



The transition of fly ash-based geopolymer gels into ordered structures and the effect on the compressive strength



Xue Ma^{a,b}, Zuhua Zhang^{c,d,*}, Aiguo Wang^e

^a State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, China

^b School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, China

^c Centre of Excellence in Engineered Fibre Composites, University of Southern Queensland, Toowoomba 4350, Australia

^d Fundamental Science on Nuclear Wastes and Environmental Safety Laboratory, Southwest University of Science and Technology, Mianyang 621010, China

^e Anhui Key Laboratory of Advanced Building Materials, Anhui Jianzhu University, Hefei 230022, China

HIGHLIGHTS

- The transition of amorphous gels into ordered structures can take place at 25 °C.
- The transition can be accelerated at 80 °C high humidity conditions.
- The transition takes place on amorphous gels randomly, rather than in pores.
- It is worthy to consider the transition at design and manufacturing stages.

ARTICLE INFO

Article history:

Received 2 February 2015

Received in revised form 8 November 2015

Accepted 6 December 2015

Available online 11 December 2015

Keywords:

Geopolymer

Fly ash

Durability

Phase

Zeolite

Cement

Crystallization

ABSTRACT

This paper reports the investigation of microstructural properties associated with the transition of amorphous gels into more ordered structures in fly ash-based geopolymers. Three typical geopolymer mixes are synthesized with Class F fly ash and slag. Accelerated ageing scheme is performed at the 80 °C hydrothermal conditions, lasting for 90 days. It is observed that under the hydrothermal conditions, the two geopolymer pastes containing solely fly ash activated with sodium hydroxide and sodium silicate exhibit a common tendency to partial crystallization after 28 days. Crystalline zeolitic phases (including analcime) are detected by XRD and FTIR techniques. The SEM observation shows that the transition from the amorphous gels into more ordered structures takes place in the binder matrix randomly, rather than in pores or from particular structures. The blending of slag can reduce the transition (crystallization) trend, which is attributed to the formation of calcium containing gels. The decrease of compressive strength of geopolymer at late ageing stage can be correlated to the phase transition. Proper molecular designs of geopolymers to kinetically control the transition must be considered for the applications of this family of materials.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Geopolymer cement is manufactured from alkali activation of solid aluminosilicate precursors at ambient or slightly elevated temperature conditions. By avoiding the high temperature calcinations of clinker, geopolymer manufacturing can save energy and reduce greenhouse gas emissions to a large extent compared to Portland cement, depending on the mixture compositions [1,2]. Driven by the increasing interests of low-CO₂ technology and econ-

omy, in the past decades, worldwide scientific research studies have been conducted on geopolymerization and related techniques, and much knowledge has been achieved, from the understanding of reaction paths to the properties control of products [3]. Geopolymer concretes manufactured by alkali activation of fly ash with a certain proportion of slag have been developed and applied since the late of 1990s in China, mostly in corrosive environments where Portland cement products deteriorate too fast [4]. Similar concretes, also called Eco-friendly concretes, are commercially available in Australia and some demonstration projects were built using these geopolymer materials [5].

Despite of the progress in both scientific research and showcase, the usage of geopolymer is still very low in volume, in fact

* Corresponding author at: Centre of Excellence in Engineered Fibre Composites, University of Southern Queensland, Toowoomba 4350, Australia.

E-mail address: Zuhua.Zhang@usq.edu.au (Z. Zhang).

near null compared to Portland cement. Except for the slow regulatory framework progress, such as standard specifications, the complex nature of this class material is probably the biggest barrier. The complexity comes from the source materials and activator and curing scheme as well. In Portland cement concrete, cement is simply mixed with water and other ingredients which are specified and well developed, so the hydration products are predictable over reaction and ageing periods. However, geopolymer concretes usually use fly ash and other industrial wastes as solid materials. These materials are highly heterogeneous and usually vary largely in reactivity. They require different dosages of alkali activators and curing temperatures or periods to achieve satisfying mechanical properties. As a result, the reaction extent of solid materials is usually unpredictable, which in turn leads to hardly controlled properties of geopolymeric gels. This leads to the wide concern of the durability of geopolymer products.

