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Research paper

Characterization of alkali activated kaolinitic clay

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ABSTRACT

Low cost building materials have been developed by chemical activation of Jordanian Hiswa kaolinite with a sodium hydroxide solution. The effect of the main parameters of synthesis and processing on the development of compressive strength was studied. An investigation of the physical, thermal, mineralogical and microstructural properties was performed. A compressive strength of 32 MPa was obtained for a mixture cured at 80 °C for 24 h. The mineralogical and microstructural results on the hardened material indicate the formation of sodium zeolite phases and feldspathoids with a Na/Al ratio of one. The high compressive strength observed is directly related to the formation of the new phases that fill the pore spaces and bind the matrix.

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1. Introduction

The production of cement clinker produces a high amount of CO₂: its main raw material is calcium carbonate which releases CO₂ upon heating, while the heating to elevated temperatures consumes important amounts of fuel. The enormous amount of concrete used worldwide leads to the figure that the production of cement contributes more than 5% to the global anthropogenic emission of carbon dioxide (Habert et al., 2011). It is known that geopolymers, among other alternatives, can replace Portland cement while having a smaller ecological footprint (Habert et al., 2011; Steveson and Sagoe-Crentsil, 2005). The CO₂ production during calcination of clay minerals is much smaller than what is obtained from Portland cement as the calcination of clay minerals is a dehydroxylation instead of a decarbonation.

The dehydroxylation occurs at a lower temperature, thus, costing less energy (Gartner, 2011). Geopolymerization is the reaction of a solid aluminosilicate with a liquid alkali component as an activator agent, forming an inorganic polymeric network of alkali aluminosilicates (Ingles, 1970; Rahier et al., 2007; Rovnanik, 2010; Rowels and O'Connor, 2003; Van Jaarsveld et al., 2002; Xu and Van Deventer, 2000). The solid aluminosilicates normally used are metakaolinite (calcined clay mineral), fly ash (dust from coal incineration), blast furnace slag (quenched slag from iron making), or other waste products from power stations and mining processes: their amorphous structure can be transformed under the action of the alkaline

activator. Several names are given to the materials obtained via alkali activation (Xu et al., 2008). Besides geopolymers, inorganic polymers (Rahier et al., 1996) and mineral polymers (Patfoort et al., 1989; Theys et al., 1991) are also used although they are considered to be of the same class of materials. The materials produced at low-temperature by activation using an alkaline liquid component can range from completely amorphous to crystalline products (analogues of natural zeolites); the alkaline liquids contain group 1 metal ions usually sodium and/or potassium. The water in the geopolymer mixture provides a reaction medium and assures the workability of the mixture during mixing and handling. Filler materials may be used to enhance desired properties including mechanical strength and density.

An environmental drawback of geopolymers is the use of silicate solutions. These are prepared by dissolution of a glass that is formed at elevated temperature, thus with a considerable emission of greenhouse gases (Habert et al., 2011; Steveson and Sagoe-Crentsil, 2005). Using a NaOH solution instead of a silicate solution and kaolinite instead of metakaolinite would thus greatly reduce the environmental impact of the construction material produced. The term alkali activation will be used here instead of geopolymerization. The reason is that the raw material (kaolinite) and the product are (partly) crystalline, contrary to the nature of geopolymers. Another difference with the above consists in the fact that no thermal treatment has to be performed on the solid aluminosilicate; it can be used in its naturally occurring state and transformed by simple technological means, which allows the method to fit into the appropriate technology for building as defined by Schumacher (1973). The elements stated above contribute to the economic viability of the alkali activation of kaolinite, with respect to cement.

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Alkali activation of clay soils has been known for a long time, for instance road stabilization in developing countries (Cuisinier et al., 2009; Gera and Volkov, 2000; Hossain and Mol, 2011; Xeidakis, 1996). The fact that zeolites can be formed from kaolinite and NaOH solutions is also known (Breck, 1974). The literature on this topic is however scarce and few studies have been carried out to improve these materials in order to obtain a quality that is good enough to use as construction materials, which can replace fired bricks, tiles or cementitious products (Shi et al., 2006; Yousef et al., 2012). The same technology has also been used to consolidate earthen architectural remains (Elert et al., 2008). Currently, an increasing number of investigations are undertaken to search for a sustainable replacement of ordinary Portland cement. A recent development by Lemouagna et al. (2011) used volcanic ash in combination with alkaline solutions.

