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Mechanical behavior of activated nano silicate filled cement binders

S. S. Shebl · L. Allie · M. S. Morsy · H. A. Aglan

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Abstract This investigation aimed to develop structural blended cement pastes with high mechanical properties for building envelope purposes. The effect of nano silicate (NS) replacement on the properties of blended white cement pastes as compared with the control paste have been studied through the measurements of indirect tensile strength (ITS). NS was thermally activated at 850 °C for 2 h and used to partially replace Portland white cement (PWC) at different ratios. The activation effect of NS on the ITS have also been studied. The cement pastes were prepared using water of consistency. The pastes were removed from the mold after 24 h and then immersed in a water bath for hydration. The 7-day aged pastes were tested after drying for 24 h at 105 °C. Different physical properties such as thermal resistivity, solar reflectivity, water absorption and apparent porosity were measured. It was found that, activation of NS decreases the porosity allowing the blended cement paste to be denser, consequently increasing the ITS. Increasing the replacement content of unactivated NS upto 2%, improved the ITS by about 40% compared with the control paste. Also, the thermal activation of the NS has a very good influence in enhancing the ITS to about 50% with respect to the 2% unactivated blended paste. The results also showed that increasing the replacement content generally increases the water absorption and the porosity of blended white cement pastes, while, slightly improving the thermal resistivity. Activation of NS reduced the solar reflectivity of blended pastes as compared with unactivated blended pastes. An optimum replacement of around 2% can be concluded from the current work.

Introduction

Portland cement is usually a mixture of limestone (calcium carbonate, $CaCO_3$) and a second material as a source of alumino-silicate. The principle clinker minerals of the Portland cement are Tri-calcium silicate, C_3S (Alite), Calcium silicate, β-C_2S (Belite), Tri-calcium aluminate, C_3A, and Ferrite phase; Tetra-calcium alumino ferrite, C_4AF (Celite). Alite compound is characterized by rapid rate of hydration within a few hours and rapid strength development during a few days, while Belite is characterized by slow rate of hydration within days and slow strength development within weeks. In contrast, Celite is characterized by a very rapid rate of hydration (a few minutes) and very rapid strength development as short as one day.

The hydration process is the chemical reaction between cement clinker minerals and water. Calcium silicates react with water producing (1) calcium silicate hydrate (CSH) gel with very poor crystallinity which consequently develops high surface area, and (2) calcium hydroxide (CH) as hexagonal crystallinity. First, the calcium and hydroxide ions release from the Alite surface with a rapid heat generation until a certain concentration where crystallization of CH occurs. This period is called temperature controlled early chemical reaction. The reaction slows and a CSH layer is formed which covers the Alite surface. As CSH layer thickness increases, time for water to penetrate

S. S. Shebl · L. Allie · H. A. Aglan (✉)
Mechanical Engineering Department, Tuskegee University,
218 Foster Hall, Tuskegee, AL 36088, USA
e-mail: aglanh@tuskegee.edu

M. S. Morsy
Housing and Building National Research Center,
P.O. Box 1770, Cairo, Egypt

the coating layer increases. Therefore, the reaction is controlled by diffusion in this period. When calcium and hydroxide ions reach to the critical concentration, calcium silicates hydrate rapidly. Finally set occurs, followed by slowing of reaction rate and the reaction is completely diffusion-dependent reaction until it reaches the steady state reaction within about 12–24 h. Tri-calcium aluminate reacts with water and gypsum from the cement, to regulate the setting time. It produces two unstable calcium hydrates. The first is calcium sulfo-aluminate hydrate which is called ettringite, with hexagonally prism-shaped crystals (needles) which are longer than CH crystals. The second is the converted mono-sulfo-aluminate hydrate, which depends on the sulfate ions supplied from gypsum. Ferrite phase also reacts slowly with water producing the same hydration products as Aluminate C_3A. Generally, the rate of hydration is in the order of Aluminate, Alite, Celite, and Belite.

