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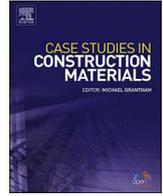
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Case study

Geopolymer materials based on natural zeolite

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ABSTRACT

One of the potential raw materials for preparation of geopolymers is the natural zeolite. In the present report, the used natural zeolite (clinoptilolite) is from huge deposit near Beli Plast, Bulgaria. Geopolymer pastes and mortars are prepared by using three different alkaline activators—sodium hydroxide, sodium silicate and sodium carbonate. The hardened geopolymers are tested for determination of mechanical properties by traditional standardized methods. The structure and the composition of the materials are studied by direct physical methods—X-ray diffraction (XRD), thermal analysis (DTA and TGA) and scanning electron microscopy (SEM). The results show variable degree of dissolutions of the raw zeolite material when using different activators and formation of solid geopolymer materials with qualitatively different structure. Despite its relatively low compressive strength, geopolymers based on natural zeolite cured at room temperature and used as coating, show very good adhesion to concrete.

1. Introduction

The main present challenge of the material science is the creation and development of new materials. Chemical resistance, mechanical properties and durability of the materials are improved by optimizing material composition. However, this should have insignificant effect on their production cost and price. During the last decades, more and more attention has been paid to energy consumption during production, emission of greenhouse gases and environmental impact. The most used material, excluding water, is Portland cement based concrete. Its good performance and low price have led to large-scale application worldwide. However, conventional concrete shows some disadvantages such as low chemical resistance against acids and salts, low thermal and fire resistance, especially at temperatures over 500 °C. Last but not least, the production of cement has a high carbon footprint – 8% of the worldwide carbon dioxide emissions originate from the cement industry [11]. Of course, this catalyses innovation and development of alternative building materials. One of the potential substitutes for cement-based composites are geopolymers.

Geopolymers are inorganic materials produced by geosynthesis from silica–alumina gels in an alkaline environment. Their microstructure consists of chains or networks of inorganic molecules linked by covalent bounds [6]. These molecules are composed from one silicon or aluminium atom connected by four oxygen atoms forming tetrahedrons, which are connected to each other in a three-dimensional network sharing one common oxygen atom.

The main raw material (precursor) for the production of geopolymers is an alumino-silicate material. Precursors can be of natural origin such as kaolin, zeolite, volcanic ash or natural pozzolans, but may also be thermally treated material such as metakaolin, fly ash, granulated blast furnace slag, calcined shales or other industrial residues. The alumino-silicate material must be activated by a second raw material, the so-called activator—alkaline solution, in general. Common activators are sodium and potassium hydroxide,

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sodium and potassium silicate solutions (water glass) and sodium carbonate. Geopolymerization starts with dissolution of alumina and silica from the raw materials as soon as they are mixed. After initial removal of surface metals such as Na^+ and Ca^{2+} by metal/proton exchange reactions, the alumina-silicates are attacked by OH^- ions. Since Al–O bonds are weaker than Si–O bonds, first Al will enter the solution as $\text{Al}(\text{OH})_4^-$ complexes. Detached Si-tetrahedra will now become easier for OH^- -attack and this results in silicon acids and oligomers, containing Si–O– groups, often written as $\text{Si}(\text{OH})_3\text{O}^-$ in solution with alkaline cations neutralizing the negative charge [7]. So, initially, there is preferential dissolution of Al, but later, a steady state is reached with stoichiometric release of Si and Al. However, the overall dissolution rate seems to decrease with increasing Al in solution. This mechanism is supported by the dissolution rate of feldspars [4]. With accumulation of silica and alumina monomers, contact between dissolved products enhances coagulation, which leads to polycondensation. The resulting alumo-silicate gel oversaturates and settles to form an amorphous product, containing a considerable amount of zeolitic phases in the form of nano-crystals, such as sodalite, faujasite, zeolite A, zeolite ZSM-5 and others [6].

The settling and hardening reactions take place at room temperature, but sometimes slightly elevated curing temperatures (up to 80 °C) are used to enhance some properties. Hardened products may possess mechanical properties comparable to ordinary Portland cement concrete (OPC) or even better. Geopolymers exhibit good thermal and fire resistance of up to 1300 °C [10] excellent sulphate resistance [2,8,9], high acid resistance [5,14] and satisfactory adhesion to iron, steel and concrete [15,18].

