Construction and Building Materials 156 (2017) 277–283

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Composition and properties of a metakaolin-based geopolymer binder suitable for shaping using a slinger

Erwin Mairitsch [a,*], Harald Harmuth [b]

[a] w&p Zement GmbH, Wietersdorf 1, 9373 Klein St. Paul, Austria
[b] Chair of Ceramics, Montanuniversitaet Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria

HIGHLIGHTS

- The designed geopolymer binder is suitable for pipe production using a slinger.
- The mechanical properties required for piping applications are met.
- Expansion due to carbonation takes place.

ARTICLE INFO

Article history:
Received 30 May 2017
Received in revised form 18 August 2017
Accepted 30 August 2017

Keywords:
Geopolymer binder
Slinger device
Metakaolin
Waterglass activation
Expansion

ABSTRACT

This paper reports the design and properties of a geopolymer binder developed for pipe production using a slinger device, and suitable for transporting low caloric gas at temperatures reaching 500 °C. The influence of curing time at ambient conditions on the durability of the resulting material was investigated. All application and shaping requirements were met. Further, a reaction with atmospheric CO_2 causing expansion during the first 10 days of curing was identified. Controlling this reaction may offer further potential for improvement.

1. Introduction

Geopolymer binders have been known since the last century and have been researched by several authors [1–11]; however, the most significant geopolymer research has occurred in the past two decades. Geopolymers exhibit several excellent properties [12–16] and numerous publications have identified them as eco-friendly binders [17–19]. Industrial interest in these materials has increased in response to recent scientific developments.

This study was developed to support industrial geopolymer applications. Synthetic resin-bounded and glass fibre-reinforced pipes are used in the paper and cellulose industries to transport low caloric gas at temperatures reaching 500 °C for gas post-treatment. The gas forms during production and can contain water vapour, organic substances, N_2, SO_2, SO_3, and small proportions of combustible gases like H_2 or hydrocarbons. These pipes are produced using a slinger and are characterised by the properties of the synthetic resin. However, the synthetic resin is not always thermally stable in this application. Geopolymers may serve as alternative binders that can offer resistance to temperatures reaching 500 °C.

The goal of this study was to design a geopolymer binder that meets material specifications and that can be produced using the slinger device currently used to produce glass fibre-reinforced, synthetic resin-bound pipes. The development of the geopolymer binder was driven by application- and production-related specifications, but the primary focus was application-related.

This application requires a geopolymer with long-term matrix stability. The specifications target the long-lasting technical availability of the shaped material and temperature stability at 500 °C. In addition, sufficient thermal shock resistance is necessary for the start-up and shutdown phases of the industrial process, where the geopolymer is heated to the gas temperature or cooled to ambient conditions.

Another important part of this study focuses on optimising manufacturing characteristics in order to enable production with existing machinery. Pipe production occurs without additional

* Corresponding author.
E-mail address: erwin.mairitsch@zement.wup.at (E. Mairitsch).

http://dx.doi.org/10.1016/j.conbuildmat.2017.08.164
0950-0618/

thermal processing. Therefore, setting and hardening the geopolymer under ambient conditions is crucial. The viscosity of the geopolymer paste is also essential to its workability in centrifugal machines. In addition, the pipe should be manufactured quickly and demoulded immediately after processing. Thus, the setting time and the period between the initial and final sets are important. Moreover, good compressive strength is required for pipe stability and post processing. Every portion of the specifications is important to ensure processability using the present equipment.

As far as the authors know, literature regarding the application of geopolymer binders to pipe manufacturing and slinger shaping is not available. Davidovits [13] addressed aluminosilicate inorganic polymers formed via aluminosilicate polycondensation. According to Davidovits [13] and other researchers [11,14,15,20,21], a wide range of aluminosilicate raw materials can be used for alkali activation. Geopolymerisation is a complex process in which the activator is essential to starting the chemical reaction and acts as a structure-forming agent [13–15,22–24]. These materials determine the reaction mechanism and the structure formed. Davidovits [13], Pacheco-Torgal et al. [14], and Provis and van Deventer [15] also showed that the structure and consequently the properties of a geopolymer binder depend on both the source materials and the binder design. The formulation significantly affects the applicability of the resulting material [25–29].