The use of replacement materials such as silica fume, fly ash, and metakaoline in Portland cement has been recently given much attention [1–3]. Also, adding of very fine particles to cement is considered an established practice in recent years. Nano scale particles can improve properties much better compared with grain scale particles of the same chemical composition. Nano silicate (NS) can improve cement hydration as reported by several studies [4–8]. The effect of using NS on the structure of cement paste to enhance the durability and the mechanical properties has been studied [4]. The hydration of cement has been accelerated and an increase in compression strength of cement pastes was noticed. The effect of using NS as a replacement in cement mortar and comparing its results with those of silica fume has also been studied [5]. Nano particles enhanced the compressive strength of cement paste much more than silica fume. It is due to the filling effect and pozzolanic reaction activation. It was concluded that the rate of pozzolanic reaction depends on the Blaine surface area available for reaction. Nano aluminate and silicate have been integrated with cement mortar as a new building material [6]. It was more effective than plain cement mortar. The use of NS as a replacement for cement in concrete has also been studied [7]. A comparison between high volume fly ash high strength concrete with those incorporating NS and control Ordinary Portland Cement (OPC) has been reported. The pozzolanic activity of NS activated the fly ash, which led to an increase in compressive strength. Addition of fly ash leads to high porosity, while NS accelerating the hydration leads to more compact structure. Nanostructured-perlite-cementitious surface compounds were developed and characterized [8]. It was a structural lightweight surface compound with improved physical and mechanical properties. Portland White Cement (PWC) was partially substituted by NS upto 4% by weight. It was found that the 2% NS improved the indirect tensile strength (ITS) of the neat PWC. This is due to the fact that nano particles fill up the individual pores and react with the residual CH and improve the microstructure when uniformly dispersed, resulting in higher strength. Other studies with nanoalumina and nanosilica as fillers have been performed to activate cementitious compounds and improve their strength [9, 10]. It was found that nanoalumina activated the slowly reactive belite phase in cements which resulted in improved mechanical strength at short cure time [9]. The compressive strength of Portland cement was also increased by the addition of nanosilica. The increased strength is attributed to the increased packing factor resulted from the nanosilica filling the interstitial voids in the cement and the pozzolanic reaction of the silicon particles from the nanosilica with the calcium oxide and hydroxide from the cement. Similar improvements in strength were obtained when thermally activated kaolin and mineral alunite was used as fillers in cements [11, 12]. However, the improvement obtained from the thermally activated kaolin cement compound was attributed to the recrystallization of the kaolin to form pozzolanic metakaolin with smaller particle sizes [11].

Many studies confirmed that the activation of replacement materials can be performed to obtain pozzolanic materials with an accelerated hydration process compared to OPC. Activation can be achieved by various techniques such as physical, chemical, and thermal techniques. The physical activation technique can be achieved by mechanically grinding, to produce very small particle size. Chemical activation involves the chemical treatment with sodium hydroxide solution, while thermal activation is done by heating the material to about 850 °C for a duration of 2 h then cooling to the room temperature. Clay was characterized before and after thermal activation by using of DTA and TGA [13]. The results clearly showed that the kaolinite of clay is transformed into an amorphous phase, which is potentially reactive with CH of cement. Fly ash was activated physically, chemically, and thermally to study its effect on corrosion resistance of concrete [14]. Thermal activation of fly ash has been done by heating at about 900–1,000 °C for 1 h then cooled to room temperature. The microstructure of the different activation treatments has been analyzed by means of Scanning Electron Microscope (SEM). The unactivated fly ash was composed of randomly distributed coarse particles, with a majority having rugged shape and rough surface. The thermal activation coarsened and grew the particles. The different activation techniques were used to activate fly ash for studying its effect on the strength of concrete [15]. The as received, physically, thermally, and chemically activated fly ash cement paste has been tested. Chemical activation could be considered as the best activation technique. It improves both compressive strength and corrosion resistance. The chemical and thermal activation of fly ash concrete showed improved compressive strength compared with OPC. The effect of chemical, physical, and thermal activation of slag on the compressive strength of mortars has also been addressed [16]. Chemical activation of slag allows it to effectively react with activation solutions and an increase in compressive strength with aging was observed. Also, physical activation could improve the compressive strength at 2 weeks of aging for 30% slag replacement and at 4 weeks of aging for 50% replacement. Thermal activation has been achieved by controlling the curing temperature at 20, 40, and 60 °C. As the curing temperature increases the compressive strength increases for short aging periods but otherwise reversed for long aging periods. This was due to the non-uniform distribution of hydration products as a result of the insufficient time to ensure uniform distribution.

