

# Effect of Nano-Silica on Alkali Activated Water-Cooled Slag Geopolymer

<sup>1</sup>H.M.Khater, <sup>2</sup>B.A.El-Sabbagh, <sup>3</sup>M.Fanny, <sup>4</sup>M.Ezzat, <sup>5</sup>M.Lottfy

Housing and Building National Research Centre (HBNRC)  
87 El-Tahrir St., Dokki, Giza, P.O. Box 1770 Cairo

<sup>1</sup>Email: [Hkhater4@yahoo.com](mailto:Hkhater4@yahoo.com)

## ABSTRACT

Ground granulated blast furnace slag is a finely ground, rapidly chilled aluminosilicate melt material separated from molten iron in the blast furnace as a by-product. Rapid cooling results in an amorphous or a glassy phase known as GGBFS or water-cooled slag (WCS). Alkaline activation of latent hydraulic WCS by 6% sodium hydroxide was studied. Nano silica is an ultrafine material that can modify mechanical, microstructural and thermal properties of geopolymer products and added to the geopolymer mix in the ratio of 0, 0.50, 1 and 1.5% of the dry weight. Curing was performed under 100% relative humidity and at a temperature of 38°C. Gelenium Ace super-plasticizer was added in the ratio of 4% from the dry weight to ensure best dispersion of the nano silica. The results showed that increasing in the percentage of nano silica results in enhancement in the mechanical properties as compared to the control mix up to 90 days. The study of thermal properties is taken place for the different ratios by experimental and mathematical evaluation. The study showed that the thermal properties as well as thermal insulation property are improved with the increase of ratio of nano silica.

**Keywords:** *Nano-silica, Geopolymer, Slag, Microstructure, Thermal properties.*

## 1. INTRODUCTION

Geopolymers are inorganic polymeric materials, firstly developed by **Joseph Davidovits** in 1970s. Geopolymerization involves a chemical reaction between aluminosilicate oxides and alkali metal silicate solutions under highly alkaline conditions yielding amorphous to semi-crystalline three-dimensional polymeric structures, which consist of Si–O–Al bonds [1], and gave a fresh insight into this class of inorganic polymer.

Geopolymerization is being considered for replacing traditional structural materials and offers a possible solution to the immobilization of toxic and radioactive wastes as well as the treatment of industrial wastes to produce value added construction materials. Therefore, there is an increasing need for multiple source materials to be jointly geopolymerised to maximally exploit the respective properties of the individual sources regarding compressive strength, stability and durability [2].

Geopolymer can be thought of as a new generation binder as a substitute for the calcium silicate hydrate which are essential components of Portland cement. Ordinary Portland Cement (OPC) is the main ingredient used in the production of concrete-the most widely used construction material in the world. In the past, concrete was simply a composite of OPC paste

with aggregates, however, modern-day concrete incorporates other cementitious materials, which act as partial replacements of OPC. The manufacturing of OPC requires the burning of large quantities of fuel, and decomposition of limestone. Both, burning of fuel and decomposition of limestone, result in significant emissions of carbon dioxide. For every ton of OPC manufactured, nearly one ton of CO<sub>2</sub> is produced depending on the production process adopted [3]. Cement plants are reported to emit up to 1.5 billion tons of CO<sub>2</sub> into the atmosphere annually [4,5]. Hence, environmental preservation has become a driving force behind the search for new sustainable and environmentally friendly composites to replace conventional concrete produced from OPC.

In 1978, **Davidovits** [6] introduced the word 'geopolymer' to describe an alternative cementitious material, which has ceramic-like properties. As opposed to OPC, the manufacture of aluminosilicate-based geopolymer does not consume high levels of energy, as water cooled slag (WCS), known also as ground granulated blast furnace slag, is already an industrial by-product. This geopolymer technology has the potential to reduce emissions by 80% [3] because high temperature calcining is not required. It also exhibits ceramic-like properties with superior resistance to fire at elevated temperatures. Geopolymer can be produced by combining a pozzolanic compound or aluminosilicate source material with highly alkaline solutions [7].

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During the period of the second half of the previous century, the terms "nano-science" and "nano-technology" were not yet familiarly used as today, however they were really practiced and successfully applied to the progress in the field of material science and technology. Concrete performance is strongly dependent on nano-size dimensions of solid material such as C-S-H particles or voids such as the gel porosity in the cement matrix and the transition zone at the interface of cement paste with aggregate or steel reinforcement, typical properties affected by nano-sized particles are strength, durability, shrinkage and steel-bond. The word nano means anything of size  $10^{-9}$ , nanoparticles is a solid particle of having size in the range 1 to 100 nm.

