

Mechanical properties of materials obtained via alkaline activation of illite-based clays of Latvia

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Abstract. Materials has been synthesized in the temperature range from 60-100 °C from two illite based clays of Latvia under activation of KOH and NaOH solutions (4-6 M). Compressive strength and apparent porosity were measured. The effect of concentration of KOH and NaOH solutions on the material mechanical properties was investigated by means of infrared spectroscopy (IR). Compressive strength data of the materials showed that via such activation could obtain building materials with good quality.

1. Introduction

Alkaline activation is a chemical process in which a powder material of an aluminosilicate nature is mixed with an alkaline activator to produce a paste that is able to set and harden in a short time [1,2]. The reaction process of this system is characterized by dissolution of alumino-silicate oxides and followed by the polymerization reaction of those dissolved species, in the presence of alkali ions for charge balancing in framework cavities nearby AlO_4 constituents. The reaction produces SiO_4 and AlO_4 tetrahedral frameworks linked by shared oxygens as polysialates or polysialate-siloxo or polysialate-disiloxo depending on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the system [2]. It is three-dimensional aluminosilicate binder obtained using inorganic raw material having pozzolanic properties such as some aluminosilicate natural minerals or clays [3]. Geopolymeric materials possess excellent mechanical properties, including fire and acid resistance [4,5]. Mentioned properties make geopolymers as alternative construction material. Kaolinite is the most often used natural raw material because of its high content of alumina [3,6]. The search for alternative easily available materials in Latvia have lead among another materials to illite-based clays. From geological point of view – Latvia is rich in clay resources to be used for material production currently and at least for centuries [7].

2. Materials and methods

Two Quaternary illite clays of Latvia (Q) and (D) were used for geopolymer synthesis were characterized by means of classic chemical analysis (table 1).

Table 1. Chemical composition of the studied clays, weight %

Deposit / Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	$\text{K}_2\text{O} + \text{Na}_2\text{O}$	LOI
Q clay	47.32	17.44	5.34	9.21	1.78	0.56	3.44	14.16
D clay	43.05	14.10	4.24	11.46	5.05	0.64	3.65	15.36



Particle size distribution was determined by sedimentation analysis and X-ray diffraction by model Rigaku, Japan, with CuK_α radiation at a scanning interval from $2\theta = 10-60^\circ$ and speed $4^\circ/\text{min}$. Results are shown in Table 2.

Table 2. Particle size distribution and mineralogical composition of the studied clays

Deposit	Particle size distribution, %			Mineralogical composition
	Sand fraction > 50 μm	Silt fraction 5 – 50 μm	Clay fraction < 5 μm	
Q clay	3.1	18.4	78.5	Illite, kaolinite, quartz, calcite, dolomite, feldspar
D clay	6.3	23.5	70.2	

In order to investigate the effect of the activators (KOH and NaOH) on the properties of the material, two series (Q and D) were tested. The potassium and sodium hydroxide solutions were obtained by dissolving dried pellets of 99 % purity in distilled water. Thus the activators were added to the clay powders and mechanically mixed. Afterwards cylindric samples ($h=25$ mm, $d=16$ mm) were made in plastic way with 25-30 % of average moisture content. Samples were cured at 60, 80 and 100 $^\circ\text{C}$ temperature for 4 hours and were allowed to mature at room temperature for 28 days to increase their mechanical strength. Final samples were used for the mechanical strength and apparent porosity measurements.

Compressive strength was determined by means of the “Compression Test Plant ToniNorm” Toni-Technic by Zwick (300 kN).

Fourier transform infrared spectroscopy was carried out on powders of hardened materials using “21 Prestige, Shimadzu Corp” FTIR spectrophotometer in transmittance mode. FTIR spectra were gathered between 400 and 1600 cm^{-1} .

3. Results and discussion

Table 1 shows differences in chemical composition between studied clays. Content of CaO is higher for clay Q than that of D clay. The CaO content of source material appears to strengthen the geopolymer by forming amorphously structured Ca-Al-Si gel during geopolymerisation. The Al_2O_3 and CaO are regarded as more significant elements than the others, because AlO_4^- and silicate oligomers combine to form geopolymers.

Moreover alkali metal cations (K^+ and Na) play a catalytic role and could contribute to strong structure formation.

