

Geopolymers from Jordanian Metakaolin: Influence of Chemical and Mineralogical Compositions on the Development of Mechanical Properties

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ABSTRACT

The present work selects four metakaolin materials; i.e., Jordanian MK, Metastar 501 MK, Fluka MK and mixed Fluka MK with quartz, to investigate the influence of chemical and mineralogical compositions on the compressive strength of geopolymers synthesized by alkali activation of metakaolin. The geopolymer cements were ageing at 25°C between 24 and 672 h. The influence of secondary phase (quartz) on the geopolymerization reaction of metakaolin has been investigated by comparing the above-mentioned four metakaolins. The bonding status and chemical environment of SiO₄ and AlO₄ tetrahedras of four different types of geopolymeric products were systematically investigated by infrared spectroscopy, and the phase changes were studied by X-ray diffraction analysis.

The results show that quartz, at the concentration used in this work, does not prevent the geopolymerization reaction. On the other hand, in the case of Jordanian MK and mixed Fluka MK with quartz, the geopolymer products form a cohesive and relatively hard solid indicating that they have large and stable compressive strength compared with the other two metakaolins (Fluka and Metastar 501 MKs).

KEYWORDS: Metakaolin, Geopolymer, X-ray diffraction, Infrared analysis, Compressive strength.

INTRODUCTION

Geopolymeric cement is a new type of CaO-free inorganic aluminosilicate cementitious material, which has received a great deal of attention across the world in recent years (Davidovits, 1989). Geopolymeric products are amorphous aluminosilicate substances with three-dimensional (3D) framework structures, whose building units primarily consist of TO₄ tetrahedras (where T is Si or Al) (Davidovits, 1988). Synthesis of geopolymeric products involves a chemical reaction between highly reactive aluminosilicates (such as metakaolin, fly ash or dehydrated clay) and strongly alkaline reagents (such as NaOH or KOH), yielding polymeric –Si–O–Al– or –

Si–O–Al–O–Si– or –Si–O–Al–O–Si–O–Si– precursors by sharing nearly all oxygen between two tetrahedral TO₄ units. According to the structural types, geopolymeric products can be expressed by the following empirical formula (Davidovits, 1994):



where, *R* is a cation such as potassium K or sodium Na and *n* is the degree of polycondensation. *z* is 1, 2 and 3; *w* is the binding water content.

Geopolymers are a class of material synthesized by alkaline activation of an aluminosilicate source at ambient or higher temperature. A relatively low temperature (600–800 °C) is required for the thermal processing of aluminosilicates derived from kaolin

sources to produce metakaolin. Due to the properties of excellent heavy metal immobilization (Zhang et al., 2008b), high temperature stability, quick solidification with high strength (Lee and van Deventer, 2002) and biological compatibility (Qudadesse et al., 2007), geopolymers are potentially used in the fields of waste treatment, fire proof construction and military engineering and even as biomaterials. Unlike conventional organic polymers, like glass, ceramic or cement, geopolymers are non-combustible, heat-resistant, formed at low temperatures and fire/acid resistant. Geopolymerization is a complicated process responsible for the formation of geopolymers. The understanding of geopolymerization process and its influencing factors is useful for the application of geopolymeric materials. However, the exact process is not fully understood so far although the involved mechanism has been studied in the last 3 decades (Davidovits, 2008; Duxson et al., 2007).

A large number of previous studies focused on the manufacture of geopolymeric products prepared from kaolinite or metakaolinite as the main precursor (Barbosa and Mackenzie, 2003; Duxson et al., 2007a), in particular for applications as adhesives, coatings and hydroceramics (Xu and van Deventer, 2002). However, if geopolymers made from clays are to be used as construction materials, large volumes of precursor will be needed, likely to come from clay deposits containing secondary minerals such as quartz and illite. This work investigates the possibility of utilizing natural Jordanian kaolin as a raw material in the production of geopolymer products. The objective of

this study is to investigate the influence of quartz as secondary phase on the compressive strength of the corresponding geopolymers, by comparing the products obtained from a pure kaolinite with those obtained from kaolin containing a large amount of quartz, from Jordan. A number of metakaolin-based geopolymer products were designed, prepared and tested for their compressive strength behaviors, by comparing the products obtained from the Jordanian metakaolin containing a large amount of quartz with those obtained from a pure metakaolin, from UK and Fluka metakaolin, from Germany. The products will be characterized by X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) Spectra.

EXPERIMENTAL PROCEDURES

Materials

In the present work, four metakaolins were used as solid precursors. One of them (symbol JMK) was a product of kaolin calcined at 650° C for 3h in air. It was obtained from Jabal Al-Hard deposit, south Jordan. The second one (symbol Metastar 501) was purchased from Imerys, Cornwall, U.K. The third one (symbol FMK) was purchased from Fluka company, Germany, and the last one was a mixture of Fluka Metakaolin and 30% quartz from Merck (symbol FMK+QZ). Potassium water glass (KWG) solution (Silirit M60) was used as alkali activator system and purchased from Cognis Deutschland, GmbH, Duesseldorf, Germany. The chemical compositions of the four types of metakaolin (precursor materials) and water glass are presented in Table 1.

Table 1. Chemical composition of metakaolins and water glass

Materials	Chemical components (%)			
	SiO ₂	Al ₂ O ₃	K ₂ O	H ₂ O
Water glass	19.3	–	24.5	56.2
Jordan metakaolin (JMK)	65.8	33.7	–	0.5
Metastar 501, UK	61.5	37.8	–	0.7
Fluka metakaolin (FMK)	60.2	39.2	–	0.6
Fluka metakaolin + 30% quartz (FMK-Qz)	64.6	34.8	–	0.6

Methods

A series of cements were prepared using Jordanian metakaolin (JMK), metakaolin Metastar 501 (Imerys, Cornwall, U.K.), Fluka Metakaolin (FMK) and

additionally a mixture of Fluka metakaolin with 30% quartz (FMK-Qz). Chemical compositions are given for comparison in Table (2).

Table 2. The chemical compositions of geopolymer cements of alkali activated metakaolins prepared using Jordanian kaolin (JMK), Fluka kaolin (FMK) and a mixture prepared using Fluka kaolin and SiO₂ (Merck 594375 or 1.07536.0250) [70% Fluka metakaolin + 30 % Merck quartz (SiO₂)]

Cement	KWG	MK	SiO₂	Al₂O₃	K₂O	Molar
	(%)	(%)	(mol)	(mol)	(mol)	Si/Al
Jordan cement						
J-Cem. 1	50	50	0.85	0.34	0.25	1.25
J-Cem. 2	55	45	0.73	0.28	0.25	1.30
J-Cem. 3	62.5	37.5	0.63	0.22	0.25	1.40
Metastar 501						
M-Cem. 1	62.5	37.5	0.60	0.25	0.25	1.20
Fluka cement						
F-Cem. 1	63.6	36.4	0.54	0.22	0.25	1.20
F-Cem. 2	58.8	41.2	0.61	0.27	0.25	1.10
F-Cem. 3	55	45	0.68	0.32	0.25	1.05
Fluka + quartz cement						
Fqz-Cem. 1	50	50	0.84	0.35	0.25	1.20
Fqz-Cem. 2	55	45	0.72	0.29	0.25	1.25

Specimen Preparation for Mechanical Test

All the geopolymer samples were prepared by hand, mixing the different metakaolin powders (as described in Table 1) in the alkaline solution of potassium water glass [(KWG) (SiliritM60)] for about 10 min, forming a homogeneous slurry. The ageing process followed at 25° C between 24 and 240 h. Transfer of the slurry to cylindrical PE-containers was carried out (20 mm in diameter and 12 mm in height) which were closed to prevent moisture loss and to slow down water

evaporation from the surface, and hence eliminate surface cracking. All alkali activated cements were sealed in plexi boxes and cured at ambient temperature between 72 and 672 h. The details of mixture proportion of the nine types of geopolymeric cement paste are given in Table 2. The variation of Si/Al ratios for cements J-cem.1, J-cem.2, J-cem.3, M-cem. 1, F-cem.1, F-cem.2, F-cem.3, Fqz-cem.1 and Fqz.cem.2 resulted from different amounts of water glass and metakaolin in each composition (Table 2).

Compressive Test

The mechanical testing measurements were carried out for a series of geopolymers to test the influential variable on the compressive strength of hardened geopolymers. The compressive strength results of geopolymers were measured on cylindrical samples of dimensions (20 mm diameter and 12 mm height), using a universal testing machine (ENERPAC P392, USA). The batch of these samples was placed in an air-conditioned room at 25 °C for 3 to 28 days. The compressive strength was calculated from the applied load at the point of sample failure.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR analysis was performed on a Bruker IFS66v FTIR spectrometer by using KBr pellet techniques in the 4000–400 cm^{-1} range, with a resolution of 1 cm^{-1} . (1 mg of fine powders previously prepared was homogeneously grinded together with 200 mg of KBr powder until the mixture had the consistency of fine flour, and then pressed into a disk).

Powder X-Ray Diffraction (XRD)

XRD analysis was recorded on a Bruker AXS D4 ENDEAVOR diffractometer using Ni filtered Cu $K\alpha$ radiation at 40 kV and 40 mA. The measurements were carried out with a step width of $0.03^\circ 2\theta$ and a measuring time of 1 second per step. The powder data were analyzed with the Stoe WinXPOW software package.

RESULTS AND DISCUSSION

Precursor Materials

The Jordanian kaolins and their respective metakaolins were fully characterized (chemical and mineralogical composition, thermal behavior and particle size distribution, and so on) in previous studies (Gougazeh and Buhl, 2010). The mineralogical composition of the JMK, Metastar 501 MK, FMK and Fqz MK samples, determined by X-ray diffraction and chemical analysis, is summarized in Table 1. The X-

ray patterns of JMK, Metastar 501 MK, FMK and Fqz metakaolin samples are illustrated in Fig. 1. For the samples obtained from the pure Metastar 501 and FMK precursor, the main feature is by far the very broad reaction at $20^\circ - 40^\circ (2\theta)$ $\text{CuK}\alpha$ assigned to the amorphous metakaolinite structure. Expectedly, for the samples obtained from the impure JMK and Fqz MK precursor, sharp reflections were recorded due to the residual crystalline quartz phase and a halo at $2\theta = 30^\circ$, indicative of an essentially amorphous compound.