The main goal of this research is to characterize the material resulting from alkali activated kaolinite as is found in the Hiswa area in South Jordan. The clay deposits in Jordan are widely used and the extracted clays have a low price (Khoury, 2002). In this paper the optimal composition and cure conditions will be discussed. A structural characterization with XRD, SEM and NMR is carried out.

2. Experimental procedure

A kaolinite (Kaol) from Jordanian Hiswa is used as aluminosilicate source. A silica sand (SiSand) from south Jordan is used as a filler material and NaOH purchased from Merck with 99% purity is used to prepare the alkali solution with distilled water. The SiSand has a particle size distribution between 90 and 250 μm . Preparation of the samples was performed in three steps:

- 1- Mixing: the amount of Kaol and SiSand were mixed using a laboratory mechanical overhead mixer. The alkali solution was prepared by mixing NaOH and distilled water in a closed plastic bottle to avoid evaporation. The cooled NaOH solution was added gradually to the Kaol/SiSand mixture and mixed for 2 min at 100 rpm and 10 min at 200 rpm to get an optimum homogeneity.
- 2- Molding: the mixture was put into a stainless steel cylinder mold (50*25 mm) and compacted with a pressure of 16 MPa by using a hydraulic compressor; the mold was then removed and the sample weighed. With each mixture at least 3 samples were prepared.
- 3- Curing: the uncovered samples were placed in a ventilated oven at 80 °C for 24 h, unless specified otherwise.

The compressive strength of the samples was measured by using a CONTROLS testing machine (Model T106 modified to suit standard testing), where the load was applied and increased by a displacement rate of 3 mm/min. An average of three samples per measurement was taken.

2.1. Optimization of ratio

The optimal component ratio was studied by preparing two series of samples with different ratios of NaOH and SiSand. In this work, the amount of distilled water added was taken as the plasticity limit for the mixture of Kaol and SiSand. As a result the mixture does not flow and must be compressed. The optimal ratio of the other components in the mixture was determined depending on the best compressive strength as will be highlighted in the Results and discussion section. Two series were prepared: One with six samples with different NaOH ratios and a second series with four samples with different SiSand ratios. The mass ratios of NaOH vary from 8, 12, 14, 16, 18, to 20 with respect to 100 Kaol mass%, 50 SiSand mass% and 22 H₂O mass%. The samples were cured at 80 °C for 24 h. The second series had different SiSand ratios of 25, 50, 100, and 150 with respect to 100 Kaol mass%, 16 NaOH mass% and 22 H₂O mass% and also cured under the same conditions.

2.2. Optimization of curing conditions

The effect of curing time on compressive strength was studied by preparing one series cured at 80 °C at six different times for 6, 12, 18, 24, 48 and 72 h. Another series was cured 24 h at four different temperatures at 50, 60, 70, and 80 °C for 24 h to check the influence of temperature.

Four series of the optimized samples without SiSand filler and with sand filler were prepared to get an idea of the influence of sand on the difference between wet and dry samples. The samples without sand also served for structural and molecular analyses. One series was left under lab conditions and another series was immersed in de-mineralized water to test the stability of samples in wet conditions. Unconfined compressive strength was measured for all series after three days.

The compressive strength of the samples was measured by using a modified motorized CBR device, at a displacement rate of 3 mm/min. Three similar samples are tested and the average of the three measurements is taken.

2.3. Characterization of the raw materials and optimized material

In order to identify the major elements of Kaol and SiSand, X-ray fluorescence spectroscopy was done on powdered samples using a Bruker System S4 Pioneer.

The mineralogical components of raw Kaol and optimized samples were investigated by X-ray diffraction (XRD), using a Siemens 500 Kristalloflex instrument, with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a scan rate of 2°/min.

