



Synthesis of stoichiometrically controlled reactive aluminosilicate and calcium-aluminosilicate powders



Brant Walkley^a, Rackel San Nicolas^{a,b}, Marc-Antoine Sani^c, John D. Gehman^{c,d}, Jannie S.J. van Deventer^{a,e}, John L. Provis^{f,*}

^a Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia

^b Department of Infrastructure Engineering, The University of Melbourne, Victoria 3010, Australia

^c School of Chemistry and Bio21 Institute, The University of Melbourne, Victoria 3010, Australia

^d GehmanLab, Woodend, Victoria 3442, Australia

^e Zeobond Pty Ltd, P.O. Box 23450, Docklands, Victoria 8012, Australia

^f Department of Materials Science and Engineering, The University of Sheffield, Sheffield S1 3JD, United Kingdom

ARTICLE INFO

Article history:

Received 7 October 2015

Received in revised form 24 March 2016

Accepted 4 April 2016

Available online 9 April 2016

Keywords:

Amorphous aluminosilicates

Powder synthesis

NMR spectroscopy

ABSTRACT

Aluminosilicate and calcium-aluminosilicate powders are synthesised via an organic steric entrapment route under conditions permitting strict stoichiometric control, utilising polyvinyl alcohol and polyethylene glycol as polymeric carriers. Polyethylene glycol is superior to polyvinyl alcohol for synthesis of calcium-aluminosilicate powders via this method, producing a more controllable product which generated less fine ash during calcination. This paper presents detailed description of synthesis and characterisation of the powders produced through this approach, including new insight into the nanostructures within the calcined powders. Aluminium environments are a mixture of 4-, 5- and 6-coordinated, while silicon is tetrahedral and shows a broad range of connectivity states. The powders are X-ray amorphous, display a high degree of homogeneity, and thus offer potential for utilisation as precursors for synthesis of hydrous aluminosilicates in the quaternary CaO–Na₂O–Al₂O₃–SiO₂ system.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, the production of ceramic powders via chemical synthesis routes has gained significant attention in academia and industry as a method of increasing energy efficiency when compared with production by traditional high-temperature solid-state reactions, as well as offering scope for production of chemical or phase compositions which are difficult to achieve via solid state routes. The Pechini process [1], for example, is a solution-polymerisation route which allows the production of homogeneous single phase mixed oxide powders by the use of an organic acid to chelate metal ions, and has been key to the development of ceramic synthesis via chemical routes.

A number of studies have used variations of the Pechini process to synthesise calcium, silicon or aluminium-containing mixed oxides by employing an organic polymeric steric entrapment solution-polymerisation route [2–6]. This method utilises a long chain organic polymer, most commonly polyvinyl alcohol (PVA), to sterically inhibit the movement of the metal cations during solution polymerisation, forming a homogeneous single phase mixed oxide powder upon drying and moderate-temperature calcination to remove the organic component

[2,5,7]. Of the studies utilising the organic polymeric steric entrapment solution-polymerisation route, most focus on the synthesis of mixed oxides for ceramic applications [2–4,6], others describe synthesis of an apparently ‘metakaolin-like’ powder which can be subsequently activated to form a geopolymeric binder [8,9], while one study described the use of this route to individually synthesise each of the reactive phases which are present in Portland cement (PC) [5].

Geopolymers, or alkali-activated binders, are produced by chemical reaction of an aluminosilicate or calcium-aluminosilicate powder with an alkaline solution to form a solid binder with properties comparable to those of hardened PC [10,11]. These materials offer a viable environmentally friendly replacement for PC, with a reduction in the associated CO₂ emissions of between 50% and 80% when compared to PC binders [12]. Furthermore, as the raw materials used to produce geopolymers are often industrial by-products such as blast furnace slag and fly ash, or readily available aluminosilicate clay-based products such as metakaolin (calcined kaolinite), they present an avenue for the use of, and add value to, these materials.

Geopolymer formulations must be carefully designed to obtain desirable rheological, chemical and physical properties, and this can only be achieved through a detailed understanding of complex particle interactions occurring within the packed geopolymer mortar and concrete systems [13–16]. This can be particularly challenging due to the wide

* Corresponding author.

