INVESTIGATING THE POSSIBILITY OF UTILIZING LOW KAOLINITIC CLAYS IN PRODUCTION OF GEOPOLYMER BRICKS

QHATANI MOHSEN*, NASSER YOSSEF MOSTAFA*.**

*Materials and Corrosion Lab (MCL), Faculty of Science, Department of Chemistry, Taif University,
888 Hawayia, Taif, Saudi Arabia
**Chemistry Department, Faculty of Science, , Suez Canal University, Ismailia, Egypt

E-mail: nmost69@yahoo.com

Low kaolinitic clays raw materials were chemically and mineralogically characterized. The manufacture of geopolymer bricks based on thermally treated clays (700°C for 2 hours) and NaOH solution or alkaline sodium silicate solutions were investigated. The activation process was conducted at different temperatures (room temperature, 75°C and 150°C). The phases formed were studied by X-ray diffraction analysis and scanning electron microscopy. The amorphous geopolymer phase was formed at all processing temperatures. The mechanical properties depended on amounts of active aluminum silicates in the starting material, the type of activator and the processing temperature. The results showed that two of the studied clays have adequate characteristics for geopolymer brick manufacture when activated with NaOH solution. However, all studied clays were suitable for geopolymer brick manufacture if activated with sodium silicate solution. Geopolymer bricks with low production costs and low production technology could be produced from clays deposits in Saudi Arabia.

INTRODUCTION

Development of products from a country's natural resources and waste by-products is very important as far as the industrialization of a nation is concerned. The western region, of Saudi Arabia, has abundance amounts of low quality clay deposits. The vast majority of existing deposits lack chemical and mineralogical characterization data. Thus, empirical knowledge is commonly used to process low value clays for traditional fired brick products, which need extensive use of energy during the production processes.

In 1970s [1], Davidovits pioneered the discovery and establishing of the research in geopolymer binders. Geopolymers are a novel class of materials that are formed by the polymerization of silicon and aluminum species. The principal binding phase in geopolymers is an amorphous aluminosilicate gel that consists of a three dimensional framework of SiO_4 and AlO_4 tetrahedra linked by corner-shared O atoms [1-3]. The negatively-charged tetrahedral Al sites in the network are charge-balanced by alkali metal cations such as Na^+ and/or K^+ [1]. However, sodalite and hydroxysodalite, which are members of zeolite group, have been detected as reaction products in some metakaolin and fly ash geoplolymer systems [3-5].

Geopolymer binders possess many advanced properties such as fast setting and hardening, excellent bond strength [1], long-term durability and better fire and acid resistance [6]. Due to such superior property, geopolymers have the potential to be used in several industrial applications [7]. The most important advantage of geopolymer binders is their low manufacturing energy consumption and low CO_2 emission [7-9], which make them to be a ''Green Material''[10-12]. The original raw material used by Davidovits is metakaolinite, activated by alkali hydroxide and/or alkali silicate [1, 8, 9]. Many researchers [7, 13-16] have demonstrated that many other aluminosilicate materials could be used as raw materials for geopolymers, such as fly ash, furnace slag, silica fume and kaoline and some natural minerals. Xu et al [7] investigated geopolymerization of sixteen natural aluminosilicate minerals with the addition of kaolinite. It was found that a wide range of natural alumino-silicate minerals provided potential sources for synthesis of geopolymers.

It has been proved that calcined materials such as metakaolinite usually display a higher reactivity during geopolymerisation compared to non-calcined materials [7, 17]. This can be explained by the fact that calcination of clay minerals change their crystalline structure into amorphous materials [13]

The variation of the activator composition is usually used to control the setting and the hardening times as well as the compressive strength. Generally, higher contents of NaOH and sodium silicate will give higher strength. However, Lee et al. [18] and Palomo et al. [4], found that too much alkali in the composition will adversely affect the strength. Thus, there should be an optimum alkali content for providing maximum mechanical properties. Many researcher [19, 20] found that the optimum Na_2O/Al_2O_3 molar ratio of one. De Silva and Sagoe-Crenstil [21] state that the initial molar content of Na_2O, Al_2O_3 and SiO_2 plays a key role in controlling transformations from amorphous to crystalline phase.

Freidin [22, 23] used geopolymerisation of waste by-products to produce cementless pressed blocks. Bassir Diop et al [24] developed low temperature bricks based on geopolymerisation of tuff using inexpensive processing. Billong et al [25] used thermally-treated lateritic soil partially activated with sodium hydroxide (NaOH) in the production of compressed blocks.

Based on the abundance of clay raw materials in Saudi Arabia, it is pertinent to develop geopolymer products based on these raw materials. The present investigation explores the possibility of utilizing low value clay raw materials in the production of pressed geopolymer bricks.

EXPERIMENTAL

Materials

Three low value clays were obtained from Saudi Arabi raw materials. Laboratory-grade NaOH reagent was obtained from Aldrich. Commercial sodium silicate ($Na_2O\%$, 14.2; $SiO_2\%$, 28.8 and Na_2O/SiO_2, 2.0) was obtained from Adwan Chemical Industries Co. Ltd, KSA. Distilled water was used throughout the research. The different clays locally named as white clay (WC), grey clay (GC) and red clay (RC) were used in this investigation. The white clay and the red clays were collected from Gada queries and the grey clay collected from Elmadina query. Pure kaolin (KA); ball clay was obtained from Colorificio Ceramico Bonet, S.A., Spain, and it was used as a reference material. The raw materials were ground in an alumina ball mill and sieved to < 120 µm. The clay raw materials were analyzed by XRF and X-ray diffraction. The clay raw materials were activated by calcination at 700°C for 2 hours. The activated clays were tested for the production of geopolymer building products and the results were compared with those of pure kaolin samples (KA).