The thermal behavior was determined by TG/DTA analysis. The analysis was done by using a Netzsch STA 409 thermal analyzer. The samples (approximately 36 mg, size <425 μm) were heated in an alumina cup at a rate of 20 °C/min, starting from 50 °C up to a maximum temperature of 1000 °C using N₂ as a purge gas.

The structural details were studied by SEM/EDX and NMR. The platinum coated samples of raw Kaol and the optimized samples were scanned using a high-energy beam of primary electrons in a raster scan pattern using model FEI-INSPECT-F50. ²⁹Si and ²⁷Al spectra were obtained using a Bruker AC250 spectrometer that operates at 49.70 MHz and 65.18 MHz for the ²⁹Si and ²⁷Al resonance frequencies, respectively. For more details on the MAS NMR conditions see Ref. (Rahier et al., 1997).

3. Results and discussion

3.1. Characterization of the raw material

The composition, expressed in oxides, for the Kaol and SiSand is given in Table 1. Silica (SiO₂) and alumina (Al₂O₃) are the major components for Kaol, representing 74% from the total content. For SiSand, the results show that SiO₂ forms about 99% from the total content, which was expected as the sand was expected to be almost pure. The presence of 0.5% Al₂O₃ is attributed to an insignificant amount of clay impurities.

Fig. 1 shows the X-ray diffractogram of the raw Kaol. The chart indicates that the mineralogical components of Kaol are mainly kaolinite (Al₂Si₂O₅(OH)₄) and quartz (SiO₂). Muscovite/illite (KAl₂Si₃AlO₁₀(OH)₂) and hematite (Fe₂O₃) are present as minor components with traces of alunite (KAl₃(SiO₄)₂(OH)₆). Gypsum (CaSO₄·2H₂O) is present as a filler material in joints and fractures of the deposit (Al-Momani, 2000). Under the supposition that Al₂O₃ is only present in kaolinite, the amount of kaolinite in Kaol would be 64 m% based on the results in Table 1.

The Kaol has a very fine particle size (picture not shown). Quartz appears as colorless particles, medium to fine grained, subrounded to angular shaped, and fractured pattern. Iron oxides (brown patches

Table 1
Major element composition of Jordanian Hiswa Kaol and SiSand.

Major oxides	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	L.O.I	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	SO ₃	TiO ₂
Kaol (wt.%)	25	0.7	7.5	1.4	12	0.2	0.0	0.2	0.2	49	2.9	0.9
SiSand (wt.%)	0.5	0.1	0.0	0.00	0.2	0.00	0.0	0.1	0.0	99	0.0	0.1

of hematite) are present as a cement material. Some black spots could not be identified.

Fig. 2 shows the TG/DTA curves of the Kaol sample. The TG curve indicates that the sample has lost about 1% of water as moisture content. The next mass loss step around 500–600 °C accounting for 9.4% is due to the removal of the OH groups of kaolinite resulting in metakaolinite. From this mass loss the amount of kaolinite can be calculated being 67%. This is somewhat higher than the amount deduced from XRF. The DTA curve shows three endothermic peaks: the first one appears in the range of 100–150 °C, corresponding to the moisture loss also seen with TGA. The second peak appears at about 565 °C and is mainly attributed to the dehydroxylation of kaolinite transforming into metakaolinite (Caglar et al., 2007; Kakali et al., 2001; Zuhua et al., 2009). This dehydroxylation is the removal of hydroxyl groups from Al–OH bonds (Rocha and Klinowski, 1990). The third endothermic peak appears at about 970 °C. At this temperature the dehydroxylation goes to the end and new more stable phases are formed. The new phases are a mixture of amorphous materials such as mullite, silica–alumina and a small amount of unreacted metakaolinite.

3.2. Optimization of mixing ratios

NaOH is used as an activator for the aluminosilicate material. The OH[−] concentration of the activator is an important parameter. The alkalinity is primarily necessary for the disintegration of the strong aluminosilicate layer (Sathia et al., 2008). As the reactivity of kaolinite is much lower than for thermally activated clays, such strong alkaline solutions need to be used (Fernandez et al., 2011). On the other hand, Na⁺ serves as the counter ion for the negative charge introduced by each AlO₄ tetrahedron formed (see section 3.4). Fig. 3 shows that the compressive strength increases almost linearly with the NaOH content. The highest compressive strength value obtained was 33 MPa, for the series that contains 16 parts of NaOH. At higher NaOH content the compressive strength again decreases.