The use of nano-particles in cement and concrete can lead to improvements in the nanostructure of building materials [8]. Nano-materials show unique physical and chemical properties that can lead to the development of more effective materials than ones which are currently available [9]. The extremely fine size of nano-particles yields favorable characteristics. Nano-particles are unique because their size affects the behavior of cement. **Ginebara et al.** [10] reported that the particle size can greatly affect the hydration kinetics of cement. Ultra small magnetic ferrite nano particles (diameter smaller than 15 nm) have a convenient size to be dispersed in a liquid carrier and provide a colloidal solution known as magnetic fluid (or Ferro fluid). Such solution, which having both the fluid and magnetic properties, may lead to numerous industrial applications [11]. Several studies were performed concerning with applications of nanotechnology and nano materials in Construction [12-18].

**Wen-Y Kuo et al.**, shown that the compressive and flexural strengths of cement mortars enhanced with  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  nano-particles [19]. It was found that the nano-particles which dispersed uniformly in a cement paste will accelerate cement hydration due to their high activity [20]. Additionally, the nano-particles will fill pores leading to increase strength and improve the microstructure of cement and the interface between the cement paste and aggregates in concrete. It was also found that nano- $\text{Fe}_2\text{O}_3$  exhibits a self-sensing of strain capability which can be useful for structural health monitoring [21]. The solid solution between Al-ettringite and Fe-ettringite  $[\text{Ca}_6[\text{Al}_{1-x}\text{Fe}_x(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}]$  was investigated [22]. Complex susceptibility of magento-fluids together with the optical band gap and surface property of the nano magnetite based particles were described in an earlier paper [23].

The main purpose of this work is the preparation of geopolymer materials by alkaline activation of amorphous water cooled slag materials. The other target is to investigate the effect of addition of different ratios of nano silica on alkali with activated cooled water slag and study its impacts on mechanical and microstructural characteristics. X-ray diffraction and SEM are used for scanning and analysis of the composite structure of nano geopolymers. While, the compressive strength measurement was used to evaluate the mechanical performance of the geopolymer mixes. Thermal properties are also used to evaluate the geopolymer characterization compared with the plain mix that without nano silica.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 Materials

The materials used in this investigation is water cooled slag or what is known as ground granulate blast furnace slag (GGBFS) sourced from Iron and Steel Factory- Helwan, Egypt; its chemical composition is illustrated in Table (1). Sodium hydroxide (NaOH) is produced by SHIDO Company with purity 99 % is used as alkali activator. Nano silica used is 99.9%  $\text{SiO}_2$ , a particle size of 8-18 nm, and  $60\text{m}^2/\text{g}$  Blaine fineness. The chemical composition of the starting raw materials was illustrated in Table (1).

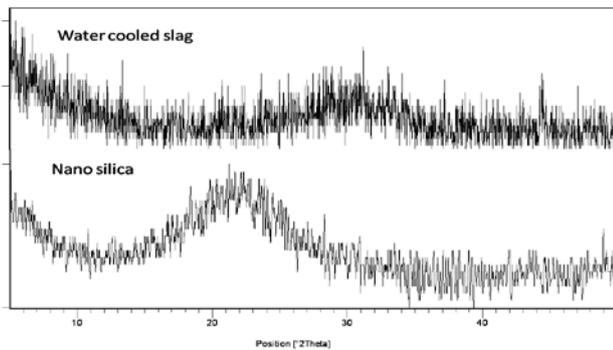
**Table(1):** Chemical composition of water cooled slag (ggbfs).(Mass,%)

Oxide Content (%)	Water – Cooled Slag (GGBFS)
$\text{SiO}_2$	35.16
$\text{Al}_2\text{O}_3$	15.68
$\text{Fe}_2\text{O}_3$	0.52
CaO	37.25
MgO	7.25
$\text{SO}_3$	1.34
$\text{K}_2\text{O}$	1.23
$\text{Na}_2\text{O}$	1.35
$\text{TiO}_2$	0.03
$\text{MnO}_2$	0.02
$\text{P}_2\text{O}_5$	0.02
Cl-	0.05
LOT	0.00
Total	99.89

Mineralogical characterization was done using X-ray diffraction analysis as represented in Figure(1). The pattern showed that water cooled slag composes

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mainly of amorphous materials, while Nano-silica composed of amorphous silica as represented in **Fig.(1)**



