Influence of Aggressive Exposure on the Degradation of Nano-Silica Admixed Cementitious Mortar Integrated with Phase Change Materials

Snehal K[1] and B B Das[1*] and Salim Barbhuiya[2]

[1]Department of Civil Engineering, National Institute of Technology Karnataka, Surathkal, Karnataka, India, 575 025.

[2]Department of Engineering and Construction, University of East London, United Kingdom

*Corresponding Author

Abstract:

The objective of the present study is to evaluate the stability of cementitious mortar incorporated with phase change material (PCM, n-octadecane) at aggressive exposure conditions such as acid (1% H_2SO_4), alkali (5% Na_2SO_4) and chloride (5% NaCl). Thermogravimetric analysis (TGA) was performed to characterize and quantify the amount of deleterious compounds such as ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, AFt), gypsum ($CaSO_4\cdot 2H_2O$ Gy) and Freidel's salt ($Ca_2Al(OH)6(Cl, OH)\cdot 2H_2O$, Fs) formed due to the action of SO_4^{2-} (acidic and alkaline media) and Cl^- (chloride media) ions at the continuous exposure period of 180 days. Mass loss associated to the thermal degradation of n-octadecane PCM ($CH_3(CH_2)_{16}CH_3$) at various exposure solutions was also calculated at the temperature boundary of 250-300 °C. This study also highlights the introduction of optimized nano-silica dosage (3%) into the PCM based cementitious mortar to counteract the undesirable facets of PCMs on cementitious system.

Results revealed that incorporation of PCM in cementitious mortar augmented the amount of AFt, Gy (at acid and alkali exposure solution) and Fs (at chloride exposure solution) formation, responsible for the amplified rate of deterioration. It is important to be noted that after long term exposure of 180 days no traces of PCM was observed in PCM based cementitious mortar mixes, which signifies the mixes no longer holds the capacity to store energy. However, co-occurrence of nano-silica (3%) in PCM based cementitious mixes curtailed the negative impact of PCM on cementitious mortars exposed to aggressive conditions significantly. Further, differential thermogravimetric (DTG) curve shows an additional endothermic peak at 250-300 °C for 3% nano-silica modified PCM based cementitious mixes even after exposure to aggressive ions that implies the ability of the mix to sustain the thermal efficiency characteristics of PCMs.

Key Words: Phase change material (PCM), nano silica, aggressive ions, durability, length change.

1. Introduction

Rapid growth in industrialization and urbanization significantly increased the consumption rate of energy. Building and infrastructures are considered to be one of the leading consumers of energy. Major part of the energy consumed in commercial and residential buildings is for maintaining thermal comforts of habitants i.e. especially for space conditioning and heating. Current estimation says that more than 50% of the global energy is being spent at space cooling and heating in building sectors [1-2]. This necessitates the need for conservation of energy and to improve the energy efficiency of the buildings and infrastructure. In this point of view, thermal energy storage and latent heat storage systems are gaining importance for various developments in energy conservation [3-4]. Phase change materials (PCMs) are one such novel sensible and latent heat storage materials which has an ability to absorb and dissipate heat when the material changes its phase from solid to liquid and vice versa [4-6]. PCMs can be incorporated in to a number of construction materials such as gypsum boards, masonry wall with bricks, concrete, asphalt etc., [7-8]. Concrete/cementitious composites are widely used global construction material, which are porous in nature and acts as an ideal media for PCMs incorporation [5-6, 9-10]. Utilization of PCMs in cementitious composites has gained lot of attention by the research community to minimize the energy loading in buildings.

Various types of PCMs can be incorporated in concrete/mortar using different techniques [7, 11]. Among several PCMs, organic types are most preferred by the researchers owing to its better stability in cementitious system [7-8]. N-octadecane is one such organic PCMs which has potential ability to store latent heat and can withstand larger thermal cycles [6, 11] . Major detriment of PCMs use in cementitious composites is loss in structural integrity owing to its leakage issue [5, 9]. This is found to be as foremost limitation for its structural utility. It is also reported that incorporation of PCMs in cementitious composites are responsible for increase in permeable porosity [10, 12]. PCM presence in cementitious system adversely affects the strength and durability performance of cementitious composites [9, 12]. From the literature it is understood that most of the studies on PCM based cementitious mortar/concrete were concentrated on the influence of PCMs on thermal and mechanical aspects of cementitious composites [6-7, 11 13-14]. It is reported that addition of PCMs reduces mechanical strength [6, 11, 13], disturbs the hydration

process [5, 9] and increases the porosity [6, 10, 12] of cementitious composites. Further, studies stated that incorporation of PCMs in cementitious composites enhances the specific/latent heat [6, 14-18] and reduces the thermal conductivity [15-17].

In the present scenario, another important deciding parameter for any structural material is that its response against aggressive environment. Country like India encompasses varied weather conditions with vast coastal area in the south. Aggressive change in climatic condition is triggered by means of speedy evolution of industries and cities over the period of time. This dramatic change in climatic condition is always been a concern in regard to the service life of concrete/cementitious composites. From various studies it is evident that cementitious composites deteriorates and loses it structural properties on exposing to aggressive conditions [19-20]. Wei et al (2017) reported that significant reduction in enthalpy (of the order 25%) was experienced when PCM based cementitious composite are exposed to sulfate bearing environment. However, very limited studies are focused on the durability aspect of PCM incorporated cementitious composites against aggressive ions [21].

Sulfate (SO_4^{2-}) and chloride (Cl^-) are the major detrimental aggressive ions that impacts the service life of cementitious composites [19]. Sulfate attack in the form sulfuric acid (acidic) and alkaline (Na, K, Mg) sulfate are responsible for the formation of expansive compounds such as gypsum (Gy) and ettringite (AFt) which hampers the cementitious system [20]. Similarly, cement based concrete or mortar also have least resistance to chloride attack. It is reported that continuous exposure of cementitious composites to chlorides may cause deleterious effects such as a) decalcification of calcium hydroxide resulting leaching of calcium chloride, b) development of porous C-S-H and c) formation of voluminous compound such as Friedel's salt and its analogous due to the reaction between calcium aluminates and chloride ions, ultimately leading to cracks in concrete [22]. At this point of time, it is very much essential to study the durability parameters of the innovative smart cementitious composite composing of PCM under different aggressive exposure conditions such as acidic, alkaline and saline media.

On the other hand, the concept of nanotechnology to improve the performance of cementitious composites by making use of nano-sized materials has opened up a new drive

in concrete history. Nano-silica, a silica enriched nano particle (with active SiO_2 content >99.5%) is the most preferred nano-scale material in cementitious composites as a performance enhancing ingredient [23]. Nano-silica is considered to be as superior pozzolanic ingredient with a potential to boost the extent of chemical reactivity owing to its high surface to volume ratio [24-25]. It was reported that incorporation of small percentage of nano-silica in cementitious composites aids in enhanced the early and later age properties of cementitious composites [23-24, 26]. Hasty pozzolanic reaction and nano-filler effect of nano-silica improved the microstructure of cement composites and thereby assisted in attaining better resistance to permeability of aggressive ions [27]. It was understood from previous experimental study carried out on PCM based cementitious mortar integrated with nano-silica that drawbacks of PCM based cementitious composites in terms of engineering, hydration and microstructure properties can be tailored by integrating a highly pozzolanic nano-silica particles [6]. But, after reviewing considerable amount of research articles it was observed that no studies have specifically focused on the combined effect of nano silica and PCM in cementitious composites with respect to aggressive ions. Further, lack of investigations on the effects of direct incorporation of bulk PCMs on the same is also noticed. Consequently, there is a need to provide more emphasis on PCMs and PCMs in combination with nano-silica performance against aggressive ions for its better usage in structures at varied climatic region.

In this perspective, the present experimental study was carried out to demonstrate the effect of direct incorporation of bulk PCM (n- octadecane) in cementitious mortar on different aggressive exposure conditions such as sulfuric acid (acidic), sodium hydroxide (alkaline) and sodium chloride (chloride). PCM was directly added to cementitious mortar mix at the levels of 1%, 3% and 5% by weight of the binder without replacement to any ingredients. Influence of aggressive ions on compressive strength, density and length changes of PCM added cementitious mortar cured for 28 days at various exposure periods were investigated. Subsequently, PCM based cementitious mixes were modified by integrating optimum dosage of nano-silica (3%) to improve the resistivity towards aforementioned aggressive conditions and the same were studied. Thermogravimetric analysis integrated with differential thermogravimetric (TG-DTG) studies were employed to quantify the formation of deleterious compounds such as ettringite (AFt), gypsum (Gy) and Freidel's salt (Fs) at

various temperature ranges of 50-150 °C, 120-150 °C and 230 to 380 °C, respectively. Further, PCM deterioration due to the same was determined on the basis of thermogravimetric mass loss at the temperature range of 250 - 300 °C.

2. Experimental investigation

2.1. Materials and material properties

Material used in this study for the preparation of cement mortar includes commercially available ordinary Portland cement (OPC) in compliance to ASTM Type I [28], organic based PCM i.e. n-octadecane (n-oct, $CH_3(CH_2)_{16}CH_3$), water-based and sodium-stabilized colloidal nano-silica (CNS, 20 nm) and zone II river sand as fine aggregate (confirming to IS 383-2016 [29]).

Material properties of the ingredients used in present study are given in Table 1 and the particle size distribution of the materials used are presented in Figure 1.

Table 1. Physical properties of the cement and fine aggregate used in the study

Material used	G	ρ m^2/kg	SC	Setting time (min)		FM	Appearance	MP (ºC)	LH (J/g)	Solid Content (w/v)	SiO_2 content
				IST	FST						
OPC	3.15	300	32	110	170	-	powder	-	-	-	-
River sand	2.56	-	-	-	-	3.14	grains	-	-	-	-
PCM * (n-oct)	0.78	-	-	-	-	-	oil	26-29	289.4	-	-
CNS*	1.7	2,00,000	-	-	-	-	liquid	-	-	40%	99.5

*Manufacturers data, G- Specific Gravity, SC- Standard Consistency, IST-Initial Setting Time, FST-Final Setting Time, FM-Fineness Modulus, ρ- fineness, MP-melting point, LH-latent heat of fusion.

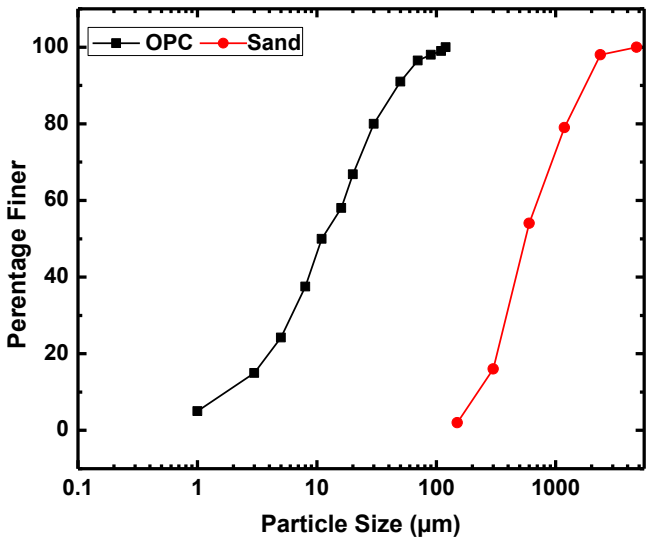


Figure 1. Particle size distribution curve of the materials used in this study

2.2. Mix proportions

Total eight mortar mixes were prepared in this study. Among these mixes one is control mix (with no PCMs and Ns) which was considered to be as reference mix. It is to be noted that PCM (n-octadecane) is directly added to the mortar mixes without replacing any of the mortar ingredients at 1%, 3% and 5% by weight of OPC. On the other hand, optimum dosage of nano-silica (3%) was used as a partial replacement to OPC [6, 23]. For all the mixes, constant water to binder ratio and water to sand ratio of 0.5 and 1:3 were adopted in this experimental study. It is to be noted that care was taken on calculating water content for particular mixes consisting of colloidal nano-silica (i.e. amount of water present in colloidal nano-silica was adjusted by deducing it from total water content). The detailed mix proportion along with mix designation for all the mixes are furnished in the Table 2.