Filler materials like sand reduce cracking and decrease the porosity of the composite. Fillers also reduce the quantity of binder paste making the resultant material less expensive. The effect of adding sand grains to the reaction mixture on the compressive strength is shown in Fig. 4. Increasing the sand content improves the workability of the mixture. The best compressive strength values are obtained for

a SiSand:Kaol ratio of 0.5 to 1. Remark that the sample in Fig. 3 with 16 parts of NaOH has the same composition as the sample one in Fig. 4 with 50 parts of SiSand. They were however made from a different batch. This shows the deviations between several batches (compressive strength of 28 compared to 33 MPa).

3.3. Optimization of curing conditions

The effect of the curing temperature on compressive strength is shown in Fig. 5. The maximum compressive strength value was 32 MPa, for the series cured at 80 °C for 24 h. The increase in curing temperature from 60 °C to 80 °C more than doubles the compressive strength. In general, temperature substantially increases the reaction rate.

The effect of curing time on compressive strength is shown in Fig. 6. The compressive strength increases with the increase of curing time. A maximum compressive strength of 48 MPa was attained after 48 h of thermal curing. After 48 h, no further gain in strength was observed. Therefore, heat-curing time needs not to be more than 48 h at 80 °C in practical applications.

To check the stability of the samples under wet conditions some optimized samples with and without sand filler were tested under dry and wet conditions 7 days after curing for 24 h at 80 °C. The average compressive strength value of the samples without SiSand was 23 MPa in dry conditions and 13 MPa in wet conditions; whereas the average compressive strength value for the samples with SiSand was 41 MPa in dry conditions and 24 MPa in wet conditions. Note that the compressive strength still increased from 32 to 41 MPa during storage for 7 days at room temperature after the curing.

As a general rule, the samples made with SiSand exhibited higher strength values than the samples made without SiSand. The strength of all mixtures has decreased by half under wet conditions. This can be partly attributed to the absorption of water by the remaining kaolinite (Reddy and Kumar, 2009), and partly by the hydrolysis of the Si–O–Si bonds in the newly formed structure. However, this drop in strength is not caused by degradation of the material; since repeated drying–wetting cycles do not further diminish the strength, this observation however, will be discussed at greater length in a subsequent paper.

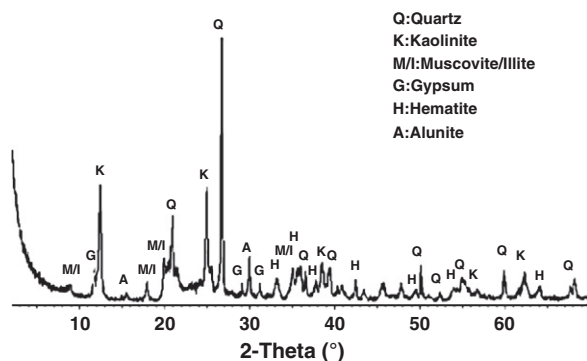


Fig. 1. XRD spectrum of the raw Kaol.

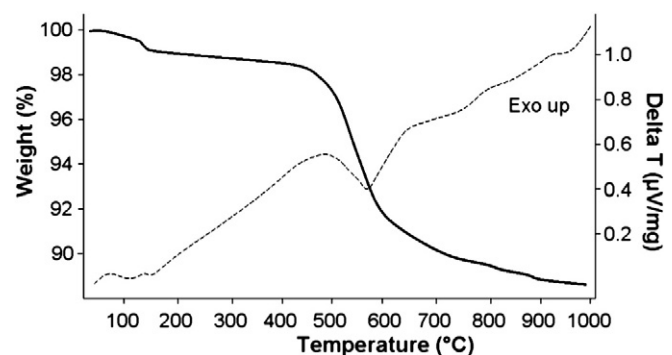


Fig. 2. TG/DTA curves of the raw Kaol.

