
ALKALI ACTIVATION OF CERAMIC WASTE

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Abstract

In ceramic tile production, because of various reasons, unsold fired products come out. These are waste tiles and only a little part of them are used. If these waste tiles were used in geopolymer production, this pollution decreases. In this study, usage of waste tile as pozzolan was studied. In this paper the effect of sodium silicate solution with different molar ratio on the compressive strength the synthesis of Egyptian ceramic waste -based geopolymers is investigated. Eight different alkaline solutions with different soluble silica contents were used to activate ceramic waste. The primary reaction product was a sodium aluminosilicate gel, while different types of zeolites appeared as minority phases. The percentage and composition of these reaction products were found to depend on both the soluble silica content present in the activating solutions and curing time. In addition, the amount of gel was observed to have a decisive effect on the mechanical strength developing in the material. X-ray diffractograms of geopolymers indicated the existence of the major amorphous phases of ceramic waste, as well as the formation of a new amorphous phase in the geopolymeric matrices. Fourier-transform infrared (FTIR) spectroscopy analysis revealed essential ceramic waste phase transformations within geopolymers that affected their mechanical strength. The results of the current research indicate that a compressive strength is increased with the increase of alkali content, as well as with the increase of sodium silicate in the synthesis of geopolymers.

Key words, alkali activation, ceramic waste, compressive strength, DTA, XRD, FT-IR

Introduction

Geopolymers are chemically hardened monolithic aluminosilicate gels formed by partial dissolution and polycondensation of aluminosilicate materials, such as fly-ash and calcined clays, in aqueous alkaline environments [1, 2]. Geopolymers have been proposed as an alternative to traditional Ordinary Portland Cement (OPC) for use in construction applications, due to their excellent mechanical properties [3], low temperatures required for synthesis and their intrinsic fire resistance [4]. Like

zeolites and some aluminosilicate gels, geopolymers are synthesised in aqueous media, albeit much lower water weight fractions, typically less than 35%. Due to their excellent mechanical properties, the bulk of literature is focussed on the effect and application of different raw materials on the compressive strength of geopolymers [5], chemical impurities [6] and the effect of the chemical composition of the alkali activating solutions [7]. Only a relatively small number of investigations have specifically studied the effects of high-temperature on geopolymeric gels [8–13]. Studies of geopolymeric gel have not explored the effect of gel Si/Al, alkali cation, raw material or impurities. Each of these factors play crucial roles in determining the mechanical properties of geopolymers at ambient conditions and should also be expected to affect greatly the properties of geopolymers at elevated temperatures. The geopolymer structure is formed from tetrahedrally co-ordinated aluminium and silicon atoms bridged with oxygen [14, 15]. The negatively charged aluminium in IV-fold coordination is balanced via association with monovalent cations, typically sodium and potassium, provided by the alkaline activating solution [1]. The resulting inorganic gel is amorphous to electron diffraction [1, 9, 16], and exhibits a single broad hump in ^{29}Si MAS-NMR spectra, similar to aluminosilicate gels [17]. However, transformation of the amorphous gel into zeolite has been observed, where structural reorganisation is rapid due to an open microstructure [5, 18, 19]. The microstructure of geopolymers has been observed to vary greatly depending on the Si/Al, a result of variation in the density of the aluminosilicate gel. The change in microstructure appears to be very important to the mechanical properties of geopolymers, with strength observed to increase generally with decreasing gel density [18]. Rahier *et al.* [13] broadly investigated some thermal properties of a geopolymer of non-prescribed composition synthesised from metakaolin and sodium silicate solution (denoted Na-geopolymer), primarily the dehydration and thermal shrinkage. The specimen investigated by Rahier exhibited shrinkage of approximately 6% during dehydration, without significant densification observed at higher temperatures (>600 °C). More recently, the thermal characteristics of Na-geopolymer with a Si/Al of approximately two has been investigated, revealing a similar region of shrinkage associated with dehydration, but also the specimen was observed to densify at approximately 800 °C [8]. The different thermal shrinkage behaviour of these systems suggests that there are differences in the thermal behaviour of Na-geopolymers with differing

composition which is yet to be elucidated by systematic investigation. Furthermore, the dehydration and densification processes occurring in Na-geopolymers have not been determined. The microstructure of Na-geopolymer is known to be highly dependent on Si/Al, which may play a significant role in determining the material's thermal properties and the effect of elevated temperatures on its physical properties [18].