The replacement materials such as silica fume, fly ash, and metakaoline that are used for enhancing the mechanical properties of cementitious systems had received little attention for their effects on the physical properties, especially the thermal resistivity [17–19]. Silica fume causes the thermal resistivity and specific heat of cement paste to be increased [20]. Also, thermally treated cement pastes showed that water loss was reversible after re-saturation, although the specimens were damaged [21]. It was proposed that the thermal treatment increased the total porosity and modified the pore structure.

The NS used in this study is modified with an ammonium salt. The ammonium is formed by protonation of ammonia. In a solution, the degree to which ammonia forms the ammonium cation depends on the pH of the solution. Any hydrogen in the ammonium ion can be substituted with an alkyl group to form a substituted ammonium ion. Depending on the number of organic radical groups, it is called primary, secondary, tertiary, or quaternary ammonium cation. Only quaternary ammonium cations are permanently charged. Generally, it has a negligible solubility in water. The NS used in the current study was Cloisite 30B and its chemical identification was alkyl quaternary ammonium bentonite. It is a hydrophobic material with a specific gravity of about 1,900–2,100 kg/m^3, and decomposed at a melting point of approximately 200 °C. This NS has been used as successful replacement for OPC and enhanced compressive strength was achieved as a result. In this study, the physically activated NS had been thermally activated by heating it at 850 °C for 2 h, and then allowing it to naturally cool to the indoor room temperature. The purpose of this study is to examine the pozzolanic behavior of the thermally activated NS and its effect on the thermal and mechanical properties of the activated NS filled cement binders for building envelopes purposes.

Materials and experimental

The materials used in this study are PWC provided by Lehigh Cement Co., and NS supplied by Southern Clay Products. The chemical compositions of the PWC and NS are summarized in Table 1. The NS is Cloisite 30B modified montmorillonite clay (Hydrated sodium calcium aluminum silicate). It is a natural montmorillonite modified with an ammonium salt that was used to improve plastic thermo-physical properties. NS replacement of 2, 5, and 10% by weight of PWC has been used as illustrated in Table 2. The NS was thermally activated at 850 °C for 2 h. Samples were made from both activated and unactivated NS using all three replacement ratios. Water of consistency was used for preparing the blended pastes. PVC molds with diameter of about 50.8 mm and height of about 12.7 mm were used for molding samples for thermal and mechanical tests. The samples were removed from the molds after 24 h, and then allowed to cure in water for 7 days. The specimens were dried at a temperature of 105 °C for 24 h in an oven. The ITS was obtained by performing mechanical tests on dried specimens. Thermal resistivity and solar reflectivity tests were also performed on dried specimens. In addition, diffusion properties, such as water absorption and apparent porosity have been obtained.