Due to their chemical composition, natural zeolites are among the possible raw materials for the production of geopolymers. Zeolites are crystalline hydrated alumino-silicates, composed of silicon and aluminium tetrahedra (SiO_4 and AlO_4) and linked by one oxygen atom [17]. Up to now there are only a few papers related to natural zeolite based geopolymers. Alcántara et al. [1] used calcium hydroxide to hydrate natural zeolite clinoptilolite and the resulting material showed a maximum compressive strength of 38.7 MPa. A mixture of sodium silicate and sodium hydroxide was used by Villa et al. [16] for the activation of natural zeolite composed of clinoptilolite mostly. The higher strength up to 33 MPa at 28 days was showed after curing at slightly elevated temperature (40 °C). Bondar et al. [3] has used Iranian natural pozzolan named Shahindej dacite which consists of some clinoptilolite to produce geopolymers. The results obtained show that the optimum water-soluble glass modulus ($\text{SiO}_2/\text{Na}_2\text{O}$ ratio), used for the study, is equal to 2.1. The best activation of the raw material is achieved by mixing potassium hydroxide and sodium water glass. The authors suggest curing at 60 °C or calcination of the material to produce structural concrete. However, the physical properties of the synthesized material depend mostly on precursors, the preparation method of the sample, the curing conditions, the particle size distribution and concentration and type of the alkaline activator.

The aim of the present study is to examine the influence of different types of activator solutions on natural zeolite clinoptilolite in order to produce geopolymer material with practical use. This is achieved by analysing the structures and properties of natural zeolite based geopolymers by means of instrumental methods such as TGA/DTA, XRD and SEM. Geopolymers were prepared from natural zeolite by using three types of activators: sodium hydroxide, sodium carbonate and sodium silicate.

2. Materials and methods

2.1. Materials

The natural zeolite (clinoptilolite) from the Beli plast deposit in the Eastern Rhodopes region, Bulgaria, is used for the research. The deposits consist of approximately 10 billion tons of natural zeolite-type Clinoptilolite [19]. The crushed zeolite is oven dried to constant mass and grounded in a ball mill down to the fineness of cement. The chemical composition of the zeolite is presented in Table 1. The analysis was conducted in University of Mining and Geology, Sofia, Bulgaria by AES ICP—method after alkali melting and dissolving with an acid, by classical chemical methods on the dried sample at 105 °C.

The mineral composition of the natural zeolite consists of 70–75% Clinoptilolite, 10% Cristobalite, 5–10% amorphous state, and under 5% of sanidine, calcite and dolomite.

The specific surface of the natural zeolite, determined by nitrogen adsorption using the BET method is 33 m²/g. The total measured relative volume (V_{total}) of pores is 0.11 cm³/g, the volume of the micropores (V_{micro}) is 0.004 cm³/g. The average diameter of micropores ($D_{\text{av,micro}}$) is 0.8 nm and the calculated value for the mesopores ($D_{\text{av,meso}}$) is 7.7 nm. The obtained pore-size distribution is presented on Fig. 1. The considerable specific surface of the zeolite leads to high water demand of the fresh geopolymer mixes. Davidovits [6] demonstrates that the added water is not chemically combined to the structure of the material, but it acts physically, providing suitable media for mixing and homogenization.

The components of the alkaline solutions are: sodium hydroxide (NaOH) on flakes (minimum 98% purity), sodium carbonate (Na_2CO_3) powder (minimum 99.8% purity) and sodium silicate water solution with molar ratio $\text{SiO}_2/\text{Na}_2\text{O} = 2.35$ and density 1.47 g/cm³.

