CHARACTERIZATION AND EVALUATION OF NATURAL ZEOLITE AS A POZZOLANIC MATERIAL

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ABSTRACT

This paper presents details about mineralogical and chemical composition of natural zeolite (NZ) from Harrat Shama for using it as a pozzolanic material. The structural properties and mineralogical composition of NZ were determined using XRF, XRD, FTIR, DSC, SEM-EDX as well as study surface texture and cation exchange capacity. The geopolymer paste was prepared using sodium silicate solution as activator for zeolite and incubated at 25 and 45 ºC up to 90 days. The compressive strength of NZ-based geopolymer was investigated up to 90 days. Five blended cement were designed by substitution for Portland cement by 0 %, 5 %, 10 %, 15 % and 20% of NZ. The compressive strength of NZ-OPC pastes were studied up to 90 days. The microstructure of NZ-Based geopolymer and hydrated NZ-cement pastes were tested. The results were shown that the sum of SiO_2, Al_2O_3, and Fe_2O_3 content in the natural zeolite was approximately 82.71.3% and mainly composed of clinoptilolite mineral. Geopolymerization of NZ gave a good dense geopolymer matrix with high early stage mechanical properties. The NZ has shown improving early stage compressive strength of all blended cement pastes up to 7 days. The incorporation of nature raw zeolite in cement, up to 10% wt, improved the compressive strength to 7-29%. Generally, Saudi Arabian natural zeoilite (NZ) have high pozzolanic properties and could be used in the preparation of geopolymers matrix and blended cement pastes.

Keywords: Natural raw zeolite; Characterization; Geopolymerization; Pozzolana; Saudi Arabia

1. INTRODUCTION

Natural zeolites are one of effective absorbents, ion-exchangers, molecular sieves which used in many applications [1]. Natural zeolites, as a cheap and locally available absorbent, were used in the energy field and their related applications were as additives, catalysts and absorbents [2, 3]. The removal of pollutants was evaluated [4-6].

Huge amounts of raw materials and energy were consuming for production of Portland cement that consider as one of the primary sources of global warming [7]. Davidovits [8] prepared a new material (geopolymer) as an alternative material for Portland cement. Geopolymer are amorphous materials prepared at ambient temperature or slightly elevated [9]. Due to the unique properties of geopolymer, it is suitable for use in many applications such as building and construction field [8, 10]. The natural raw materials and industrial waste which are based on aluminum silicate minerals are suitable for preparing of geopolymers such as fly ash [11, 12] natural pozzolana [13], metakaolin [14]. The natural zeolite is considered as one of the suitable materials for fabrication of geopolymer. The mechanical properties of metakaolin-based geopolymer were enhanced by addition of natural zeolite as filler [15]. Bulgaria natural zeolite was activated by different alkaline activators. The results showed that the sodium silicate (water soluble glass) gave the highest compressive strength at 28 days [16]. Natural zeolite cement mortar was designed, and the result showed that the early strength was dramatically

increased and the strength at 7 days was higher than that of the OPC [17].

Pozzolana usually used to improve the physico-chemical and mechanical properties of cement pastes and concrete [18]. The pozzolana is mainly composed of silica and aluminates that have ability to react with calcium hydroxide for forming components have binding properties. These materials may be industrial by-products such as silica fume, slag and fly-ashes or natural such as vitreous pumice, diatomite earths, metakaolin and zeolitic tuffs [19, 20]. Natural zeolite (NZ) is hydrate alumino-silicates which have large quantities of reactive SiO_2 and Al_2O_3. In this respect, a number of investigations were attempted to monitor the performance of NZ as supplementary cementitious materials. The engineering properties of the blended cement pastes and concrete containing natural zeolite were presented. The results of some studies showed that the replacement of cement with 20% zeolite is considered the best ratio [21, 22]. The effects of calcination temperature on the pozzolanic activity of natural zeolites were investigated. The blended cement with calcined forms of zeolite showed less water/cement ratio, improve workability of the pastes and increase the mechanical properties [23]. Burris and Juenger [24] observed the milling of natural zeolites that used as pozzolana materials to improve the activity of zeolites. Uzal and Turanl [25] confirmed that no free $Ca(OH)_2$ in hardened pastes, containing high(above 20 %) volume of natural zeolite, at 28 days. Karakurt and Topçu [26] reported that the durability of concrete against alkali-silica reaction and sulfate effects were improved by the addition of natural zeolite as pozzolanic material. The evolution of the early hydration of cements blended with natural zeolites showed that their addition accelerates the onset of C_3S hydration and precipitation of CH and AFt [27]. Tydlitát et al [28] concluded that the addition of natural zeolite to Portland cement up to 40 % accelerates the early hydration process due to the effect of aluminate of zeolite towards the AFt-AFm conversion process. Addition 10 %

of natural zeolite to concrete has been proven to increase its density, ultrasonic pulse velocity and freeze-thaw resistance compared to that of normal concrete [29]. It was found that the concrete mixtures which contain silica fume or natural pozzolana had high resistance against chloride diffusion [30]. Addition of clinoptilolite and silica fume to cement delayed the dissolution of gypsum in the early period of hydration [31].

In King of Saudi Arabian (KSA), many of the extensive areas of aluminosilicates material deposits were not economically exploited. This is mainly related to lack of sufficient studies to illustrate their applications. Due to this fact, this study aims to characterize Harrat Shama natural raw zeolite deposits and study their potentials as raw materials for blended cement and geopolymer.

2. MATERIALS AND METHODS

2.1 Materials

The Harrat Shama (HS) is located in the western part of Saudi Arabia, about 120 km southeast of Jeddah city near to Shuaiba water desalination plant (Lat: 20° 41′ 1.66 and Long: 39° 41′ 45.15). It is a part of lava fields that founding in the Arabian Plate [32], (Fig. 1). Motelib et al. [33] were studied the different volcanic sequences in Harrat Shama (HS). According to their results the HS is divided into two sequences lower and upper whereas zeolite-bearing bedded tuffs were found in the lower sequence. Zeolite-bearing bedded tuff is occurred as volcanic cone and its thickness over ~ 30 m. We collected a representative sample of natural zeolite (about 20 kgs) from a natural deposit at Jabal Shamah (Tuffil). The zeolite sample was ground to pass from sieve No. 200, homogenized and dried at 100 ºC ± 5 ºC for 24 hr.

