Geopolymers based on natural zeolite clinoptilolite with addition of metakaolin

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Abstract: *Geopolymers based on natural zeolite clinoptilolite and addition of up to 50% metakaolin were synthesized using binary sodium/potassium alkali activator. The influence of metakaolin addition was evaluated on apparent density, water absorption, relative mass loss after watering and microstructure (XRD) of the prepared geopolymers. The addition of metakaolin greatly influenced the physical and mechanical properties of the obtained geopolymers. Minimal/optimal metakaolin addition was estimated to 30% in the respect of sufficient strength (11 MPa) and the high price of metakaolin. The resulted geopolymer based on natural zeolite and metakaolin (30%) contained residual unreacted clinoptilolite which could be beneficial for properties of future geopolymer products. Potential applications of obtained geopolymer-clinoptilolite agglomerates are: waste or radioactive water decontamination, passive cooling systems, plasters in residential buildings, etc.*

Keywords*: GEOPOLYMER, NATURAL ZEOLITE, CLINOPTILOLITE, METAKAOLIN*

1. Introduction

Carbon dioxide (CO_2) emissions are one of the most significant challenges encountered by humanity nowadays. In 2020, slightly reduced CO_2 emissions were triggered by the ongoing COVID-19 pandemic [1]. Still, Portland cement industry is responsible for 8% of global CO_2 emissions of which 55% of decarbonisation of limestone and 40% of heating the kilns to temperature about 1450 ° C [2]. In recent years, ecological building materials are in the focus of the global research. A potential alternatives of Portland cement are geopolymers. Geopolymers are synthetic inorganic polymers which act as binder to produce monolith stone-like materials. Usually, the geopolymers are comprised of two components– aluminosilicate powder precursor and activator solution. The precursor could be a raw material or industrial by-product consist of high amount of reactive Al_2O_3 and SiO_2. The breakthrough precursor was metakaolin from which first geopolymers was synthesized by Joseph Davidovits in the late 1970s [3]. The metakaolin is a calcined kaolinite clay at temperature about 750 ° C. Geopolymer cements do not rely on limestone and generate much less CO_2 during manufacture, i.e. a reduction in the range of 40% to 80-90%, compared to Portland cement materials [4]. The properties of the geopolymers are similar to Portland cement and even superior as better fire and chemical resistance [5–7]. High strength [8,9] and rapid hardening geopolymers [10] are also reported. This allow geopolymers to partially or entirely replace Portland cement materials.

In general, aluminosilicate binder materials activated by alkali hydroxides or silicates under high-pH conditions are classified as geopolymers [11]. Nowadays, the focus of potential geopolymer precursors is aimed to industrial by-products such as fly ash and slags from heavy metal productions. The benefits of utilizing industrial waste are of ecologic and economic aspects. One of the main drawbacks is the non-persistent chemical and mineralogical composition. Moreover, the industrial waste often consists of undesirable elements such as iron, magnesium, heavy or radioactive metals. Numerous studies reported geopolymer immobilization of hazardous elements [12], but still such materials should not be used in residential buildings. Geopolymer precursors could be of natural origin such as volcanic tuffs, perlite, zeolite, clay, rock dust, etc. Geopolymers based on natural materials are more suitable for residential buildings.

