



## Research paper

## Influence of metakaolin characteristics on the mechanical properties of geopolymers

C. Kuenzel<sup>a,b</sup>, T.P. Neville<sup>c</sup>, S. Donatello<sup>d</sup>, L. Vandeperre<sup>b</sup>, A.R. Boccaccini<sup>b,e</sup>, C.R. Cheeseman<sup>a,\*</sup><sup>a</sup> Department of Civil and Environmental Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom<sup>b</sup> Centre for Advanced Structural Ceramics, Department of Materials, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom<sup>c</sup> Centre for CO<sub>2</sub> Technology, Department of Chemical Engineering, University College London, Gower Street, London WC1E 6JE, United Kingdom<sup>d</sup> Cement and Materials Recycling Department, Eduardo Torroja Institute of Construction Sciences, Madrid 28033, Spain<sup>e</sup> Institute of Biomaterials, University of Erlangen-Nuremberg, Cauerstrasse 6, 91058 Erlangen, Germany

## ARTICLE INFO

## Article history:

Received 16 November 2012

Received in revised form 8 August 2013

Accepted 11 August 2013

Available online 18 September 2013

## Keywords:

Metakaolin

Geopolymer

Reactive content

Weibull statistics

## ABSTRACT

The relationship between the properties of geopolymers and the characteristics of metakaolin samples used in their preparation has been investigated. Three commercial metakaolin samples have been characterised using <sup>27</sup>Al-NMR to determine the coordination number of Al (IV, V and VI), and by acid and alkali dissolution to determine the reactive Si and Al content. The setting and mechanical properties of geopolymers formed from the metakaolin samples under identical conditions are reported, using Weibull statistics to analyse strength data. Although the metakaolin samples contained different levels of five coordinated aluminium (Al (V)) the mechanical properties of the geopolymers formed were very similar. The reactive fraction of metakaolinite determined by dissolution in 8 M NaOH provides the most relevant long-term indicator of geopolymer performance.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Geopolymers are made from a range of different aluminosilicates that have received significant attention in recent years (Duxson et al., 2007a; Khale and Chaudhary, 2007; Komnitsas and Zaharaki, 2007). Forming geopolymers involves mixing an aluminosilicate with highly alkaline activating solution to form a flowable paste. Dissolution/precipitation reactions cause the paste to harden to a solid geopolymer network structure that can have excellent mechanical properties. The majority of geopolymer research has investigated the use of coal fly ash, blast furnace slag and metakaolin (MK) based systems (Kuenzel et al., 2012; Rahier et al., 2007a; Somna et al., 2011). Coal fly ash and slags are relatively cheap and readily available industrial by-products, but they exhibit significant variations in chemical and physical properties. MK is produced by controlled calcination of naturally occurring kaolinite, and has the advantage of consistent chemical composition and properties. Coal fly ash and slag-based geopolymer concretes are proposed as alternatives to Portland cement concrete and have the potential to reduce the carbon footprint of construction (Chindaprasirt et al., 2007; Hardjito et al., 2004; Palomo et al., 1999a; van Jaarsveld et al., 2004). More expensive MK based geopolymers have been investigated for use in specialist applications such as the encapsulation/immobilisation of nuclear wastes, where chemical/physical property consistency and long-term availability of raw materials are required (Bell et al., 2009a,b; Blackford et al., 2007;

Kuenzel et al., 2010; Perera et al., 2005, 2006). Additional important geopolymer properties are excellent resistance to fire and bacterial attack, and the development of rapid early strength (Cheng and Chiu, 2003; Hermann et al., 1999; Palomo et al., 1999b).

Although the chemical composition of MK is generally consistent, very little has been reported on the comparative performance of geopolymers made from different MK samples or the desirable characteristics of MK for geopolymer production. International standards are not currently available to regulate production of MK from kaolinite and therefore the content of reactive Al and Si can vary significantly due to changes in feedstock purity and processing conditions (Sanz et al., 1988).

An important factor that determines the reactivity of MK is reported to be the Al coordination number (Davidovits, 2008). This can be tetrahedral (IV), pentahedral (V) or octahedral (VI). Despite relatively little supporting data it is generally accepted that the quantity of Al (V) in MK influences the mechanical properties of geopolymers (Sagoe-Crentsil and Weng, 2007) and increases MK reactivity. However, the authors are not aware of previous research that has directly correlated Al (V) content with the content of reactive Al as measured by HF or NaOH dissolution, and the resulting geopolymer properties (Ruiz-Santaquiteria et al., 2011).