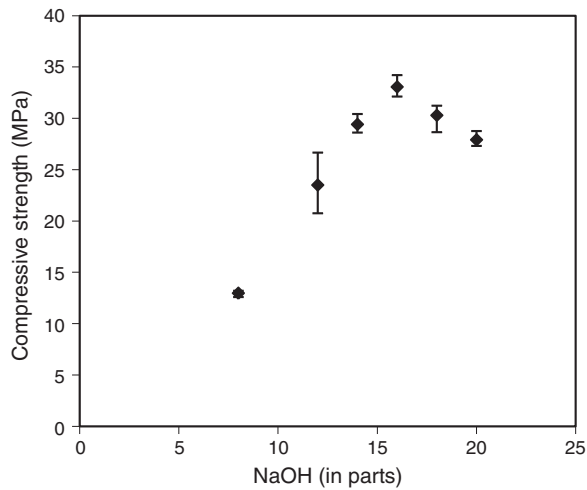


Fig. 3. NaOH ratio vs. compressive strength. Samples with composition 100 Kaol, 50 SiSand and 22 H₂O and cured for 24 h at 80 °C.

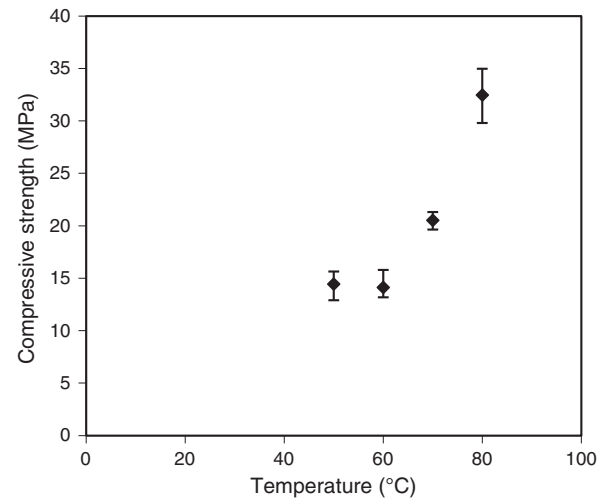


Fig. 5. Curing temperature vs. compressive strength. Samples with composition 100 Kaol, 100 SiSand, 16 NaOH, and 22 H₂O and cured for 24 h.

3.4. Structural characterization of the optimized material

Fig. 7 shows the X-ray diffractogram of the optimized alkali-activated material. The chart indicates that the reaction of kaolinite with NaOH results mainly in new alkaline sodium aluminosilicate phases. These phases are Na-zeolitic minerals namely: phillipsite ((Na,K,Ca)_{1–2}(Si,Al)₈O₁₆·6H₂O) and natrolite (Na₂Al₂Si₃O₈·2H₂O). A feldspathoid phase of hydroxysodalite (Na₂Si₂Al₂O₅(H₂O)₆) is also identified. Quartz occurs as a major phase in the sample due to the added SiSand filler along with the remains of kaolinite, muscovite/illite, and hematite from the raw material. Remark that in these minerals the ratio Na⁺/Al³⁺ = 1 as is the case for geopolymers (Rahier et al., 1996). If the ratio of Na/Al = 1 is valid for all the reaction products formed, including any amorphous products, then the amount of kaolinite consumed can be calculated since 2 mol of NaOH will react with 1 mol of kaolinite (Al₂O₃·2SiO₂·2H₂O). In our samples 16 parts of NaOH were used to 100 parts of Kaol. Taking account of the molar mass 16 parts of NaOH are only enough for to react with 52 parts of Kaol. From the characterization of the clay an amount of 64% (XRF) to 67% (TGA) of kaolinite is present in the Kaol while only 52% can react. As a consequence, some kaolinite will remain unreacted.

Fig. 8 shows the TG/DTA curves of the optimized sample. The TG curve indicates that the sample loses about 1.45% water between 80

and 340 °C. This is accompanied by an endothermic signal in DTA. The second step shows the transformation of kaolinite to metakaolinite as the remaining OH groups are eliminated. This can be observed in the mass loss as well as in the heat flow signal. An attempt was made to determine the amount of unreacted kaolinite via the mass loss by dehydroxylation of unreacted kaolinite. However, the mass loss in Fig. 8 shows that this step is higher than expected. This is explained by an overlap with some newly formed phase. As such the amount of residual kaolinite cannot be measured accurately. The loss of this chemically bound water will make the material less suited for elevated temperature applications.