One of potential ecological geopolymer precursorc are natural zeolites. Zeolite rocks are composed of zeolite minerals, such as clinoptilolite, mordenite, phillipsite, chabazite, etc - over 30 species. The major world deposits are located in USA, Cuba, Japan, Bulgaria, Russia, China, Italy, Mexico, Slovakia and others [13]. The natural zeolite deposits in Bulgaria are mostly clinoptilolite type – located in Eastern Rhodopes. The only commercially available is near Beli Plast village (Kardzhali region). The quality is very good, as the amount of clinoptilolite reaches 90% of the rock composition. The zeolites are crystalline, hydrated, aluminosilicates with lattice structure. Their three dimensional network is composed of SiO_4 and AlO_4 tetrahedra sharing oxygen atoms. The zeolite structure contains channels and connected cavities of different sizes, where water molecules and cations are located, necessary to balance the negative balance of the structure. The cations are mobile and could be exchanged [14]. The density of zeolites varies from 1.9 to 2.3 g/cm^3 depending on the type of cations. The structure of clinoptilolite contains micropores with dimensions corresponding to molecular diameters. This gives the zeolite function of a molecular sieve. The water molecule can enter the network of channels, but other, heavier (large) molecules remain "locked" in. The pores of clinoptilolite are heterogeneous, with two types of pores observed. The main porosity is microporosity (0.5 nm - 2.5 nm) composed of the clinoptilolite three-dimensional aluminosilicate lattice, which forms a nanosystem of channels. The second type of pores are mesopores and macropores (2.5 nm – 50 nm), which may contain water [15]. The specific structure of zeolites gives a variety of useful properties in different areas of application. Zeolites are used as molecular sieves, ion exchangers, catalysts and others. Based on these characteristics, devices and technologies with high efficiency and diverse focus have been created: enrichment of the air with oxygen, extraction of radioactive elements from solutions [16], purification of wastewater and domestic water [17], removal of ammonia from wastewater, extraction of acidic components from wastewater, separation of gases, separation of normal and aromatic hydrocarbons, extraction and separation of rare alkaline (Rb, Cs, Li), colored (Cu, Zn, Pb), heavy (Ag) and alkaline earth (Sr) elements. Zeolite is also used in various fields of catalysis [18]. In many countries, from ancient times zeolite rocks are used as a building material [19]. Recently, zeolite raw material has been used to produce new, non-traditional building materials such as geopolymers [20–22].

In previous studies the potential of natural zeolite as geopolymer precursors was evaluated [23–25]. The results showed that geopolymers based on natural zeolite possess excellent adhesion to concrete [26]. However, geopolymers based on natural zeolite slowly gain strength at normal temperature and undergo high shrinkage [27]. The aim of the present work is to study the influence of metakaolin addition to properties of geopolymers based on natural zeolite.

2. Materials and methods

2.1. Method of analysis

The density was measured by hydrostatic weighing method and calculated using Equation 1:

$$D = \frac{m_d}{m_w - m_{w,w}}, g/cm^3$$

, where:

m_d – mass of dried specimens after watering

m_w – mass of water absorbed specimens

$m_{w,w}$ – mass under water of water absorbed specimens

Equation 1. Calculation of density by hydrostatic weighing method

The relative mass loss was calculated based on dried mass before and after watering of the specimens.

The mechanical properties were evaluated using 3 cubic specimens with side area 10 cm^2 each series.

The XRD patterns were obtained by Panalytical Empyrean at 40 kV and 30 mA. The chemical composition was analyzed by X-ray fluorescence apparatus - Rigaku Supermini 200 using 30 mm pressed tablets.

3.1. Materials

The main geopolymer precursor in the present experiment was natural zeolite from Beli Plast, Bulgaria, provided by Imerys, a commercially available product with particle size < 0.15 mm. The chemical composition of the natural zeolite is presented in Table 1.

Commercial metakaolin, provided by Kaolin EAD, Bulgaria, was used in order to enhance the properties of the geopolymer. The metakaolin is produced by calcination of local kaolinite clay. The wet residue on 45 μm sieve of the metakaolin is 0.40%. The chemical composition of the natural zeolite is presented in Table 1.

Table 1. Chemical composition of the geopolymer precursor - natural zeolite clinoptilolite(NZ) and metakaolin (MK)

	SiO_2	Al_2O_3	CaO	K_2O	MgO	Fe_2O_3	Na_2O	TiO_2
MK	53.94	43.2	0.15	0.62	0.09	1.14	0.11	0.74
NZ	78.89	11.71	3.43	3.09	1.13	1.11	0.44	0.19

The activator solutions were prepared by using solid KOH pellets, sodium water glass with molar modulus about 3 and tap water. The ingredients were mixed by magnetic stirrer a day prior the synthesis of geopolymers.

2.3. Geopolymer synthesis

Total of 6 series were prepared with different concentration of the activator. The composition design is presented at Table 2 in molar ratios. Sample ZM20 was designed with higher SiO_2/Al_2O_3 by addition of more water glass. The recipes are based on best results from previous studies on geopolymers based on natural zeolite [26] and metakaolin [28], separately.

The geopolymer precursor and activator solution were mixed and homogenized with mechanical stirrer for 1 min. The mixtures were rested to mature for 5 min, then mixed again for 30 seconds. From each series certain amount of the geopolymer paste was taken for microstructural examination (XRD). To determine mechanical and physical properties the fresh geopolymer paste was mixed with quartz sand (zeolite to sand = 1:2 by mass) and homogenised mortar was poured in steel cubic moulds. The samples were stored in plastic bags for three days at laboratory conditions (20 ^oC), then placed at 80 ^oC for 24 hours.