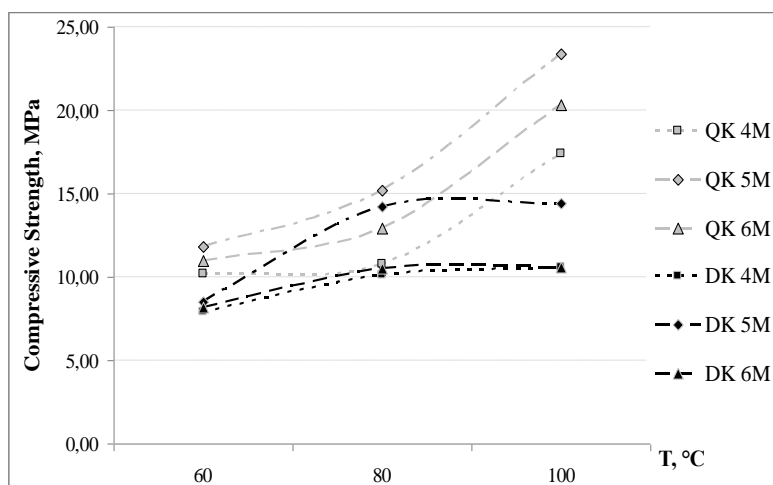
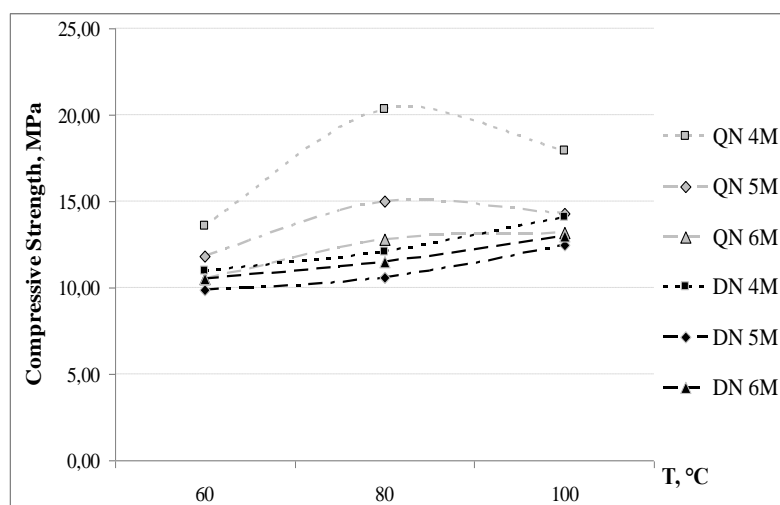


Fig. 1 presents the role of KOH as chemical activator on the compressive strength of final materials obtained from both studied clays and cured at different temperatures. KOH solution with higher used concentration (6M KOH) did not promote the strength enhancement for both clays.

Figure 1. Compressive strength evolution vs. KOH concentration at different curing temperatures.

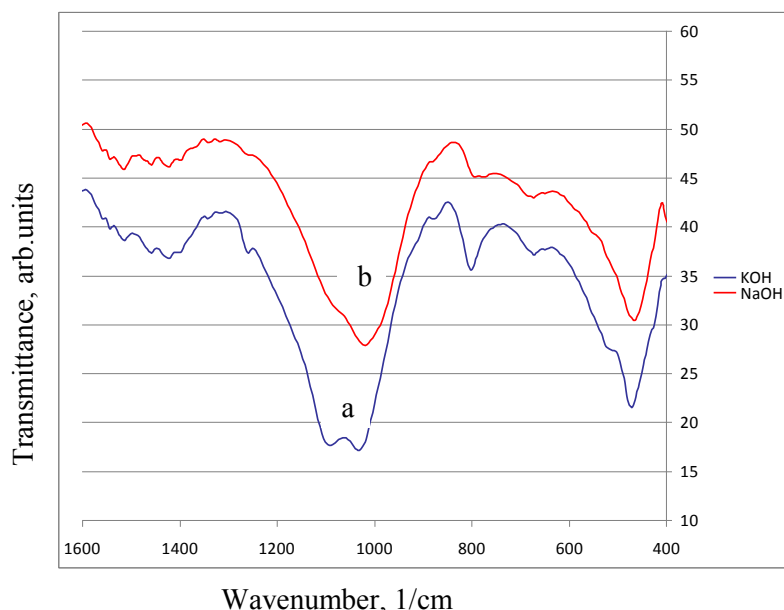
The higher compressive strength (23 MPa at 100 °C) showed Q clay activated with 5 M KOH solution. By activation with 4 M and 6 M compressive strength of materials obtained from Q clay was lower (17 and 20 MPa, accordingly). Obviously higher concentration of KOH solution facilitates the dissociation of different silicate and aluminate species, thus promoting further polymerization resulting in higher compressive strength. However, if a very high alkaline environment is used, the connectivity of silicate anions may be reduced resulting thus in poor polymerization and lower compressive strength. Compressive strength increases with an increasing of curing temperature in all cases. Contrary to Q clay compressive strength is lower when D clay is treated with KOH solution reaching the best value (14 MPa) when curing at 80 °C temperature took place.



Results presented in Fig. 2 shows effect of NaOH solution on the compressive strength of materials obtained from both used clays. Strength increased along with decrease of NaOH concentration for Q clay.

Figure 2. Compressive strength evolution vs. NaOH concentration at different curing temperatures.

