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The Suitability of Chemically and Thermally Activated Quaternary Clays of Latvia as Raw Material for Geopolymer Binders

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It is now accepted that new binders are needed to replace Portland cement (PC) for enhanced environmental and durability performance. The urge to reduce emissions of carbon and the fact that PC structures having built a few decades ago are already facing disintegration problems points out the handicaps of PC binders. Research works carried out in developing of alkali-activated binders show that this new type of binder could have a huge potential to become as alternative building material. Latvian Quaternary clays were studied from the point of view of the national economy, analyzing the physical properties and chemical composition of those sediments in connection with the possibilities of their utilization in the manufacture of geopolymer materials. Quaternary clay minerals dominate by illite with admixture of chlorite. Quaternary clay typically is rich in fine, scattered carbonates. The aim of this study was to synthesize geopolymer product from illite clays of Latvia under alkaline activation. Results of the investigations showed the influence of alkalies on the transformation of clay/illite structure by curing of activated clays at different temperatures for various time. Obtained results showed that illite-based clays of Latvia could play a role of the raw material for production of geopolymer binders.

Keywords: *alkaline activation, inorganic polymers, mechanical strength, quaternary clays of Latvia.*

1. Introduction

Alkaline activation is a chemical process in which a powder material of an alumosilicate nature, such as clay, is mixed with an alkaline activator to produce a paste that is able to set and harden in short time (Duxson et al. 2007), (Pacheco-Torgal et al. 2008), (Fernández-Jiménez *et al.* 2008), (Xu and van Deventer 2000).

The properties and characteristics (strength, shrinkage, porosity, etc.) of the resulting materials depend on nature of the raw materials and on process variables (activator, curing temperature and time, etc.). These materials, frequently termed alkaline inorganic polymers or geopolymers, constitute a new family of products which among other interesting properties can combine qualities typical of cements with those of traditional ceramics and zeolites (Dimas et al. 2009). Inorganic polymers possess good mechanical properties, including fire and acid resistance. Mentioned properties make geopolymers as alternative construction material. It is reasonable to emphasize that the type and nature of the used starting material will directly affect the final physical and chemical properties of geopolymer (Komnitsas et al. 2009).

Illite clayey deposits are one of the dominating mineral raw materials in the sedimentary cover at present area of Latvia. The Quaternary clays of Latvia are useful for various kinds of traditional ceramic production such as bricks, building blocks, roof tiles as well as sorbents and precursors for promoting of sinterability of new ceramic products. Quaternary clay deposits mostly are of glaciolacustrine origin and formed in the Pleistocene glacial meltwater basins. Their grain-size is various, content of clay minerals are dominated by illite (75-80 %) with admixture of kaolinite (Kurss and Stinkule 1997). Preliminary studies (Granizo et al. 2002), (Yip et al. 2003), (Yip et al. 2005), (Dombrowski et al. 2007), (Yip *et al.* 2008) have shown that the addition of moderate amount of calcium containing material can have a significant effect on the mechanical properties of final material. Besides illite and kaolinite mentioned clays as natural additives contain carbonates such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$).

The aim of this study was to synthesize geopolymer product from illite-based Quaternary clays of Latvia under alkaline and thermal activation.

2. Methods

In order to investigate the effect of the activator on the properties of material obtained from AP, SP and PR clays 5 and 6 M KOH solutions were used. The potassium hydroxide solution was obtained by dissolving dried pellets of 99 % purity in distilled water. Thus the obtained activator was added to the clay powders and mechanically mixed. Afterwards cylindric samples (h = 20 mm, d = 20 mm) were made in plastic way with 25 % of average moisture content in order to obtain good paste workability. One set of prepared samples was stored in the ambient atmosphere of the laboratory. Another set of prepared samples were allowed to cure at 40, 60, 80 and 100 ^{o}C temperature for 4, 3, 2 and 1 hour, accordingly and afterwards stored at an ambient atmosphere of the laboratory for testing. Compressive strength of samples was tested 7, 14, 21 and 28 days after synthesis. Compressive strength of samples was determined on the hardened geopolymer materials using compressive strength test set "Compression Test Plant ToniNorm, Toni-Technic by Zwick" (300 kN workload). Fourier transform infrared spectroscopy was carried out on powders of activated clays (after hardening) using FTIR spectrophotometer 21 Prestige, Shimadzu Corp. in transmittance mode (interval of wave number ranging was 1300-400 cm^{-1}). All clays and some activated materials were characterised by X-ray diffraction (model Rigaku Ultima^{+}, Japan, with CuK_{α} radiation at a scanning interval from $2\theta = 10–60^{o}$ and speed 4 ^{o}/min). The mineralogical identifications were made using an XRD pattern database (International Centre for Diffraction Data, ICDD).

