Construction and Building Materials 149 (2017) 248–256

Contents lists available at ScienceDirect

Construction and Building Materials

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

Development of mixture design of heat resistant alkali-activated aluminosilicate binder-based adhesives

Pavel Krivenko *, Oleg Petropavlovsky, Hrygorii Vozniuk

V.D.Glukhovsky Scientific Research Institute for Binders and Materials, Kiev National University of Construction and Architecture, Ukraine

HIGHLIGHTS

- Thermo-resistant adhesives are based on alkali-activated aluminosilicate binders.
- Reaction products of the formulated binders are represented by zeolites.
- The adhesives are intended for work at high temperatures (up to 900 °C).

ARTICLE INFO

Article history:
Received 28 February 2017
Received in revised form 11 May 2017
Accepted 15 May 2017

Keywords:
Adhesive
Alkaline activation
Aluminosilicate
Binder
Heat resisting
Zeolite

ABSTRACT

The study was aimed at producing adhesives with improved thermo-mechanical properties and environmental friendliness and heath safety using alkali-activated aluminosilicate binders in order to meet today's requirements.

A relationship between phase composition of the reaction products after hardening in normal conditions and heating has been established and properties of the formulated alkali-activated aluminosilicate binders and adhesives based on them have been determined.

Optimization of binder composition in terms of strength characteristics after hardening and heating has been performed using a two level factorial experiment design with three factors. The results of the study suggested showing that high performance properties of the binders could be provided through a proper choice of optimal ratios of sodium and potassium gel and crystalline structures (zeolites) that were capable to smooth dehydration and following recrystallization into anhydrous compounds of the nepheline and leicite types. These anhydrous compounds determine thermal stability of the resulted artificial stone under action of high temperatures (up to 900 °C). The study held allowed to establish optimal ratios of oxides: $[(0.5–0.75)Na_2O + (0.25–0.5)K_2O]/Al_2O_3 = 1$; $SiO_2/Al_2O_3 = 4$; $H_2O/Al_2O_3 = 12$.

The developed adhesives exhibit high values of thermo-mechanical characteristics in the conditions of use temperatures reaching 900 °C (adhesion strength – 0.92 to 1.6 MPa, compressive strength up to 68 MPa, coefficient of liner thermal expansion up to $8.51 \cdot 10^{-6}\,C^{-1}$, residual adhesion strength up to 88%, shrinkage up to 1.72%).

The developed adhesives have been tried on a pilot scale and used in commercial-scale production of fire resistant structures such as lift doors and frames, as well as tried in bonding heat insulation boards to boilers with surface temperatures over 500 °C.

1. Introduction

With consideration of today's requirements with regard to adhesives, these are: reduced energy consumption in production, high workability (easiness-in-work) in application, high performance properties (good adhesion to various materials, ability to harden not only in normal conditions but at high temperatures, combination of high strength and thermo-resistance at use temperatures up to 900 °C), as well as health safety and environmental friendliness, an assumption was put forward that the best solution to meet these requirements could be adhesives based on alkali-activated aluminosilicate binders [1]. Starting 1957, the Scientific Research Institute for Binders and Materials has been involved in the works on development of inorganic polymers based on alkaline – alkaline earth metal compounds [2]. Studies on directed synthesis of alkaline – alkaline earth aluminosilicate hydrates which at

* Corresponding author.
E-mail addresses: pavlo.kryvenko@gmail.com (P. Krivenko), petropavlovskii@mail.ru (O. Petropavlovsky), belinea2005@ukr.net (H. Vozniuk).

http://dx.doi.org/10.1016/j.conbuildmat.2017.05.138
0950-0618/

the moment of formation and crystallization are able to expose binding properties have been taken as theoretical bases [3].

According to the classification proposed in [4], the alkali-activated aluminosilicate binders belong to the first class of alkali-activated cements – geocements, basic composition of hydration products of which is represented by alkaline and alkaline earth aluminosilicate hydrates – analogs of natural minerals of the zeolite and feldspathoid types [5–7], which are themselves inorganic polymers with three-dimensional framework structure [8]. The geocement-based materials are capable to polycondensation and can acquire quickly a required form at low temperatures (within a few hours at 30 °C and a few minutes at 140 °C), thus predetermining a possibility to use them as thermo-reactive resins. They exhibit high rigidity, weather resistance and ability to withstand high temperatures [9]. With consideration of the data on stability of phase transformations in the alkali-activated aluminosilicate binders when heated [10] and the experience collected from their use in various applications connected with service in high temperature conditions [11–15]. Since previous attempts did not satisfy completely the current needs, the purpose of the study was to develop adhesives from the alkali-activated aluminosilicate binders for high temperature uses with higher characteristics and to check their efficiency in pilot and industrial application.