**Fig.(1):** X-Ray diffraction pattern of the used raw materials.

## 2.2 Synthesis of Nano- Silica

Silica nanoparticles are synthesized by using a standard procedure with experimental conditions. A quantity of 5 ml of TEOS (Tetra Ethyl Ortho Silicate) was first dissolved in 30 ml of absolute ethanol under low frequency ultrasound at room temperature for 10 min. Then 1 ml of distilled water was dropped into the reaction media with the feed rate  $0.2 \text{ ml}\cdot\text{min}^{-1}$ , to facilitate hydrolysis of TEOS in the ultrasonic bath. After 1.5 h, 2 ml of ammonia (catalyst) was fed into the reaction mixture at feed rate of  $0.01 \text{ ml}\cdot\text{min}^{-1}$ . Sonification was continued for 3 hrs. Gelation was allowed for 1 hour. The gel was centrifuged at for 397 min with a speed of 6.000 rpm, washed with ethanol and distilled water and dried using vacuum dryer for overnight.

## 2.3 Geopolymerization and curing

Geopolymer was made by hand-mixing raw materials of each mixture passing a sieve of  $90 \mu\text{m}$  with the alkaline solution for 10 min. and a further 5 min. with a mixer. All investigations involved using 6% NaOH of dry mixes based on previous investigation [24].

The water-binder material ratio (w/b) was about 0.27 by mass. Nano silica was added to the binding material (Blast furnace slag) in small quantities 0, 0.5 and 1.5 %, mixed well with part of the total water using a magnetic stirrer, the other part of water is mixed with the 6 % alkali activator (NaOH) then it is added to the binding material in the mixer followed by the deflocculated Nano-silica and finally 4 % super plasticizer (Gelenium Ace) is added to the mix. Paste mixture were cast into  $25\times 25\times 25 \text{ mm}$  cubic-shaped moulds, vibrated for compaction and sealed with a lid to minimize any loss of evaporable water.

All mixes were left to cure undisturbed under ambient temperature for 24 hour, and then subjected to curing temperature of  $38^\circ\text{C}$  with a 100 % relative humidity. At the end of the curing regime, the specimens were subjected to the compressive strength measurements and then the resulted crushed specimens were subjected to stopping of the hydration process using solution of alcohol/acetone (1:1), followed by washing with acetone as recommended by **Saikia et al. [25]** in order to prevent further hydration and for further analysis and followed by drying of the crushed specimens for 24 hours at  $80^\circ\text{C}$  and then preserved in a well tight container until the time of testing.

## 2.4 Methods of investigation

Chemical analysis was carried out using Axios, WD-XRF Sequential Spectrometer (Panalytical, Netherland, 2009). Compressive strength tests were carried out using five tones German Brüf pressing machine with a loading rate of  $100\text{kg}/\text{min}$  determined according to **ASTM-C109-07[26]**. The XRD analysis was carried out using a Philips PW3050/60 Diffractometer. The data were identified according to the XRD software. The microstructure of the hardened alkali activated water cooled slag was studied using SEM Inspect S (FEI Company, Netherland) equipped with an energy dispersive X-ray analyzer (EDX). The removal of free water was accomplished by using alcohol/acetone method as recommended as recommended by **Saikia et al.[25]**. The investigation of thermal properties; instantaneous thermal conductivity K and U- value are also measured as represented in figure (2).



**Fig. (2):** Test Set Up for both K and U values

## 3. RESULTS AND DISCUSSION

### 3.1 Mineralogical, SEM and mechanical characteristics

XRD pattern of alkali activated water cooled slag mixes that partially replaced with Nano-silica in the ratio from 0 up to 1.5% from the total dry weight are shown in Figure (3). The pattern illustrates that mix with super plasticizer (SP) provides a broad band in the region of  $6-10^\circ 2\theta$  for aluminosilicate gel and broad

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bands in the region of 17-35° 2θ which characterize the glassy phase of the geopolymer component. Those last two regions are getting broader when using SP as compared with that with no SP; giving an indication about good compatibility of the geopolymer mix and better enhancement in geopolymerization by using SP. Using 0.5 % NS, the amorphous glassy phases band become more broader which increases with 1 and 1.5 % NS. a noticeable crystalline quartz peak appeared upon using 1.5 % NS, while the glassy band turned to be intense which may be due to transformation of the amorphous component in the geopolymer into crystalline one with increase of Nano-silica content which is positively reflected on their microstructural and mechanical properties.

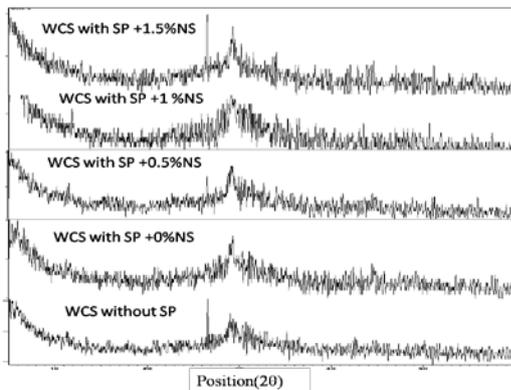


Fig.(3): X-Ray diffraction pattern of 90 days alkali activated WCS mixes (water/binder of 0.27%) having various doses of nano silica.

