



# The effect of limestone on sodium hydroxide-activated metakaolin-based geopolymers



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## HIGHLIGHTS

- Matrix consisted of calcium silicate, alkali aluminosilicate, calcium carboaluminates.
- The heat treatment increased reaction of limestone only at higher 5 mol NaOH.
- The leaching from limestone–metakaolin is controlled by equilibrium considerations.

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## ABSTRACT

Blends of metakaolin and limestone can be alkali-activated with NaOH to form solid binders, which show relatively low strength but offer potential as a model system by which the reaction processes of more complex systems can be better understood. The effects of curing procedure, limestone content and alkalinity of the activator are able to be related to the mineralogy, mechanical properties and microstructure of hardened pastes. The presence of limestone enhances the release of Al and Si ions from metakaolin, with the Al released in the early stages of the reaction being bound into AFm-type phases. Dissolution of LS is slightly higher when a lower alkalinity sodium hydroxide activator is used. The heat treatment of pastes activated with 3 M NaOH solution resulted in a lower extent of reaction of limestone, while with 5 M solution, heat-curing at early age resulted in more reaction. The main alkali-activation product in metakaolin–limestone–NaOH pastes is a geopolymer gel with inclusions of unreacted metakaolin, limestone particles, zeolite A, and AFm phases, with different zeolites such as faujasite-like and hydrosodalite phases also identified at higher reaction temperatures.

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## 1. Introduction

Materials containing significant amounts of alumina and silica such as blast furnace slag, metakaolin or fly ash can either be combined with Portland cement to produce blended binders with improved technical, environmental and/or economic performance [1,2], or activated by alkaline solutions [3,4], to produce binders suitable for application in the construction industry. Significant research has been conducted in the area of alkaline activation since the 1940s [5–11], which has led to the commercial-scale utilization of these binders in various civil infrastructure contexts in Europe, Asia, Australia and the Americas [3,4,7,12–14]. The alkali activation process can be divided into three main phases: dissolution of the

solid aluminosilicate precursor, polymerization of alumina/silica-hydroxy species (monomers and oligomers), and then a polycondensation and stabilization phase during which oligomers and small gel units are transformed into extensive cross-linked networks via through-solution reorganization [15].

The most common types of low-calcium alkali-activated binders, or ‘geopolymers’ [7], are produced from fly ash or metakaolin as solid aluminosilicate precursors [10]. Metakaolin is produced from natural clays by calcination at a moderate temperature, which renders the material reactive by disrupting its crystal structure, buckling the silicate and aluminate layers through dehydroxylation [16,17]. Geopolymers derived from metakaolin tend to have high water content and permeability [18], meaning that it is of interest to find inexpensive calcium sources to supplement this aspect of the system chemistry and improve both mechanical and durability-related properties of the binders [19–23]. Incorporation of appropriate contents of additional components rich in Ca, in the presence of suitable activator chemistry, results in

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formation of stable binding phases which can include coexisting N–A–S–H and C–A–S–H gels [20,24].

The mechanical properties of alkali silicate-activated binders are often comparable with the properties of Portland cements, reaching 28-day compressive strengths which would be suitable for use in highly demanding civil engineering applications. However, many alkali-activated binder systems are also designed for lower-cost production, with the use of inexpensive aluminosilicate precursors and/or activators (e.g. sodium hydroxide or carbonate) showing lower 28-day compressive strengths (below 10 MPa) and slower strength development [25], but still with potential application in small precast concrete blocks and bricks, where high strength development is less of a priority.

Additionally, there has been a high degree of interest recently in ternary Portland cement–metakaolin–limestone blended binder systems, where the use of finely ground limestone as a supplementary cementitious material can provide improved material properties through the formation of additional carboaluminate phases [26,27]. Alkali-activated hybrid systems containing clinker, metakaolin, limestone and an alkaline component have also been developed as a sustainable cementing option [28]. The mechanistic details of the hydration chemistry of the limestone and metakaolin in such systems remain incompletely understood, and so it is interesting to isolate the metakaolin–limestone–alkali hydroxide sub-system to provide further information about these reaction processes. In this scenario, the alkali hydroxide solution is used to approximate the pore solution environment of a hydrating cement; the alkalinities used in alkali-activation are much higher than in a blended Portland cement binder or an alkali-hybrid cement containing a sulfate activator, and this will alter some of the phase relationships observed, but it is anticipated that important information will nonetheless be elucidated through the study of this system.

Therefore, the main objective of this research is to study the interactions between ground limestone, metakaolin, and alkali hydroxide solutions of moderate to high concentration. The influence of precursor blend, curing conditions and alkali hydroxide concentration on the dissolution and geopolymerization process in the metakaolin–CaCO<sub>3</sub>–NaOH system will therefore be investigated.

## 2. Materials and methods

### 2.1. Materials

The metakaolin used was produced by Imerys Minerals, UK under the brand name of Metastar 402. The chemical composition of metakaolin (MK) and limestone (LS) determined by X-ray fluorescence (XRF) are shown in Table 1.