177 **Table 2.** Mix proportions for various mortar mixes used in present study

Mix	Mix Designation	OPC	Ns	PCM	Cement	Ns	PCM	Sand	Water
		%			Quantity (kg/m^3)				
Control	CM	100	-	-	568.35	0	0	1705.1	284.2
OPC + nano-silica - 3%	CNS-3M	97	3	-	551.30	17.05	0	1705.1	258.6
OPC + n-octadecane-1%	oct-1M	100	-	1	568.35	0	5.68	1705.1	284.2
OPC + n-octadecane-3%	oct-3M	100	-	3	568.35	0	17.05	1705.1	284.2
OPC + n-octadecane-5%	oct-5M	100	-	5	568.35	0	28.42	1705.1	284.2
OPC + 3% nano-silica + n-octadecane-1%	CNS/oct-1M	97	3	1	551.30	17.05	5.68	1705.1	258.6
OPC + 3% nano-silica + n-octadecane-3%	CNS/oct-3M	97	3	3	551.30	17.05	17.05	1705.1	258.6
OPC + 3% nano-silica + n-octadecane-5%	CNS/oct-5M	97	3	5	551.30	17.05	28.42	1705.1	258.6

178 2.3. Experimental methodology

179 2.3.1. Sample preparation

180 Initially, n-octadecane PCM (in molten form) and CNS (for mortar mixes containing nano-
181 silica) was added to water and uniformly dispersed by means of continuous stirring. Next,
182 OPC and sand were dry mixed for 120 sec at low speed using 5 liter capacity automatic
183 mortar mixer. Finally, water comprising of PCM/Ns or both are added gently and mixed
184 for 120 sec (30 sec at slow speed + 90 sec at high speed). The fresh mortar samples prepared
185 using automatic mortar mixer were cast in designated moulds of the size 70.6 mm x 70.6
186 mm x 70.6 mm (for measuring density and strength losses associated to different chemical
187 exposures) and 25 mm x 25 mm x 285 mm (for measuring change in length associated to
188 different chemical exposures). Then, samples were made to store in laboratory condition
189 (Temp: 27 ± 2 °C and RH: 95%) for 24 hrs. After 24 hrs samples were demoulded and
190 subjected to saturated water curing for a period of 28 days.

191 2.3.2. Testing methodology

192 Cubical mortar samples of size 70.6 mm x 70.6 mm x 70.6 mm were used to measure the
193 resistance to aggressive chemicals (acid alkali and chloride) in terms of density loss and

strength loss. After the specified period of water curing i.e. 28 days, samples were taken out of the water submerged condition and allowed to attain saturated surface dry condition. Compressive strength of all the mixes cured for 28 days were determined using compressive strength testing machine of 2000 kN capacity at the loading rate of 35 $N/mm^2/min$ (IS 4031 (part 6)-1988) [30] and that was noted as initial compressive strength value ($\sigma_{initial}$) of the respective mix. Next, initial density ($\rho_{initial}$) of the samples before exposing to any chemical solutions were recorded using weighing balance (precision 0.1 g). Subsequently, all the samples were exposed to differed chemical solutions by submerging the samples in an independent containers comprising of 1% sulfuric acid (acid environment, pH 0.3), 5% sodium sulfate (alkali environment, pH 12.0) and 5% sodium chloride (chloride environment, pH 7.0) solutions [19-20, 31]. Samples were kept exposed to solutions for the period of 30, 60, 90, 120 and 180 days. Chemical solutions were sporadically checked for pH and maintained accordingly till the long term exposure period of 180 days. After the accomplishment of specified exposure periods, samples were taken out of the exposure media and allowed to attain surface dry condition. Subsequently, checked for final density (i.e. ρ_{final}) and compressive strength (σ_{final}) at particular period of exposure. Density loss (ρ_{loss}) and strength loss (σ_{loss}) percentage of particular mix exposed to certain type and period of exposure were calculated with respect to initial density and strength values [19]. Average of three cubical samples was considered as density loss and strength loss value for corresponding mix at specified type and duration of exposure.

Mortar bars of size 25 mm x 25 mm x 285 mm were cast to measure the change in length of the samples exposed to acid, alkali and chloride solutions. Length comparator apparatus (ASTM C490/490M) [32] was used in this study to measure the associated length change of the samples exposed to various exposure media. Prism samples water cured for 28 days were allowed to attain saturated dry condition and the initial comparator reading was noted. Then, all the samples were made to immerse in different chemical solutions such as 1% sulfuric acid (acid environment, pH 0.3), 5% sodium sulfate (alkali environment, pH 12.0) and 5% sodium chloride (chloride environment, pH 7.0) using independent containers with maintained pH throughout the period of exposure. Change in length were checked and kept recording at the exposure periods of 1, 3, 7, 14, 30, 60, 90, 120 and 180 days. Length change of samples were measured in compliance to ASTM C 157/C157M (acid and saline

exposure) [33] and ASTM C 10212/1012M (sulfate exposure) standards [34]. Change in length in terms of micro strains for mortar samples was calculated as per ASTM C596-18 standards [35].

Thermogravimetric analysis was carried out using TG/DTA analyzer (Rigaku-TG/DTA 8122). Crushed and grinded mortar samples passing through 75 micron sieve were used to characterize the thermal mass loss of the chemically exposed PCM based mortar samples. Test was carried out at nitrogen purge environment (heating rate: 10 °C/min and purge rate: 20 ml/min), at the temperature range of 50–900 °C. On the basis of obtained TGA results, deleterious compounds formed due to acid and alkali attack i.e. ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, AFt) and gypsum ($CaSO_4\cdot 2H_2O$, Gy) were quantified using the Eqs. 1 and 2, respectively considering the mass loss at particular temperature boundaries of 50-120 °C and 120-150 °C, respectively [19, 36]. Freidel's salt ($Ca_2Al(OH)6(Cl, OH)\cdot 2\ H_2O$, Fs) formed due to chloride exposure was quantified using the Eq. 3 by considering the mass loss at specific temperature range of 230-380 °C [19, 37].

$$\text{AFt (\%)} = m_{AFt} \cdot \frac{M_{AFt}}{26M_H} \quad (1)$$

$$\text{Gy (\%)} = m_{Gy} \cdot \frac{M_{Gy}}{2M_H} \quad (2)$$

$$\text{Fs (\%)} = m_{Fs} \cdot \frac{M_{Fs}}{6M_H} \quad (3)$$

Where, m_{AFt}, m_{Gy} and m_{Fs} describes the percentage mass loss linking to AFt, Gy and 6 molecular layer of water from Fs at the temperature ranges of 50-120 °C, 120-150°C and 230- 380 °C, respectively. M_{AFt}, M_{Gy}, M_{Fs} and M_H represents the molecular weight of AFt, Gy, Fs and H_2O i.e, 786.7 g/mol, 172.17 g/mol, 561.3 g/mol and 18.02 g/mol, respectively.

Further, percentage of mass loss associated to thermal degradation of PCM based hydration product (Δm_{PCM}) at the temperature boundaries of 250-300 °C was calculated using Eq. 4.

$$\Delta m_{PCM}(\%) = m_{250°C} - m_{300°C} \quad (4)$$

3. Results and Discussion

3.1 Thermogravimetric analysis (TG-DTG) - before exposure to aggressive chemicals

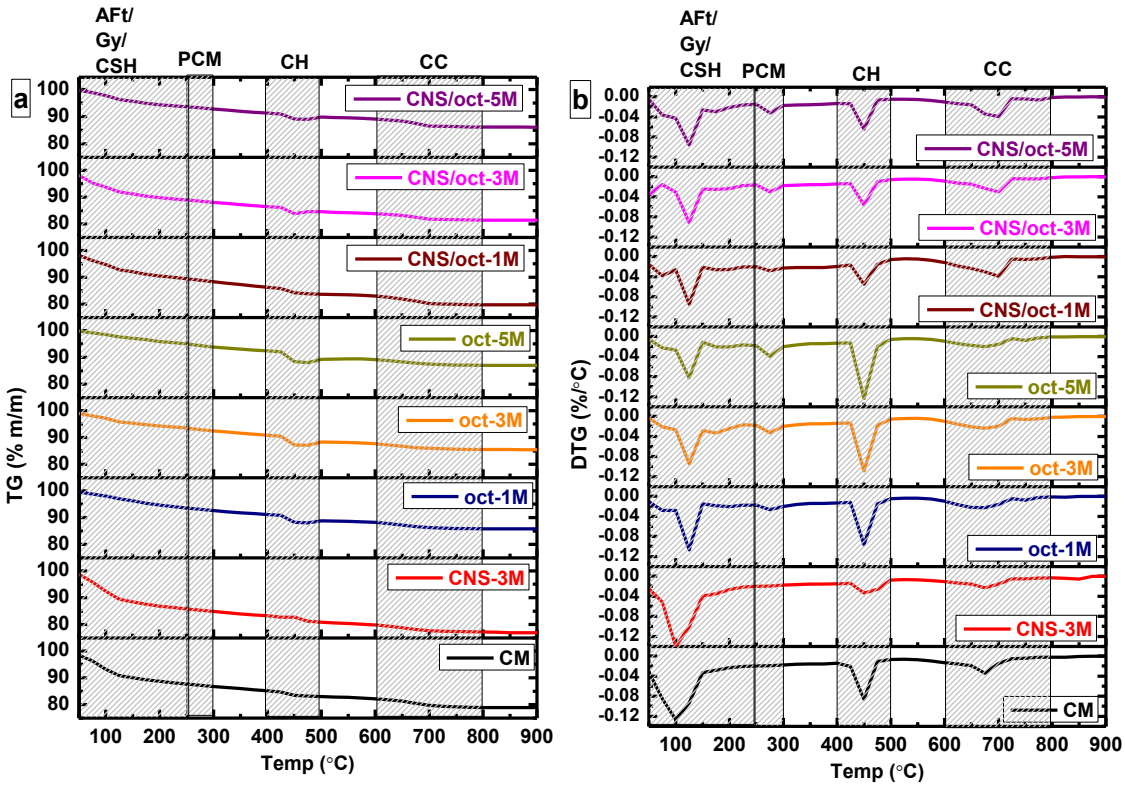


Fig. 2 TG-DTG curve for all the mixes at the curing age of 28 days before exposure to aggressive chemicals

Fig. 2 represents the TG-DTG plot for all the cementitious mortar mixes at the curing age of 28 days (without any chemical exposure). Quantification and identification of phases in cementitious composites are made by considering the moss loss associated to the endothermic peaks at specific boundaries of temperature i.e., 50-200 ºC, 200-300 ºC, 400-500 ºC and 600-800 ºC. It is reported that formation of phases at the temperature range of 0-200 ºC in cement matrix are complex. Mass loss at 0-50 ºC relates to the removal of free molecules of water. Subsequently, mass losses at 50-120 ºC [36], 120-150 ºC [36] and 150-300 ºC [23] signifies the decomposition of ettringite (AFt), gypsum (Gy) and dehydration of calcium silicate hydrate (CSH), respectively. Further, dehydroxylation of calcium hydroxide (CH) and decarbonation of calcium carbonate (CC) are associated to the mass losses at the particular temperature ranges of 400-500 ºC and 600-800 ºC, respectively [6, 23]. It is important to note that all PCM added

cementitious composite mixes showed additional endothermic peak (Fig. 2b) at the temperature range of 250-300 ºC indicating the PCM decomposition [5-6]. This study emphasis on the formation of secondary compounds such as AFt, Gy and Fs due to the action of aggressive SO^{4-} and Cl^{-} ions. In this regard, amount of AFt and Gy present in all the mixes at the age of 28 days before exposure to chemical solutions were quantified and presented in the Fig. 3. There was no endothermic peak relating to the decomposition of Fs (i.e., 230- 380 ºC) was observed in case of non-exposed mixes. It is for this reason, plot related to the quantified amount of Fs is not being presented here.