Table 1

The chemical composition of natural zeolite clinoptilolite from Beli Plast, Bulgaria, measured by AES ICP.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	MnO	P_2O_5	SO_3	TiO_2	LOI	Humidity
62.74	9.68	0.74	6.73	2.90	2.79	0.29	0.03	< 0.03	< 0.03	0.12	13.74	5.00

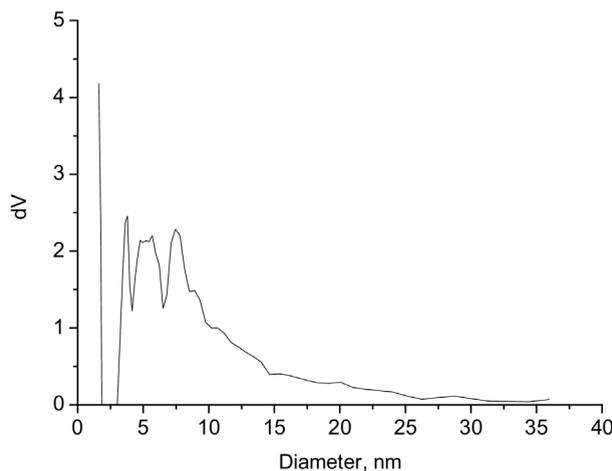


Fig. 1. Pore-size distribution of natural clinoptilolite from the Beli plast deposit, made by DFT theory.

2.2. Specimen preparation

Three series of specimens are prepared with different types of alkaline activators: sodium water soluble glass (sodium silicate solution $MR = 2.35$), water solution of sodium hydroxide with concentration—6 M, 8 M, 10 M and water solution of sodium carbonate (soda/zeolite by mass – 0.16, 0.24, 0.32 – marked as 1C, 2C, 3C respectively). The activating solution is tempered to room temperature before use. The high specific surface of the zeolite leads to considerable water demand. All geopolymeric mixtures are prepared at a fixed liquid to solid ratio of 0.55. This guarantees that all samples have the same initial total pore volume. The physical tests are carried on geopolymer pastes. The geopolymer mortars are produced by adding quartz sand (sand/zeolite = 3:1 by mass) for measuring the compressive strength.

The geopolymeric specimens were prepared by hand mixing of the zeolite and the activating solution. The resulting pastes and mortars are casted in cubic steel moulds of $40 \times 40 \times 40$ mm. Each sample was compacted by pressing and the moulds including the samples were kept in polyethylene bags to avoid excessive evaporation. After 10 days, the specimens were demoulded and put back into the polyethylene bags until testing at 28 days. Efflorescence is observed in all samples activated with sodium carbonate. The specimens were tested for compressive strength and sample pieces were taken from ones with highest strength for XRD, TGA/DTA and SEM.

2.3. Analytical methods

The samples taken from specimens tested for compressive strength were dried to constant mass and ground in a porcelain poulder to full passing through a sieve with a clear square opening of $63 \mu\text{m}$. The resulting powders were tested by X-ray diffraction by using a Bruker D8 diffractometer with $\text{CuK}\alpha$ radiation generated at 30 mA and 40 kV.

Other subsamples were examined by differential thermal and gravimetric analysis. Simultaneous DTA and TGA measurements were performed by using SETSYS Evolution TGA-DTA/DSC/MS between 20°C and 1000°C at heating rates $10^\circ\text{C}/\text{min}$.

Fragments from the tested specimens were examined by scanning electron microscopy. SEM-photos are obtained with different magnification of 500, 1000, 2000 and 5000 times by using electron microscope – SEM 515 with WEDAX-3A & Everhart Thorney detector – “Philips”.

3. Results and discussion

3.1. Compressive strength

The compressive strength is measured at 28 days, the results are presented in Fig. 2, and they show the highest strength for zeolite activated with water glass (3.7 MPa). Samples with sodium hydroxide show the highest strength at 8 M concentration (2.7 MPa), followed by the samples with sodium carbonate (3C) with ratio soda/zeolite = 0.32 by mass. The natural zeolite shows slow rates of strength gain at normal curing temperature (20°C), which combined with the addition of sand (3:1 by mass) leads to low compressive strength.

However, the result indicates that sodium silicate gives better results, which correspond to other studies of geopolymers.