Table 1 The chemical composition of starting material

Oxide composition	PWC (%)	NS (%)
CaO	66.3	–
SiO_2	22.5	99.9
Al_2O_3	5.4	–
Fe_2O_3	0.4	–
MgO	1	–
SO_3	2.8	–
Na_2O	0.17	–
K_2O	–	–
TiO_2	–	–
Ignition loss	1.7	0.1

Table 2 The dry mixes composition of blended binders (mass %) (C refers to unactivated NS, A refers to activated NS)

Mixes	PWC	NS[a]	Mixed water[a]
C0	100	0	0.28
C2	98	2	0.3
C5	95	5	0.32
C10	90	10	0.34
A2	98	2	0.3
A5	95	5	0.32
A10	90	10	0.34

[a] % calculated based on mass of binder (PWC + NS)

Testing procedures

Mechanical properties (Indirect tensile strength)

The indirect tensile tests have been performed on a material testing system (MTS 810), using cylindrical samples with about 50.8 mm diameter and about 12.7 mm thickness. The loading rate on the cylinder is 2.54 mm/min. Five samples per batch were tested and the average ITS was calculated according to the following equation:

$$\sigma = \frac{2P_{\max}}{\pi D t}, \tag{1}$$

where σ is the indirect tensile strength (ITS), (MPa); $P_{\max}$ the maximum applied load, (N); D the diameter, (mm); and t the thickness, (mm).

Physical properties (Thermal resistivity and solar reflectivity)

Thermal conductivity device, Quickline-10, was used for testing the blended cement pastes. It works according to ASTM E-1530 [22], which follows the guarded heat flow meter method. This method can be summarized as follows: the sample is located under a reversible compressive load between two polished cooper surfaces, each controlled at a different temperature. The upper plate acts as heat source while the lower acts as heat sink. The lower contact surface is part of a calibrated heat flux transducer. To insure good contact on the test sample without any air gaps, an axial load of 275 kPa was applied. As heat flows, an axial temperature gradient is established. By measuring the temperature difference across the sample, along with the output from the heat flux transducer, the thermal conductivity of the sample can be determined when the thickness of the sample is known. The reciprocal of thermal conductivity is the thermal resistivity.

An RT-060 reflectance/transmittance integrated sphere was used for measuring the surface reflectance of the nano-structured cement pastes. It is designed for use in the 250–2,500 nm wavelength range. Reflectance is the percentage of incident flux reflected by a material. A reference material of known reflectance is used for calibration.

Diffusion properties (Water absorption and apparent porosity)

The water absorption was determined according to ASTM C140-01 [23]. The samples were immersed in a water bath for 24 h. The samples were then removed from the water allowing it to drain. A damped cloth was used to remove any visible surface water. The weight of the samples was recorded as saturated weight (W_s). The samples were dried in a ventilated oven at 105 °C for at least 2 days. The final weight of the samples was recorded as dry weight (W_d). The water absorption [23] and water porosity [21] were calculated as follows:

$$\text{Water absorption}\,\% = \frac{(W_s - W_d)}{W_d} \tag{2}$$

$$\text{Porosity}\,\% = \frac{(W_s - W_d)}{\rho_w V}, \tag{3}$$

where ρ_w is the water density; V the volume of the sample.

Results and discussion

Figure 1 shows the variation of the DSC thermograms of NS and the thermally activated NS. There are two endothermic peaks for the unactivated NS. The first peak is located at about 185 °C, and the second peak is located at about 420 °C. However, there was only one endothermic peak for the thermally activated NS, located at about 455 °C and the disappearance of the first peak could be noticed. Evidently, the unactivated NS starts to decompose at 185 °C, while the activated NS starts at about 455 °C. This is due to the fact that the modified NS is a hydrophobic material and the activation process destroyed the ammonium ions on the NS making it a hydrophilic material. The crystalline structure is destroyed into amorphous structure and this will enhance the hydration process of the cement.