In this case the lower $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$ ratios promoted the strength improvement than higher ones in the case of Q clay. Obviously using higher than 4M NaOH concentration for chemical activation, excess hydroxide ion concentration caused aluminosilicate gel precipitation at the very early stages, resulting in lower compressive strength. The highest compressive strength (20 MPa) showed material activated with 4M NaOH and cured at 80 °C. Chemical treatment of D clay with different NaOH concentrations gave lower compressive strength results comparing with Q clay at similar curing and chemical conditions.



FTIR analysis shows increased sensitivity for structures of short-range structural order and is considered as an appropriate technique for studying the structural evolution of amorphous aluminosilicates exhibiting high heterogeneity. Infrared absorption bands enable identification of specific molecular components and structures.

Figure 3. FTIR spectra of materials from Q clay cured at 100 °C: a – activated with 5 M KOH solution; b – activated with 5 M NaOH solution.

The difference in absorption frequencies between differently activated Q and D clays predicts transformations taking place during material synthesis. The most characteristic difference observed between the FTIR spectra of differently activated Q clay is concerning the band at around 800 cm^{-1} which is related to the AlO_4 vibrations [8].

The bands at 470 cm^{-1} seen for both specimens are due to bending vibrations of Si-O-Si and O-Si-O bonds indicating that quartz is almost chemically inert in the strong alkaline activating solutions [9,10]. The small band seen at $\sim 530\text{ cm}^{-1}$ only for material obtained by activating with KOH solution is mainly due to the symmetric stretching vibrations of Si-O-Si and Al-O-Si [8], which are referred to the formation of amorphous to semi-crystalline aluminosilicate materials. Small bands at 680 cm^{-1} represent the Si-O symmetrically stretching showing that 6-coordinated Al changed into 4-coordinated one, and participates in the formation of framework structure [11]. The very small band seen at 870 cm^{-1} corresponds to dissolved silicate and/or aluminosilicate species and indicates that dissolution of raw materials takes place [12]. Characteristic band at 1033 cm^{-1} have been assigned to asymmetric stretching of Al-O and Si-O bonds originating from within individual tetrahedra. All bands at around 1088 cm^{-1} are a major fingerprint of the inorganic polymer matrix and define the extent of polysialation or aluminium incorporation; they are also due to asymmetric stretching of Al-O and Si-O bonds originating from within individual tetrahedra [9]. The very small band seen at 1270 cm^{-1} may be due to Si-O-Si or Al-O-Si asymmetric stretching vibration as a result of SiO_4 and AlO_4 reorganisation that takes place during synthesis [12].

4. Conclusions

Geopolymers are materials rapidly developed during last decades and they are quite new ones in Latvia. Illite-based geopolymer materials through activating of two Quaternary clays of Latvia by KOH and NaOH solution were synthesized. Compressive strength of the geopolymers were greatly dependent both on curing conditions and the concentration of activation solution. It was shown that higher compressive strength demonstrated activated Q clay containing higher clay and lower sand fraction. Better compressive results showed Q clay cured at $100\text{ }^\circ\text{C}$ and activated with KOH. Obviously KOH provides more inorganic polymer precursors compared to NaOH since the larger K^+ favours the formation of larger silicate oligomers with which $\text{Al}(\text{OH})_4^-$ prefers to bind, thus higher compressive strength is acquired in this temperature. Curing in lower temperatures gave decreased compressive strength of materials in the case of activation with KOH solution. Using NaOH as activator better results reached Q clay as well.

References

- [1] Duxon P, Fernández-Jiménez A, Provis JL, Lukey GC, Palomo A and van Deventer JSJ 2007 *J. Mater. Sci.* **42** 2917
- [2] Steins P, Poulesquen A, Diat O and Frizon F 2012 *Langmuir* **28** 8502
- [3] Kuenzel C, Vandeperre LJ, Donatello S, Boccaccini A and Cheeseman C 2012 *J. Amer. Ceram. Soc.* **95** 3270
- [4] Davidovits J 1991 *J. Therm. Anal.* **37** 1633
- [5] Davidovits J 2008 *Geopolymer chemistry & applications*. 2nd edition, Saint-Quentin: Institute Géopolymère 333
- [6] Elimbi A, Tchakoute Kouamo H and Njopwouo D *Constr. Build. Mat.* 2011 **25** 2805
- [7] Seglins V 2008 *Scientific Proceedings of Riga Technical University, Material Science and Applied Chemistry Riga* **17** 62
- [8] Bakharev T 2005 *Cem. Concr. Res.* **35** 1224
- [9] Van Jaarsveld JGS, Van Deventer JSJ, Lukey G C 2002 *Chem. Engin. J.* **89** 1-3 63
- [10] Lee W K W, Van Deventer JSJ 2002 *Colloids Surf. A: Physicochemical and Engineering Aspects* **211** Issues 2-3 49
- [11] Zhang Y, Wei S, Zongjin L 2012 *Appl. Clay Sci.* **47** 271
- [12] Rees CA, Provis JL, Lukey GC, Van Deventer JSJ 2007 *Langmuir* **23** 8170