3.2. X-ray diffraction

The results from XRD analysis of zeolitic raw material and the activated materials are presented on Fig. 3. The X-ray patterns are

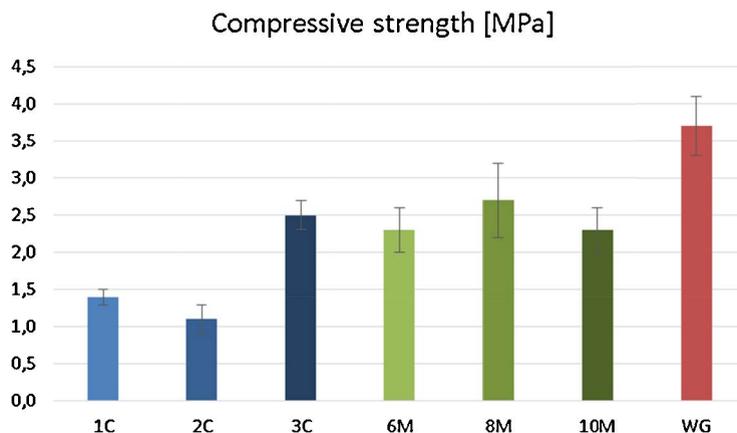


Fig. 2. Compressive strength of geopolimer mortars at 28 day.

placed one above the other. The graph of natural zeolite is at the bottom, followed by the graph of samples activated by sodium carbonate (3C), water glass and sodium hydroxide (8 M), respectively. Based on these X-ray diffraction patterns, significant difference can be observed between the quantity and the quality of the newly formed geopolimeric matrices for the different types of alkaline activators.

Almost no change of the structure of the geopolimer made with sodium carbonate can be seen, in comparison with the raw material, except considerable quantity of unreacted soda detected as trona—new peaks are located at $33.84^{\circ}2\theta$, $29.05^{\circ}2\theta$ and $18.12^{\circ}2\theta$. That means that not the whole quantity sodium carbonate is involved in geopolimerization process and some of the residual soda contact with water and carbon dioxide to transformed back to the parent mineral trona— $\text{Na}_3(\text{CO}_3)(\text{HCO}_3)\cdot 2\text{H}_2\text{O}$.

There is partial dissolution of Ca-clinoptilolite, sanidine and cristobalite in the samples activated with water soluble glass.

