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Super high strength metabentonite based geopolymer

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Abstract

The paper presents the results of the study on the effects of the combination of the low liquid/solid (l/s) ratio and pressure compaction of the fresh pastes on the properties of the hardened based geopolymer paste. It is very well known that the mentioned combination gives the possibility to prepare cement composites with the excellent engineering properties. The object of the study was the metabentonite based geopolymer. The results obtained shown the metabentonite based geopolymer prepared under the combination of the low l/s ratio value and pressure compaction as a super strength material. This strength effect was evidently a consequence of the found high dense nano- or near-nano pore structure of the geopolymer.

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1. Introduction

A significant motivation driving the geopolymer research is to catch up the high quality of the engineering properties of the geopolymers. The variations and combinations of the concrete technology processing factors along this line are very interesting. It is well known that when very low water/cement ratios are used they result in a significant increase of strengths, durability and the quality of the others engineering properties of concretes may be achieved [1,2].

The object of the paper is to characterize the properties of the metabentonite based geopolymer prepared under the use of the combination of the very low w/c ratio and pressure compaction of the fresh mixture.

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2. Experimental procedure

2.1. Test specimens' preparation and their testing

For the study the metabentonite pastes were prepared with activator solution/metabentonite ratio (l/s) 0.08. The test specimens were 20 mm-edge cubes. The reference test specimens were prepared with l/s 0.70. The alkali activator sodium hydroxide solution was added to the mixture. The portion of the activator corresponded to 7 wt. % of the weight of the metabentonite.

The preparation of the fresh mixtures represented an intensive mixing for 3 min using electrical mixer. The forms were filled by the mixture. Then the mixture with l/s ratio 0.08 was compacted under the application of the uniaxial pressure 300 MPa with the endurance of 1 min. The preparation of the reference test specimens (l/s ratio 0.70) was the same but the manual compaction was used. Then the pressure compacted test specimens hardened 24 hours and the reference test specimens due to their slow hardening 5 days. The ambient temperature of the hardening was 20 °C and relative humidity 95%. After the demoulding, their testing followed. The test specimens were dried at 105 °C and these properties were estimated: bulk weight, compressive strength, specific weight, phase composition, pore structure and morphology of the particles of the matrix.

2.2. Methods used

Bulk weight was calculated using the estimated weight and dimensions of the test specimens. For the estimation of compressive strength a destructive method using the loading press was used. For specific weight estimation the equipment Pentapyc 5200e QUANTACHROME CORPORATION was used. Thermal analysis was carried out on the METTLER TOLEDO, TGA/DSC 1, STAREe System, the sample mass 45 mg, heating rate 10 °C/min, ramping from ambient temperature to 1000 °C in an air atmosphere. For pore structure analysis Pore Master 60 automated mercury porosimeter, using the wetting contact angle 141.3 ° and mercury surface tension 0.48 N·m⁻¹ was used [3]. Using the pore analyzes results the water permeability coefficients were calculated [4]. The morphology of the samples was studied by scanning electron microscopy using a Carl Zeiss – EVO 40 HV microscope. Before the scanning process, all samples were coated with gold to enhance the electron conductivity.

2.3. Materials

The metabentonite used was the product of bentonite heat-treatment at 650 °C for 4 hours. The data on the chemical composition, based on the results of the current chemical analytical methods, and specific weight of the both materials are given in Table 1. As it can be seen the consequences of the heating was the increase in the content of SiO₂ and Al₂O₃, and the specific weight. It was evidently a consequence of minimizing the ignition loss content due to the heating. The resulted increase of SiO₂ and Al₂O₃ content seems to be interesting effect because their molar ratio used to be appreciated as a significant factor of the development of geopolymers with performed mechanical properties. This ratio is considered as a main synthesis parameter among alkali content Na₂O/Al₂O₃, water to aluminosilicate ratio, and processing parameters such as curing time and curing temperature and others [5].

Table 1. Chemical composition and specific weight of bentonite and metabentonite.