These two elements are able to form highly concentrated aqueous solutions and solvate large amounts of silicon and aluminium, both of which are critical for geopolymerisation. Geopolymeric materials synthesised with different alkali cations exhibit marked differences in Si/Al ordering [20,21], thermal stability [22-24] and setting properties [24]. To some extent, the effect of alkali cation on the mechanical properties of geopolymers has been observed [24-28]. Despite the apparent effects of alkali, there has been no systematic investigation to determine the extent to which alkali type will affect the development of the mechanical properties of geopolymers. Alkali cations are associated with aluminium, where the AlO_4 groups have a single negative charge due to aluminium (III) being in tetrahedral co-ordination. A study of the effect of alkali cations (sodium and potassium) on the molecular ordering of the geopolymer gel concluded that the concentration of silicon in the activating solution plays a large role in aiding the incorporation of aluminium into the matrix via solution phase speciation with silicon [20]. Similarly, the nature of the alkali cation also contributes to the level of reaction of the solid aluminosilicate source, as well as the level of aluminium incorporation [20]. The effect of the concentration of silicon in the alkali activating solution has been investigated on systems utilising both fly-ash [28,29] and metakaolin [30, 31] as solid aluminosilicate sources. Furthermore, the relationship between geopolymer composition, microstructure and mechanical properties has recently been conducted by the study of geopolymers synthesised from metakaolin with composition $Na(SiO_2)_zAlO_2 \cdot 5.5H_2O$, where $1.15 \leq z \leq 2.15$ [31].

Geopolymers possess excellent physico-chemical and mechanical properties, including low density, micro-porosity or nano-porosity, negligible shrinkage, high strength, thermal stability, high surface hardness, fire and chemical resistance [32-34]. Due to these properties, they are viewed as alternative materials for certain industrial applications in the areas of construction, transportation, road building, aerospace, mining and metallurgy. Certain industrial wastes, such as coal-fired fly

ash, blast furnace slag and mine tailings contain sufficient amounts of reactive alumina and silica, in order to be used as source materials for the geopolymerization process. Therefore, geopolymerization can be considered as an economically viable technology for the transformation of industrial wastes and/or by-products of aluminosilicate composition into attractive construction materials [32, 35, 36].

The aim of the present study was to explore the effect of the sodium oxide and soluble silica content in a series of activating solutions on the physico-mechanical properties of ceramic waste – base geopolymer as well as study the effect of curing temperature on the to identify and quantify such products and their impact on mechanical development in the material.

Materials And Methods

The materials used in this investigation were ceramic waste, Commercial grade sodium hydroxide in pallets form (97% -100% purity) as well as sodium silicate solution ($\text{Na}_2\text{O}=10.3\%$, $\text{SiO}_2=28.9\%$, Water = 60.8%) were used to preparation of alkali activators.

The ceramic waste was activated with a series of alkaline solutions, all with a practically constant silicon oxide content ($\approx 28\%$), but with varying proportions of sodium oxide. The chemical composition and certain other properties of each solution are given in Table 1, which also shows the differences in both the sodium oxide and the water content achieved by mixing sodium silicate and sodium hydroxide in different proportions. Eight different alkali solutions with different soluble silica contents were used to activate ceramic waste.

