

Effect of Silica Fume on the Characterization of the Geopolymer Materials

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ABSTRACT

The application of geopolymer technology offers the opportunity to address a variety of sustainability issues such as converting by-products currently treated as wastes to useful and valuable products, enhancing product features across the materials market and reducing greenhouse gas emissions by significant amounts, particularly in the cement industry. The influence of silica fume (SF) - byproduct of the reduction of high-purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys- addition on properties of geopolymer materials produced from alkaline activation of alumino-silicates metakaolin and waste concrete produced from demolition works has been studied through measurement of compressive strength, FTIR, XRD and SEM analysis. Alumino-silicate materials are coarse aggregate included waste concrete and fired kaolin (metakaolin) at 800°C for 3 hours; both passing a sieve of 90 µm. Mix specimens containing silica fume were prepared at water/binder ratios in a range of 0.30 under water curing. The used activators are an equal mix of sodium hydroxide and silicate in the ratio of 3:3 wt. %. The control geopolymer mix composed of metakaolin and waste concrete in an equal mix (50:50, wt %). Silica fume was partially replaced waste concrete by 1 up to 10wt. %. Results indicated Compressive strengths of geopolymer mixes incorporating SF increases up to 7 % substitution and then decreases up to 10% but still higher than the control mix; where 7% SF digested calcium hydroxide (CH) crystals, decreased the orientation of CH crystals, reduced the crystal size of CH gathered at the interface and improved the interface more effectively.

Keywords: silica fume, geopolymer, waste concrete, metakaolin.

1. Introduction

Silica fume known as micro-silica is a byproduct of the reduction of high-purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys. Because of its extreme fineness and high silica content, Silica fume is a highly effective pozzolanic material. Silica fume is used in concrete to improve its properties like compressive strength, bond strength, and abrasion resistance; it reduces permeability; and therefore, helps in protecting reinforcing steel from corrosion

Silica fume has been used as a high pozzolanic reactive cementitious material to make high-performance concrete in the severe conditions [Kohno (1989), Gautefall (1986)]. This mineral admixture has highly been used in severe environmental conditions despite its several mixing and curing problems, because of its acceptable early age strength development [Cheng and Feldman (1985), Grutzeck et al. (1983)]. The hydration mechanism and properties of secondary C-S-H made by pozzolanic reaction have been studied by many investigators [Cheng and Feldman (1985)]. However, C-S-H formed by silica fume-calcium hydroxide reaction might be different in respect of the amount of molecular water, C/S ratio and density [Cohen and Bentur (1988)]. Moreover, because of its rather different characteristics, pozzolanic gel has high potential to con-

tribute in reactions with other internal or external ions such as Al, Cl and alkalis [**Maage (1989), Sellevold and Nilson (1988)**].

On the other hand, the search for a new environmentally friendly construction material that will match the durability of ancient concrete has provoked interest into the study of alkali activated cementitious systems over the past decades. Alkali activated cements refer to any system that uses an alkali activator to initiate a reaction or a series of reactions that will produce a material possesses cementitious property [**Yip et al. (2005)**].

Alkali activated cement, alkali activated slag and fly ash, and geopolymers are all considered to be alkali activated cementitious systems; however, it is expected that the structures of these materials are vastly different and result from different chemical mechanistic paths. It is commonly acknowledged that calcium silicate hydrate (CSH) is the major binding phase in Portland cement [**Taylor (2000)**] and alkali activated slags [**Richardson and Cabrera (2000)**]; however, the binding property of geopolymers is generally assumed to be the result of the formation of a three-dimensional amorphous aluminosilicate network [**Van Jaarsveld and Van Deventer^a (1999), Davidovits (1991), Phair and Van Deventer (2002), Lee and Van Deventer (2002)**].

The production of geopolymeric precursors is carried out by calcinations of aluminosilicates natural clay materials. Their source can be also some industrial aluminosilicate waste materials. The result of the hardening mechanism is a three dimensional zeolitic framework unlike traditional hydraulic binders in which hardening is the result of the hydration of calcium aluminates and silicates [**Davidovits (1991), Phair and Van Deventer (2002), Lee and Van Deventer (2002), Davidovits (1993)**]; this circumstance is a cause of significant differences in the quality and variety of the engineering properties of the composites based on geopolymer and current cements. As a means of converting waste materials to useful products, the value of geopolymer technology lies primarily in its ability to produce a high-performance binder from materials that are rich in silica and alumina that are the bases of geopolymerization process.

Davidovits (1991) proposed that Geopolymers are formed by the polymerization of individual aluminate and silicate species, which are dissolved from their original sources at high pH in the presence of alkali metals. The resultant products are reported to have the general formula $M_n-[-Si-O_2]_z-Al-O]_n \cdot wH_2O$ where M is the alkali element, - indicates the presence of a bond, z is 1, 2 or 3 and n is the degree of polymerization. Theoretically, any alkali and alkali earth cations can be used as the alkali element (M) in the reaction; however the majority of research has focused on the effect of sodium (Na^+) and potassium (K^+) ions [**Phair and Van Deventer (2002), Van Jaarsveld and Van Deventer^b(1999)**]. It has not been clearly proven whether other alkali and alkali earth cations, including calcium will participate in the reactions in a similar way.

The target of the present paper is to study the effect of silica fume addition in the performance of geopolymer materials and investigate its effect on the mechanical and microstructural properties of the geopolymer constituents.

2. Experimental

2.1. Materials:

Aluminosilicate materials used in this investigation are fired kaolin clay and coarse aggregate included waste concrete; both well grinded and passing a sieve of 90 μm . an aluminosilicate Kaolin material with high kaolinite residue was utilized in the synthesis of geopolymeric binder, sourced from Al- Dehesa, Sinai governorate, Egypt, was thermally treated at 800°C for 3 hrs with a heating rate of 5°C/min, to produce metakaolin (Mk).