Table 2. Composition design in molar ratios and water to solid ratio (w/s) of the prepared geopolymers

Series	Molar ratio			w/s
	SiO_2/Al_2O_3	Al_2O_3/M_2O	H_2O/M_2O	
ZM5	11.70	0.32	10.19	0.51
ZM10	10.43	0.36	10.43	0.52
ZM20	8.55	0.43	10.90	0.54
ZM20W	9.41	0.40	10.91	0.54
ZM30	7.23	0.51	11.40	0.56
ZM50	5.51	0.65	12.37	0.59

3. Results and Discussion

3.1. Physical and hydrophysical properties

The outside appearance of the geopolymer series was characterized by visible with bare eye cracks in decreasing manner with the addition of metakaolin. The physical and hydrophysical properties of the prepared geopolymer mortars are presented at Table 3. The apparent density of the geopolymers increased with the increase of metakaolin addition up to 30%, then at 50% slight decrease was observed. The water absorption was lower at 20% metakaolin addition, then steady increased and the value was about 20% at 50% metakaolin. The lack of straightforward correlation between metakaolin addition and density and water absorption is probably due to different water to solid ratio of the series. However, the relatively high water absorption (about 14-20%) and relatively low density is a sign for well-developed porous structure.

The relative mass loss was very high at low level of metakaolin additions. The samples lost mass probably because they contained water soluble unreacted activator and/or partial disintegration due to low strength. The relative mass loss was about 1% or less at 30% or more metakaolin addition.

The usage of more water glass (ZM30W) led to higher density and lower water absorption.

Table 3. Apparent density, water absorption and relative mass loss after watering of the prepared geopolymers

Series	Density, g/cm^3	Water absorption, %	Relative mass loss, %
ZM5	1.56	18.0 ± 0.1	8.0 ± 0.4
ZM10	1.63	16.3 ± 0.1	6.0 ± 0.3
ZM20	1.69	15.4 ± 0.3	3.1 ± 0.3
ZM20W	1.72	13.6 ± 0.2	3.3 ± 0.1
ZM30	1.70	17.5 ± 0.1	1.3 ± 0.1
ZM50	1.65	20.4 ± 0.1	0.7 ± 0.1

3.2. Compressive strength

The results of compressive strength tests of the prepared geopolymer mortars are presented at Figure 1. The addition of metakaolin up to 20% showed no beneficial effect on strength, thus geopolymers was characterized by only about 3 MPa. Significant strength increase was observed with addition of 30% and 50% metakaolin, respectively – 11 and 20 MPa. Minimal/optimal metakaolin addition is determined at 30% in the respect of sufficient strength and the high price of metakaolin, respectively minimal amount of addition.

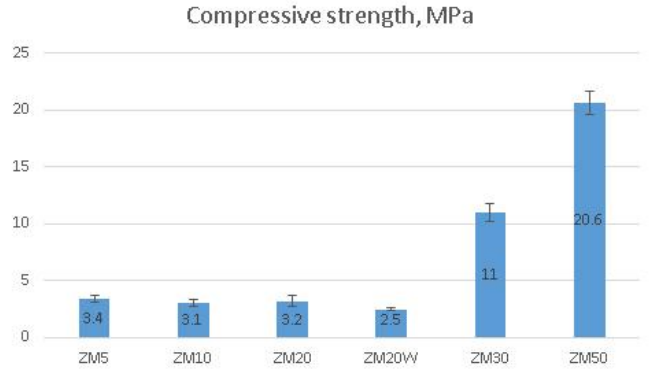

Figure 1. Compressive strength of the prepared geopolymers

3.3. Powder XRD

The natural zeolite, metakaolin and the prepared geopolymers were examined by Powder X-ray diffraction. The results are presented in **Грешка! Източникът на препратката не е намерен.**. The natural zeolite was comprised of clinoptilolite (~80%) and opal-cristobalite. Metakaolin showed amorphous structure presented by broad halo between 15 – 30 2θ° , and quartz inclusion. The geopolymer samples ZM30 showed characteristic amorphous halo for geopolymers between 22 – 37 2θ° . Opal-cristobalite presented in the natural zeolite was completely dissolved to take part of geopolymerization process. The clinoptilolite reacted partly thus geopolymer contains residual clinoptilolite which could be beneficial for the future properties of the geopolymer product.