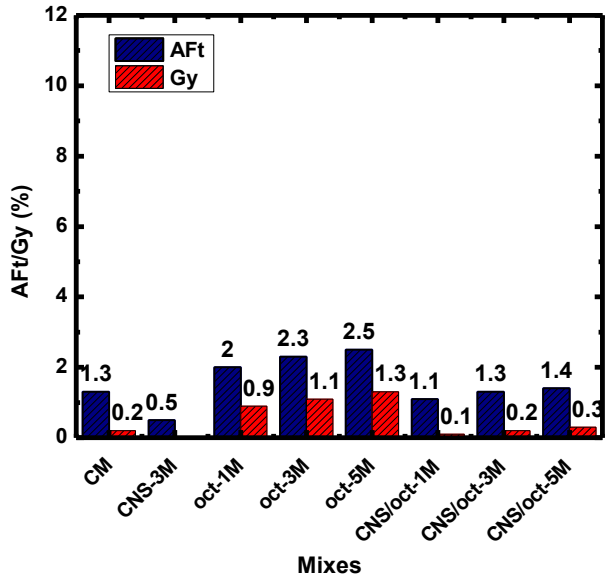
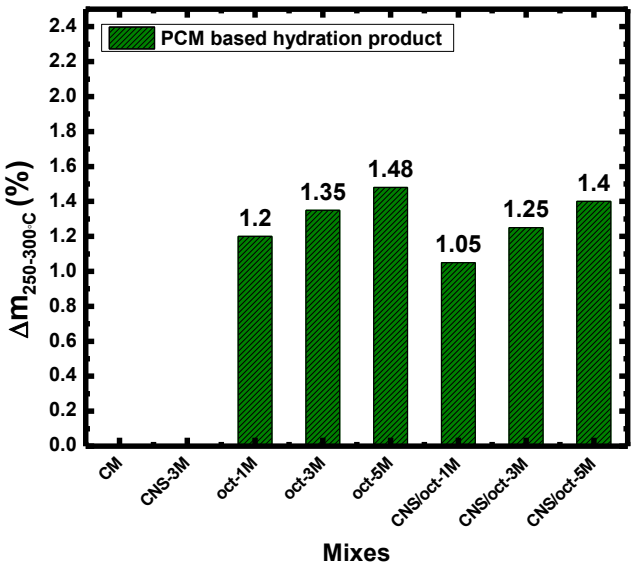


Fig. 3 Quantified amount of AFt and Gy formed for all the mixes at the curing age of 28 days

It can be observed from the Fig.3 that percentage of AFt and Gy formed for all the mixes at the curing age of 28 days falls below 3%. Amount of AFt and Gy formed for control mix was found to be 1.3% and 0.2%, respectively. Resulted amount of AFt and Gy for CNS-3M mix was found to be negligible at the age of 28 days i.e., 0.5% and 0%, respectively. While the mixes composing of PCM showed higher percentage of AFt and Gy, that found to be increased by 52%-90% and 50%-90%, respectively in correspondence to control mix. It is important to note that formation of AFt and Gy was found to be reduced significantly for 3% nano-silica modified PCM based cementitious mixes with respect to PCM based cementitious mixes without nano-silica i.e., 50%-60% and 60%-80%, respectively. This is mainly attributed to the difference in hydration activity exits due to the occurrence of PCMs [5, 6, 9].



286

287 **Fig.4** Mass loss percentage related to decomposition of PCM based hydration product at the
288 curing age of 28 days

289 Mass loss percentage related to decomposition of PCM based hydration product at the curing
290 age of 28 days is presented in Fig. 4. Mass loss percentage for PCM added cementitious
291 composites (i.e. oct-mixes) at the temperature boundary of 250-300 ºC is found to be in the
292 range of 1.2% to 1.5%. While, for 3% nano-silica modified PCM based cementitious mixes
293 (CNS/oct-mixes) it was seen to be reduced by 5%-10%. It is to be noted that PCM based
294 cementitious mixes both with and without nano-silica showed the existence PCM in
295 cementitious matrix after the curing age of 28 days. However, it is reported that compressive
296 strength of cementitious composites drastically reduces due to the crosslinking action of PCM
297 with hydration product (C-S-H). Further, intrusion of optimum dosage of nano-silica stabilizes
298 the disturbed PCM based cementitious matrix [6]

299 3.2 Exposure to acid (H_2SO_4) solution

300 3.2.1 Density loss, strength loss and length change

301 Resulted density and strength loss values for PCM added cementitious mortar mixes (with and
302 without nano-silica) in comparison to control and optimized nano-silica (CNS-3M) mixes
303 exposed to sulfuric acid solution for the contact periods of 30, 60, 90, 120 and 180 days are
304 presented in Fig. 5 and Fig. 6, respectively.

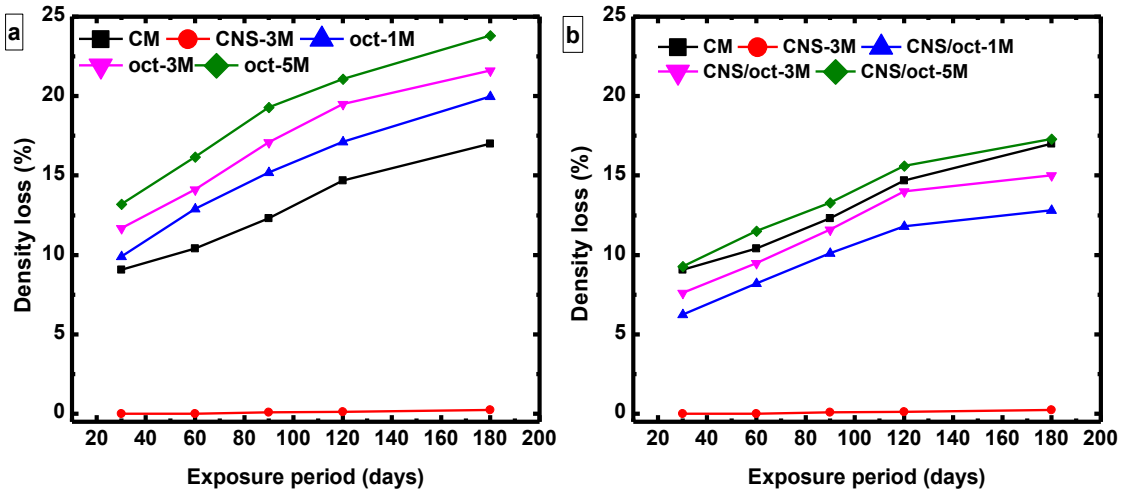


Fig. 5 Percentage of density loss for a) PCM added cementitious composite (oct-mixes) b) 3% nano-silica modified PCM added cementitious composite (CNS/oct-mixes) exposed to sulfuric acid (H_2SO_4)

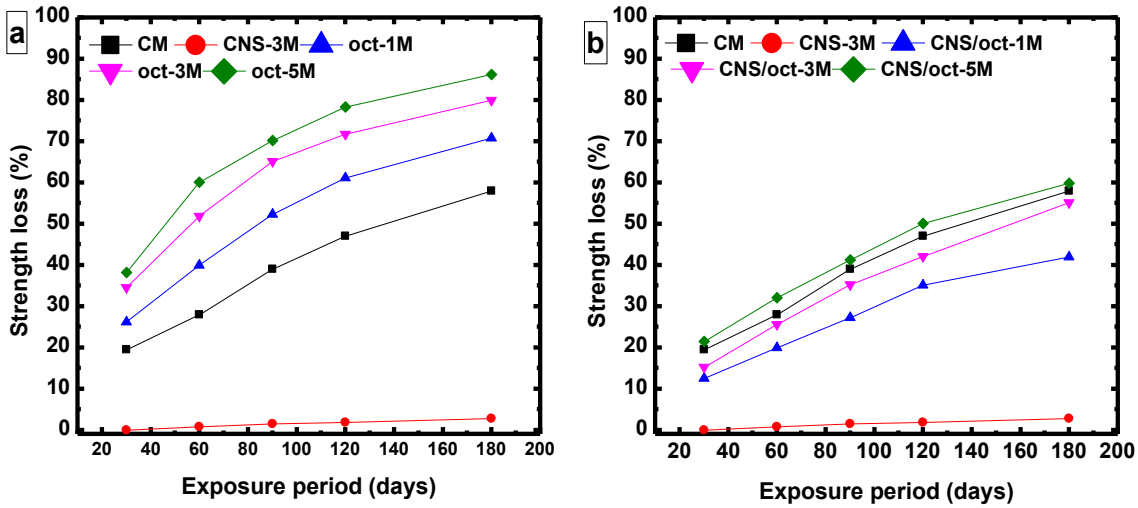


Fig. 6 Percentage of strength loss (%) for a) PCM added cementitious composite (oct-mixes) b) 3% nano-silica modified PCM added cementitious composite (CNS/oct-mixes) exposed to sulfuric acid (H_2SO_4)

It can be observed from Figs. 5 and 6 that among all the mixes CNS-3M mix showed the least deterioration. Percentage of density and strength loss for CNS-3M mix at the exposure period of 180 days was found to be 0.23% and 2.4%, respectively i.e. 98% (density loss) and 96% (strength loss) lower compared to that of control mortar mix. This is ascribed to the high pozzolanic reactivity of nano-silica which aids in reducing initial calcium

hydroxide (CH) content. Further, amplified reactivity of nano-silica led to the densification of cementitious matrix and assists in controlling the further diffusion of aggressive ions. While, rate of deterioration was observed to be higher for PCM added cementitious mortar (oct-mixes) mixes in proportionate to PCM dosage as compared to that of control mortar. Density and strength loss percentage experienced by 5% PCM added cementitious mortar (oct-5M mix) was 25% and 85%, respectively at the exposure period of 180 days. This is mainly attributed to the deleterious act of sulfuric acid (H_2SO_4) on the weak cementitious matrix comprising of PCM and it is also augmented through the combined act of acid and sulfate attack [38]. Exposure to H_2SO_4 would cause dissolution and leaching of acid-susceptible constituents such as calcium hydroxide leading to the formation of gypsum, a soft sulfate di hydrate mineral [39]. Further, this compound along with other sulfate compounds reacts with aluminate phases of cement to form voluminous hydrous calcium aluminium sulfate mineral identified as ettringite [39-40]. It is reported that this action results in an increase in capillary porosity, loss of cohesiveness and eventually losses the strength [38]. It can be understood from the obtained results that by incorporating 3% nano-silica to PCM based cementitious mortar (CNS/oct) which are vulnerable to H_2SO_4, the rate of deterioration can be minimized. Figs. 5b and 6b also depicts that CNS/oct-1M and CNS/oct-3M exhibits lower percentage of density and strength losses compared to that of control mortar irrespective of exposure period. While, density and strength losses for CNS/oct-5M found to be 2% and 3%, higher to control mortar, respectively. Hence, it can be inferred that to reduce the deterioration of the PCM based cementitious matrix occurred due to the intrusion of acid, it is desirable to incorporate highly active pozzolanic ingredient that aids in improving the density and uniformity of the cementitious matrix.

Fig. 7 demonstrates the variation in length change for 1%, 3% and 5% PCM based cementitious mortar mixes (with and without nano-silica) in comparison to control and optimized nano-silica (CNS-3M) mixes, when exposed to 1% H_2SO_4 solution for different periods of exposure.

