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Effect of Nano-Clay on Alkali Activated Water-Cooled Slag Geopolymer

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Authors' contributions

This work was carried out in collaboration between all authors. Author HMK designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors BAE, MF managed the analyses of the study and review the final form of the manuscript. Authors ME, ML managed the literature searches and experimental procedures. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

Ground granulated blast furnace slag is a finely ground, rapidly chilled aluminosilicate melt material that is 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 clay is an ultrafine material that produced from firing kaolin material up to 800ºC for 2hrs with a heating rate of 5ºC/min; this can modify mechanical, microstructural and thermal properties of geopolymer products and added to the geopolymer mix in the ratio of 0 up to 7% of the dry weight. Curing was performed under 100% relative humidity and at a temperature of 38ºC. Gelenium Ace super-plasticizer was added in the ratio of 4% from the dry weight to ensure good dispersing of the used nano clay. Results showed that increasing the percentage of nano clay up to 1% results in an enhancement in the mechanical properties as compared with control mix up to 90 days, while higher ratio leads to matrix dilution and so negatively affect mechanical characteristics of the resulting products. The study of thermal properties is taken place for the different ratios by experimental and mathematical evaluation. Study shown that the thermal properties as well

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as thermal insulation properties improved with the increased ratio of nano clay in ratio 1-1.5%.

Keywords: Nano-clay; 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 alumino-silicate 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. Geopolymers may have a lower impact on global warming than OPC but on the other side they have a higher environmental impact regarding other impact categories [3].

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_2 is produced depending on the production process adopted [4]. Cement plants are reported to emit up to 1.5 billion tons of CO_2 into the atmosphere annually [5,6]. 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 [7] 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% [4] 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 [8].

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 practicized 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 [9]. Nano-materials show unique physical and chemical properties that can lead to the development of more effective materials than ones which are currently available [10]. 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. [11] 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 [12]. Several studies were performed concerning with applications of nanotechnology and nano materials in Construction [13-20].

Khater et al. [21] studied the alkaline activation of latent hydraulic WCS by 6% sodium hydroxide. 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^{o}C. Gelenium Ace super-plasticizer was added in the ratio of 4% from the dry weight to ensure good dispersing of the used nano silica. The results showed that increasing the percentage of nano silica results in an enhancement in the mechanical properties as compared with 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 shown that the thermal properties as well as thermal insulation property are improved with the increase ratio of nano silica.

Wen-Y Kuo et al., shown that the compressive and flexural strengths of cement mortars enhanced with SiO_2 and Fe_2O_3 nano-particles [22]. It was found that the nano-particles which dispersed uniformly in a cement paste will accelerate cement hydration due to their high activity [23]. 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-Fe_2O_3 exhibits a self-sensing of strain capability which can be useful for structural health monitoring [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 clay 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 geopolymer. 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 clay.

2. MATERIAL AND METHODS / EXPERIMENTAL DETAILS / METHODOLOGY

2.1 Materials

The material 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. Kaolin material used for preparation of nano-clay brought from Middel East for Mining Investment Co., Egypt. The chemical composition of the starting raw materials was illustrated in Table (1).

Table(1) : Chemical composition of the used raw materials (Mass, %).

Material	Source	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	MnO_2	P_2O_5	Cl^-	L.O.I.	Total	Notes
Water – Cooled Slag (GGBFS)	Iron and Steel Factory – Helwan	36.95	10.01	1.48	33.07	6.43	3.52	0.74	1.39	0.52	3.44	0.10	0.05	0.00	97.69	BaO= 3.0
Kaolin before firing	Middle east mining investment company	49.86	34.10	0.30	0.09	0.26	0.59	0.02	0.03	0.88	0.01	0.35	-	13.44	99.92	
Kaolin After firing	Middle east mining investment company	57.53	38.63	0.35	0.11	0.30	0.56	0.03	0.01	1.02	0.01	0.41	-	0.93	99.88	

Mineralogical characterization was done using X-ray diffraction analysis as represented in Fig. (1). The pattern showed that water cooled slag composes mainly of amorphous materials, while Nano-clay composed of about 95% kaolin and 5% quartz.