Table (1): Chemical analysis of starting materials, mass %

Oxide content %	CTW	SSL	AA1	AA2	AA3
SiO_2	47.23	30.7	30.7	30.7	30.7
Al_2O_3	17.39	--	--	--	--
Na_2O	10.08	10.3	14.3	18.3	29.3
CaO	1.06	--	--	--	--
MgO	14.77	--	--	--	--
K_2O	3.70	--	--	--	--
SO_3	0.15	--	--	--	--
Fe_2O_3	0.01	--	--	--	--
TiO_2	0.01	--	--	--	--
P_2O_5	4.76	--	--	--	--
H_2O	0.00	59.0	55.0	51.0	40.0

L.O.I	0.79	--	--	--	--
Total	99.21	100.0	100.0	100.0	100.0

Mixing of all the materials were done manually in the laboratory at room temperature. The ceramic waste and the alkali solution were mixed homogeneously. The “solution/ash” ratio used was 0.5 by weight. The fresh geopolymer paste was used to cast cubes of size 2x2x2 cm to determine its compressive strength. The molar oxide ratio of H₂O:Na₂O was kept constant at 10. At this value the water content of the sodium silicate mixture was adequate to facilitate geopolymerization without deterioration of the mechanical properties of the geopolymer. The specimens were prepared according to the method followed by Hardjito et. al.[37]. Each cube specimen was cast in three layers by compacting manually as well as by using vibrating machine. The specimens were wrapped by plastic sheet to prevent loss of moisture and placed in an oven.

The bulk density was determined from weights of hydrated paste in air and suspended in water according to Archimedes principle [38]. The determination of compressive strength of cement pastes was carried out according to ASTM designation: C 109-80 [39] using compressive strength machine. After each experiment, the material was grinded (size 65 μ) and mixed with a small volume of acetone in order to dehydrate the system and then to prevent the material evolution. The combined water (W_n), was determined from the ignition loss of dried samples at 1000 °C. The XRD pattern ceramic waste -base geopolymer was recorded on (M/S. Shimadzu Instruments, Japan) diffractometer XRD 7000 with Ni filtered CuK α as a radiation source at 2 θ scan speed of 4° min⁻¹. XRD. IR spectrometer (Perkin-Elmer 880). The FTIR spectra in the wave number range from 400 to 4000 cm⁻¹ were obtained in atmosphere using the KBr pellet technique. The pellets were prepared by pressing a mixture of sample and dried KBr (sample : KBr approximately 1:200) at 8 t/cm². Finally, for the characterization of the surface morphology and the analysis of microstructure compositions a JOEL JSM-type scanning electron microscope was used.

Results and Discussion

Alkali activation of ceramic waste at room temperature):-

Chemically combined water contents:-

The chemically combined water contents of alkali activated ceramic waste cured at room temperature with different alkali activators up to 90 days, are seen in Figures(1-3). It is clear that the chemically combined water contents increase with time for all activated pastes. This is mainly due to the progress of alkali reactions of activator with ceramic waste phases. As the activation time of granulated slag

progresses, more hydration products are formed then the chemically combined water content increases. Also the chemical combined water content increases with sodium hydroxide from AA1 into AA2 and then decreases at AA3. This is mainly due to the progress of alkali activation reaction and formation of hydration products that have water high contents. This is also due to the decrease of $\text{Na}_2\text{O}/\text{SiO}_2$ which tends to form more CSH with higher water contents [40].

Figure (1): Chemically combined water contents of alkali activated ceramic waste by AA1 cured at room temperature, up to 90 days

Figure (2): Chemically combined water contents of alkali activated ceramic waste by AA2 cured at room temperature, up to 90 days

Figure (3): Chemically combined water contents of alkali activated ceramic waste by AA3 cured at room temperature, up to 90 days

Bulk density

The bulk density of alkali activated ceramic waste cured at room temperature up to 90 is seen in Figures (4-6). It is clear that the bulk density increases with curing time up to 90 days, for all activated pastes as a result of the activation reaction of alkali activator with ceramic waste components. On the other side the bulk density increases with alkali content from AA1 into AA2 and then decreases at AA3. This is mainly due to increasing the hydration products. This hydrate have tendency to leading then the porosity increases, therefore, the bulk density decreases. The bulk density values of the activated ceramic waste are lower than those of the alkali activated slag. This may be due to the decrease of Ca^{2+} in the ceramic waste; therefore, the activated ceramic wastes have lower amounts of CSH which is the main source of mechanical properties of the cement pastes. As the Na_2O content increases the bulk density decreases due to the formation Na. rich CSH with low bulk density and high porosity [41, 42].