Characteristics	Components (%)	
	Bentonite	Metabentonite
Humidity	5.23	0.95
Ignition loss	6.19	1.98
SiO ₂	71.10	76.56
Al ₂ O ₃	9.94	11.74
Fe ₂ O ₃	2.33	3.62
CaO	3.46	3.62
MgO	1.65	1.51
Specific weight (<i>kg·m⁻³</i>)	2273	2501
SiO ₂ :Al ₂ O ₃ mol. ratio	12.08	11.10
dehydroxylation degree α (%)	68.0	

The used metabentonite accounted the SiO₂/Al₂O₃ molar ratio 11.10 indicating the high SiO₂ content what is promising. The significance of the high SiO₂/Al₂O₃ molar ratio is based on the fact that a high silicate dosage is necessary for synthesizing aluminosilicate gel that provides good interparticle bonding and physical strength of geopolymers. Moreover, the silica content controls the dissolution and polymerization of silica and alumina in aluminosilicate gel [5–7]. The major quantitative criterion for evaluation of the performance of clay by thermal treatment is the dehydroxylation degree α [8]:

$$\alpha = 1 - \left(\frac{M}{M_{\max}} \right) \quad (1)$$

Where: M and M_{max} are residual and maximum sample mass loss, respectively.

Using data on the ignition loss from Table 1 the value of dehydroxylation degree of bentonite used was calculated $\alpha = 68.0\%$. It shows the deficient dehydroxylation of bentonite. Evidently, the higher calcination temperature should be used for the total dehydroxylation and accomplishing the α value 100%.

3. Results and discussion

3.1. Mechanical properties and pore structure

The results of the estimation of bulk weight and compressive strength are summarized in Table 2. The significant difference in the values at the pressure compacted and reference pastes are very evident. It documents 43.9% and 55750% increased bulk weight and compressive strength in the benefit of the pressure compacted paste.

Table 2. Mechanical characteristics of metabentonite based geopolymers.

Hardened paste	Bulk weight (<i>kg·m⁻³</i>)	Compressive strength (MPa)	Increase opposite to the reference (%)	
Preparation conditions			Bulk weight	Compressive strength
Pressure compaction 300MPa, l/s ratio 0.08 hardening conditions 1 day, 20 °C, 95% RH	1497	111.5	43.9	55 750
Reference paste, l/s ratio 0.70, ,hardening conditions, 5 days, 20 °C, 95% RH	1040	0.20	-	

An adequate relationship can be observed when the pore structure parameters, shown in Table 3, are taken in the account. It can be seen a significant decrease of the total porosity, pore median, pore volume and water permeability coefficient at pressure compacted paste opposite to the reference one. The decrease represented 65.2% at total porosity, 80.8/83.7 % at total/micro pore median, 75.5/78.0 % at total /micro pore volume, and at water permeability coefficient 92.7%. The difference between surface area was minimal with the values 18.6 (pressure compacted paste) and 17.1 $m^2 \cdot g^{-1}$ (reference paste). A reverse, unparalleled relationship shown the macropore content increase with the values 24.4% (pressure compacted paste) opposite to the 17.2% (reference paste).

On the whole, these results document the formation of high dense pore structure under the use of the low l/s ratio and pressure compaction. The direct consequence was high compressive strength of the pressure compacted paste 111.5 MPa opposite to the reference showing the value only 0.20 MPa.

The detected presence of the mildly increased macro pore content in the pressure compacted paste was probably able to some degree to depress the positive effect of the technology. The causes of the phenomenon are not yet known. But it can be expected that its elimination will increase the effectivity of the technology with the further increase of the compressive strength. Therefore, the elimination of the negative effect of the macropore content in the pressure compacted composites seems to be an interesting and important research topic.

Table 3. Pore structure parameters of the geopolymers.

Hardened paste	Total porosity (%)	Pore median (nm)	Pore volume ($cm^3 \cdot g^{-1}$)	Specific surface area ($m^2 \cdot g^{-1}$)	Macro pore content (%)	Coefficient of water permeability ($K \cdot 10^{-13} m \cdot s^{-1}$)
		Total/micro	Total/micro			
Preparation conditions						
Pressure compaction 300MPa, l/s 0.08, hardening conditions 1 day, 20 °C, 95% RH	17.9	39.4/24.0	0.12/0.09	18.6	24.4	4
Reference paste, l/s ratio 0.70, hardening conditions, 5 days, 20 °C, 95% RH	51.4	205.5/146.9	0.49/0.41	17.1	17.2	55

Total pore radius range 2 – 200000 nm,

Micro pore radius range 2 – 7500 nm

Water permeability coefficient calculated using the mercury porosimetry results [4]

Specific surface area calculated from porosimetry results.