By using metakaolin, a relatively pure and reactive solid material, the recent research has suggested that the alkali activated products have zeolite like structures (mainly analcime-group) at several angstroms [6,7]. These XRD-amorphous products can be regarded as zeolite precursors, which are easily transferred into crystalline zeolites by elevating the reaction temperature, for example, from 25 °C to 40 °C [8], or transformed into dehydrated zeolite phases by heating to a certain temperature [7]. This directly leads to the deduction that the products are thermodynamically unstable. With the assumptions of the thermodynamic parameters of the eventual products, Zhang et al. [8,9] calculated the theoretic reaction extents of both sodium hydroxide and sodium silicate activated systems and proposed that the 'thermodynamical maturity' of the products was only 0.2–0.4 at the corresponding Al/Si and Na/Al ratios, meaning a far way to reach the final crystalline status. This raises the concern of late transition and its consequent impacts. In Lloyd's research [10], accelerated ageing at 95 °C promoted the crystallization of geopolymeric gels in metakaolin-based geopolymer with the designed bulk composition of $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot 13\text{H}_2\text{O}$. The amount of zeolite Na-P1 phase increased significantly (up to ~50 wt.%) during the 28 days of aging and the pores were become larger, accompanying with significant compressive strength loss, by 70%. This partially explained the previous observed strength loss of the metakaolin-based geopolymers by water bath curing at 80 °C for 7 days, which did not show notable volume change [11].

When fly ash is used as solid material, however, the transition from amorphous gels to crystalline zeolites seems to become complex. In Lloyd's research [10] under the same aging conditions of 95 °C, the same zeolite Na-P1 was observed in fly ash-based geopolymers but the content was only about 2–20 wt%, depending on alkali concentrations. The formation of zeolite in fly ash-based geopolymer was found to have less or no accompanying strength loss. It was speculated that the crystallization takes place in the hollows left by reacted ash instead of in the binder itself, which may lead to contribution the strength increase rather than deterioration [12]. The geopolymers that activated by the sodium hydroxide and the mixture of sodium hydroxide and sodium silicate both exhibited increased compressive strength with the 85 °C curing period extended from 5 h to 7 days while the concentrations of crystalline hydroxysodalite and herschelite increased as well [13]. Longer curing periods resulted in more zeolite formed but the compressive strength continued to grow [14]. These results provide some evidences and suggest that fly ash-based geopolymers could be long-lasting materials for building products and construction purposes. However, Mishra et al. [15] reported that the tensile strengths of fly ash-based geopolymers that activated by the mixtures of a sodium silicate and two sodium hydroxide solutions of 10 M and 12 M decreased by about 15% and 40%, respectively, only extending the 60 °C curing from 48 h to 72 h,

while the compressive strength increased. This again raises the concern of the possible late transition in fly ash-based geopolymer products under certain service conditions and its unclear impacts on their macroscale properties.

Understanding the phase stability and relevant kinetics is therefore critical to the durability of geopolymer products. However, it is also very difficult because of the complexity of alkali-activation systems. This study aims to investigate the microstructure evolution during phase transition of the fly ash-based geopolymers that subjected to different ageing conditions. Three typical fly ash-based geopolymers are synthesized: one is activated using concentrated NaOH solution, one is activated using modified sodium silicate activator, and one is blended with 20% slag and activated with sodium silicate activator. This study will contribute the fundamental knowledge to understanding the stability of geopolymer gels and the possible consequence due to later phase transition.

