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Research Article

Nano Silica and Micro Silica Effect on Mechanical Attributes of Ferrochrome Slag Based Geopolymer

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ABSTRACT

Considering global trends in sustainable and green development as well as the major drawbacks of conventional hydraulic cement, accelerate attempt for finding a suitable alternative and likely cause further development of geopolymeric cements in future. Influences of Nano scale Materials in improving the mechanical properties of ordinary Portland cement have been obviously proved. Despite the widespread use of these materials in different fields of science, for instance, chemicals engineering, materials engineering and even ordinary Portland cement, the effect of Nano scale materials in geopolymers has not been investigated deservedly. The purpose of this study is creating bridges to mitigate these gaps and shortcomings. Very fine silica particles (micro and Nano-silica) effects in ferrochrome slag based geopolymer have been evaluated in this research. Elazığ ferrochrome slag was used as the main aluminosilicate source and then it was blended with Nano silica or silica fume in little amounts in order to accelerate geopolymerization. Nano-silica and silica fume have been used at 2,4,6,8 and 10% of total binder weight in this study due to probe fine silica effect on the mechanical specification of produced material such as compressive strength, Static modulus of elasticity, Tensile Strength and microstructural change. The experimental results show all of these mention mechanical properties have been improved with adding fine silica in geopolymer mixes in optimum percentage of total binder weight. The best percentage of fine silica partial replacement instead of FS is 6% at all of silica fume and three Nano particle size (15, 30 and 45 nm). SEM images assessment demonstrated homogenous and denser texture with acceptable chemical bonds improvements for samples with optimum Nano-silica dosage. Compressive strength increase can be explained by densification of the matrix texture by using of Nano-silica and silica fume at optimum dosage.

Keywords: Compressive strength; Geopolymer; Nano-silica; SEM; Splitting Tensile Strength

Nano ve Mikro Ölçekli Silis Malzemesinin Ferrokrom Cüruf Bazlı Geopolimerlerin Mekanik Özelliklerine Katkısı

ÖZET

Geleneksel çimentoların dezavantajları uluslararası sürdürülebilir ve yeşil kalkınma planları üzerinde yoğun talep yaşanmasına neden olmaktadır. Geopolimer malzemenin daha fazla geliştirilmesi veya alternatif malzemenin araştırılmasına dayalı çalışmaların gelecekte hızlanması beklenmektedir. Sıklıkla kullanılan Portland çimentosunun mekanik özelliklerinin geliştirilmesinde nano ölçekli malzemelerin katkısı literatürde kanıtlanmıştır. Nano ölçekli silika malzemeler, kimya ve malzeme mühendisliği gibi farklı bilim dallarında ve hatta sıradan Portland çimentosu üretiminde bile yoğun kullanılmasına ve araştırılmasına rağmen geopolimer üretiminde yeterince incelenmemiştir. Bu çalışmanın amacı bu konudaki boşlukları azaltmak ve önceden elde edilen bilgileri geopolimerler üzerine aktarmaktır. Bu çalışma esnasında nano ve mikro ölçekli silis malzemelerin ferrokrom cüruf bazlı geopolimerler üzerindeki etkisi değerlendirilmiştir. Elazığ ferrokrom cürufu alümino-silis kaynağı olarak bu çalışmada kullanılmıştır. Geopolimerleşme sürecini hızlandırmak için Nano-silis ve silis dumanı cüruf ağırlığının %2, %4, %6, %8 ve %10 oranlarında kullanılmıştır ve üretilen malzemelerin basınç ile çekme mukavemeti, elastisite modülü ve mikro yapısı üzerindeki etkisi incelenmiştir. Deney sonuçlarına göre,

geopolimer karışıma uygun miktarda ince silis malzemesinin eklenmesiyle malzemenin yukarıda bahsedilen mekanik özelliklerinde iyileşme meydana gelmiştir. Ferrokrom cüruf yerine farklı mikro ve nano boyutlarında (15, 30 ve 45 nm) silis kullanım oranı optimum %6 olarak belirlenmiştir. Numunelerde uygun değerde Nano-silis kullanımı, malzemenin kimyasal bağlarında iyileşme, homojen ve daha yoğun dokuya sahip olmasını sağlamıştır ve SEM görüntülerinde bu durum açıkça görülmektedir. Basınç mukavemetinin artışının, Nano-silis ve silis dumanının uygun değerde kullanılması sonucunda malzemenin dokusunun yoğunlaşmasından ve kimyasal bağlarının iyileşmesinden kaynaklandığı düşünülmektedir.

Anahtar Kelimeler: Basınç Dayanımı; Geopolimer; Nano-Silis; SEM; Yarmada Çekme Dayanımı

I. INTRODUCTION

In not so distant future, Building Engineering Society is required to implement the concepts of sustainable development. The most used building material in the world is concrete. It is also necessary to use conventional cement until finding the right alternative for ordinary Portland cement. Based on done evaluations, the annual cement production per capita is one ton. On the other hand, the production of cement leads to the production of carbon dioxide gas, which is the main greenhouse gas and 1-ton cement production produces 1-ton carbon dioxide gas. Also, according to researches, Five to eight percent of the world's carbon dioxide (CO_2) emissions are formed by cement factories [1]. It is clear that this amount of greenhouse gas does not match with the concepts of sustainable development. According to the Copenhagen deal, which its aim was to limit the temperature increase to less than two-centigrade degrees, we need to find a good alternative for ordinary Portland cement [2-5]. By reducing the production of carbon dioxide, this alternative will play a significant role in reducing the unpleasant global phenomenon.

Geopolymer cements due to their friendly environment nature and the fact that alkaline reactions are not considered in class that have significant danger for human being developed quickly. On the other hand, geopolymer binders have acceptable mechanical properties even in some cases they have more advantages than ordinary cement which stabilize its position as the most important alternative for ordinary Portland cements. Geopolymer binders have great properties that among them durability and resistant to fire and acids can be mentioned. Currently the main activity to reduce carbon dioxide in cement plant is to use pozzolanic additives in cements. Often For this purpose, plants pozzolanic by-products like fly ash, palm oil [6] ash and silica fume or natural pozzolans like perlite [7] and pumice [8-10] have been used. Mostly These pozzolanic materials are milled as large as cement fineness. Extensive researches have been done on cements made by addition of pozzolanic materials and materials that are rich of alumino-silicate. In spite of considerable benefits (advantages) of these types of cements, including reducing production costs, increasing durability and reducing produced greenhouse gases by Increasing the percentage of these pozzolanic materials in conventional cements mechanical strength of concrete and mortars made from these cement types have been reduced significantly. As a result, there are limitations in using of these materials in cement production [11].