Figure (4): Bulk density of alkali activated ceramic waste by AA1 cured at room temperature, up to 90 days

Figure (5): Bulk density of alkali activated ceramic waste by AA2 cured at room temperature, up to 90 days

Figure (6): Bulk density of alkali activated ceramic waste by AA3 cured at room temperature, up to 90 days

Compressive strength:-

The compressive strength values of alkali activated ceramic waste cured at room temperature with different types of alkali activators up to 90 days, are seen in Figures (7-9). It is clear that the compressive strength of activated ceramic waste increases with time for all activated pastes. Also, the compressive strength increases with the temperature as well as alkali content from AA1 up to AA2 and then decreases at AA3. This is mainly due to the increasing of dissolution of component with alkali and enhances the performance of geopolymerization reaction. Also, the compressive strength increases with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ due to the increases of CSH as the main factor of compressive strength. As a result of the free alkali formation and

dilution effect in addition to the formation of Na-Calcium aluminosilicate hydrate with low strength. The low Na-CASH and CSH gives low strength. Formation of the geopolymer framework is greatly dependent up on the dissolution of the ceramic waste particulates, which is directly affected by concentration of alkali solution. Activator solution with higher concentration of NaOH up to AA2 provides better dissolving ability to ceramic waste particulates and produces more reactive bond for the monomer, which will increase inter-molecular bonding strength of the geopolymer. The compressive strength of alkali activated ceramic waste is lower than those of the alkali activated slag. This may be due to the decrease of Ca^{2+} in the ceramic waste; therefore, the activated ceramic wastes have lower amounts of CSH which is the main source of mechanical properties of the cement pastes [42].

Figure (7): Compressive strength of alkali activated ceramic waste by AA1 cured at room temperature, up to 90 days

Figure (8): Compressive strength of alkali activated ceramic waste by AA2 cured at room temperature, up to 90 days

Figure (9): Compressive strength of alkali activated ceramic waste by AA3 cured at room temperature, up to 90 days

FTIR spectra

Figure (10) shows FTIR-Spectra of alkali activated ceramic waste cured at room temperature at 90 days, with different types of alkali activators. It is seen in Fig. 10 that the band centered at about 1016 cm^{-1} in raw ceramic waste, corresponding to the Si–O asymmetric stretching in tetrahedral [43, 44] is shifted to lower wavenumbers. That increases with alkali concentration up to A5 and then return to higher wavenumbers. Also, the intensity of band increases with alkali concentration. The shift toward the low wave number may be attributed to the partial replacement of SiO₄ tetrahedron by AlO₄ tetrahedron, resulting in a change in the local chemical environment of Si–O bond. The formation of the geopolymer is also indicated by the band at about 870 cm^{-1} linked to Al–O symmetric stretching in tetrahedral [44], which is absent in the spectrum of ceramic waste. Other bands related to the formation of the geopolymer are those at about 1420 and 1650 cm^{-1} related to O–H bending and H₂O stretching, respectively [45]. The band at about 1460 cm^{-1} is related to the formation of carbonate by reaction of alkali metal hydroxide with atmospheric CO₂.