2.2. Preparation of NZ- base geopolymer paste

Sodium silicate with $SiO_2/Na_2O =1.7$ and density 1.68 g/cm^3 was employed as an activator solution. An activator/powder ratio of 0.6 was used to prepare the geopolymer paste;

it was poured into cylinder molds after mixing poured with a diameter of 2.5 cm and a height of 2.5 cm for 24 hr and then demolded. The geopolymers G-NZ1 cylinders were incubated at ambient temperature and G-NZ2 cylinders at 45 ℃ for 3, 7, 28, and 90 days curing times. Three cylinders were crushed in order to determine compressive strength for the geopolymer samples up to 90 days. The hardened zeolite based geopolymer cured for 28 days were investigated by XRD and FTIR, DSC and the selected samples were investigated using SEM-EDX after treatment with acetone/methanol mixture to terminate the geopolymerization process [34].
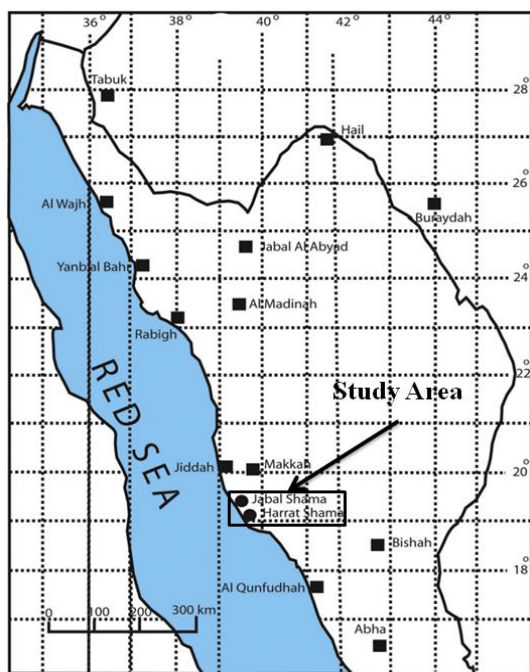

Fig. 1. A map of the Arabian Plate showing location of the Harrat Shama.

2.3. Preparing of natural zeolite blended cement

OPC type CEM I42.5 R was used to prepare blended cements of natural zeolite. The chemical composition of cement is shown in Table 1. Five blended cements were prepared by substitution of OPC (Ordinary Portland Cement) with 0, 5, 10, 15 and 20 mass % of natural raw zeolite. These blended cements

were coded as OPC, OPC-NZ5, OPC-NZ10, OPC-NZ15 and OPC-NZ20. The ingredients of each mixture were mixed in an agate mortar to homogeneity. The water/powder ratio was 0.42 in all cases. The NZBC pastes were molded into cylinder molds with an internal diameter of 2.5 cm and a height of 2.5 cm, compacted and then covered. The specimens were incubated at 25 ℃ and at 100% relative humidity for 24 h, and then de-molded. The hardened blended cements were kept under water up to 90 days. Three cylinders were used for determining the compressive strength at 3, 7, 28 and 90 days of curing. The compressive strength measurements were carried out using an automatic compression test machine. A commercially available, Microwave oven was used for stopping the hydration of cement pastes [35]. Some selected samples were investigated using FTIR, DSC, XRD and SEM-EDX techniques.

2.4. Analytical instruments

The chemical composition of zeolite sample was analyzed by X-Ray Fluorescence (XRF) (Pnalytical Axios advanced XRF). The low-temperature nitrogen adsorption/desorption isotherms (77.4 K) were determined using a surface area Quanta Chrome Nova 2000 USA. Field emission scanning electron microscopy, a JEOL JSM 6360 DLA, was used for determination the morphology of the samples. CEC of the natural zeolite was determined by ammonium acetate method as [36]. XRD patterns of natural zeolite, geopolymers and blended cement samples were recorded using An XRD 7000 (Shimadzu Instruments, Japan) at a 2θ scan speed of 4∘ min−1, λ = 0.154 nm with Cu Kα as a radiation source. The FTIR spectra of natural zeolite, geopolymers and blended cement samples were record using A JASCO Asia Portal - FT/IR-6300 Spectrometer. The thermal behaviour of natural zeolite, geopolymers and blended cement samples were performed on DSC (NETZSCH STA 409 C/CD instrument). The samples were investigated up

to 1000 °C using a rate of 10 °C/min in an He atmosphere.

3. RESULTS AND DISCUSSION

3.1. Characterization of natural raw zeolite

Physical properties and chemical composition of the natural zeolite is listed in Tables 1 and 2. They indicate that the total SiO_2, Al_2O_3, and Fe_2O_3 contents in the zeolite is 83.19 % approximately, matching with the requirements stated in ASTM C618 [37] for a natural pozzolana. Furthermore Chakchouk et al. [38] indicated that materials having a total percentage of SiO_2, Al_2O_3, and Fe_2O_3 greater than 50% are suitable to produce a good pozzolanic material. It can be seen from these data that, the Si/Al ratio for NZ sample is 4.6. According to Perraki and Orfanoudaki [39] the zeolite is a clinoptilolite type [40].

Fig. 2a illustrates the XRD patterns of the raw zeolite. The XRD peaks of clinoptilolite mineral appeared at 2Ɵ values of 9.8º, 11.17º, 22.3º, 22.7º, 26.1º, 28.14º, 30.0º and 32.08º (JCPDS No 00-025-1349) [41]. The cowlesite mineral relates to the natrolite subgroup as a fibrous zeolite in the Dana classification, where Strunz placed it in a separate series [42]. The cowlesite has peaks at 2Ɵ of 5.8º, 4.46º, 19.8º and 30.07º [43] while cristobalite appeared at