FTIR Analysis

FTIR Analysis of Metakaolin-Based Geopolymer

Figs. 2-12 represent the IR spectra of Jordan Metakaolin (JMK) and a series of alkali activated cements produced after different curing times at room temperature. The absorption pattern of raw aluminosilicate (JMK) exhibits peaks at: 460 cm^{-1} , 588 cm^{-1} , 675 cm^{-1} , 803 cm^{-1} and 1080 cm^{-1} (Fig. 5). The band at 460 cm^{-1} is related to Si-O in-plane bending vibration, while the band at 675 cm^{-1} is assigned to Si-O symmetrically stretching vibration (Yunsheng et al., 2008). A peak at 588 cm^{-1} is also seen in the spectrum of alkali activated in a geopolymer. The 803 cm^{-1} band is caused by six-coordinated Al-O stretching vibration, which disappears in IR spectrum of alkali-activated series (J-Cems., M-Cems., F-Cems. and Fqz-Cems.). This means that in the dissolution process six-coordinated Al transforms into coordination.

Comparison of the IR Spectra between Jordanian Geopolymer Cement (J-Cem. 3) and Metastar Geopolymer Cement (M-Cem. 1)

Figs. 2 and 3 illustrate the IR spectra of J-Cem.3 and M-Cem.1, respectively. Series of the IR spectra of alkali activated cement were measured after different curing times. The analysis was performed for geopolymers characterized with the same composition, curing conditions and preparation time, several times showing the same results. The spectra of potassium water glass and metakolin have been given to show the

relation between IR spectra of raw materials and corresponding geopolymer.

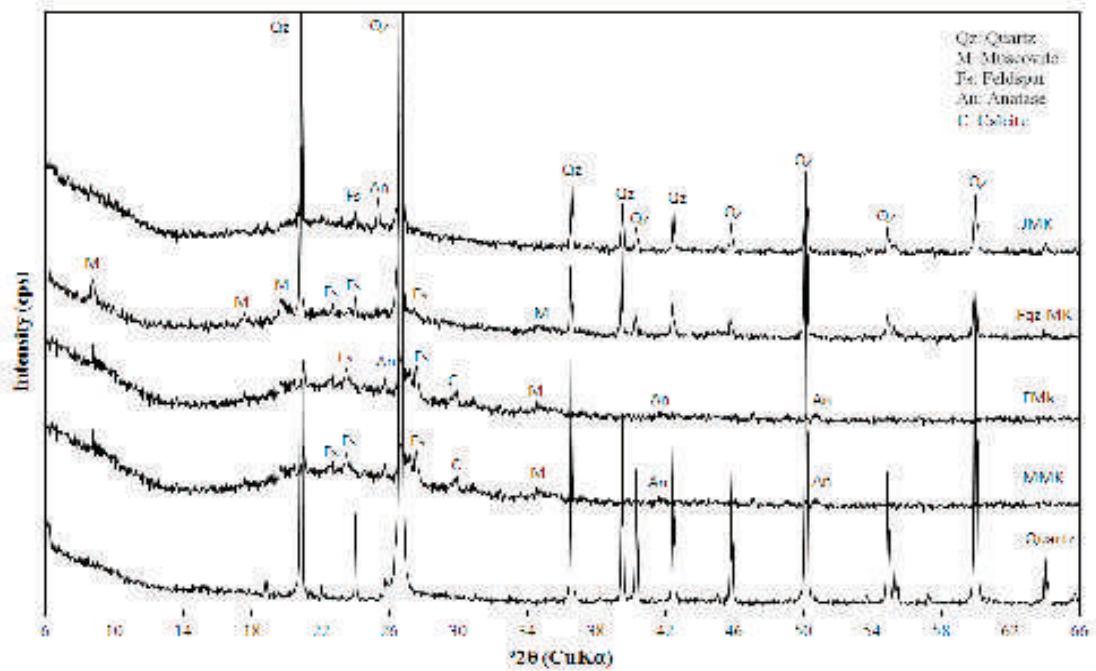


Figure 1: X-ray diffraction patterns of quartz, Metastar metakaolin (MMK), Fluka metakaolin (FMK), mixture of Fluka + 30 % quartz metakaolin (Fqz MK) and Jordanian metakaolin (JMK) samples

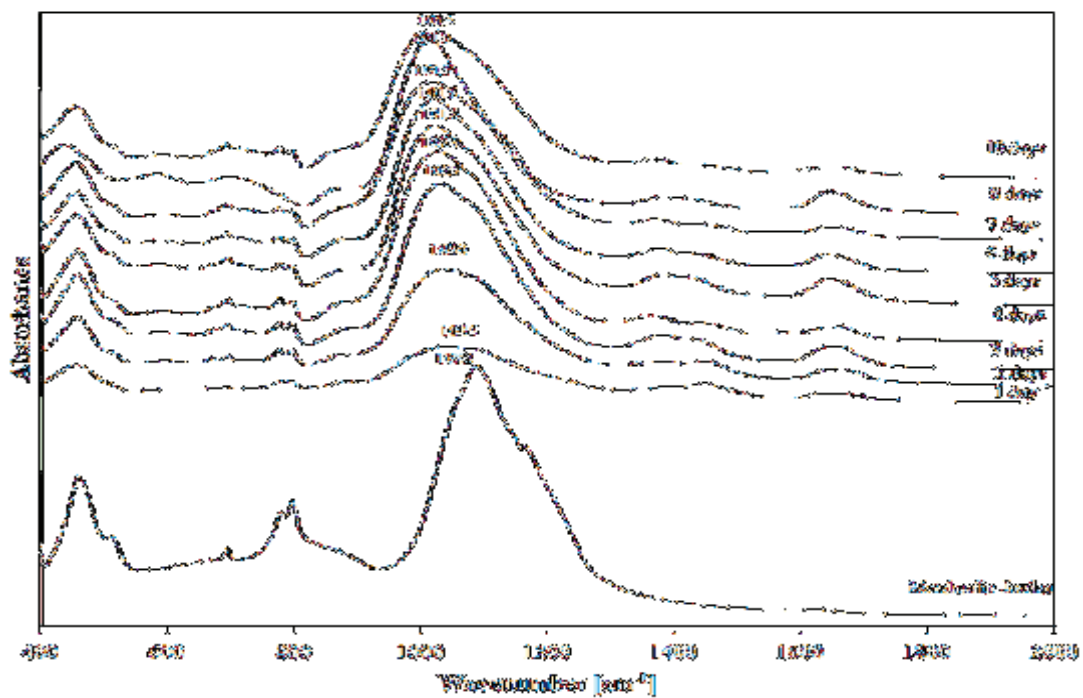


Figure 2: IR spectra of alkali-activated metakaolin (J-Cem. 3) during 10 days of ageing at room temperature, and metakaolin-Jordan

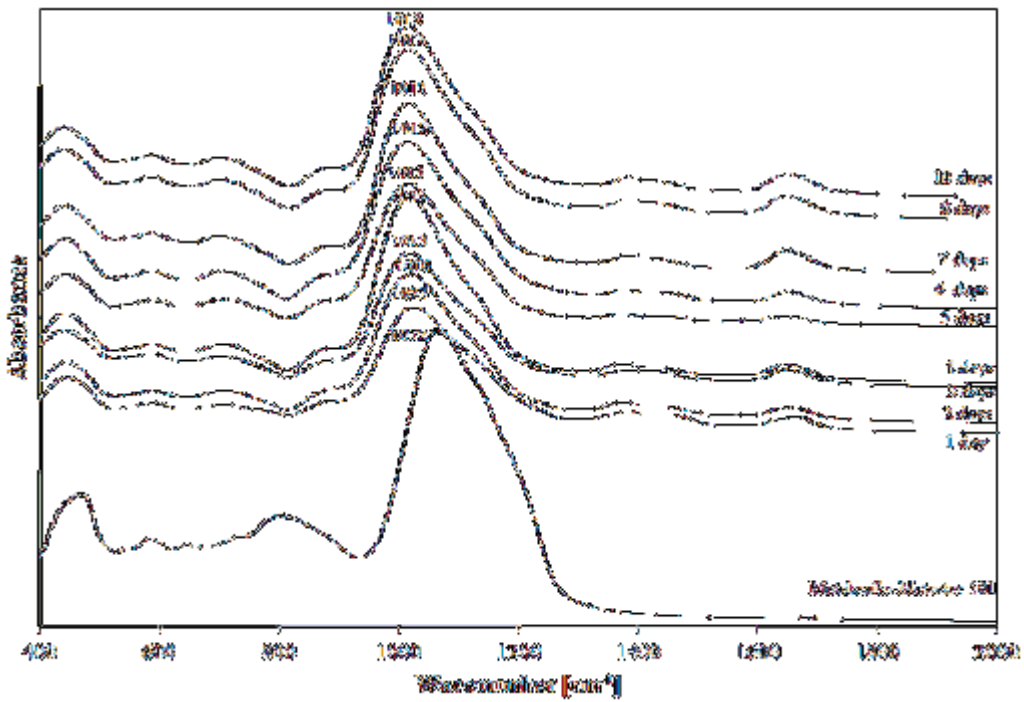


Figure 3: IR spectra of alkali-activated metakaolin (M-Cem. 1) during 10 days of ageing at room temperature, and metakaolin Metastar 501

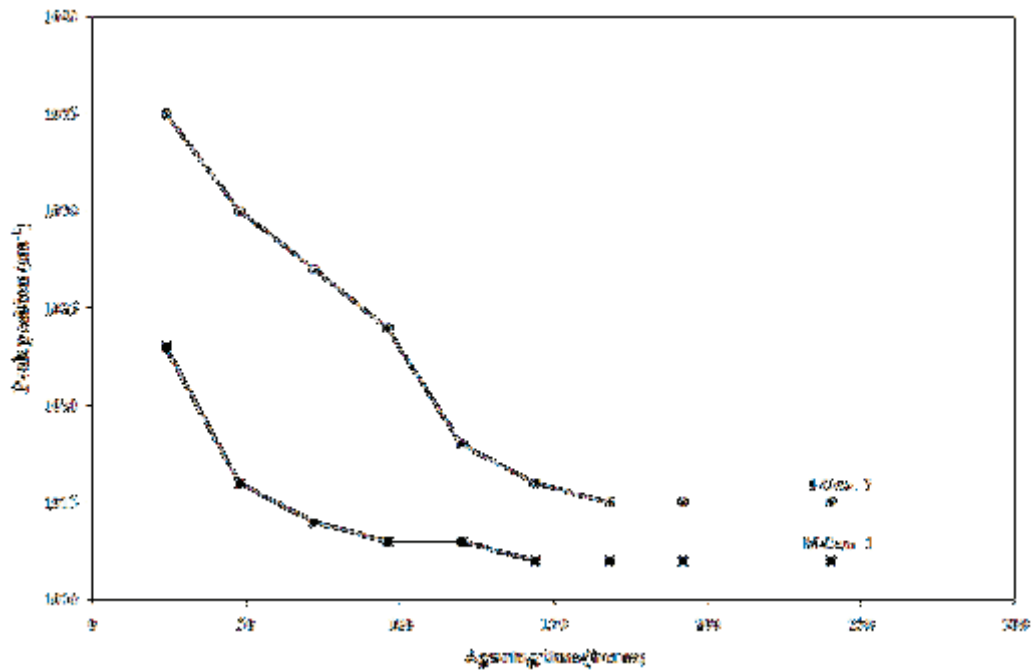


Figure 4: The dependence between DOSPM of asymmetrical stretching and ageing time of Jordanian geopolymer (J-Cem. 3) and Metastar geopolymer cement (M-Cem. 1) estimated from FTIR study of ageing process given in Figs. 3 and 4