Preparation of geopolymer bricks

Geopolymer bricks, activated with NaOH solution, were prepared as follows; The predetermined amount of NaOH was dissolved in mixing water then mixed with calcined clays in a porcelain mortar for 5 min. Geopolymer bricks activated with NaOH + sodium silicate solutions were prepared as follows; a constant calcined clays: sodium silicate solution weight ratio of 3 was used for all raw materials. The predetermined amount of NaOH was dissolved in sodium silicate solution then mixed with calcined clays in a porcelain mortar for 5 min. The Na_2O/Al_2O_3 molar ratio was fixed at one, and a constant total amount of mixing water was used (15 % by weight of the total ingredients). The resulting mass was moulded into cylindrical specimens 2.015 cm in diameter and 2.0 cm in height, under a moulding pressure of 15.0 MPa in a special steel mould, using a hand-operating, hydraulic press. The molded samples were allowed to mature at room temperature for 24 hours before curing at different temperatures. Curing temperatures included; (a) room temperature for 3 days; (b) 75°C for 24 h; and (c) 150°C for 24 h. Four samples from each mix were subjected to compressive strength test. The hydration products of samples were investigated by XRD and SEM.

Methodology

The chemical analysis was carried out by X-ray fluorescence (XRF) using AXIOS, Wavelength Disper-sive-XRF Sequential Spectrometer. X-ray diffraction (XRD) analysis was performed using an automated diffractometer (Philips type: PW1840), at a step size of 0.02°, scan rate of 2° in 2θ unit, and a scan range from 10° to 80°. Water absorption measurements of the bricks were carried out according to ASTM C140-01 [26]. The percentage absorption was calculated using the equation:

$$\text{Absorption (\%)} = [(W_2 - W_1)/W_1] \times 100$$

where W_1 = weight of specimen after complete drying at 105°C, W_2 = final weight of surface dry sample after immersion in water for at least 24 hours. The fracture surfaces of the fired samples were investigated using SEM (JOEL, Model: JSM-5600, Japan.) equipped with secondary electron detector and EDX. All samples were coated with gold.

RESULTS

Raw materials characterization

Table 1 shows the chemical composition of the clay raw materials in comparison with pure kaolin (KA). All clays contain SiO_2 and Al_2O_3 as the most predominant oxides. These oxides are mainly associated with the clay minerals. The SiO_2 content is also associated with free quartz particles. The relatively high SiO_2/Al_2O_3 ratio of all clays raw materials, with respect to pure kaolin, is an indication of low amounts of clay minerals.

Iron oxide, Fe_2O_3, is the main colorant in the clay rocks. According to Table 1, the increase of Fe_2O_3 in clays is associated with the progress increase of the dark color. Clay WC presents the lowest amount of Fe_2O_3,

which reflects its white color. Gray clay (GC) and red clay (RC) have a comparatively high amount of Fe_2O_3. GC clay has the highest amount of alkali; 1.83% K_2O and 0.68% Na_2O, and has 6.08 % CaO, which indicates the presence of calcite.

Table 1. The chemical compositions of the raw materials.

Material	Kaolin (KA)	White clay (WC)	Grey clay (GC)	Red clays (RC)
SiO_2	48.28	70.23	50.77	47.49
TiO_2	0.06	0.61	0.93	1.79
Al_2O_3	35.69	11.79	15.84	22.49
Fe_2O_3	0.97	6.49	9.01	14.89
MnO	-	0.17	0.15	0.26
MgO	0.07	0.44	2.47	0.46
CaO	0.05	1.13	6.08	1.03
Na_2O	0.28	0.16	0.68	0.22
K_2O	1.42	0.27	1.82	0.21
P_2O_5	0.12	0.21	0.34	0.19
SO_3	0.11	0.11	0.08	0.13
Cl	-	0.14	0.14	0.11
L.O.I	12.75	8.15	11.50	11.5
Total	99.8	99.9	99.81	100.77

Table 2 gives the mineralogical composition of different raw materials determined using XRD. The major crystalline components of the pure grade kaolin (KA) as supplied are kaolinite (84 %) and illite (16 %). WC comprises predominantly montmorillonite (30 %), and quartz (70%). The relatively high quantity of the free silica as quartz in the WC clay materials, is confirmed by the high SiO_2/Al_2O_3 ratio and low loss on ignition (LOI) as shown in Table 1. It should be noted that colored clays (GC & RC) have their major peaks associated with kaolinite, montmorillonite, quartz and hematite as a colorant. GC comprises predominantly kaolinite (32 %), calcite (15 %), quartz (15%) and montmorillonite (8 %) with considerable amounts of albite (7 %) and microcline (13 %). The latter accounts for the high amount of alkali in this material. GC clay is the only raw material that contains calcite; $CaCO_3$ (15 %), as the principal non-clay mineral. This was also confirmed by the results of chemical analysis, as this sample shows high CaO content of 6.08 %.