2. Experimental

2.1. Materials

Class F fly ash obtained from Callide Power Station, Queensland, Australia, was used in this work as aluminosilicate source material. Blending slag in fly ash-based geopolymer concrete has been a very common method to obtain fast setting and high early strength in practice. To examine the effects of blending slag, a commercially available granulated blast furnace slag obtained from a local cement company was used in the blend of 80% fly ash and 20% slag. The chemical compositions of the fly ash and slag were determined by X-ray fluorescence (XRF), and the results are shown in Table 1. Fig. 1 shows their mineral compositions tested by XRD using an ARL 9900 Series X-ray workstation (Thermo Scientific) with Co K_α radiation, operated at 40 kV and 40 mA, with a step of 0.02° and count time of 0.33 s from 8° to 80° (2 θ). The fly ash contains certain amounts of crystalline phases, including mullite ($\text{Al}_{1.83}\text{Si}_{1.08}\text{O}_{4.85}$, ICSD# 43298), quartz (SiO_2 , ICSD# 89280), magnetite (Fe_3O_4 , ICSD# 43001), and hematite (Fe_2O_3 , ICSD# 15840). The majority of the slag is amorphous while the calcium silicate (Ca_3SiO_5 , ICSD# 81100) detected is expected due to the contamination of cement clinker when the slag was grounded using the miller at the cement company. A semi-quantitative analysis by XRD indicates that the amorphous phase in the fly ash is about 75% and it is 95% in the slag.

Two activator solutions including a NaOH solution (SH) and a NaOH modified sodium silicate solution (SS) were used. The SH was prepared by solving NaOH pellets (purity of 99%) in water to 12 mol/L, and cooled to room temperature. The SS was a mixture of D-Grade™ (PQ Australia Pty. Ltd.) liquid sodium silicate and the prepared NaOH solution in a ratio of 100:22.1 (in mass) to reach the desired composition of $\text{SiO}_2 = 24.08$ wt.%, $\text{Na}_2\text{O} = 16.58$ wt.% and $\text{H}_2\text{O} = 59.34$ wt.%. This activator solution was allowed to equilibrate for at least 3 h prior to use. Distilled water was used throughout the experimental program.

2.2. Specimen synthesis and ageing

Geopolymer paste specimens were designed at Si/Al ratios of about 1.5 (Table 2). They were synthesized by adding the activator solutions to the solid materials (fly ash, or the blend of fly ash and slag) at a constant Na_2O /precursor mass ratio of 5.8%. The fresh pastes were poured into $\text{Ø}23$ mm \times 24 mm cylindrical molds, covered with plastic sheet (or name sealed) and subjected to curing at 25 °C, RH = 90% for 1 d in an environmental chamber. This initial low temperature curing was employed due to the proven benefit to the strength development in other studies where fly ashes were used as raw materials [16,17]. The specimens were then de-moulded, denoted as 'F100-SH', 'F100-SS' and 'F/S-SS', as shown in Table 2, and subjected ageing at 80 ± 1 °C and 25 ± 3 °C in sealed glass containers, which contained water at bottom to provide high humidity conditions, but not in contact with the specimens. At 1, 7, 14, 28 and 90 days, the specimens were taken out from containers, equilibrated to room temperatures and tested for compressive strength (Table 2). Before testing, the two end surfaces of each cylindrical specimen were carefully sanded flat and parallel. The loading speed of compression was 0.5 mm/min. Four or five specimens were tested for each mix at different ages to give average values. The crushed specimens were stored and grounded in acetone, dried at 105 °C for 6 h for microstructural analysis.

2.3. Characterization

Selected samples were firstly analysed using an ARL X'TRA XRD (Thermo Scientific) at 45 kV, 30 mA, with Cu K_α radiation. The scanning step size was 0.02° and the count time was 3 s. Those shown detectable zeolite phases were further analysed by quantitative XRD analysis. A high purity corundum ($\alpha\text{-Al}_2\text{O}_3 > 99.99\%$)

Download English Version:

<https://daneshyari.com/en/article/256295>

Download Persian Version:

<https://daneshyari.com/article/256295>

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