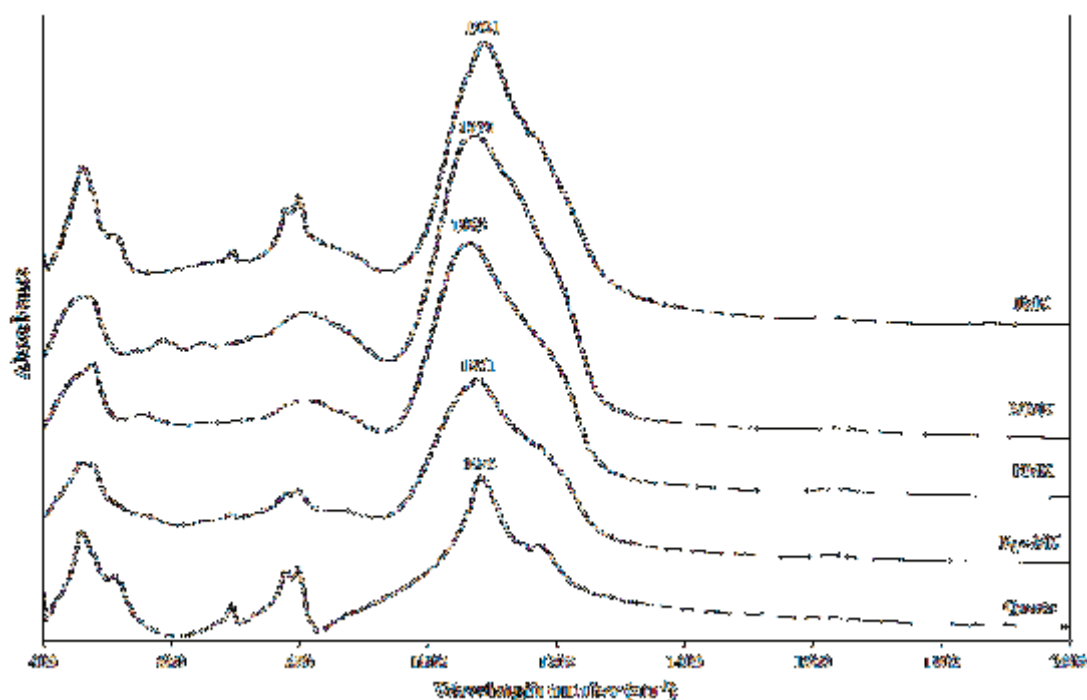


Figure 5: IR spectra of quartz and different alkali-activated metakaolin, JMK: Jordanian metakaolin, MMK: Metastar 501 metakaolin, FMK: Fluka metakaolin and Fqz. MK: mixture of Fluka and 30 % quartz metakaolin,

After one day of ageing, bending mode shifts from 452 cm^{-1} to 435 cm^{-1} (M-Cem.1) and from 453 cm^{-1} to 450 cm^{-1} (J-Cem.3) and remains at the same position for both cements during further ageing.

Strong changes both at earlier and later stages of geopolymerization are observed in the range of asymmetrical stretching. The position of the maximum of this peak will be called DOSPM (density of states peak maximum). After stirring the metakaolin diluted with alkaline solution and taking a spectrum after 1 day and 2 days, the DOSPM shows maximum at about 1035 cm^{-1} and 1030 cm^{-1} , respectively for J-Cem.3 and 1023 cm^{-1} and 1016 cm^{-1} , respectively for M-Cem.1. Above about 5 days of ageing, the DOSPM remains at the same position for J-Cem.3, whereas above about 3 days for M-Cem.1. This indicates that M-Cem.1 was faster dried and matured than J-Cem.1 (Fig. 4).

Comparison of the IR Spectra between Metakaolin and Various Geopolymeric Products

The structure of geopolymeric products is totally different from the layered structure of metakaolin, as shown in Fig.1. In order to better understand the bonding status and chemical environment of the predominant building units (SiO_4 and AlO_4 tetrahedras) in the polymeric chains for the nine types of the geopolymeric product, the IR spectra of various geopolymeric products are presented in Fig.1. The detailed comparisons of the IR spectra between metakaolin and various geopolymeric products are also performed in order to explore the formation mechanism of geopolymeric products. The FTIR spectra of various geopolymeric cement matrices are presented in Figs. 5-12. The chemical shifts of main FTIR bands and the corresponding species are determined based on

(Akolekard et al., 1997; Valeria et al., 2000) by carefully comparing FTIR spectra; the following

observations can be drawn:

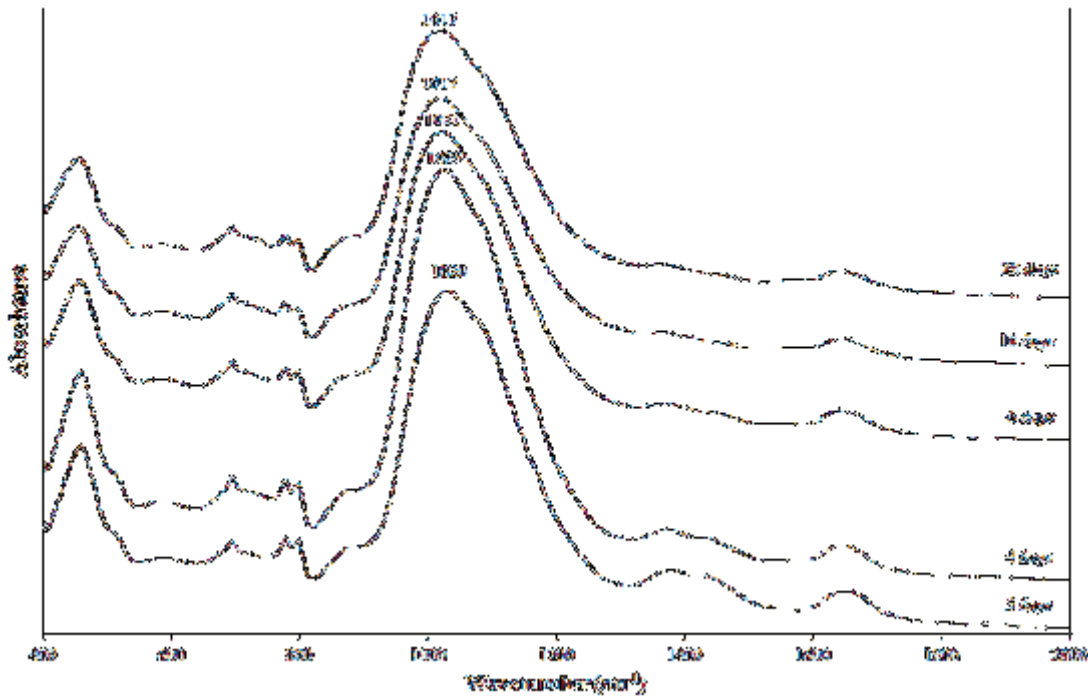


Figure 6: IR spectra of alkali-activated metakaolin (J-Cem. 1) during 28 days of ageing at room temperature, and Jordan-metakaolin

1) It is seen from Figs. 5-12 that there is a large diffuse band at about $1003\text{-}1035\text{ cm}^{-1}$ in IR spectra of the nine types of geopolymeric product (J-Cem. 1, J-Cem. 2, J-Cem. 3, M-Cem. 1, F-Cem. 1, F-Cem. 2, F-Cem. 3, Fqz-Cem. 1 and Fqz-Cem. 2). This indicates that various geopolymeric products are actually amorphous ones consisting of randomly developed Si-Al polytetrahedras with a lack of periodically repeating Si-Al atomic ordering.

2) The strong band at 1080 cm^{-1} , 1063 cm^{-1} and 1072 cm^{-1} in the IR spectrum of Jordanian metakaolin, Fluke metakaolin and Fluka + quartz (30%) metakaolin, respectively shifted towards the low wavenumber after hydration reaction of geopolymeric cements after 28 days. The chemical shift is very large, ranging from 51 cm^{-1} for Fluka cements, 59 cm^{-1} for mixture of Fluka and quartz cements to 65 cm^{-1} for

Jordan cements. In addition, the strong band at 1072 cm^{-1} in the FTIR spectrum of metakaolin (Metastar 501) shifted approximately 60 cm^{-1} after geopolymerization reaction of geopolymeric cement after 10 days. This demonstrates that an obvious change in microstructure takes place during hydration reaction, resulting in a formation of new products with different microstructures from the layered metakaolin.

Similar results are also seen in the XRD patterns, as shown in Figs. 16-22. According to (Akolekard et al., 1997; Valeria et al., 2000), peaks at 1063 , 1072 and 1082 cm^{-1} are caused by stretching vibration of Si-O bond, while peaks at 1012 , 1013 and 1015 cm^{-1} are ascribed to asymmetrical vibration of Si-O bond. The large shift toward the low wave number may be attributed to the partial replacement of SiO_4 tetrahedron by AlO_4 tetrahedron, resulting in a change in the local

chemical environment of Si-O bond. In addition, The band at 1006 cm^{-1} is very strong, but a lack of sharp feature is indicative of the general disorder in the Si(Al)-O- network, reflecting the wide distribution of the SiQn (mAl) unit in the polymeric molecular chains of geopolymeric cement products. A SiQn (mAl) unit is the conventional notation used to describe the structural units in aluminosilicates, where “n” represents the degree of condensation of SiO_4 tetrahedra. If $n = 0, 1, 2, 3$ and 4 , then silicon is respectively in isolated monogroup (SiO_0), in disilicates and chain end groups (SiO_1), in middle groups in chains (SiO_2), in sheet sites (SiO_3) and in three-dimensional cross-linked sites (SiO_4). The letter “m” represents the number of aluminum atoms in the second coordination sphere of silicon. In general, if there is no aluminum atom in the second coordination sphere of silicon, the notation becomes SiQn(nSi). The stretching modes of Si-O bonds of SiQn units are IR active in the $850\text{-}1200\text{ cm}^{-1}$ region with the absorption bands of the SiQn unit with $n = 4, 3, 2, 1, 0$ centered at around $1200, 1100, 950, 900,$ and 850 cm^{-1} , respectively (van Jaarsveld et al., 1999). These values shift to lower wavenumbers when the degree of silicon substitution by aluminum in the second coordination sphere increases, as a consequence of the weaker Al-O bond.