2Ɵ of 21.7º [41]. Semi-quantitative XRD analysis shows that NZ was mainly consisted of clinoptilolite (45 wt %), cowlesite (41 wt %) and cristobilite (14 wt %).
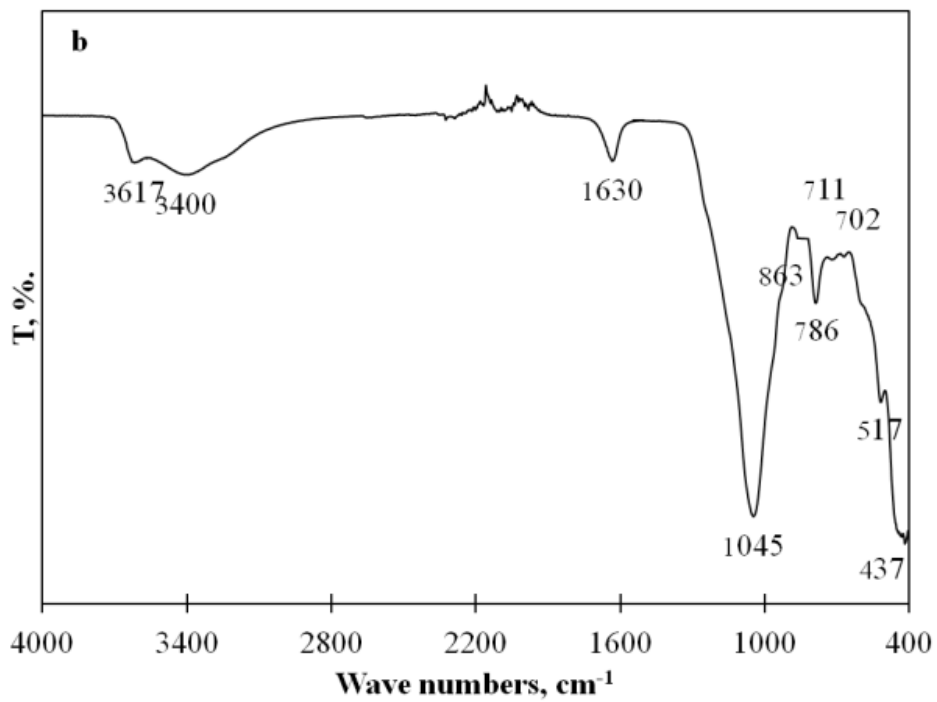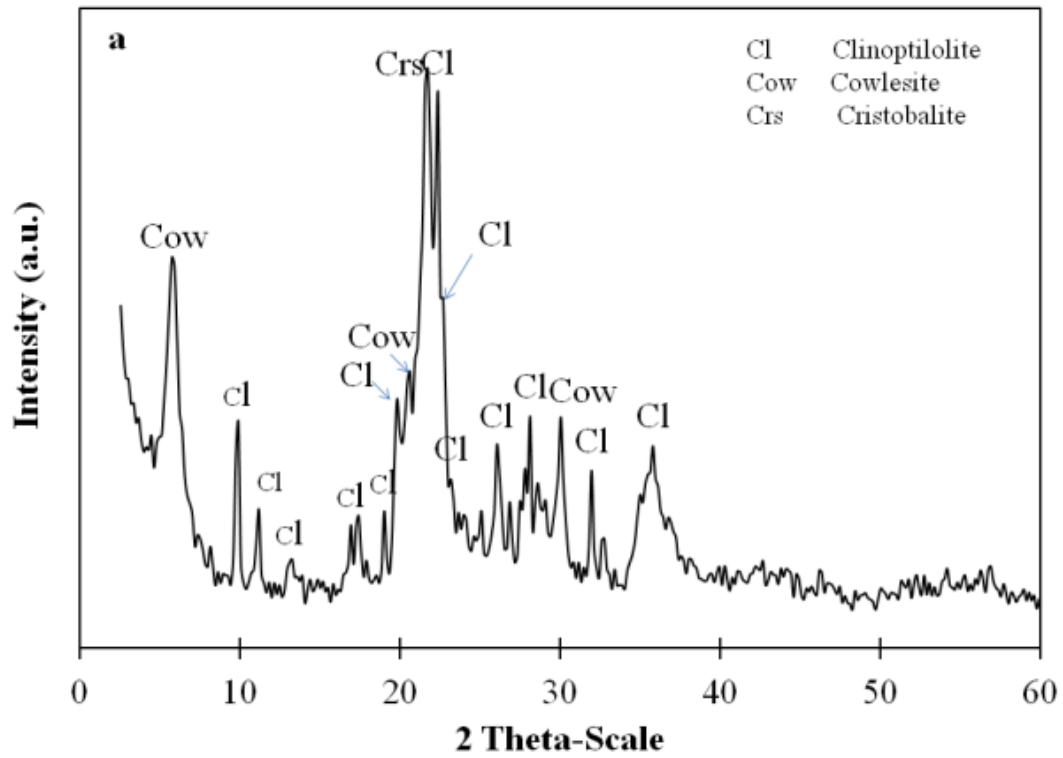
Fig. 2b shows FT-IR spectra of natural raw zeolite in the region between 400 and 4000 cm^{-1}. The structure of zeolite can be estimated through its FTIR spectrum [44]. It is clearly shown different absorption bands at 437, 517, 786, 1045, 1630, 3400 and 3617 cm^{-1}. The strong band at 1045 cm^{-1} is related to the T-O stretching vibration. This band gives estimation about aluminum content in the framework of zeolite mineral, where it shifts to higher frequencies with decreasing number of Al atoms in the framework tetrahedral sites. The band at 437 cm^{-1} is assigned to a T–O bending mode and intensity of this band is independent on the degree of crystallinity [39]. The water has several forms in zeolite structure; the band at 3617 cm^{-1} is connected to interaction of the water hydroxyl with the cations. A band at 3400 cm^{-1} is due to vibration of the bonds O–H···O i.e. attributed to the hydrogen bonding of the water molecule to surface oxygen, A band at 1630 cm^{-1} is attributed to the bending mode of the water. Bands in the region 500–800 cm^{-1} are due to pseudo-lattice vibrations and show the nature of the channel cations [40].

Table 1: Chemical composition of natural raw zeolite and cement in mass %.

Component	SiO_2	Al_2O_3	CaO	K_2O	MgO	Fe_2O_3	Na_2O	SO_3	TiO_2	LOI	Total
NZ	66.96	15.17	3.80	2.20	1.53	1.06	0.16	-	0.08	10.2	99.40
CEM I 42.5 R	20.88	6.08	63.00	0.01	1.5	3.18	0.02	1.6	-	1.9	99.88

Table 2: Physical properties of natural raw zeolite

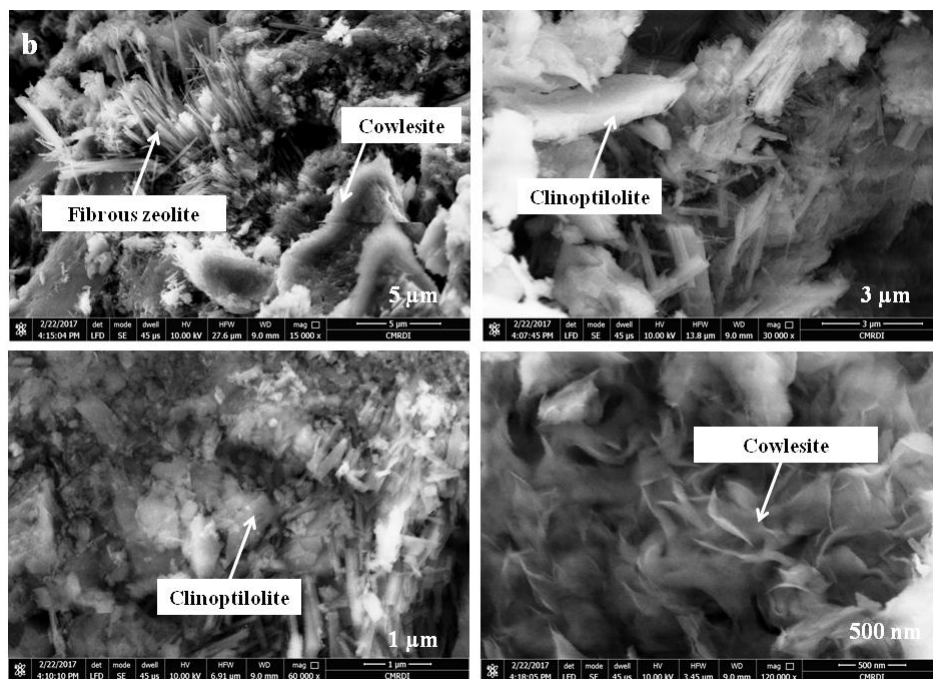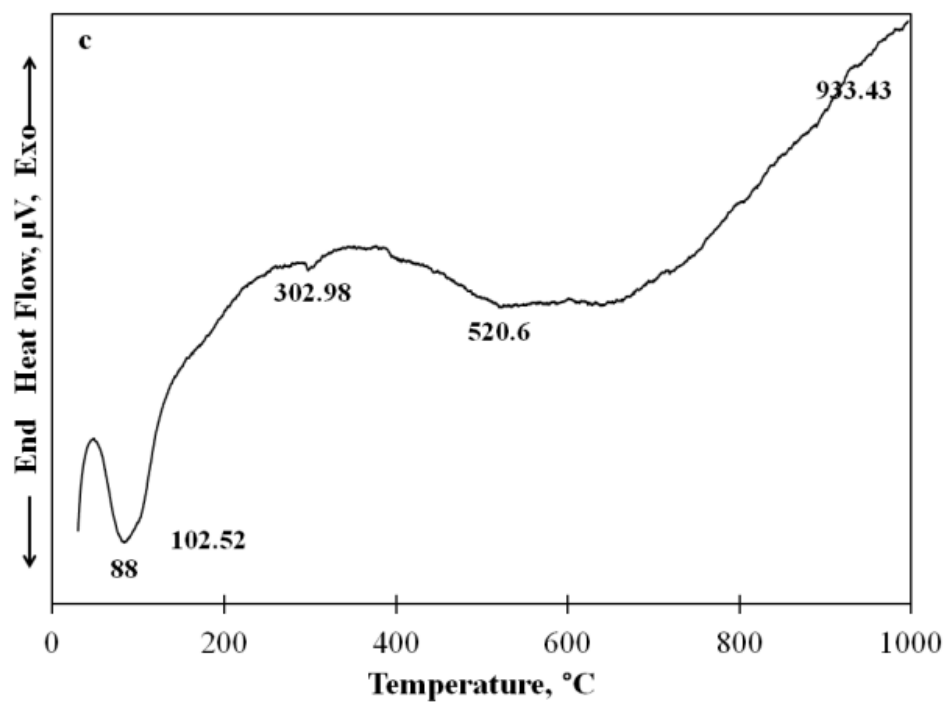|	
Cation-exchange capacity	2.8 meq /100 g
Specific gravity	2.1 g cm^{-3}
Mineralogical composition	Clinoptilolite (45%), Cowlesite (41%), and Cristobalite (14%)
Particles size	100% < 43 μm
Surface area, N_2- adsorption	38.3 m^2/g
Pore radius	17.39 Å
Porous volume	0.085 cc/g