This temperature was chosen on the basis of an earlier research work [Kakali et al. (2001), Wenying et al. (2008), Cioffi et al. (2003)]. The most important characteristics of this calcined product (Mk) are: chemical composition ($\text{SiO}_2 + \text{Al}_2\text{O}_3$ about 95%), fineness (surface area between 15 and 20 m^2/g), passing a sieve of 90 μm and its poorly crystalline nature. Raw materials used in this investigation were characterized by means of chemical analysis as represented in Table (1).

Silica fume sourced from Suez Cement Company (Helwan plant) also known as micro-silica is a byproduct of the reduction of high-purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys; it was in the powder form with 95% SiO_2 , an average particle size of 8 μm as represented from its laser particle size distribution (Fig.1).

Table (1): Chemical composition of starting materials. (Mass, %)

Sample name	SiO2	Al2O3	Fe2O3	CaO	MgO	Na2O	K2O	SO3	TiO2	P2O5	Loss	Total
Kaolin	56.38	27.61	1.32	0.18	0.06	0.08	0.04	0.06	3.73	0.13	10.17	99.97
Metakaolin	59.03	35.33	0.89	0.43	0.13	0.05	0.05	0.03	2.46	0.72	0.79	99.91
Waste Concrete	77.63	1.57	1.19	8.61	0.24	0.24	0.12	2.31	0.01	0.03	7.61	99.56
Silica Fume	94.92	0.02	1.28	0.03	0.01	0.28	0.15	0.02	—	—	3.28	99.99

Median Size : 7.00413(μm)
 Mean Size : 7.82009(μm)
 Mode Size : 8.2495(μm)
 Diameter on Cumulative % : (1)10.00 (%) 1.3360(μm)
 : (2)50.00 (%) 7.0041(μm)
 : (3)90.00 (%) 15.0121(μm)

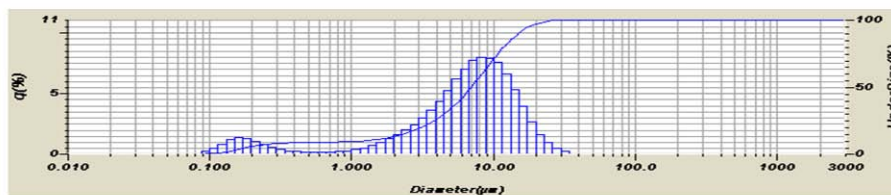


Fig. (1): Laser particle size distribution of silica fume.

Mineralogical characterization of the raw materials was done using X-ray diffraction analysis as represented in Fig.(2), where coarse aggregate included waste concrete has a major content of quartz and little calcite content. Kaolin on the other hand is composed mainly of kaolinite and quartz, while silica fume is completely amorphous silica.

Sodium silicate solution and sodium hydroxide were used as alkali activators. Sodium hydroxide (NaOH) produced by SHIDO company with 99% purity and liquid sodium silicate (LSS) from Fisher company consists of 32%SiO₂ and 17%Na₂O with Silica modulus SiO₂/Na₂O equal 1.88 and density 1.46 g/cm³ (Na₂SiO₃· 9H₂O).

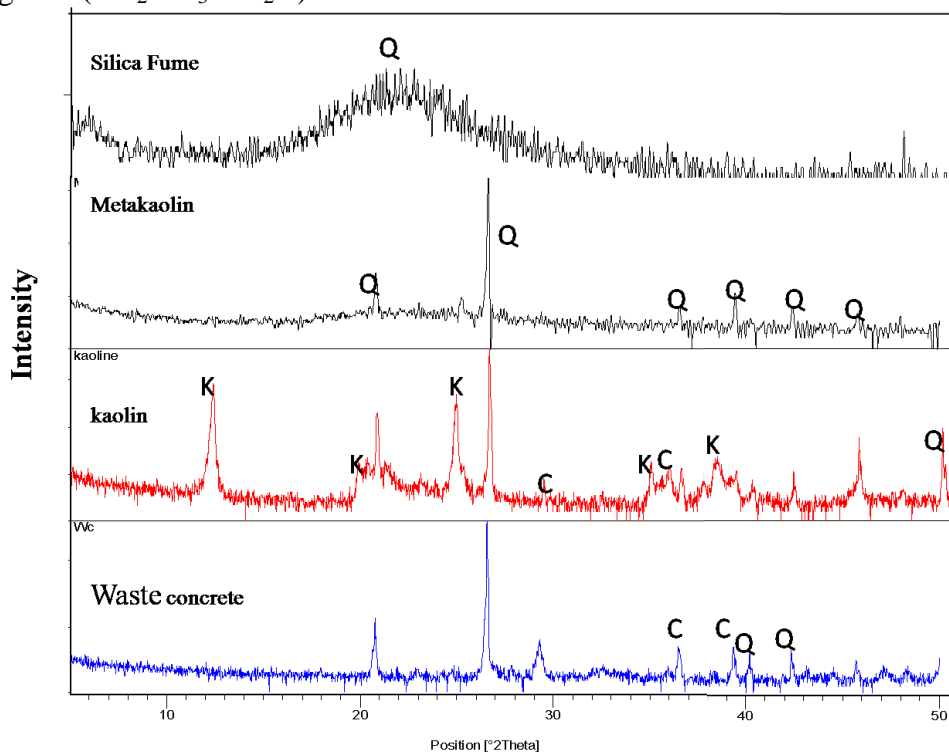


Fig. (2):XRD analysis of the used raw materials. [Q:Quartz, C:Calcite, K:Kaolin]

2.2. Synthesis and curing

Geopolymers were made by hand-mixing raw materials of each mixture, passing a sieve of 90 μm as represented in Table (2), with the alkaline activator solution and with the mixing water for 10 minutes followed by a further 5 minutes using rotary mixer and mixed at medium speed (80 rpm) for another 30 s; the mixture was allowed to rest for 90 s and then mixed for 1 min at high speed.

