HIGH STRENGTH METAKAOLIN BASED GEOPOLYMER

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The unique properties of aluminosilicates have made them valuable in the wide range of industrial applications. One branch of application is represented by building materials.

A significant factor of the level of the quality of engineering properties of building materials anyhow is the water/binder ratio. It is well known that its decreasing value effectively increases strength and quality of other engineering properties of the material. Due to the accompanying effect impairing workability of the mixture for processing the pressure compaction is needed.

The subject of the paper are the results of the study of the properties of metakaolin based geopolymer prepared under the use of the combination of very low water/metakaolin ratio (0.08), pressure compaction of the fresh mixture by applying an uniaxial compressive stress of 300 MPa and alkali activation. The effect of preparation conditions was systematically studied by a thermal analysis (DTA, GTA), mercury intrusion porosimetry, coupling of scanning microscopy and EDX, and compressive strength estimation of the geopolymer. The used metakaolin was a product of calcination of the source material at 650 °C for 4 hours. It was an amorphous material showing an increased thermodynamic instability and herewith an increased reactivity in comparison with the unheated solid. The pressure compacted geopolymer reached after 24 hrs of the hardening the compressive strength of 146.6 MPa whereas the reference paste only 0.03 MPa. It represents 2540 times increase in behalf of the pressure compacted paste. High compressive strength was evidently the consequence of the found high homogeneous and dense pore structure of the pressure compacted paste.

Keywords: geopolymer, microstructure, metakaolin, pore structure, compressive strength

1.   Introduction

Geopolymers are a class of aluminosilicates formed by reaction of solution of alkali hydroxides with dehydroxylated clay or analogous solid waste materials under high alkaline conditions. The hardening mechanism involves the chemical reaction of geopolymeric precursors, such as alumino-silicate oxides, with alkali polysilicates yielding polymeric Si-O-Al bonds. The result of the hardening mechanism is a three dimensional zeolitic framework unlike traditional hydraulic binders in which hardening is the result of the hydration of calciumaluminates and silicates (Schulze, 1999; Naragaj et al., 1996; Appa Rao, 2001; Freiden et al., 2007; Zhongzi et al., 1993; Zhongzi et al., 1993; Della Roy et al., 1972). This circumstance is a cause of significant differences in the quality and variety of the engineering properties of the composites based on geopolymer and current cements. Geopolymers can gain strength more rapidly than Ordinary Portland ce-

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ment. The dependence of the engineering properties of concretes and other cement composites on the value of water/cement ratio (w/c) is very well known. Also the fact that their strengths, durability and the quality of other engineering properties are increased when the w/c ratio values are decreased (Schulze, 1999; Naragaj et al., 1996; Appa Rao, 2001). A significant factor limiting the use of these positive effects is the workability worsening that can be partially solved by use of plasticizers and superplasticizers. An illustration of the influence and significance of the w/c ratio values used is in Figure 1 (Zivica, 2009).
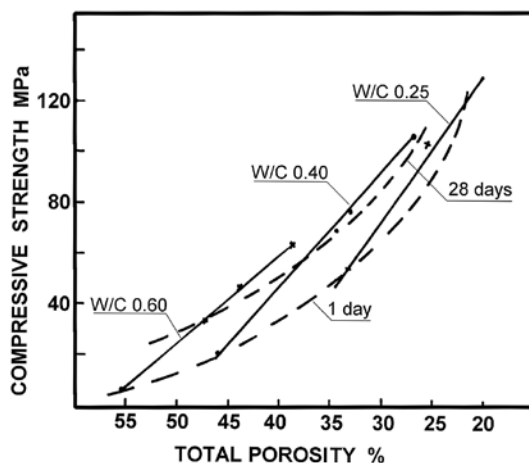

Figure 1. Dependence of compressive strength of the cement paste on total porosity and changes of (w/c) ratio (Zivica, 2009)

A very attractive solution represents the combination of super low *w/c* ratios, under *w/c* 0.1, resulting in a submicroscopic pore structure and an adequate high quality of the engineering properties of the composite (Freiden et al., 2007; Zhongzi et al., 1993; Della Roy et al., 1972 and 1973; Durekovic et al., 1995; Roessler et al., 1985). It appears that the low porosity cement composites have a great potential of reconsideration and modification of composition and structure (Zhongzi et al., 1993). All mentioned dependences and effects are common also to geopolymer systems distinguishing from the related cement materials only by the specific properties of geopolymer as a binder. The significance of the water: cement ratio for the geopolymer systems is reported (Barbosa et al., 2000). According to the authors the effects of the changes of water are: cement ratio on the properties of the geopolymers are the same as at cement materials. Similar is the effect of ambient temperature increase showing the setting time decrease as a consequence of increase of rapidity of polymerization and the hardening more rapidly than OPC cement. But only the temperature increase to 90 °C seems to be optimal (Chindaprasirt et al., 2007; Chang et al., 2008; Kong et al., 2000 and 2010; Rodríguez et al., 2013).