Figure 2 illustrates the ITS for the different cement pastes at 7 days aging. Unactivated and thermally activated blended cement pastes with NS content upto 10% were tested. It was evident that, the ITS of blended cement pastes increased with increasing unactivated NS content upto 2%, then slightly decreased to 5%, which agrees with M. S. Morsy and H. A. Aglan [8]. They reported an improvement of about 28% and 22% for the blended paste of 2% and 4% NS content, respectively. This agrees with the results of the current study which is about 40% and 20% for the blended paste of 2% and 5% NS content, respectively. The increase of ITS of the blended cement may be due to the pozzolanic reaction of the silica elements in the clay and the lime elements in the cement, which in turn has an effective contribution in increasing the bonding forces between particles. Increasing the NS replacement much more than 5% slightly increases the ITS upto 10%. The compressive strength is considered to be an indication of pores or intermolecular spaces. Decreasing the pores by filling them with very fine filler causes the compressive strength to increase. On the other hand, the tensile strength is considered to be an indication of the ability of the particles of a substance to hold together with each other. The effective element in this process is the binder.

Fig. 1 DSC Thermograms of the unactivated and thermally activated NS

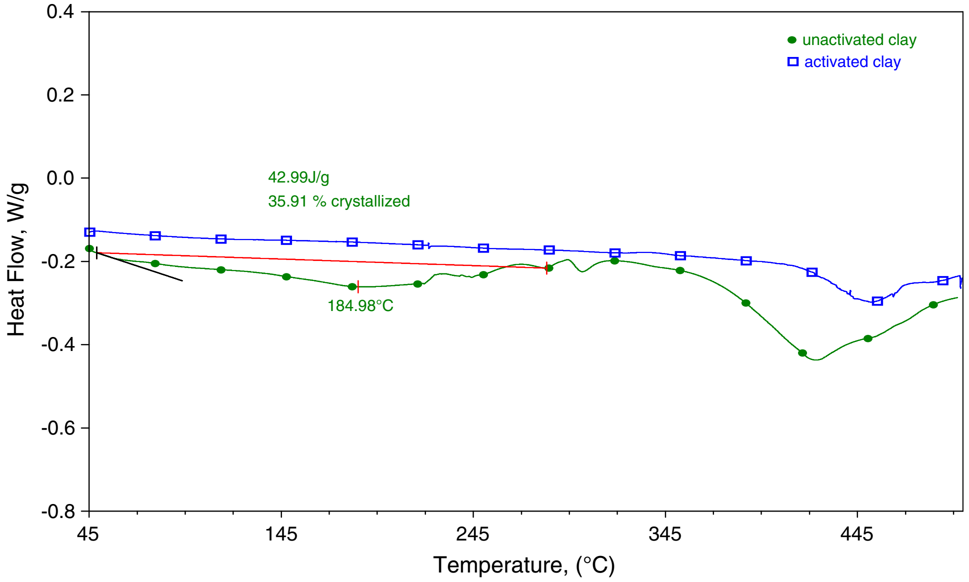
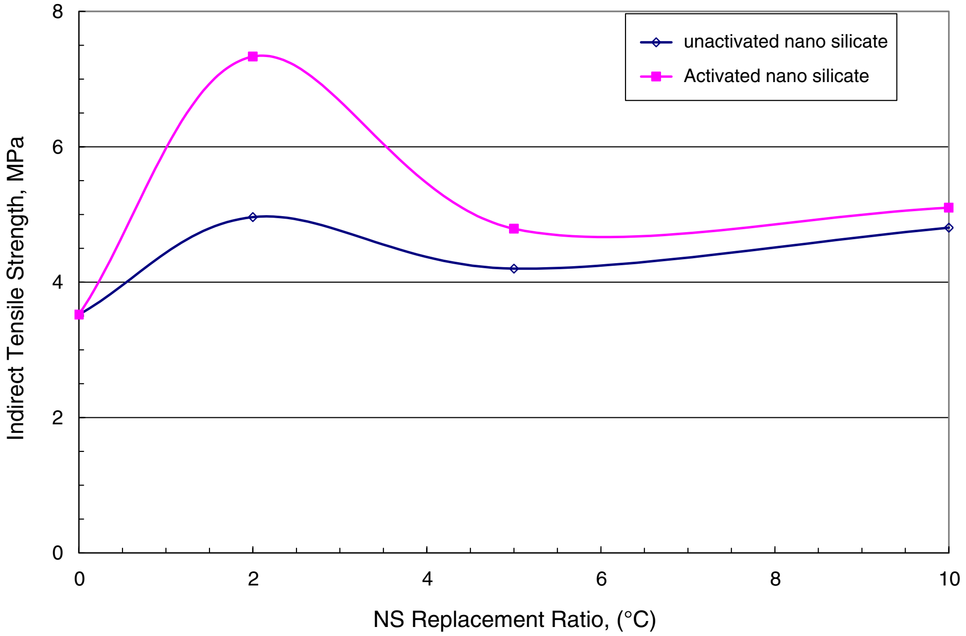