Table (2): Composition of the geopolymer mixes.(Mass, %)

Mix no.	Waste concrete (WC),%	Metakolin (Mk), %	Silica fume (SF), %
S0	50	50	0
S1	49	50	1
S3	47	50	3
S5	45	50	5
S7	43	50	7
S10	40	50	10

All investigations involved using of Na_2SiO_3 and NaOH in the ratio of 3:3wt. % of dry mixes, respectively; this ratio was chosen based on previous investigations [El-Sayed et al. (2011), Abd.El-Aziz (2010)]. Water-binder ratio (w/b) was 0.30 by mass. Paste mixtures were cast into $25 \times 25 \times 25$ mm cubic-shaped moulds and sealed with a lid to minimize any loss of evaporable water.

All mixes were left to cure undisturbed under ambient temperature (23°C) for 24hrs, demolded and then some specimens were left to be water cured under room temperature. At the end of the curing regime, the specimens were removed from their curing condition, dried well at 80°C for 24 hrs then exposed to compressive strength measurements and then the resulted crushed specimens were subjected to stopping of hydration process using stopping solution of methanol/acetone (1:1 by volume) followed by washing with acetone as recommended by different investigators [Saikia et al. (2004), Khater (2010)]; to prevent further hydration and for further analysis followed by drying of crushed specimens for 24 hours at 80°C , and then preserved in a well tight container until time of testing.

2.3. Methods of investigation

Chemical analysis was carried out using Axios (PW4400) WD-XRF Sequential Spectrometer (Panalytical, Netherland). $\text{Cu-K}\alpha$ source with a post sample $\text{K}\alpha$ filter. XRD patterns were collected from 0° to 50° 2θ (step size 0.02° 2θ and speed $0.4^\circ/\text{min}$). Silica quartz was used as an internal standard. Data were identified according to the XRD software (pdf-2: database on CD-Release 2005). Particle size analysis was done using Laser scattering particle size distribution Analyzer (Horiba LA-950). Stopping of the hydration was performed on crushed specimens by subjecting to stopping solution of alcohol/acetone (1:1) followed by washing with acetone as recommended by different investigators [Saikia et al. (2004), Khater (2010)]; to prevent further hydration. Micro-structure of the hardened activated specimens were studied using SEM Inspect S (FEI Company, Netherland) equipped with an energy dispersive X-ray analyzer (EDX). Bonding characteristics of alkali activated specimens were analyzed using Jasco-6100 Fourier transformed infrared spectrometer FTIR. The wave number was ranging from 400 to 4000 cm^{-1} [Panias et al. (2007)].

3. Results and discussion

XRD patterns of alkali activated geopolymer mix that made without silica fume and water cured from 1 up to 180 days is shown in Fig.(3).The patterns illustrate a broad band in the region of 6-

$10^{\circ}2\theta$ for aluminosilicate gel and broad bands in the region of $17-35^{\circ} 2\theta$ which characterize the glassy phase of the geopolymer constituents. These two regions are considered as a vital role in geopolymer characterization, where any increase in these regions will be reflected on the performance and efficiency of the geopolymer composition. An increase in the CSH content is also noticed with the increase of curing time as indicated from the increased broadness at 29.4° that results from interaction of free dissolved silica with Ca-species in the matrix forming CSH; which accumulate in the open pores and transformed into crystalline form at the later curing ages.

XRD patterns of alkali activated geopolymer mix containing various ratios of silica fume from 0 up to 10% as a partial replacement of the used waste concrete and water cured up to 180 days is shown in Fig. (4).

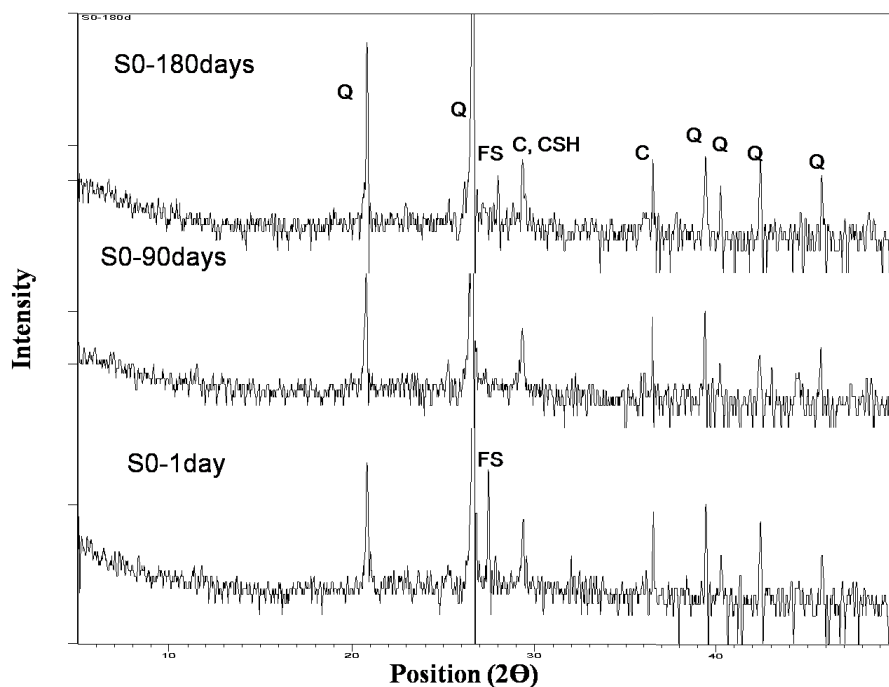


Fig. (3): XRD pattern of geopolymer mix without silica fume at different curing ages. [Q:Quartz, FS:Feldspar, C:Calcite, CSH: Calcium silicate hydrate]

The patterns illustrate the decreased calcite content up to 7 % SF, then increased again upon using 10 % SF, which is due to the ability of silica fume material with its higher specific surface area in interacting with dissolved calcium from waste concrete materials and forming CSH that positively affect geopolymerization process by forming nucleation centers for formation and accumulation of geopolymer. Increasing the silica fume content beyond 7% results in a negative effect by forming an agglomerates which concentrate in a small area and so hinder the formation of both CSH and geopolymer phases. It can also be noticed an increase of the broad band in the region of $6-10^{\circ}2\theta$ for aluminosilicate gel and broad bands in the region of $17-35^{\circ} 2\theta$ which characterize the glassy phase

of the geopolymer constituents by increasing silica fume content up to 7%, while decrease with the addition of 10 % SF.