The aim of the presented work was to study on the possibilities of the use of effects of the combination of very low w/c ratio and pressure compaction in the geopolymer systems. As a model the alkali activated metakaolin system was used. Metakaolin used was a product of heating the kaolin at 650 °C for 4 hours (Mánayai et al., 1970; Pennel et al., 1991).

Progressive heating of clays leads to the removal of free, adsorbed and structural water, which is followed by the formation of new minerals. In open atmospheric conditions include reversible dehydration of loosely bound water when dry-heated between 100 °C and 300 °C, irreversible removal of interlayer water and loss of swell potential at temperature above 400 °C, dehydroxylation or release of hydroxyl groups from the crystal structure of clays between 500 °C and 1 000 °C, silicate recrystallization and the formation of new minerals at above 800 °C (Mitchel, 1976; Wang et al., 1990; Kuhnel et al., 1993).

Some physico-chemical properties of clays such as swelling, plasticity, cohesion, compressibility, strength, cation exchange capacity, particle size, adsorptive properties, pore structure, surface acidity, and catalytic activity as well mineralogy are greatly affected by thermal treatment. The investigation of these effects and their influence on the properties of the clays has a great importance (Jaarsveld et al., 2002; Hua, X. et al., 2003; Lee et al., 2002).

The thermal transformation of clays is dependent on the heating parameters such as temperature, heating rate and time, as well as, cooling parameters significantly influence the dehydroxilation process. The major quantitative criterion for evaluating the performance by thermal analysis is a degree of dehydroxilation. In dehydroxilation region the activity of heated material increases along with the temperature but decreases abruptly in the `spinel` region. The activities can be measured by the compressive strength of prepared geopolymer. Along with the temperature increasing, compressive strength of kaolinit based geopolymer increases to a maximum at about 900 °C, sustains until 950 °C, with a little decrease and sharply decreases at 1 000 °C (Jaarsveld et. al., 2002; Lee et al., 2002; Yang et al., 2008; Hua, H. et al., 2003; Bágeľ et. al. 1997; Jambor 1961).

2.   Methods, test specimens and materials

2.1.Methods

Bulk density was calculated using the determined weight and dimensions of the test specimens. For the estimation of compressive strength there was used a destructive method using the loading press.

Thermal analysis was carried out on the equipment Thermal analysis (simultaneous TG and DTA curves) SDT 2960 device T.A. Instruments: the sample mass 20 mg, heating rate was10 °C/min, ramping from ambient temperature to 1 000 °C in air atmosphere. TG mass losses and DTA effects were analyzed using the T.A.I. Thermal Analyst Package.

Pore structure was analyzed using the automated mercury intrusion porosimeter Quantachrome Poremaster 60G (QUANTACHROME INSTRUMENTS). The maximum applied pressure of mercury was 414 MPa, equivalent to a Washburn pore radius of 1.8 nm. The contact angle 141.3° and surface tension 480 dyn/cm of mercury for the calculation of pore analysis results were used. The porosimeter results were completed by histograms of pores size distribution.

The morphology of the samples was studied by scan 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. The samples were also examined by energy dispersive X-ray analysis (EDX) with spectrometer Quantax 400 to analyse chemical composition. Solution heat was estimated by the method of kinetics of heat development (Jambor 1961 and 1962).

2.2. Test specimens preparation and their testing

For the study the metakaolin pastes prepared with activator solution/metakaolin ratio (l/s) 0.08 and compacted in the fresh state by applying the uniaxial pressure of 300 MPa were used. The test

specimens were 20 mm-edge cubes. The reference test specimens were prepared with l/s 0.70 compacted by hand. 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 metakaolin. Depending on the l/s ratio used, molar ratio H_2O/Na_2O was 22.3 at the reference paste and 0.023 at the pressure compacted paste.

The preparation of the fresh mixtures represented an intensive mixing for 3 min using electrical mixer. The forms were filled by the mixture and then exposed to the uniaxial pressure of 300 MPa with the endurance of 1 min. The preparation of the reference test specimens was the same but manual compaction was used. The prepared test specimens hardened 24 h in the forms, at temperature 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 density and compressive strength, specific gravity (density), phase composition, pore structure and morphology of the matrix.

2.3. Materials

The data on the chemical composition and specific weight of the original kaolin and metakaolin are given in Table 1. With the aim to compare the reactivity of both materials also their solution heat was determined using the method of the kinetics of its development (Jambor, 1961 and 1962). The kaolin used was from the locality Sedlec Czech Republic.