Fig. 2 Effect of thermal activation of NS on the indirect tensile strength of 7-day aged nano silicate filled cement binders with different replacement ratios



The results also show that the activation of NS strongly enhanced the ITS of the nano structured blended cement pastes. There was an improvement in the ITS for the 2% activated NS blended paste by about 50% compared with the unactivated NS blended paste. This is due to the activation process of NS that transforms its structure from crystalline silica into amorphous silica and causes the hydrophilic effect, which accelerates the hydration process leading to the enhancement in ITS. In addition, the pozzolanic reaction between the CH in the cement and the amorphous silica from the activated nanosilicates would normally be slow during a prolonged period of moist curing. However due to the very small sizes of the nanosilicates compared to the sizes of the cement particles (20 µm), a very large surface area is produced. This large surface area causes the nanosilicates to react rapidly with the CH to form calcium silicate in alkaline environments such as the pore solution of Portland cement paste [8, 10]. Increasing the replacement content above 2%, lowered the ITS. The higher loading of NS, which is rich with silica gives the chance of transformation of CSH into tobermorite and increases the extent of silicate polymerization [8]. Also, there was an increase in porosity that indicates a weak structure which is accompanied by a decrease in density and in conjunction leading to decrease in ITS. Hence, the improvement of ITS of the blended cement pastes can be summarized as follows: 2% replacement had the best improvement reaching to about 108% for activated NS and about 40% for unactivated NS compared with control paste.

The improvement in ITS is because when activated NS cement is mixed with water, the NS particles will absorb significant amounts of the mixing water. The Ca-montmorillonite has a large water adsorption producing crystalline swelling but the Na-montmorillonite has a large water adsorption resulting in macroscopic swelling. The crystalline swelling (Ca-montmorillonite) is easier to separate and increase the rate of the hydration reaction of the cement pastes but the macroscopic swelling (Na-montmorillonite) is the most difficult to separate and decreases the rate of hydration. Therefore, the higher ITS of activated NS cement can be explained as the improvement of the bonds between cement grains due to the hydration of un-hydrated cement grains; producing additional CSH deposited in the pore system. Evidently, the increase of NS replacement increases the mixed water which leads to the formation of more porosity.

Figure 3 demonstrates SEM micrographs of cement pastes with unactivated and thermally activated NS at 7 days. More pores can be noticed for the unactivated NS filled cement binder compared to the activated one as seen in Fig. 3a and b. It can be seen that CSH is predominant with less CH crystals. Also, it can be seen that the activated NS cement paste has produced a more dense structure and compact formation of hydration products than the unactivated NS cement paste, which explains the enhancement in ITS.

The physical and diffusion properties were measured and tabulated in Table 3. The results show that the activation of NS decreases the porosity of the blended cement which agrees with the SEM micrographs. The results also show that, increasing the replacement content of unactivated NS generally decreases the density and increases the water absorption and the porosity of blended white cement pastes. It has a very small influence on both the thermal resistivity and the UV solar reflectivity. Activation of NS allows all the properties to have the same trend, except the solar reflectivity. Activation of NS had a negative effect by