3. Results and discussion

Three Quaternary clays of Latvia (AP, SP and PR) with different Si/Al ratio used for geopolymer synthesis were characterised by means of chemical analysis (table 1). Results of chemical composition show that Si/Al ratio varies from 2.7 (clay PR), 3.5 (clay SP) and up to 3.8 (clay AP).

Table 1. *Chemical composition of the used Quaternary clays (weight %)*

Oxides	Clay AP	Clay SP	Clay PR
SiO_2	53.82	51.82	45.95
Al_2O_3	14.32	14.69	17.07
Fe_2O_3	5.76	5.47	6.78
TiO_2	0.53	0.59	0.58
CaO	6.93	8.27	5.95
MgO	2.56	2.52	3.86
Na_2O	0.42	0.53	0.17
K_2O	3.40	3.35	3.93
LOI	12.26	12.76	15.71

LOI: loss on ignition at 1000 °C.

All clays were characterized by X-ray diffraction analysis (Fig. 1). Figure shows that the basic clay mineral is illite with some content of kaolinite. Besides all clays contain more or less carbonates, such as calcite and dolomite, but clay PR – plagioclase as well. Clays are more or less rich in quartz.

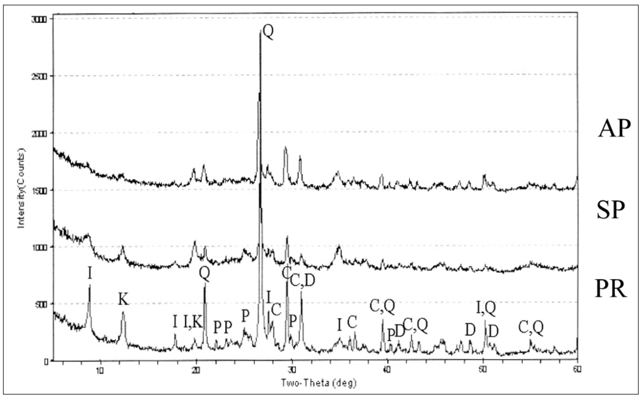

Fig. 1. *X-ray diffractograms of the used clays: I – illite, K – kaolinite, Q – quartz, C – calcite, D – dolomite, P – plagioclase*

Compressive strength measurements are widely used as an indicator to assess the success of inorganic polymer technology. This is due to the low cost, simplicity as well as due to the fact that strength development is a primary measure of the utility of these materials in various applications (Provis et al. 2005). Curing took place at different temperatures for 7 up to 28 days in order to enhance structural bonding and then the hardened products were subjected to mechanical (compressive) strength testing.

Table 2 presents the initial compressive strength of three carbonates containing clays synthesized using an alkaline activator (5M and 6M KOH solution) and cured (thermally activated) for different time at different temperatures.

Table 2. *Initial mechanical (compressive) strength of materials*

Raw material	Curing temperature, °C	Mechanical strength, MPa			
		After 7 day hardening		After 14 day hardening	
		5 M KOH	6 M KOH	5 M KOH	6 M KOH
Clay AP	20	0	0	0	3.7
	40	0	3.9	3.8	6.0
	60	3.8	4.0	8.9	7.5
	80	4.3	4.0	9.1	8.3
	100	0	4.0	4.6	7.4
Clay SP	20	0	0	3.6	4.1
	40	4.0	4.8	8.9	9.5
	60	7.8	7.6	11.2	8.3
	80	5.8	5.3	8.7	8.3
	100	4.6	4.9	7.7	9.2
Clay PR	20	3.8	5.0	4.5	5.3
	40	4.4	10.5	5.3	10.9
	60	8.9	10.6	20.5	21.2
	80	28.1	34.0	33.3	36.0
	100	44.2	49.9	52.1	58.4