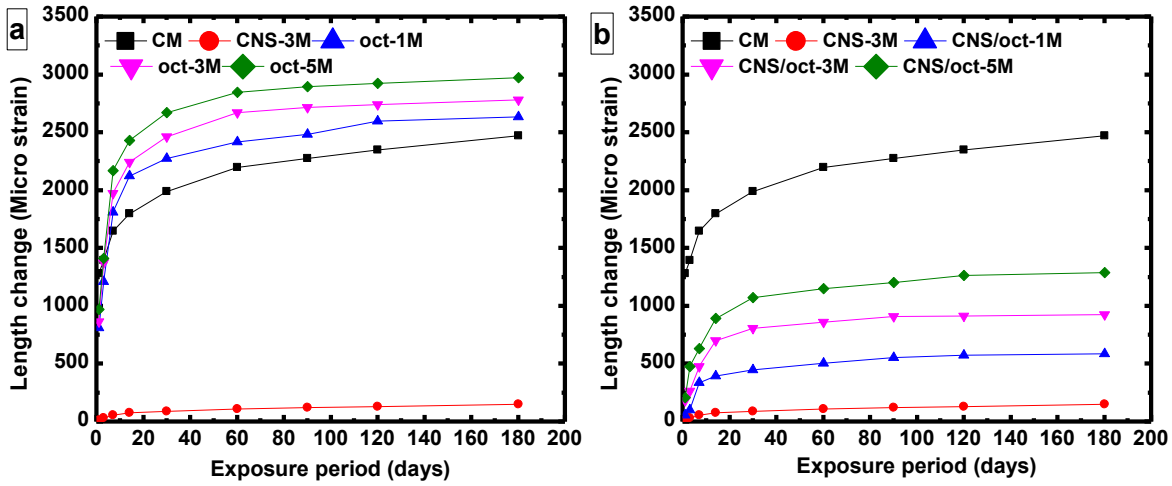


Fig. 7 length change in micro strain for a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sulfuric acid (H_2SO_4) solution

It can be seen from the Fig. 7 that all mortar specimens with and without PCMs exposed to H_2SO_4 undergoes expansion over the period of exposure. This expansion is caused due to the reactivity of sulfate ions with calcium aluminates (C_3A) and calcium hydroxide (CH) leading to the development of expansive compounds such as secondary ettringite (AFt) and secondary gypsum (Gy) [39-40]. It can be perceived from the Fig. 7 that control mortar experiences a length change of approximately 2500 micro strains at the exposure period of 180 days. Results also shows that CNS-3M mortar mix comprising of 3% nano-silica experiences negligible change in length as compared to that of control mortar and other PCM based mortar mixes. Maximum value of length change for CNS-3M was observed to be as 130 micro strain at the exposure age of 180 days. This could be ascribed to the reduction in CH content and improved microstructure of cementitious mortar owing to the high pozzolanic and nano-filling action of nano-silica particles. It can be perceived from the figure that in case of PCM based cementitious mortar mixes (oct-mixes) rate of expansion found to be increased with the increase in PCM dosage and seen to be higher than that of control mix. Length change values for oct-1M, oct-3M and oct-5M at the maximum exposure age of 180 days were seen to be 2636 micro strain, 2781 micro strain and 2975 micro strain, respectively. This can be attributed to the existence of higher percentage of calcium hydroxide owing to the addition of PCMs [6]. In addition to that cross linking of PCM with hydration products weakens the microstructure

of cementitious matrix thereby making the system susceptible to deleterious ions [9]. Increased level of CH in PCM based cementitious system increased the amount of Gy and AFt formation which are highly expansive compounds responsible for voluminous changes in cementitious composites. It is reported that these compounds are responsible for increase in volume of cementitious system by about 1.2 and 2.5 times, respectively [41]. It is to be noted from the figure that PCM based cementitious mortar integrated with 3% nano-silica (i.e. CNS/oct) experiences a length change in the range of 586 to 1289 micro strain that falls lower to that of control mortar. It is evident from the results that rate of expansion of PCM based cementitious mortar corresponding to H_2SO_4 exposure can be controlled by introducing optimized dosage of highly reactive nano-silica particles which has a potential to imbibe lime, fore most susceptible compound in the formation of secondary expansive compounds.

3.2.2 Thermogravimetric analysis (TG-DTG)

In order to understand the influence of H_2SO_4 on PCM added cementitious composites thermogravimetric analysis (TG-DTG) was carried out. Figs 8 and 9 demonstrate the TG and DTG plots for 1%, 3% and 5% PCM based cementitious mortar mixes (with and without nano-silica) in comparison with control and optimized nano-silica (CNS-3M) mixes, when exposed to 1% H_2SO_4 solution for the period of 180 days.

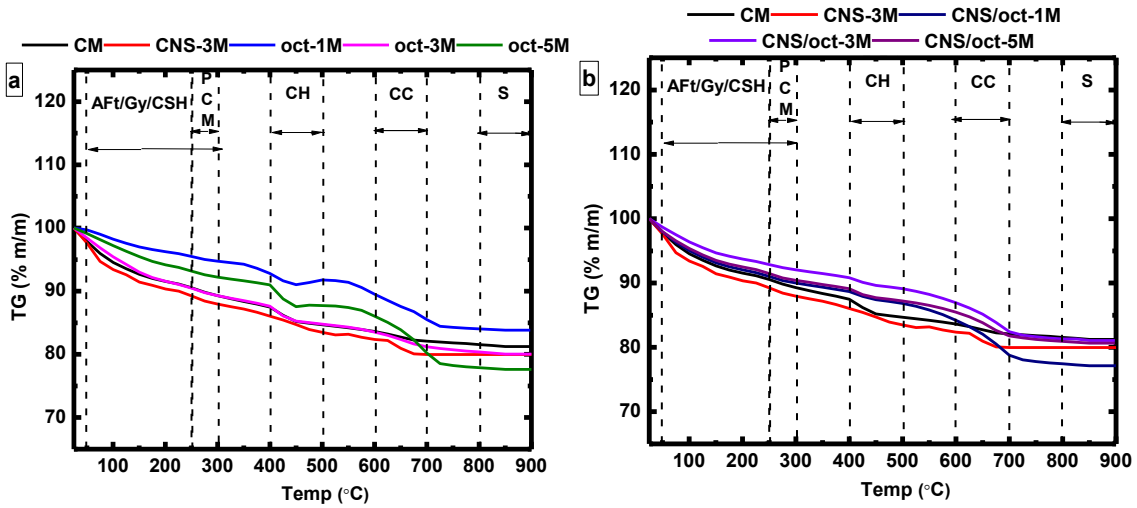


Fig. 8 TGA plot of a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sulfuric acid (H_2SO_4)

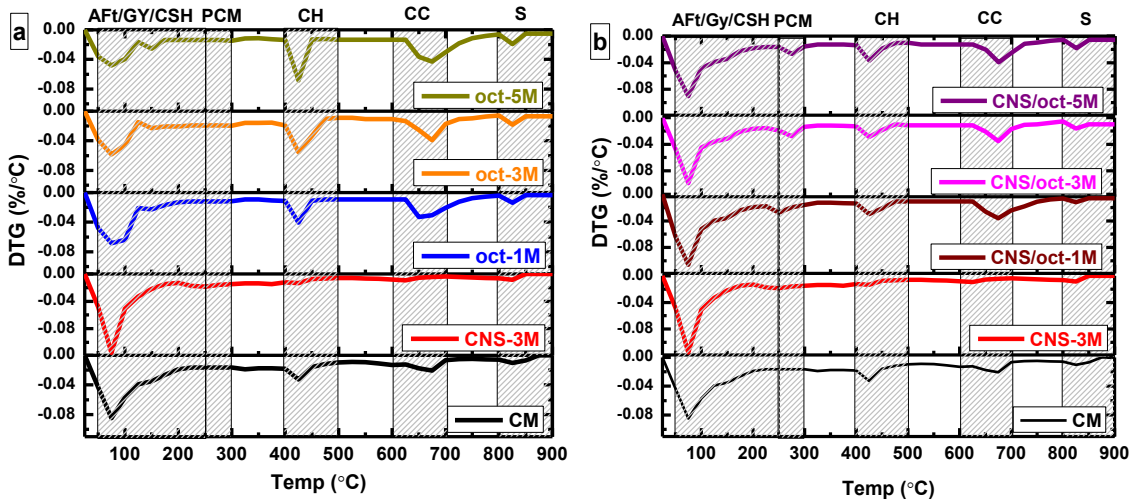


Fig. 9 DTG plot of a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sulfuric acid (H_2SO_4)

Ettringite (AFt) and gypsum (Gy) are the two major compounds formed due to the deleterious action of SO^{4-} ions, which are responsible to the deterioration of cementitious composites. On the basis of TG-DTG results amount of AFt and Gy formed for all the mixes during 180 days of H_2SO_4 exposure were quantified using Eqs 1 and 2 at specific temperature ranges of 50-120 °C and 120-150 °C, respectively. The same are graphically presented in Fig. 10.

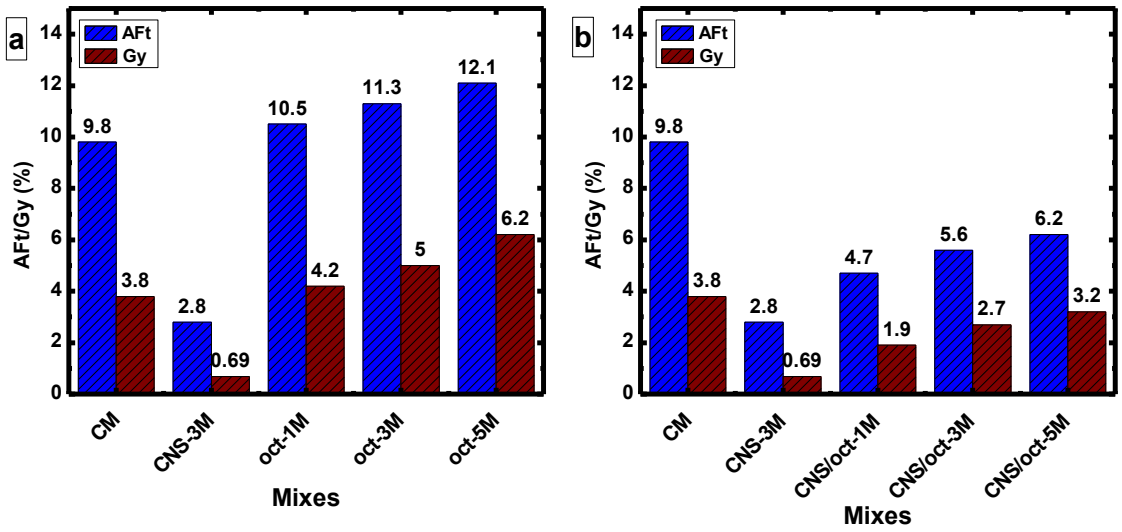


Fig. 10 Quantified amounts of AFt and Gy for a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sulfuric acid (H_2SO_4) solution for 180 days

It can be observed from the figure that least formation of AFt and Gy was obtained for CNS-3M mix. This is attributed to the greater consumption of CH by means of high reactivity rate of nano-silica and formation of densified cementitious matrix owing to its physico-chemical activity [42]. It can also be inferred from the figure that AFt and Gy content for oct-mixes found to be increased with the increase in PCM dosage. Further, it is evident from the figure that AFt and Gy content for PCM added cementitious mixes (oct-mixes) found to be increased by 8-24% with respect to that of control mix. This is ascribed to the increase in CH content with increased dosage of PCM in cementitious mixes. This can be substantiated through the increase in endothermic peak height associated to dehydroxylation of CH (at 400-500 °C) with the increase in PCM content (Fig. 2b). It is to be noted from the Fig. 10 that amount of formation of AFt and Gy for PCM based cementitious mixes were found to be modified by the integration of 3% highly reactive nano-silica particles i.e., CNS/oct mixes. Formation rate of AFt and Gy content for CNS/oct mixes were found to be reduced by ≈50% with respect to PCM based cementitious mixes (oct-mixes). This is mainly attributed to the progressive action of nano-silica on PCM added cementitious mixes by minimizing the pores generated through the incorporation of PCMs, instigating the pozzolanic reactivity and reducing the concentration of CH with in the PCM based cementitious system [6].

In addition, it is important to note from the Fig. 9 that for CNS/PCM mixes there exists an extra endothermic peak at the temperature boundaries of 250-300 °C, which indicates the decomposition of PCM (octadecane) linked calcium silicate hydrate. However, endothermic peak referring to PCM was found to be absent in PCM based cementitious mixes without nano-silica (oct-mixes). This could be attributed to extermination of PCM in cementitious mixes exposed to H_2SO_4. Whereas, presence of nano-silica in PCM based cementitious mixes controlled the deterioration of PCM caused due to H_2SO_4 exposure owing to the refined microstructure of cementitious matrix through the action of nano-silica. This demonstrates that in case of CNS/oct mixes PCMs are still active as a thermal storage material even after the 180 days of H_2SO_4 exposure. In this regard, percentage of mass loss associated to the decomposition of PCM based hydration product (at 250º C-300 °C) was calculated for all PCM added cementitious composites (with and without nano-silica) and the results are presented in Fig 11.