The third endothermic peak appears at about 970 °C and does not finish below 1000 °C. It is likely this corresponds to the transformation of metakaolinite into more stable phases, but also to the decomposition of other minerals that are present such as carbonates and sulfates (Rocha and Klinowski, 1990).

Fig. 9 shows the SEM micrograph and EDX microanalysis for the new sodium aluminosilicate phase that grows as a result of the reaction. The new phase occurs mainly as rosettes of spherulitic aggregates filling the pore spaces and binding with the other particles. The relicts of kaolinite indicate that the reaction is not complete, confirming the XRD and TG/DTA results. EDX microanalysis (arrow in Fig. 9) of a new phase indicates the presence of aluminum (Al),

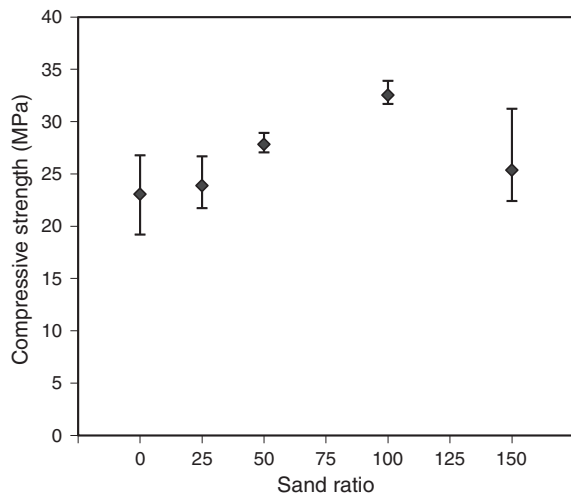


Fig. 4. Sand ratio vs. compressive strength. Samples with composition 100 Kaol, 16 NaOH and 22 H₂O and cured for 24 h at 80 °C.

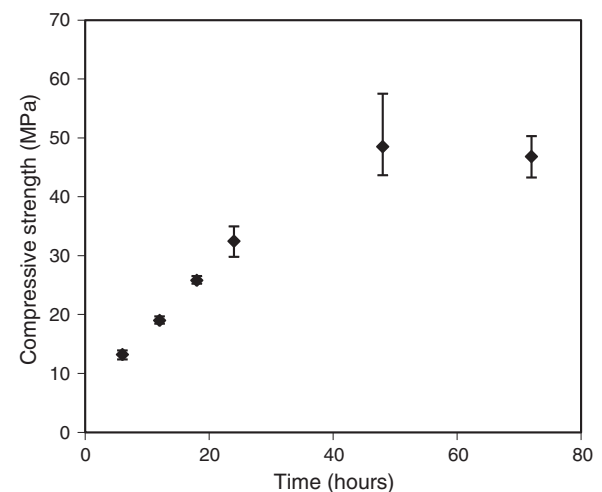


Fig. 6. Curing time vs. compressive strength. Samples with composition 100 Kaol, 100 SiSand, 16 NaOH, and 22 H₂O and cured at 80 °C.

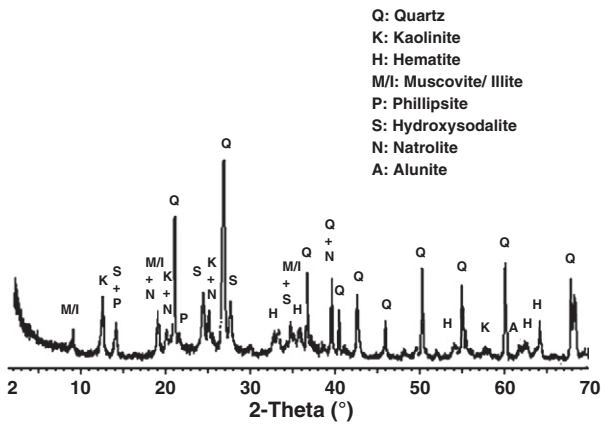


Fig. 7. XRD spectrum of the optimized sample. Samples with composition 100 Kaol, 100 SiSand, 16 NaOH, and 22 H₂O and cured at 80 °C for 24 h.