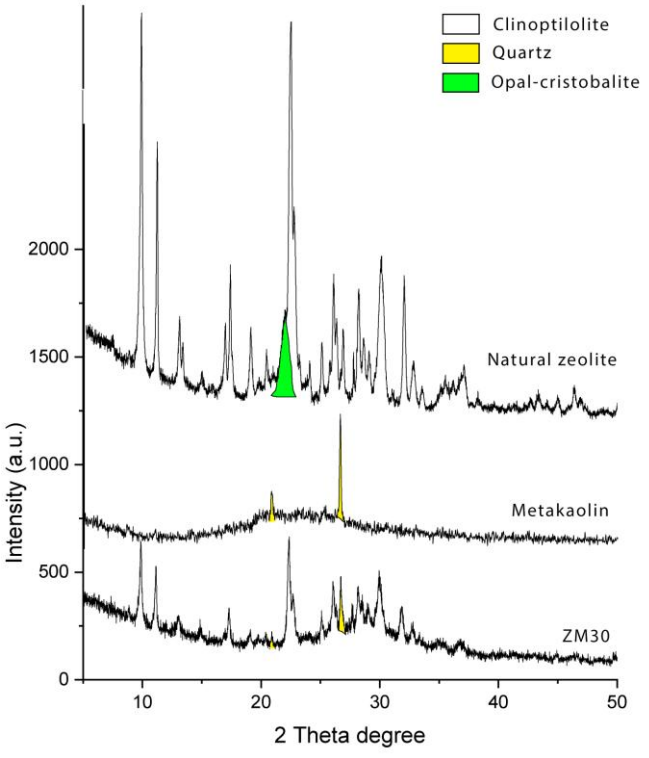

Figure 2. Powder XRD diffractograms of the precursors and geopolymer series ZM30

4. Discussion on possible applications

The different metakaolin addition to the synthesized geopolymers greatly influenced the physical and mechanical properties of the final material. The addition of 30% or more metakaolin guarantees satisfactory integrity of the synthesized geopolymers clinoptilolite agglomerates. The result was synthetic geopolymer-clinoptilolite agglomerate consist of geopolymer gel phase and unreacted clinoptilolite. Moreover, the filler from quartz sand could be replaced with fractionized crushed natural zeolite in order to increase the zeolite content. The shape of the geopolymer-clinoptilolite agglomerates could be designed from irregular - produced in moulds, to spherical shapes fabricated by granulation techniques, or layered plaster on surface. Both clinoptilolite and geopolymer gel possess sorption and ion-exchange properties [16,29,30]. Consequently, geopolymer-clinoptilolite agglomerates probably could be utilized in waste water treatment for heavy metal and radioactive decontamination. However, the high pH and high alkali content of the geopolymer must be also considered. More studies are needed to evaluate sorption capacity and selectivity of the synthetic geopolymer-clinoptilolite agglomerates.

Rising temperatures in big cities are an increasing problem, especially at arid areas, or in summer. This effect arises from the increasing amount of heat generated by human activities and cumulative surface areas covered by artificial materials with high solar absorption capacity. This warming phenomenon is known as "heat island effect". One of the possible methods for counteracting the "heat island effect" is application of passive cooling systems using evaporation of water absorbed by porous material [31]. Both natural zeolites and geopolymers are suitable for passive cooling materials [31,32]. The synthesized geopolymer-clinoptilolite agglomerates appears to be candidate for materials with passive cooling properties. More studies are required to evaluate application of the synthetic geopolymer-clinoptilolite agglomerates in passive cooling systems.

5. Conclusion

The metakaolin greatly influenced the physical and mechanical properties of prepared geopolymers based on natural zeolite clinoptilolite. The addition of up to 20% metakaolin did not bring beneficial effect to the properties of the prepared geopolymers. Minimal/optimal metakaolin addition was estimated to 30% in the respect of sufficient strength (11 MPa) and the high price of metakaolin. The resulted geopolymer based on natural zeolite and metakaolin (30%) contained residual unreacted clinoptilolite which could be beneficial for the future properties of the geopolymer product. Potential applications of obtained geopolymer-clinoptilolite agglomerates are: waste or radioactive water decontamination, passive cooling systems, plasters in residential buildings.

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