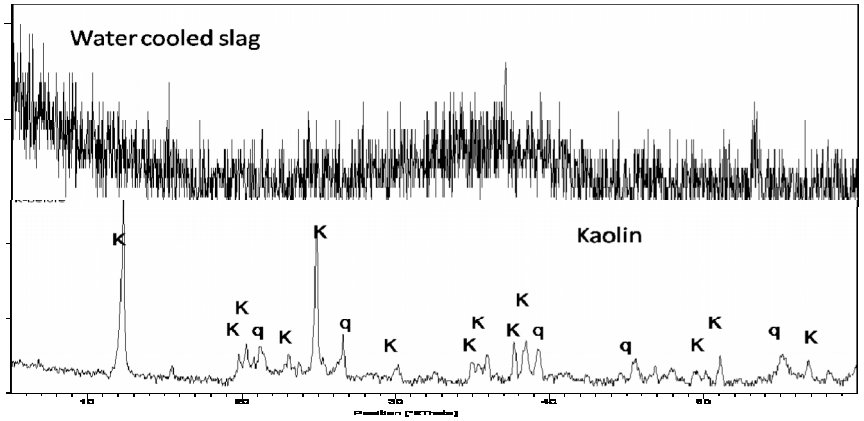

Fig.(1): X-Ray diffraction pattern of the used raw materials.

2.2 Synthesis of Nano- Clay

Clay nanoparticles are synthesized by firing high pure kaolin at 800 degree for 2hrs with a heating rate of 5^{o}C/ min to form an amorphous nano precusrsors. Nano clay firing results in the formation of nano clay particles with the average particle size 35-53nm, while its raw materials before firing has a grain size about 100% <10μm as indicated from the TEM [Fig.

(2)]. Fig. (3) illustrate XRD pattern of fired and unfired kaolin materials, the pattern reflects that mostly all the kaolin residues are distorted and dehydrated forming amorphous nano-clay material.

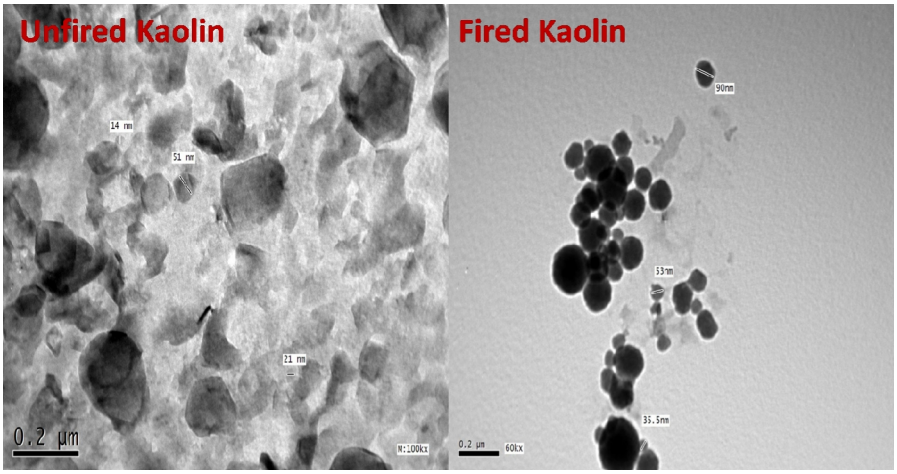

Fig.(2): Transmission electron micrograph of fired and unfired bentonite Kaolinite material provided from Middle East for mining investment.