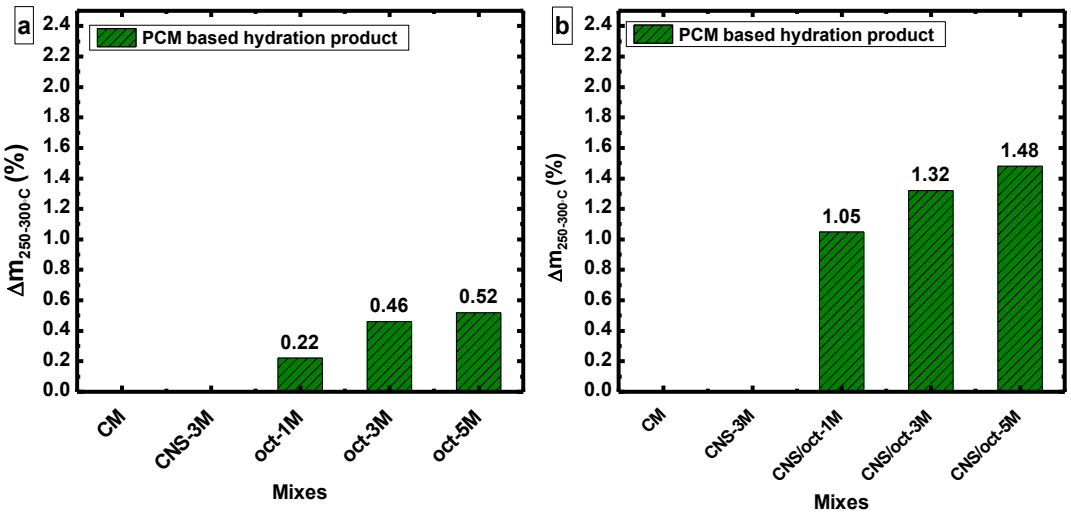


Fig. 11 Percentage mass loss of PCM based hydration product at 250º C-300 °C for a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sulfuric acid (H_2SO_4) solution for 180 days

It can be seen from the Fig. 11 that percentage of mass loss occurred at 250º C-300 °C for oct-mixes is lower to that of CNS/oct mixes. However, for oct- mixes mass loss at that particular temperature relates to the stretching of peaks linking to Aft/Gy/CSH compounds, there is no additional endothermic peak indicating the existence of PCM traces was noticed at this particular range of temperature. Whereas, in case of CNS/oct-mixes prominent endothermic peak was observed at the temperature range of 250º C-300 °C and this specifies the occurrence of PCM cross-linked C-S-H phase i.e. PCM based hydration product. It is reported that thermal decomposition of tobermorite phase of C-S-H that comprises of microstructural crystalline regions with disordered layer structures such as 11 Å/9 Å tobermorite and 11 Å jennite happens at the temperature boundaries of 80º C-300 °C [43]. Here, in case of PCM based mixes owing to the cross linking of PCM with the tobermorite phase of C-S-H, the associated endothermic found at the temperature range of 250º C-300 °C.

3.3 Exposure to alkali (Na_2SO_4) solution

3.3.1 Density loss, strength loss and length change

Figs. 12 and 13 shows the density loss and strength losses endured by 1%, 3% and 5% PCM based cementitious mortar mixes (with and without nano-silica) along with control and

optimized nano-silica (CNS-3M) mixes, when exposed to 5% Na_2SO_4 solution for the exposure periods of 30, 60, 90, 120 and 180 days.

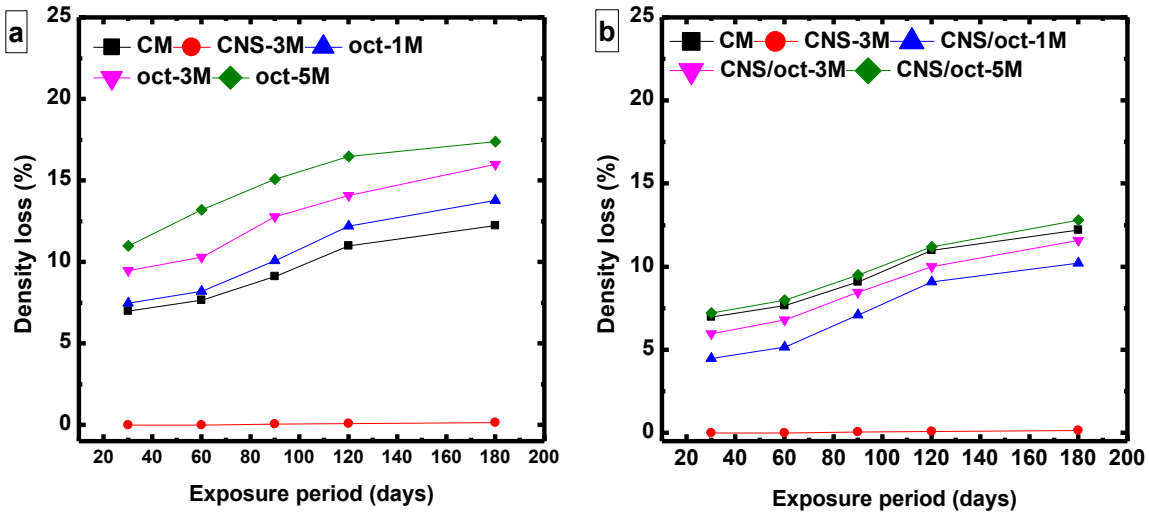


Fig. 12 Density loss (%)) of a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sodium sulfate (Na_2SO_4)

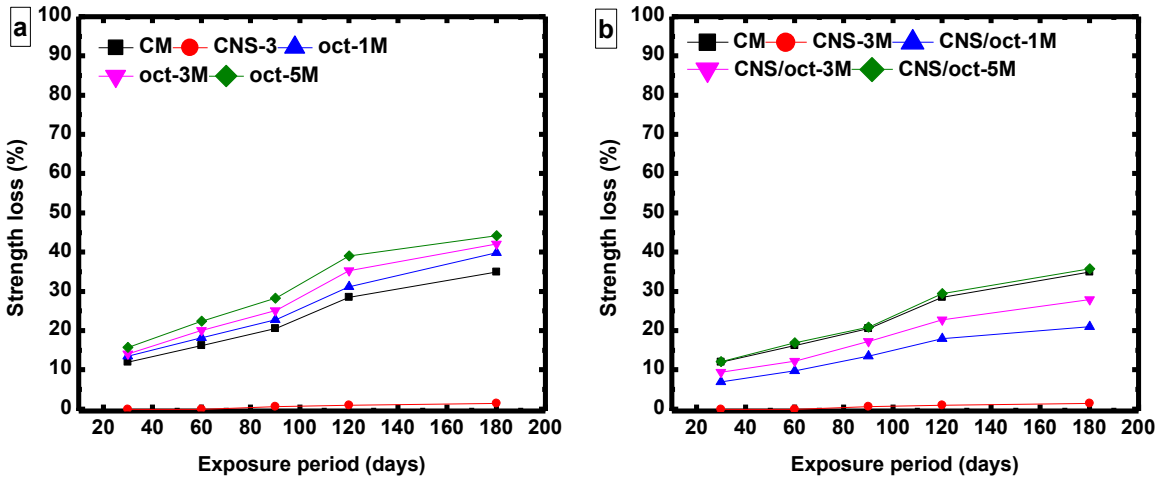


Fig. 13 Strength loss (%) of a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sodium sulfate (Na_2SO_4)

It can be observed from the Figs 12 and 13 that as like H_2SO_4 exposure, CNS-3M mix showed least deterioration in correspondence to alkali (Na_2SO_4) exposure as well. Density loss and strength loss values for CNS-3M mix at Na_2SO_4 exposure period of 180 days was found to be 0.16% and 1.5%, respectively. On the other hand, PCM based cementitious mortar mixes (oct- mixes) experienced greater deterioration as compared to that of control mortar (Fig. 13a).

However, alkaline based Na_2SO_4 solution found to be less aggressive compared to that of acidic H_2SO_4 solution. Among PCM based cementitious mortar mixes, mix comprising of 5% PCM (oct-5M) suffered highest deterioration with maximum density and strength loss values of 17% and 44%, respectively at the exposure period of 180 days. Further, it can be understood from the Fig. 13b that PCM based cementitious mortar mixes when integrated with 3% nano-silica (CNS/oct- mixes) rate of deterioration caused due to Na_2SO_4 exposure found to be reduced. Density and strength losses experienced by CNS/oct-1M and CNS/oct-3M were found to be lower to that of control mortar. It is to be noted that density loss and strength loss experienced by CNS/oct- mixes were found to be reduced by around 27% and 35%, respectively with respect to that of oct-mixes at the exposure period of 180 days. This controlled level of deterioration was due to the presence of nano-silica which compensated the negative impact of PCMs on the performance of cementitious composites.

Length change results of different proportion of PCM added cementitious mixes with and without nano-silica in comparison to control and 3% nano-silica mix is presented in Fig. 14.

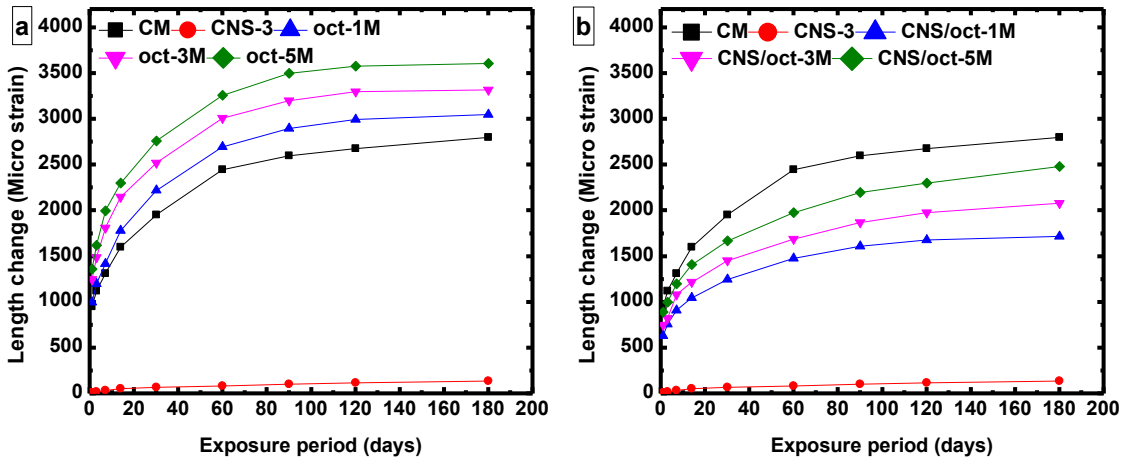


Fig. 14 length change in micro strain for a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sodium sulfate (Na_2SO_4) solution

From the obtained results it can be noticed that all the mixes tends to expand when exposed to Na_2SO_4 solution and found to be higher to that of H_2SO_4 exposure. This could be attributed to the immediate interaction of sulfate ion with the aluminate phases to form voluminous compounds such as AFt and Gy [44]. It can be noticed from the figure that expansion rate for CNS-3M mix with 3% nano-silica (as partial replacement to cement)

was found to be least i.e. 152 micro strain at 180 days of exposure. High pozzolanic nature of nano-silica significantly reduced the amount of CH and C_3A content, which are susceptible for the formation of expansive secondary compounds such as AFt and Gy. Further, Fig. 14a also illustrates that with increase in the addition of PCM content in cementitious mortar, rate of expansion also found to be increased. PCM added cementitious mixes (oct-mixes) showed higher expansion than control (2700 micro strain) i.e. in the range of 3050 to 3610 micro strain. This could be ascribed to the presence of PCMs that disturbed the hydration process by a) cross linking with the hydration products to form larger traces of calcium hydroxide (Fig. 2), b) diminishing the formation of C-S-H and c) leading to the larger formation of AFt and Gy content. But, the rate of expansion of PCM based cementitious mixes can be reduced with the addition of 3% nano-silica. Rate of expansion for CNS/oct- mixes was found to be reduced by 31% - 44% with respect to oct-mixes. This could be due to the presence of nano-silica which accelerated the pozzolanic and hydration activity of CNS/oct- mixes thereby resulting in lesser formation of AFt and Gy.