The general trends observed from table 2: mechanical strength of alkali activated clays are greatly dependent on (1) source material and (2) curing conditions. During the alkali attack of the alumosilicate material containing clays, an initial nucleation phase takes place where the alumosilicate species are dissolved. When the nuclei reach a critical size, they start to crystallize, but this is a very slow process so it may be completed after a definite time depending on clay composition. Depending on the different SiO_2/Al_2O_3 ratio in the used clays (2.7 for clay PR, 3.5 for clay SP and 3.8 for clay AP) decreases the initial rate of the hardening. Clay PR with smaller SiO_2/Al_2O_3 ratio possesses higher initial mechanical strength in comparison with clays AP and SP.

Comparative results of mechanical strength of chemically and thermally activated clays after 28 day hardening are shown in figures 2 and 3.

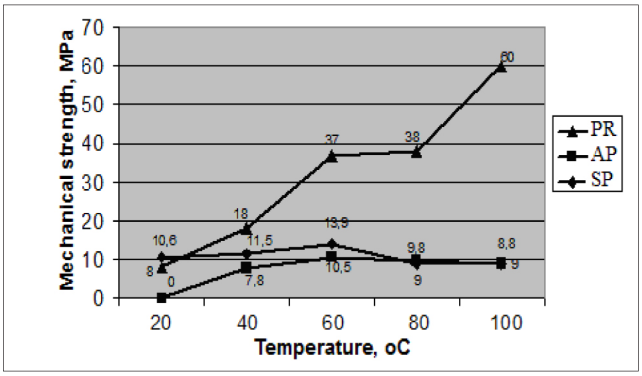

Fig. 2. Mechanical strength of samples activated with 5 M KOH after 28 days of hardening.

Both figures show that strengths have increased with increasing of curing temperature only for clay PR (using for activation both 5M and 6M KOH solution). Clay AP showed the best values of mechanical strength cured at 60 °C temperature (using for activation 5M KOH solution) and at 40 °C temperature (using 6M KOH). Clay SP showed higher mechanical strength activated by 5M KOH solution and cured at 60 °C temperature.

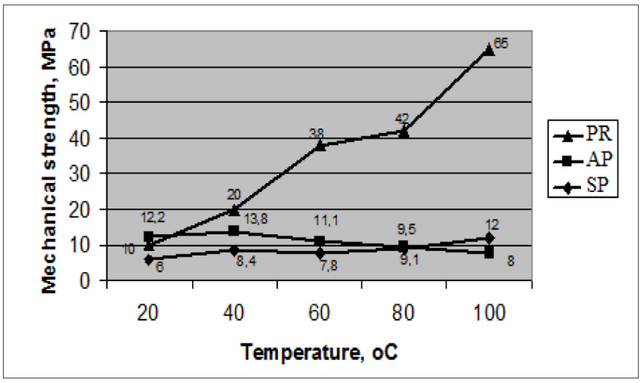

Fig. 3. Mechanical strength of samples activated with 6 M KOH after 28 days of hardening.

Comparing results on obtained activated clays by different KOH solutions, obviously not always higher concentration of KOH solution facilitates the dissociation of different silicate and aluminate species, but prevents further polymerization resulting in lower compressive strength. On the other hand, with the rising of curing temperature increases mechanical strength up to definite value afterwards mechanical strength decreases because both the connectivity of silicate anions may be reduced resulting thus in poor polymerization and increases the amount of unreacted material so leading to the lowering of the strength values.

It is known that the type of cation involved in the activation reaction differently affects the microstructural development of the material. The presence of alkali metal cation plays a catalytic role, controls all stages of inorganic polymer formation, in particular gel hardening and crystallization and enables an appropriate structure formation (Phair and Van Deventer 2002), (Xu and Van Deventer 2000). Al-Si mineral with higher content of Na_2O (plagioclase in PR clay) positively affect the geopolymerisation in KOH solution. Thus the best mechanical strength values have been reached using PR clay – 60 and 65 MPa depending on activator alkalinity (5M or 6M KOH).