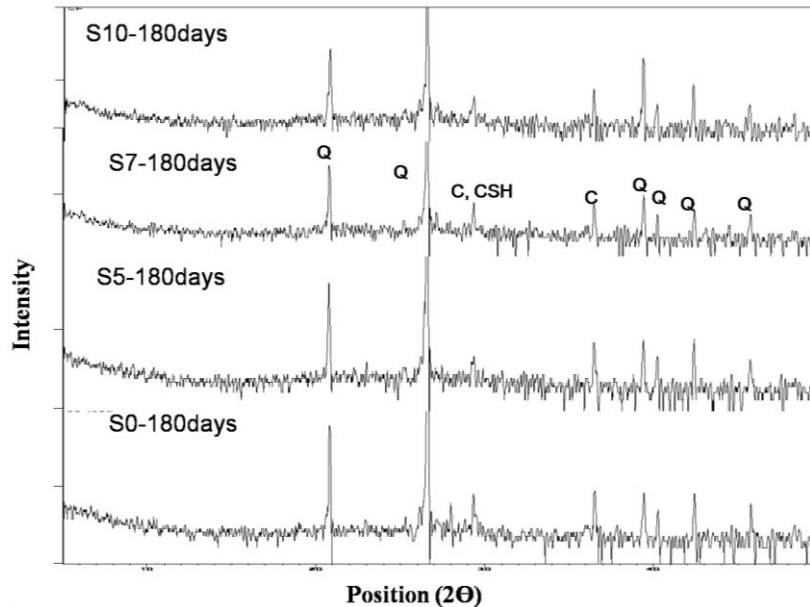


Fig. (4): XRD pattern of geopolymer mixes having various ratios of silica fume, water cured at 180 days. [Q:Quartz, C:Calcite, CSH: Calcium silicate hydrate]

Morphology and microstructure of 1 and 180 days water cured reference geopolymer specimens made without silica fume content are shown in Fig. (5). Evidently, Fig. (5a) shows the low contribution of Geopolymer constituents where most of the geopolymer are in the oligomer state after on day of hydration; the CSH phases are also appeared within the microstructure and bound most of the formed oligomer by forming nucleation sites for accumulation of geopolymer [Temuujin et al.(2009), Khater (2012)]. After 180 days of hydration, the oligomer condensation and precipitation of the formed geopolymer are clearly distinguished in Fig. (5b), where a crystalline plate of geopolymer constituents fill the pore forming a well compact and dense structure.

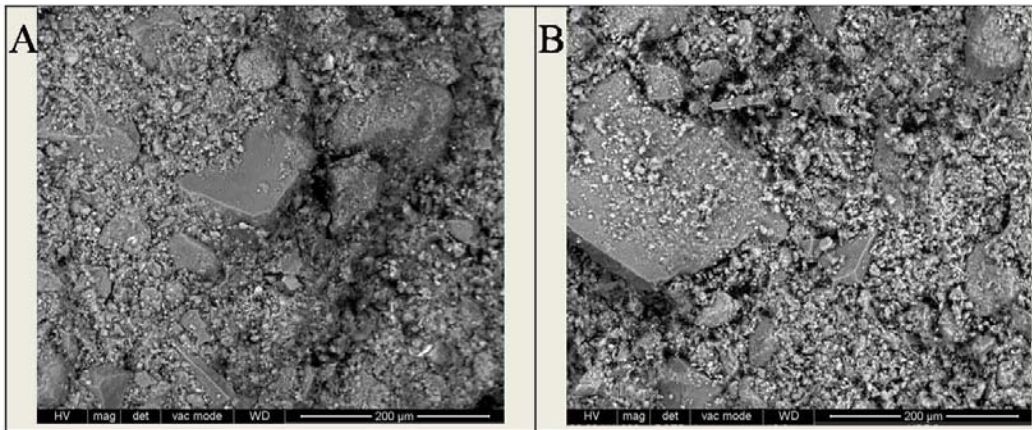


Fig. (5): SEM micrographs of hydrated Geopolymer mix made without silica fume, water cured at: (a) 1 day and (b) 180 days

Fig. 6 shows representative SEM micrographs of geopolymer binder containing 0, 5, 7 and 10 wt. % of silica fume after water cured up to 180 days. The micrograph of geopolymer mix made without silica fume displayed oligomer condensation and precipitation of the formed geopolymer (Fig. 6a), where crystalline plates of geopolymer constituents fill the pores forming a well compact and dense structure. Increasing silica fume to 5% results in an increase in the content of the formed CSH as most of liberated free lime are consumed by the added silica fume; this will be positively reflected on the morphology of the formed geopolymer leading to a well compact structure (Fig.6b).

Further addition of silica fume (7%) leads to a complete consumption of free hydrated lime and so leads to the coexistence of CSH(I) that has a CaO/SiO_2 ratio <1.5 with a fibrous structure and CSH (III) with a denser-almost spheres form with CaO/SiO_2 ratio <1.5 [Taylor (1992), Diamond(1986), Malhotra and Mehta(1996), Gleize et al. (2003)] as represented in (Fig.6c); these compact CSH phases results in an enhancement in the microstructure performance providing an additional strengthen to the sample specimens, in addition to its vital rule in the formation of additional nucleation or polymerization-condensation centers for precipitation of geopolymer as was indicated from the specimen morphology where a massive platy geopolymer layer fill mostly the matrix composition.