3) The intensities of the bands at 914 cm^{-1} and 798 cm^{-1} in IR spectrum of metakaolin, caused by 6-fold coordinated Al(VI)-OH swing vibration and 6-fold coordinated Al(VI)-O stretching vibration, respectively, considerably reduced or disappeared after hydration reaction of geopolymeric cement. In addition, a similar trend is also found for the Si-O symmetrically stretching band at about 697 cm^{-1} . This shows that 6-coordinated Al(VI) may be changed into 4-coordinated Al and participate in the framework formation of geopolymeric products during the process of hydration reaction.

4) A weak band at around 840 cm^{-1} can be observed in some geopolymeric products. The band cannot be found in the IR spectrum of metakaolin. The new band

is assigned to the bending vibration of Si-OH. This can be caused by some bond breakage sites in the network structure of geopolymeric products. The existence of Si-OH will result in a decrease in the degree of condensation, thus a reduction in mechanical strength. Based on the above analysis of FTIR spectra, we can conclude that during geopolymerization reaction of geopolymeric cement, SiO_4 and AlO_4 tetrahedron will be released from the surface of metakaolin particles under the attack of the strongly alkaline solution. The VI-coordinated Al introduced by metakaolin will also be leached out in the strongly alkaline solution, and the coordination state will transform from VI to IV. As the dissolution proceeds, more and more SiO_4 and AlO_4 tetrahedrons go into the alkaline solution. After undergoing structural reorientation to a certain extent, SiO_4 and AlO_4 tetrahedrons will produce a polycondensation reaction, thus a formation of geopolymeric cement products with a framework structure. It is the bonding of AlO_4 (IV) with SiO_4 that causes the great changes in the original Si-O chemical environment, resulting in different chemical shifts as well as a reduction or disappearance of some characteristic bands in FTIR spectra. When the mixture proportion of geopolymeric cement matrix is not properly designed, incomplete polycondensation reaction will occur, thus resulting in some bond breakages in the framework structure.

Strong changes both at earlier and later stages of geopolymerization are observed in the range of asymmetrical stretching. The position of the maximum of this peak will be called DOSPM (density of states peak maximum).

The steep increase in compressive strength coincides with the DOSPM from 1030 cm^{-1} , 127 cm^{-1} and 1024 cm^{-1} to 1015 cm^{-1} , 1013 cm^{-1} and 1012 cm^{-1} for (Jordanian geopolymers), (Fluk + quartz geopolymers) and 1024 cm^{-1} for (Fluka geopolymers) products, respectively. This indicated the slowly growing aluminosilicate and probably crosslinking network covering the polysilicate chains.

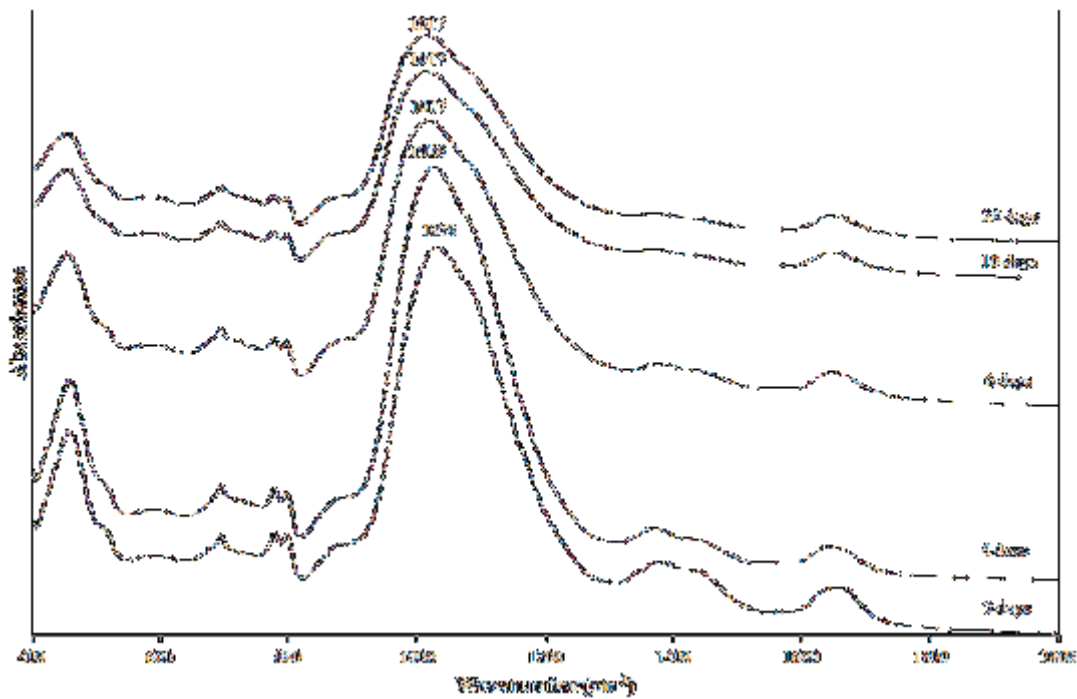


Figure 7: IR spectra of alkali-activated metakaolin (J-Cem. 2) during 28 days of ageing at room temperature, and Jordan-metakaolin

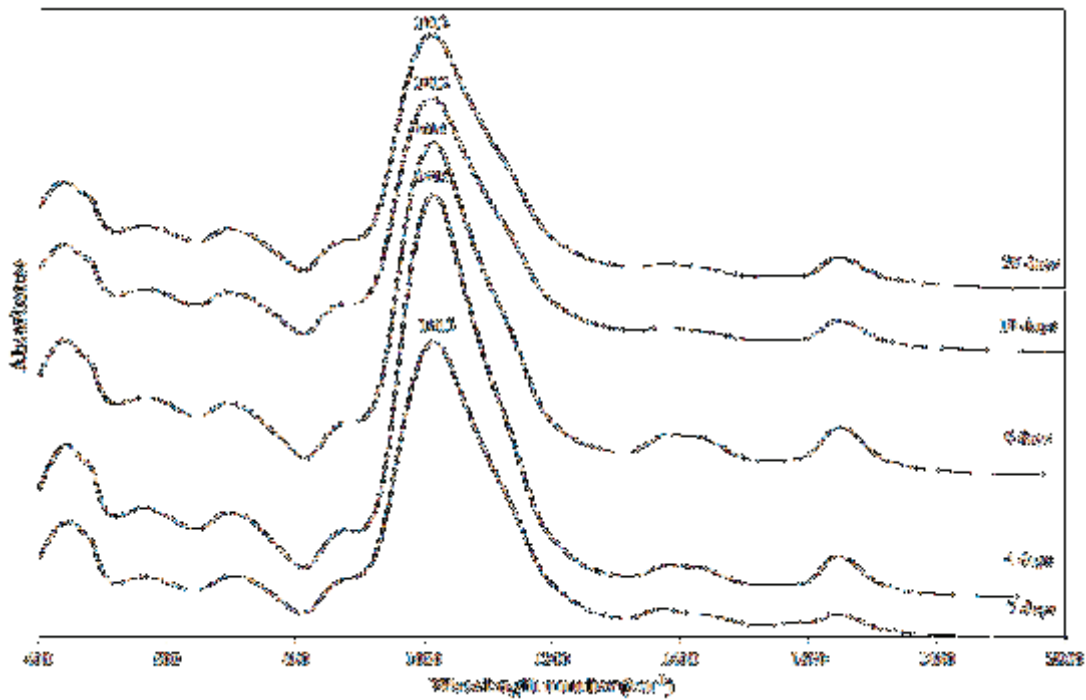


Figure 8: IR spectra of alkali-activated metakaolin (F-Cem. 1) during 28 days of ageing at room temperature, and Fluka-metakaolin

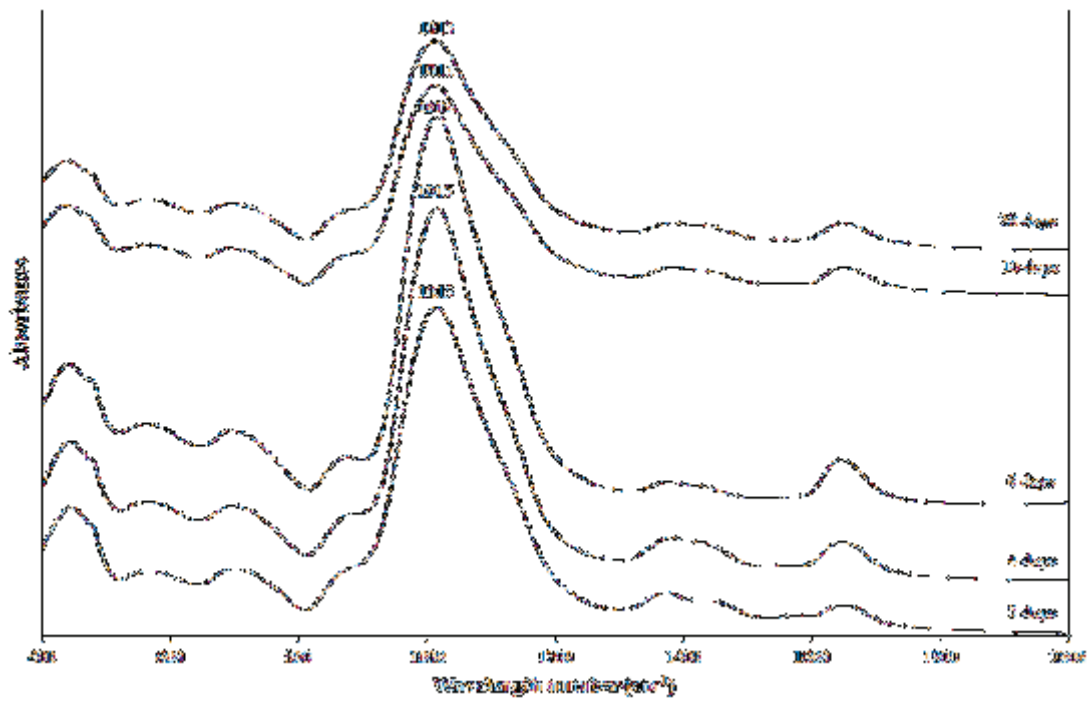


Figure 9: IR spectra of alkali-activated metakaolin (F-Cem. 2) during 28 days of ageing at room temperature, and Fluka-metakaolin