The SEM microstructure of 90 days cured WCS specimens using 6 % NaOH as activator is shown in Fig.(4). The micrograph of mix specimens without SP shows the spreading of microcrack within the matrix structure, while upon using SP a good compatibility and homogeneity appeared; where using super plasticizer provides good workability during mixing which enhance materials intact with each other. Also, Geopolymer materials are spreading in both mixes but it appears more in SP-specimens as results of high performance geopolymerization products.

The SEM microstructure of 90 days cured WCS specimens using 6 % NaOH as activator is shown in Fig. (5). The micrograph of geopolymer specimens with no nano-silica depict that structure is slightly heterogeneous with dispersing of geopolymer structure over the surface (Fig.5A); where geopolymer activation with 6% NaOH positively affect degree of polymerization, that is strongly affected by the soluble silicate and aluminates of the geopolymeric system and directly increase dissolution rate of Si and Si-Al phases improving the effectiveness of the geopolymerization process. With addition of 0.5% NS (Fig. 5B), an increase in the

amorphous geopolymer content within the microstructure was noticed. Using 1 & 1.5% NS, the amorphous geopolymer structure posses a massive layer of geopolymer materials which increases with Nano-silica as represented in Fig.(5C,D), respectively.

The results of compressive strength for hardened geopolymer mixes along with various activator cured at 100% relative humidity and at 38° C up to 90 days are shown in Fig.(6).The results show the increase of strength in all mixes along with hydration age is mainly attributed to the proceeding of pozzolanic reaction in slag pastes. It is known that a dosage of 6 % NaOH (NH) achieved better gain in compressive strength where it provides a high pH (more than 12) as mentioned latter, suitable for WCS activation and enhancing geopolymeric structure. It is noticed that on using of super plasticize the compressive strength values increased significantly, where a good workability of the geopolymer specimens resulted in a homogeneous composition and thus lead to increase in compressive strength values.

On the other hand, nano silica with its amorphous and high specific surface area possesses an extra enhancement in geopolymerization process. This is may be due the fact that highly reactive nano silica will consumes the liberated hydrated lime from hydration reaction and result in the formation of CSH that acts as nucleating sites for geopolymer formation and accumulation[27], the reaction of NS (that has many unsaturated bonds of ≡Si-O-) with hydrated lime is illustrated in the following equations:

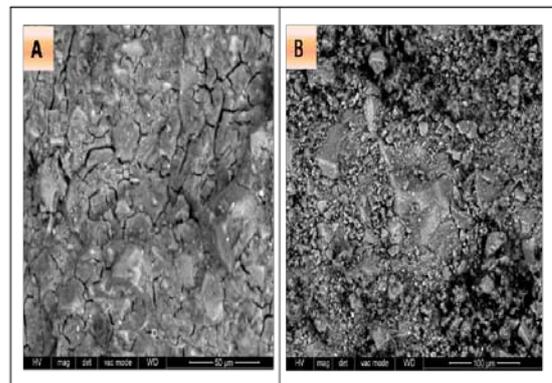
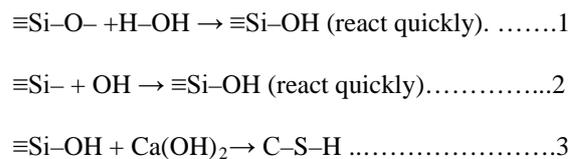


Fig.(4): SEM micrograph of alkali activated WCS mixes (water/binder of 0.27%) with : A) without superplasticizer B) with Gelenium Ace superplasticizer.

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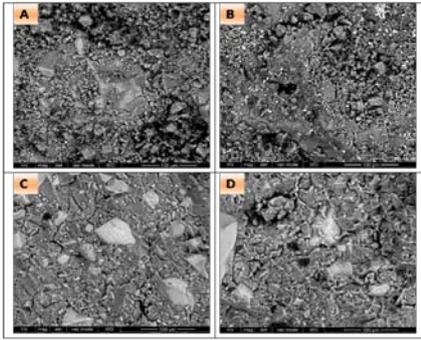


Fig.(5): SEM micrograph of 90 days alkali activated WCS mixes (water/binder of 0.27%)having : A) 0%NS, B) 0.5%NS, C) 1%NS and D) 1.5%NS.