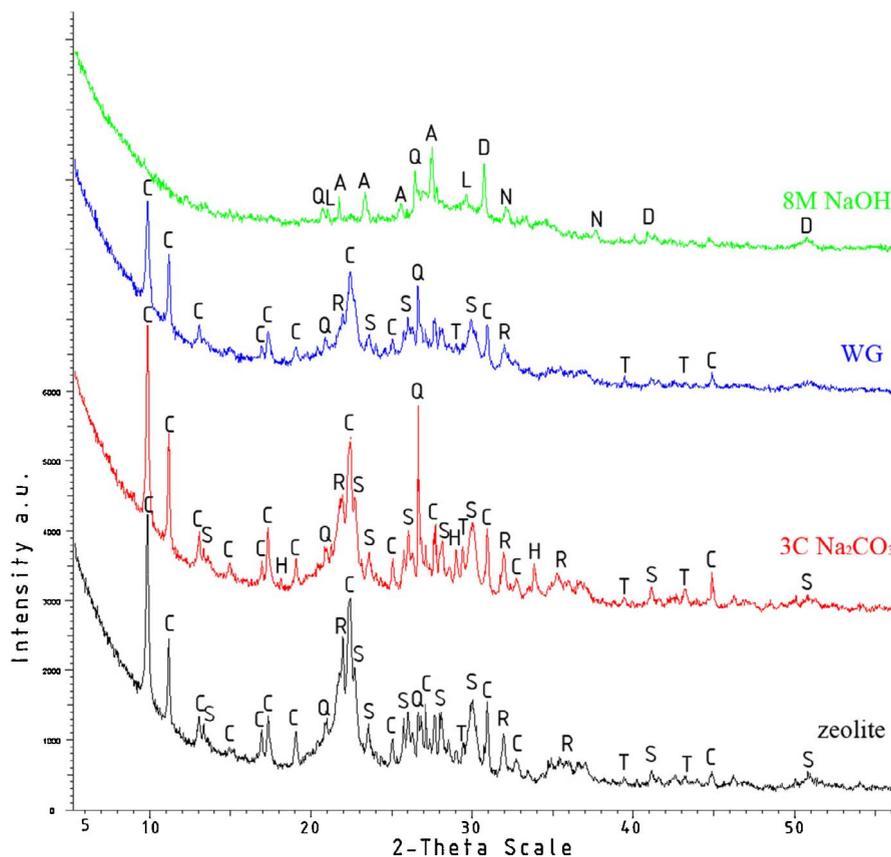


Fig. 3. X-ray patterns of the zeolite raw material and the geopolymers obtained by activation with sodium carbonate (3C), water glass and sodium hydroxide (8M) (C = clinoptilolite-Ca, R = cristobalite, Q = quartz, A = anorthite (disordered); D = dolomite; S = sanidine; T = calcite, N = thermonatrite, L = calcium aluminium silicate, H = trona.

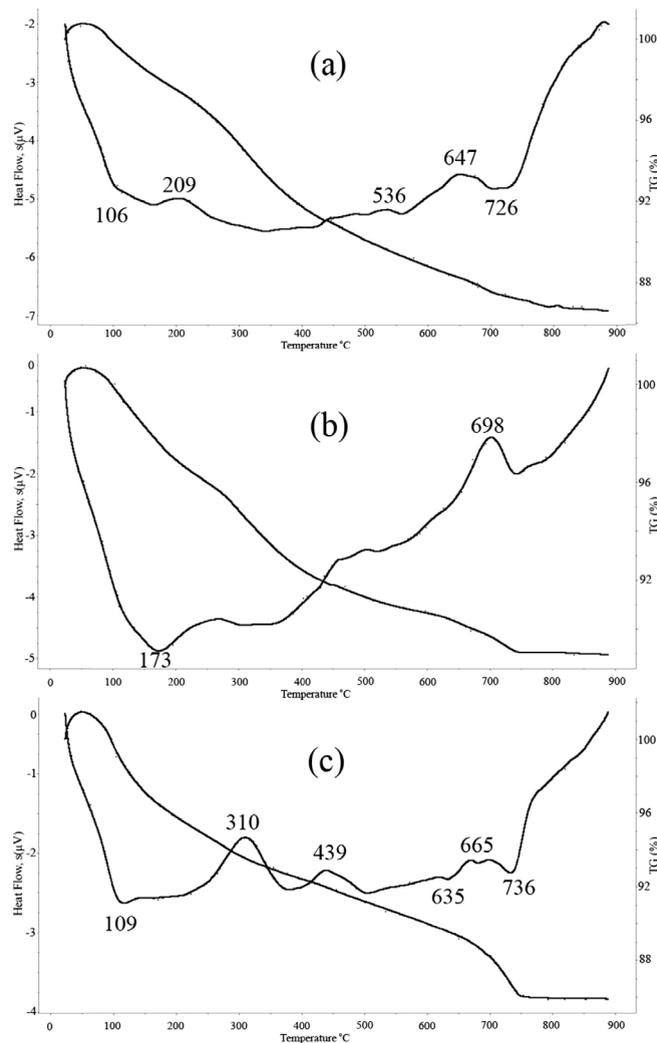


Fig. 4. DTA/TG for geopolymers obtained by activation with sodium hydroxide (a), water glass (b) and sodium carbonate (c).

When sodium hydroxide is used as an activator, a typical X-ray pattern for an amorphous geopolymer structure can be observed with only some minor peaks of crystalline phases. The peaks, corresponding to Ca-clinoptilolite and cristobalite completely disappear, supposing a high degree of geopolymerization. Some new phases have been formed, possibly dolomite, disordered anorthite, thermonatrite and aluminosilicates. The hardened geopolymer activated with sodium hydroxide had a lower compressive strength at 28 days than water glass activated one, despite of higher degree of geopolymerization. This is explained with higher tendency of shrinkage and higher relative volume of the pores observed in geopolymer pastes based on NaOH, compared to sodium silicate based [12].

3.3. Differential thermal and thermogravimetric analysis (DTA/TGA)

In Fig. 4, the DTA/TGA thermographs of the geopolymers obtained by the activation of the zeolitic raw material are presented: activated by sodium hydroxide (Fig. 4a), by water soluble glass (Fig. 4b) and by sodium carbonate (Fig. 4c).