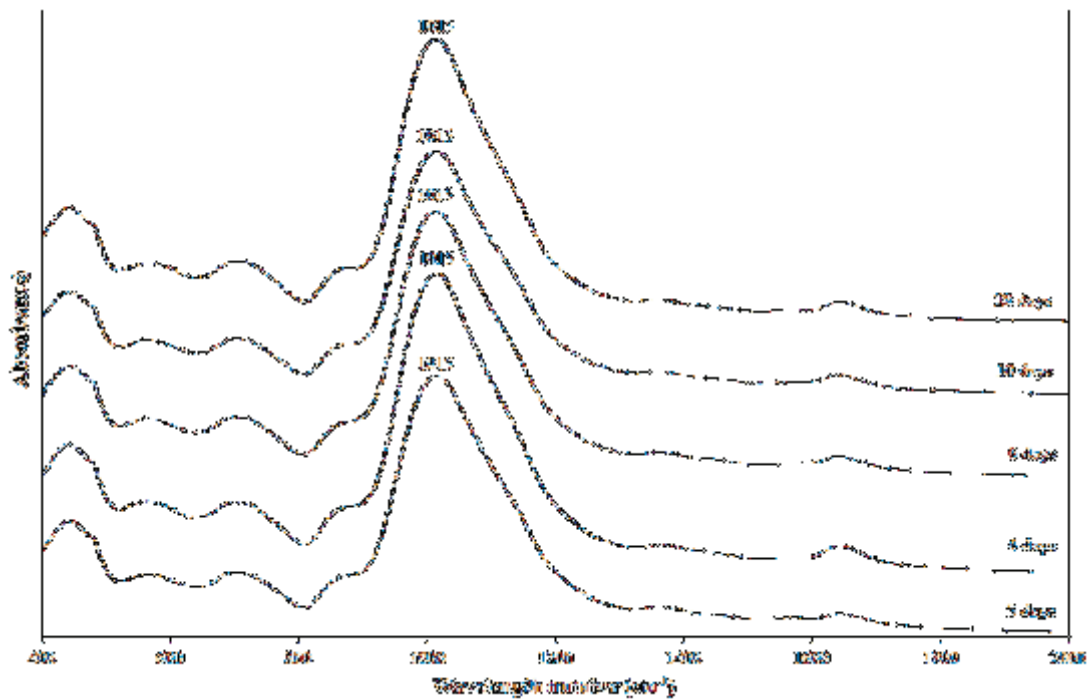


Figure 10: IR spectra of alkali-activated metakaolin (F-Cem. 3) during 28 days of ageing at room temperature, and Fluka-metakaolin

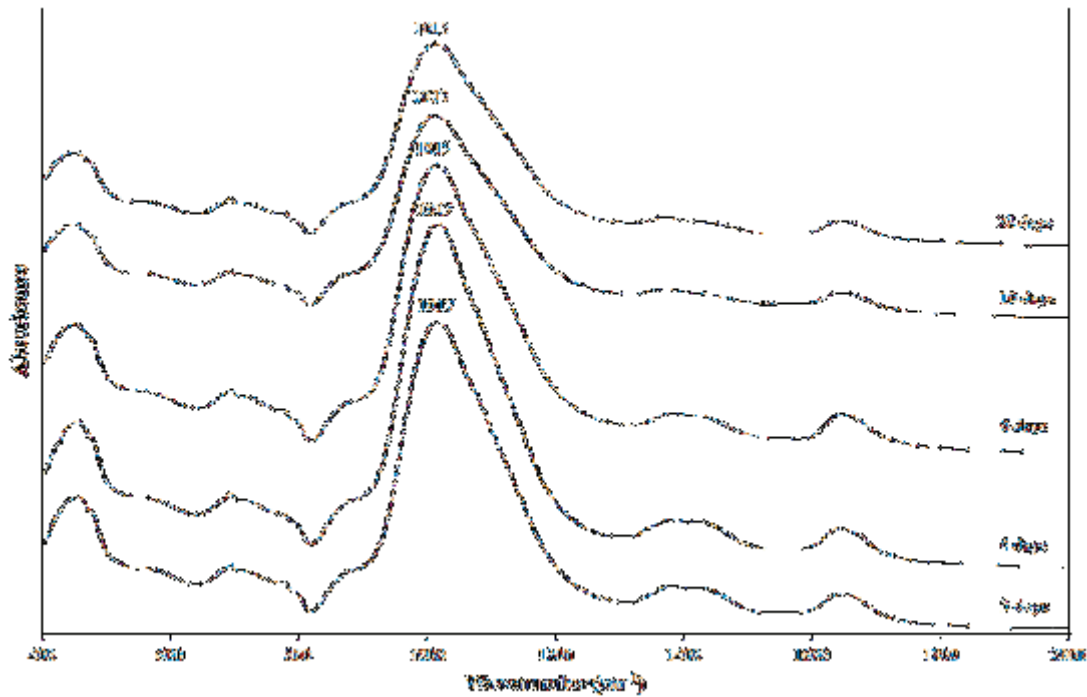


Figure 11: IR spectra of alkali-activated metakaolin (Fqz-Cem. 1) during 28 days of ageing at room temperature

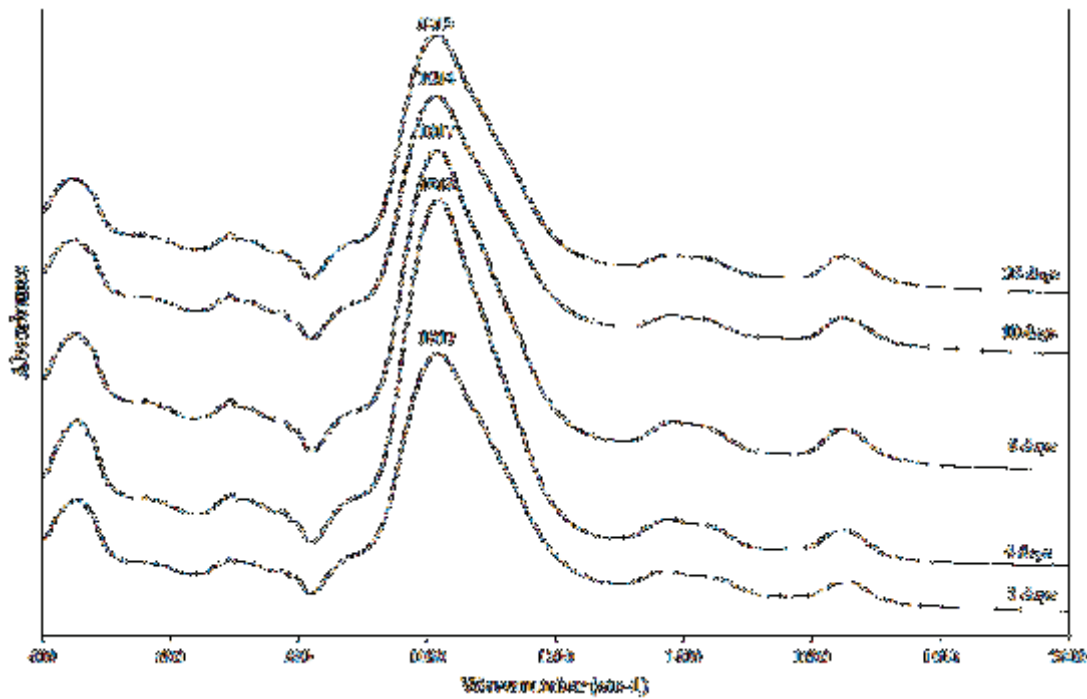


Figure 12: IR spectra of alkali-activated metakaolin (Fqz-Cem. 2) during 28 days of ageing at room temperature

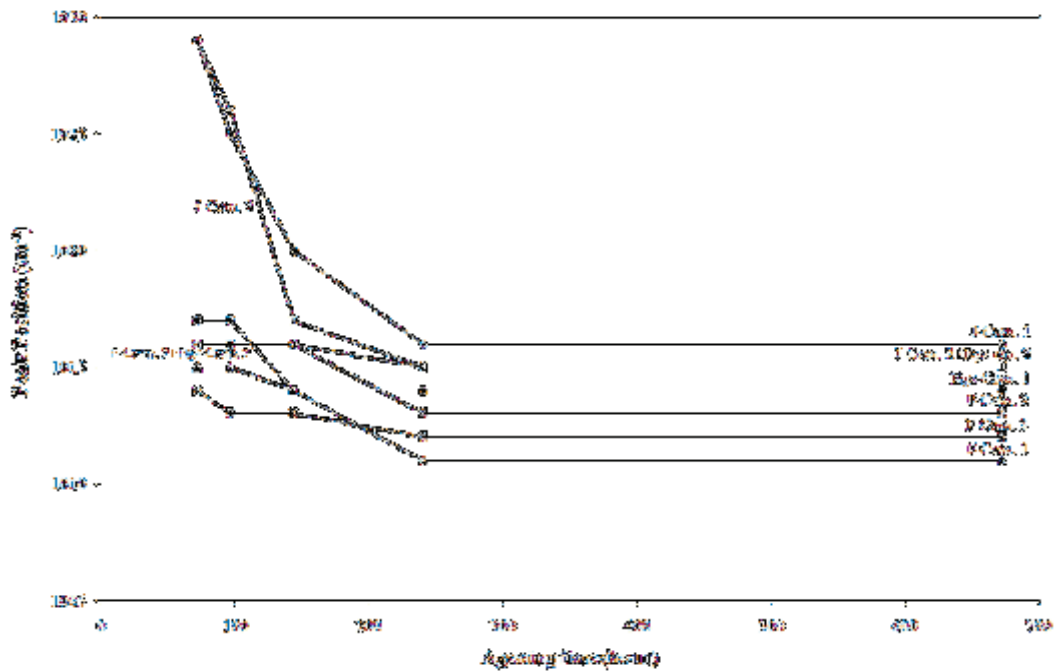


Figure 13: The dependence between DOSPM of asymmetrical stretching and ageing time of Jordanian geopolymer cements and other geopolymer cements estimated from FTIR study of ageing process given in Figs. 6-12