In some research work, Nano materials have been used as pozzolanic additive particularly Nano scale pozzolanic materials that extract from industrial plant by products. In one of these studies, the use of Nano copper oxide with fly ash has increased the compressive strength of pozzolanic cements [12].

In recent decades, remarkable advancement has been made in natural and artificial pozzolan activation. The purpose of this new emerging research field is producing totally different binder with different mechanism and curing process, without any dependence on ordinary Portland cement, optimal use of inexpensive natural pozzolanics and industrial plant by product or waste by their activation. We can produce cement that has distinctive features from hydraulic cement.

The geopolymer name was chosen for this new cement product by Joseph Davidovits in 1970. Also, the application of the geopolymerization interpretation for causative reactions was invented by Davidovits

[4]. Indeed, the optimal use of waste and sometimes toxic is possible by this method. In addition to the environmental benefits, Financial Profitability of this kind of cement is predictable.

A. GENERAL REVIEW OF GEOPOLYMER MATERIAL

The structure of geopolymers is approximately the same as the structure of zeolites. As it is extracted from the name of geopolymer, the main atom in this type of polymer is silicon that found abundantly in the earth's crust. In this type of polymer, a network structure is formed of the bond between the atoms of oxygen and silicon and aluminium. And the main difference between geopolymers and zeolites is their amorphous texture because zeolites have mostly crystalline structures. At laboratory condition, geopolymers can gain enough strength in few hours at 85 °C curing temperatures this time can decrease for only few minutes by other methods that will mention. It is possible to use an autoclave or microwave to accelerate the geopolymerization process. The specific gravity of the geopolymers is about 1300-2100 kg/m^3. The principal factors that can be mentioned in geopolymer activation are specific surface of powdered grains, curing temperature and curing period. The most applicable method in activation is chemical activation method and usually NaOH or KOH are used as activator in this method. The use of water glass solution increases polymer length and also enhances the mechanical strength and properties of produced geopolymers. In the next section, the geopolymers producing mechanism will be described in details [13].

B. GEOPOLYMERIZATION PROCESS

Polymerization is in fact a set of chemical reactions in which small molecules produce large chain-shaped or three-dimensional macromolecules. And all of these reactions are also exothermic. According to some researchers, indeed, this material is zeolite but main distinctive feature of geopolymer and zeolit is their molecular structure. Geopolymers has amorphous or semi crystalline molecular structure inverse zeolites that have crystalline structure but their synthesis method is the same. The three main steps in these reactions can be summarized as follows:

- Solution o alumino silicates under the influence of an alkaline solution
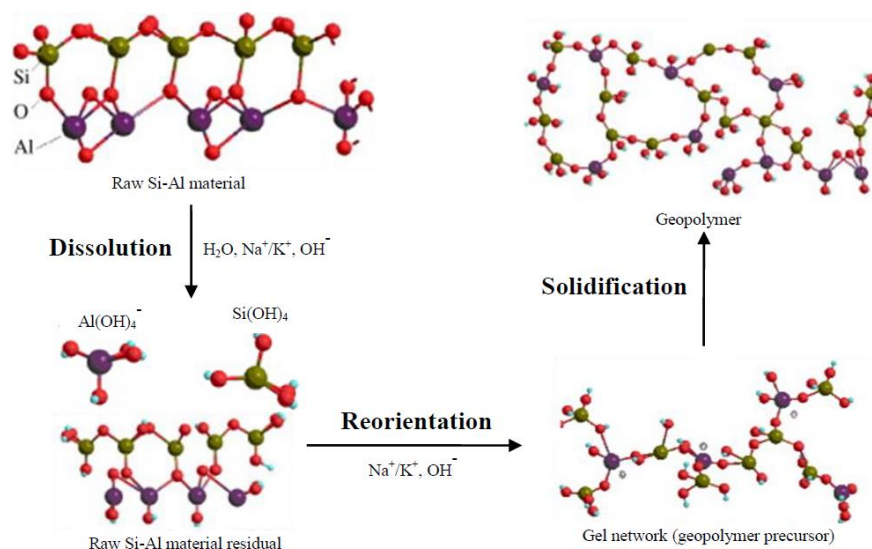- Reorientation
- Solidification

Figure 1. Schematic Sketch of typical geopolymerization [14]

In addition, heat is one of the most important factors and chemical reaction catalysts in geopolymerization [10, 15, 16].

C. A SUMMARY OF PREVIOUS RESEARCH ON NANO-MATERIALS

Usually materials that have geometric dimensions in Nano scale or a volume of materials that include Nano scale materials are called Nano-materials. Substances smaller than 100 nm are referred as Nano materials. Nano materials often have significant and excellent physical and chemical properties. In the case of using Nano materials in binders, they improve their mechanical properties, especially increase their compressive strength some of these materials used in scientific work are as follows Nano silica , Nano-aluminium oxide, Nano-Titanium Dioxide, Nano-Calcined Kaolin , Nano-Ferric oxide , Nano-Zinc peroxide and Nano-clay [17].

In several scientific researches carried out by the researchers, different methods for developing of mortar and concrete enhanced with Nano scale materials have been investigated. When the Nano-materials are mixed with cement particles, we can see blocking of free water. Because, Nano materials fill the gaps and empty spaces between cement particles and this feature is known as Nano-particles filler effect. Also, Nano particles exhibit better pozzolanic properties and show better performance in secondary C–S–H gel production they also improve and enhance the mechanical properties of the transitional region (The transition region is referred to the area between the mortars or concrete aggregates and the cementitious phase) and reduces the cracks in this region. In addition to the issues mentioned, Nano scale materials enhance the strength of existing chemical bonds. In a comparative manner, when nanoparticles and Nano scale materials have been used, the cementitious materials that produced from these materials exhibit characteristics quite distinct and different if compared with cementitious materials that using conventional fine materials. As mentioned, one of the most effective factors in the improvement of properties such as compressive strength, creep and contractions caused by shrinkage is the filler effect of Nano-scale materials. Nano filler can decrease gaps between matrixes. The fineness of Nano scale materials is one of the most influential factors in secondary C-S-H gel production, since specific surface of the material play a more colourful role in the pozzolanic reactions; we know the more specific area the more pozzolanic reaction.