Fig. 2. (a) X-ray diffraction, (b) FTIR spectra, (c) DSC curve, (d) FESEM images of natural raw zeolites.

Fig. 2c shows the DSC curve of the natural raw zeolite. There is only one continuous water loss peak at 50 °C - 200 °C. This endothermic effect is mainly due to loss of the weakly bound water [45]. The nature of water molecules in the zeolite depends on many factors, from which number and the type of the cations in the structure of the zeolite [46]. It is no secret that the climate of Saudi Arabia is dry and very hot, affecting the water content of rocks and natural minerals. Alver et al. [47] showed that the dehydration behavior of the clinoptilolite could be controlled by the exchangeable cations and the sites occupied by cations. Fig. 2c shows the enthalpy of the water loss is 22.38 J g^{-1} that agreement with XRD results (NZ have about 45 wt % clinoptilolite). Castaldi et al. [45] conformed the zeolite with monovalent ions has the lowest loss of weakly bound water than polyvalent. As seen from Fig. 2c there is no apparent endothermic peaks at 450 °C [48]. This assures that the sample consists mainly of clinoptilolite mineral whereas heulandite is thermally unstable and undergoes structural collapse below 450 °C [47]. A weak endothermic effect in the temperature range of 440–580 °C is related to dehydroxylation process of the surface OH groups [49].The endothermic effects at 302 °C and 520 °C are related to the distortions of the framework structure of cowlesite due to dehydration process. The morphology of natural zeolite was investigated by FESEM and the corresponding images are shown in Fig. 2d. There are three different structural variations. The flattened platy or tabular crystals are typical of the clinoptilolite zeolite while cowlesite mineral appears as hemispheres of delicate with very thin blades. Also, there are chain-like structures whose minerals form acicular or needle-like prismatic crystals related to cowlesite of other fibrous zeolite minerals [50].

3.2. Characterization of NZ-based geopolymer paste

A photograph of NZ-based geopolymer is shown in Fig. 3a. The results for compressive strength of NZ based geopolymers (each sample was triplicated) as a function of time and curing temperature are illustrated in Fig. 3b. Geopolymer samples were coded as G-NZ1 and G-NZ2 with respect to the curing temperature at ambient and 45 °C, respectively. It can be seen that the prepared zeolite geopolymers have increasing compressive strength with curing time up to 90 days. Both samples show slight increase in compressive strength in the first week of curing and enhanced sharply after this period up to 28 days. The geopolymer sample that cured at 45 °C shows a greater compressive strength than that cured at room temperature up to 90 days. This is due to the effect of temperature on enhancing the interaction between activated solution and zeolite, resulting in increased reaction products and improved mechanical properties [18].