The XRD pattern emphasize the increase of strength with Nano silica, as it appears from the crystalline quartz peak in addition to transformation of glassy band in the region of  $17-35^{\circ} 2\theta$  to intense which may be due to transformation of amorphous component in the geopolymer into crystalline one; this is also confirmed by mapping examination of Nano-silica addition Fig. (5c-d) as the massive crystalline geopolymer plates are spread all over the surface and increase with Nano silica addition.

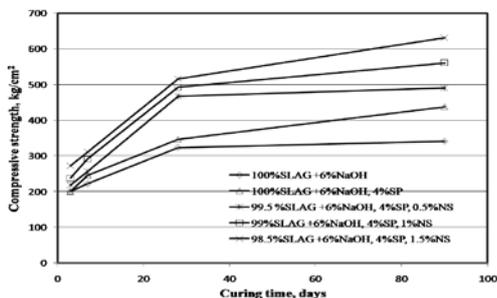


Fig.(6): Compressive strength of alkali activated WCS mixes (water/binder of 0.27%)having various doses of Nano -silica.

### 3.2 Evaluation of Thermal and physical properties

The measured U- value for the studied mixes with the thickness of 2.5 cm and given evaluation of U-value is compared for different thickness 5, 10, 15 and 20 cm of these materials; with common wall thickness of 10-20 as a reference value (in exact building). These results are illustrated in Fig. (7), where decrease in slope is noticed upon using of NS which may be due to nucleation Geopolymers formation, also U- value decreases by about 20% on using of 1.5% NS than the binder (control with no sp). It is also shown that the increasing of thickness up to 20 cm decreases U- value by about 40% than that of 2.5 cm thickness.

The time lag from the measurements and the decrement factor for the studied geopolymer samples of thickness 2.5 cm increased for the control sample and as

well as samples with NS, The highest value is noticed for sample with 1.5% NS which increase with increasing of the thickness. The decrement factor has an opposite behavior; it decrease with increasing in percent of NS and with increasing of the thickness as illustrated in Fig. (8). Also, it is obvious that the thermal time constant ( $T_c$ ) is dependent on the measured time lag which is can be considered as a mean for evaluation for different thickness. The  $T_c$  increased with increasing NS ratio which may be due to the formation of massive layers of Geopolymers materials, as well as it is noticed that  $T_c$  increase with the thickness.

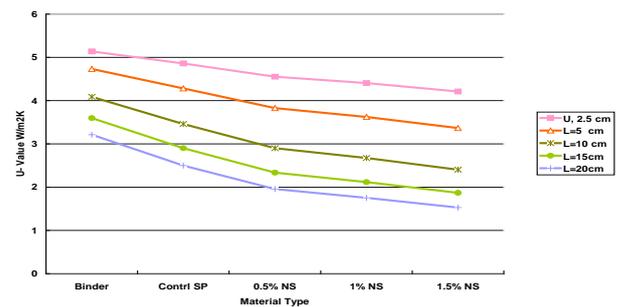


Fig (7): Variation of the U-value for the studied material types with different thickness

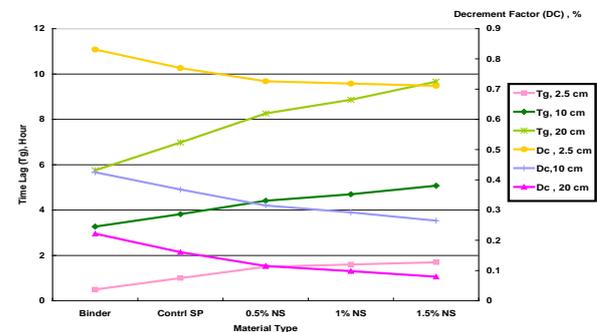


Fig (8): Variation of the time lag and decement factors for the studied materials types of different thickness

### 4. CONCLUSION

1. Mechanical and microstructural properties are positively affected with the superplasticizer addition.
2. Addition of Nano silica results in an enhancement in geopolymer microstructure leading to the formation of high performance geopolymer composite which affects the compressive strength leading to an increase in their values as compared with specimens without nano silica.
3. It is seen from the thermal study results that the thermal factors are suitable for most Egyptian Climatic Regions and confirmed with the factors given by the NS sample with thickness 15 & 20 cm thickness; with U-values between 1.5-1.8  $w/m^2 \cdot C$ , time lag around 8-10

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hours, thermal time constant between 28-48 hours and decrement factor of 0.07-0.1. These values are found to be very suitable for Egyptian climatic conditions and performs as an approach to a good thermal insulation materials with Exception to its heat storage which is out of our scope of this work.

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