



Development of inorganic polymer by alkali-activation of untreated kaolinitic clay: Reaction stoichiometry, strength and dimensional stability



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HIGHLIGHTS

- Kaolinite can be alkali activated resulting in hydroxysodalite.
- Reaction product is a strong and stable building material.
- Maximum mechanical strength (50 MPa) is obtained at about 50% of kaolinite conversion.

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ABSTRACT

An environmental friendly building material was developed by alkali-activation of untreated kaolinitic clay using sodium hydroxide. The reaction was studied using differential scanning calorimetry. The chemical structure of the produced inorganic polymer was deduced from infrared spectroscopy, X-ray powder diffraction, thermogravimetric analysis, and scanning electron microscopy to be the tetrahydrate phase of hydroxysodalite with a Na/Al ratio of 4/3. Its strength and stability were evaluated in terms of compressive strength under dry and saturated conditions using different ratios of mixing water and NaOH. The compressive strength of dry samples ranges between 45 and 50 MPa. The wet samples after soaking in water show a strength between 20 and 25 MPa, and the wet samples after alternating cycles of drying and wetting also show a strength of 20–25 MPa.

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1. Introduction

The development of building materials by alkali-activation of aluminosilicate materials has been studied extensively, due to their potential in producing binding materials competitive to ordinary Portland cement in terms of strength and durability [1–7] while less CO₂ is emitted [8–10]. Different terms are used to describe the alkali-activation products of aluminosilicate materials but the most appropriate broad term is inorganic polymers [1,11].

As during the reaction a three dimensional silicate network is formed, the term ‘inorganic polymer’ is appropriate. The backbone consists of Si–O and Al–O bonds, forming an inorganic material with an infinite structure. To make the distinction between a polymer and a three dimensional structure that cannot be called a polymer, the behavior in the molten state or in solution is looked at. A polymer retains some of its properties in the molten state. That is the reason why the viscosity of silicates is very high in the melt, while the viscosity of molecular or ionic solids such as NaCl is comparatively low. Another way to make the distinction is via the theory of fragile and strong solids/liquids. Also from this theory it is clear that most silicates are polymers.

In this work inorganic polymers are formed from a two component systems including reactive aluminosilicate powder and

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alkaline activator. For workability and reactivity reasons, most aluminosilicate materials used for the alkali-activation process are thermally activated materials such as metakaolinite [12,13], industrial wastes such as fly ash [14,15], or (blast furnace) slag [16–18]. Some work also has been presented on the production of inorganic polymers from untreated kaolinite and NaOH [5,6]. The most used alkaline activator is a mixture of alkali–metal hydroxide (NaOH, or KOH) with an alkali–metal silicate solution ($n\text{Na}_2\text{O}\cdot\text{SiO}_2$, or $n\text{K}_2\text{O}\cdot\text{SiO}_2$) [1–4].

Life Cycle Assessment (LCA) shows that the alkali–silicate solution used as activator has a large contribution to the ecological impact [10]. Replacing the silicate solution by NaOH or KOH would be beneficial. Also using naturally occurring aluminosilicate materials such as kaolinite without being thermally activated would further reduce CO_2 emissions [8,9]. At the Department MEMC of VUB, several unpublished master thesis works have investigated between 1985 and 2000 the stabilization of kaolinitic soils or B-horizon of latosols with NaOH solution for use as building material.

Compared to previous work on the alkali-activation of kaolinite [5–7] and to the best of the authors knowledge, neither the influence of cure temperature nor the stoichiometry of the reaction have been investigated in detail. Hence, the present work aims at studying these aspects. Next to a kaolinite containing clay a reference kaolinite will be used as a model system. Calorimetry will be used to estimate the reactivity and to get a first idea of the stoichiometry. For construction applications, the produced inorganic polymer specimens are tested under dry and saturated conditions to evaluate their strength and stability.

2. Materials and methods

2.1. Materials

Jordanian kaolinitic clay (JC) was collected from Batn el-Ghoul deposit, which is located in the southern part of Jordan about 280 km from Amman. The clay reserve of this deposit was estimated by the Natural Resources Authority of Jordan (NRA) to be around 2200 Megatons [19]. Homogeneity of the clay sample was insured by collection of 2 ton gross sample which was crushed using a cone crusher (TRIO model TC36) equipped with micro-filters to produce particles with size $<425\ \mu\text{m}$, which were packed in 50 kg plastic bags. According to the sieve analysis [20] about 95% of the particles are less than $20\ \mu\text{m}$. The plastic limit of the clay was determined according ASTM D4318 [21] to be 24%.

As a reference, a standard kaolinite (SC) sample known commercially as KGa-1a clay was supplied by the Source Clay Minerals Repository (University of Missouri, Columbia) with a purity of 98%. KGa-1a is a well crystallized kaolinite from Washington Country, Georgia [22].

Silica sand was used as filler material during the evaluation of the inorganic polymers' strength and stability. Commercial silica sand type M31 was supplied by S.C.R Sibelco (Belgium). The average grain size was about $260\ \mu\text{m}$.

The NaOH solution was prepared by adding a weighed amount of demineralized water to NaOH pellets (Merck, 98.0%) in a plastic bottle. The bottle was closed to avoid evaporation and carbonation. The solution was allowed to cool down to ambient temperature before mixing with the other components.

2.2. Analytical techniques

2.2.1. DSC measurements

Differential scanning calorimeter (Mettler Toledo, DSC822E) equipped with mechanical cooling system was used to determine the lowest temperature that is needed to initiate the kaolinite alkali-activation reaction, as well as the temperature and NaOH ratio that achieve the maximum yield of the product. About 30 mg sample of paste was placed in a reusable high pressure gold plated stainless steel pan. The samples were heated from 30 to $290\ ^\circ\text{C}$ with a scan rate of $5\ ^\circ\text{C}/\text{min}$. The second heating scan was used to produce the baseline for calculating the total reaction heat. Each experiment was conducted twice and the reported enthalpy of the reaction is the mean of two experiments.