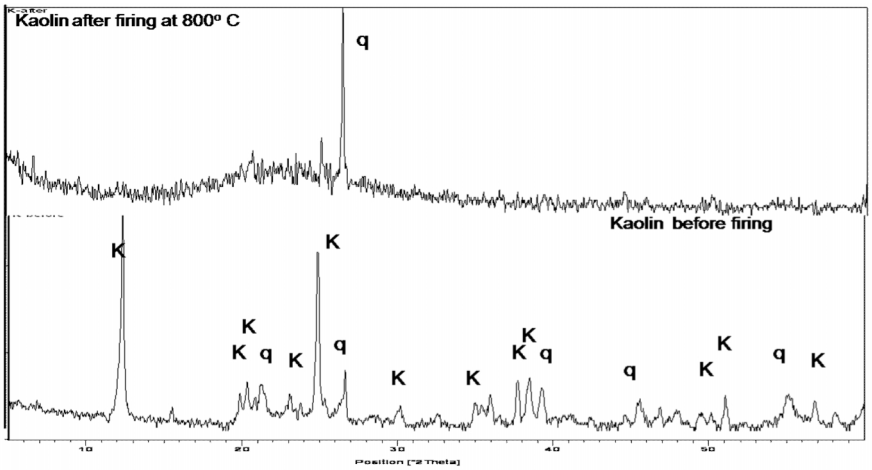

Fig.(3): X-Ray diffraction pattern of kaolin material before and after firing. (provided from Middle East for mining investment) [K: kaolin, Q: quartz]

2.3 Geopolymerization and Curing

Geopolymer was made by hand-mixing raw materials of each mixture passing a sieve of 90 µm 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 [23]. The water-binder material ratio (w/b) was about 0.27 by mass. Nano clay was added to the binding material (Blast furnace slag) in small quantities 0, 1, 1.5, 3, 5 and 7 % as illustrated in Table

(2), 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-clay (NC) and finally 4% super plasticizer - Gelenium Ace (SP) is added to the mix. Paste mixture were cast into 25×25×25 mm cubic-shaped moulds, vibrated for compaction and sealed with a lid to minimize any loss of evaporable water.

Table (2). Mix design of incorporation of nano-clay in mixes of water cooled slag materials

Mix	slag	NC, %	NaOH, %	Sp, %	Density, kg/m^3
A1	100	0	6	4	2105
A2	100	0	6	4	2094
K1	99.5	0.5	6	4	1912.3
K2	99.0	1.0	6	4	1827.9
K3	98.5	1.5	6	4	1835.1
K4	97.0	3.0	6	4	1829
K5	95.0	5.0	6	4	1790.1
K6	93.0	7.0	6	4	1716.2

All mixes were left to cure undisturbed under ambient temperature for 24 hour, and then subjected to curing temperature of 38^{o}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. [24] in order to prevent further hydration and for further analysis and followed by drying of the crushed specimens for 24 hours at 80ºC 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 100kg/min determined according to ASTM-C109-07[25]. 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 by Saikia et al. [24]. The investigation of thermal properties; instantaneous thermal conductivity K and U (measure of the rate of heat loss)-value are also measured as represented in Fig. (4).

Fig. 4. Test set up for both K and U values

3. RESULTS AND DISCUSSION

3.1 Mineralogical and Mechanical Characteristics

The results of compressive strength for hardened geo polymer mixes along with various Nano-clay content and cured at 100% relative humidity and at 38^{o} C up to 90 days are shown in Fig. (5) and represented in Table (3) .The results show the increase of strength in all mixes along with hydration age which is attributed to the continuing 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 [23]; suitable for GGBS activation and enhancing better geopolymeric structure.

Table (3). Compressive strength of nano-clay and water cooled slag mixes (Kg/Cm^2)

Mix	3 days	7 days	28 days	90days
A1	200.00	222.03	323.63	341.01
A2	200.65	246.43	346.47	437.38
K1	170.14	256.55	340.44	376.50
K2	197.72	287.97	378.85	393.31
K3	158.88	234.52	263.81	284.14
K4	141.17	155.86	222.36	237.05
K5	137.09	146.64	211.59	214.04
K6	120.28	129.66	135.37	182.95

It is noticed that using super plasticizer positively affect compressive strength values where a good workability of the geo polymer specimens resulted in a homogeneous composition and so increase in compressive strength values. It is also noticed an increase of strength with nano clay addition up to 1 % while it is slightly decreases by addition of 1.5 % nano

clay, this increase may be due to the fact that highly reactive nano clay 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 [26], the added nano clay positively affect the reaction by contributing with its alumina and silicon oxides into geopolymer formation; however its ultra fine composition hinder the progress of the reaction if added in a higher dose.