Diffusion of Na_2SO_4 into cementitious matrix also leads in the formation of voluminous compounds such as AFt and Gy. TG-DTG results of control, optimized nano-silica and PCM based (with and without nano-silica) cementitious mixes exposed to 5% Na_2SO_4 solution for the period of 180 days are presented in Figs. 15 and 16.

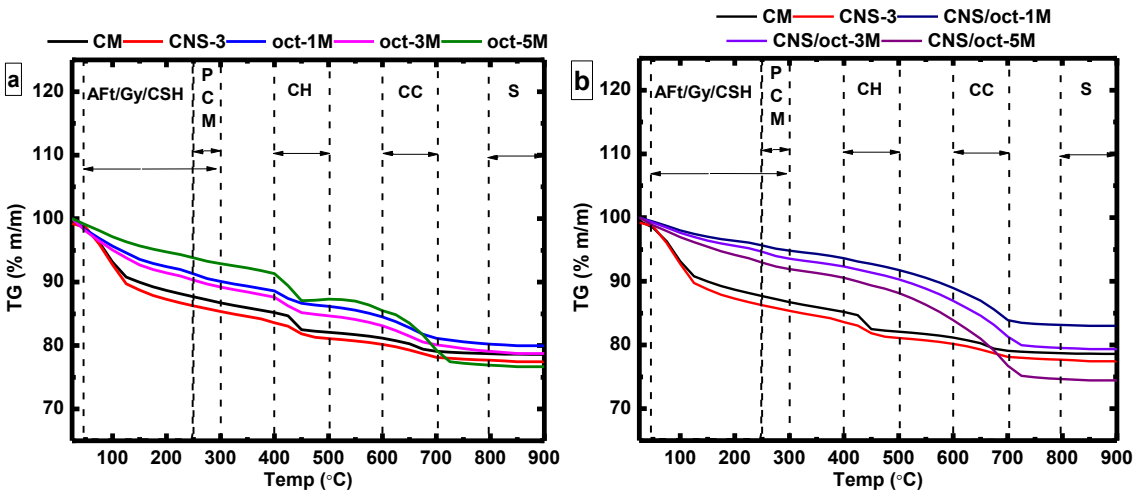
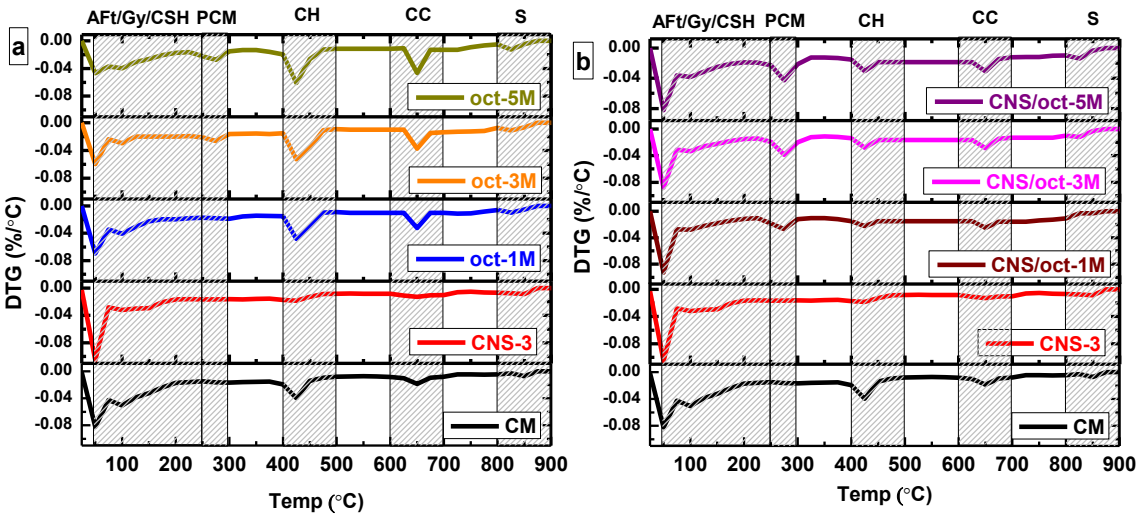


Fig. 15 TGA plot of a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sodium sulfate (Na_2SO_4)



512

513 **Fig. 16** DTG plot of a) PCM added cementitious composite b) 3% nano-silica modified
514 PCM added cementitious composite exposed to sodium sulfate (Na_2SO_4)

515 It can be observed from the figure that the trend of TG (Fig.15) and DTG (Fig. 16) curves
516 for Na_2SO_4 exposed PCM based cementitious mixes were found to be similar to H_2SO_4
517 exposure condition. It is important to note that in case of Na_2SO_4 exposure condition
518 endothermic peak at the temperature range of 250-300 °C which signifies the PCM
519 decomposition was also seen to be exist in oct-3M and oct-5M mixes without nano-silica.
520 This indicates the occurrence of PCM in alkali exposed cementitious mixes at 3-5% PCM
521 dosages. Further, AFt and Gy formed during Na_2SO_4 exposure of PCM based cementitious
522 mixes leads to the deterioration of cementitious system.
523 Quantified amount of AFt and Gy for control, 3% nano-silica, PCM (n-octadecane) and
524 nano-silica modified PCM added mortar mixes exposed to Na_2SO_4 solution for 180 days
525 are plotted in the form of histogram and presented in Fig. 17 (a-b).

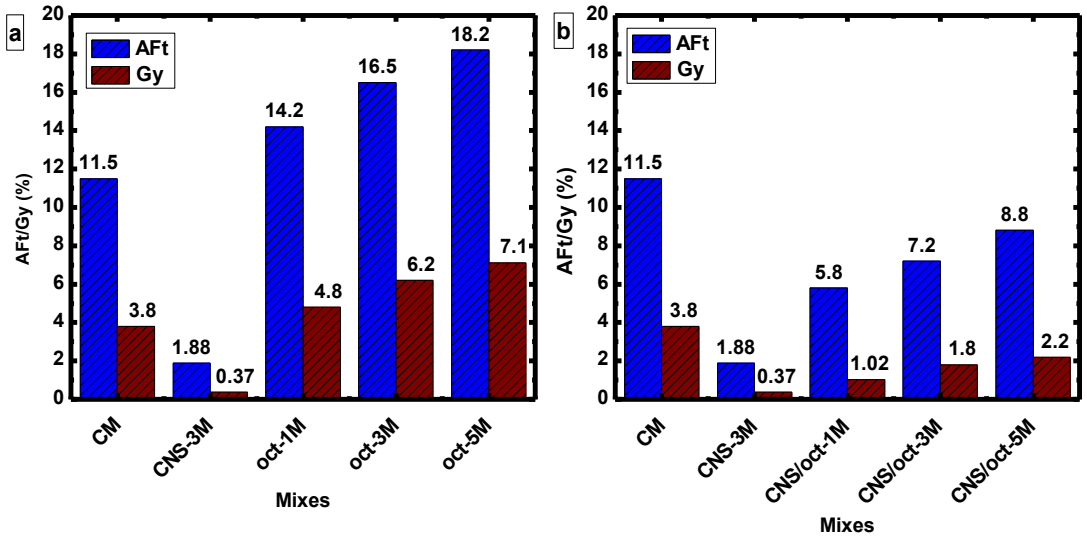


Fig. 17 Quantified amounts of AFt and Gy for a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sodium sulfate (Na_2SO_4) solution for 180 days

It can be seen from the Fig. 17 that CNS-3M mix with 3% nano-silica tremendously reduced the formation of voluminous compounds such as AFt and Gy. This can be attributed to the existence of negligible traces of CH that can be evinced from the mass loss curve associated to dehydroxylation of CH (Figs 15 and 16). On the other end, the rate of formation of AFt and Gy for Na_2SO_4 exposure condition was higher for PCM based cementitious mixes and found to be increased with the increase in percentage of PCM. AFt and Gy content for oct-mixes were found to be increased by 23 - 58% and 26 - 87%, respectively with respect to that of control mix at the exposure age of 180 days. This is attributed to the increase in free lime (CH) and larger availability of un-hydrated aluminate compounds such as C_3A and C_4AF in cementitious matrix owing to the presence of PCM and 100% OPC as a binder. It is reported that PCMs are responsible for increase in capillary porosity in cementitious paste owing to its negative impact on binding, as it gets adsorbed over the surface of cement grains and hydrated compounds [5, 9]. Further, it can be noticed from the Fig.17 that for CNS/oct- mixes formation of AFt and Gy were seen to be curtailed in correspondence to oct-mixes. Amount of AFt and Gy formed for CNS/oct- mixes were found to be reduced by 51 -60% and 69 -79%, respectively in correspondence to PCM based cementitious mixes without nano-silica (oct-mixes). This could be due to the occurrence of highly reactive nano-silica that yields to the reduction of CH

concentration and also complemented in minimizing the capillary pores generated through PCM as well as by CH.

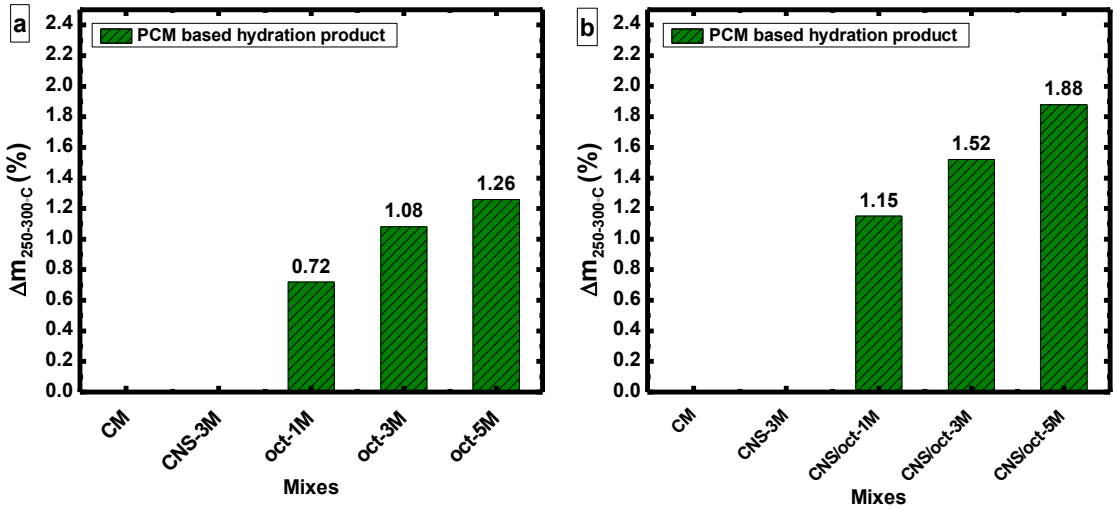


Fig. 18 Percentage mass loss of PCM based hydration product at 250º C-300 °C for a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sodium sulfate (Na_2SO_4) solution for 180 days

Fig. 18 demonstrates the calculated percentage of mass loss linking to the decomposition of PCM based hydration product for the mixes exposed to 5% Na_2SO_4 solution for 180 days. It can be noticed from Fig. 18 that the trend of variation in histogram of PCM based hydration product for Na_2SO_4 exposure found to be in similar to that of H_2SO_4 exposure. In contrast, in case of Na_2SO_4 exposure there could notice a signature of endothermic peak in the specific temperature range of 250 - 300 °C for oct-3M and oct-5M mixes. This signposts that percentage of mass loss for oct- mixes related to the PCM cross-linked hydration product. Further, it is to be noted that percentage of mass loss associated to PCM based hydration product seen to be increased for CNS/oct-mixes and that found to be highest for CNS/oct-5 M mix (1.89%). It is reported that tobermorite phase of C-S-H decomposes at the temperature range of 80-300 °C and the results indicate that n-octadecane based PCM gets adsorbed over the tobermorite phase of C-S-H (PCM based hydrated product), therefore endothermic peak shifts towards the right i.e. at 250-300 °C [43]. Further, it is understood that this particular phase of C-S-H remains stable.