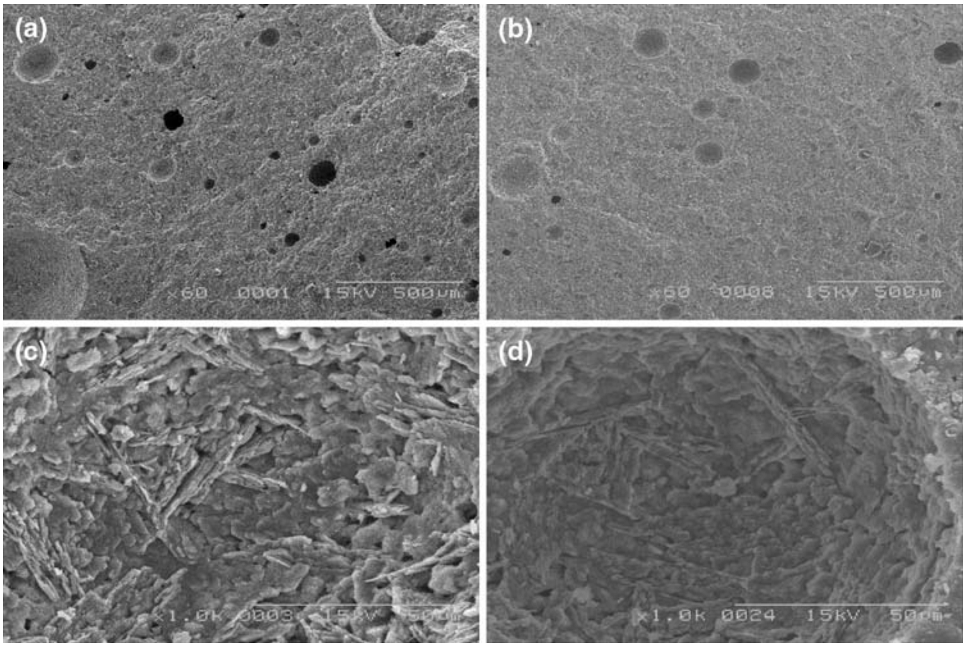


Fig. 3 SEM micrographs of 7-day aged nano silicate filled cement binders **a** unactivated at 60× **b** activated at 60× **c** unactivated at 1,000× **d** activated at 1,000×

Table 3 Physical and diffusion properties of nano silicate filled cement binders

Property	Unactivated NS/binder				Activated NS/binder		
	0%	2%	5%	10%	2%	5%	10%
Density (kg/m^3)	1,900	1,840	1,700	1,635	1,865	1,820	1,755
Porosity (%)	26.4	39.1	40.4	42.9	32.3	34.1	34.9
Water absorption (%)	12.3	14.9	16.9	19.7	14.2	14.9	18.3
Thermal resistivity (mK/W)	1.5	1.5	1.6	1.8	1.5	1.7	1.7
Solar reflectivity (%)	90	89	91	91	83	81	75

reducing the solar reflectivity of blended pastes as compared with unactivated blended pastes and a downward trend as the NS content increased could be observed. Upon activation, the originally white nanosilicate became dark brown. This change in color has affected the whole blend and made it darker in color than the unactivated blend. A darker blend will result in lower solar reflectivity. Activation of NS lowers the porosity and water absorption of the blended cement pastes, while increasing the density and there was almost no effect on the thermal resistivity.

Conclusions

Activation of nanosilicate and its effect on the thermal and mechanical properties of activated NS filled cement binders is presented. The main conclusions that were derived can be summarized as:

- Activation of nanosilicate is helpful in enhancing the tensile strength of cement paste and an optimum replacement within 2% can be concluded. There was an enhancement by about 50% compared with the unactivated nanosilicate blended paste.
- Activation of nanosilicate had a negative effect by reducing the solar reflectivity of blended pastes as compared with unactivated blended pastes. Increasing the activated nanosilicate content of the blended paste further decreased the UV solar reflectivity.
- Activation of nanosilicate slightly increased the density and decreased the porosity and water absorption of the blended cement paste compared with those with unactivated nanosilicate.

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