E-mail address: j.provis@sheffield.ac.uk (J.L. Provis).

variation of chemical and physical characteristics exhibited by commercial geopolymer precursors where a range of chemical reactivity is observed, meaning it is often difficult to distinguish reactive from inert species. This is further complicated by the introduction of alkali-reactive aggregates in geopolymer concrete systems [17,18].

A large number of studies are focused on understanding the chemistry of geopolymers and alkali-activated binders, however the literature is often conflicting and experimental analysis involves a large number of unconstrained parameters. To gain insight into the effect of precursor chemical composition on the chemical and physical interactions occurring within the complex particulate system formed during geopolymer synthesis, a method of studying geopolymers which permits strict stoichiometric control must be developed. This, in turn, can only be achieved through synthesis of aluminosilicate and calcium-aluminosilicate powders via a route through which strict control of the chemistry is obtained.

The present study applies the knowledge gained through development of the aforementioned chemical synthesis routes for ceramic powder production. Specifically, the organic polymeric steric entrapment solution-polymerisation route is refined and adjusted, including the use of PEG rather than PVA for calcium-containing systems, to develop a novel class of laboratory synthesised, stoichiometrically controlled reactive high-purity geopolymer precursor powders.

2. Experimental

2.1. Powder synthesis

2.1.1. Aluminosilicates

A 5 wt% polyvinyl alcohol (PVA) solution was made by adding 98–99% hydrolysed PVA (Sigma Aldrich, molecular weight 31–50 kDa) to distilled water. PVA of this molecular weight has been shown to produce more reactive calcium silicate and calcium aluminate powders with higher specific surface areas, compared to longer-chain PVA [5]. The polymer was added to distilled water in small increments over heat and the resulting solution was stirred at 60 °C for 1 h. Aluminium nitrate nonahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma Aldrich 98.5 wt%) was added to distilled water to produce a 40 wt% solution, which was then added to the 5 wt% PVA solution and stirred at 60 °C for 1 h before addition of colloidal silica (Sigma Aldrich Ludox HS-40 colloidal silica (SiO_2), 40 wt% in water). The stoichiometry was designed to achieve the elemental ratios outlined in Table 1, as well as ensuring that the number of metal cations (M^{x+}) in solution was significantly more than the number that the PVA could chemically bind through its OH groups ($\text{M}^{x+}/\text{OH} = 4$) [2,5]. Water was evaporated from the resulting solution by stirring over heat at 80 °C, to form a viscous aerated gel. A portion of each aerated gel was kept for analysis by differential thermogravimetric analysis (DTG), while the remaining dry aerated gel was calcined by heating at 3 °C/min to 550 °C in a laboratory muffle furnace, with a 1 h hold time at 550 °C and then cooling in air, to produce a fine white powder which was subsequently ground by hand before characterisation.

2.1.2. Calcium-aluminosilicates

A 5 wt% polyethylene glycol (PEG) solution was produced by adding PEG (Sigma Aldrich, MW 20 kDa) to distilled water. The requirement for

Table 1
Molar ratios, polymer carrier and metal valence (M^{x+}) to hydroxyl functionality (OH) ratio for each sample.

Sample	Empirical formula	Ca/(Al + Si)	Al/Si	Polymer	M^{x+}/OH
A	$2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$	0.000	1.000	PVA	4
B	$4\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$	0.000	0.500	PVA	4
C	$0.800\text{CaO} \cdot \text{SiO}_2 \cdot 0.078\text{Al}_2\text{O}_3$	0.692	0.156	PEG	2
D	$1.214\text{CaO} \cdot \text{SiO}_2 \cdot 0.078\text{Al}_2\text{O}_3$	1.050	0.156	PEG	2
E	$0.709\text{CaO} \cdot \text{SiO}_2 \cdot 0.026\text{Al}_2\text{O}_3$	0.675	0.051	PEG	2
F	$1.104\text{CaO} \cdot \text{SiO}_2 \cdot 0.026\text{Al}_2\text{O}_3$	1.050	0.051	PEG	2