It can be concluded from the DTA results that the type of activator affects the process of heat transformation. Endothermic peaks in the range of 100–170 °C are observed for all samples. Such peaks, caused by evaporation of the adsorbed water are normal for mineral materials. The higher endothermic peak at 173 °C in the water soluble glass activated sample is an evidence for a denser structure of the material.

The samples activated with water soluble glass (Fig. 4b) show a clear exothermic peak at 698 °C, due to transition of amorphous alkaline silicates to their crystalline form (cristobalite). This is supported by XRD results from similar samples of natural zeolite activated with sodium silicate, thermally heated to 1000 °C [13].

A sequence of thermal effects is observed for geopolymers obtained by sodium carbonate activation (Fig. 4c). Such peaks are also characteristic for pure Na_2CO_3 , which means that a considerable portion of the activator has not taken part in the activation reactions

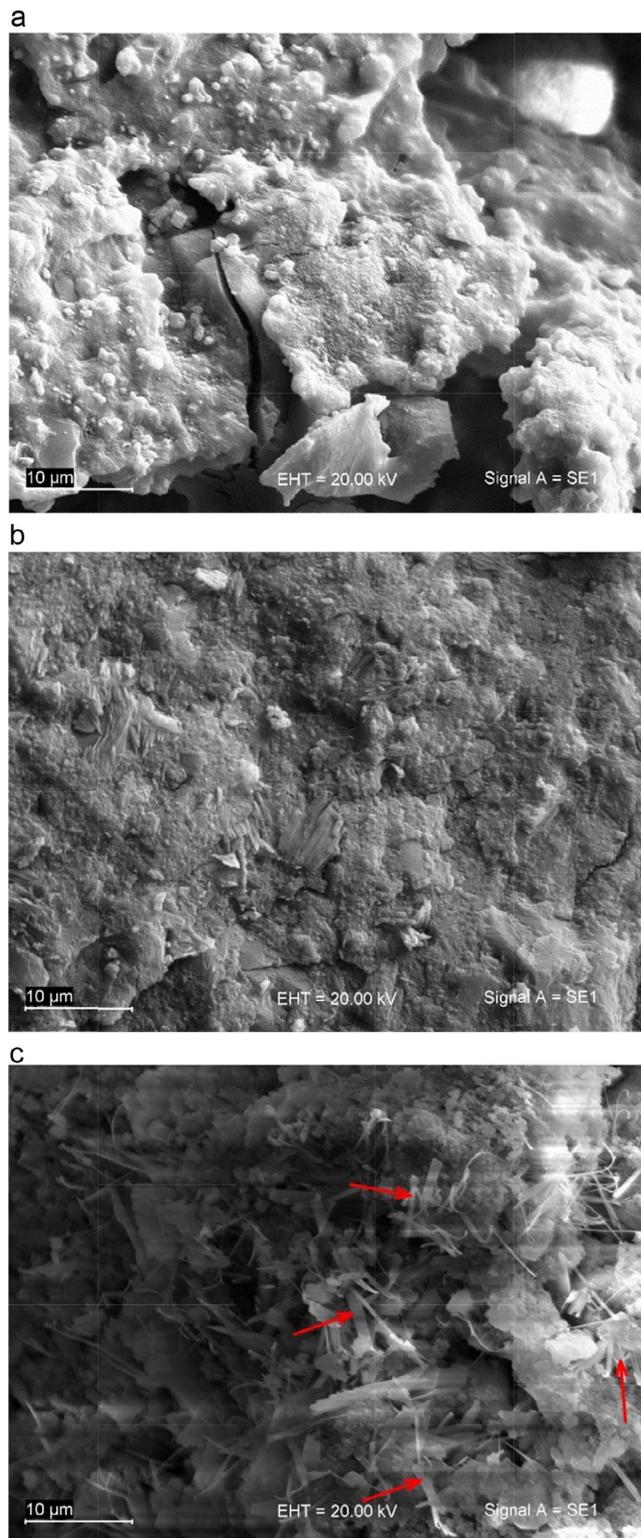


Fig. 5. (a) SEM image of material activated with sodium hydroxide. (b) SEM image of material activated with water soluble glass. (c) SEM image of material activated with sodium carbonate.