3.3 Exposure to chloride (NaCl) solution

3.3.1 Density loss, strength loss and length change

Figs 19 and 20 presents the density loss and strength loss values for 1%, 3% and 5% PCM based cementitious mortar mixes (with and without nano-silica) along with control and optimized nano-silica (CNS-3M) mixes, when exposed to 5% sodium chloride (NaCl) solution for the duration of 30, 60, 90, 120 and 180 days.

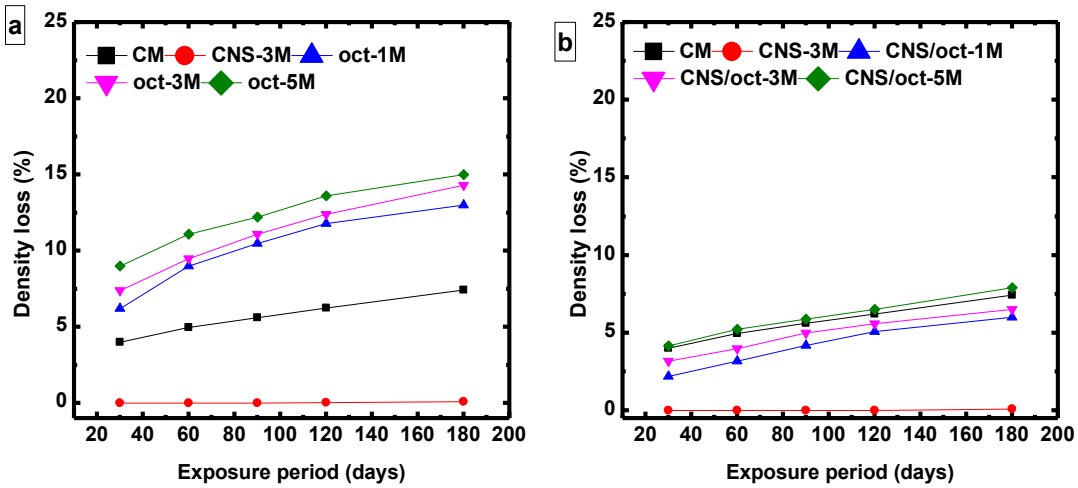


Fig. 19 Density loss (%) of a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sodium chloride (NaCl)

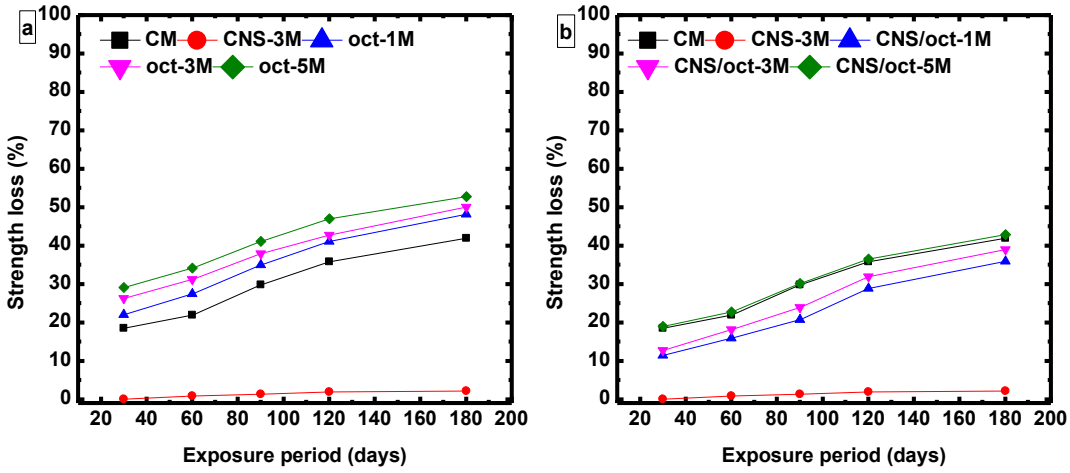
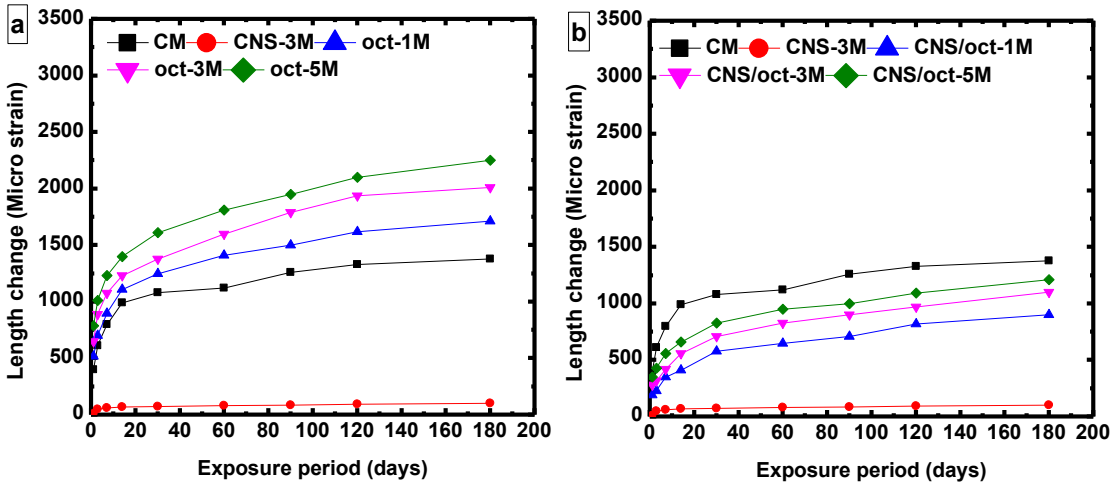


Fig. 20 Strength loss (%) of a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sodium chloride (Na_2SO_4)

It can be observed from the figure that as like acid and alkali exposure, CNS-3M mix showed the least rate of deterioration. It is understood that nano-silica has a greater role in resisting the action of chloride ions on cementitious system owing to its enhanced physical

583 and chemical activity. In contrast, PCM added cementitious mortars (oct-mixes) showed
584 highest rate of deterioration at 5% NaCl exposure. Density and strength losses suffered by
585 oct-mixes were found to be increased by 75-90% and 20-30%, respectively with respect to
586 control mix at 180 days of exposure. This could be ascribed to the deleterious facts such as
587 decalcification, leaching of calcium chloride and formation of porous C-S-H [45]. Further,
588 integration of optimized nano-silica content (i.e. 3%) into the chloride susceptible PCM
589 added cementitious mortar (CNS/oct- mixes) altered the rate of deterioration. Density and
590 strength losses experienced by CNS/oct- mixes were found to be reduced by 47-55% and
591 26-30%, respectively in correspondence to oct-mixes without nano-silica. This can be
592 attributed to the reduced rate of diffusion of chloride ions into the cementitious system
593 owing to the modified microstructure of PCM added cementitious mortar in the presence
594 of highly reactive nano-silica.
595 Change in length associated to the NaCl exposure for PCM added cementitious mortar
596 mixes and nano-silica modified PCM added cementitious mortar mixes in comparison to
597 control and 3% nano-silica mixes are presented in Fig. 21.



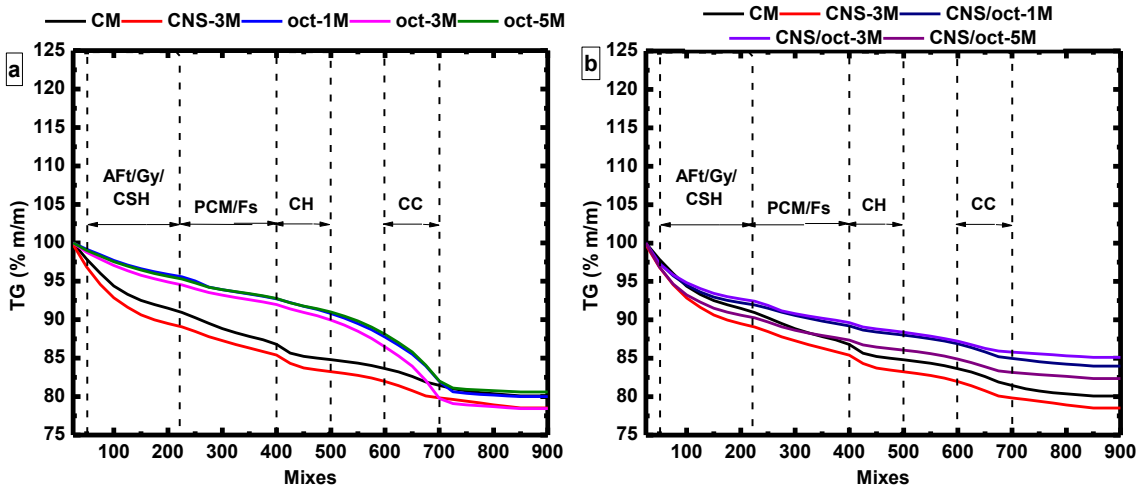
598

599 **Fig. 21** length change in micro strain for a) PCM added cementitious composite b) 3%
600 nano-silica modified PCM added cementitious composite exposed to sodium chloride
601 (NaCl) solution

602 It can be observed from the figure that the trend in variation of length change for control, CNS-
603 3M and all PCM added cementitious mortar (with and without nano-silica) specimens exposed
604 to 5% NaCl solution was found to be similar to acid and alkali exposure. CNS-3M mix

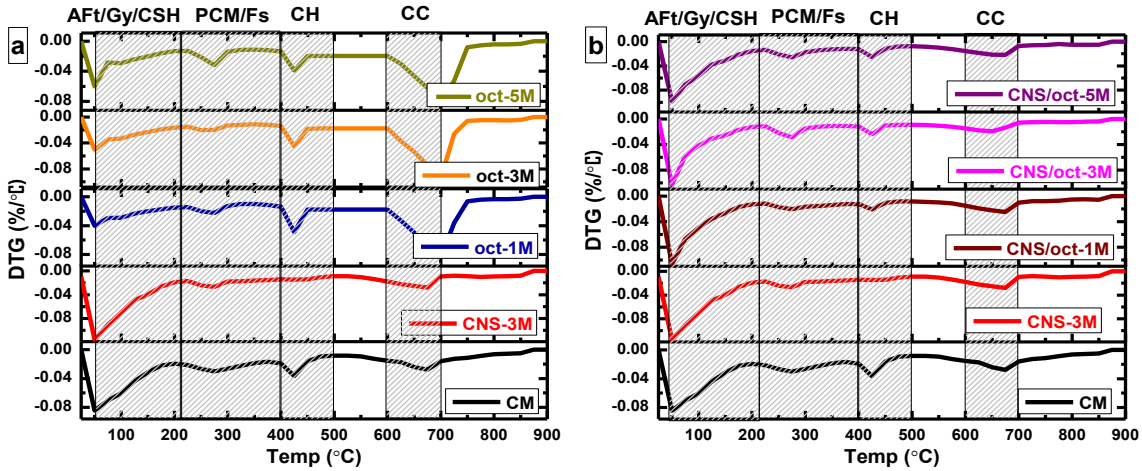
605 comprising of 3% nano-silica showed greater resistance to chloride exposure. Expansion value
606 of CNS-3M mix at the exposure age of 180 days was seen to be less than 100 micro strain.
607 This can be attributed to the least formation of Fs owing to the increased consumption rate of
608 unhydrated/hydrated aluminates phases in the cementitious system and filler property of nano-
609 silica, which resisted the diffusion of chloride ions responsible for the formation of Fs [19].
610 PCM added cementitious mortar mixes (oct-mixes) showed highest rate of expansion.
611 Expansion value for oct-mixes at the exposure age of 180 days was found to be in the range of
612 1750-2250 micro strain which is greater to that of control mix (1300 micro strain). This is
613 mainly attributed to the increased porosity owing to the excessive formation of CH and
614 disturbed hydration system in cementitious composite [6]. Further, leading to the enhanced
615 ingression of chloride ions into the system, thereby develops expansive stress through the
616 voluminous nature of Fs formed within the hardened cementitious system. It is important to
617 note that incorporation of nano-silica in PCM added cementitious mixes controlled the rate of
618 expansion caused due to NaCl solution. Expansion value for CNS/oct-mixes at the age of 180
619 days falls in the range of 750-1150 micro strain. PCM based cementitious mortar in the
620 presence of nano-silica exhibited better-quality microstructure by tailoring the interruption
621 caused by PCM.