the use of PEG instead of PVA is due to the presence of the calcium, and will be discussed in more detail below (Section 2.2). The polymer was added to distilled water in small increments over heat, and the resultant solution was stirred at 60 °C for 1 h. Aluminium nitrate nonahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma Aldrich, 98.5 wt%) and calcium nitrate tetrahydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (BDH Prolabo, VWR International, 99.0 wt%) were each added to distilled water to produce 40 wt% solutions by mass of anhydrous salt, and these solutions were subsequently added to the 5 wt% PEG solution and stirred at 60 °C for 1 h before addition of colloidal silica (Sigma Aldrich Ludox HS-40 colloidal silica (SiO_2), 40 wt% in water). As in the aluminosilicate powder synthesis, the stoichiometry was designed to achieve the elemental ratios outlined in Table 1, as well as ensuring that the number of metal cations (M^{x+}) in solution was significantly more than the number that PEG polymer carrier could chemically bind through its OH groups ($\text{M}^{x+}/\text{OH} = 2$). Water was evaporated from the resulting solution by stirring over heat at 80 °C to form a viscous aerated gel which was then placed in a drying oven at 100 °C overnight to remove any remaining water. A portion of each aerated gel was kept for analysis by differential thermogravimetric analysis (DTG), while the remaining dry aerated gel was calcined at 3 °C/min to 900 °C in a laboratory muffle furnace, with a 1 h hold time at 900 °C and then cooling in air, producing a fine white powder which was subsequently ground by hand before characterisation.

The stoichiometric ratios for these samples were chosen to provide a chemically simplified model system for aluminosilicate and calcium-aluminosilicate alkali-activated binder precursors. Samples A and B (empirical formulas $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ and $4\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$, respectively) were chosen to represent the range of bulk silicon and aluminium content typically found in fly ashes, with A also representing the approximate composition of metakaolin (see Fig. 1) [19]. Samples C, D, E and F (empirical formulas $0.800\text{CaO} \cdot \text{SiO}_2 \cdot 0.078\text{Al}_2\text{O}_3$, $1.214\text{CaO} \cdot \text{SiO}_2 \cdot 0.078\text{Al}_2\text{O}_3$, $0.709\text{CaO} \cdot \text{SiO}_2 \cdot 0.026\text{Al}_2\text{O}_3$ and $1.104\text{CaO} \cdot \text{SiO}_2 \cdot 0.026\text{Al}_2\text{O}_3$, respectively) were chosen to enable synthesis of binders exhibiting chemistry in regions of the quaternary $\text{CaO}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system which are important for the study of sodium- and aluminium-substituted calcium silicate hydrate gels, the main reaction product present in alkali-activated slag binders [11,20].

2.2. Practical considerations

An organic steric entrapment solution-polymerisation route utilising PVA has been previously reported to enable synthesis of a range of cementitious phases including dicalcium silicate, tricalcium silicate,

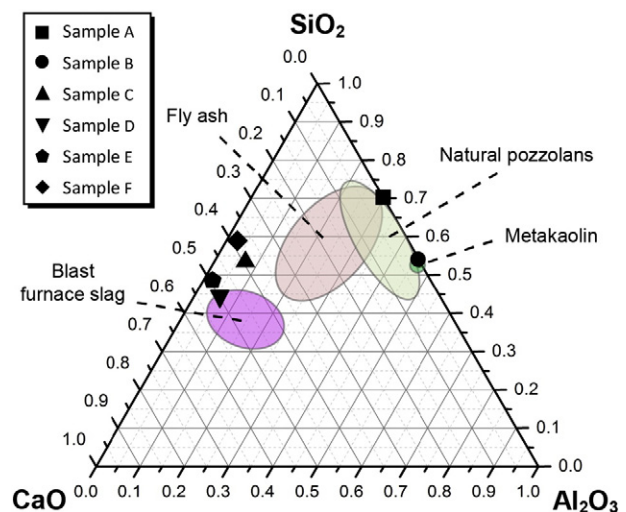


Fig. 1. Projection of powder chemistry onto the ternary Ca–Al–Si system showing elemental composition (mass basis) of each powder, as well as the compositional range for common supplementary cementitious materials based on [21].

Download English Version:

<https://daneshyari.com/en/article/6676587>

Download Persian Version:

<https://daneshyari.com/article/6676587>

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