Table 1. Chemical composition and properties of kaolin and metakaolin used

Chemical composition (%)	Kaolin	Metakaolin
	Components	
Humidity	0.94	0.35
Ignition loss	12.20	1.95
SiO_2	48.06	53.68
Al_2O_3	36.76	42.00
Fe_2O_3	1.42	1.70
CaO	0.33	0.21
MgO	0.24	0.10
Density ($kg\ m^{-3}$)	2 631	2 582
Solution heat ($J\ g^{-1}$)	278.2	5 563

The comparison of the chemical composition showed an increase in the SiO_2, Al_2O_3 and Fe_2O_3 contents of the metakaolin as a direct consequence of the decrease of the ignition loss due to the heat-treatment. Further, interesting effects could be observed: a significant (ca. 20 times) increased solution heat and, on the contrary, a decreased specific weight of the metakaolin. The increased solution heat indicated the increased reactivity of metakaolin opposite to the kaolin. The found specific weight decrease indicated the decreased compactness of metakaolin. This effect was confirmed by the porosimetry results showing 31.8 % increase of pore volume and 20.2 % increase of total porosity. Further, the found 40.7 % decrease of macro-pore content and 689.8 % increase of specific surface area indicating the metakaolin as a material significantly finer than the starting kaolin (Tab. 2). All the mentioned effects were undoubtedly the consequence of the process of the heat-treatment producing the amorphous or near-amorphous SiO_2-Al_2O_3-Fe_2O_3 product. Its presence in the metakaolin is confirmed

from the DTA-curves by a very broad endotherm between ca. 200 and 950 °C, instead of the sharp endotherm peak at 511 °C visible on the DTA-curve of the kaolin (Fig. 2). According to the results the used metakaolin was the material with SiO_2 / Al_2O_3 molar ratio 2.22 showing significantly increased fineness and solution heat both contributing to the increase of its reactivity as a partner in the process of the geopolymer formation (Pacheco-Torgal et al., 2008; Granizo, 1998; Weng et al., 2005).

Table 2. Pore structure parameters of kaolin and metakaolin used

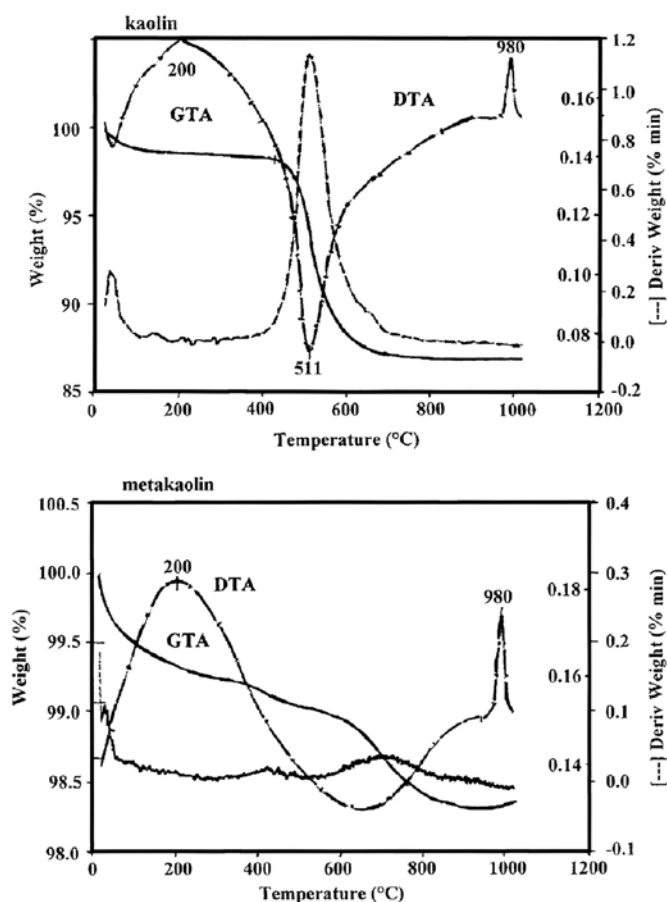| Pore structure parameter	Kaolin	Metakaolin
Pore volume ($mm^3 g^{-1}$)	771	1 016 (+ 31.8 %)
Macro-pore portion (%) r > 7 500 nm	26.8	15.5 (− 40.7 %)
Pore median (nm)	1102	772 (− 29.9 %)
Total porosity (%)	77.8	93.5 (+ 20.2 %)
Specific surface area calculated from porosimetry data ($m^2 g^{-1}$)	4.9	38.7 (+ 689.9 %)