Mechanical properties

The compressive strengths of geopolymer brick samples activated with NaOH and cured at different temperature are given in Figure 1. The strength of the reference mix (KA) increases with increasing curing temperature from room temperature up to 150°C. All samples made with clay materials attains lower strength than reference mix (KA). This was expected because KA had the highest amount of aluminosilicate active constitutents. The strength of bricks made with clay materials depends on the composition of the raw materials and curing temperature. The strength increases with an increase in the curing temperature from room temperature to 75°C. However, increasing the curing temperature to 150°C resulted in a slight reduction in strength. GC sample attains no strength at room temperature.

The compressive strengths of geopolymer brick samples activated with alkaline sodium silicate solution and cured at different temperatures are given in Figure 2. Generally, bricks activated with a mixture of NaOH and sodium silicate solutions attain much higher strengths than those activated with only NaOH solutions. The strength of the reference mix (KA) increases with increasing curing temperature from 25 to 75°C, then decline with further increasing temperature to 150°C. The compressive strengths of WC samples increase more than the reference mix at curing temperatures 75°C and 150°C.

Water absorption

Water absorption is an important property that influences the durability of bricks. The lower water absorption the higher the resistance to water infiltration and to environmental damage. The results of the total water absorption for all the bricks are presented in Table 3. From these results, it can be seen that all absorption values of the geopolymer bricks were lower than the limit of ASTM C90 standard specification (17 % wt.) for loadbearing masonry unites. Geopolymer bricks activated with NaOH and sodium silicate solution have much lower water absorption values than those activated with only NaOH solution.

Table 2. Mineralogical composition of different clays and pure kaolin.

Phase	Kaolin (KA)	White clay (WC)	Grey clay (GC)	Red clays (RC)
Kaolinite ($Al_2Si_2O_5(OH)_4$)	84	-	32	40
Illite ($K_{0.8}Al_2(Si_{3.2}Al_{0.8})O_{10}(OH)_2$)	16	-	-	-
Montmorillonite ($Al_2Si_4O_{11} \cdot H_2O$)	-	30	8	12
Calcite ($CaCO_3$)	-	-	15	-
Quartz (SiO_2)	-	70	15	18
Hematite (Fe_2O_3)	-	-	2	4
Albite ($NaAlSi_3O_8$)	-	-	7	26
Microcline ($KAlSi_3O_8$)	-	-	13	-

Microstructure evaluation

Figures 3, 4, 5 and 6 show the SEM micrographs of different geopolymer bricks made with different activators and processed at different temperatures. Generally, gel that results from geopolymer bricks activated with sodium silicate are quite denser than those activated with NaOH alone. This may explain the low water absorption of bricks activated with NaOH and sodium silicate solution.