A geopolymer binder was designed and characterised based on these requirements. The influence of curing time at ambient conditions on the resulting matrix and the durability of the hardened paste are discussed in the present paper. The effect of curing was investigated via compressive strength and length-change testing, X-ray powder diffraction (XRD), and scanning electron microscopy (SEM). Although it is not required for durability, the freeze–thaw resistance was also examined.

2. Materials and methods

2.1. Materials

2.1.1. Metakaolin

The aluminosilicate raw material used in this study was metakaolin (MK) Metaver R, supplied by NEWCHEM AG, Switzerland. The chemical composition was analysed via X-ray fluorescence (XRF) spectrometry (Axios mAX, PANalytical B.V., Netherlands), with results summarised in Table 1. The raw material comprised 93.31 wt% silica (SiO_2) and alumina (Al_2O_3). The SiO_2-to-Al_2O_3 mass and molar ratios were 2.37:1 and 4.02:1, respectively. The residual oxides included CaO, MgO, Fe_2O_3, K_2O, Na_2O, TiO_2, and MnO. The particle size distribution (PSD) was determined using a particle size analyser with a laser diffraction sensor (Helos BF, Sympatec GmbH, Germany). The PSD indicated that 100% of the volume was smaller than 174.00 μm, with a d_{50} value of 18.10 μm. The bulk density (ÖNORM EN 196-6:2010 [30]), specific surface area (Blaine [30] and Brunauer–Emmett–Teller (BET)), and grain size distribution characteristics are presented in Table 2. The BET specific surface areas were measured via nitrogen adsorption. XRD indicated the presence of quartz, mullite 3:2, dickite, muscovite, calcite, dolomite, and anatase. The phase composition was determined quantitatively by adding an internal standard (20 wt% rutile) and performing Rietveld refinement. The majority of the sample was amorphous (58.3 wt%). The X-ray analysis showed that the major crystalline phase was quartz (30.9 wt%). The residual crystalline fraction comprised dickite (4.1 wt%), muscovite (2.1 wt%), and calcite (2.1 wt%) with small portions of mullite 3:2, dolomite, and anatase. The particle morphology was studied via SEM. The backscattered SEM micrograph (Fig. 1) shows irregularly shaped particles with various grain sizes. SEM investigation does not indicate spherical morphologies.

2.1.2. Waterglass alkali activator solution

The alkaline activator solution was produced by combining two commercial potassium waterglasses (KWs) of Betol K 35 T (KW1) and Kaliumsilikat K 57 M (KW2), supplied by Woellner GmbH, Germany. The chemical composition, SiO_2/K_2O and H_2O/K_2O molar ratios (MRs), and physical properties of both waterglasses were provided by the supplier as given in Table 3. KW2 has an alkali concentration three times that of KW1. Both KWs have similar dissolved silicate contents. The solid contents ($SiO_2 + K_2O$) of KW1 and KW2 are 34.82 wt% and 52.00 wt%, respectively. KW1 has SiO_2/K_2O and H_2O/K_2O MRs of 3.4 and 4 times higher than those of KW2, respectively. KW1 is slightly less viscous and less dense than KW2. The fabrication of the alkali activator solution is described in Section 2.2.

2.2. Specimen preparation

2.2.1. Binder design

The design of the geopolymer binder was determined by the material requirements described in Section 1, and by production-related specifications necessitated by the existing slinger device (Fig. 2). Pipe manufacturing was performed using existing slinger devices in ambient conditions. The process was almost continuous and could be divided into formation by a centrifugal machine and rectification of rejects via methods such as cutting or surface treatment, followed by storage. The material was conveyed between the different steps mechanically. Centrifugal casting required a continuous binder supply to the rotating mould, which resulted in a defined wall structure and high dimensional accuracy. The binder was introduced by the feeder arm via the nozzle into the mould. The forward and backward movement of the feeder arm allowed an even distribution of the binder. The large centrifugal forces were controlled via the roller speed to enable high compaction of the material. Shaping proceeded rapidly and the resulting pipe could be directly demoulded afterwards. A pipe length of 800 mm and outside diameter of 300 mm were specified in order to fit existing machinery.