Figure (11) shows FTIR-Spectra of alkali activated ceramic waste with A5 activator, cured at room temperature up to 90 days. It is shown that the intensities of the bands related to the geopolymer formation increase as the polycondensation time

increases. On the other side, the intensity of characteristics band of slag decreases with time. This is mainly due to the dissolution of ceramic waste components in the alkali medium and shifted to lower wavenumbers. The sequence of spectra in this figure also shows that the band centred at about 460 cm^{-1} (Si–O bending) undergoes a very small shift towards higher wave numbers as a consequence of the incorporation of alumina in the geopolymer [44]. This band would be shifted much more considerably towards higher wavenumbers in the case of a geopolymer only made of SiO_4 tetrahedral [46]

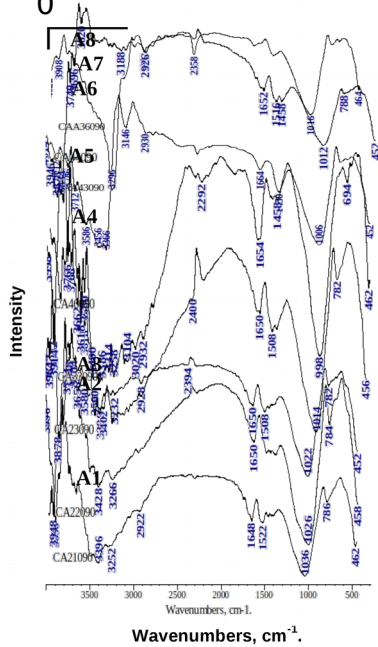


Figure (10) FTIR spectra of alkali activated ceramic waste with different types of activator, cured at 90 days.

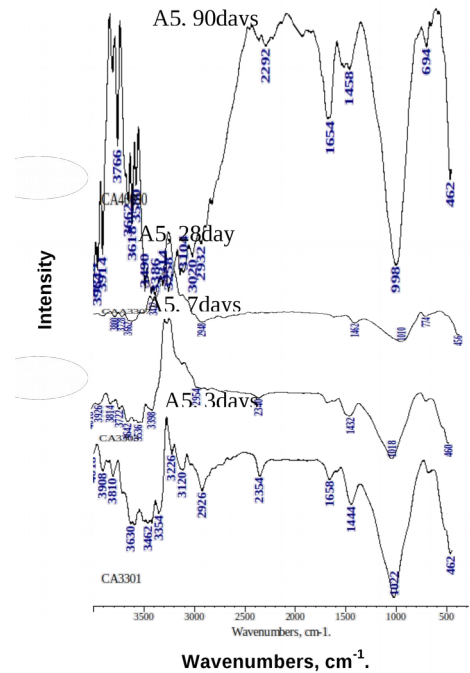


Figure (11) FTIR spectra of alkali activated ceramic waste with activator A5, cured up to 90 days

XRD pattern

Figure (12) show XRD pattern of alkali activated ceramic waste cured at room temperature at 90 days, with different types of alkali activators. Ceramic waste based geopolymer have a large diffuse halo peak at about 20–40° (2θ max Cu K). This means that the ceramic waste based geopolymeric products are mainly X-ray amorphous materials. Also, indicating the formation of an alkaline aluminosilicate gel [47]. In addition, several sharp characteristic peaks are also seen. The other signals detected corresponded to zeolite structures such as hydroxysodalite (Na₄Al₃Si₆O₁₂-OH, JCPDS 11-0401) and herschelite (NaAlSi₂O₆·H₂O, JCPDS 19-1178) or alkaline bicarbonates. Other zeolite-type crystalline phases also appeared after activation, which varied depending on the nature of the activating solution used and curing time [48].

Figure (13) shows XRD pattern of alkali activated ceramic waste with A5 activator, cured at room temperature up to 90 days. The intensity of the characteristic

peaks of zeolite products decreases with time and also appears new at other position. These changes can be explained by the fact that zeolite are metastable and may undergo successive transformation into one or several more stable phases [48].

