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Metakaolin-based geopolymer mortars with different alkaline activators (Na^+ and K^+)

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HIGHLIGHTS

- Mortars produced with potassium silicate exhibited a homogeneous microstructure.
- The elastic moduli were influenced by the type of the alkaline-activating solution.
- Mortars activated with potassium silicate are more thermally stable.

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ABSTRACT

In this study, the influence of different alkaline activators (Na^+ and K^+) on the mechanical, thermal, and microstructural behaviors of metakaolin-based geopolymer mortars was investigated. Four types of mortars were manufactured, and the only difference between them was the alkaline-activating solution. Potassium and alkaline sodium silicates and potassium and sodium hydroxides were used in combination as the alkaline-activating solutions. Compressive strengths, indirect tensile strengths, and longitudinal moduli of elasticity of the mortars were evaluated along with thermal property analysis (thermogravimetric analysis and differential thermal analysis) and scanning electron microscopy (SEM). All the mortars exhibited similar compressive strength, >80 MPa, at 28 days. It was possible to observe a high gain in the mechanical strength in the early ages, which is characteristic of geopolymers. The increase in mechanical strength ranged approximately from 72% to 81% after 3 days and from 86% to 93% after 7 days with respect to the strength at 28 days. Mortars produced with alkaline sodium silicate exhibited a heterogeneous microstructure with a large number of pores, while those containing potassium silicate were denser and exhibited low porosity. Such different morphologies of the mortars are a result of the type of the alkaline cations used; their effect could also be perceived in the thermal performance of the mortars, with better performance induced by potassium silicate and potassium hydroxide.

1. Introduction

Geopolymers are relatively new materials, which were first developed by Joseph Davidovits and patented in the 70s. They are inorganic polymeric materials with chemical compositions similar to zeolites, but their structure is either amorphous or semi-crystalline. They are produced from a mixture of several aluminosilicate materials (with high contents of Si and Al) along with an alkaline-activating solution (mostly Na^+ or K^+ silicates and hydroxides). After their development as alternatives to thermoset polymers in fire-resistant applications, geopolymers were used mainly for civil construction [1]. This is due to their potential to replace concrete and similar products containing Portland cement owing to their excellent mechanical properties, durability, and adherence to iron and conventional concrete.

The reaction mechanism of geopolymers, geopolymerization, is exothermic in nature due to polycondensation. Palomo et al. [2] reported that alkali-activation, sometimes called geopolymerization, is a chemical process that allows the transformation of vitreous structures (partially or totally amorphous and/or metastable) into very compact and luting composites. Van Jaarsveld et al. [3] suggested that for geopolymerization to occur, a strongly alkaline medium is required. This is necessary for it to dissolve silica and alumina, as well as to hydrolyze the surfaces of the particles of

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raw materials. Such an environment can be achieved using alkaline solutions in a simple or combined form for activation.

Several parameters must be analyzed when selecting the raw materials to produce geopolymers. Of these, reactive silica content (amorphous) and particle size are the most important [4]. Some studies showed that alterations in the amount of Si and Al affect the properties of the geopolymers significantly. Hence, a complete understanding of the reactivity of alkaline-activated raw materials is important, mainly to set the optimum compositions and achieve the desired properties in the final product.

Theoretically, any material containing aluminum and silicon can be a solid source of aluminosilicates for geopolymerization, but the most often used materials are blast furnace slags and ash from the burning of coal and calcined clay. The most commonly used clay is kaolin, which upon thermal activation changes into metakaolin. When metakaolin is used as the aluminosilicate source, the resulting geopolymer is purer and can be more easily characterized compared to the geopolymers produced from agroindustrial wastes. The geopolymers produced with metakaolin are considered a "model-system" without the complexities introduced by the use of fly ash, slags, and other alternative raw materials, which contain several hard-to-characterize amorphous phases. Fly ash, for example, is not a well-defined material, but it comprises several crystalline and vitreous phases [5].

The activator requires an alkaline compound in the aqueous form. Hence, the traditionally used compounds are hydroxides (Na^+, K^+, and Ca^{2+}), silicates (Na^+ and K^+), and even carbonates or sulfates [6]. Normally, a mix between silicates (liquid or solid dissolved in water) and hydroxides (solid dissolved in water) is used [7]. The silicate of the produced solution is an additional SiO_2 source, while the hydroxide assures high alkalinity in the solution [8]. During geopolymerization, the alkaline solution plays an important role and affects the development of mechanical strength. Its selection depends mostly on its reactivity and the cost of the materials employed.