Certain properties must be considered to support manufacturability. In particular, the binder must set and harden in ambient conditions, without thermal processing. A certain viscosity (ISO 2555:1989 [31]) is also required for centrifugal casting. For rapid, continuous fabrication, the setting times (ÖNORM EN 196-3:2009 [32]) and the period between initial and final sets must be within specified limits. Sufficient compressive strength is required for stability and post processing. These requirements are the key characteristics resulting from the production of glass fibre-reinforced, synthetic resin-bound pipes by means of the centrifugal casting process using existing slinger devices. Each of these properties must be within the established limits to ensure successful pipe production. The specifications for and characteristics of the geopolymer binder are shown in Table 4.

The structure and properties of a geopolymer binder depend both on the characteristics of the source materials and on the proportions of the activator solution and aluminosilicate material used. The literature presents a common method of designing a geopolymer by targeting MRs using component chemical analysis data [1,2,12–15,26]. These ratios are Si/Al, K_2O/Al_2O_3, SiO_2/K_2O, and H_2O/K_2O. The molar ratio Si/Al is fundamental to the matrix and thus provides an opportunity for classification by application [2,12,27–29]. Davidovits et al. [2] proposed the use of Si/Al ratios above 3 for temperatures reaching 600 °C. The K_2O/Al_2O_3 ratio affects the structure and properties like strength and durability of the hardened paste. A ratio of 0.8–1.6 is required for high strength and durability. Obviously, a value of at least unity is needed to balance the charge caused by the presence of tetrahedral Al^{3+} instead of Si^{4+}; a value of 1.00–1.14 is recommended [9,14,27]. K^+ was chosen due to its ability to form large aluminosilicate oligomers [22] and because it enables faster polycondensation than Na^+. These characteristics result in a denser framework and a steady geopolymer matrix [13,14,16,22]. The activator solution is characterised by the SiO_2/K_2O ratio, which particularly affects the resolution of the raw material and the polycondensation capabilities of the monomer and oligomer units. The literature suggests that a ratio of 1.0–1.5 is needed for high resolution and a high degree of polycondensation [14,23–25]. The H_2O/K_2O ratio influences the workability of the fresh geopolymer paste. Davidovits [13] proposed a molar ratio of 10–25 for good workability. The geopolymer binder was formulated by using preliminary tests to investigate the specification limits. The binder composition and associated MRs are presented in Table 5.

2.2.2. Mixing and curing methods

Sample preparation and manufacturing steps, other than binder formulation (Section 2.2.1), were performed in accordance with the ÖNORM EN 196-1:2005 standard [33]. This standard describes specimen preparation as well as strength determination for cement-based mortars. The activator solution was prepared in advance by mixing both potassium waterglasses listed in Table 3 for 60 s. The geopolymer paste was produced using a Hobart mixer (Model 1551, Toni Technik GmbH, Germany). Because of the fineness of the material, the metakaolin was added to the activator solution within the first 60 s of mixing. After homogenisation, the fresh paste was poured into the prepared moulds, compacted, and wrapped in plastic film to prevent water evaporation. The specimens were cured for 24 h at 20 ± 2 °C and 50 ± 10% r.h. The samples were removed from the moulds after 1 d. Depending on the analytical needs, either testing started immediately or the samples were stored in the conditions previously described until testing.

Table 1
Chemical composition of metakaolin used in this work, as measured via XRF (LOI = loss of ignition).

Composition [wt%]	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Na_2O	TiO_2	MnO	LOI
Metakaolin	65.63	27.68	1.16	0.33	2.79	0.36	0.23	1.59	0.24	1.69