Figure 3, represents the microstructure of bricks made from KA. Samples activated with NaOH solution (Figure 3a) are more plate-like than the equivalent samples activated with alkaline sodium silicate solution
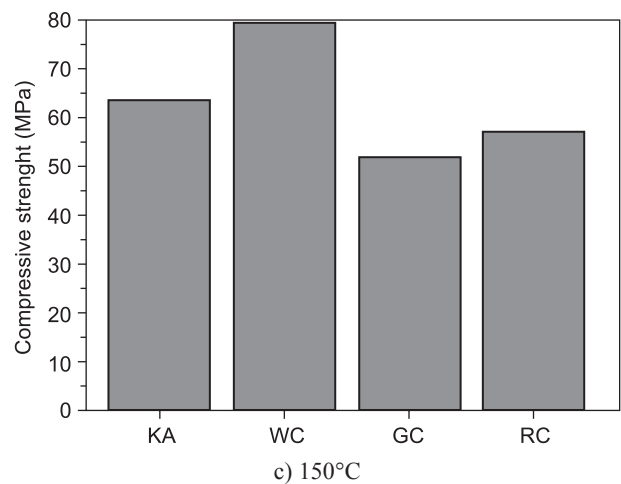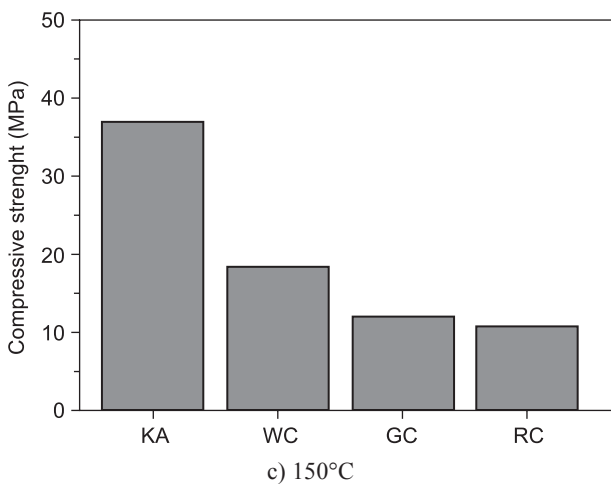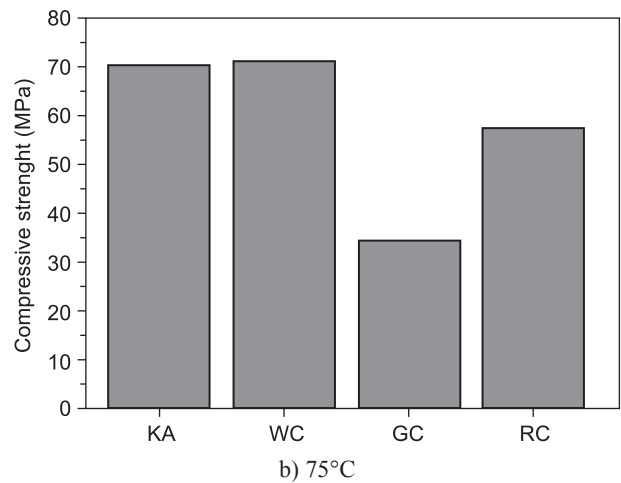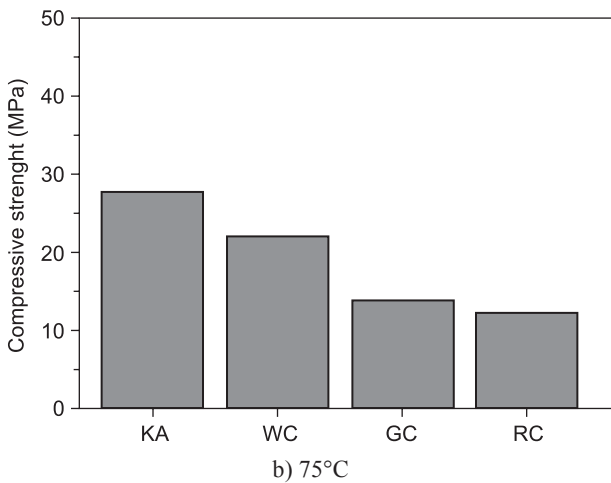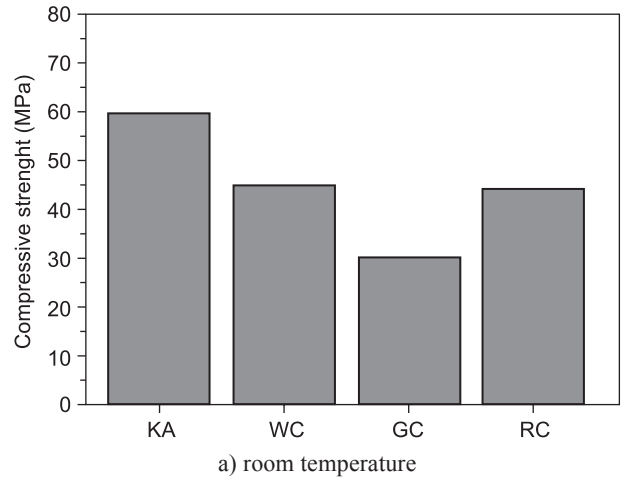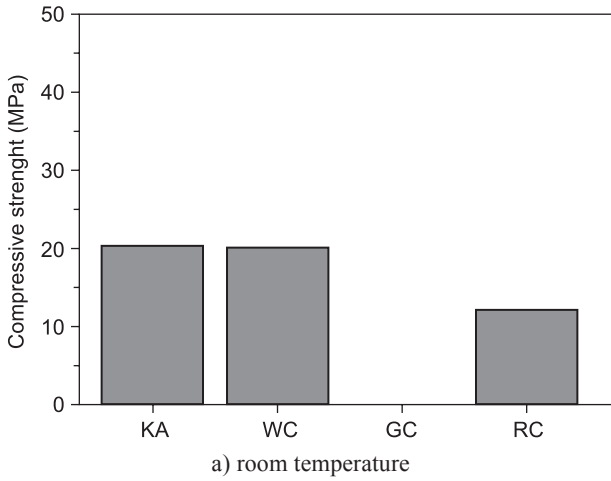

Figure 1. Compressive strength of NaOH activated bricks cured at different temperatures.

Figure 2. Compressive strength of alkaline sodium silicate activated bricks cured at different temperatures.

(Figure 3b). The latter samples are fine grained and dense in appearance which reflects the advances of the geopolymerization reaction of samples activated with alkaline sodium silicate solution.

Table 3. Water absorption (%) of bricks processed at different temperatures.

Activator	Sample	Processing temperature		
		Room	75°C	150°C
NaOH	KA	8.2	7.5	8.6
	WC	11.3	10.6	10.8
	GC	9.8	9.4	9.5
	RC	9.5	9.2	9.7
NaOH + Na silicate	KA	5.3	5.1	5.1
	WC	6.8	5.8	5.5
	GC	6.4	5.1	5.0
	RC	5.6	4.8	4.7

Figures 4a and 4b represent the microstructure of RC bricks activated with NaOH solution and activated with alkaline sodium silicate solution respectively, and processed at room temperature. Samples reveal the same microstructure as bricks prepared from KA (Figure 3).