It should be noted that using a higher content of silica fume must be accompanied by adjustment of the water and superplasticizer dosage in the mix in order to ensure that specimens do not suffer excessive self desiccation and cracking. However, addition of 10% silica fume in this work did not include the addition of superplasticizer so lead to sample cracking and hinder the propagation of three dimensional geopolymer networks as indicated from the morphology of the formed geopolymer composition (Fig.6d); also, the increase of silica content leads to the formation of two dimensional cross-linked poly-sialate with rode like structure that produced as a result of the increase of Si/Al ratio more than 3 times, and known by lower mechanical and hardening properties as compared with three dimensional network that formed at $\text{Si/Al} = 1.5-2$ [Davidovits (1999)]. It can be noticed also the presence of small geopolymeric content which fill the pores with low conjunction with each other leading to low compaction of the formed geopolymer composite.

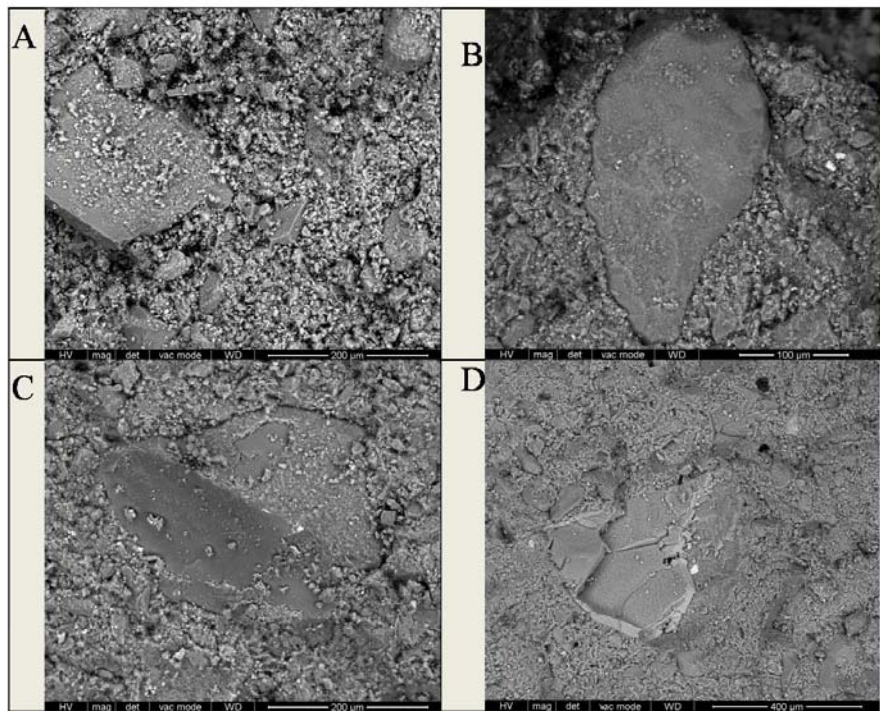


Fig. (6): SEM micrographs of hydrated geopolymer mixes containing different silica fume ratios, water cured at 180 days: (a) 0% SF, (b) 5% SF, (c) 7% SF and (d) 10% SF.

After 180 days of hydration, the FTIR spectra of geopolymer mix specimens containing various silica fume contents are shown in Fig. (7). Bands description are as follows: stretching vibration of O-H bond in the region $3429-2300\text{ cm}^{-1}$, bending vibration of (HOH) in the region of $1595-1628\text{ cm}^{-1}$, stretching vibration of CO_2 located at about 1430 cm^{-1} , asymmetric stretching vibration of (T-O-Si) at about $980-1100\text{ cm}^{-1}$ where T=Si or Al, Si-O stretching in the region of 880 cm^{-1} , symmetric stretching vibration (Si-O-Si) between $770-780\text{ cm}^{-1}$, symmetric stretching vibration of (Si-O-Si and Al-O-Si) in the region $675-685\text{ cm}^{-1}$ and bending vibration of (Si-O-Si and O-Si-O) in the region $450-460\text{ cm}^{-1}$.

The most characteristic difference observed between the FTIR spectra of geopolymer specimens made with various silica fume concerning bands attributed to the asymmetric stretching vibrations (T-O-Si) that increase in its intensity and broadness with silica fume addition up to 7%; while the pattern of 10% subjected to lowering in this band broadness. Bending vibration of (Si-O-Si) both appeared to be increase in sharpness with increasing silica fume up to 7% then slightly decrease with 10% silica fume content. Bending vibration band of (HOH) increases in broadness with silica fume addition up to 7% and decreases sharply with further increase of SF. The broadness of HOH band implying the overlap of more bands with higher intensity which is mainly related to the combined water in CSH and so the increase of this peak reflect the increase of binding materials of this specimen. This band decreases sharply with addition of 10% silica fume as a result of inclusion of added SF in the formation of two dimensional polysialatedisiloxo cross linked (which has a two

dimensional structure with low hardness than three dimensional one) than forming CSH which in turn acts as a seeding agent for geopolymer accumulation. The symmetric band of CO₂ located in FTIR spectra looks nearly similar for all specimens.