Figure 2. Thermograms of kaolin and metakaolin used
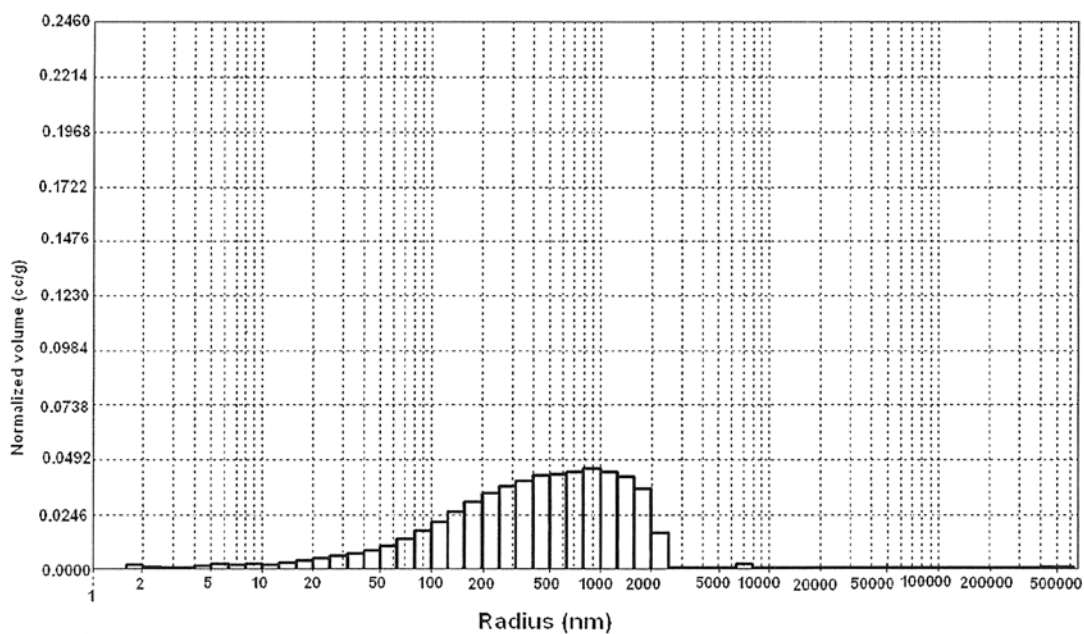
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Figure 3. Histogram of pore size distribution in kaolin used
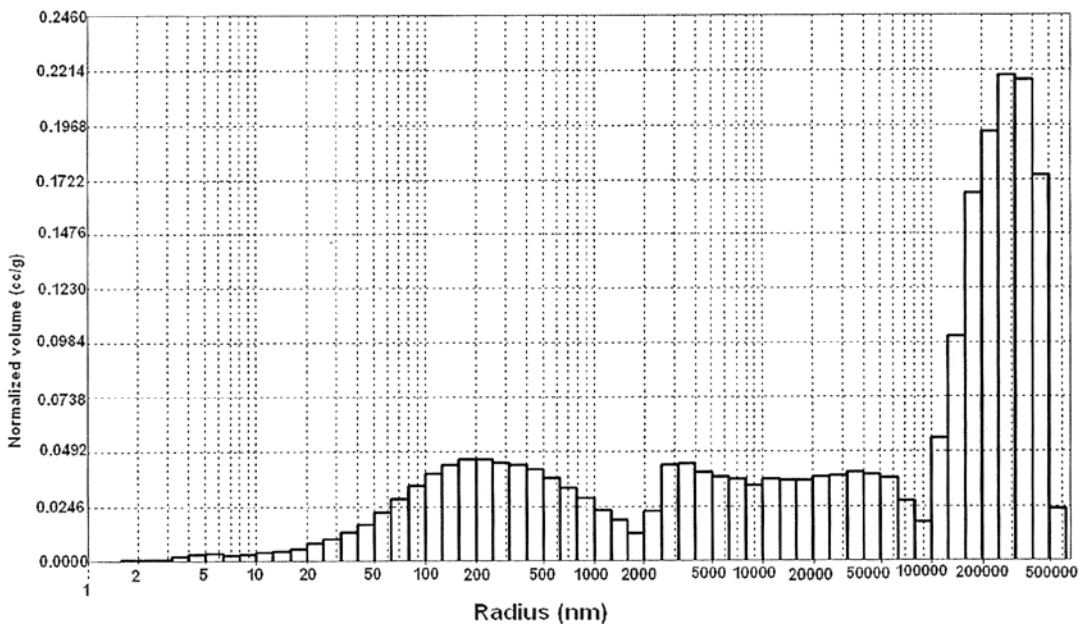

Figure 4. Histogram of pore size distribution in metakaolin used

The results given in Table 2 have shown the heat treatment as a process promoting the development of more open pore structure. It can be seen in the increase of total porosity, total pore volume, macro pore portion and total pore median. This effect of accessibility increase can be clearly seen at the comparison of the histograms of the original and thermally treated kaolin (Figs. 3 and 4) when a significantly increased volume of pore with radius over 2000 nm can be seen. The resulted accessibility is able to increase the access of the activator solution into pore space and its contact with the activated solid and finally to contribute to the process of geopolymerization and development of the properties of the binding systems.

3. Results and discussion

3.1. Mechanical properties and pore structure results

The results of the estimation of bulk weight, compressive strength and pore structure parameters are summarized in Table 3. The significant difference between the pressure compacted and reference pastes is evident. An increase in the benefit of pressure compacted paste is 128.7 % at the bulk weight and ca. 500 times at the compressive strength values.

Adequate relationship values of total porosity and pore median of the pressure compacted probes opposite to those of reference paste occurred (Tab. 3). At the same time corresponding content of macro-pores (r > 100 nm) is 4 % at the pressure compacted paste and 93 % at the reference one, and a reverse ratio 96 % and 4 %, at micropores contents (r < 100 nm).