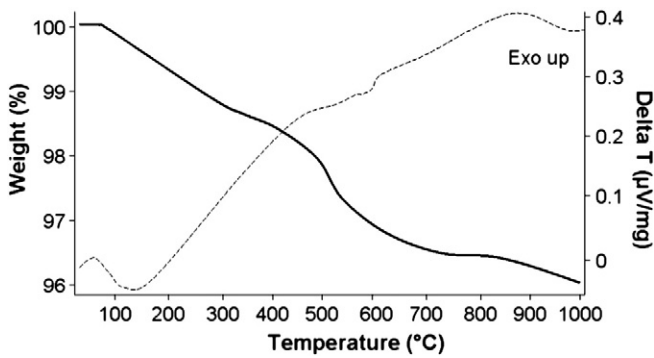


Fig. 8. TG/DTA curves of the optimized sample. Samples with composition 100 Kaol, 100 SiSand, 16 NaOH, and 22 H₂O and cured at 80 °C for 24 h.

silicon (Si), potassium (K) and sulfur (S) originating from Kaol, while the presence of sodium (Na) is due to the addition of alkali activator (NaOH).

Fig. 10a describes the chemical shifts of ²⁹Si MAS NMR for a sample without SiSand compared to the raw Kaol. The ²⁹Si spectrum shows that Kaol shows a single resonance at −91 ppm characteristic

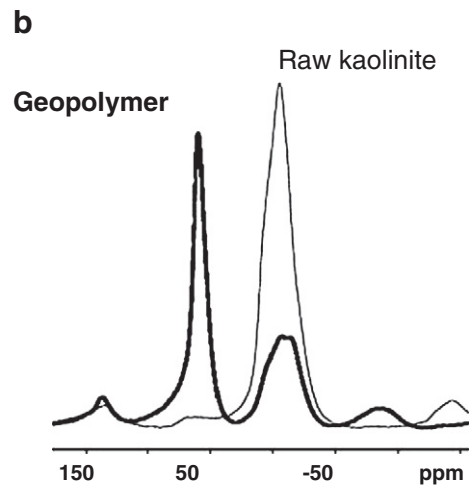
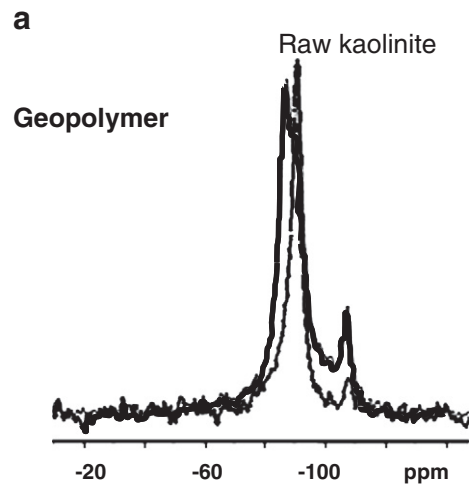


Fig. 10. a) ²⁹Si MAS NMR spectrum and b) ²⁷Al MAS NMR of Kaol and optimized sample. Samples with composition 100 Kaol, 100 SiSand, 16 NaOH, and 22 H₂O and cured at 80 °C for 24 h.