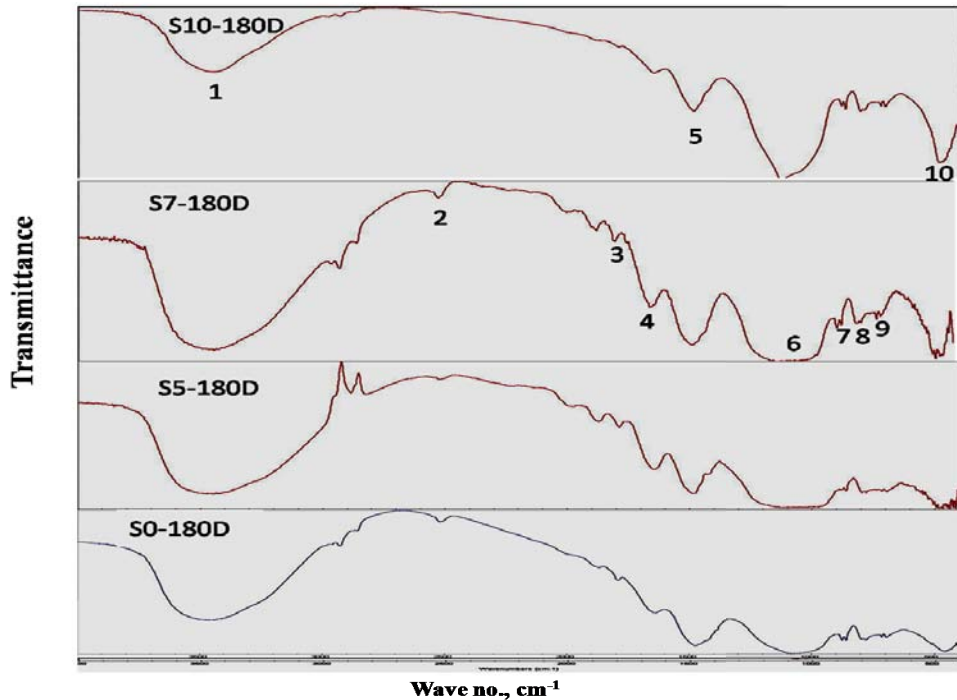
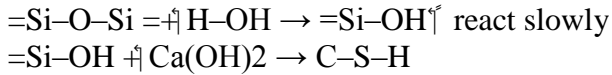


Figure (7): FTIR spectra of 180 days water cured geopolymer specimens having various ratio of silica fume. [1,2 : Stretching vibration of O-H bond, 3,4: Bending vibrations of (HOH), 5: Stretching vibration of CO₂, 6,7: Asymmetric stretching vibration (T-O-Si), 8: Symmetric stretching vibration of Si-O, 9:Symmetric stretching vibration (Si-O-Si and Al-O-Si), 10: Bending vibration (Si-O-Si and O-Si-O)]

Compressive strength values of hydrated geopolymer mixes containing different SF contents from 0 up to 10 wt.% as partial replacement of waste concrete at different curing times of 1, 7, 28 and 90 days at room temperature are shown in Fig. (8). Evidently, the compressive strength of mixes increases with the increase of curing time as a result of progressive hydration forming CSH as well as geopolymer formation leading to a fine and homogeneous structure. The results indicated also the increase of strength with increasing SF content up to 7%, then decreases up to 10%. The increase in strength with increasing SF up to 7% then decrease up to 10%. Strength increase with silica fume up to 7% is due to highly effective pozzolanic activity of silica fume which improve its properties like compressive strength, bond strength, and abrasion resistance. Also, silica fume is assumed to be as the reactant to produce secondary C-S-H by consuming calcium hydroxide. The decreased calcium hydroxide content of the cement matrix and increased amount of C-S-H gel together with filler effect of SF contribute to safeguarding of the matrix against external ingressive ions.

It is known that SF has many saturated bonds, =Si-O-Si=, and little unsaturated bonds at the surface, so the reaction mechanism of silica fume with hydrated lime is as follows:



However, it should be noted that using a higher content of silica fume more than 7% must be accompanied by adjustment of the mixing water and superplasticizer dosage of the mix in order to ensure that specimens do not suffer excessive self desiccation and cracking. But in this work, there is no superplasticizer used and the mixing water is in a constant ratio of 0.3% for better comparison of the reaction products. Otherwise, using this much quantities of silica fume could actually lower the strength of composites instead of improving it as indicated from the strength results.

On the other hand, there is a huge gap between the strength of mix that made without silica fume and that contains 7%SF where silica fume represents an enrichment source for amorphous silica and enhancing geopolymerization. It is known that mechanical properties and microstructure of geopolymer strongly depends on the initial Si/Al ratio. Better strength properties have been reported for mixtures with SiO₂/Al₂O₃ ratios in the range of 3.0–3.8. Changes in the SiO₂/Al₂O₃ ratio beyond this range usually result in low strength systems [De Silva et al. (2007)]. In spite geopolymer may be formed in the absence of alumina forming a homogeneous polysiloxo structure.

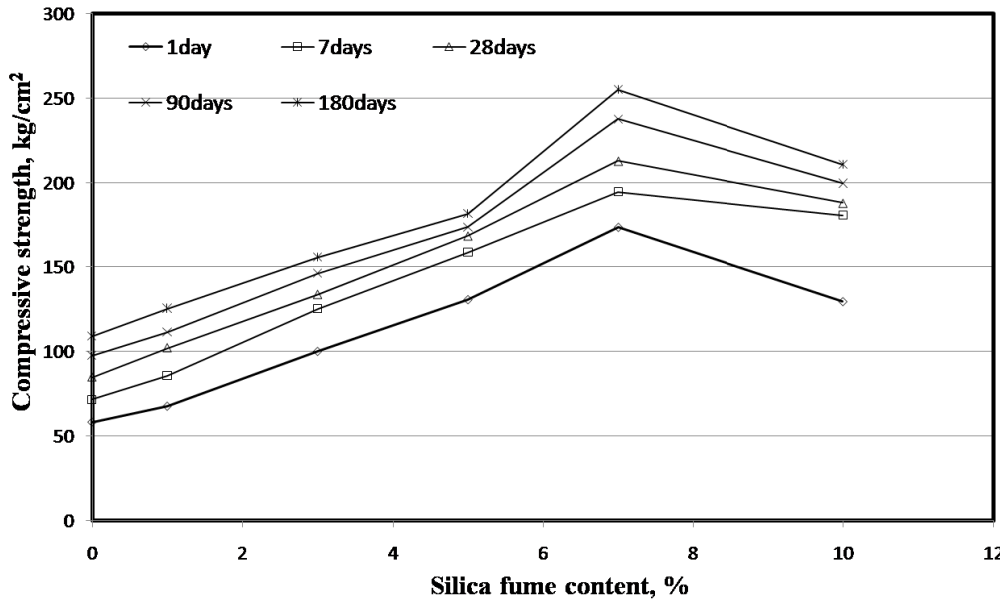


Fig. (8): Compressive strength of geopolymer mixes having various ratios of silica fume.