The histograms and pore size distribution curves shown in (Figs. 5 and 6) provide a suitable illustration about the character of pore structure. At the comparison it can be seen at the pressure compacted paste a significant shift of pore size curve and the character of the histogram in the area of nano-pores with radius under 100 nm. It shows the pressure compacted paste as a material with the increased pore structure homogeneity and much finer pore structure. It may have an interesting and significant consequence for the strength characteristics of the material. In the sense with the Griffith's law it can cause an increase of the critical tension in the benefit of the pressure compacted paste (Griffith, 1920).

Table 3. Bulk density, compressive strength and pore structure parameters of metakaolin based geopolymer pastes after 24 h of hardening

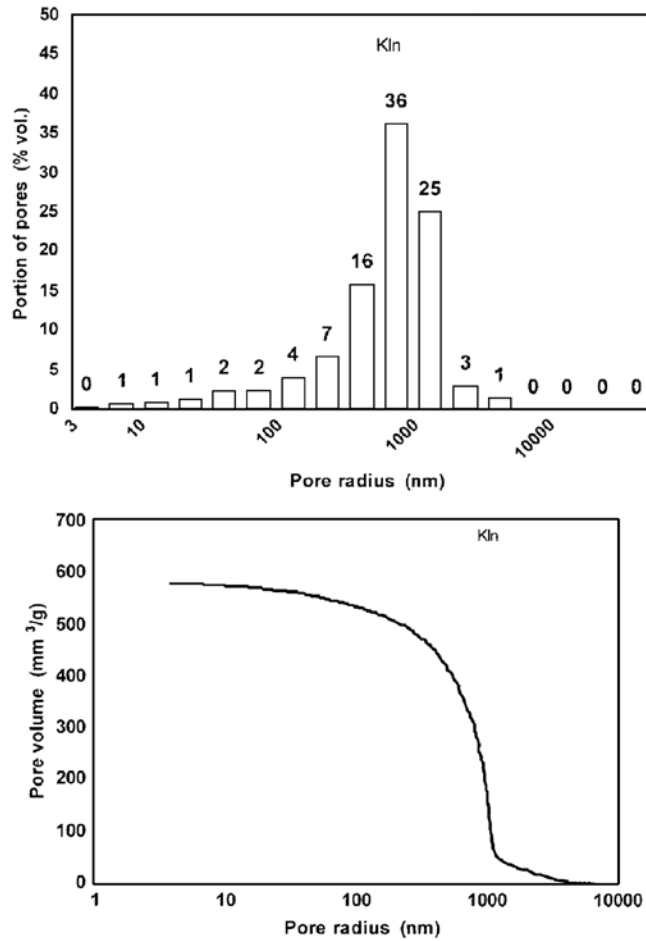|	Bulk density $(kg\ m^{-3})$	Compressive strength MPa	Total porosity %	Pore median nm	Specific surface area $m.g^{-1}$	Portion o pores (%) r < 100 nm r > 100	
Pressure compacted paste	1862	146.6	15.7	59	5.5	69	4
Reference paste	814	0.03	54.5	814	5.8	7	93

Figure 5. Histogram and pore size distribution curve of reference metakaolin based geopolymer paste after 24 hours of hardening

The found significantly high compressive strength of pressure compacted paste is undoubtedly based on its advanced pore structure developed under the use of the low l/s ratio and pressure compaction. The metakaolin paste prepared under these conditions was able to very significantly overcome the paste prepared under the current conditions. It means under the use of the current l/s ratio and without the pressure compaction.

As it is reported in the literature the currently prepared metakaolin pastes reached the compressive strength 5 MPa after 1 day (l/s ratio 0.70) and ca. from 15 to 90 MPa after 7 days of the hardening (Buchwald et al., 2007; Duxson et al., 2007). The compressive strength values between 0.40 to 64 MPa and 38 MPa are also reported (Rowles et al., 2003; Kong et al., 2007; Zivica, 2009).
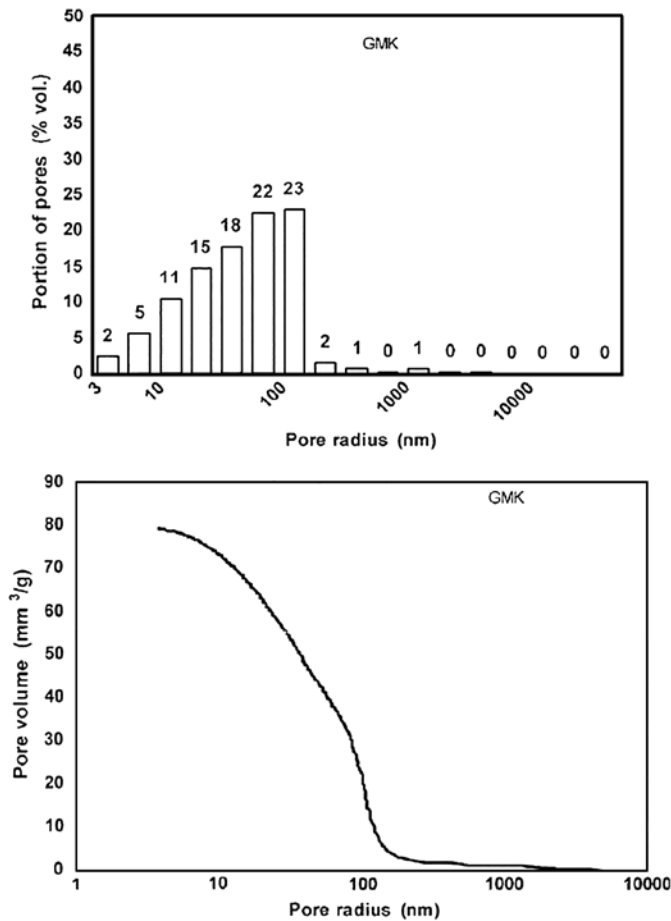
Figure 6. Histogram and pore size distribution curve of pressure compacted metakaolin based geopolymer paste after 24 hours of hardening