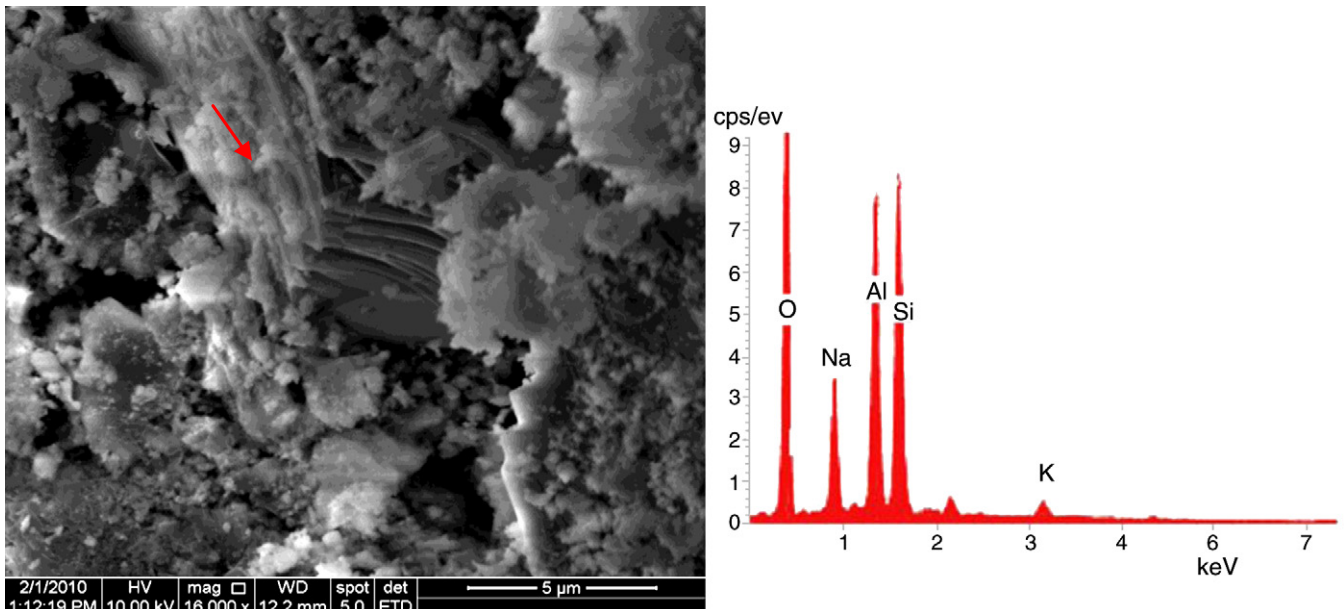


Fig. 9. SEM/EDX of the optimized sample. Samples with composition 100 Kaol, 100 SiSand, 16 NaOH, and 22 H₂O and cured at 80 °C for 24 h.

for the Si in the SiO₄ layer of kaolinite (Rocha and Klinowski, 1990). This Si is linked over an oxygen bridge to three other Si atoms with mainly covalent bonds. The resonance at −108 ppm which is characteristic of Si covalently linked to four other Si atoms is related to the quartz in the raw material. In the reacted sample, there is a new separate resonance observed at −87 ppm. This resonance is related to newly formed sodium aluminosilicate phases. The ²⁷Al spectrum in Fig. 10b shows a broad resonance at −5 ppm assigned to 6-coordinated Al in Kaol (Xu and Van Deventer, 2000). This again shows that the kaolinite is not completely consumed. The new phases show a resonance at 57 ppm attributed to 4-coordinated Al. This transformation to tetrahedral Al is comparable to the geopolymerization process.

4. Conclusions

The Jordanian clay from the south Hiswa area is predominantly composed of kaolinite and quartz, in addition to a considerable amount of muscovite/illite, hematite and possibly alunite and gypsum. Alkali activation of the raw kaolinite with an aqueous solution of sodium hydroxide was studied. The compressive strength and the workability of the formed samples are influenced by the proportions and properties of the components of the reaction mixture. An increase of silica sand content up to a one to one ratio with respect to kaolinite has led to improvements in the workability of the mixture and an increase in the compressive strength. By optimizing the ratios and curing conditions a compressive strength of up to 48 MPa under dry conditions and 23 MPa under wet conditions was obtained. This loss of compressive strength under wet conditions is acceptable. A major decline in the kaolinite content was confirmed by several analytical techniques. However, it was not possible to obtain a quantitative measurement for the amount of kaolinite remaining. The crystalline reaction products were found to be sodium aluminosilicate phases from the zeolitic group, namely phillipsite, atrolite and hydroxysodalite. These phases fill the pore spaces and bind the matrix, this differs from many geopolymers, as these phases contain chemically bound water. In a following paper the durability of this material will be studied.

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