The trend of variation of compressive strength is in coincide with XRD data, FTIR spectrum and SEM observations, where the amorphous content of geopolymer materials increase with increasing SF content as it forms precipitation sites for geopolymer accumulation and precipitation when interacts with free lime in the medium forming CSH. Further increase in silica fume leads to insufficient wetting of the medium and hinder the propagation of geopolymer chains and so weaken its mechanical properties; in spite it exceeds that has no silica fume content as its higher pozzolanic activity leads to increase the formed CSH and hence possess higher mechanical and microstructural characteristics.

Water absorption of geopolymer mixes containing SF in the ratios from 0 up to 10 wt.% at different curing ages are shown in Fig. (9). Obviously, the results of Fig.(9) indicate the decrease of water absorption with the increase of curing time as a result of progressive hydration with the formation of CSH and geopolymer leading to more denser structure. Evidently, it decreases with increasing SF content up to 7% and then increases slightly up to 10%. The decrease of water absorption with increasing SF is due to the fact that when a material with high specific surface area is added to a mix specimen, it acts as a micro-filler of the matrix particles, which can reduce the amount of water that filled in the voids of the blending materials. However, replacing cement with a high specific surface material would increase the wettable surface area and the amount of water adsorbed. Thus, the final water requirement will depend on which of the two above-mentioned factors will be superior. With replacement of less than 7% in this paper, the former factor may be superior for SF. [30].

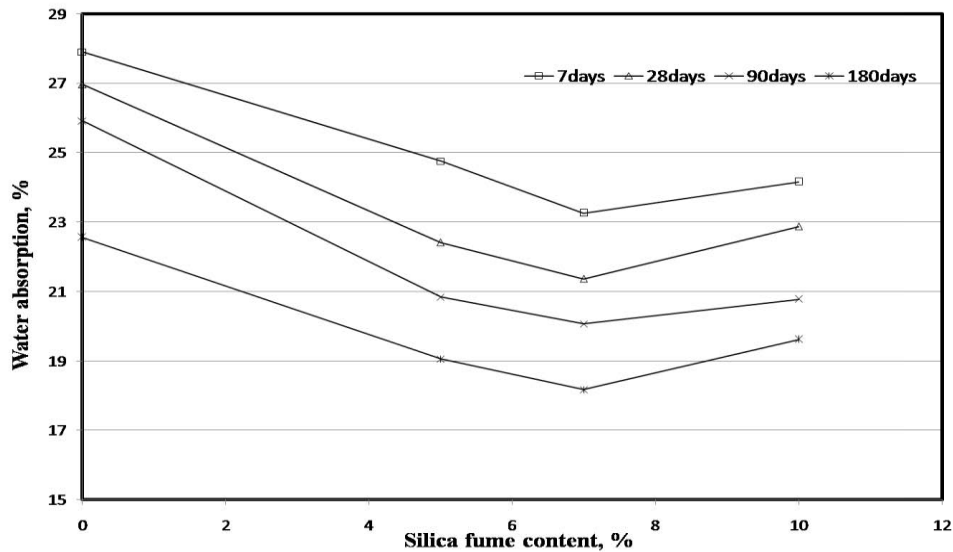


Fig.(9): Water Absorption of geopolymer mixes having various ratios of silica fume.

4-Conclusion

Alkaline activation of aluminosilicate wastes in the presence of silica fume and metakaolin using sodium hydroxide and sodium silicate in the ratio of 3:3 wt. % of the dry weight leads to the formation of an aluminosilicate geopolymer that possess an enhancement in both mechanical and microstructural properties. Silica fume addition is likely to result in the formation of nucleation CSH sites for precipitation of geopolymer product. Metakaolin inclusion improves greatly the geopolymeric structure. Silica fume addition up to 7% enhances greatly the geopolymerization process with the formation of well refined and compact matrix, while further increase of SF content leads to decrease in the mechanical characteristics of the reaction product. Alkaline activation of these aluminosilicate wastes can help in an ideal utilization of demolition wastes in disposal landfills all over the world and producing valuable sustainable materials that can be better applied in building industry.