Factor playing an important role during activation process is the calcium content in clays. It is stated that the form of added Ca^{2+} plays a significant role in determining the mechanical properties of the final material (Yip et al. 2004). All clays contain calcite (in addition clay PR – calcium containing plagioclase) (see Fig.1) being not chemically inert in the alkaline activated systems. Calcite obviously is beneficial because it diminish the amount of dissolved water preventing the hydraulic attack. Some authors (Yip and Van Deventer 2003) reported that calcium increases mechanical strength after alkaline activation due to the formation of Ca-Al-Si amorphous structures. It was found the development of calcium silicate hydrate and possibly coexistence with geopolymeric gel reinforcing the geopolymeric structure and as the result increasing of the mechanical strength.

Fig. 4 shows the XRD diffractogramms of the activated PR clay in comparison with unactivated one. XRD analysis reveals the formation of new phase (CSH) – only in activated samples. Furthermore it could be noticed the decrease of intensities of the present phases – kaolinite, illite and calcite. There is also registered halo peak between $2\Theta = 26°$ and 28° (marked with red semicircle) and is attributed to an amorphous silicate phase consisting of a SiO_4 tetrahedra sharing oxygen atoms and lacking a long-range order. Halo peak for sample cured at 100 °C temperature is higher than that of sample cured at 60 °C temperature confirming the different mechanical strength values of the obtained samples. 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 alumosilicates exhibiting high heterogeneity (Lee and van Deventer 2002). Infrared absorption bands enable identification of specific molecular components and structures. The difference in absorption frequencies among activated clays predicts transformation taking place during material synthesis.

The FTIR spectra of chemically and thermally activated clays are shown in Fig. 5. All observed peaks were quite broad absorption bands, indicating the structural disorder in the silicate network and thus the amorphous character of the gelatinous silicate phases. The peaks at 470 cm^{-1} are attributed to in-plane bending of Si-O and Al-O linkages originating from within individual tetrahedra (Van Jaarsveld et al. 2002). This is a result of the presence of kaolinite some part of which remaining unreacted.