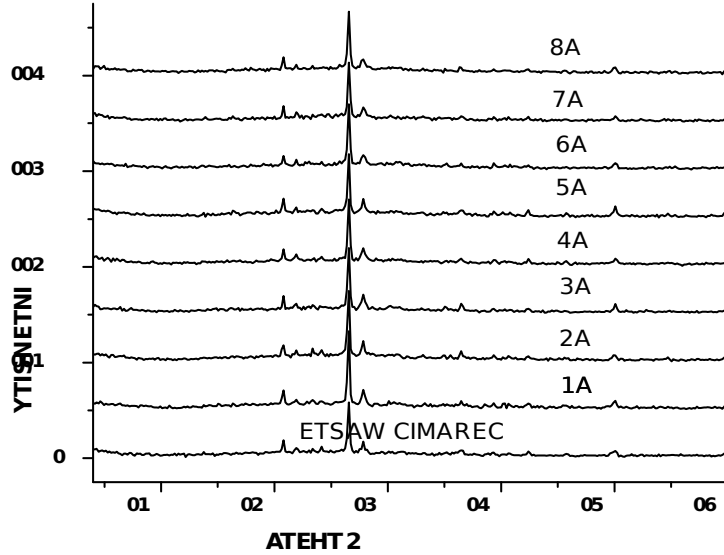


Figure (12): XRD pattern of alkali activated ceramic waste with different activators, cured at 90 day

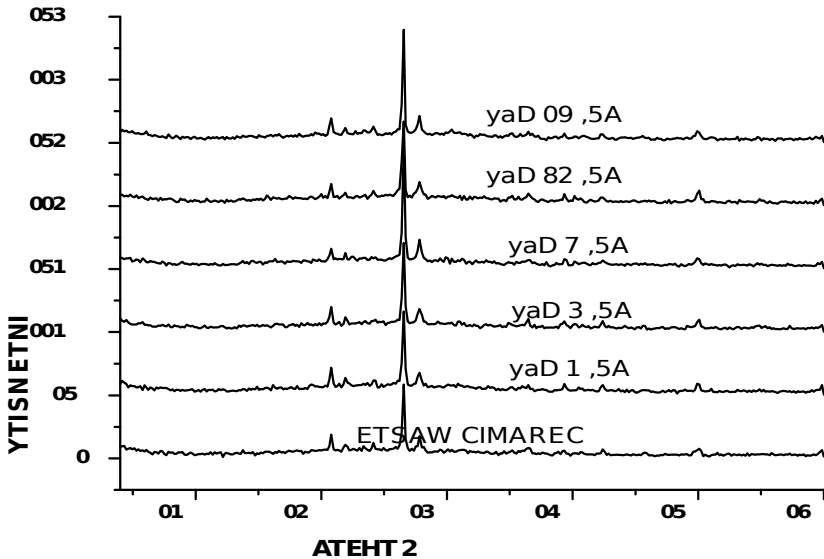


Figure (13): XRD pattern of alkali activated ceramic waste with different activators, cured up to 90 day

Scan electron microscope investigation

The scanning electron micrograph of ceramic waste based geopolymer activated with A5 cured at ambient temperature up to 90 days are shown in Figure (14). This sample gave the highest value of compressive strength. Microstructural observations by SEM were very much consistent with the phase transformations observed by XRD. The microstructure of mixtures was characterized by dense and homogeneous phases which accounted for their high strengths. However, a detailed examination (at higher magnification) of the amorphous-looking phases revealed that, there were embedded pockets of crystalline growths [49]. Irregularly shaped macropores are clearly seen as well as spherical cavities which either can be due to air bubble entrapment or are part of the interface between the unreacted spherical ash particles and the geopolymeric matrix [50]. Simplified geopolymerization reactions can be described as initial dissolution of the aluminium and silicon from ceramic waste followed by their polymerisation, gelation and hardening. Van Deventer and co-workers suggested that presence of calcium in solid waste materials will provide extra nucleation sites for precipitation of dissolved species and cause rapid hardening [51, 52].