Fig. 3c shows the XRD patterns of NZ - based geopolymer cured for 3 and 28 days at an ambient temperature and 45 °C. It is obvious that changes in mineralogical composition of NZ with curing time and temperature and the enhanced halo pattern between 2Θ 18º and 38º indicates presence of amorphous nature of geopolymer [22]. At 3 days of curing the crystalline phases of zeolite dominate in their XRD patterns for both samples cured at ambient temperature and 45 °C, while peak intensities of these mineral became slightly higher at 45 °C. The peak observed with d-spacing value of 15.2 Å, which correspond to cowlesite and peak with d-space 4.089 Å which related to cristobalite in raw zeolite, totally disappeared. This indicated dissolution in geopolymeric reaction [16].
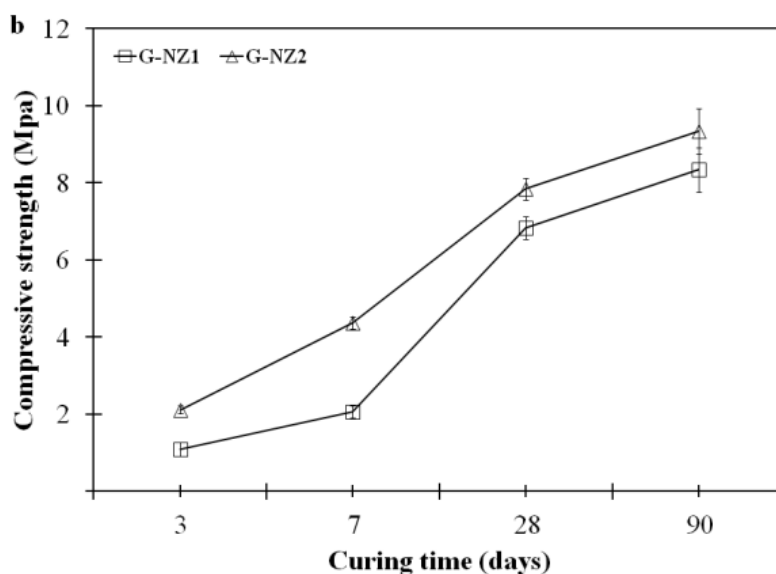
The FTIR spectra of NZ-base geopolymer are shown in Fig. 3d. The peaks in the range 950–1222 cm^{-1} may be related to asymmetric stretching vibration band of Si-O-Si and Al-O-Si. In this study it is assumed the formation of aluminosilicate gel [51]. The peak was observed at 790 cm^{-1} which may refer to symmetric stretching vibration of Si–O–Si. However, peak at 468 cm^{-1} attribute to the bending vibrations Si-O-Si and O-Si-O. The
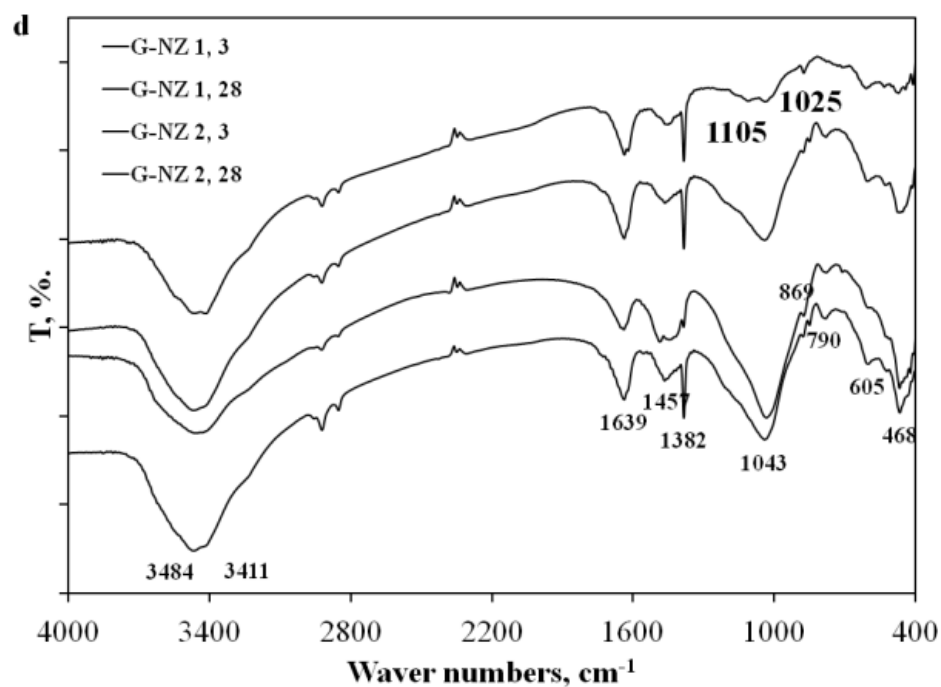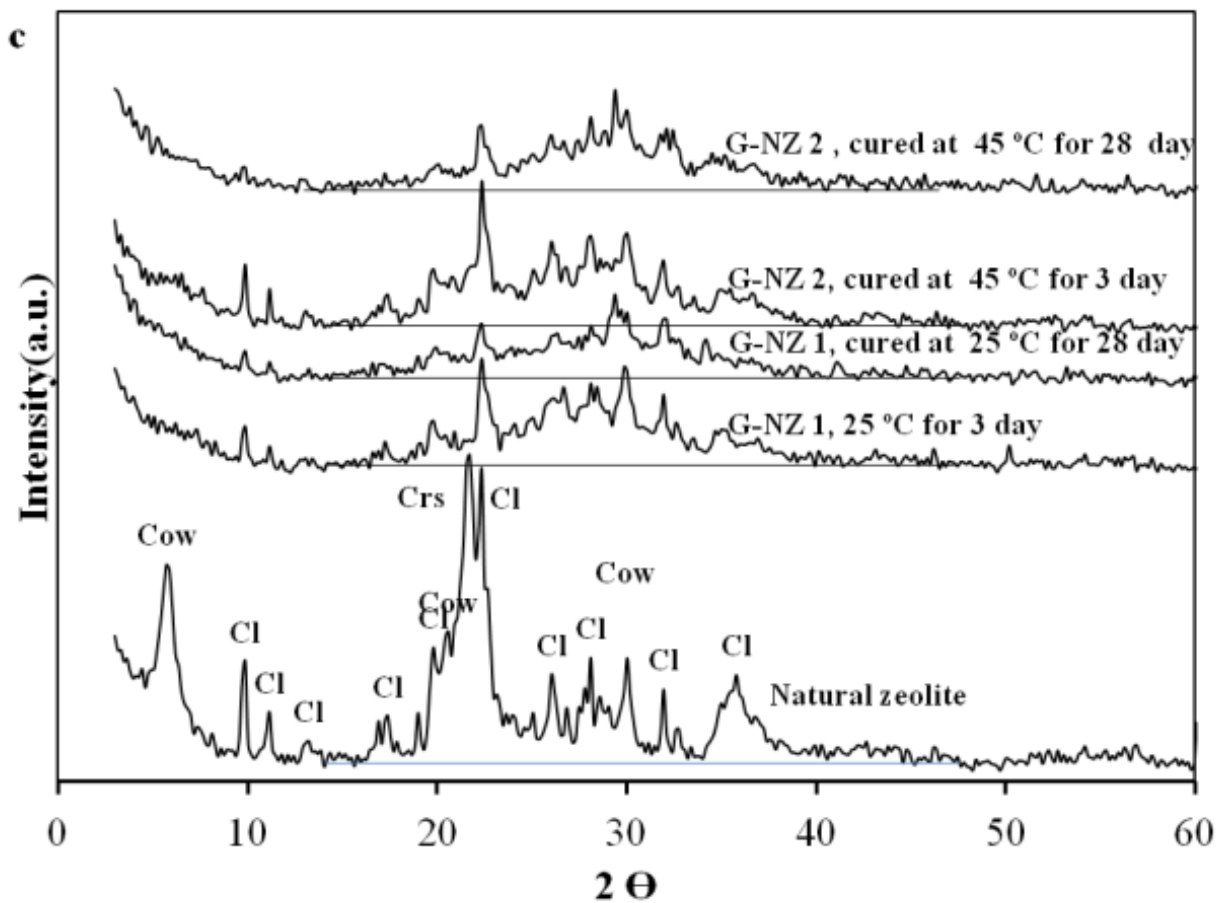
intensities of this band decrease with curing time and temperature and shifted to higher frequencies than that of original zeolite (Fig. 3e). The stretching vibration of carbonates, which formed during carbonation of geopolymer, appears at 1382 cm^{-1} [52]. The peak ranged from 2850-3700 cm^{-1} is related to stretching vibration of chemically compound water while the other peak at 1611–1684 cm^{-1} is attributed to bending vibration of physically water [53]. The intensities of these peaks reduced with curing temperature as a result of evaporation of water.

The DSC curves of geopolymer cured for 3 and 28 days at ambient and 45 ºC are illustrated in Fig. 3e. These curves show only one characteristic endothermic peak ranged from 55-175 ºC which is related to evaporation of free water and interstitial water in the geopolymer pores [54]. Other peaks can be that related to the thermal stability of geopolymer [55]. Fig. 3f shows SEM micrographs and EDX results for hardened geopolymer cured for 28 days and at ambient temperature. A dense matrix of geopolymerization overwhelmed the micrographs with modification of Si/Al ratio to 7.23 which indicates presence of geopolymer gel. In addition, some amount of Clinoptilolite appears.

c

Intensity(a.u.)

G-NZ 2 , cured at 45 °C for 28 day

G-NZ 2, cured at 45 °C for 3 day

G-NZ 1, cured at 25 °C for 28 day

G-NZ 1, 25 °C for 3 day

Crs

Cl

Cow

Cl

Cl

Cl

Cl

Cow

Cow

Cl

Cl

Cl

Cl

Natural zeolite

2 Θ

d

—G-NZ 1, 3
—G-NZ 1, 28
—G-NZ 2, 3
—G-NZ 2, 28

T, %.