The mechanical performance of geopolymers is highly influenced by the Si/Al ratio [9,10], hydroxide concentration [9], effectiveness of the geopolymerization reaction [11], type of cation used [12], and curing conditions [13,14]. Geopolymers can exhibit different mechanical, chemical, and thermal behavior according to the materials employed or depending on their molar ratio.

Hence, the purpose of this study is to compare the influence of the type of activating solution on the development of the microstructure and mechanical and thermal properties of geopolymeric mortars. To this end, four metakaolin-based geopolymers mortars were developed with different alkaline-activating solutions by combining different materials, including sodium silicate (Na_2SiO_3), potassium silicate (K_2SiO_3), sodium hydroxide (NaOH), and potassium hydroxide (KOH).

2. Materials and methods

2.1. Source materials

The precursor used in the geopolymers was metakaolin, a highly reactive mineral clay, which is the main source of silica (SiO_2) and alumina (Al_2O_3). Its chemical composition was evaluated by semiquantitative analysis using an X-ray fluorescence spectrometer with a 3-kW tube and a rhodium target. The chemical composition, specific mass, and loss on ignition of the metakaolin used in this study are shown in Table 1.

The particle size distribution in the precursor was analyzed by laser granulometry assay and the results are included in Table 2.

The alkaline-activating solutions were composed of alkaline sodium silicate (Na_2SiO_3), potassium silicate (K_2SiO_3), sodium hydroxide (NaOH), and potassium hydroxide (KOH). Their chemical compositions, according to the technical reports supplied by the manufacturers are shown in Table 3. The combinations prepared by mixing silicates (s) and hydroxides (h) and the mortar nomenclature are described in Table 4.

The fine aggregates used consisted of river quartzite sand with a specific mass of 2.64 g/cm^3 and modulus of fineness of 2.51. The selected granules could pass through a 1.18 mm aperture sieve.

To assess the influence of the alkaline-activating solution on the performance of the metakaolin-based geopolymer mortars, four types of mortars were produced with the same mass ratio of the precursor and fine aggregates (1:1). Each alkaline-activating solution complies with specific molar ratios, as shown in Table 5.

2.2. Sample preparation

Metakaolin-based geopolymers mortars were produced according to the following procedure. Initially, the alkaline-activating solution was mixed for 5 min twenty-four hours prior to molding. Subsequently, metakaolin was manually mixed for 1 min with the alkaline-activating solution using a metal spatula. The obtained mixture was further stirred in a 5 L revolving mixer for 3 min at a low speed; the revolving mixer was switched off for 1 min to

Table 1
Physical and chemical characteristics of the metakaolin used in this study.

Chemical composition	Metakaolin
SiO_2 (%)	48.4
Al_2O_3 (%)	44.8
Fe_2O_3 (%)	2.4
CaO (%)	0.1
SO_3 (%)	0.2
Na_2O (%)	0.2
K_2O (%)	1.5
TiO_2 (%)	1.4
Loss on ignition (%)	3.3
Specific mass (g/cm^3)	2.65

Table 2
Particle size of metakaolin (D_{10}, D_{50}, D_{90}, and D_{medium}).

Diameter	Metakaolin (μm)
D_{10}	2.9
D_{50}	18.8
D_{90}	47.3
D_{medium}	23.0

Table 3
Chemical composition of Na_2SiO_3, K_2SiO_3, NaOH, and KOH.

Chemical composition (%)	Na_2SiO_3	K_2SiO_3	NaOH	KOH
H_2O	53.1	60.3	21.9	12.9
SiO_2	32.2	27	–	–
Na_2O	14.7	–	75.2	–
K_2O	–	12.8	–	87.1

Table 4
Geopolymeric mortar nomenclature and activating compounds used.

Geopolymeric mortar	Silicate	Hydroxide
s.Na-h.Na	Na_2SiO_3	NaOH
s.Na-h.K	Na_2SiO_3	KOH
s.K-h.K	K_2SiO_3	KOH
s.K-h.Na	K_2SiO_3	NaOH