Fig. (6), shows the XRD result of Mixes K1, K3, K5 and K6 respectively corresponding to different nano clay ratio (0.5, 1, 3, 7) added to slag geo polymer, there is an indication of complete dissolution of the alumina-silica constituents into fully poly condensed amorphous phase as confirmed by the presence of the dominant amorphous hump from 2 theta =17º to 2 theta = 35º in the XRD pattern. However, K3 with 1 % of nano clays additive achieved the best compressive strength at 28 days of curing compared to other mixes due to highest amorphous geo polymer content which gave rise to formation of compact microstructure.

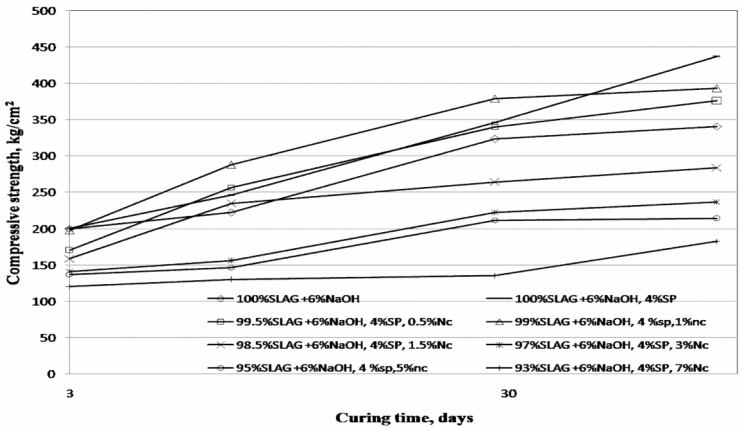

Fig.(5): Compressive strength of alkali activated slag geopolymer specimens having various dosages of nano-clay, cured at 38°C and 100% relative humidity.

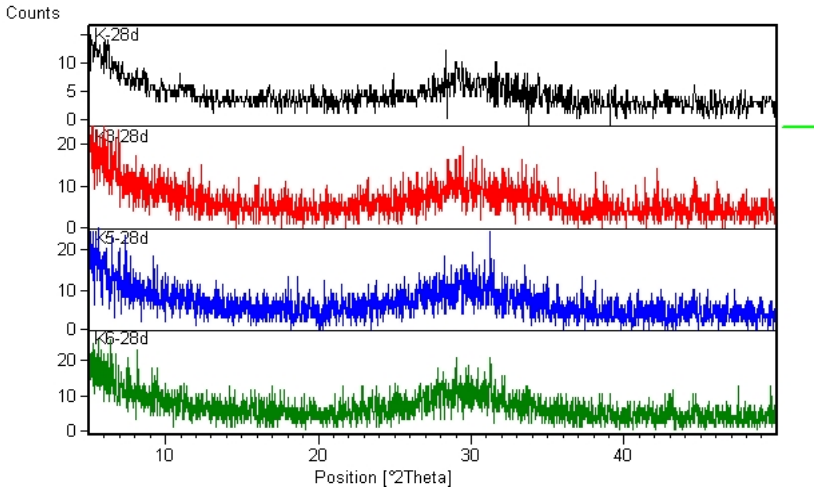

Fig. (6). XRD of slag geopolymer with different nano-clay and cured at 28 days

3.2 Evaluation of Thermal and Physical Properties

This work carried out to study the thermal physical properties of a nano clay geopolymer mixes that contains 0, 0.5, 1, 1.5, 3, 5, and 7% NC as a partial replacement of slag precursor. The measurements are taken place for the control sample and for each new sample K' each of thickness 2.5 cm. The measurements are taken for the external and internal sample face, the external and internal air and for the shaded air. The passed heat fluxes are measured through each sample. The thermal parameters that will be used to evaluate the materials are:

i. **U value:** the measure of the rate of heat loss.
ii. **Thermal time constant value: (**lumped capacity analysis method) for thermal systems, used when objects cool or warm uniformly under the influence of convective cooling or warming.
iii. **Time lag value:** time delay due to the thermal mass; the thicker and more resistive the material, the longer it will take for heat waves to pass through.
iv. **Decrement factor:** the ratio of the amplitude of the temporal evolution of the temperature on the inner surface of the multi-layer material to that of the sol-air temperature or the outer surface temperature.

The U value are evaluated from the measurements for the thickness 2.5 cm and evaluated theoretically for other thickness 5 cm, 10cm, 15 cm and 20 cm. These results are shown in Fig. (7).

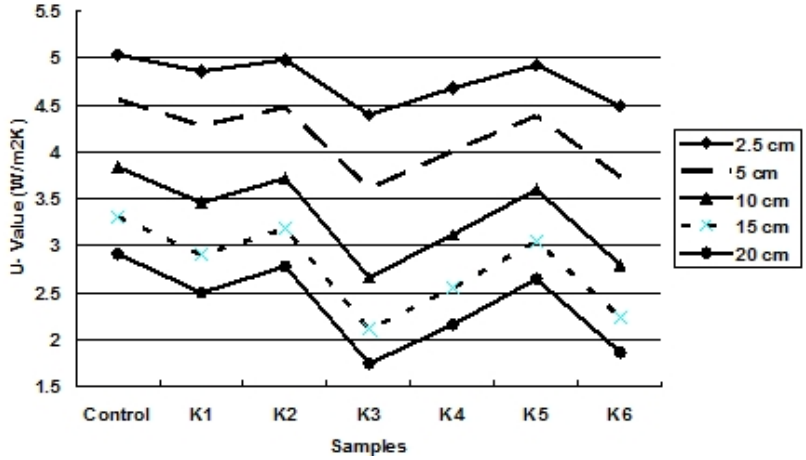

Fig. (7). The variation of U- value for different thickness of samples group K

Fig. (7), shows that K' samples have U- values lower than that of control sample , But K2 and K5 have value nearly to that of control sample. While K3 and K6 have the lowest value, which can be confirmed with the required U value that given in Egyptian Energy Code No. 306/1 -2006.The Thermal time constant Tc use evaluated for the studied samples of different Thickness; depends on the measured data as shown in Fig. (8).

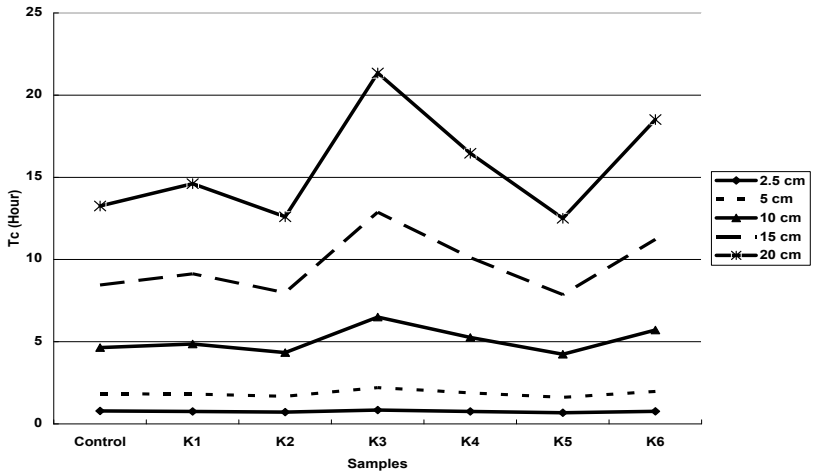

Fig. (8). The variation of Thermal time constant Tc with the studied K- samples of different thickness

Fig. (8) illustrated that the control and K3 sample has the highest values, which is confirmed with that value required for Cairo and Delta Regions in Egypt. It is clear from Fig. 1 and Fig. 2 that K2 and K3 with 1, 1.5% NC has the best values of both U, Tc values. The time lag and the decrement values are also evaluated depending on the Tc evaluation and given in Fig.(9) illustrating that K3 has the highest value of Tg and the lowest value of Dc, which indicated that it has good thermal performance. While control sample and K2 and K5 are in contrast with the value of Tg & Dc that given for K3.