5-References

1. **Abd.El-Aziz, H.**, (2010) "Physico-Chemical Studies of Alkali Activated Slag Pastes", Master Theses, Zagazig University, Zagazig, Egypt.
2. **Cheng-Yi, H.; Feldman, R.F.**, (1985) "Hydration reactions in Portland cement– silica fume blend", *Cem. Concr. Res.*; 15, 585–592.
3. **Cioffi, R.; Maffucci, L.; Santoro, L.**, (2003) "Optimization of geopolymer synthesis by calcinations and polycondensation of a kaolinitic residue", *Resources, Conservation and Recycling*, **40**, 27–38.
4. **Cohen, M.D.; Bentur, A.**, (1988) "Durability of Portland cement–silica fume pastes in magnesium sulfate and sodium sulfate solutions", *ACI Mater. J.* 85 (3), 148– 157.
5. **Davidovits J.** (1993) "Geopolymer cements to minimize carbon-dioxide green house warming", *Ceram Trans*, 37; 165–82.
6. **Davidovits, J.**, (1999) "Chemistry of Geopolymeric Systems Terminology" proceeding of, Second International Conference Geopolymer, 9-40.
7. **Davidovits, J.**, (1991) "Geopolymers: inorganic polymeric new materials", *J. Therm. Anal.*; 37, 1633–1656.
8. **De Silva, P.; Sagoe-Crenstil, K.; Sirivivatnanon, V.**, (2007) "Kinetics of geopolymerization: role of Al_2O_3 and SiO_2 ", *Cem Concr Res.*, 37(4), 512–8.
9. **Diamond, S.**, (1986) "The microstructures of cement paste in concrete". In: *Proceedings of the VIII Congress on Cement Chemistry*, Rio de Janeiro, Brazil, 122–47.
10. **El-Sayed, H.A.; Abo El-Enein, S.A.; Khater, H.M.; Hasanein, S.A.**, (2011) "Resistance of Alkali Activated Water Cooled Slag Geopolymer to Sulfate Attack", *Ceramics – Silikáty*, **55 (2)**, 153-160.
11. **Gautefall, O.**, (1986) "Effect of CSF on the diffusion of chloride through hardened cement paste", in: *Proceedings of the 2nd International Conference on the Use of Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete*, American Concrete Institute Publication SP-91, Madrid, Spain, 2,991– 998.
12. **Gleize, P.J.P.; Müller, A.; Roman, H.R.**, (2003) "Microstructural investigation of a silica fume–cement–lime mortar", *Cement & Concrete Composites*, 25, 171–175.
13. **Grutzeck, M.W.; Atkinson, Scott; Roy, Della M.**, (1983) "Mechanism of Hydration of Condensed Silica Fume in Calcium Hydroxide Solution, Fly Ash, Silica Fume, Slag and Other Mineral By-Products in Concrete", *American Concrete Institute Publication SP-79*, Detroit, 643– 665.
14. **Kakali, G.; Perraki, T.; Tsivilis, S. and Badogiannis E.**, (2001) "Thermal Treatment of Kaolin: The Effect of Mineralogy on The Pozzolanic Activity", *Applied Clay Science*, **20**, 73–80.
15. **Khater, H.M.**, (2010) "Influence of Metakaolin on Resistivity of Cement Mortar to Magnesium Chloride Solution", *Ceramics – Silikáty journal*, 54 (4); 325-333.
16. **Khater, H.M.**, (2012) "Calcium Effect on Geopolymerization of Alumino silicate Wastes", *J. Mater. Civ. Eng.*, 24(1), 92-102.
17. **Kohno, K.**, (1989) "Relative durability properties and strengths of materials containing finely grounded silica and silica fume", in: *Proceeding of the 3rd International Conference on the use of Fly Ash, silica fume, Slag and Natural Pozzolans in Concrete*, American Concrete Institute Publication SP-114, Trondheim, Norway, 2, 815–826.
18. **Lee, W.K.W.; Van Deventer, J.S.J.**, (2002) "Structural reorganisation of class F fly ash in alkaline silicate solutions", *Coll. Surf. A*; 211, 49– 66.
19. **Maage, M.**, (1989) "Efficiency factors for condensed silica fume in concrete", *Third Canmet/ACI Int. Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete*, Trondheim, Norway.
20. **Malhotra, V.M; Mehta, P.K.**, (1996) "Pozzolanic and cementitious materials", *Advances in concrete technology*, vol. 1. Ottawa, Canada: Overseas Publishers Association.
21. **Panias, D.; Giannopoulou, I.P.; Perraki, T.**, (2007) "Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers", *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **301**, 246–254.
22. **Phair, J.W.; Van Deventer, J.S.J.**, (2002) "Characterizations of fly-ash based geopolymeric binders activated with sodium aluminate", *Ind. Eng. Chem. Res.*; 41, 4242– 4251.

23. **Richardson, I.G.; Cabrera, J.G.**, “The nature of C–S–H in model slag cements” ,*Cem. Concr. Compos.*; 22 (2000); 259–266.
24. **Saikia, N.; Usami, A.; Kato, S.; Kojima, T.**, (2004) “Hydration behavior of ecocement in presence of metakolin”, *resource progressing journal*, 51(1), 35-41.
25. **Sellevoid, E.J.; Nilson, T.**, (1988) “Condensed Silica Fume in Concrete: A World Review”, *Tomas Telford Publications*, 165–246.
26. **Taylor, H.F.W.**, (1992) “Cement chemistry”. 2nd ed. London: Academic Press.
27. **Taylor, H.F.W.**, (1964) “The Chemistry of Cements”, 1; 1st ed., Academic Press, London.
28. **Temuujin, J.; Van Riessen, A.; Williams, R.**, (2009) “Influence of calcium compounds on the mechanical properties of fly ash geopolymer pastes”, *Journal of Hazardous Materials* **167**(1-3), 82-88.
29. **Van Jaarsveld, J.G.S.; Van Deventer, J.G.J.**, (a) (1999) “The effect of metal contaminants on the formation and properties of waste-based geopolymers”, *Cem. Concr. Res.*; 29 (8), 1189–1200.
30. **Van Jaarsveld, J.G.S.; Van Deventer, J.S.J.**, (b) (1999) “Effect of the alkali metal activator on the properties of fly ash-based geopolymers, *Ind. Eng. Chem. Res.*; 38, 3932– 3941.
31. **Wenying, G.; Guolin, W.; Jianda, W.; Ziyun, W.; Suhong, Y.**, (2008) “Preparation and Performance of Geopolymers”, *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, **23**(3).
32. **Yip, C.K.; Lukey, G.C.; van Deventer, J.S.J.**, (2005) “The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation”, *Cement and Concrete Research*; 35, 1688– 1697.