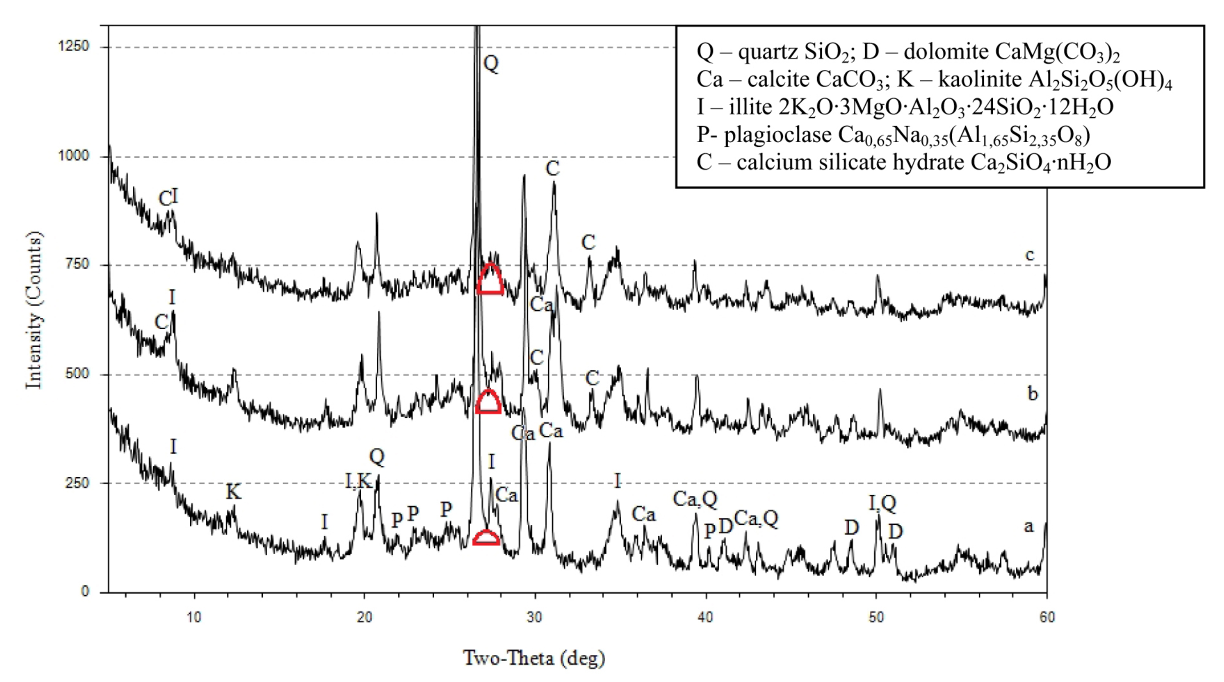

Fig. 4. X-ray diffractograms of unactivated PR clay (a) and activated ones: b – activated with 6 M KOH and cured at 60 °C temperature, c – activated with 6 M KOH and cured at 100 °C temperature

The peak at approximately 671 cm^{-1} (only for activated PR clay) represents the functional group of AlO_2. Broad band at 802 cm^{-1} is attributed to the symmetric stretching of the Si-O-Si bonds (Lee and Van Deventer 2003). Very small peak at 879 cm^{-1} (only for activated PR clay) corresponds to dissolved silicate and/or alumosilicate species and indicates that dissolution of source clay have taken place (Rees *et al.* 2007).

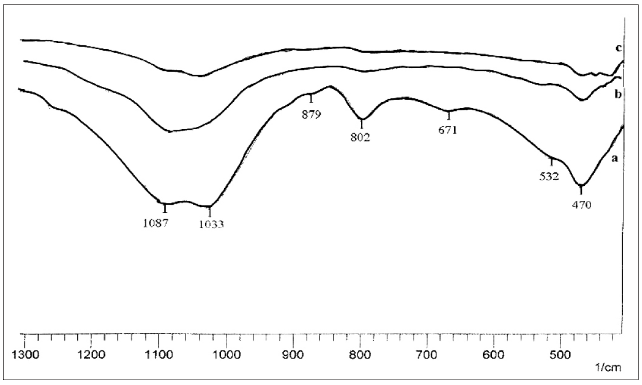

Fig. 5. FTIR spectra of activated clays (all clays activated with 6 M KOH and cured at 100 °C temperature): a – clay PR, b – clay SP and c – clay AP

Characteristic vibrations at 1033 cm^{-1} have been assigned to asymmetric stretching of Al-O and Si-O bonds originating from within individual tetrahedra. All characteristic vibrations around 1087 cm^{-1} are a major fingerprint of the geopolymer matrix and define the aluminium incorporation. This absorption band is attributed to asymmetric and symmetric vibrations of Si-O-Si and Si-O-Al bonding individual AlO_4 and SiO_4 tetrahedrons of geopolymers (Barbosa et al. 2000).

4. Conclusions

Illite-based geopolymer product through activating of three Quaternary clays of Latvia by KOH solution was investigated. In this study the effect of curing temperature on the mechanical properties of different Quaternary clays was investigated by measuring compressive strength over time. Depending on the different SiO_2/Al_2O_3 ratio in the used clays (2.7 for clay PR, 3.5 for clay SP and 3.8 for clay AP) decreases the initial rate of hardening. The best initial rate of hardening showed clay PR with smaller SiO_2/Al_2O_3 ratio. It can be also concluded that with the increase of Si/Al ratio in the source clays appears the difference in the mechanical strength measurements with the increasing of curing temperature higher than 20 °C. Curing temperature had not an essential influence on mechanical strength of activated clay AP and SP, but strength increased with increasing of curing temperature only for activated clay PR (using for activation both 5M and 6M KOH solution) reaching 60 and 65 MPa, accordingly. FTIR spectra and XRD results confirmed the differences among activated clays developing the diverse final strength of the obtained samples.

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