1105

1025

1639

1457

1382

869

790

605

468

1043

3484   3411

Waver numbers, cm^{-1}

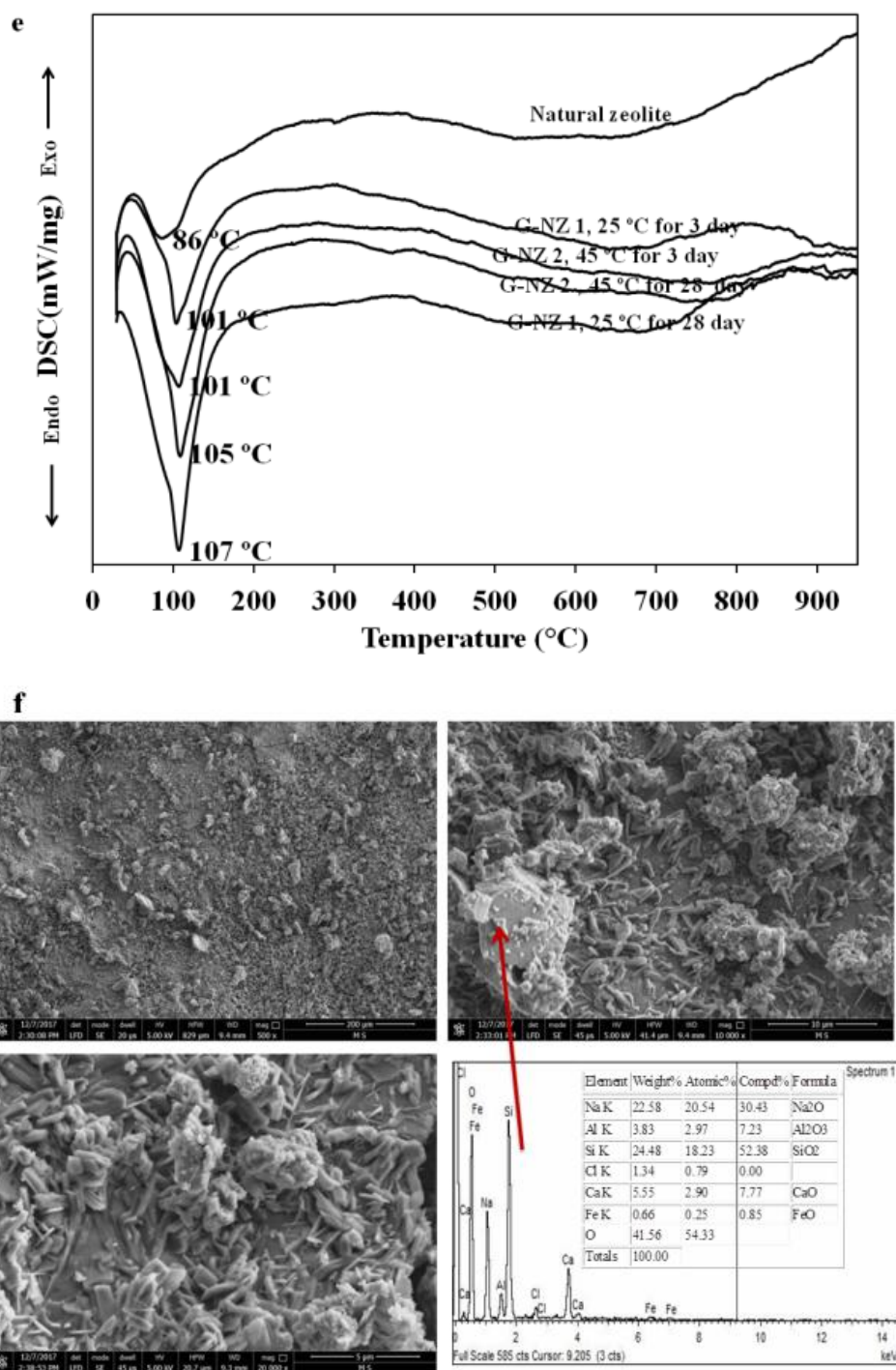MOHAMED EL-SHAHATE ISMAIEL SARAYA, and MOHAMED SAYED THABET

Fig. 3. (a) Photograph of prepared geopolymer, (b) Compressive strength of hardened geopolymer, (c) X-ray diffraction, (d) FTIR spectra, (e) DSC curve for hardened geopolymer cured at 25 ºC and 45 ºC, (f) SEM-EDX images of hardened geopolymer cured at 25 ºC and 45 ºC.

3.3. Characterization of NZ-Cement pastes

The average compressive strengths of cement pastes containing 0%, 5%, 10%, 15% and 20% of NZ cured up to 90 days are shown in Fig. 4a and Table 3. For all OPC paste and OPC -zeolite blended cement pastes, the hydration and pozzolanic reactions contributed to increase the compressive strength up to 90 days. OPC-NZ 10 has the highest compressive strength value in comparison to the reference paste (OPC). The strength activity index (SAI) (Fig. 4b) values show compressive strength for all OPC-NZ pastes higher than OPC at 3 days (29.0, 28.8, 18.6 and 119 % greater than OPC). However progressive hydration reduced values except for OPC-NZ 10. The increasing of strength in early age related to the filler effect of NZ that leads to accelerating the rate of cement minerals hydration. The dilution effect of cement is considered the main reason for reducing the compressive strength between 3 and 28 days, especially in the case of 20 % of NZ. In addition, the presence of Na^+ and K^+ ions that realized from NZ decreased the strength [56, 57].

Fig. 4c illustrates the XRD patterns of the blended samples with 0%, 5%, 10%, 15% and 20% of NZ cured for 28 days. Most of the hydration products have semi-amorphous nature except of portlandite. They showed only one crystalline product portlandite together the characteristics peaks of anhydrous clinker phases. As it is seen, the characteristic peaks of the portlandite (d ~ 4.90, 3.10, 2.62, 1.92, 1.79 Å) decreased in intensity with increasing the NZ dose in the blended cement pastes, accompanied by decreasing the intensity of the distinctive peaks of anhydrous calcium silicate minerals (d~ 3.02, 2.77, 2.6, 2.3 Å). The characteristic peaks of zeolite appeared in samples OPC-NZ15 and OPC-NZ20 to indicate that still some amounts of zeolite did not react at this age of hydration. The increasing of background in the 2Θ range 25–35º conformed presence of CSH [39].

Fig. 4c shows the heat flow of OPC and OPC-NZ blended cement cured for 28 days.

Only one endothermic effect appears in the range 50-200 ºC for NZ with an enthalpy 22.5 of J/g that related to realizing of water. The DSC curves of OPC and blended cement show several thermal effects related to changing in sizes and shapes with the amount of the NZ. The endothermic peak at 50-250 ºC is due to liberation of physical water and dehydration of calcium silicate hydrate as the main hydration product of OPC. The amounts of different hydration phases in the hardened cement pastes can be determined from the enthalpy of the corresponding peak [58].