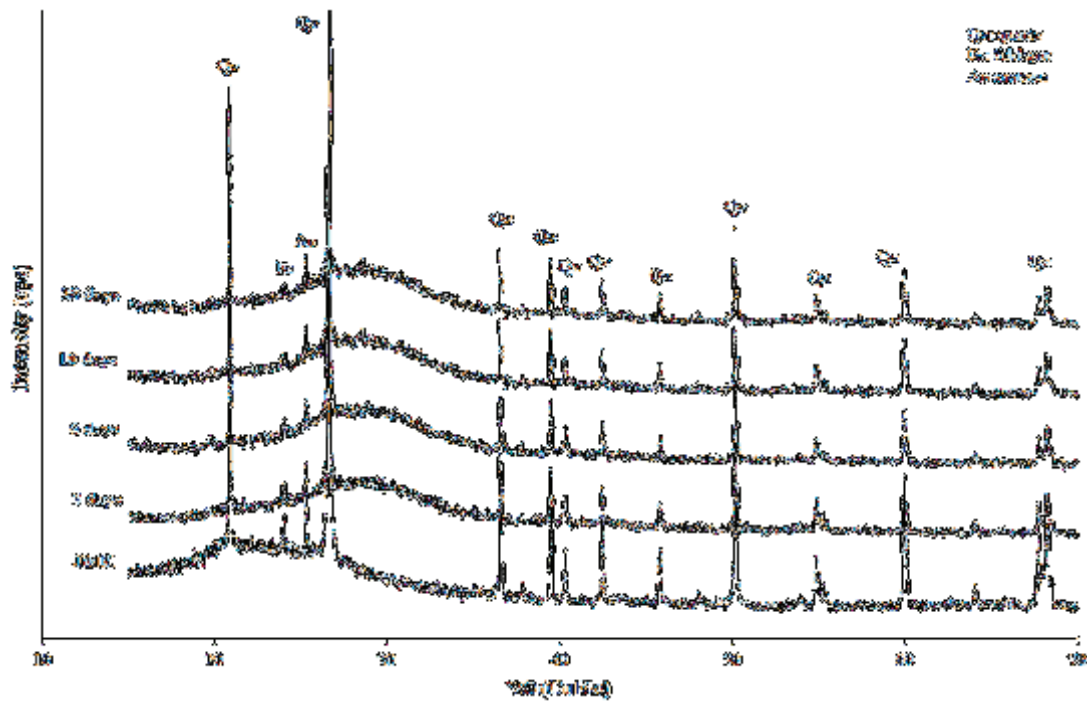


Figure 14: X-ray diffraction patterns of geopolymers obtained from JMK1 during 28 days of ageing at room temperature

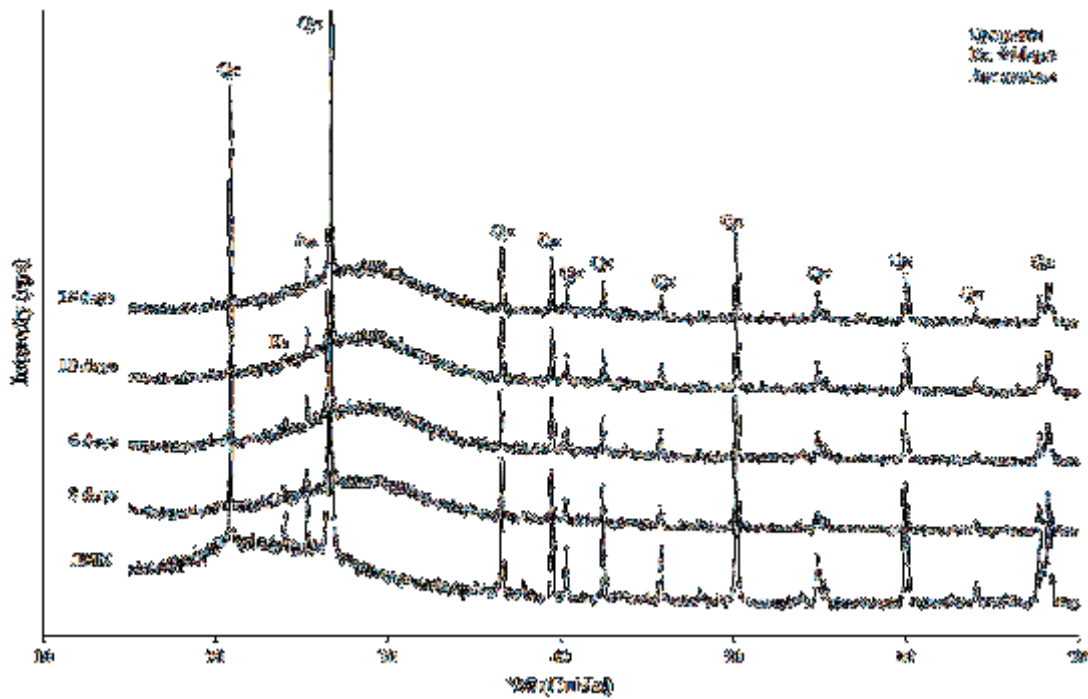


Figure 15: X-ray diffraction patterns of geopolymers obtained from JMK2 during 28 days of ageing at room temperature

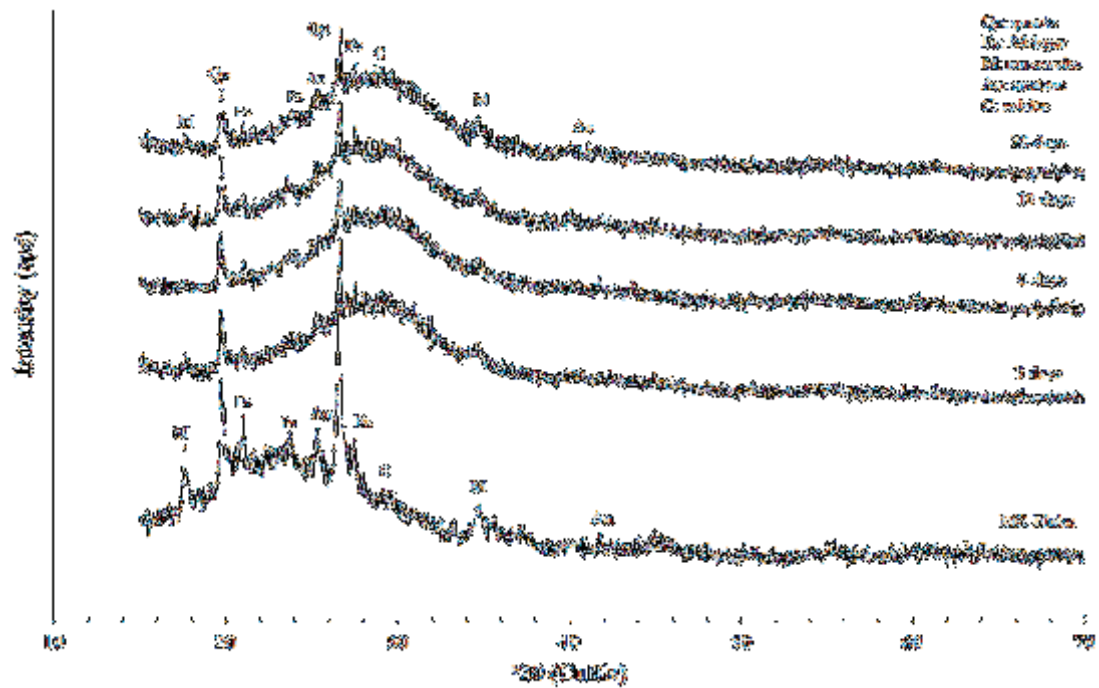


Figure 16: X-ray diffraction patterns of geopolymers obtained from FMK1 during 28 days of ageing at room temperature

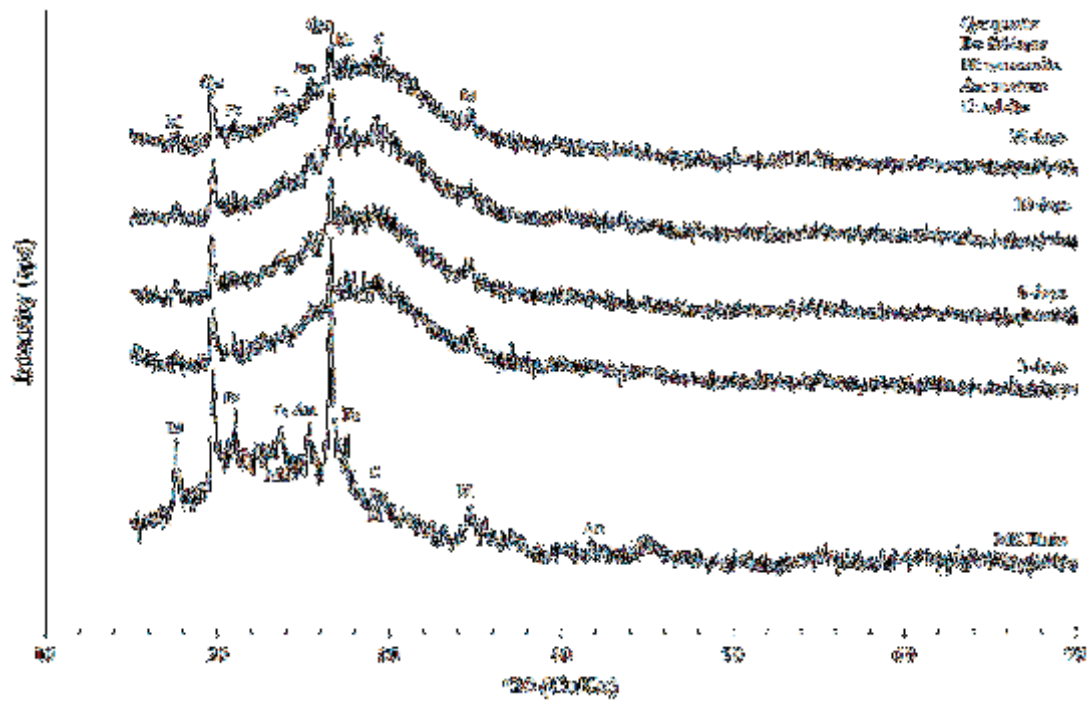


Figure 17: X-ray diffraction patterns of geopolymers obtained from FMK2 during 28 days of ageing at room temperature