A suitable and demonstrative illustration of the pore structure character provide Fig. 1 and 2 as the pore size distribution histograms. When they are compared it can be seen a significant restriction of pore size distribution histogram area of the pressure compacted paste opposite to the reference paste representing the decrease 73%, along with an almost vanishing of pores with radius over 500 nm. Only a sporadic occurrence of little amount of the pores between radius ca 2000 nm to ca 10000 nm and a coherent occurrence of the pores between 50000 to 500000 nm could be observed. Therefore, the pressure compacted paste as the material with the high degree of pore structure homogeneity and fineness opposite to the reference paste is appeared.

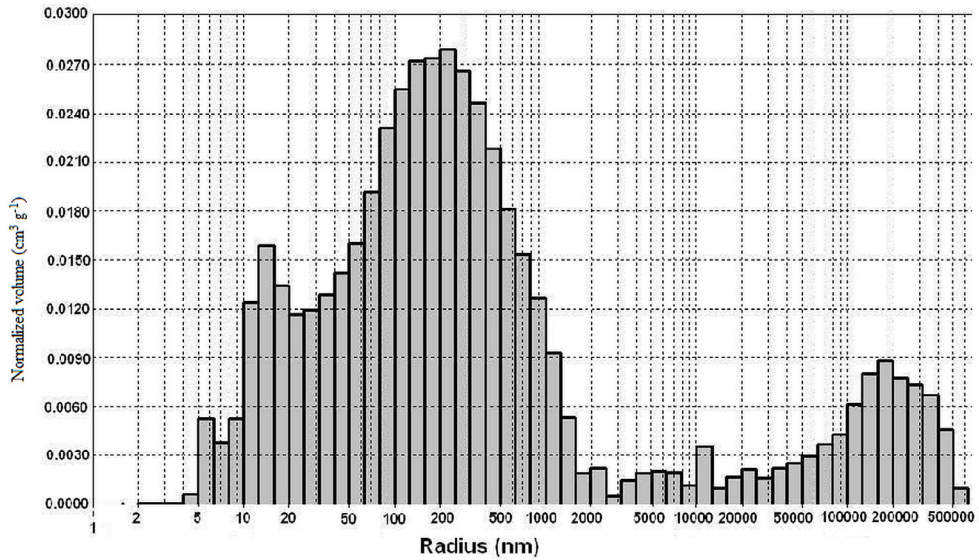


Fig. 1. Pore size distribution histogram of the reference metabentonite paste after 5 day of the hardening.

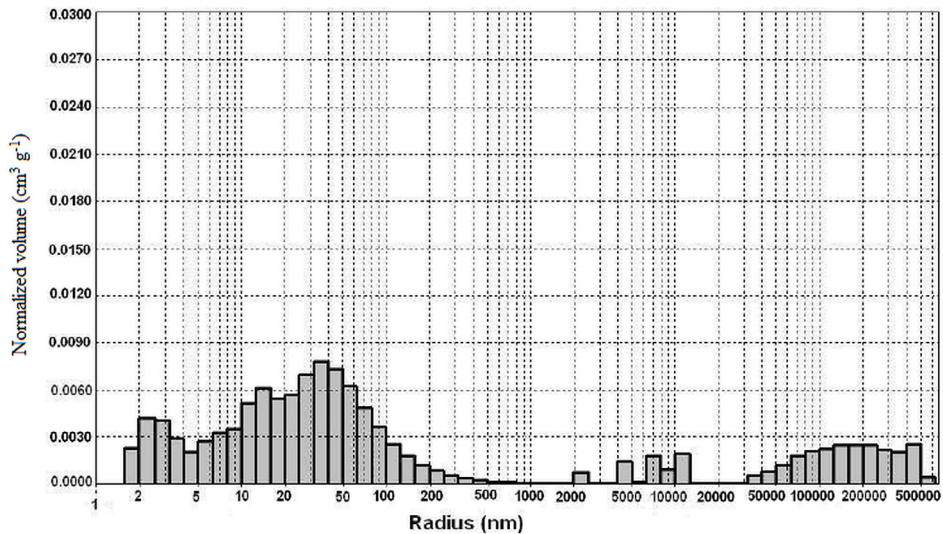


Fig. 2. Pore size distribution histogram of the pressure compacted metabentonite paste after 1 day of the hardening.