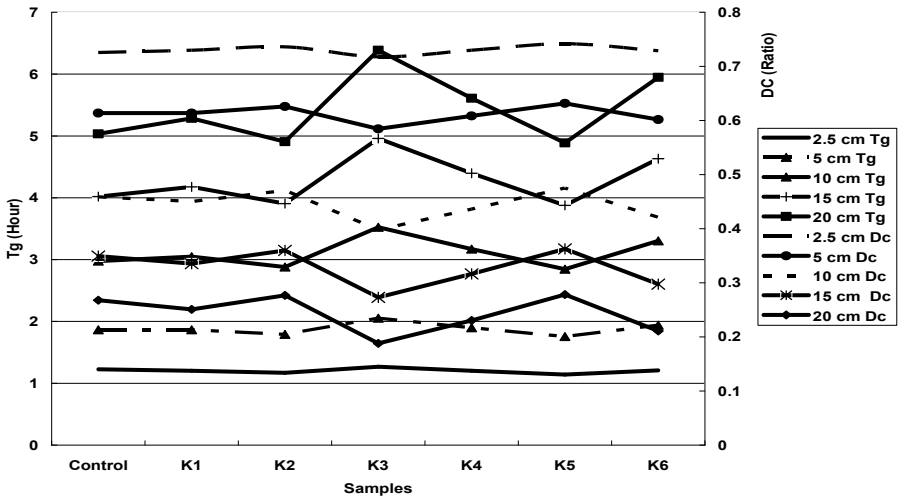

Fig. (9). The variation of time lag Tg and Decrement factor Dc for K' samples of different thickness

4. CONCLUSION

1. Mechanical and microstructural properties are positively affected with the super-plasticizer addition.

2. Addition of Nano clay 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 clay up to 1%, while further increase results in a negative effect on the mechanical properties.

3. The study shows that the addition of 1-1.5%NC possess the lowest value of U-value and Dc ratio and has the highest value of Tc and Tg values, which reflect good thermal performance and low energy consumption.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Davidovits J. Chemistry of geopolymeric systems, in: Terminology. Geopolymer'99 Second International Conference, Saint-Quentin, France. 1999;9–39.
2. Krivenko PV. Peculiarity of formation of the contact zone (slag alkaline cement–mineral wool). In: Cement and Concrete Technology in the 2000, Second International Symposium, 6–10 September, Istanbul, Turkey. 2000;553–561.
3. Habert G, de Lacaillerie J, Roussel N. An environmental evaluation of geopolymer based concrete production: reviewing current research trends. Journal of Cleaner Production, 2011;11:1229-1238.
4. McLellan B, Williams R, Lay J, Van Riessen A, Corder G. Costs and carbon emissions for geopolymer pastes in comparison to ordinary Portland cement. J Cleaner Prod. 2011;19:1080–90.
5. Hasanbeigi A, Price L, Lin E. Emerging energy-efficiency and CO2 emission-reduction technologies for cement and concrete production: A technical review. Renewable and Sustainable Energy Reviews. 2012;16:6220–6238.
6. Ali M, Saidur R, Hossain M. A review on emission analysis in cement industries. Renewable and Sustainable Energy Reviews. 2011;15:2252–2261.
7. Davidovits J. Geopolymer cement to minimize carbon-dioxide green house warming. Ceram Trans. 1993; 37:165–82.
8. Wang SD, Scrivener KL. Hydration products of alkali activated slag cement. Cem. Concr. Res. 1995; 25:561–571.
9. Aiu M. The Chemistry and Physics of Nano-Cement. Loyola Mary mount University, Advisor: Dr. C.P. Huang Submitted to: NSF-REU University of Delaware August 11, 2006.

