

Synthesis of geopolymers using natural resources for green construction materials

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Abstract: This work aims to investigate the use of alkali activated metakaolinite from natural kaolinitic soil as precursors for the production of geopolymer cement for green construction materials. Geopolymer cement was synthesized using metakaolinite, and alkaline activators, namely sodium silicate (Na_2SiO_3) and sodium hydroxide. For metakaolinite preparation, Kaolinitic soil sample was collected from kaolin deposit (Saudi Arabia), which is located in Riyadh region. XRD analysis showed that kaolinite phase, was diminished due to calcination and geopolymerization. The geopolymer cement exhibits a residual metakaolin layers bonded by geopolymer gel as shown by SEM analysis. The produced geopolymer cement exhibited a flexural strength of 12.3MPa, and compressive strength of 32MPa and 44.2MPa under immersed and dry conditions. The produced geopolymer was characterized by relatively low density, 1.45 g/cm³, and comparable water absorption, 15% (w/w), compared with other cement-based materials. The general evaluation of the produced geopolymer cement from kaolinitic soil indicates its potential for a number of applications including green construction materials.

Key-Words: Geopolymers, Kaolinite, SEM, Construction, Minerals, Water absorption, Strength

1 Introduction

As a result of geopolymerization, aluminosilicates such as kaolinite can be stabilized and transformed into geopolymers [1-3]. Geopolymers consist of an amorphous, structure resulting from the transformation of aluminosilicate monomers in an alkaline solution [4,5]. The geopolymerization setting reactions involving polycondensation of hypothetical monomers, i.e. orthosialate ions, has been proposed. As a result of these reactions, solid, hard, and stable materials similar to hydroxysodalite, feldspatoid or zeolite are formed [6]. These geopolymers are composed from SiO_4 and AlO_4 tetrahedra linked alternately by sharing all the oxygen atoms. When aluminum is four coordinated to oxygen atoms, a negative charge is created and therefore the presence of cations such as

(Na^+ , K^+ , Li^+ , Ca_2^+ , Ba_2^+ , NH_4^+ , and H_3O^+) is essential to balance the negative charge of Al in the fourfold coordination [7].

Geopolymers cement has recently received wide attention in view of their advantages over other cementitious materials, like Portland cement. Some of the advantages are high strength, low environmental impact, chemical resistance and thermal stability [8-10]. Geopolymer cement results from the geopolymerization of aluminosilicate monomers in an alkaline solution; the products obtained are considered ceramic-like materials. Kaolin clay is an abundant natural resource and readily commercially available. The objective of this work is to determine if a low purity kaolin mineral from mineral deposits in Saudi Arabia can be successfully used to produce alkali-activated

geopolymer cement. The investigation addressed the synthesis and evaluation of geopolymer cement using low purity kaolinite from Saudi Arabia, in terms of microstructure, mechanical, and physical properties. The significance of this research is to encourage the commercializing of the geopolymer cement by using low cost, and available in large amounts precursors such as low purity kaolin from local deposits [11-16].

2 Materials and methods

2.1 Materials

Geopolymer cement was synthesized using kaolinite from natural deposit, sodium silicate (Na_2SiO_3) and sodium hydroxide. Untreated kaolinite was collected from a deposit in Riyadh region (Saudi Arabia) with the assist of Saudi Ceramic Company. Preparation of the kaolinite samples involved crushing of oven dried clay (at 105°C) with a grain size less than $60\ \mu\text{m}$. The powdered clay was heated at 750°C for 4 h in a laboratory furnace to obtain its respective metakaolinite. The chemical composition of kaolinite was determined by X-ray Fluorescence (XRF) (Bruker System S4 Pioneer) and is given in Table 1. Na_2SiO_3 and NaOH solutions were used as alkaline activators for the dissolution of aluminosilicate phases. Sodium silicate solution (Merck, Germany) contained 27% SiO_2 and 8% Na_2O . The hydroxide solution with a concentration of 6.0 M was prepared using sodium hydroxide (NaOH) flakes of 98% purity (Merck) and distilled water.