As shown from Fig. 4e and Table 3 the DSC peak temperature and enthalpy of CSH changed with the increasing the NZ content in the samples. The sample with 10 % NZ shows the highest enthalpy and the lowest CSH decomposition temperature. The second peak at the temperature range 469-483 ºC is connected with decomposition of portlandite ($Ca(OH)_2$) [59]. This peak shift to the lower temperature side with addition of NZ can be related to presence of disordered calcium hydroxide. In addition, the area of this peak decreased with the increases of amount of NZ as a result of pozzolanic reaction with zeolite [60]. The endothermic effect appears in 680-780 ºC is which can be devoted to the decomposition of calcium carbonate. The enthalpies of calcium carbonate for samples containing NZ are similar but less than those containing OPC.
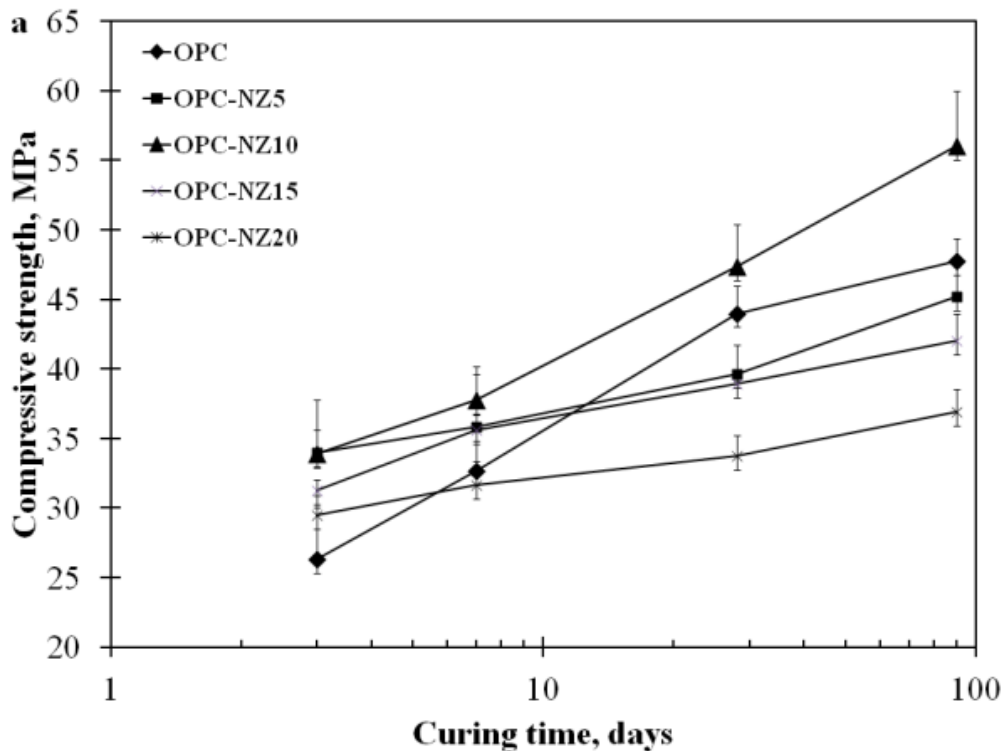
Fig. 4d illustrates the FTIR spectra of cement-zeolite pastes hydrated for 28 days. The band at 3644 cm^{-1} is related to the OH vibration (associated to CH), where there is a remarkable decrease of its intensity, especially for the sample loaded with 10 % of NZ and more. The decrease of this band confirms the reaction of NZ accordance of the pozzolanic reaction. The broad band at about 3444 cm^{-1} is attributed to the chemically bound water molecules while that at 1637 cm^{-1} to physically water. The adsorption bands of carbonates appeare at 1477 and 871 cm^{-1} due to carbonation of samples during handling [61]. The main IR band at 997 cm^{-1} (for cement paste) demoted to Si-O
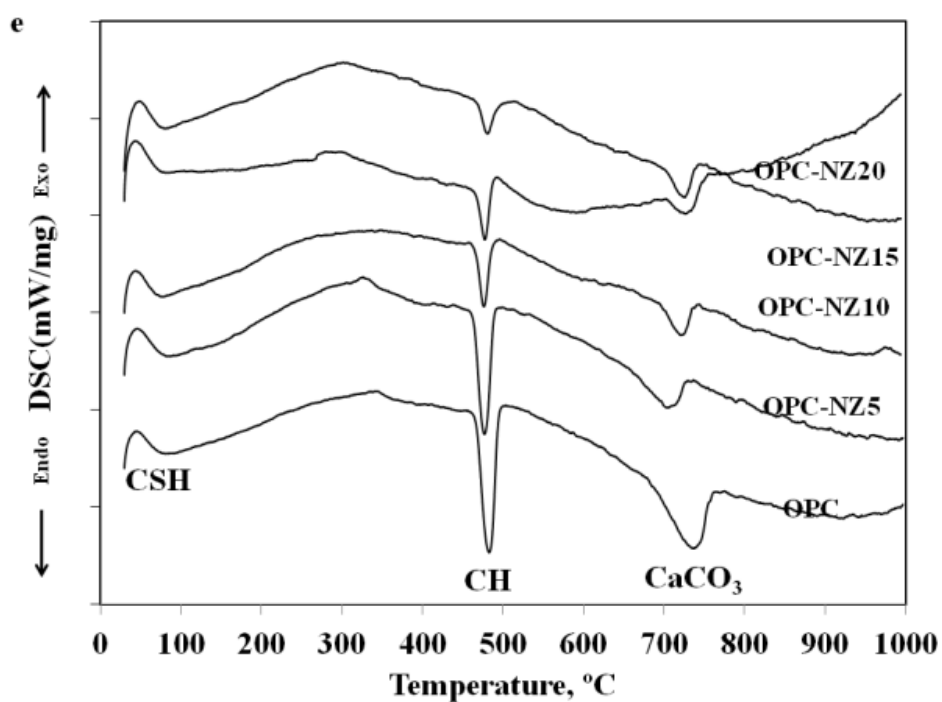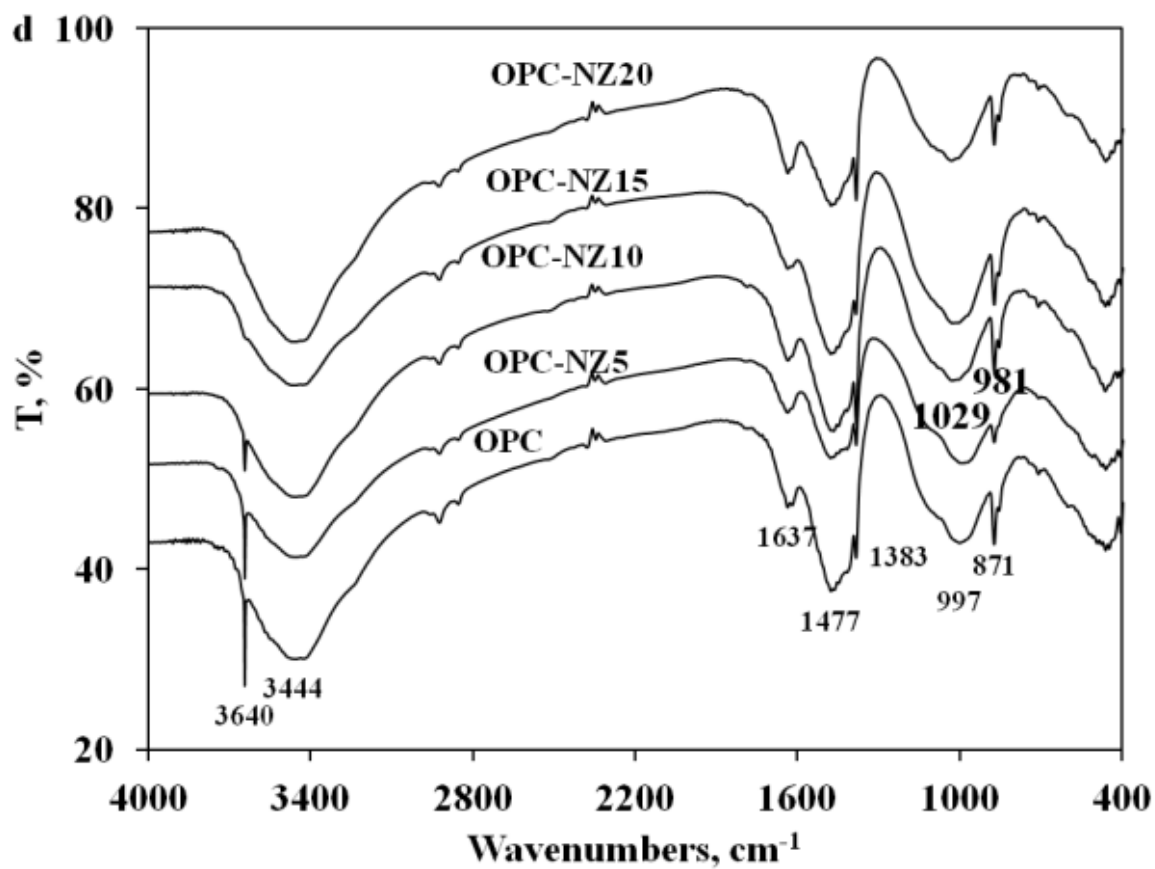
vibration for CSH. These bands could be changed in intensity and/or frequency with change of the Ca/Si ratio. This band is shifted to a lower frequency i.e. 991 cm^{-1} with addition of 5% of NZ (OPC-NZ 5) while with increasing the NZ dose it is shifted to high-frequencies 1029 cm^{-1}, 1029 cm^{-1} and 1031 cm^{-1} for OPC-NZ 10, OPC-NZ 15 and OPC-NZ 20, respectively [62]. The hardened NZ-cement past (OPC-NZ10) cured for 28 days subjected to SEM - EDX analysis to examine its microstructure (Fig. 4f). The micrograph shows CSH crystals with a fibrous morphology [63]. The relating EDX spectrum given in Fig. 4f indicates that the Ca/Si =2 conforming the reaction occurring between NZ and portlandite [64].

