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Research paper

The effect of natural zeolite on microstructure, mechanical and heavy metals adsorption properties of metakaolin based geopolymers

S. Andrejkovičová [a,*], A. Sudagar [a], J. Rocha [b], C. Patinha [a], W. Hajjaji [a], E. Ferreira da Silva [a], A. Velosa [c], F. Rocha [a]

[a] Geosciences Department, Geobiotec Research Unit, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
[b] Chemistry Department, CICECO, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
[c] Civil Engineering Department, RISCO, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

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ABSTRACT

This work investigates the effect of clinoptilolite, a natural zeolite, as filler on the mechanical performance and heavy metal's adsorption capacity of the metakaolin-based geopolymers. Clinoptilolite was chosen as an inexpensive additive with high adsorption capacity, replacing metakaolin (0, 25, 50 and 75%) in the synthesis of four different geopolymers (MK100, MK75, MK50 and MK25, respectively). To produce geopolymers with low environmental impact, during the geopolymerization processes the SiO_2/Al_2O_3 and Na_2O/Al_2O_3 molar ratios were kept constant at 1, to reduce sodium silicate and sodium hydroxide to a minimum. The final products were studied by powder X-ray diffraction, ^{27}Al and ^{29}Si solid-state NMR and Scanning electron microscopy. Moreover, strength parameters and heavy metals Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+} and Cr^{3+} adsorption tests were performed. The results show that geopolymerization in the presence of zeolite leads to an increase of the compressive strength of all blended geopolymers, with an optimal metakaolin precursor/zeolite filler ratio of 50:50, affording the highest strength (8.8 MPa at 28 days). The adsorption of metal cations on geopolymers was well fitted using the Langmuir model ($0.97 < R^2 < 0.99$). The geopolymers adsorbed heavy metals in the order $Pb^{2+} > Cd^{2+} > Zn^{2+}$, $Cu^{2+} > Cr^{3+}$. The maximum adsorption capacity of Cu^{2+} and Cr^{3+} was highest for geopolymer with 100% of metakaolin (MK100), while for Pb^{2+}, Cd^{2+} and Zn^{2+} the highest adsorption capacity is for geopolymers with 75% of metakaolin (MK75), indicating that 25% zeolite addition to geopolymers has efficiently improved the adsorption capacity.

1. Introduction

Ordinary Portland cement (OPC) is the construction material par excellence. However, because it generates almost 1 ton of CO_2 per 1 ton of Portland cement produced, this binder is one of the primary causes of global warming. Moreover, OPC consumption has grown practically exponentially in the last 20 years and in 2020 overall demand is estimated to extent 3.6×10^9 tons, which will transform into an unsustainable flow of CO_2 emissions (Garcia-Lodeiro et al., 2015).

These factors foster the study and development of new alternative binders with lower energy and environmental costs. To overcome these problems, geopolymers emerged as a possible solution (Khale and Chaudhary, 2007). Geopolymer binders can provide comparable performance to traditional cementitious binders in a range of applications with the added advantage of significant reduction of greenhouse gas emissions (Duxson et al., 2007b). Geopolymers are a class of largely X-ray amorphous aluminosilicate materials, generally synthesised at ambient or slightly elevated temperature by reaction of a solid aluminosilicate powder with a concentrated alkali metal silicate or hydroxide solution (Davidovits, 1991). Many materials composed of silica and alumina can be used in order to synthesize geopolymers. Indeed, several investigators have used metakaolin, kaolinitic clays, fly ashes and blast furnace slags as raw materials (Pacheco-Torgal et al., 2008a, 2008b). Moreover, rapid growth of an industrial society leads to a significant increase in the demand for water. Nevertheless, industrial wastewater has an extremely negative impact on the environment. Disposal of inadequately treated wastewater can cause soil contamination, and particularly wastewater containing heavy metals results in severe environmental damages (Cheng et al., 2012). Therefore, the elimination of metal ions from industrial waste water is necessary. Recently, adsorption has become the central research focus due to its protocol simplicity, effectiveness, and low cost. Zeolites are used as representative solid adsorbent for metal ions (López et al., 2014). The structure of geopolymers consists of a polymeric Si—O—Al framework, similar to that found in zeolites. Geopolymers are then expected to have the unique properties as well as zeolites (López et al., 2014).

Geopolymer based materials are attractive for use in practice because of excellent mechanical properties such as high early strength, high durability, freeze-thaw resistance, low chloride diffusion rate, abrasion resistance, thermal stability and fire resistance (e.g.

* Corresponding author at: Department of Geosciences, Geobiotec Research Unit, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal.
E-mail address: slavka@ua.pt (S. Andrejkovičová).

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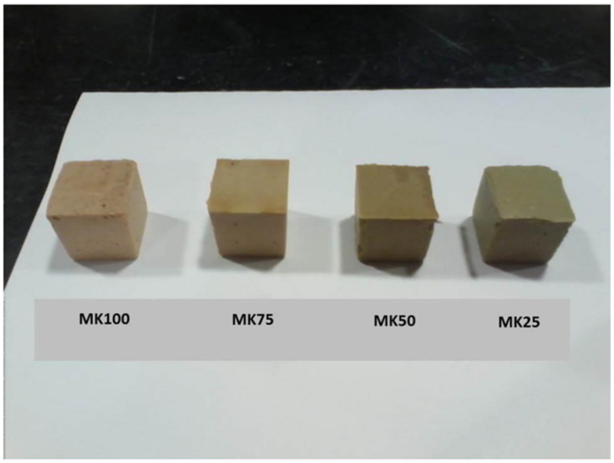

Fig. 1. Geopolymer cubic specimens.

