

Natural and calcined zeolite (metazeolite) based geopolymers

Геополимери на основата на природен и калциниран зеолит (метазеолит)

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Introduction

Geopolymers are chains or networks of mineral molecules linked with co-valent bonds (Davidovits, 2011). The precursors are usually aluminosilicate materials with natural origin (kaolin, volcanic ash, zeolite, etc.), thermally treated materials (metakaolin, calcined shales, etc.) or industrial byproducts (fly and bottom ash, metal industry slag, silica fume, etc.). The raw material is mixed with alkali or acid solution to initiate geosynthesis. The final product is x-ray amorphous material with appropriate mechanical properties, chemical resistance, thermal and fire resistance (Provis, Deventer, 2009). Previous studies show that natural zeolite mixed with sodium silicate solution hardens at normal temperature and the final geopolymer possesses sufficient compressive strength and excellent adhesion to concrete (Nikolov et al., 2017).

Materials and methods

The raw material used in the present study was natural zeolite from a large deposit Beli Plast, Bulgaria. The zeolite consists mainly of clinoptilolite, cristobalite and small amount of glass. The chemical composition

of the raw zeolite (in wt%) measured by XRF is: SiO₂ 69.4, TiO₂ 0.17, Al₂O₃ 10.30, Fe₂O₃ 0.98, Mn 0.08, MgO 0.99, CaO 3.02, Na₂O 0.39, K₂O 2.72; total 88.06.

The alkaline hardener is produced by using solid KOH, tap water, potassium silicate solution (molar ratio SiO₂/K₂O=3.34).

The XRD patterns were recorded on a Bruker D-8 Advance with Bragg-Brentano geometry with Co K α source. The morphology of the samples was studied using scanning electron microscope JEOL JSM-6010LA. The DTA/TG study was performed with apparatus LABSYSEvo in range 20–1000 °C and heating rate 10 °C/min.

Results

The DTA result of the natural zeolite shows that full amorphization of the clinoptilolite is reached at about 900 °C, then at 980 °C the crystallization of cristobalite takes place. The natural zeolite was thermally treated at 900 °C for four hours in muffle furnace in order to increase the reactivity of the material. The morphology and size of the particles is visible in SEM images (Fig. 1). The XRD analysis of zeolite and cal-

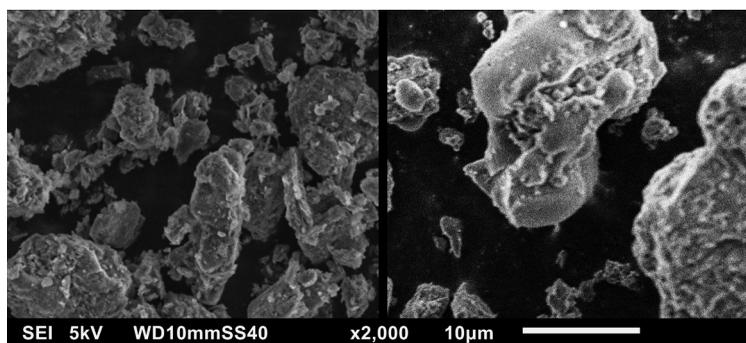


Fig. 1. SEM images of raw zeolite (left) and calcined zeolite – metazeolite (right)