Table 3 : DSC peak temperature and enthalpy for zeolite blended samples cured for 28 days and 3- 28-day compressive strength up to 90 days.

Peak	OPC		OPC-NZ5		OPC-NZ10		OPC-NZ15		OPC-NZ20	
	T(C)	J/g	T(C)	J/g	T(C)	J/g	T(C)	J/g	T(C)	J/g
CSH	82	29.9	85	27.3	78	32.6	81	24.9	82	24.2
CH	482	19.3	479	18.30	479	9.40	479	6.60	481	5.25
CaCO$_3$	735	18.8	705	9.15	723	8.5	730	6.9	726	7.76
Crystallization	-	-	-	-	975	3.2	-	-	-	-
Compressive strength (MPa)										
3 days	26(3.69)		27(3.81)		34(1.69)		31(0.79)		29(1.39)	
7 days	33(5.30)		36(3.80)		38(2.38)		36(1.08)		32(1.69)	
28 days	44(2.00)		40(2.12)		47(3.06)		39(0.23)		34(1.51)	
90 days	48(1.62)		45(2.43)		56(4.00)		42(2.00)		37(1.62)	

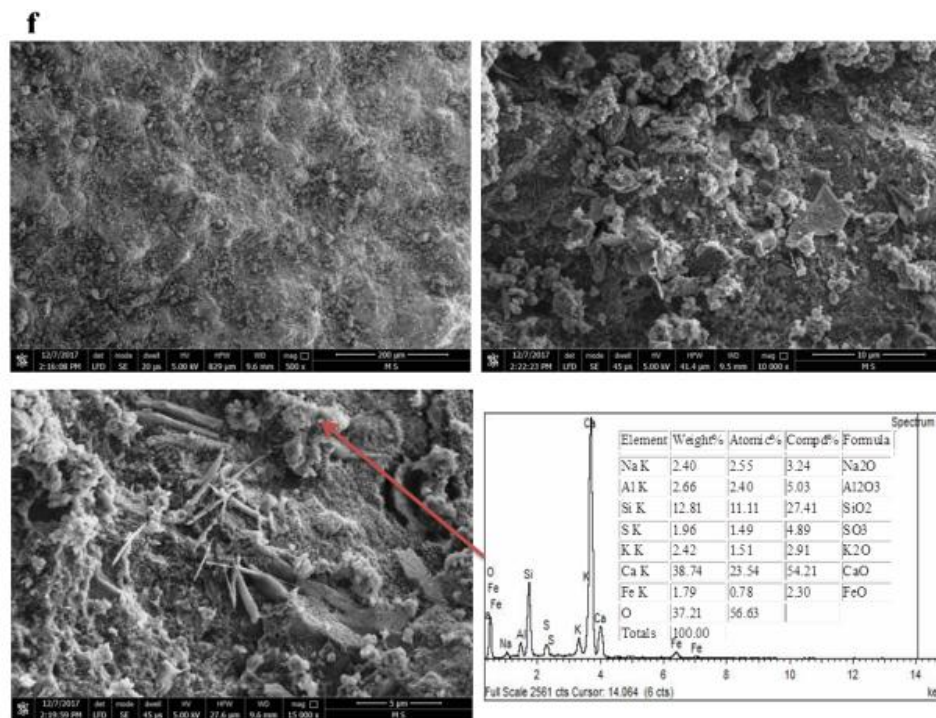| Element	Weight%	Atomic%	Compd%	Formula
Na K	2.40	2.55	3.24	Na2O
Al K	2.66	2.40	5.03	Al2O3
Si K	12.81	11.11	27.41	SiO2
S K	1.96	1.49	4.89	SO3
K K	2.42	1.51	2.91	K2O
Ca K	38.74	23.54	54.21	CaO
Fe K	1.79	0.78	2.30	FeO
O	37.21	56.63		
Totals	100.00			

Fig. 4. (a) Compressive strength of hardened cement-NZ pastes, (b) S.A.I., (c) X-ray diffraction, (d) FTIR spectra, (e) DSC curve, (f) SEM images of hardened OPC-NZ10 paste cured at 28 days.

4. CONCLUSIONS

The following conclusions are resulting from the study of natural raw zeolite as pozzolanic material for preparation of geopolymer and blended cement:

- According to ASTM C618 requirements, the natural raw zeolite from Harrat Shama (Tuffil) is a good pozzolanic material.
- It is composed of clinoptilolite, cowlesite and cristobilite and considered as clinoptilolite -zeolite class.
- The NZ reacted with activator solution to give a geopolymer matrix that has been conformed using XRD, FTIR, DSC, SEM-EDS results. The compressive strength of geopolymer paste is enhanced with increasing curing temperature.
- The addition of nature row zeolite to Portland cement accelerates the hydration of cement especially at early ages. The incorporation of 10% by mass can be considered as a limit for its effective use. Above this limit, a substantial part of zeolite reduced compressive strength.
- Finally, we can be concluded that the natural raw zeolite needs to thermal activation in order to improve its pozzolanic activity.

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