3.2. SEM and EDX results

The positive character of pore structure was confirmed by the SEM images (Figs.7 and 8).

As it can be seen the microstructure for the reference paste is highly non compact structure, with the large grains and pores observed as dark places. The occurrence of flake-like layer structure of metakaolinite particulates is an evidence of the low development of the geopolymerization process. Evidently, only a small quantity of the geopolymer product is taking place at the surface layer of the metakaolin particulates (Wang et al., 2005; Valeria et al., 2000). Due to the use of the different magnification the comparison of the SEM results enabled only limited information on the influence of the combination and the low l/s ratio and high-pressure compaction on the morphology of the particles of the system. But in principle SEM results have shown the same tendency of the influence like it can be seen at the porosimetry results.

The microstructure of the pressure compacted paste is distinctly different. In this material, a 'grain' structure is still apparent, but the intervening material is of more homogeneous nature, with small pores. This observation was linked to a strong correlation in the compressive strength increase found but also reported in the paper (Kuhnel et al., 1993).

The coupling of the SEM with an EDX provided an analysis of the surface of the studied materials. It should be expressed that the data obtained have only semiquantitative value (Figs. 9 and 10). The presence of the main elements O, Si, Al, Na and minor elements K, Fe and Mg can be seen in the EDX spectra of the geopolymers. Table 4 shows the composition of the geopolymers occurring in the studied pastes calculated using EDX data.
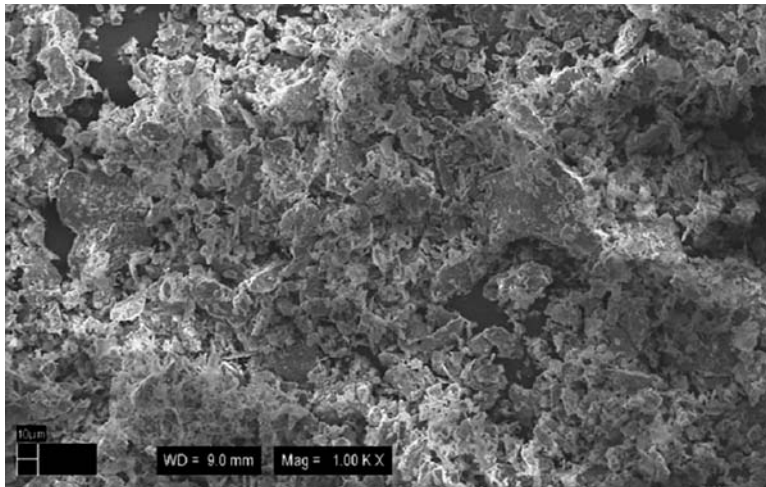

Figure 7. SEM images of the pressure compacted metakaolin based geopolymer paste after 24 hours of hardening
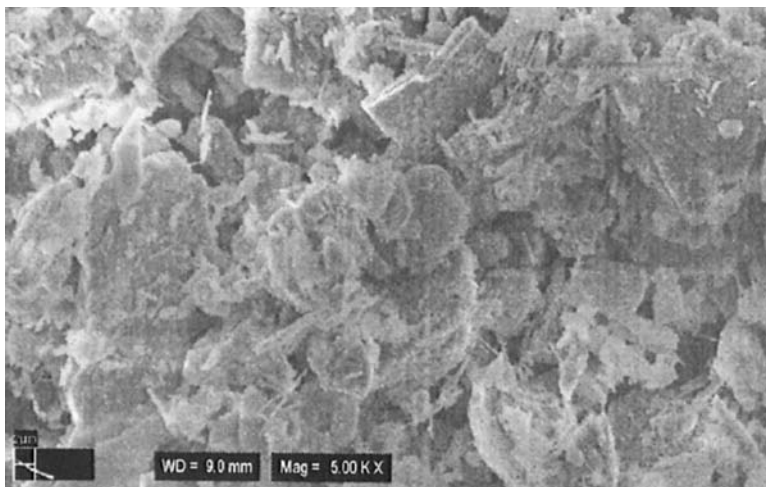

Figure 8. SEM image of the metakaolin based geopolymer reference paste after 24hours of hardening