The filling effect of Nano scale materials will produce homogeneous and denser gels, thereby improving the quality of geopolymers. In terms of hydration, materials with a nanoscale dimension have a better hydration rate. Increasing the C-S-H gels caused by the pozzolanic function causes a significant increase in compressive strength. Nanotechnology is one of the most modern methods for producing materials with enhancing mechanical properties. The mechanical properties and properties that are considered in the sustainable development and friendly environment can be improved by this method. Aly, M. et al In their research have mentioned to new nano material research papers and works and then they continue about the effect of clay with Nano scale on geopolymers thermal properties. According to the researches, there are still many deficiencies in the use of Nano scale materials in concrete and geopolymer mortars. Among the names listed for nano-materials, Nano silica is generally better known in terms of filler effect and pozzolanic properties also for increasing the hydration speed in ordinary cements it has been used extensively as additive in ordinary Portland cement. The impact of different parameters such as w/c ratio or the use of super plasticizers has been studied in some research works. And the best percentage for compressive strength gaining and durability by Nano-silica has been assessed approximately 9% [18].

We should also note that it is true that the performance and compressive strength of geopolymer is increased by using of Nano-silica and the cavities in the matrix are reduced, but because less workability the need for water and super plasticizers increases [19].

II. EXPERIMENTAL

A. MATERIALS

Because of the availability, the feasibility of using of slag in production of green construction material and decreasing environmental pollution of the plant waste Elazig Ferrochrome slag (FS) was utilized as precursor material in this study. The used slag was powdered in the mill and sieved on 63 μm. For determining the specific surface in this study, the Blaine method has been used, which according to this method, the used particles have a specific surface of 3960 cm^2/g.

The particles granulometry of powdered ferrochrome slag has been shown in Figure 2. FS was utilized as the principal pozzolanic source to generate geopolymer in this study. Because the common materials used as alkaline activators in producing geopolymer are sodium silicate solution and sodium hydroxide solution, these chemical materials have used in our work too.

The chemical mixture of FS, NaOH and Na2SiO3 solutions are presented in Table 1, Table 2 and Table 3, in order. To replace FS at different percentages, silica fume and Nano-silica have been used. In order to investigate the effect of Nano-silica particles, Nano-silica particles in different sizes of 15, 30 and 45 nm and micro size have been used in this study and their properties are shown in Table 4.

Due to desired flow ability and appropriate dispersion of Nano particles super plasticizer has been used. Properties of super plasticizer have been given in Table 5.
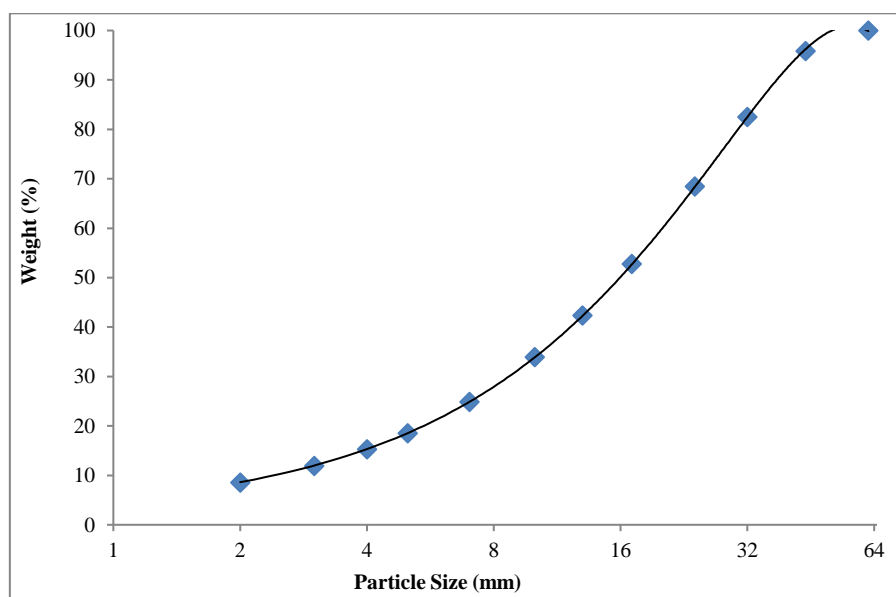

Figure 2. *Particles granulometry of powdered ferrochrome slag*

Table 1. *Specification of Elazığ ferrochrome furnace slag*

Chemical composition	PC (%)
SiO_2	33,80
Al_2O_3	25.48
Fe_2O_3	0,61
CaO	1,10
MgO	35,88
Cr_2O_3	2,12

Table 2. *Specification of sodium hydroxide (Physical and chemical)*

Chemical Formula	NaOH (wt %)	H₂O (wt %)	Appearance	Specific Gravity (20°C)
$NaOH \cdot xH_2O$	32-33	67-68	Gel	1,35

Table 3. *Specification of sodium silicate (Physical and chemical)*

Chemical Formula	SiO₂ (wt %)	Na₂O (wt %)	H₂O (wt %)	Visual Appearance	Density (20°C)
$Na_2O \cdot SiO_2 \, xH_2O$	22-24	11-12	64-67	Gel & Colourless	1,380-1,397

Table 4. *Properties of silica fume and Nano silica*

Chemical composition	(%)
SiO₂ (%)	99,7
Loss in ignition (%)	0,3
(Physical Properties)	(m^2/g)
*SSA of silica fume particle size of 15 nm	20
*SSA of Nanosilica particle size of 15 nm (m^2/g)	180
*SSA of Nanosilica particle size of 30 nm (m^2/g)	80
*SSA of Nanosilica particle size of 45 nm (m^2/g)	50

*specific surface area=SSA

Table 5. *Properties of super plasticeizer*

Density	1,023~1,063
Chlorine	<0,1%
color	green
Homogeneity Status	Homogenous
Chemical content	synthetic Polymer based

B. EXPERIMENTAL TECHNIQUES AND SAMPLE PREPARATION

For determining the principal mix design research, primer mix proportion of slag based geopolymer without silica fume and Nano-silica has been prepared and summarized as Table 6. The powdered slag was blended with an alkaline solution with three different L/S (Alkaline liquid/Slag) ratio which were 0,333 0,666, and 1.

Meantime, for alkaline activator preparation three alkaline solutions were prepared according to the Na_2SiO_3/NaOH solutions ratio i.e. 2,0 , 2,5, and 3,0. Alkaline solution and super plasticizer mixed at 300 rpm for approximately 1 minute. Then Ferrochrome slag was added and allowed mixing at 150 rpm for another 30 second. Then mixing has been continued for another 2 minute at high speed i.e. 300 rpm. Then the samples are casted into pre-prepared moulds. The surface of these moulds are lubricated with special mould oil to prevent possible reaction between moulding metal and geopolymer paste, as well as to facilitate the de-moulding samples without likely damaged.