Figures 5 and 6, represent the microstructure of bricks prepared from KA and RC respectively and processed at 150°C for 24 hours. The microstructure of NaOH activated samples show a loose grained structure with unreacted clays particles (Figures 5a and 6a). These imperfect microstructures of geopolymer bricks would be one of the main causes of poor compressive strength. KA sample that cured at 150°C (Figure 5b) shows somehow unfastened structure but RC sample (Figure 6b) cured at the same temperature shows fused-like structure It is clearly observed that non-dissolved sand and uncreacted clay particles in raw materials are enclosed within an amorphous aluminosilicate matrix acting as a binder.
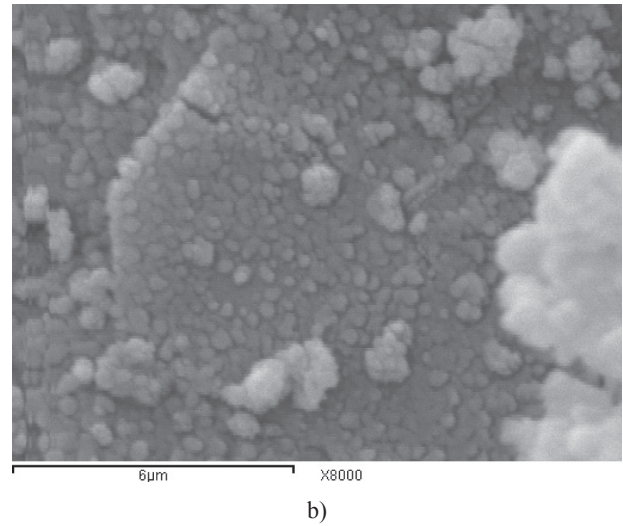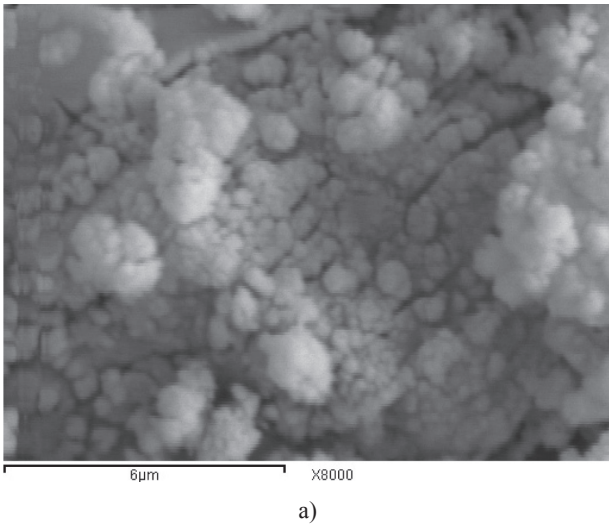

a)

b)

Figure 3. KA-based geopolymer bricks activated with; (a) sodium hydroxide solution and (b) alkaline Na-silicate solution and cured at room temperature.
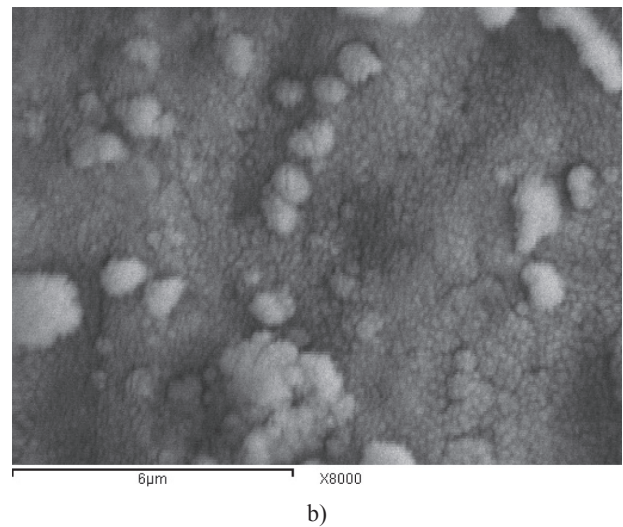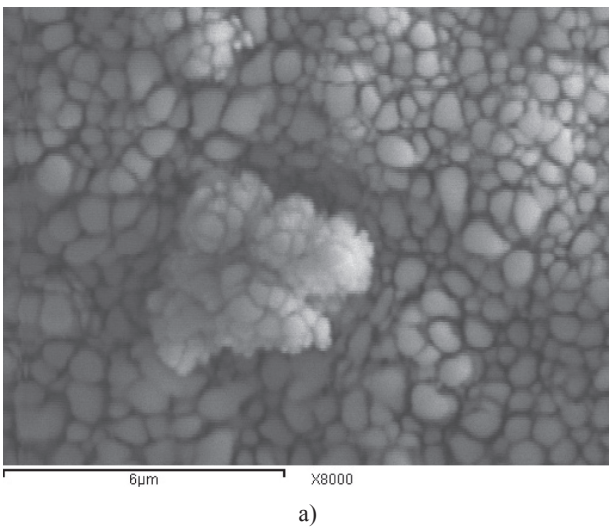

a)

b)

