# Pozzolanic activity of mechanochemically and thermally activated kaolins in cement

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## ARTICLE INFO

## ABSTRACT

This paper reports on the mechanochemical activation by intensive grinding as an alternative way to produce pozzolanically reactive metakaolin. The physicochemical properties, pozzolanic reactivity and impact on cement hydration of mechanochemically and thermally activated kaolinitic clays were compared. Mechanochemical activation of kaolin led to an amorphous hydrous material with increased specific surface area and high water content. Unlike in thermally activated kaolins, the Al coordination environment was partially retained during mechanochemical treatment. At low clinker replacement levels of 10%, the use of mechanochemically activated kaolins accelerated the hydration of the blended cement. The pozzolanic reaction reduced portlandite contents strongly and from early on. The combined effect of enhanced cement hydration and pozzolanic reaction at early ages was reflected in a higher early age strength development (up to 7 days). The differences between mechanochemically and thermally activated kaolins largely disappeared at later ages.

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## 1. Introduction

Thermally activated kaolins have been used as SCMs in blended cements since the 1950s and their effect on cement and concrete properties has been extensively studied as reviewed in [1,2]. Heat treatment transforms kaolinite into metakaolin, a highly pozzolanically reactive material. The potential applications of metakaolin depend on the kaolinite grade. Low grade, inexpensive kaolins may be used as a major constituent of blended cements. Recent research has demonstrated that clinker factors can be reduced down to 0.50 by using a combination of low grade metakaolin and limestone without compromising cement performance [3]. On the other hand, high grade, expensive metakaolin has been shown to be a viable alternative for silica fume in high performance concrete. Typically used at low clinker replacements of 10–15 wt.%, highly reactive metakaolin used in high performance concrete was reported to result in a similar strength development [4,5] and an improved chemical resistance [4–6] compared to silica fume. However, widespread application remains limited due to the comparatively high price of high quality metakaolin. Current shortages and increasing prices of silica fume have changed this situation and directed renewed attention to highly reactive metakaolins.

Metakaolin is described as a complex amorphous structure in which the aluminium in the kaolinite octahedral layer becomes mostly tetrahedrally and pentahedrally coordinated during structural reorganization

induced by thermal dehydroxylation [7–10]. The temperatures needed for complete dehydroxylation depend on the structural layer stacking order. Disordered kaolinites dehydroxylate between 530 and 570 °C, while ordered kaolinites dehydroxylate between 570 and 630 °C [11]. Dehydroxylated disordered kaolinites also show a higher pozzolanic reactivity [12,13]. Activation temperatures for optimal compressive strength are typically somewhat higher than the dehydroxylation temperature and cluster around 650–50 °C [14], although the optimum temperature can be as low as 550 °C at long periods of calcination [15].

Activation and structural disorder in kaolinite can also be induced by intensive grinding. Impact and friction-based grinding as in vibratory and planetary milling equipment results in alteration of the crystal structure and amorphization. The loss of crystallinity and the increase in surface energy by grinding or mechanochemical treatment increases the chemical reactivity [16]. The activation of kaolinite by mechanochemical treatment has been applied mostly to Al-extraction in the field of hydrometallurgy [16,17] or to the acceleration of high-temperature reaction kinetics for ceramics [18,19]. In the case of cements, reports on the use of mechanochemical activation are few and scattered. A number of publications on mechanochemical activation of slag and fly ash exist [20,21], however here the distinction between the effects of particle size reduction (mechanical) and structural transformation of the material (chemical) remains unclear due to experimental difficulties in describing amorphous phases. Other studies have reported on the mechanochemical activation of crystalline materials such as $\gamma$-$C_2S$ [22] or steel slag [23], a significant increase in reactivity was found when the material was amorphized during grinding. Mechanochemical activation for binder

production finds its most notable application in the production of Celitement®, a proposed novel cementitious binder, based on mechanochemically activated $\alpha$-$C_2SH$ [24]. In contrast, little work on the pozzolanic activity of mechanochemically activated kaolinite has been published. The scarce data available seem to indicate that the reactivity of mechanochemically activated kaolinite is similar to or slightly inferior to that of thermally activated kaolinite [25,26]. However, a general description of the effect of mechanochemically activated kaolinite on the hydration reactions and properties of blended cements is lacking.

This paper compares the pozzolanic reactivity of two mechanochemically activated kaolinites to their thermally activated counterparts and a reference metakaolin. Considering the additional cost of mechanochemical activation, low levels (10%) of activated clay in blended cements were studied. Compositional and structural differences between mechanochemically and thermally activated kaolinites are described and related to their impact on the hydration of blended cements. Finally, the potential of mechanochemical treatment as a means to kaolinite activation is discussed.

## 2. Materials and methods

### 2.1. Material selection and preparation

Kaolins from Zonouz (north west of Iran) (K_IR), and Zettlitz (Czech Republic) (K_CZ); high purity commercial metakaolin (MKB) from Burgess USA; and Portland cement (HeidelbergCement, Germany) (OPC) were used as raw materials in this study. K_IR and K_CZ kaolins were activated by thermal and mechanochemical treatment. A quartz filler was used as a reference inert material to be compared with the thermally and mechanochemically activated kaolins. The chemical and mineralogical compositions of the raw materials are given in Table 1. K_IR is a low grade kaolin (56 wt.% kaolinite) containing additional quartz (37 wt.%), K_CZ is a high grade kaolin (88 wt.% kaolinite). The characterization methods are detailed in Section 2.2.

For calcination of the K_IR and K_CZ kaolins, 50 g of material were put in an alumina crucible and were then fired in a laboratory furnace at temperatures of 700 °C for 3 h. After thermal treatment, cooling was done rapidly by removing the crucibles from the furnace and spreading the material on a steel plate at ambient conditions.