The moulds that have been used in this study were cubic in size 50*50*50 mm^3. After casting the geopolymer paste into the moulds, these specimens are placed on vibration table for one minute in order to compact the samples completely. Due to prevent water evaporation of in the samples during curing process in the oven, the samples are covered with a thin film of polyethylene. Because of the exothermic nature of geopolymeric reactions, covering the samples by thin film is essential. After the samples were cured in the oven chamber under a 70 °C and 36 hours, samples de-moulded and polyethylene coating opened then they maintained at laboratory conditions until the age of 28 days and three samples of each mix have been selected for determining 3 days' compressive strength. After that, the samples are ready to be made under test to determine their mechanical properties such as compressive strength or tensile strength at 7, 28 and 90 days. After finding the best alkaline solution by compressive strength results this process can repeat by adding Nano silica and silica fume with a slight change in mixing process. Fine silica particles were blended with alkaline solution and super plasticizer at 300 rpm for approximately 1 minute. Then Ferrochrome slag was added and allowed mixing at 150 rpm for another 30 second. Then mixing has been continued for another 2 minute at high speed i.e. 300 rpm. The rest of the curing is similar to the previous one (without micro-silica and Nano-silica Additive). ASTM C109/C109M standard has been used for compressive strength test in this research. Average of Three samples has been used to estimate mechanical properties. The rate of increase in load has been 0,30 MPa/s for hydraulic press machine. Crushed parts after compressive strength have been evaluated in laboratory in terms of microstructure change SEM observations [18-20].

Table 6. Primer mix proportion of slag based geopolymer

Mix No	Liquid/Ferrochrome slag ratio	Na$_2$SiO$_3$/NaOH Solution ratio	Compressive strength (MPa)
1		2,0	32,20
2	0,333	2,5	38,15
3		3,0	43,92
4		2,0	18,18
5	0,666	2,5	26,12
6		3,0	31,82
7		2,0	15,00
8	1,000	2,5	15,92
9		3,0	17,18

For evaluating the effect of fine silica, a primary control mix is needed so initial mix designs with Liquid/binder ratio and Na2SiO3/NaOH parameters were designed as Table 6. These samples that were without fine silica were produced according to the stated method i.e. 2.2 and were subjected to compressive strength test by ASTM C109/C109M standard. Based on the results shown in the Table 6, the highest compressive strength of this initial mixing plan is 43.92 (MPa) related to third mix. Therefore the third mix was chosen as the main mixing plan for our research. The main parameters of this mixing plan are Liquid/Ferrochrome slag ratio and Na2SiO3/NaOH Solution ratio, which their values are 1/3 and 3 respectively. In the following the main subject i.e. Nano silica and micro silica effect on mechanical attributes of ferrochrome slag based geopolymer was investigated. For this purpose, one type of silica fume and three different types of Nano silica have been applied in this research. Specifications of silica fume and nano silica have been presented in Table 4. also, the percentages of fine particles are 2%, 4%, 6%, 8% and 10% . The main mix design for investigation of Nano silica and micro silica effect has been shown in Table.7.

Table 7. Mix proportions

Mix No	Liquid / (Ferrochrome slag+NS or MS) ratio	Ferrochrome slag (g)	NS	MS	Alkaline liquid (g)	Na_2Sio_3 solution (g)	NaoH solution (g)	Superplasticizer (g)
S	0,45	1000	0	0	430	322,5	107,5	20
SMS2	0,45	980	0	20	430	322,5	107,5	20
SMS4	0,45	960	0	40	430	322,5	107,5	20
SMS6	0,45	940	0	60	430	322,5	107,5	20
SMS8	0,45	920	0	80	430	322,5	107,5	20
SMS10	0,45	900	0	100	430	322,5	107,5	20
*SNS2	0,45	980	20	0	430	322,5	107,5	20
*SNS4	0,45	960	40	0	430	322,5	107,5	20
*SNS6	0,45	940	60	0	430	322,5	107,5	20
*SNS8	0,45	920	80	0	430	322,5	107,5	20
*SNS10	0,45	900	100	0	430	322,5	107,5	20

*In all samples Na_2Sio_3/NaoH=3
* Liquid/(Ferrochrome slag+NS or MS) ratio=0,43
*the mix design is similar for three Nano-silica particle size i.e. 15, 30, 45

B.1. Elastic Modulus

Knowledge of the elastic modulus is essential in the determination structures deflection of. As a rule in general, the higher elastic modulus shows the better concrete quality. Elastic modulus is usually divided in two: static and dynamic. Usually, the dynamic modulus is larger than the static modulus. Because the specimens are not affected by the creep [21]. The static modulus of elasticity is a property that expresses the ratio, within the elastic limit, between a certain range of unit stress and the corresponding strain or unit elongation. In this section, only the static modulus of elasticity will be studied and an attempt is made to provide information about traits of alkali activated ferrochrome slag. Specimens have been subjected to uniaxial compression and deformation has been measured. The samples dimensions are cubic $50\times50\times50$ mm^3 as defined previously, ASTM C469 i.e. has been used for determination of static modulus of elasticity in this research by using LVDT, similarly to author's previous work [7].

B.2. Tensile Strength

A main weakness of geopolymers and concrete is its low resistance to tensile stress. Different tests are applied to estimate the tensile strength. The three main tests used for this purpose are direct tension test, flexure test, and splitting tension test. In this section, the tensile strength is determined by the splitting cylinder test, which is most commonly used as indirect measure of tensile strength. The result will be discussed in this section. Typically, the most important parameters in the tensile strength are the materials contained in the mixing plan and their amounts. The curing method also has a significant impact on tensile strength [20, 22].

III. RESULTS and DISCUSSION

The results of 3, 7, 28, 90 days' compressive strength tests and 28 days' Static modulus of elasticity as well as 28 days' Splitting Tensile Strength has been presented in Table 8.

The 3 days' compressive strength of the sample without fine particles, i.e., micro-silica and Nano-silica is 18,95 MPa. The average values of compressive strength samples with micro-silica, Nano-silica15, Nano-silica30 and Nano-silica45 samples at 3 days' are 20,02 MPa, 25,06 MPa, 23,97 MPa and 24,93 MPa respectively, which are greater than 18,95 MPa (related to sample without fine particles). Therefore, it can be concluded that, in general, 3 days' compressive strength of samples increase by adding fine-silica. Among the samples with micro-silica, the best 3 days' compressive strength related

to sample by 6 percent silica-fume and its value is 20,93 MPa. The same as previous case, the Nano-silica15 samples have the highest 3 days' compressive strength for the sample with 6% Nano-silica and its values is 26,78 MPa. In Nano-silica30 and Nano-silica45 samples, the maximum values are 26,15 and 25,73 respectively, by percentages of 10 and 6 respectively. The highest increase is related to SNS6-15 sample with 41,31%.