Figure 4. RC-based geopolymer bricks activated with; (a) sodium hydroxide solution and (b) alkaline Na-silicate solution and cured at room temperature.
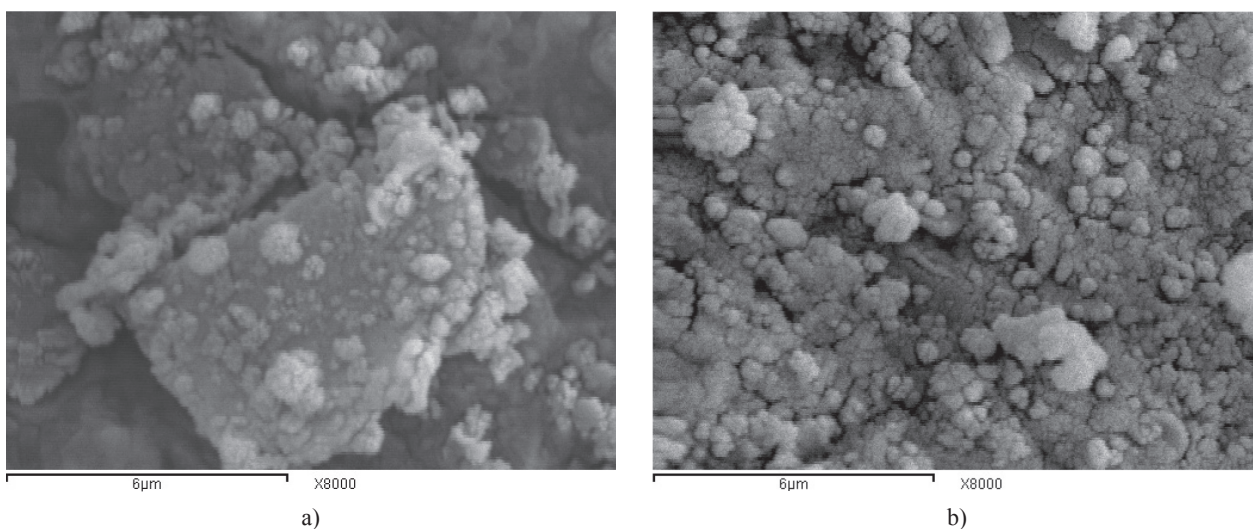
Figure 5. KA-based geopolymer bricks activated with; (a) sodium hydroxide solution and (b) alkaline Na-silicate solution and cured at 150°C.
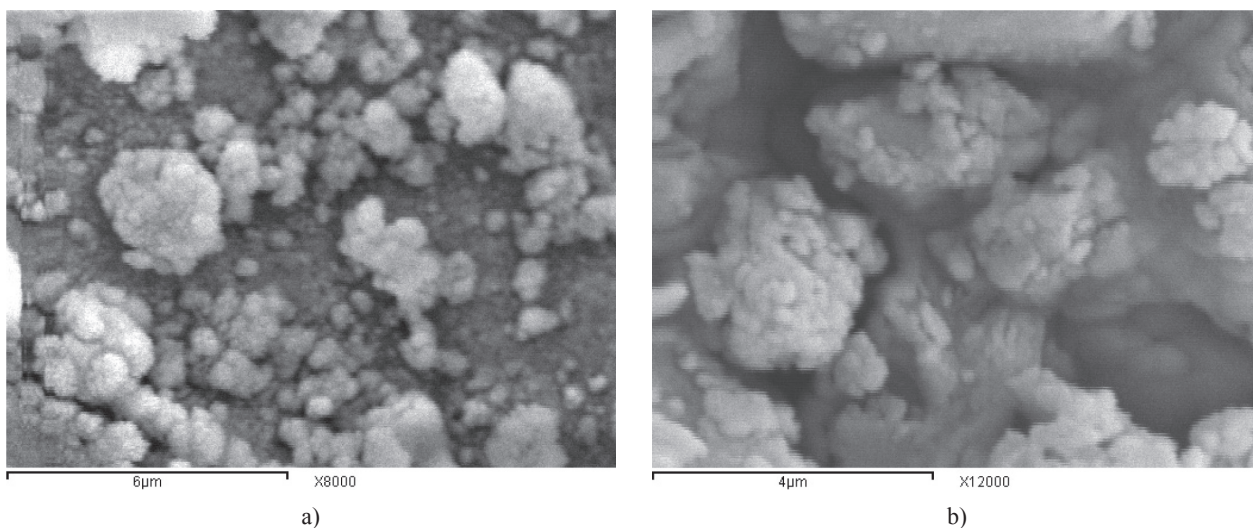

Figure 6. RC-based geopolymer bricks activated with; (a) sodium hydroxide solution and (b) alkaline Na-silicate solution and cured at 150°C.

XRD analysis

Figure 7 show the X-ray diffractograms of the starting calcined materials and the diffractograms of the products resulting from activation with alkaline sodium silicate solutions and cured at different temperatures. All the calcined clays and pure calcined kaolin exhibit a hump at $2q = 20\text{-}30°$, which is characteristic of structurally disordered metakaolin, and a set of peaks corresponding to minor crystalline quartz. The small broad peak that characterizes metakaolin appears at $2q = 20°$ for all samples.

After alkaline activation at different curing temperatures, the previously described hump shifts to the right, towards high $2q$ values. This shift is related to the formation of the amorphous sodium aluminosilicate gel which is the main binding phase. KA sample shows the presence of a minor amount of natrolite (PDF # 99–100 –0371) zeolite. This type of zeaolite was detected in other slag based geopolymers [27, 28].

DISCUSSION

For clay raw materials activated with only NaOH solution, curing at 75°C gives the best compressive strength. This can be explained by the fact that with increasing temperature from room temperature to 75°C, the reaction between the activation solution and the calcined clay increases. However, increasing curing temperature to 150°C causes a decline in compressive strength. This decline is due to the stopping of geopolymerization reaction due to vaporization of mixing water. Also, increasing temperature to 150°C may