10. Li H, Xiao H, Ou Jin-ping. Microstructure of cement mortar with nano particles. Composites: Part B. 2004;35:185-189.
11. Ginebra MP, Driessens FCM, Planell JA. Effect of the particle size on the micro and nano structural features calcium phosphate cement: a kinetic analysis. Biomaterials. 2004;25:3453-3462.
12. Zins D, Cabuil V, Massart R. New aqueous magnetic fluids. Journal of Molecular Liquids. 1999;83:217-232.
13. Ge Z, Gao Z. Applications of Nanotechnology and Nano materials in Construction. First International Conference on Construction In Developing Countries (ICCIDC-I) "Advancing and Integrating Construction Education, Research & Practice" August 4-5, Karachi, Pakistan; 2008.
14. Hanehara S, Ichikawa M. Nanotechnology of cement and concrete. Journal of the Taiheiyo Cement Corporation. 2001;141:47-58.
15. Scrivener KL. Nanotechnology and cementitious materials. In: Nanotechnology in construction: proceedings of the NICOM3 (3rd international symposium on nanotechnology in construction). Prague, Czech Republic. 2009;37–42.
16. Sobolev K, Ferrada-Gutiérrez M. How nanotechnology can change the concrete world: part 2. Am Ceram Soc Bull. 2005;84(11):16–9.
17. Sobolev K, Shah SP. SP-254 Nanotechnology of concrete: recent developments and future perspectives. Detroit: American Concrete Institute; 2008.
18. Bartos PJM, de Miguel Y and Porro A, editors, NICOM: 2nd international symposium on nanotechnology for construction. Bilbao, Spain: RILEM Publications SARL; 2006.
19. Bittnar Z, Bartos PJM, Nemecek J, Smilauer V, Zeman J editors. Nanotechnology in construction. Proceedings of the NICOM3 (3rdinternational symposium on nanotechnology in construction). Prague, Czech Republic: Springer-Verlag Berlin Heidelberg. 2009;438.
20. Jayapalan AR, Kurtis KE. Effect of nano-sized titanium dioxide on early age hydration of Portland cement. In: Bittnar Z, Bartos PJM, Nemecek J, Smilauer V, Zeman J, editors. Nanotechnology in construction: proceedings of the NICOM3 (3rd international symposium on nanotechnology in construction). Prague, Czech Republic. 2009;267–73.
21. Khater HM, El-Sabbagh BA, Fanny M, Ezzat M, Lottfy M. Effect of Nano-Silica on Alkali Activated Water-Cooled Slag Geopolymer. Proceeding of the Second International Conference on Microstructural-related Durability of Cementitious Composites, 11-13 April 2012, Amsterdam, and the Netherlands.
22. Kuo Wen-Yih, Huang Jong-Shin, Lin Chi-Hsien. Effects of organo-modified montmorillonite on strengths and permeability of cement mortars. Cement and Concrete Research. 2006;36:886-895.
23. Li H, Xiao H, Ou Jin-ping. "A study on the mechanical and pressure sensitive properties of cement mortar with nano phase materials", Cement and Concrete Research. 2004;34:435-438.
24. El-Sayed,HA,Abo El-Enein SA, Khater HM, Hasanein SA. Resistance of Alkali Activated Water Cooled Slag Geopolymer to Sulfate Attack. Ceramics – Silikáty. 2011;55(2):153-160.
25. Saikia N, Usami A, Kato S, Kojima T. Hydration behavior of ecocement in presence of metakaolin. resource progressing journal. 2004;51(1):35-41.
26. ASTM C109M- 07. Standard Test Method for Compressive Strength of Hydraulic Cement Mortars; 2007.

27. Khater HM. Effect of Calcium on Geopolymerization of Aluminosilicate Wastes. Journal of Materials in Civil Engineering. 2012;24(1):92-101.

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