Compressive strength is a basic characterisation property for geopolymers, although comparing results can be difficult due to variations in specimen size, test geometry, loading rate, testing apparatus and mixing/curing procedures used (Provis et al., 2005). Analysis of strength data using Weibull statistics allows prediction of failure probability under a given applied load and requires test data between 20 and 30

\* Corresponding author. Tel.: +44 207594 5971; fax: +44 207 594 6124.

E-mail address: [c.cheeseman@imperial.ac.uk](mailto:c.cheeseman@imperial.ac.uk) (C.R. Cheeseman).

samples to give accurate results (Khalili and Kromp, 1991). Using Weibull statistics in combination with fracture toughness data also allows the critical defect size to be determined.

The aim of the research was to investigate how the characteristics of MK samples influence the setting reactions and mechanical properties of geopolymer paste samples.

## 2. Materials and methods

### 2.1. Materials

Three different MK samples have been characterised and used to form geopolymers under identical processing conditions. The MK samples used were MetaStar 501 (Imerys, UK), Argical M1200 (Imerys, UK) and MetaMax (BASF, Germany). These were characterised using X-ray fluorescence (XRF, Spectro 2000 XRF analyser, Germany) and loss on ignition. Particle size distribution data was determined by laser diffraction (Beckman Coulter LS100, USA). The crystalline phases present in the MK samples were determined by X-ray diffraction (XRD, PAN analytical X-Pert Pro MPD, Philips, The Netherlands). Samples were analysed using a stepwise scan from 15 to 60  $2\theta$  with steps of  $0.033^\circ$  and 20 s per step. The  $\text{CuK}\alpha$  radiation was generated at 40 kV and 20 mA.

### 2.2. Al coordination and dissolution analysis of MK samples

The coordination number of Al in the MK samples was determined using solid  $^{27}\text{Al}$ -MAS NMR (Advance 600 solid state NMR, Bruker, Germany) at room temperature with a resonance frequency of 104.3 MHz and spinning rate of 12 kHz. In order to determine the relative amounts of IV, V and VI coordinated Al, spectra were analysed using the computer program dmfit and by applying a Gaussian model to the peaks (Massiot et al., 2002).

A range of different dissolution techniques have been proposed to determine the reactive Al and Si content in MK (Fernandez-Jimenez et al., 2006; Ruiz-Santaquiteria et al., 2011). In this study the amount of reactive Al was determined by dissolving MK samples in either 1% HF or 8 M NaOH and analysing the resulting insoluble residue (Ruiz-Santaquiteria et al., 2011). 1 g of each MK was mixed with 100 ml of 8 M NaOH or 100 ml 1% (mass) HF solution for 20 h at ambient temperature prior to separating the residual solids by filtration. Previous work has shown that 20 h is sufficient to dissolve all the reactive phases in MK under these conditions (Kuenzel, 2013). The residual solids collected on ash free filter paper were washed in deionised water until the pH of the filtrate was neutral. The mass of retained solids was determined by calcining the filter paper and retained solids at 1000  $^\circ\text{C}$  for 1 h. Separate fractions of the filtered solids were also dried at 110  $^\circ\text{C}$  and analysed by XRD to determine the changes in the crystallinity of MK caused by the dissolution process.

### 2.3. Preparation of MK geopolymers

All MK geopolymers were prepared using a molar Al:Si:Na ratio of 1:2:1. This is reported to be an ideal Al:Si ratio to produce geopolymers with good mechanical properties (Duxson et al., 2005, 2007b,c). The molar  $\text{H}_2\text{O}$ :Al ratio used was 8 in order to obtain a low viscosity mix. Previous studies have varied the molar  $\text{H}_2\text{O}$ :Al ratio between 5.5 and 12 (De Silva et al., 2007; Duxson et al., 2005, 2007b; Fletcher et al., 2005; Poulesquen et al., 2011; Rowles and O'Conner, 2003).