Table 4. Composition of the metakaolin based geopolymer pastes after 24 h of hardening analysed by EDX

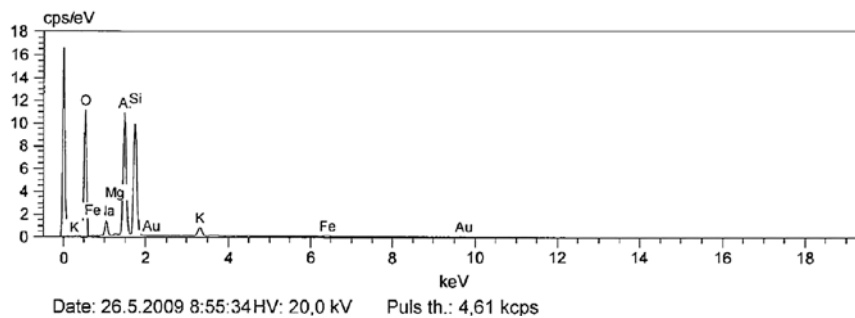| Element as oxide %	Pressure compacted paste	Reference paste	Metakaolin
SiO_2	37.32	49.71	53.68
Al_2O_3	33.41	39.44	42.00
Na_2O	8.38	6.60	–
SiO_2/Al_2O_3 molar ratio	1.90	2.14	2.17
Na_2O/Al_2O_3 molar ratio	0.41	0.26	–

Figure 9. EDX spectrum of pressure compacted metakaolin based geopolymer paste after 24 h of hardening

The decreased SiO_2 and Al_2O_3 contents in both hardened pastes opposite to the starting values are expressed at the pressure compacted paste. The principle of the effect is not clear. It can be only assumed as a consequence of the effect of the geopolymer formation. The content of Na_2O in the pressure compacted paste is by 30 wt. % higher opposite to that of reference paste. One reason could be the different concentrations of the used activator solutions given by the different l/s ratios. These caused that under the use of the same NaOH quantity of 7 wt. % but at the different l/s ratios the concentration of the activator solution was 46.7 wt. % at the pressure compacted paste but only 9.1 wt. % at the reference one. The significance of the NaOH concentration in the process of geopolymer formation is unquestioned. Rowles and O´Connor reported that the compressive strength of geopolymer depends significantly also on the Na:Al ratio together with Si:Al. The compressive strength is increased as the both ratios are increased (Rowles et al., 2003). It is well known that variation of the SiO_2/Na_2O ratio significantly modifies the degree of polymerization of the dissolved species in a silicate solution (Duxson et al., 2007). This plays a significant role in determining the structure and properties of geopolymer gels. In the case of the NaOH activator with low concentration, there would be insufficient amount of OH^{1-} ions to completely dissolve Si^{4+} and Al^{3+} from metakaolin, and insufficient Na^{1+} to allow for complete polymerization of the network. These both lead to unreacted metakaolin part and, therefore, lower strength of material. In the case the high sodium content, there would be excess OH^{1-} ions allowing for a complete dissolution of Si^{4+} and Al^{3+} from metakaolin.
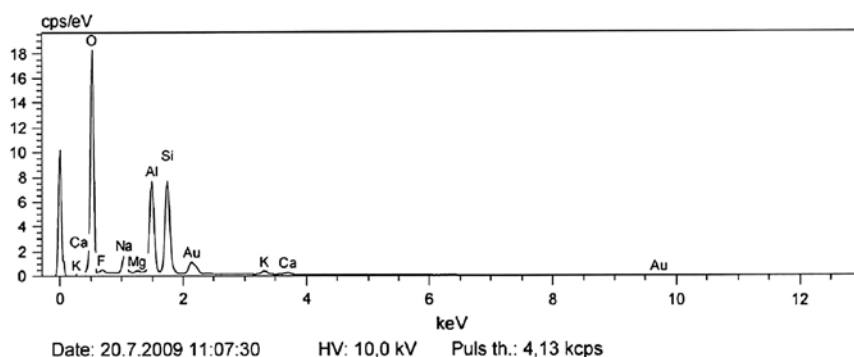
Figure 10. EDX spectrum of metakaolin based geopolymer reference paste after 24 h of hardening