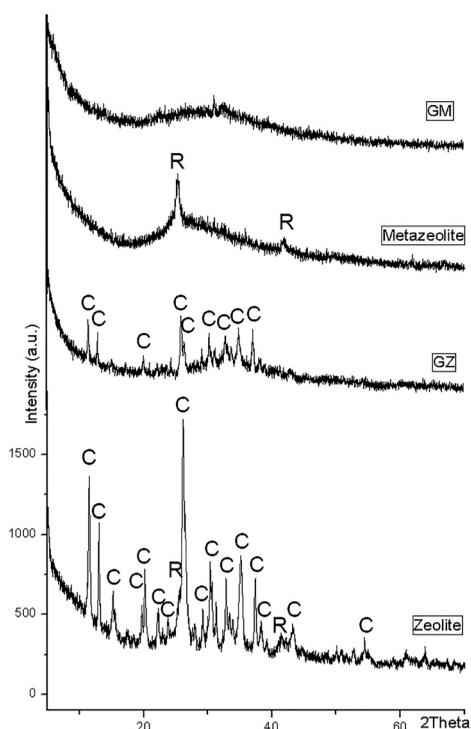


Fig. 2. XRD patterns: C, clinoptilolite and R, cristobalite

cined zeolite shows the total amorphization of the clinoptilolite and preserving the cristobalite (Fig. 2). The fully calcined zeolite is named “metazeolite” as in the case of kaolin – metakaolin.

The raw zeolite/metazeolite was mixed with hardener to prepare two series of geopolymer specimens GZ and GM, respectively. The molar ratios of both series are: $\text{SiO}_2/\text{Al}_2\text{O}_3=13$, $\text{H}_2\text{O}/\text{M}_2\text{O}=10$ (where M is the sum of K and Na). The water to solid weight ratio is 0.45 for GZ and 0.40 for GM because of the different water demand of zeolite and metazeolite. The fresh geopolymer mixture with metazeolite shows better rheological properties (thixotropic behavior). The precursor and activator were homogenized and poured in cylindrical molds (50×30 mm). After 3 days curing at 20 °C, the samples were placed at 80 °C for 3 days. On 28th day the density, shrinkage and compressive strength were measured (Table 1).

According to XRD analysis the clinoptilolite in raw zeolite was partially dissolved after geopolymerization, while the cristobalite was fully dissolved in both raw and meta-zeolite (Fig. 2). The geopolymer based on metazeolite was x-ray amorphous with slightly dif-

Table 1. Properties of geopolymer specimens at 28th day

Series	Density, g/cm ³	Shrinkage, %	Compressive strength, MPa
GZ	1.59	14.29	25.53±2.62
GM	1.84	7.22	43.11±4.17

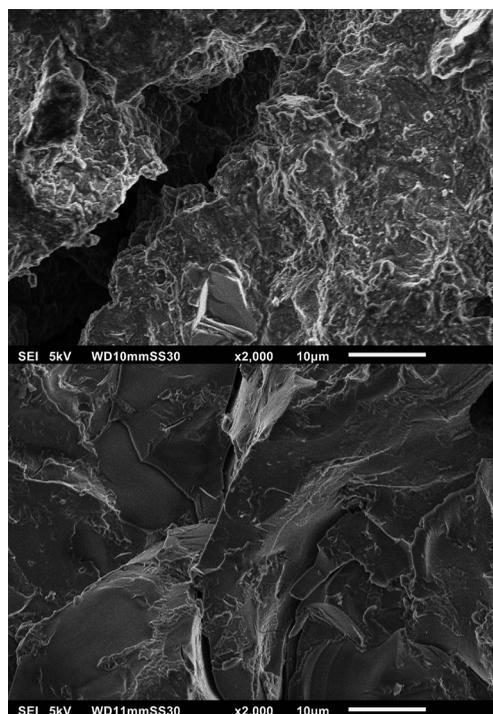


Fig. 3. SEM images of geopolymer based on natural zeolite (top) and metazeolite (bottom)

fused halo peak between 20° and 40°. SEM images of geopolymer specimens showed a less porous structure for metazeolite-based geopolymer (Fig. 3).

Conclusion

The calcination of the natural zeolite at 900 °C leads to full dehydroxylation and amorphization of the clinoptilolite structure thus transforming the natural zeolite into metazeolite. The metazeolite-based geopolymer is an x-ray amorphous material with better mechanical properties than that of the geopolymer based on natural zeolite. The shrinkage of the final product is reduced twice when metazeolite is used as a geopolymer precursor.

In practice, more valuable and economic is to calcine the zeolite at lower temperature (500–700 °C) in order to partially preserve the structure of the clinoptilolite thus increasing its reactivity as geopolymer precursor. In this way, the beneficial properties of the clinoptilolite (like ion exchange and sorptivity) could be retained in the final geopolymer material.

References

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