Fig. 6. Adhesion specimen after testing.

with zeolite and therefore it remains as free sodium carbonate.

The thermogravimetric curves show the lowest mass loss for geopolymers produced with water soluble glass (11.08%), followed by NaOH (13.35%) and Na_2CO_3 (14.10%).

3.4. Scanning electron microscopy (SEM)

The SEM photos taken with magnification $5000\times$ of the samples activated with sodium hydroxide, sodium water soluble glass and sodium carbonate are presented at Fig. 5a–c, respectively.

It can be seen from the SEM photographs (Fig. 5) that geopolymers produced from water glass and sodium hydroxide are microscopically similar. The main difference between them is the clear globular microstructure of sodium hydroxide based geopolymer. A shrinkage crack is observed on Fig. 5a.

The sample based on sodium carbonate is difficult to work with. The material is brittle and is not well covered with gold, which compromises the conductive coating, as a result unwanted horizontal lines on the photographs are observed. However, it can be confirmed that the structure of the sodium carbonate based sample is more porous in comparison to the others and it shows more newly formed platy and needle-like crystals of sodium carbonate (pointed on Fig. 5c).

3.5. Discussion

The present research shows that geopolymers based on Bulgarian natural zeolite increase strength relatively slowly at normal temperature. At the same time, the solid geopolymer is characterized by low strength and high tendency to shrinkage. These properties limit the practical use of the building material. This motivates the research team to look for specific niches and applications. The effect of high shrinkage could be minimized by casting of the material in thin layers—for example in plasters, stucco, screed or coatings. Meanwhile, the compressive strength is not as an important characteristic of the plasters as the adhesion to different surfaces.

The adhesion of hardened geopolymer paste to concrete at direct tension is determined by pull-off test. Two series of specimens are prepared—with and without fibre reinforcement. The polypropylene micro fibres—monofilaments, with length = 4 mm and diameter = $18\ \mu\text{m}$, in quantity 1% by volume, are added in one of the series, in order to reduce excessive shrinkage.

3.6. Adhesion to concrete

The preparation of the concrete substrate is realized by brushing and moisturizing. The thin layer geopolymer paste, with an approximate total thickness of 2 mm, is applied using a steel trowel. The specimens are cured without cover in laboratory conditions ($23 \pm 2\ ^\circ\text{C}$, $\text{RH } 65 \pm 5\%$). There is no presence of the shrinkage cracks on the surface of the coatings after four weeks hardening when the adhesion test is performed. The failure type is cohesive, in the geopolymer coating (Fig. 6), at all tested samples.

The obtained adhesion strength is relatively high—over 2 MPa, making geopolymer based on natural zeolite suitable for plasters and coatings.

4. Conclusion

Taking into account the results from the studies conducted, it can be concluded that the mixing of natural zeolite with different

types of alkaline activators leads to the formation of a solid material with qualitatively different structure.

Sample based on sodium silicate (water soluble glass) shows highest compressive strength at 28 days. The results show partial dissolution of main minerals presented in natural zeolite—clinoptilolite and cristobalite, when sodium silicate is used as an activator. On the other hand, when sodium hydroxide is used total dissolution of zeolite is observed and amorphous phase is formed with some crystalline inclusion. Only partial reaction with the zeolite is observed in case of sodium carbonate activation, and the final product consists of significant amount of unreacted soda ash.

The geopolymer paste, used as surface coating of concrete substrate, shows an excellent adhesion characteristic, making natural zeolite based geopolymer suitable for plasters and coatings.