2.2.2. IR, XRD, TGA and SEM characterizations

The reaction stoichiometry that governs the alkali-activation of kaolinite and its products, was studied by IR, XRD, TGA and SEM. The infrared spectra were taken using a Thermo Scientific Nicolet spectrometer (model IS50R) coupled with a Thermo Scientific Smart iTR single reflectance diamond crystal (ATR attachment).

The sample was mounted directly onto the ATR crystal and clamped with a built-in press delivering pressures up to 60 MPa to obtain good contact. Spectra were collected from 4000 to $650\ \text{cm}^{-1}$ at a resolution of $2\ \text{cm}^{-1}$.

The mineralogical composition was investigated by XRD, using a Siemens 500 Kristalloflex instrument, with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418\ \text{\AA}$) and a scan rate of $2\ ^\circ/\text{min}$. The thermal behavior of the inorganic polymer was studied by TGA analysis. The analysis was performed by using TA Instrument equipment (model TA-TGA Q5000). The samples (approximately 36 mg) were heated in a platinum cup at a rate of $10\ ^\circ\text{C}/\text{min}$, starting from $50\ ^\circ\text{C}$ up to a maximum temperature of $1000\ ^\circ\text{C}$ using N_2 as a purge gas.

A PhenomProX scanning electron microscope with EDX system was used for SEM/EDX analysis at the acceleration voltage of 15 kV. The samples were placed on carbon tape on a sample holder.

2.2.3. Mechanical strength characterization

The prepared specimens were tested in terms of density, water absorption, and uniaxial compressive strength. The density was measured in order to evaluate the degree of grain packing after the mixing and compacting process. The density after curing (d_{dry}) was determined by considering the mass using an analytical balance (Sartorius-BP4100S, $\pm 0.01\ \text{g}$) and dimensions using a digital caliper ($\pm 0.01\ \text{mm}$).

Water absorption was evaluated after immersion of specimens in demineralized water for one week, by calculation of the amount of absorbed water as given in Eq. (1):

$$W_{\text{abs}} = ((M_s - M_d)/M_d) \times 100\% \quad (1)$$

where W_{abs} is the absorption of water, expressed as a mass percentage, M_d is the mass of the specimen after curing (g), and M_s is the mass of the specimen after immersion (g).

Uniaxial compression test was performed using a universal testing machine (INSTRON 1195). The load was applied at a controlled displacement rate of 2 mm/min. The unconfined compressive strength was determined according to Eq. (2):

$$S = F/A \quad (2)$$

where S is the compressive strength (N/mm^2 or MPa), F is the maximum load applied before failure (N) and A is the cross section of the specimens (mm^2).

2.2.4. Fabrication of inorganic polymer specimens and pre-test treatment

Throughout the present work preparation of the specimens involved mixing of specific ratios of the clay, sand, NaOH and water. The produced inorganic polymer was identified by the ratios of the above-mentioned materials used to produce it. The procedure of specimens' fabrication and pre-test measurements involved three stages (Fig. 1). Ten different samples with different compositions were prepared to study the thermal behavior of the alkali-activation progress (stage 1), and the reaction stoichiometry (stage 2), as shown in Table 1. The NaOH solution was prepared by using equal mass amounts of NaOH and demineralized water, and added in mass amounts to the JC and SC clay ranging from 20% to 100%. The sample code used is the mass ratio of clay:sand:NaOH:water preceded by the clay type, where the clay mass is as a reference set to 100. For the thermal behavior study, paste samples were characterized immediately after mixing the ingredients (clay, NaOH and water).

The reaction stoichiometry study was done on inorganic polymer powder samples, which were first cured in a ventilated oven at $80\ ^\circ\text{C}$ for 24 h, and afterwards crushed and sieved ($<75\ \mu\text{m}$) before characterization.

The evaluation of the strength and stability of the inorganic polymers produced with the Jordanian kaolinitic clay (JC), (stage 3), was performed on cylindrical specimens following standard test procedure [23]. Sand was used as filler material in this stage. It has been reported [24] that the strengthening effect of fillers on concrete material derives from improving the particle packing or pore structure, and reducing drying cracks caused by drying shrinkage. The mass ratio of clay:sand was fixed to be 100:100 by experience, based on workability and compactibility of the fresh mixture. Moreover, the addition of sand permits to reduce the amount of activator, which is the most costly component. It was found [4,5] that for a good compromise between mixture workability and strength properties, the optimal ratio of water should be close to, but lower than the plasticity limit of the clay material (24%).

Nine series of cylindrical specimens were prepared with different composition ratios of NaOH and mixing water (Table 2). A first series was produced to investigate the influence of the amount of water on the strength. A minimum ratio of 16 was needed to provide enough cohesion needed for compaction and demolding, so ratios of 16, 18, 20 and 22 were studied. A second series kept the ratio of water constant at the obtained optimum, while the ratio of NaOH was increased from 10 to 18 to investigate its influence on the obtained strength.

Cylindrical specimens were prepared by mixing clay and sand for 5 min at 107 rpm using a Hobart planetary mixer (model A200). The NaOH solution was mixed with the solid components for 10 min at 198 rpm. Each mixture was divided into nine specimens (about 50 g each) and molded immediately in a stainless steel cylinder (internal diameter 25 mm, height 150 mm) with a plunger at a pressure of 15 MPa. The demolded specimens were cured for 24 h at $80\ ^\circ\text{C}$ using a – ventilated

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