3.2. Thermal analysis

The DTA curves of the bentonite and its metaproduct in Fig. 3 are shown. It can be seen that the DTA curve of the metabentonite with the miniaturized endodeflections, especially at 88 °C and 165 °C, less at 625 °C and 669 °C makes tracks of the DTA curve of the bentonite, without the possibility of the assessment their phase affiliation. The observed miniaturization effect shows the destruction of the phases containing water present. It is evident that DTA was of the able to provide only very limited information on the phase composition and the changes of the systems.

It was evidently the consequence of the known amorphous or near-amorphous character of the constituents of the geopolymers. TGA curves shown in Fig. 4 and 5 accounted near levels of total weight loss 10.34 (pressure compacted paste) and 9.79% (reference paste). That loss represents the releasing of humidity, adsorbed and chemically bound water in the hydrates.

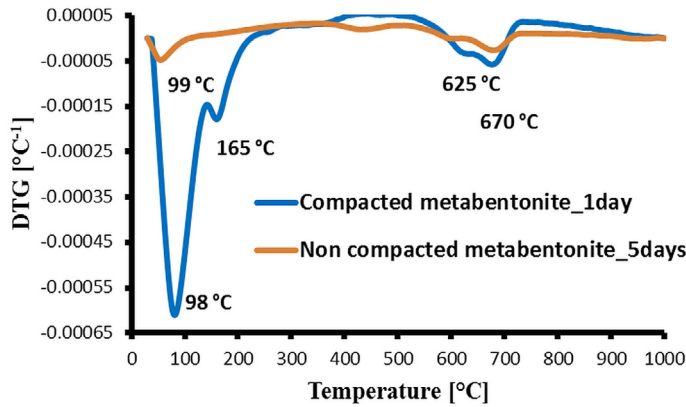


Fig. 3. DTA curves of the pressure compacted metabentonite and reference paste after 1 and 5 days of the hardening.

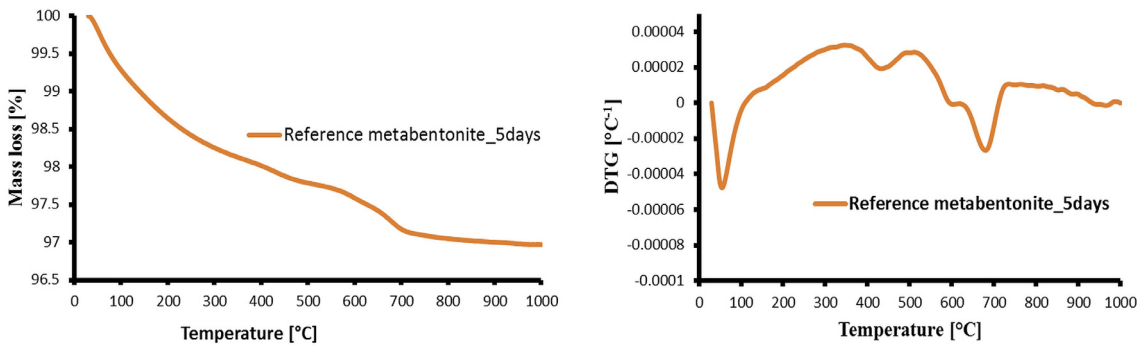


Fig. 4. TG and DTG curves of the reference metabentonite paste after 5 day of the hardening.

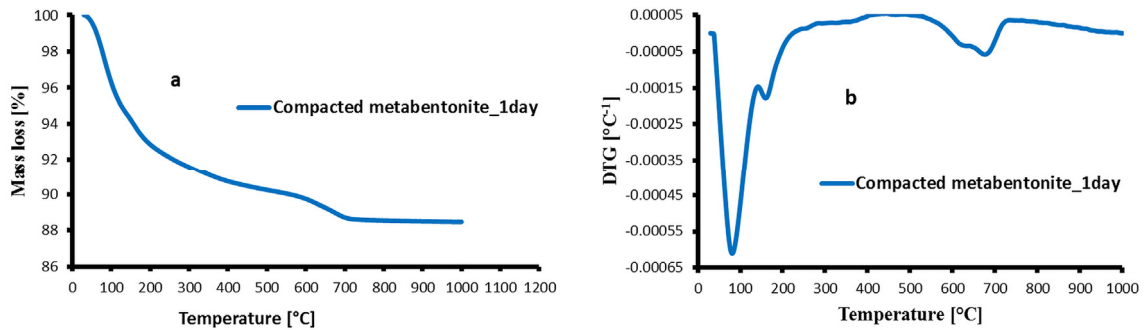


Fig. 5. TG and DTG curves of the pressure compacted metabentonite paste after 1 day of the hardening.