In the case of a seven days' case, the compressive strength of the sample without fine particles is 30,92 MPa, which has the lowest compressive strength, compared with 20 other mix design. In other words, in all cases, the 7 days' compressive strength has been enhanced with the using of fine-silica. The maximum 7 days' compressive strength is related to SNS6-15 sample by 45,91 MPa. Similar to early ages i.e. 3 and 7 days, the best compressive strength of 28 and 90 days is related to the SNS6-15 specimens, which are 53,85 MPa and 53,90 MPa respectively. The 28 days' Static modulus and 28 days' Tensile Strength are also the highest for SNS6-15 mix sample. Obviously, the best mix design is for Nano-silica15 sample with optimal percentage of 6%. These results have been illustrated in Figure 3.

Table 8. Mechanical test Results for mixtures

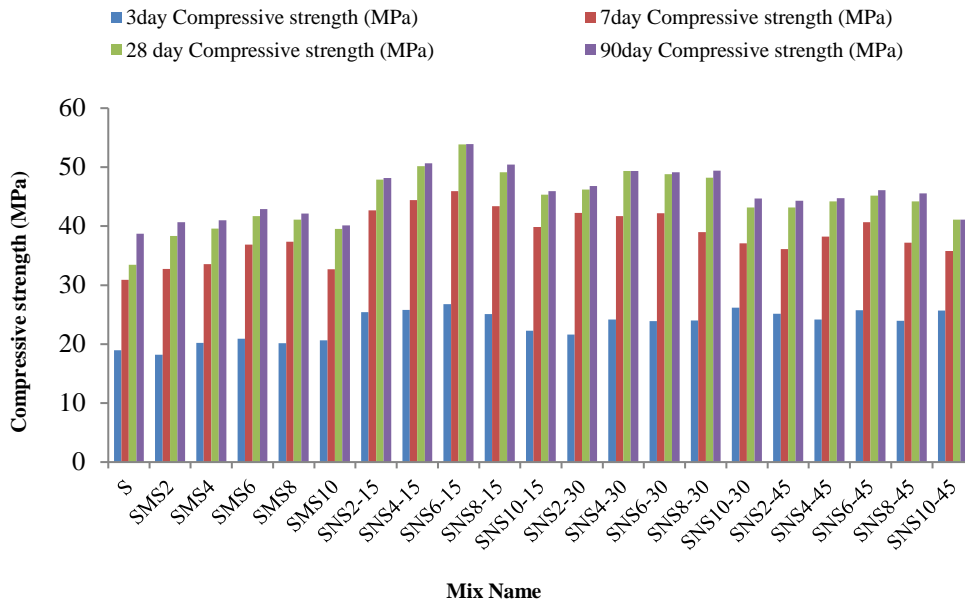| No	Mix No	3days Compressive strength (MPa)	7days Compressive strength (MPa)	28days Compressive strength (MPa)	90 days Compressive strength (MPa)	28days Static modulus of elasticity (GPa)	28days Splitting Tensile Strength (MPa)
1	S	18,95	30,92	33,43	38,70	30,20	2,41
2	SMS2	18,18	32,76	38,33	40,67	39,08	2,62
3	SMS4	20,20	33,55	39,60	40,98	31,98	2,82
4	SMS6	20,93	36,86	41,70	42,90	41,22	2,93
5	SMS8	20,17	37,36	41,12	42,15	34,78	2,89
6	SMS10	20,65	32,67	39,51	40,13	38,87	2,59
7	SNS2-15	25,41	42,68	47,89	48,16	44,00	3,11
8	SNS4-15	25,77	44,42	50,15	50,65	41,62	3,24
9	SNS6-15	26,78	45,91	53,85	53,90	46,24	3,67
10	SNS8-15	25,09	43,37	49,16	50,45	43,91	3,38
11	SNS10-15	22,26	39,87	45,35	45,93	38,17	3,15
12	SNS2-30	21,61	42,25	46,18	46,79	42,17	3,12
13	SNS4-30	24,18	41,71	49,36	49,37	41,06	3,40
14	SNS6-30	23,91	42,19	48,81	49,11	44,66	3,36
15	SNS8-30	24,01	39,00	48,19	49,43	42,22	3,32
16	SNS10-30	26,15	37,10	43,17	44,68	39,57	3,12
17	SNS2-45	25,15	36,12	43,17	44,28	38,87	2,85
18	SNS4-45	24,15	38,25	44,19	44,73	39,32	3,18
19	SNS6-45	25,73	40,68	45,18	46,11	40,04	3,14
20	SNS8-45	23,94	37,18	44,17	45,57	39,31	2,86
21	SNS10-45	25,69	35,76	41,10	41,12	36,38	2,79

Figure 3. Compressive strength results according mixtures age

According to Figure 4 for 28 days' compressive strength of specimens used in this study (in all fine-additive i.e. micro-silica, Nano-silica15, Nano-silica30, Nano-silica45), we have a steep slope increase in compressive strength, by adding two percent of the fine-particle. After that, for 4%, additive the compressive strength increases, but the slope of the increase is lower than the previous one. The maximum compressive strength is for SNS15-6 mix design. By increasing the amount of fine-additives to more than 6%, we see a decrease in compressive strength. According to Table 8, these results are similar to 3, 7 and 90 days' compressive strengths. Fineness increasing or fine particle increasing will increase the specific surface of these materials naturally. This will facilitate the chemical reactions of geopolymerization, but if these fine-particles increase from optimal amount, it will have a reverse effect, such as reducing compressive strength and deteriorating mechanical properties. Principal reason for this is excessive need for alkaline solution or water. In the absence of sufficient solution, the workability of the samples is greatly reduced and optimal blending will not be possible.

As a result, it will not be possible to obtain a homogeneous paste. On the other hand, if excessive alkaline solution use, an increase in the free unused sodium radicals will occur in the produced geopolymer. We know that sodium has strong interest in reaction with water and if it presents in hardened specimens, will reduce the durability and life of the produced geopolymer, and this will not be consistent with the concept of sustainable development which is important to us. In addition to the above mentioned, if water exceed the optimum amount after hardening of the specimen it will leave a lot of porosity in the specimens and porosities will reduce specific gravity, compressive strength and other mechanical properties of the product.