Table 1, Chemical analysis of untreated kaolinite

Compound	Composition%
MnO	0.3
Cr_2O_3	0.4
CaO	1.1
K_2O	0.1
P_2O_5	0.9
Fe_2O_3	9.3
Al_2O_3	22.5
SiO_2	38.1
TiO_2	14.2

2.2 Production of geopolymer cement

The ratios used during the alkaline activation process were: SiO_2 (in sodium silicate

solution)/ Al_2O_3 (in metakaolinite) molar ratio of 1, and Na_2O (in sodium silicate and NaOH solutions)/ Al_2O_3 (in metakaolinite) molar ratio of 1. The $\text{H}_2\text{O}/\text{Na}_2\text{O}$ molar ratio was 13. The aqueous solution of Na_2SiO_3 , NaOH and H_2O was mechanically mixed for 1 min. Metakaolinite was mixed with the sodium hydroxide and sodium silicate solutions for 15 minutes. The final pulp was poured into three rectangular molds ($160\text{mm}\times 15\text{mm}\times 30\text{mm}$ each) which were cured in a ventilated oven (Binder-ED115, Germany) at 40°C for one day. After curing, specimens were removed from the molds and cooled at room temperature. In addition, three discs ($2\text{cm}\times 2\text{cm}\times 1\text{cm}$) were prepared from each mixture, to carry out microstructural and mineralogical studies using XRD, TGA and SEM.

2.3 Mineralogical analyses

X-ray diffraction (XRD) analyses were carried out on powdered samples to identify major crystalline and potentially newly formed phases using a Shimadzu diffractometer-6000 (Japan) with a Cu tube and a scanning range from 5° to $80^\circ 2\theta$ at a scan rate of $2^\circ/\text{min}$. Qualitative analysis was carried out using the crystalline phases were identified by detecting and analyzing the positions of the peaks using the software package supplied with the instrument. The morphology of the specimens was studied using an Inspect F50 scanning electron microscope (Netherlands). The samples were pre-coated with platinum under an argon atmosphere. Energy-dispersive X-ray spectroscopy (EDX) was used for elemental analysis and chemical characterization of samples.

2.4 Mechanical and physical characterizations of geopolymer cement

The fabricated specimens for each series were tested for the water absorption, the density, the flexural strength and the compression strength. Water absorption of the immersed specimens (Group-2) was calculated for each series according to the following equation.

$$W \% = ((W_w - W_d)/W_d) \times 100 \%$$

Where, $W\%$ is the absorption of water expressed as percentage; W_w and W_d are the weights of the immersed specimen and of specimens after drying, respectively. For density measurements, the eight specimens after the curing were weighed using an electronic balance and their dimensions were measured using a digital micrometer. The specimens

were tested in three-point bending and in compression. Testing was performed at room temperature with a universal testing machine. The bending specimen's dimensions were: height=15 mm, width=30 mm and length 160 mm, the distance between the supports was 120 mm and the speed of the machine head during testing was 0.1 mm/minute. Compression tests were performed on the failed bending specimens, placed on their side with a loading area=40×15 mm² and height=30 mm. The speed of the machine head during testing was 2 mm/minute.

3 Results and discussion

3.1 Microstructural characteristics and phase composition

The XRD patterns of kaolinitic soil and produced geopolymer cement are reported in Fig.1. The results show that most the identified peaks are corresponding to kaolin, Fig1-up. As a result of calcination and metakaolinite-alkali geopolymerization a high background seen in XRD patterns, Fig. 1-down, between 20° to 40° indicates the presence of amorphous phases [17]. The amorphous phase detected could be albite since the K⁺ content in the reactants (kaolinite and Na-silicate solution) is very low compared to Na⁺. The diminishing of XRD peaks corresponding to kaolinite and the formation of amorphous phase (gel) indicate to the high percentage of the geopolymerization of kaolinitic soil. The geopolymer gel is considered as the binder material of the end products as shown by the SEM analysis, Fig.2. The formation of high amount of binder material is an indication of the high mechanical performance and stability of the produced geopolymer cement [3].