### 2.2. Test specimens and testing procedure

All paste mixes were alkali-activated with 3.0 M or 5.0 M NaOH solution, at a water to binder ratio of 0.70. All mixes were workable and easily molded. The proportions (by mass) of LS to MK varied from 30/70 to 70/30, Table 2. All specimens were produced using a low-volume vacuum mixer and were cast into Teflon molds without addition of any release oil. The use of a vacuum mixer enabled us to produce smaller specimens with higher homogeneity of the hardened paste due to a very low amount of air, which would otherwise be entrapped during mixing. Specimens were cured in sealed conditions either at 80 °C or at 20 °C. After 24 h of curing, specimens were removed from molds and stored either in water (wet cured) or

**Table 2**  
Mix compositions of pastes.

Mix	W/B ratio	LS (wt%)	MK (wt%)	NaOH (mol/L)
100MK	0.7	0	100	3.0 and 5.0
50LS/50MK	0.7	50	50	3.0 and 5.0
30LS/70MK	0.7	30	70	3.0 and 5.0
70LS/30MK	0.7	70	30	3.0 and 5.0

under ambient laboratory conditions (dry cured). In both cases the curing temperature was 20 °C. Strength was determined using paste beams having dimensions of 10 × 10 × 60 mm, and 3 replicates per mix; beams were broken in flexion (3-point bending) and the compression test was conducted on the unstressed ends of the beam obtained from bending. The testing apparatus was a Roell + Kortheus instrument, with a load rate of 0.35 mm/min. The microstructure of the 28-day cured paste specimens was studied using a backscattered electron detector (BSE) in an Environmental Scanning Electron Microscope (ESEM), Electroscan E3. The operating parameters of the ESEM were: accelerating voltage 20 keV, chamber pressure 2.5 torr and working distance 13.3 mm. All ESEM studies were conducted using resin-impregnated polished paste specimens. Samples were cut using a diamond saw with ethanol as a lubricant, stored for 24 h in ethanol to remove the capillary water, followed by resin impregnation in vacuum, then samples were ground and polished using diamond pads (125 and 25 μm) and diamond spray (6, 3, 1 and 0.25 μm).

The chemistry of the raw materials and the hardened paste specimens was studied using X-ray diffraction analysis (XRD) and thermogravimetry (TG). Both tests used crushed and hand ground powders. The particle size distribution of the powdered samples was verified using a Coulter laser particle size analyzer, and the mean particle size was around 20 μm. All XRD measurements were done at the age of 10 days, and the TG at 10 days and 3 months. The TG analysis was conducted using a thermogravimeter type 951 from Du Pont Instruments, updated with a Temperature Programmer Interface (TPI) controller. The heating rate was 20 °C/min to a maximum temperature of 1000 °C. Measurements were made in an inert helium atmosphere using a flow rate of 40 mL/min. The X-ray diffraction (XRD) analysis was conducted using a Philips PW1830 diffractometer. The XRD has a Cu LFF type of tube anode and the following setup was used: generator voltage of 40 kV, generator current of 40 mA.

The leaching tests were undertaken using suspensions of either metakaolin (MK), limestone (LS), or mixtures of the two. Sodium hydroxide solutions with molarities 1, 3, and 5 M were used for mixes containing pure MK or LS, while mixtures consisting of MK/LS combination used 3 M NaOH solution, Table 3. The leaching tests were performed at a liquid/solid mass ratio of 1/50 in a 1 L sealed vessel, with agitation at 200 rpm for 24 h. Elemental analysis was achieved using a Perkin–Elmer Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) instrument to characterize samples extracted after 1, 2, 3, 4, 5, 8 and 24 h. The suspension temperature was kept at around 20 °C throughout the experiments.

## 3. Results and discussion

### 3.1. Characterization of raw materials

The X-ray diffractograms of metakaolin (MK) and limestone (LS) are shown in Fig. 1; the LS consists mostly of calcite (CaCO<sub>3</sub>) and some traces of mica, feldspar and kaolinite. The MK appeared as a highly amorphous material, with a minor muscovite impurity, and traces of quartz. The differential thermogravimetry (DTG) data for the two precursors, Fig. 2, show two decomposition peaks at 100 and 600–800 °C (minor) in the case of MK, and one at 800 °C for LS. The small mass loss in the metakaolin at 600–800 °C can be related to further dehydroxylation of residual kaolinite-like structures present, while the mass loss in the limestone is due to decarbonation of CaCO<sub>3</sub>.

**Table 1**  
Chemical composition of metakaolin and limestone determined by XRF analysis, and particle size data from laser diffraction and nitrogen sorption analysis. LOI is loss on ignition at 1000 °C.

	Mean particle size (μm)	Specific surface area (cm <sup>2</sup> /cm <sup>3</sup> )	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	LOI
Metakaolin	4.2	3.0 × 10 <sup>4</sup>	0.1	54.8	40.4	0.8	0.4	2.7	0.1	1.1
Limestone	10.7	2.0 × 10 <sup>4</sup>	53.5	1.5	0.3	0.2	1.7	0	0	42.8

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