Maybe we can say that stiffness is the most important feature of solid mechanics and structural design. The modulus of elasticity depends on parameters such as impurities, non-homogeneity and existing chemical bonds in tested samples. Additionally, compressive strength and elastic modulus are closely related and increasing the compressive strength increases the elastic modulus.
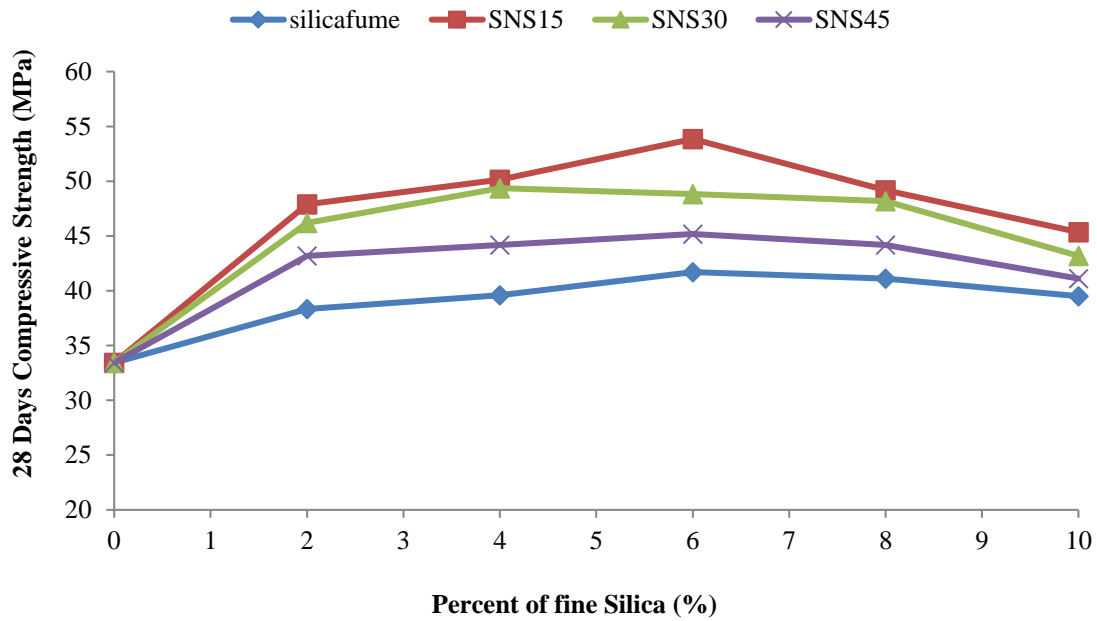
Figure 4. *Relationship between percent of powdered silica with 28 days' compressive strength*

As is deduced from the Figure 5, the highest modulus of elasticity is related with Nano-silica15 and by optimal percentage of 6%. In the other three samples, the best percentage for high modulus of elasticity is 6% too. According to the results of Table 8 and Figure 5, the modulus of elasticity associated with four fine samples are 41,22, 46,24, 44,66, and 40,04 GPa for Silica-fume, Nano-silica15, Nano-silica30, Nano-silica45 respectively. Obviously compressive strengths related to these samples are also considerable. In the case of establishment of regression relationship between them, as shown in Figure 5 an almost strong relationship is seen and its coefficient of determination is $R^2=0,727$.
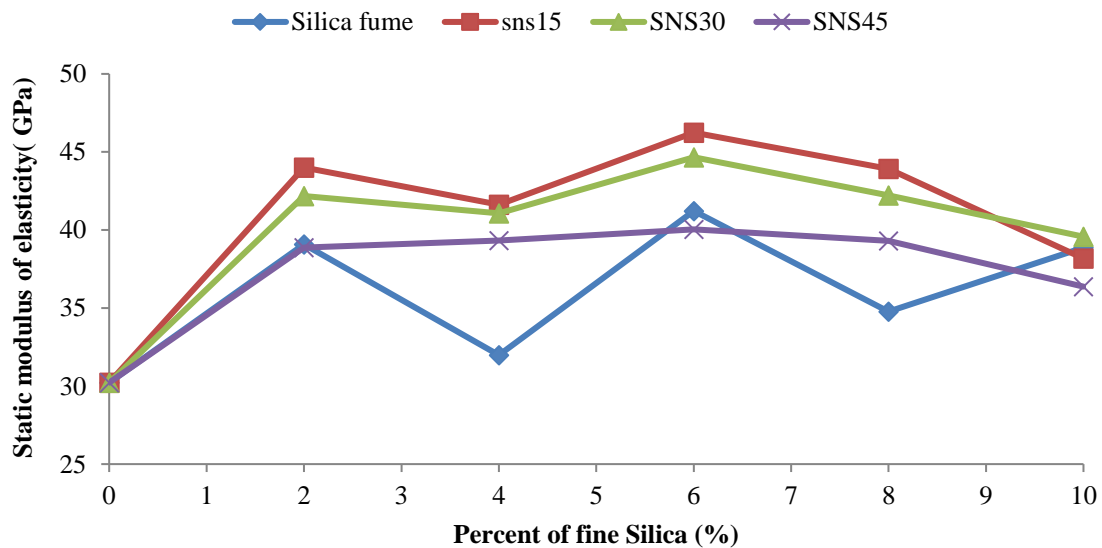

Figure 5. *Relationship between percent of powdered silica with static modulus of elasticity*
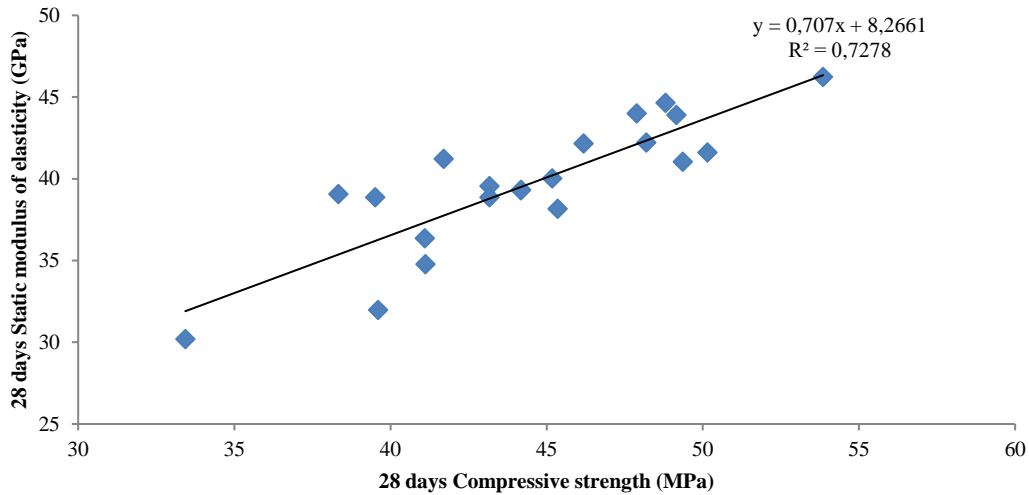
357