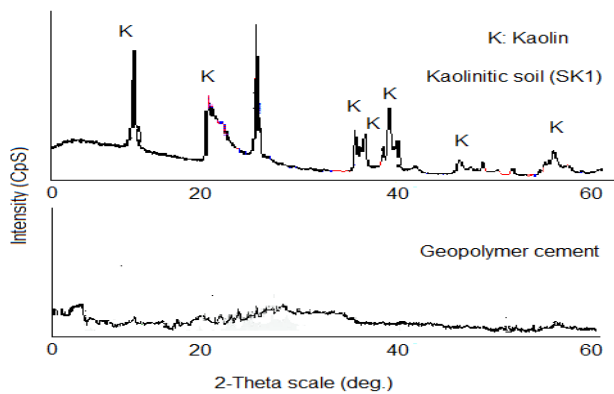


Fig. 1, Qualitative XRD patterns of powdered kaolinitic soil, and powdered geopolymer cement

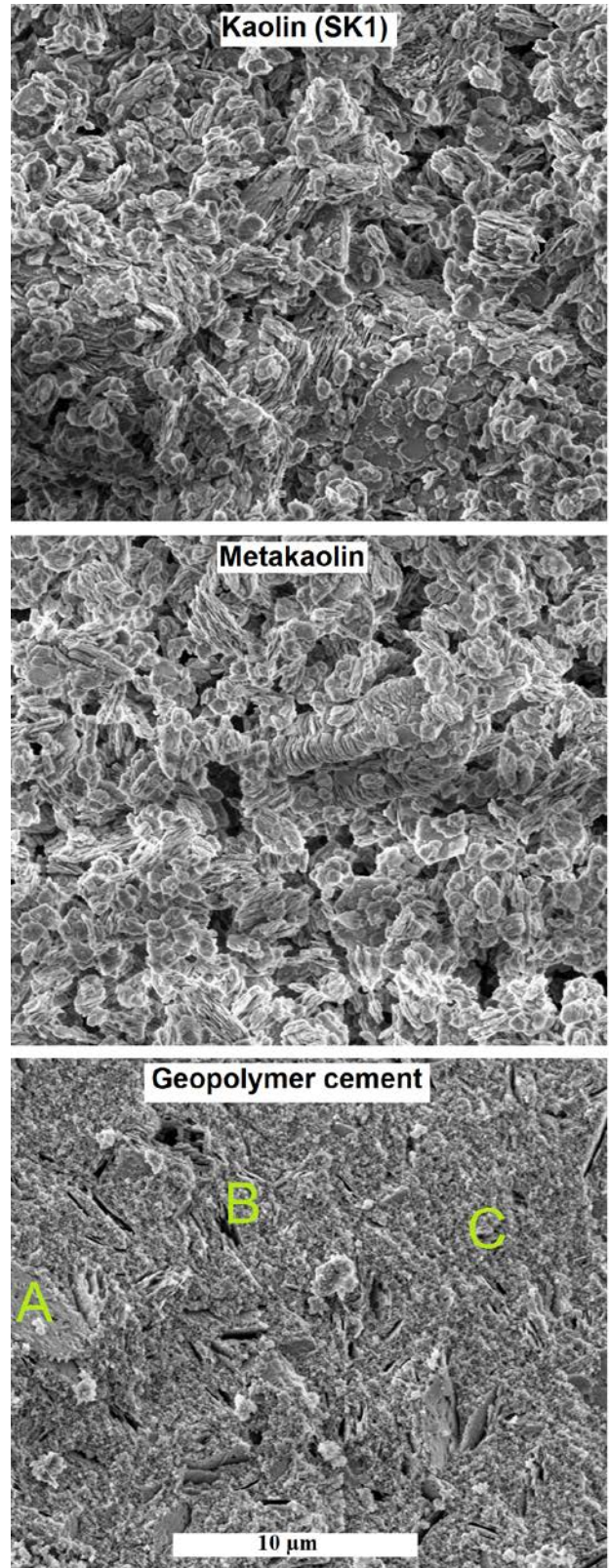


Fig. 2. SEM image of geopolymer cement; A: partially transformed metakaolin, B: fully transformed metakaolin, C: amorphous sodium aluminum silicate phase (geopolymer gel).

The layers of metakaolin are reported by the SEM as shown in Fig. 2-middle. These layers were distorted due to the calcination of kaolinite at 750°C. SEM analysis indicates that the microstructure of metakaolinite-based geopolymers, is characterized by the coexistence of geopolymer gel and partially unreacted metakaolinite layers (Fig. 2-down). This SEM image reveals also that due to geopolymeric reactions the gaps between partially reacted metakaolinite layers have been filled with formed geopolymeric gel (sodium aluminosilicate matrix).