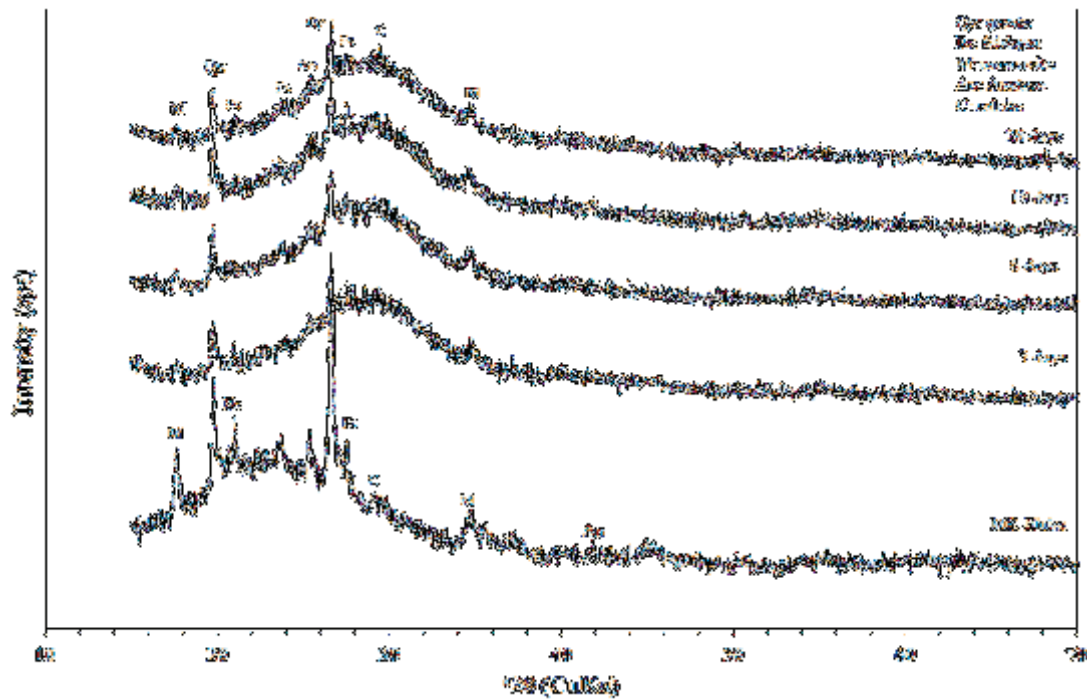


Figure 18: X-ray diffraction patterns of geopolymers obtained from FMK3 during 28 days of ageing at room temperature

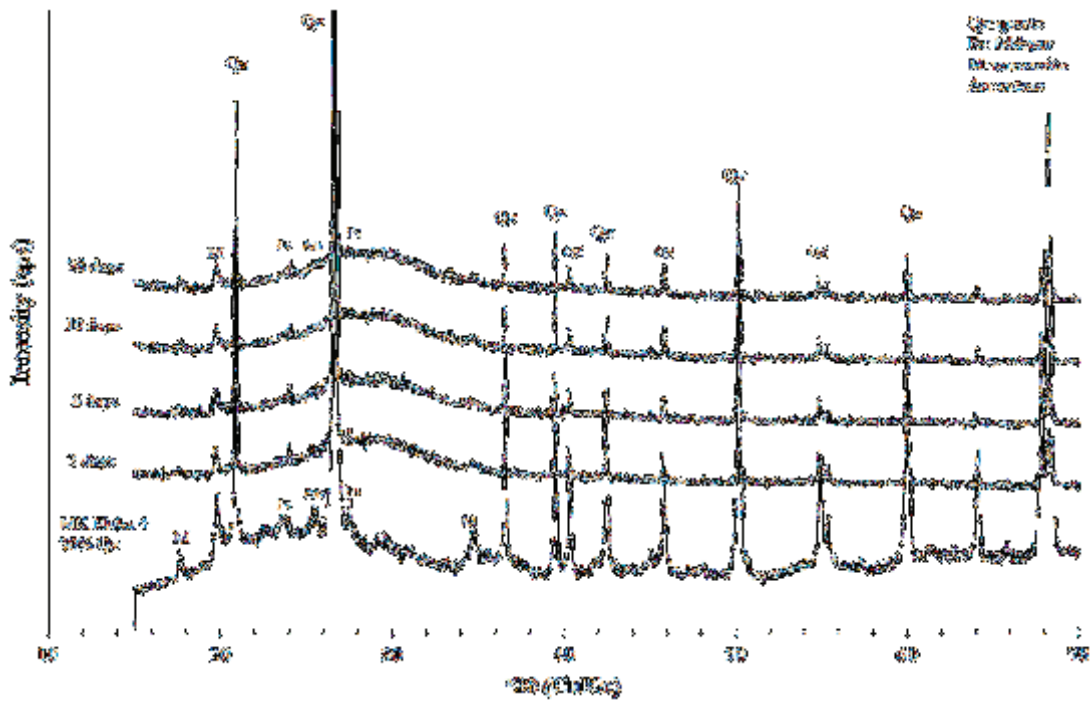


Figure 19: X-ray diffraction patterns of geopolymers obtained from MK1 (Fluka+30 % quartz) during 28 days of ageing at room temperature

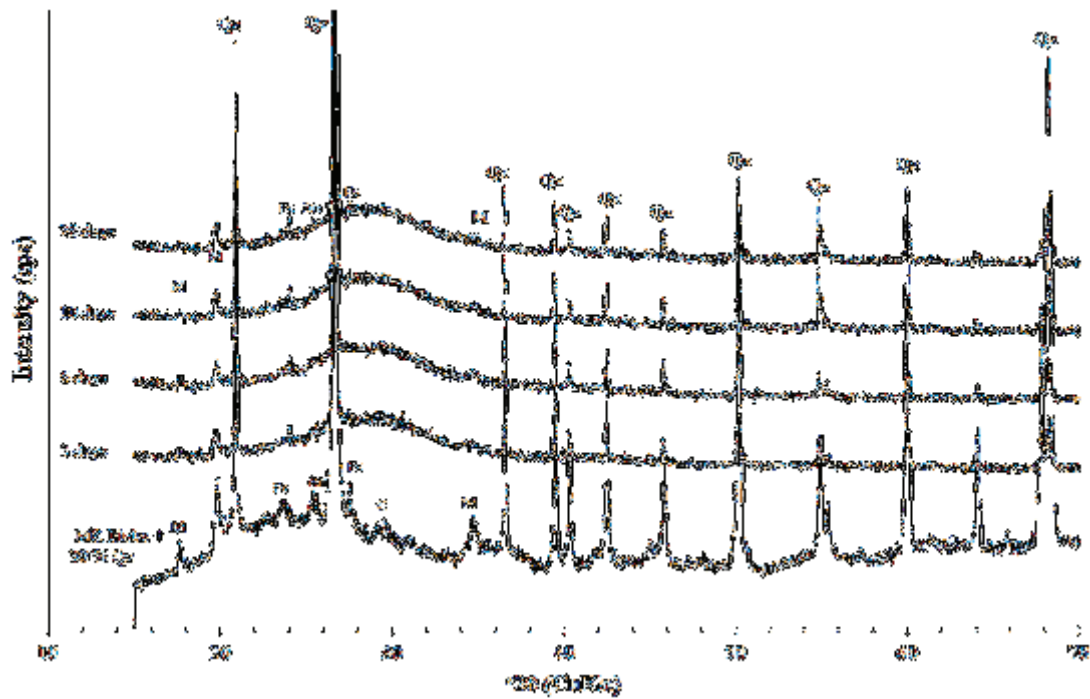


Figure 20: X-ray diffraction patterns of geopolymers obtained from MK2 (Fluka +30 % quartz) during 28 days of ageing at room temperature

The IR results show that in the spectrum after 3 and 4 days of ageing, the DOSPM shows the maximum at about 1030 cm^{-1} , 1025 cm^{-1} (for Jordanian geopolymer cements), 1025 cm^{-1} , 1020 cm^{-1} (for Fluka cements) and 1027 cm^{-1} , 1020 cm^{-1} (for Fluka + quartz cements), respectively (Fig. 13). This demonstrated that the position of maximum peaks was observed at an earlier stage of geopolymerization in the range of

asymmetrical stretching. On the other hand, after 6-day ageing it reaches the position at 1015 cm^{-1} , 1013 cm^{-1} and 1012 cm^{-1} for Jordanian cements, mixture of Fluka and quartz cements and Fluka cements, respectively. The IR results indicated that the DOSPM remains at the same position above 6 days or 10 days of ageing for the three examined materials.

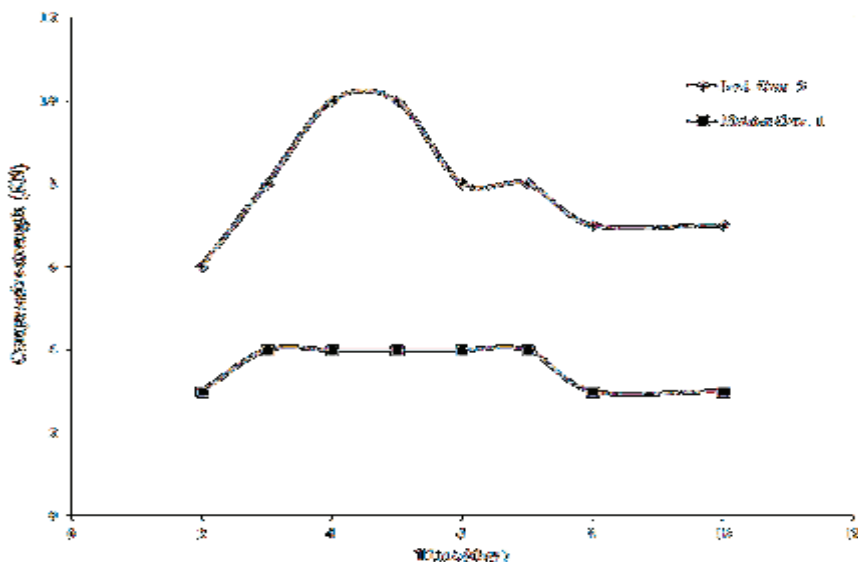


Figure 21: Compressive strength of the Jordanian geopolymer cement (J-Cem. 3) and Metastar geopolymer cement (M-Cem. 1)

XRD analysis

The XRD patterns of the geopolymer of JMK obtained from impure Jordanian metakaolin (JMK) precursor show the formation of an amorphous phase. In addition, several sharp peaks at 4.26 \AA and 3.34 \AA are also seen from Figs. 14 and 15. According to the XRD patterns, these sharp peaks are identified as quartz. With respect to X-ray diffractogram of metakaolin, quartz is an impurity in the metakaolin and does not take part in geopolymerization reaction. This mixture forms a cohesive and relatively hard solid. This is the signature of geopolymerization.

The XRD patterns of the geopolymer of FMK (Fluka metakaolin) show the formation of an amorphous phase and trace phases such as muscovite,

quartz, anatase and metakaolin (Figs. 16-18). For the geopolymer products obtained from the pure FMK precursor, the main feature is by far the very broad reaction (large diffuse halo peak) at 20° 2θ $\text{CuK}\alpha$ in X-ray diffractogram of the fully-reacted geopolymeric cement matrix. This indicates that geopolymeric cement products are mainly X-ray amorphous materials and assigned to the amorphous metakaolin structure.