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References

- [1] E. Alcántara, Ch. Cheeseman, J. Knight, M. Loizidou, Properties of alkali-activated clinoptilolite, *Cem. Concr. Res.* 30 (2000) 1641–1646.
- [2] T. Bakharev, Durability of geopolymer materials in sodium and magnesium sulfate solutions, *Cem. Concr. Res.* 35 (2005) 1233–1246.
- [3] D. Bondar, C.J. Lynsdale, N. Milestone, N. Hassani, A. Ramezani-pour, Effect of type, form, and dosage of activators on strength of alkali-activated natural pozzolans, *Cem. Concr. Res.* 33 (2011) 251–260.
- [4] W.H. Casey, H.R. Westrich, G.R. Holdren, Dissolution rates of plagioclase at pH = 1 and 3, *Am. Mineral.* 76 (1991) 168–173.
- [5] J. Davidovits, L. Buzzi, P. Rocher, D. Gimeno, C. Marini, S. Tocco, Geopolymeric cement based on low cost geopolymer materials. Results from the European Research Project GEOCISTEM, *Geopolymer' 99 Proceeding* (1999) p83–p96.
- [6] J. Davidovits, *Geopolymer—Chemistry & Application*, second ed., Geopolymer Institute, Saint-Quentin, France, 2951482051, 2011, pp. 63–422.
- [7] P. Duxson, J.L. Provis, Designing precursors for geopolymer cements, *J. Am. Ceram. Soc.* 91 (2008) 3864–3869.
- [8] A. Fernández-Jiménez, I. García-Lodeiro, A. Palomo, Durability of alkali activated fly ash cementitious materials, *J. Mater. Sci.* 42 (2007) p3055–p3065.
- [9] A. Palomo, M.T. Blanco-Valera, M.L. Granizo, F. Puertas, T. Vázquez, M.W. Grutzeck, Chemical stability of cementitious materials based on metakaolin, *Cem. Concr. Res.* 29 (1999) 997–1004.
- [10] J.L. Provis, J.S.J. Deventer, *Geopolymers: Structures, Processing, Properties and Industrial Applications*, Woodhead Publishing, Saint-Quentin, France, 200910:184569449X.
- [11] N. Müller, J. Harnisch, A blueprint for a climate friendly cement industry, How to Turn Around the Trend of Cement Related [Report], WWF International, 2008, pp. p1–p2.
- [12] A. Nikolov, I. Rostovsky, V. Naidenov, Geopolymeric materials based on natural zeolite, 13th International Scientific Conference VSU'2013 (2013) ISSN 1314-071X (IV 66-71).
- [13] A. Nikolov, I. Rostovsky, Structural study of geopolymers based on natural zeolite and sodium silicate after thermal treatment of up to 1000 °C, Annual of the University of Architecture, Civil Engineering and Geodesy, Sofia, Fascicule VIII-A, Scientific Research-I, 2014–2015, University of Architecture, Civil Engineering and Geodesy, Sofia, 2014ISSN 1310-814X.
- [14] T. Silverstrim, H. Rostami, J. Clark, J. Martin, Microstructure and properties of chemically activated fly ash concrete, *Proc. 19th Int. Conf. Cem. Microsc.*, Int. Cement Microscopy Assoc. (1997) p355–p373.
- [15] T. Ueng, S. Lyu, H. Chu, H. Lee, T. Wang, Adhesion at interface of geopolymer and cement mortar under compression: an experimental study, *Constr. Build. Mater.* 35 (2012) p204–p210.
- [16] C. Villa, E. Pecina, R. Torres, L. Gómez, Geopolymer synthesis using alkaline activation of natural zeolite, CIMAV, S.C., Compl. Ind. Chihuahua, C.P. 31109, Chihuahua, Chih., Mexico, ESI-UAdeC, Blvd. Adolfo López Mateos S/N C.P. 26830, Nueva Rosita, Coah., Mexico, FIME-UANL, Ciudad universitaria, San Nicolás, Nuevo León, Mexico, (2010), *Constr. Build. Mater.* 24 (2010) p2084–p2090.
- [17] R. Xu, W. Pang, J. Yu, Q. Huo, J. Chen, *Chemistry of Zeolites and Related Porous Materials: Synthesis and Structure*, WILEY, Clementi Loop, Singapore, 978-0-470-82233-3, 2007, p. p24.
- [18] S. Yong, D. Feng, G. Lukey, J. Deventer, Chemical characterisation of the steel–geopolymeric gel interface, *Colloids Surf., A: Physicochem. Eng. Aspects* 302 (2007) p411–p423.
- [19] V.I. Smirnov, M.D. Zhelyazkova-Panayotova, A.I. Ginzburg, et al., *Geology of the Ore Deposits*, Science and Art Publishing, 1986, p. 350 (in Bulgarian).