The metakaolinite, which is considered as precursor in this study, was attacked by the alkaline solution during geopolymerisation as shown in Fig. 3 and was partially consumed. The residual metakaolin was amorphous, as seen in Fig. 2-middle. Due to the alkaline attack, macro holes filled with new formed Na-aluminosilicates are widely scattered between the residual metakaolin layers.

Microstructural observations, through SEM analyses (Fig. 2), reveal phase inhomogeneities. Although the residual metakaolinite shows similar morphology to the initial metakaolinite, its chemical composition could be different. This is because the alkaline solution attacks only the surface of metakaolinite layers without altering their overall structure. It is likely that homogenization cannot be achieved before complete dissolution of the reactive materials takes place. At the onset of gelation (polycondensation), species transferred into solution react locally, viscosity increases rapidly and hence, the gel formed prevents further homogenization [7].

3.2 Physical and Mechanical properties of geopolymers

Experimental results show that flexural strength of the produced geopolymers is around 12.3MPa, Fig. 3. It is reported also that compressive strength of the produced geopolymer is 32MPa and 44.2MPa under immersed and dry conditions respectively. The bulk density, 1.45g/m³, and water absorption 15% (w/w). These results are comparable with geopolymer produced from pure kaolin [3,6,9].

Earlier studies also mention that participation of gel in geopolymerization reactions and formation of a new binding mineral matrix results in geopolymeric products with improved mechanical properties [3]. Usually, a more homogenous microstructure which is related with the increase in the volume of geopolymeric gel at a relatively constant nominal density, results in products with improved mechanical properties [6]. The results of the present study show that using calcined natural kaolinitic soil

as precursor material in the starting mixture affects to a certain degree microstructure and strength of the produced geopolymers. The mechanical properties of metakaolin – based geopolymers is comparable with the ordinary concrete [13]. The geopolymeric matrix has been used to fabricate different standard laminate composite plates with carbon, glass, and silicon carbide fibers, sandwich structures using syntactic foam, and strengthening of brick, masonry, and reinforced concrete elements [17]. Therefore, low purity metakaolin – based geopolymers satisfy the criteria to be used for housing and general construction applications.

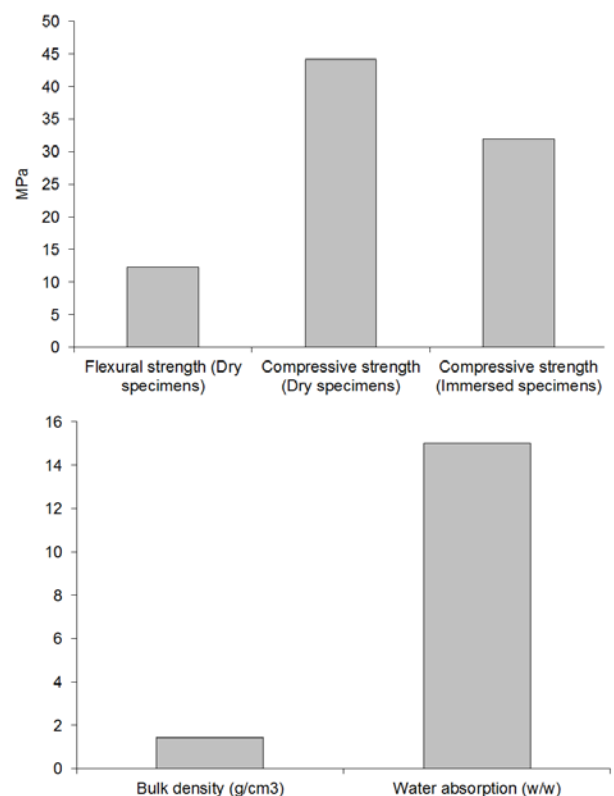


Fig.3, Physical and mechanical properties of geopolymers produced from natural kaolinitic soil.

4 Conclusions

Geopolymers have been successfully produced by alkali-activation of natural and untreated kaolinitic soil from mineral deposits in Saudi Arabia. The products composed mainly from geopolymer gel and broken kaolinite layers. An important finding of the present study is that the possibility of using low cost mineral deposits in Saudi Arabia for mass production of geopolymer cement with high mechanical performance and acceptable physical properties compared with Portland cement.

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