The significance of the concentration of NaOH solution for the mechanical properties of the geopolymers is confirmed also by the results reported in the paper (Valeria et al., 2000). An increase of a compressive strength from ca. 35 to 65 MPa has been shown when the NaOH solution concentration increased from 4 to 2 mol L^{1-}. This effect is attributed to the enhanced dissolution of the metakaolin particulates and hence the speeded condensation of the monomer in the presence of NaOH with higher concentration.
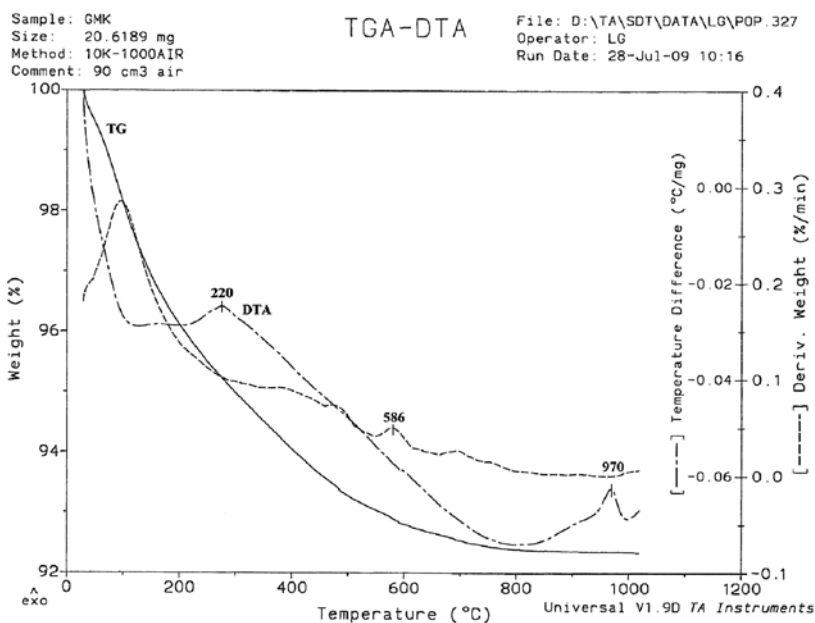
3.3. Thermal analysis results

Figure 11. Thermogravimetric (TG) and differential thermal (DTA) analysis curves of the pressure compacted metakaolin based geopolymer paste after 24 h of hardening

The results of the thermal analysis of studied materials are shown in (Figs. 11 and 12). As it can be seen these results enable only limited information on the phase composition of system. It is evidently the consequence of the amorphous or near-amorphous character of the constituents of the materials studied, thus a use of any method is rather restricted. DTA-curves are characterized (i) by the occurrence of the effects in the region about 100 °C which are due to the loss of evaporable water, and (ii) by the occurrence of the exotherms at 970 °C which are caused by the mullite formation. TG curves shown in both pressure compacted and reference pastes very near levels of weight loss 7.2 and 7.9 wt. %. Besides the adsorbed water, the loss is also due to the chemically bound water typical for a series of hydraulic hydrates. The thermo-analytical data strongly favour a qualitative similarity of phase composition of pressure compacted and reference probes, thus supporting the data interrelations of pore structure and mechanical tests on the densification and strength development as a unique effect of pressure compaction.
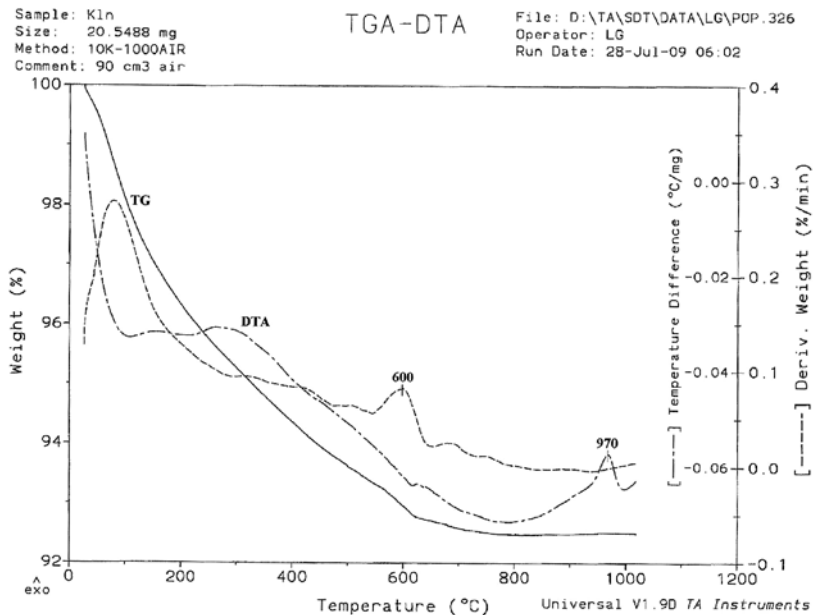

Figure 12. Thermogravimetric (TG) and differential thermal (DTA) analysis curves of the reference metakaolin based geopolymer paste after 24h of hardening

4. Conclusion

The combination of the low alkali activator solution: binder ratio (l/s) with the pressure compaction of the fresh mixture as a significant accelerator of the development of the pore structure and on it dependent strength has been shown. At the given case the use of l/s 0.08 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 ca. 500 times. The found positive effect of the combination of the low l/s ratio and high-pressure compaction also at another alkali activated alumino-silicate materials can be expected. The Si:Al ratio in the

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starting alumino-silicate materials, fineness, the portion and type of alkali activators used, curing regime, and other parameters are undoubtedly important for the development of the properties of the geopolymer composites with the potential in the quality differences of the systems based on the various aluminosilicates. Therefore, these factors are worthy of the more detailed study because the pressure compacted geopolymer composites seem to be very interesting materials and technology.

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