also reduce the mechanical properties by introducing shrinkage cracks. The strength of the samples made with WC raw materials are higher than those with RC and GC, although they have high amount of active aluminumsilicate materials.
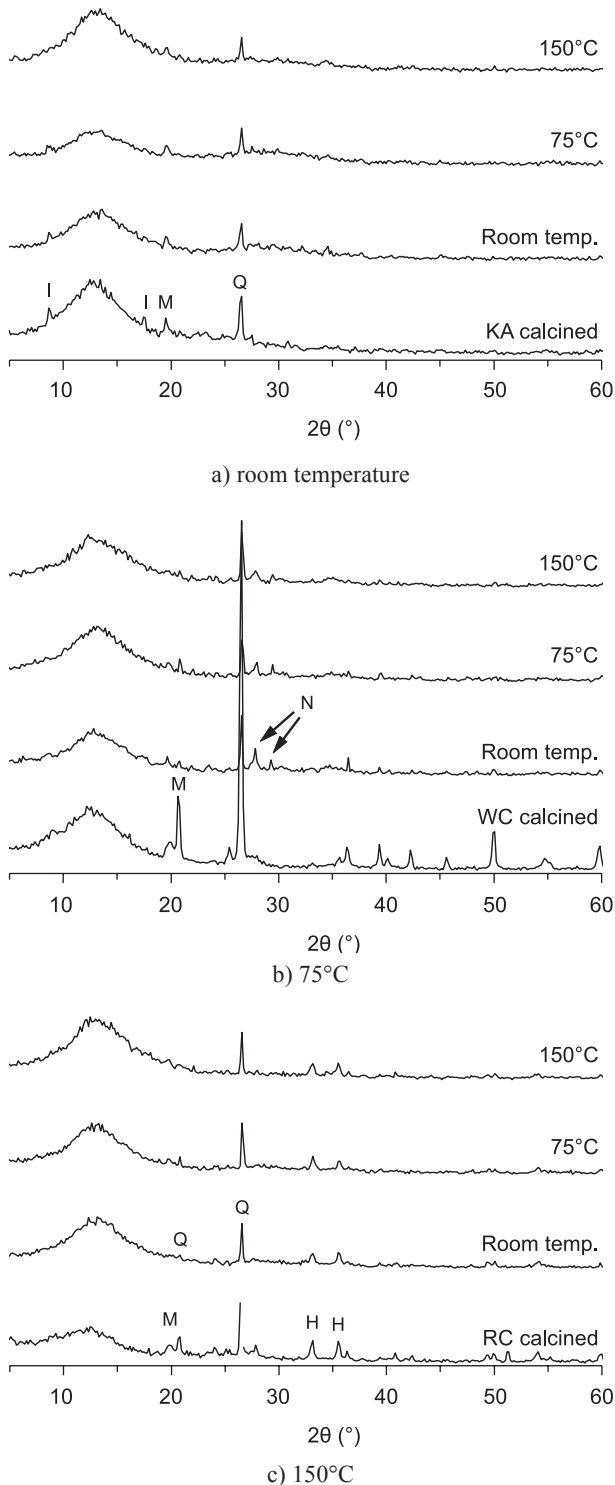

a) room temperature

b) 75°C

c) 150°C

Figure 7. XRD of different calcined raw materials and bricks activated with alkaline sodium silicate solution at different temperatures; (Q = quartz, H = Hematite, M = metakaolinite, I = albite and N = natrolite).

Generally, bricks activated with a mixture of alkaline sodium silicate solutions attain much higher strengths than those activated with only NaOH solutions. The compressive strengths of WC samples increase more than the reference mix at curing temperatures 75°C and 150°C. The strength difference seems to arise from the presence of high amount of sand as filler in WC raw material, which forms compsites with geopolymer matrix.

At present, there is no specification for geopolymer building units, therefore ASTM specification for different types of bricks (C62, C216 and C902) and loadbearing concrete masonry units (C90) are used for evaluating brick quality. Table 4, summarizes the minimum compressive strengths and the maximum water absorptions for different types of bricks and loadbearing concrete masonry units.

Water absorption values for the geopolymer bricks were lower than the limits of ASTM specifications for all brick types except ASTM C902 requirement for pedestrian and light traffic paving brick exposed to severe weathering conditions (SW). Water absorption of samples activated with only NaOH solutions exceeds ASTM C902 requirement.

Strength of WC brick samples activated with NaOH solution passes all ASTM specifications except for ASTM C902 requirement for pedestrian and light traffic paving brick exposed to severe weathering conditions (SW). GC and RC samples activated with NaOH solution pass only ASTM C90 for Loadbearing masonry units and ASTM C62 for building bricks exposed to negligible or no weathering

The geopolymer brick samples prepared from all raw materials and activated with alkaline sodium silicate solutions exceed the strength requirements of all brick types specified in ASTM (Table 4) if they are cured at 75°C or 150°C, except GC sample. In the case of GC samples, the average strength is slightly lower than ASTM C902 requirement for pedestrian and light traffic paving brick exposed to severe weathering conditions (SW). However, such small strength deficiencies can be readily corrected by processing adjustments such as adding fine aggregate. Bricks activated with NaOH and sodium silicate solutions and cured at room temperature pass all ASTM specifications of bricks except for ASTM C902 requirement for pedestrian and light traffic paving brick exposed to severe weathering conditions (SW).

CONCLUSIONS

Three clay raw materials were tested for geopolymer brick production. The calcined clays were activated by sodium hydroxide (NaOH) or by alkaline sodium silicate solutions. The physical and mechanical properties of the bricks were tested compared with the specifications

of ASTM for different types of bricks and loadbearing concrete masonry units. The following conclusions may be drawn:

1. The present study has shown that low value clays can be used as raw materials for geopolymer bricks and panels production after calcination. Both NaOH and alkaline sodium silicate solutions can be used as activators for the geopolymerization reaction.

2. Processing at ambient temperature may be unfeasible for samples activated only with NaOH solution due to low mechanical properties. However, processing at 75°C for 24 hours resulted in satisfactory mechanical properties.