Figure 6. *Regression Relationship between compressive strength (MPa) and Static modulus of elasticity for all geopolymer samples at 28 days*

As shown in Figure 7, with an increase in fine materials until 4% the tensile strength of the samples also increases in all mixes. The highest tensile strength is related to Nano-silica15 with 6% fine Nano-silica. For percentage more than 6 percent, the tensile strength decreases with increasing fine particles. Perhaps the reason is the reduction in the homogeneity of geopolymer paste. The reason for the heterogeneity is the lack of water, which also reduces the workability of the geopolymer paste. In addition and this water deficiency reduces geopolymerization reactions. In the case of establishment regression relationship between tensile strength and compressive strength as Figure8 an excellent relationship is seen between them and its coefficient of determination is $R^2=0,90$. In other words, in geopolymers with fine silica additives in their mix design, it is possible to predict tensile strength of geopolymers by compressive strength without need for destructive test by 90% accuracy. This result is similar to results concluded from fly ash based geopolymer [23].
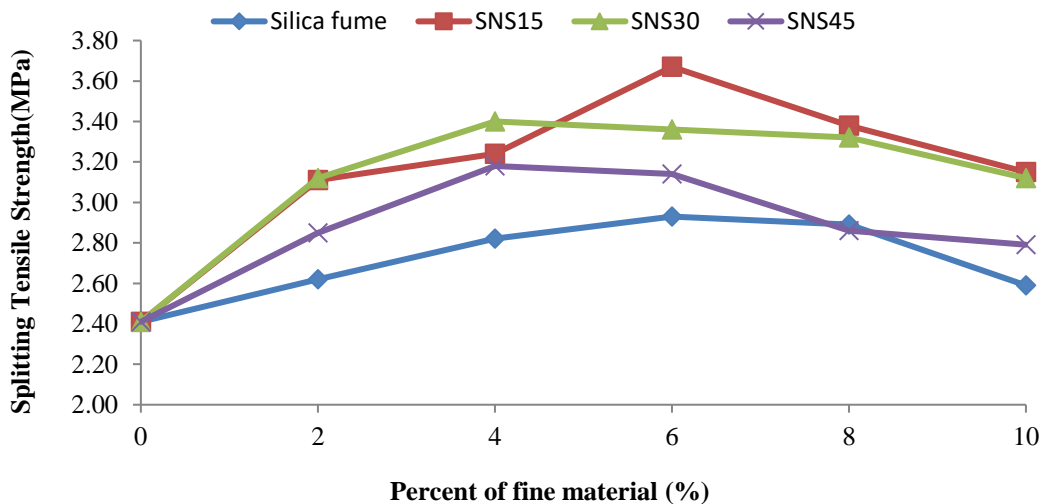

Figure 7. *Relationship between percent of powdered silica with splitting tensile strength*
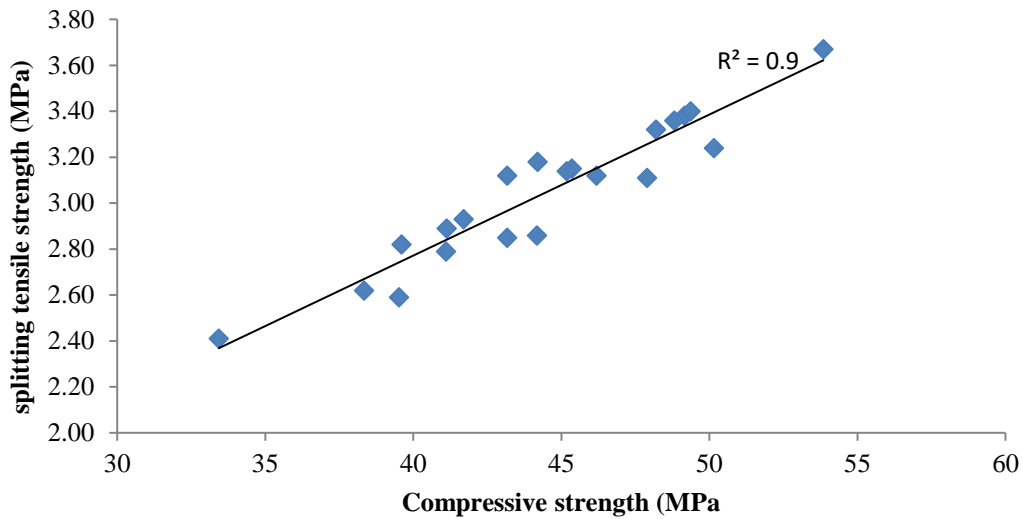
Figure 8. Regression between splitting tensile strength and compressive strength of all geopolymer samples