3.3. Scanning electron microscopy

A high and significant difference between character of the microstructure of geopolymer matrix of pressure compacted and reference pastes is observable at comparison of Fig. 7 and 8. As it can be seen the microstructure for the reference paste is highly incompact, with the large grains and pores shown as dark places. The occurrence of flake-like layer structure of metabentonite particulates is an evidence of the low development of the geopolymerization process. Evidently, only a small quantity of the geopolymer product is taking the place at the surface layer of the metabentonite particulates [9]. This microstructure character reminds the matrix observed at metakaolin and metahalloysite based geopolymers [10,11].

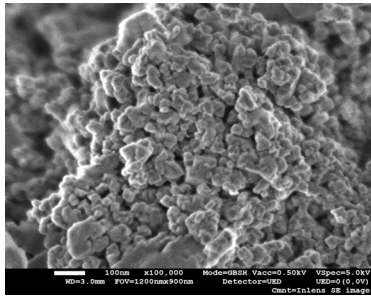


Fig. 6. SEM image of metabentonite.

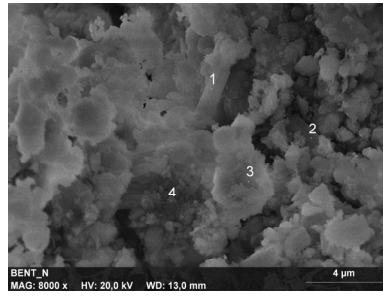


Fig. 7. SEM image of the reference metabentonite based geopolymer after 5 days of the hardening.

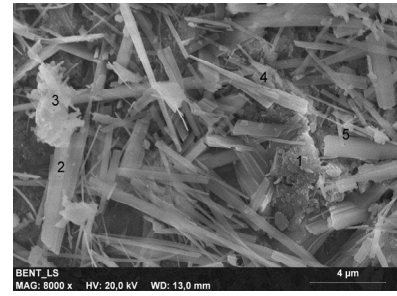


Fig. 8. SEM image of the pressure compacted metabentonite based geopolymer after 1 day of the hardening.

The microstructure of the pressure compacted paste is diametrically unlike (Fig. 8). The intervening material is of more homogeneous nature, with small pores shown as dark places. These appear smaller in comparison to those observed at the reference paste. This observation is in a strong correlation with the porosimetry results showing finer pore structure of the aggregated material. However, for the pressured paste is markedly characteristic, an abundant occurrence of stick particulates. Their uniqueness conclusively also by the SEM image of the metabentonite (Fig. 6) is confirmed. The occurrence of the stick particles is very interesting phenomenon suggesting the possibility different hardening mechanism of the geopolymers under the use of very low l/s ratio values.

The stick particulate occurrence seem to be significant and important topic due to the possibility of their feasible effect on the strength of the material. The influence of particle shape on the rheology and performance of Portland cement based concretes is reasonably well understood, and is reviewed in some detail in most concrete texts. However, this issue has not previously been explored in detail in the scientific literature for the case of alkali-activated materials. It is therefore obvious that there is much which remains to be determined regarding the effect of particle geometry on the behavior of geopolymer pastes undergoing alkaline activation [12–14].

4. Conclusion

- The combination of the low l/s ratio with the pressure compaction of the fresh mixture as a significant accelerator of the pore structure development and on it dependent strength of geopolymer has been shown.
- The used l/s 0.08 ratio and 300 MPa compaction pressure resulted in the very dense near nano-pore structure with the high degree of the homogeneity and the compressive strength overcoming the reference material over ca. 56000 times.
- The found occurrence of the sticky particles in the pressure compacted paste seems to be very interesting research topic. As a cause of their existence the very low l/s ratio comes into the consideration. A possible synergetic effect of the sticky particles on the high compressive strength of the pressure compacted geopolymer is also actual.

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