Alkali activating solutions were prepared using sodium silicate (26%  $\text{SiO}_2$ /8%  $\text{Na}_2\text{O}$ , VWR International, Pennsylvania, USA) and sodium hydroxide pellets (NaOH, Fischer Scientific International, New Hampshire, USA) dissolved in deionised water to give the required Si and Na ratio. Activating solutions were prepared by mixing appropriate quantities of  $\text{Na}_2\text{SiO}_3$  solution with water and NaOH and stirring for 24 h. The activating solution was then mixed with MK using an

automatic mixer (65-L0006/AM, Controls, Italy) for 3 min and the slurry cast into stainless steel moulds ( $10 \times 10 \times 50$  mm). A vibrating table was used for 10 min to remove air bubbles, with the samples then placed in sealed polyethylene (PE) bags and cured at ambient temperature ( $22 \pm 3$   $^\circ\text{C}$ ). After two days the samples were de-moulded and placed in sealed PE bags and cured for a further 54 days at ambient temperature.

### 2.4. Characterisation of geopolymer samples

Setting under ambient conditions was monitored using a Vicat needle penetrometer (Vicatronic Automatic Single Station Vicat Needle Apparatus, Qualitest, USA) following BS EN 196-3 (Standard, 2008). Due to the water soluble nature of MK pastes at very early ages, oil was used instead of water to cover the sample and prevent surface drying during setting.

Isothermal conduction calorimetry (Wexham Developments Ltd., UK) was used to determine the heat output during the dissolution and poly-condensation reactions that characterise the geopolymerisation process, with the external temperature maintained at  $20.0 \pm 0.1$   $^\circ\text{C}$ .

Compressive strengths of geopolymers were measured on 10 mm cube samples cut from the original samples (Zwick/Roell Z10, Germany). The crosshead speed was 0.5 mm/min and the edges of the specimen were lightly chamfered prior to testing.

Flexural strength and fracture toughness were determined using three point bend testing of  $10 \times 10 \times 50$  mm samples using a crosshead speed of 0.5 mm/min and a support span of 40 mm. Before measuring the flexural strength, the edges of samples were lightly chamfered.

The  $10 \times 10 \times 50$  mm geopolymer samples were notched using a 0.2 mm thick diamond blade to a depth of approximately 2 mm to measure the fracture toughness ( $K_{Ic}$ ). The  $K_{Ic}$  was calculated using the following equation (Rooke and Cartwright, 1976):

$$K_{Ic} = \frac{3PL\Psi\sqrt{\pi a_0}}{2bW^2} \quad (1)$$

where  $P$  = force,  $L$  = span length,  $a_0$  = notch depth,  $b$  = sample width,  $W$  = sample height, and  $\Psi$  is given by the following equation:

$$\Psi = 1.11 - 1.55\left(\frac{a_0}{W}\right) + 7.71\left(\frac{a_0}{W}\right)^2 - 13.5\left(\frac{a_0}{W}\right)^3 + 14.2\left(\frac{a_0}{W}\right)^4 \quad (2)$$

The statistical behaviour of strength was modelled using the Weibull function (Weibull, 1951). The probability of failure  $P_f$  can be described by the following equation:

$$P_f = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_0}\right)^m\right] \quad (3)$$

where  $m$ , the Weibull modulus, is related to the scatter of strength values during a test (Lawn and Wilshaw, 1975) with higher  $m$  indicating reduced scatter,  $\sigma_0$  is the reference strength and  $\sigma$  is the nominally applied stress. This equation contains two unknowns,  $m$  and  $P_f$ . To determine  $P_f$ , Lawn suggested using the mean rank. However, for tests limited to less than 50 samples the following equation was proposed (Bergman, 1984; Masson and Bourgain, 1992):

$$P_f = \frac{i-0.5}{N} \quad (4)$$

where  $N$  represents the total number of samples and  $i$ , each individual sample. The Weibull parameter can then be calculated by combining and rearranging Eqs. (3) and (4) to give:

$$\ln\left[\ln\frac{1}{(1-P_f)}\right] = m \ln\left(\frac{\sigma}{\sigma_0}\right) \quad (5)$$

Download English Version:

<https://daneshyari.com/en/article/1694897>

Download Persian Version:

<https://daneshyari.com/article/1694897>

[Daneshyari.com](https://daneshyari.com)