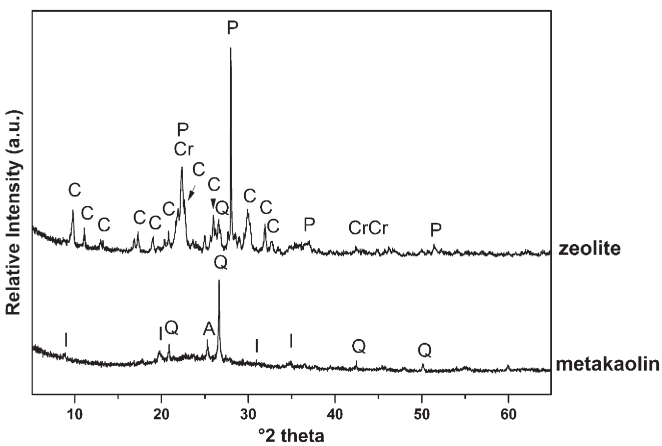

Fig. 2. X-ray diffraction patterns of metakaolin and zeolite. (A-anatase TiO_2, Cl-clinoptilolite $(Ca,K_2,Na_2,Mg)_4Al_8Si_{40}O_{96}.24\ H_2O$, Cr-cristobalite SiO_2, I-illite $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$, P-plagioclase $NaAlSi_3O_8–CaAl_2Si_2O_8$, Q-quartz SiO_2).

Schmücker and MacKenzie, 2005; Duxson et al., 2007a; van Deventer et al., 2007; Davidovits, 2011; Ferone et al., 2013). Due to their lower Ca content, they are more resistant to acid attack than Portland cement (OPC) based materials (Janotka, 1999; Palomo et al., 1999; Allahverdi and Škvára, 2005; Thokchom et al., 2009).

These characteristics make them interesting products for adsorbents as used with concrete replacements in various environments. Combination of high adsorption capacities of zeolites and geopolymers in regards to heavy metals, have been recently the focus of several authors. Yousef et al. (2009) studied the effects of zeolitic tuff on the adsorption capacity of geopolymers. They confirmed high adsorption capacity in relation to Cu(II) and that adsorption capacity of the specimens towards Cu(II) increases significantly with increase of pH.

Influence of various kaolin/zeolite ratio in geopolymers on adsorption of Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) was examined by El-Eswed et al. (2012) concluding that the adsorption capacity of the geopolymers of 150 g:50 g (zeolite:kaolin) content was higher than that of the raw materials separately. The experimental results obtained by Alshaaer et al. (2014) show that the maximum adsorption efficiency 7.8 mg Cu^{2+}/g of adsorbent, was observed for geopolymer with zeolitic tuff/metakaolin ratio of 0.5.

El-Eswed et al. (2015) investigated the efficiency and mechanism of immobilization of Pb(II), Cu(II), Cd(II) and Cr(III) metal solutions in kaolin/zeolite based geopolymers. The results of the authors showed that heavy metals were successfully immobilized in kaolin/zeolite based geopolymers mainly when high metal concentrations were employed. The objective of this study is to prepare lower cost geopolymeric materials with as low environmental impact as possible, exhibiting high heavy metals adsorption capacity and high mechanical performance for construction purposes. To achieve these goals, zeolite was used as an additive (25, 50 and 75%) to metakaolin based geopolymers. The target of zeolite addition is to provide a low cost natural geomaterial with suitable mechanical properties and high adsorption capacity for heavy metals. Metakaolin was chosen as the main precursor, as several researches consider metakaolin as ideal raw material for manufacture geopolymers due to its high reactivity and purity compared to other clays (e.g. Yip et al., 2004; Cheng et al., 2012). According to Habert et al. (2011) the production of most standard types of geopolymer concrete has a slightly lower impact on global warming than standard Ordinary Portland cement (OPC) concrete. They also reveal that the production of geopolymer concrete has a higher environmental impact regarding other categories than global warming. This is due to the heavy effects of the production of the sodium silicate solution. For this reason, molar ratios of SiO_2/Al_2O_3 and Na_2O/Al_2O_3 were kept at 1 (minimum value possible) to reduce amount of sodium silicate and sodium hydroxide activators, to make the final geopolymer products more eco-friendly.

2. Materials and methods

2.1. Materials used for geopolymerization

Geopolymers were prepared using commercial metakaolin (1200S, AGS Mineraux, France, $D_{50} = 1.1$ μm, bulk density = 296 g·dm^{-3}), zeolite (ZeoBau micro 50, from Nižný Hrabovec, Zeocem, Slovakia, CEC = 83 meq/100 g, SSA = 1663 m^2/kg, particle size 0–0.05 mm, bulk density = 500–600 g·dm^{-3}, more information about Nižný Hrabovec deposit is available on http://www.iza-online.org/natural/), hydrated sodium silicate (Merck, Germany Merck, Germany; 8.5 wt.% Na_2O, 28.5 wt.% SiO_2, 63 wt.% H_2O) and sodium hydroxide (ACS AR Analytical Reagent Grade Pellets).

The role of the above ingredients in the preparation of geopolymers is as follows: metakaolin was used as a precursor of aluminium; zeolite was used as filler with high specific surface area and cation exchange capacity; sodium silicate was used as a source of silicon and sodium hydroxide as an alkaline activator for dissolution of aluminosilicate. Water was the reaction medium.

Table 1
Chemical analyses of materials.

	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	L.O.I.
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Metakaolin	54.39	39.36	1.75	0.01	0.14	0.10	nd	1.03	1.55	0.06	1.90
Zeolite	70.61	12.06	1.78	0.03	0.85	3.38	0.31	3.65	0.19	0.04	6.89