2. Materials and testing

2.1. Constituent materials

The alkali-activated aluminosilicate binders were prepared using metakaolin with fineness of 8500 cm^2/g (specific surface by Blaine) as an aluminosilicate constituent and amorphous silica with fineness of 8000 cm^2/g (by Blaine) as a siliceous constituent. When required, in order to accelerate hardening process in air-dry conditions a ground granulated blast-furnace slag (ggbs) with fineness of 4000 cm^2/g (by Blaine) in quantities up to 10% of binder mass was added.

Chemical composition of the constituents according to the product data sheets of the suppliers is given in Table 1.

Soluble sodium silicate (silicate modulus $M_s = 2.8$ and density $\rho = 1400 \pm 10$ kg/m^3) was used as an alkaline component. Sodium and potassium hydroxides were added, when required.

According to X-ray powder diffraction data (Fig. 1, Curve 1), phase composition of the metakaolin is represented by X-ray amorphous substance, kaolinite relicts (low intensity peaks with d = 0.712, 0.357, 0.261) and β-quartz (d = 0.424, 0.334, 0.187).

The X-ray patterns of the amorphous silica showed high degree of its amorphization (Fig. 1, Curve 3).

The alkali-activated aluminosilicate binders of the composition Me_2O-Al_2O_3-SiO_2-H_2O varying in ratios of constituent oxides: $Na_2O/Al_2O_3 = 0.5$ –1, $K_2O/Al_2O_3 = 0.25$ –0.5 at $(Na_2O + K_2O)/Al_2O_3 = 1$, $SiO_2/Al_2O_3 = 3$ –5 and $H_2O/Al_2O_3 = 10$ –14 have been chosen.

Gels of aluminosilicate composition varying in ratios of basic structure- forming oxides have been synthesized in order to study

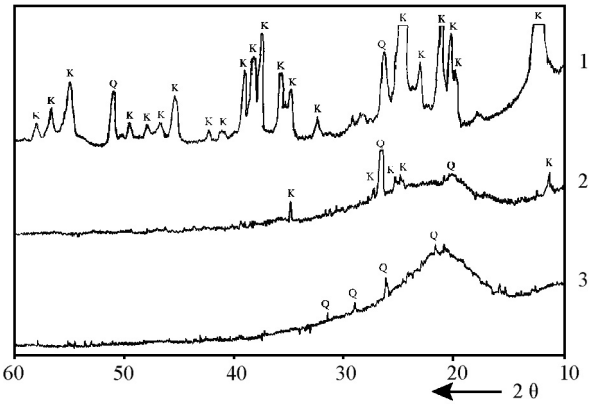

Fig. 1. X-ray patterns of the constituent materials: 1 – kaolin, 2 – metakaolin (K – kaolinite, Q – β - quartz), 3 – amorphous silica.

reaction products of the formulated binders. The ratios of oxides which would allow to synthesize zeolites of the required composition have been taken with account of recommendations given in [16–20].

Quartz sand and chamotte fines (both composed of fractions 0.14 and 0.315 mm)(both in quantities from 90 to 110% of binder mass) as well as mica (commercial product– "Mika 40") (0–10% of binder mass) were used as fillers.

2.2. Examination and testing techniques

Choice of examination and testing techniques was determined by intended use of the adhesives.

Phase composition of the constituent materials and that of the alkali-activated aluminosilicate binder reaction products were identified with the help of set of physico-chemical examination techniques, these were: X-ray powder diffraction, differential-thermal analyses, scanning electron microscopy and infrared spectroscopy.

X-ray powder diffraction analysis was done using a diffractometer DRON-2 M on powder samples. The patterns were acquired - from the angles $2\Theta = 10$ to 60° at speed of counter rotation of 2°/min. The X-ray phases were identified using ICDD–PDF2 database (Reliese 2000) after the formulated binders hardened for 28 days in air-dry conditions and after treatment at 80 °C.

Scanning electron microscopic examination of the resulted microstructure was done using a microscope REMMA – 101A by a method of copper replica in accordance with the procedure described in [21]. Identification of the reaction products was done using the data given in [22] after the formulated binders hardened for 28 days in air-dry conditions and after treatment at 80 °C.

Infrared spectroscopy was done using an infrared spectrophotometer IKS-40 with application of standard procedure by grinding a sample to fine powder and mixing of the powder in vaseline oil with KBr and placing into a cell, after this a spectrum was taken within the range of 400–4000 cm^{-1}. An accuracy of measurement of oscillation frequencies of adsorption was ±0.5%. Identification

Table 1
Chemical composition of constituent materials according to the product data sheets.

Constituent material	Mass percentage of oxides and chemical elements												
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	S	Al	C	SO_3	LOI
Kaolin	48.40	37.27	0.43	0.29	0.25	0.05	Traces	Traces	–	–	–	0.13	13.18
Metakaolin	53.16	43.19	0.76	0.73	0.51	Traces	0.74	0.25	–	–	–	0.13	<0.49
Amorphous silica	92.2	0.94	0.25	–	1.49	–	Traces	0.36	0.08	0.23	1.5	–	2.87
Ground granulated blast-furnace slag (ggbs)	38.28	6.52	–	–	45.46	0.24	–	–	1.89	–	–	–	–