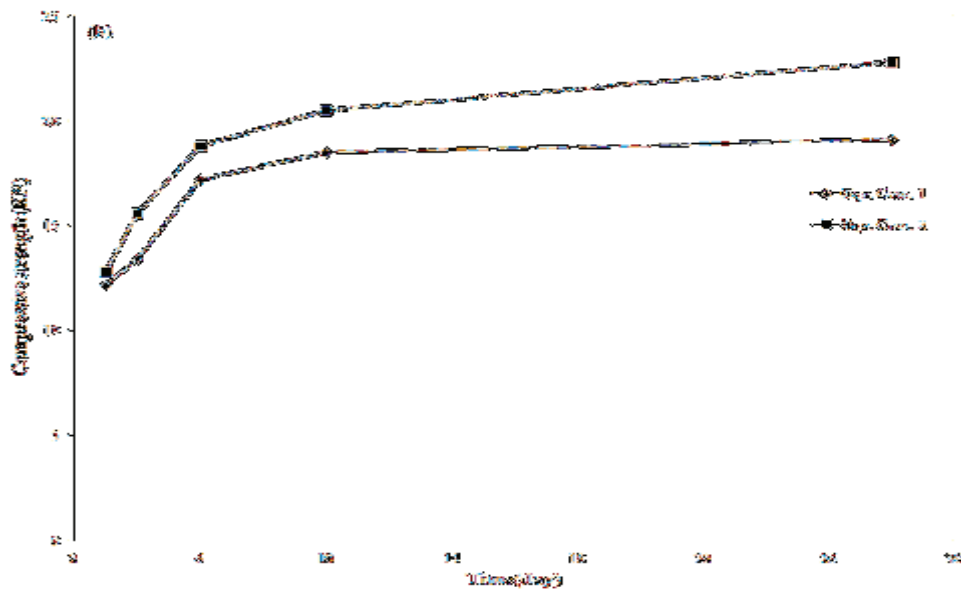
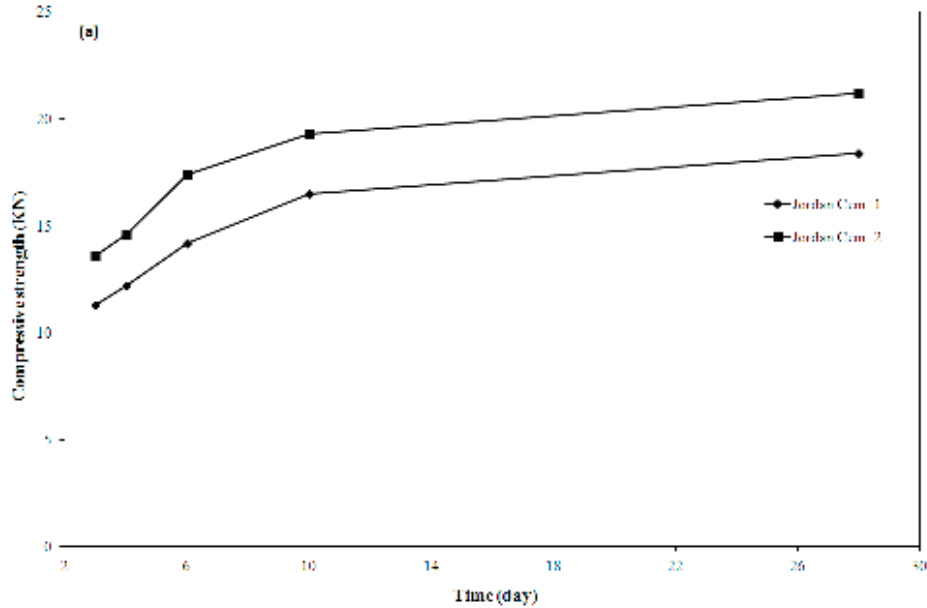
In the XRD patterns of the geopolymer of FMK (Fluka metakaolin + 30 % quartz), a large part of the structure was of amorphous content and minor amounts of impurity such as muscovite and quartz (Figs. 19 and 20). For the geopolymer products obtained from FMK + quartz precursor, sharp reflections due to the residual

crystalline of quartz phase are also observed alongside the broad reflections. As in the case of geopolymer products from Jordanian metakaolin (JMK), quartz is an impurity in the metakaolin produced from Fluka kaolin and 30% quartz and does not take part in geopolymerization reaction.

Compressive Strength

Figs. 21 and 22 show the compressive strengths of

geopolymer specimens of the four families of geopolymer products synthesized at different Si/Al ratios from alkali solutions (potassium water glass solution). Cements with different water glass contents exhibit similar compressive strengths at a given Si/Al ratio, suggesting that the difference in mechanical properties between cement series of different Si/Al ratios is in the order of 5% - 10 %.



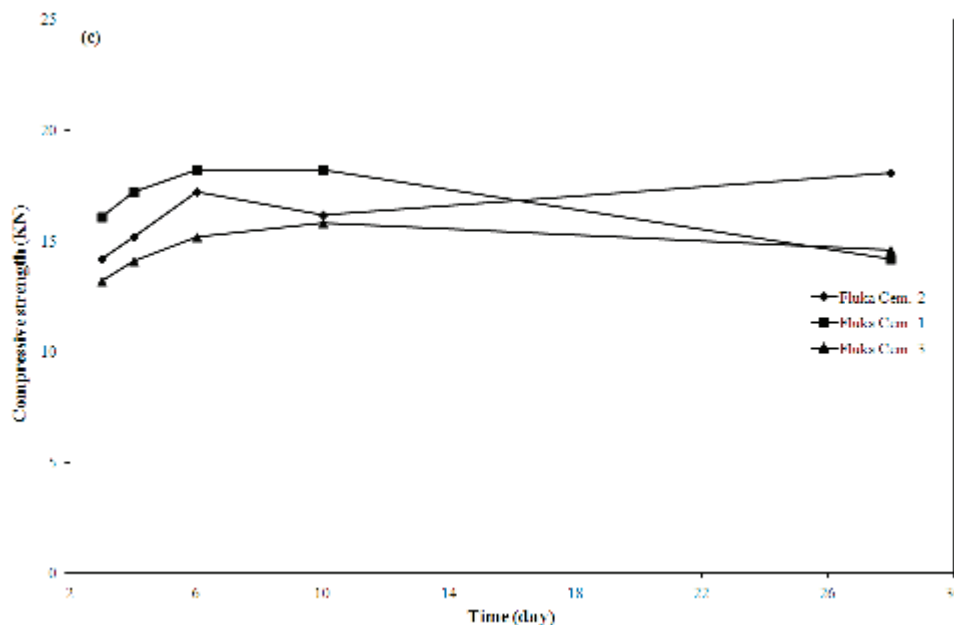


Figure 22: Compressive strength of the produced geopolymer cements:
 (a) Jordanian geopolymer cements
 (b) Mixture of Fluka + 30% quartz geopolymer cements
 (c) Fluka geopolymer cements

From Fig. 21 and Fig. 22, it can be observed that Jordanian MK and mixed Fluka MK + quartz cements exhibit higher compressive strengths than that of Fluka geopolymer. The compressive strength exhibits slightly greater values at the highest Si/Al ratios of 2.7, 2.5 and 2.4 than those at 2.5, 2.4 and 2.1 for Jordanian, mixture of Fluka + quartz and Fluka cements, respectively. It can be observed in the present investigation that the compressive strength increases for the large Si/Al ratio. A comparison of the compressive strength of the geopolymer cements ageing at 3, 4, 6, 10 and 28 days is presented in Fig. 22. The largest changes in strength occur after 28 days and decrease in Fluka geopolymer cements. With the exception of MKF cement 1 and mixture of MKF + quartz cement 1, other produced cements exhibit a trend of strength that it increases after 10 days or remains stable at 28 days, suggesting that the geopolymer cements (Fluka and Metastar cements)

produced from pure precursor materials are somehow increasingly unstable at high Si/Al ratio. In contrast, the other mixed-geopolymer cement series (Jordanian and Fluka +quartz cements) exhibits remarkably stable compressive strength in all Si/Al ratios. Fig. 22 shows that there are systematic changes or significant increases to the compressive strength for the mixed produced cements (Jordanian and Fluka +quartz cements) occurring as a result of ageing. The compressive strength of the produced Jordanian and mixed Fluka MK + quartz cement compositions was higher than those reported by previous authors (Duxson et al., 2007; Ruescher et al., 2010) which is believed to be related to the high quartz content of the present mixtures.

Geopolymerization is a highly complex transient reaction system. All of the important chemical processes and physical properties of the material are greatly altered at different stages of reaction, including

synthesis, early strength development and long-term ageing (Lee and van Deventer, 2002). Although geopolymers nearly reach the maximum strength after only 10 days (Fig. 23), the changes in compressive strength and crystallinity of specimens in the present work suggest that the transient nature of geopolymerization extends into longer time periods and that the development is dependent on the combination of K/Al and Si/Al ratios.

CONCLUSIONS

The composition, structure, microstructure and properties of the polymers formed in the alkali activation of metakaolin depend on the concentration, volume and type of activator used, as well as the characteristics of the metakaolin itself (composition, fineness and so on) (Barbosa et al., 2000; Duxson et al., 2005a; Granizo et al., 1997; Steveson and Sagoe-Crentsil, 2005). The product of metakaolin activation with NaOH solutions is an amorphous cementitious material (Granizo et al., 1997; Granizo et al., 1998; Granizo et al., 2002; Singh et al., 2005) with good mechanical properties (Granizo et al., 1997).

The X-ray patterns of JMK, Metastar MK, MKF and mixed MK +quartz are shown in Figs. 1-4. For the samples obtained from the pure Metastar and Fluka precursors, the main feature is by far the very broad reflection assigned to the amorphous metakaolinite structure. Expectedly, for the samples obtained from the impure JMK and mixed MK +quartz precursors, sharp reflections due to the residual crystalline quartz and metakaolin phases are also observed alongside the broad reflection. Illite is an aluminosilicate which can

react in alkaline conditions. Its presence in the Fluka MK material is therefore a significant feature which can affect geopolymerization.

The compressive strength of specimens exhibited two distinctly different trends after 28-day curing. For geopolymer cements obtained from Metastar 501 and Fluka metakaolins precursor exhibited reduced values after 28-day curing, whereas in cements obtained from Jordanian MK and mixed Fluka MK with quartz precursor exhibited maximum compressive strength values. The development of mechanical properties of geopolymers investigated in the present work highlights the importance of IR analysis of geopolymers of different precursor metakaolins with varied Si/Al ratios with time to determine the basis for the maximum or reduction in compressive strength of the geopolymer cements after 28-day curing.

The main result of the work presented in this paper is that kaolin deposits from Jordan containing as much as 30% of secondary minerals are still suitable, after moderate heat treatment, for the synthesis of cohesive, yet castable, geopolymer-type solids by alkaline activation. Considering the large deposits of impure kaolins in many parts of the world, this opens the way to the large scale utilization of these mineral resources for the production of green construction materials. One source of concern though is the chemical lability of the products, especially at low Si/Al ratio in the reactive solution.

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