For the mechanochemical treatment, a planetary ball mill – QM-3SP2 – was used with 500 $cm^3$ plastic containers and 10 mm diameter zirconia balls (5.7 $g/cm^3$). The grinding took place at ambient temperature. The mass of powders for grinding in the plastic containers was 20 g, giving a balls-to-powder mass ratio of approximately 25. Samples were ground for 1, 3, 5, 7 and 12 h and the applied rotational speed was 450 rpm. It should be noted that the long grinding times were specific to the low mechanical load grinding device used in this study. As shown by various other researchers [16,17,25,26], the use of more energy intensive grinding equipment such as disc mills or high speed planetary ball mills enables grinding times of less than 1 h.

### 2.2. Material characterization

The chemical compositions of the kaolinitic clays, the Burgess metakaolin (MKB), the quartz filler and the Portland cement were determined by XRF. The loss on ignition (LOI) was measured by heating for 2 h at 1050 °C.

The particle size distributions (PSD) were measured with a Malvern Mastersizer type S laser beam granulometer. The cement was dispersed in isopropanol, whereas the kaolinitic clays, the reference metakaolin, and the thermally and mechanochemically activated kaolinites were dispersed in a solution of water with 0.01% polyacrylic acid dispersing agent. 15 min ultrasonication was carried out on all suspensions before the PSD measurements. The real and imaginary refractive indices of cement were considered to be 1.7 and 0.1, respectively, while the refractive index of isopropanol was 1.39. In the case of the kaolins and the reference metakaolin, the real and imaginary refractive indices used were 1.529 and 0.01, dispersed in water with a real refractive index of 1.33.

The Brunauer–Emmet–Teller (BET) specific surface area of the samples was determined with a Micromeritics Gemini 2375 V4 instrument using nitrogen gas at liquid nitrogen temperature. Note that in order to make sure that the powders were well dried and outgassed, they were kept in the BET tubes under nitrogen gas for 16 h at 80 °C before the measurement.

The morphological, compositional and structural alteration of the kaolin samples by mechanochemical and thermal activation was studied by scanning electron microscopy (SEM), thermogravimetry (TG), X-ray diffractometry (XRD), Fourier-transform infrared (FTIR) spectroscopy, and $^{27}Al$ nuclear magnetic resonance (NMR) spectroscopy. The morphology of carbon coated kaolinite powders was studied before and after mechanochemical and thermal treatment by SEM using a SFEG XL 30 in high resolution (through the lens detector) mode. Thermogravimetric (TG) measurements of the powders were acquired using a Mettler Toledo TGA/SDT 851 instrument. The samples were heated at a constant rate of 10 °C/min from 30 to 950 °C in a $N_2$ flow of 30 mL/min. XRD data were recorded using a PANalytical X'Pert Pro diffractometer with $CuK\alpha_{1,2}$ radiation in $\theta$-$\theta$ reflection configuration. The X-ray tube was operated at 45 kV and 40 mA. Incident beam Soller slits of 0.04 rad were inserted and the incident divergence slit was fixed at 0.5°. An X'Celerator linear position-sensitive X-ray detector with a length of 2.122° 2θ was used for data acquisition. All scans were measured over an angular range of 7 to 70° 2θ with 0.017° 2θ step size and accumulated time per step of 29.8 s, resulting in a total measurement time of about 15 min per scan. The samples were spun during measurement. FTIR spectroscopy measurements of powder samples were acquired in Diffuse Reflectance Infrared Transmission (DRIFT) mode on a Jasco FT/IR 6300A spectrometer. IR spectra were collected over the 600–4000 $cm^{-1}$ range, 50 scans were accumulated with a spectral resolution of 4 $cm^{-1}$. $^{27}Al$ NMR spectra of powder samples were collected using a Bruker Avance I 400 solid state spectrometer at a 20 kHz spinning rate and 11.7 T magnetic field.

**Table 1**
Chemical and mineralogical composition of the selected low-grade kaolins, the reference high-grade metakaolin, the quartz filler and the Portland cement.

| Oxides (wt.%) | K_CZ | K_IR | MKB | Quartz filler | PC | Phase (wt.%) | K_CZ | K_IR | PC |
|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 45.05 | 65.18 | 50.62 | 97.91 | 19.27 | Kaolinite | 88 | 56 | |
| $Al_2O_3$ | 38.88 | 24.10 | 46.91 | 1.00 | 5.65 | Illite | 10 | 7 | |
| $Fe_2O_3$ | 0.91 | 0.45 | 0.38 | 0.05 | 3.63 | Quartz | 2 | 37 | |
| CaO | 0.30 | 0.93 | 0.02 | 0.02 | 63.65 | $C_3S$ M3 | | | 63.6 |
| MgO | 0.23 | 0.25 | 0.09 | / | 1.62 | Beta-$C_2S$ | | | 8.9 |
| $SO_3$ | / | / | 0.08 | / | 3.16 | $C_3A$ | | | 6.5 |
| $Na_2O$ | 0.02 | / | 0.28 | / | 0.15 | $C_4AF$ | | | 14.2 |
| $K_2O$ | 0.87 | 0.34 | 0.18 | 0.77 | 1.24 | Periclase | | | 0.4 |
| $TiO_2$ | 0.29 | 0.03 | 1.29 | 0.03 | 0.29 | Anhydrite | | | 4.0 |
| LOI | 13.04 | 8.57 | 0 | 0.15 | 0.75 | Arcanite | | | 2.3 |
| $d_{50}$ (μm) | 5.37 | 4.68 | 5.13 | 11.3 | 8.6 | | | | |
| BET ($m^2/g$) | 19.1 | 8.1 | 9.64 | 1.71 | 0.87 | | | | |