3. The type of chemical activators; NaOH or alkaline sodium silicate solutions, is crucial for achieving high compressive strength. This is most likely due to enhanced dissolution of aluminum silicate active materials of the raw materials.

4. Strength of the geopolymer brick develops rapidly when it is cured at higher temperature than at room temperature. However, increasing processing temperature over 100°C decreases compressive strength due to rapid vaporization of mixing water.

5. The production of geopolymer brick on a small scale can be accomplished with traditional tools of casting and room temperatures curing. The processing of geopolymer bricks does not generate chemical pollutants like fired clay bricks.

Acknowledgements

References

1. Davidovits J.: J Therm. Anal. *35*, 429 (1989).
2. Van Jaarsveld J.G.S., Van Deventer J.S. J.: Miner. Eng. *10*, 659 (1997).
3. Provis J. L., Lukey G.C., Van Deventer J. S. J.: Chem. Mater. *17*, 3075 (2005).
4. Palomo A., Grutzec M. W., Blanco M. T.: Cem. Conc. Res. *29*, 323 (1999).
5. Slavik R., Bednarik V., Vondruska M., Skoba O., Hanzlicek T.: World Congress, p. 17-19. Saint Quentin. France 2005.
6. Phair J. W., Van Deventer J. S. J.: Miner. Eng. *14*, 289 (2001).
7. Xu H., Van Deventer J. S. J.: Int. J. Miner. Process *59*, 247 (2000).
8. Davidovits J. in: Proceedings of the World Congress Geopolymer, p. 9-15, Ed. Davidovits J., Saint Quentin, France 2005.
9. Davidovits J., Comrie D.C., Paterson J.H., Ritcey D.J.: Conc. Int. *12*, 30 (1990).
10. Davidovits J.: US Patent No. 5925449, 1999.
11. Davidovits J., Buzzi L., Rocher P., Gimeno D., Marini C., Tocco S.: In: Proceedings of the 2nd International Conference on Geopolymer '99, p. 83-96, Eds. Davidovits J., Davidovits R., James C., Saint Qunentin, France 1999.
12. De Silva P., Sagoe-Crenstil K., Sirivivatnanon V.: Cem. Conc. Res. *37*, 512 (2007).
13. Xu H., Van Deventer J.S.J.: Miner. Eng. *15*, 1131 (2002).
14. Phair J.W., Van Deventer J.S.J.: Int. J. Miner. Process *66*, 121 (2002).
15. Komnitsas K., Zaharaki D., Perdikatsis V.: J. Mate. Sc. *42*, 3073 (2007).
16. Panias D., Giannopoulou I., Perraki T.: Colloids and Surfaces A: Physicochemical Engineering Aspects *301*, 246 (2007).
17. Xu H., van Deventer J. S. J.: Colloids and Surfaces A: Physicochemical and Engineering Aspects *216*, 27 (2003).
18. Lee W.K.W., Van Deventer J. S. J.: Colloid. Surf. A *211*, 115 (2002).
19. Stevenson M., Sagoe-Crentsil K.: J. Mate. Sc. *40*, 2023 (2005).
20. Duxson P., Provis J. L., Lukey G. C., Mallicoat S. W., Kriven W. M., Deventer J. S. J.: Colloids Surf . A Physicochem. Eng. Asp. *269*, 47 (2005).
21. De Silva P., Sagoe-Crenstil K.: Cem. Conc. Res. *38*, 870 (2008).
22. Freidin C.: Cons. Build. Mat. *21*, 12 (2007).
23. Yang K. H., Song J. K., Ashour A. F., Lee E. T.: Cons. Build. Mat. *22*, 1981 (2008).
24. Diop M. B., Grutzeck M. W.: Cons. Build. Mat. *22*, 1114 (2008).
25. Billong N., Melo U. C., Louvet F., Njopwouo D.: Cons. Build. Mat. *23*, 2457 (2009).

Table 4. ASTM Specifications for different bricks and load-bearing concrete masonry units [29-32].

Title of specification	ASTM designation	Weathering conditions	Minimum compressive strength (MPa)	Maximum water absorption (%)
Building brick	C62	SW*	20.7	17
		MW*	17.2	22
		NW*	10.3	No limit
Facing brick	C216	SW	20.7	17
		NW	17.2	22
Pedestrian and light traffic paving brick	C902	SW	55.2	8
		MW	20.7	14
		NW	20.7	No limit
Loadbearing masonry units	C90	-	13.1	17

* SW indicates severe weathering, MW indicates moderate weathering, and NW indicates negligible or no weathering

26. ASTM C140-01, Standard test methods for sampling and testing concrete masonry units and related units, (2001).
27. Yao J. Z., Yong L. Z., Hai H. L., De Long X.: J. Mater. Sci. *34*, 7141 (2008).
28. Zaharakid., Komnitsas K.: Global NEST Journal *11*, 137 (2009).
29. ASTM C62, Standard Specification for Building Brick (Solid Masonry Units Made From Clay or Shale), 2001.
30. ASTM C216, Standard Specification for Facing Brick (Solid Masonry Units Made from Clay or Shale), 2001.
31. ASTM C902, Standard Specification for Pedestrian and Light Traffic Paving Brick, 2001.
32. ASTM C90-02, Standard specification for loadbearing concrete masonry units, the American Society for Testing and Material, 2001.