According to the classification scheme proposed by Davidovits, when Si:Al=1 it is a sialate ($-\text{Si}-\text{O}-\text{Al}-\text{O}-$), for Si:Al=2 it is a sialatesiloxo ($-\text{Si}-\text{O}-\text{Si}-\text{Al}-\text{O}$) for Si:Al=3 it is a sialate-disiloxo ($-\text{Si}-\text{O}-\text{Al}-\text{O}-\text{Si}-\text{O}-\text{Si}-$) and when Si:Al>3 it is deemed to be sialate link, poly (sialate-multisiloxo) [53]. Generally, the three-dimensional amorphous geopolymeric network with a general formula of $\text{R}_n-[-\text{Si}-\text{O}_2]_z-\text{Al}-\text{O}]_n \cdot w\text{H}_2\text{O}$ (R represents a cation such as sodium, potassium, or calcium; n is the degree of polycondensation; z = 1, 2, or 3; and w is the amount of binding water) is often argued to be the phase that gives the binding property to the geopolymeric gel. The ratio of Si/Al should be 1–3, and the ratio of Na/Al should be 1. During the geopolymerization reaction process, Si/Al ratios in the original ceramic waste, the reactive ceramic waste sphere, and the reaction products of ceramic waste are changing [54].

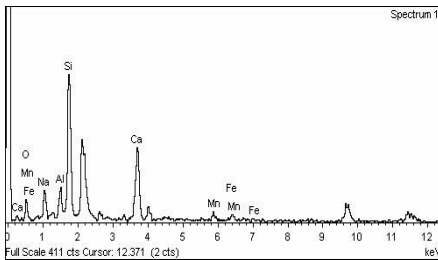
The physical and mechanical properties of geopolymers were a function of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios [55]. EDXA analysis is conducted on the sample and the results are listed in Table (2). It was found that the elemental composition was dominated by Si, Al and Na as well as Ca. According to the chemical

compositions and The SiO₂/Al₂O₃ ratios of 4.5 and 3.6, and Na₂O/Al₂O₃ ratios of 1.90 and 0.34 confirmed the presence of continuous mass of strong geopolymer. Also, it is suggested that phase might be a geopolymeric binder, which has similar characteristics to the PSS type of geopolymeric binder. This observation is also consistent with previous observations by Yip et al. [56, 57].



a-Low magnification micrograph

b-High magnification micrograph



c- EDAS analysis and

Figure (14) SEM images and EDAS spectra at room temperature

Conclusions

The effect of the main synthesis factors on the development of ceramic waste -based geopolymers is investigated during the last decades. They are developed during the last decades. They are based on aluminosilicate oligomers that are formed by the reaction of aluminosilicate materials under strongly acidic conditions. The activation of aluminosilicate oligomers raises the development of a three-dimensional polymeric framework, in

Element	App	Intensity	%Weight	%Weight	%Atomic
	.Conc	.Corn		Sigma	
O K	0.17	0.4207	36.10	3.96	51.14
Na K	0.07	0.4968	11.82	1.71	11.65
Al K	0.04	0.5286	6.21	0.96	5.22
Si K	0.19	0.5869	27.91	2.10	22.51
Ca K	0.14	0.8926	13.67	1.13	7.73
Mn K	0.02	0.7976	2.27	0.57	0.94
Fe K	0.02	0.8289	2.02	0.58	0.82
Totals			100.00		

which the undissolved solid particles are bonded and the whole system hardens in a final durable structure.

Water plays important roles during dissolution, polycondensation and hardening stages of geopolymerization. So the amount of water is constant in all samples whereas reduction of water content in the synthesis of geopolymers improved their compressive strength. Sodium hydroxide content in the synthesis of geopolymers was found to affect significantly their compressive strength. Sodium hydroxide concentration in the aqueous phase of the geopolymeric system acts on the dissolution process, as well as on the bonding of the solid particles in the final structure.

Geopolymers synthesized with either, lower or greater NaOH concentration in the aqueous phase developed lower compressive strength. The amount of sodium silicate solution in the synthesis of geopolymers was evidenced to have a substantial effect on the obtained compressive strength. Sodium silicate solution controls the soluble silicate concentration and the predominant silicate species in the geopolymeric system, improving the mechanical strength of the produced materials.

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