In Figure 9, in all mix samples, the evolution of strength gaining in produced geopolymers can be seen. The initial steep gradient in the graph on the first seven days shows the immense importance of these seven days in gaining compressive strength. After seven days, the strength gaining process continues with a moderate slope. After 28 days, the increase amount in compressive strength will no longer be significant and there will be very few incremental changes. Therefore, it can be said that in geopolymers, similarly to conventional concrete, 28-day compressive strength can be used as a criterion in structural design. This result is consistent with author previous work [8].
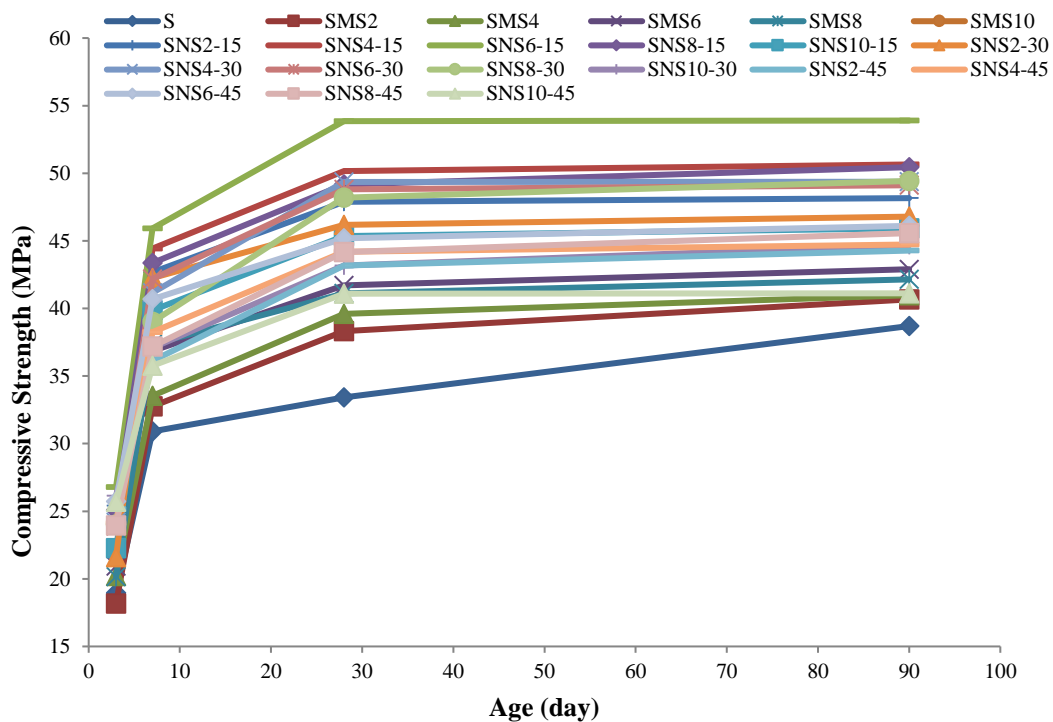

Figure 9. Relation between Compressive strength and samples age

A. FINE PARTICLES EFFECT ON GEOPOLYMER MICROSTRUCTURE

A.1. SEM Analyses

To evaluate fine particles effect on the microstructure of produced geopolymers, a sample that has the highest compressive strength from each fine particle groups has been selected and has been assessed by SEM. It is observed that in all samples empty spaces, holes and cracks are much lower by using of fine particles and Samples are more homogeneous and denser similar to Khater work [24]. Due to the more mechanical strengths of the samples, it can be deduced that likely the fine silica's have a good filler effect and have filled well free space between the produced gels in the geopolymer matrix. In addition to the item mentioned because the higher specific surface and higher fineness, these fine materials are more likely to participate in alkali activation chemical reactions and produce more bonds, thus improving the mechanical properties of the produced geopolymer.
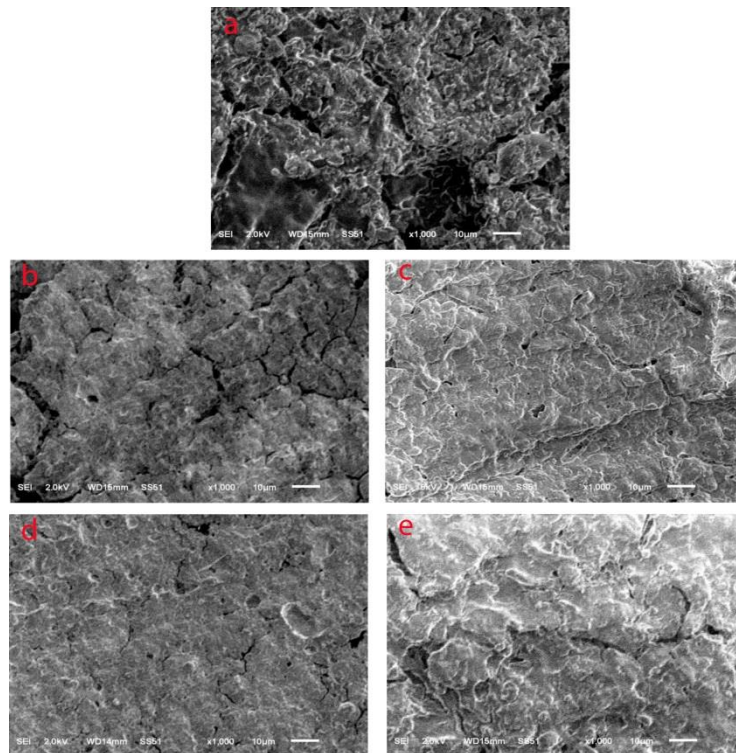

Figure 10. *SEM images samples (a) without Nano or micro-silica (b) with silica fume (c) Sample with Nano silica15 (d) Sample with Nano-silica30 (e) Sample with Nano-silica45*

We can see geopolymer precursor in Figure 10(a) for sample without fine silica. Similarly cracks and cavities are seen for geopolymer with silica fume in Figure 10(b). As can be seen in Figure 10(c,d,e) , the samples with nano-silica are much denser and have fewer cracks. In addition the width of the cracks in samples with nano silica is smaller than other samples (samples without Nano or micro-silica and samples with micro-silica) Figure 10(d). In the specified ellipsoid part in Figure 10(c,e) we can see much denser geopolymer matrix.

IV. CONCLUSIONS

This work reports fine silica influence on the most important mechanical properties of geopolymer i.e. Compressive strength, aging and tensile strength and try to find optimum size and optimum replacement content of silica fume or Nano silica replacement instead of ferrochrome slag. The most important results extracted from this research can be summarized as follows:

1. Silica fume and Nano-silica have significant effect on improving and enhancing the mechanical specification of geopolymers than silica fume.
2. Silica fume and Nano-silica can be applied as an additive in geopolymer and hybrid cements. These particles can fill empty spaces between cement particles and can reduce the cracks in the transition region. For this reason; they can increase the samples compressive strength and improve the mechanical attributes. In addition, Nano silica can accelerate chemical reactions due to their high specific surface area (in the vicinity of ordinary Portland cement or without cement.)
3. According to the results of the study, from three Nano particle size (15, 30 and 45 nm) and silica fume, the best results are related for a 15 nm sample. The reason for reducing the compressive strength for samples by 15 nanometres particle size more than 6% is inhomogeneous particle distribution and particles agglomeration.
4. The best percentage of Nano silica partial replacement instead of FS is 6% at all of silica fume and three Nano particle size (15, 30 and 45 nm).
5. The results of the SEM analysis confirm a denser and homogeneous microstructure for Nano silica samples. This result justifies the high compressive strength of these specimens.
6. In almost all specimens, the rate of increase in compressive strength is high in the early days, but this increase rate is not perceptible after 28 days.

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