622 Interaction of NaCl with un-hydrated and hydrated phases of aluminates of cementitious
623 system leads to the formation of Friedel's salt (Fs) and its analogues.
624 To analyze the action of NaCl on PCM added cementitious samples thermogravimetric
625 analysis (TG-DTG) was carried out for the samples exposed to the duration of 180 days.
626 TG and DTG plot for the same are presented in Figs. 22 and 23, respectively.



627

628 **Fig. 22** TGA plot of a) PCM added cementitious composite b) 3% nano-silica modified
629 PCM added cementitious composite exposed to sodium chloride (NaCl)



630

631 **Fig. 23** DTG plot of a) PCM added cementitious composite b) 3% nano-silica modified
632 PCM added cementitious composite exposed to sodium chloride (NaCl)

633 It can be observed from the Figs. 22 and 23 that 180 days NaCl exposed PCM based mortar
634 mixes (with and without nano-silica) also undergoes series of thermogravimetric mass
635 losses at various temperature ranges similar to acid (H_2SO_4) and alkali (Na_2SO_4) exposed
636 mixes. It can be noticed from the Fig. 23 that in case of NaCl exposed mixes, there exists
637 endothermic peak for all the mixes at the temperature range of 230-400 °C which indicates
638 the overlapping of endothermic peaks developed through the decomposition of two
639 compounds i.e. Friedel's salt (Fs, 230-380 °C) and PCM (250-300 °C). Accordingly,
640 endothermic peak in this particular range of temperature is observed to be broadened.

Quantified amount of chemically bound Fs content for control, nano-silica, PCM (n-octadecane) and nano-silica/PCM based mortar mixes exposed to 5% NaCl solution is shown in Fig. 24.

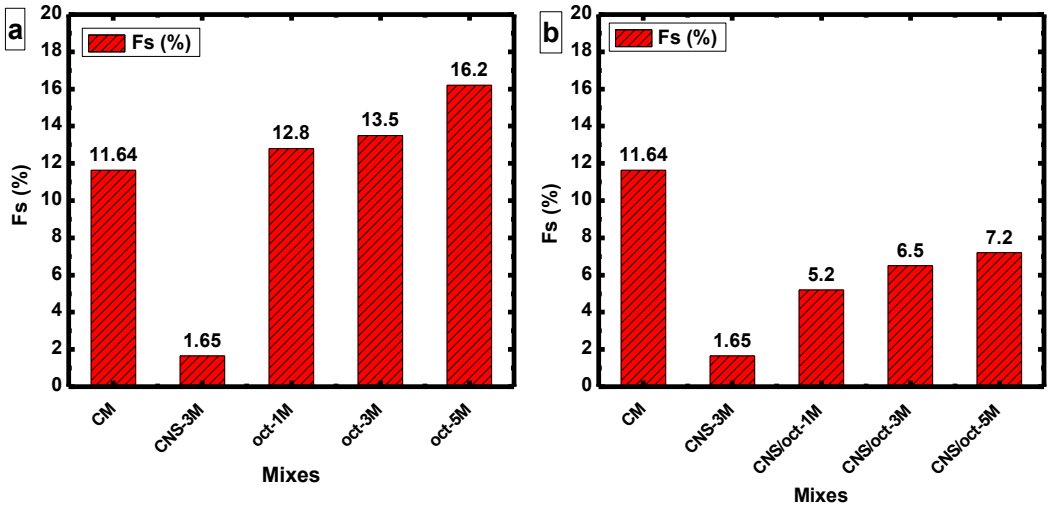


Fig. 24 Quantified amounts of Fs for a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sodium chloride (NaCl) solution for 180 days

Fig. 24 demonstrates the significant drop in Fs content for CNS-3M mix i.e. 86% lower to that of control mix. This could be attributed to the following actions of nano-silica: a) consuming the CH, b) supplementary formation of dense C-S-H, c) nano filler effect and d) reduced concentration of chloride vulnerable compounds such as C_3A and C_4AF. At the same time, amount of Fs formed for PCM added cementitious mixes (oct-mixes) were found to be increased by 10-40% with respect to that of control mix and are directly proportional to the percentage of PCM added. This could be attributed to the occurrence of higher concentration of portlandite (CH) and aluminate phases (C_3A, C_4AF and AFm) [5, 9, 46]. Further, in case of nano-silica modified PCM added cementitious mixes (CNS/oct- mixes) despite of the disruption in hydration process caused by PCM, presence of highly reactive nano-silica scaled down the formation of Fs. Amount of Fs formed in CNS/oct mixes were found to be reduced by 47-50% and 52-55% in correspondence to control and PCM based cementitious mixes (oct-mixes), respectively. This indicates that resistance to chloride ion for PCM added cementitious mixes can be enhanced by integrating 3% of nano-silica.

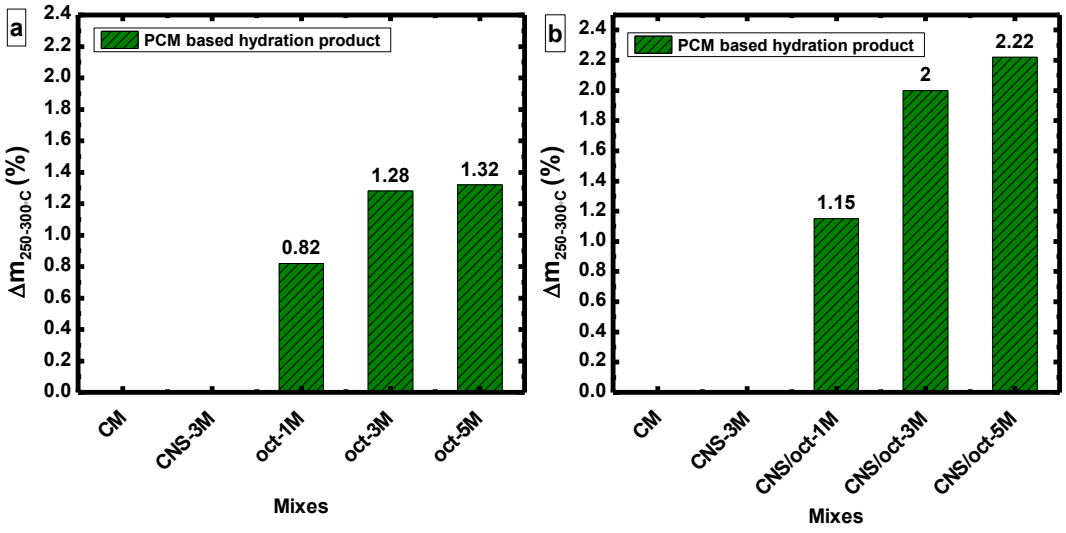


Fig. 25 Percentage mass loss of PCM based hydration product at 250º C-300 °C for a) PCM added cementitious composite b) 3% nano-silica modified PCM added cementitious composite exposed to sodium chloride (NaCl) solution for 180 days

Percentage of mass loss derived from TG-DTG analysis for decomposition of PCM at temperature boundaries of 250 to 300 °C is plotted in Fig. 25. It can be noticed from Fig. 23 that all the mixes displays the endothermic peak at this range of temperature indicating the decomposition of hydration product linking to PCM. It can be inferred from Fig. 25 that PCM added cementitious mixes containing 3% nano-silica (CNS/oct- mixes) exhibits greater Percentage of mass loss associated to decomposition of PCM based hydration product and it is found to be 50-68% higher to that of oct-mixes. This is ascribed to presence of PCM in cementitious system are responsible for the increase in the permeable porosity of cementitious composites owing its interruptive nature and incompatibility with that of hydrated cementitious system [5, 19]. This leads to the increase in diffusion of chloride ions into the transpired pores and acts as a barrier to the function of PCM, further aggressive chloride media causes deterioration of PCM. Nano-silica being a loftier material aids to the significant reduction in porosity, simultaneously adds to the development of dense CSH in the cementitious system due to its nucleation mechanism [23] that attributes to the protection of PCM incorporated cementitious composite from aggressive ions. Further, it is clear from the obtained results that incorporation of nano-silica does not weakens the thermal performance of integrated PCM in cementitious system. Due to this action, strategy of incorporating nano-silica into PCM added cementitious system found to

be promising in tackling the influence of aggressivity with retaining the thermal ability. However, it is important to note that in case of chloride exposed mixes there found a discrepancy in the calculated mass loss percentage for PCM based hydration product, since there subsists superimposition of endothermic peak (Fig. 23) responsible for the decomposition of compounds such as Fs and PCM linked C-S-H phase (tobermorite like) in the range of 200-400 ºC.

4. Conclusion

In this paper, change in phase compositions (AFt, Gy, Fs, PCM based hydration products) happened before and after the action of aggressive solution such as 1% sulfuric acid, 5% sodium hydroxide and 5% sodium chloride were quantified using TG/DTG technique. The effect of PCM (n-octadecane) in the presence and absence of nano-silica (optimal content 3%) on aggressive exposure solutions for all the mixes were investigated.

All PCM based cementitious mixes (with and without nano-silica) used in this study showed an endothermic peak at 250-300°C relating to the decomposition of PCM cross linked hydration product at the curing age of 28 days and that indicates both the series of PCM mixes are thermally effective. At the same time endothermic peak height at 400-500°C associated to dehydroxylation of portlandite phase increased with the increase in PCM dosage, nevertheless endothermic peak height reduced with the incorporation of highly pozzolanic nano-silica particles.

PCM added cementitious mixes experiences extensive loss in density, compressive strength and volumetric stability when exposed to SO_4^{2-} and Cl^- ions. In contrary, 3% nano-silica modified PCM added cementitious mixes minimized the vulnerability to aggressive ions and resistivity found to be more compared to that of control mix especially at 1% and 3% PCM dosages. Sulfuric acid attack on the weak cementitious matrix in the presence of PCM is more deleterious due to the combined act of acid and sulfate. Formation of voluminous secondary ettringite (AFt) and gypsum (Gy) when exposed to SO_4^{2-} ions (at both acid and alkali media) and Friedel's salt (Fs) when exposed to Cl^- ions (at Chloride media) greatly increased for PCM added cementitious mixes (oct-mixes) and 50% reduction is seen in the PCM based cementitious mix comprising of nano-silica.

It is important to note that after exposing to aggressive solutions (SO_4^{2-} ions and Cl^- ions) endothermic peak occurred at 250º C-300 °C for PCM mixes disappeared. However, for PCM mixes modified with 3% nano-silica, prominent peak was observed at 250º C-300 °C that specifies the occurrence of thermally active PCM. PCMs at this phase cross linked with tobermorite like C-S-H with disordered layer structures such as 11 Å/9 Å tobermorite and 11 Å jennite, and the peak shifts from 80º C-300 °C to 250º C-300 °C.

At this point of time it is well understood from the study that there is an essential need to amalgamate highly reactive pozzolanic material like nano-silica to PCM added cementitious mixes in order to have better thermo-mechanical and durability performance.

References

[1] M. De Gastines, E. Correa, A. Pattini, Heat transfer through window frames in energyplus: model evaluation and improvement. Adv. Build. Energy Res. 13 (2019) 138–155.

[2] M. Balbis-Morejón, J. J. Cabello-Eras, J. M. Rey-Hernández, F. J. Rey-Martínez, Energy evaluation and energy savings analysis with the 2 selection of ac systems in an educational building. Sustainability. 13 (2021) 7527.

[3] I. Sarbu, C. Sebarchievici, A comprehensive review of thermal energy storage, Sustainability. 10 (2018) 191.

[4] W. Aftab, A. Usman, J. Shi, K. Yuan, M. Qin, R. Zou, Phase change material-integrated latent heat storage systems for sustainable energy solutions, Energy Environ. Sci. 14 (2021) 4268-4291.

[5] K. Snehal, B. B. Das, Effect of phase-change materials on the hydration and mineralogy of cement mortar, Proc. Inst. Civ. Eng.: Constr. Mater. (2020) 1-11.

[6] K. Snehal, B. B Das, S. Kumar, Influence of integration of phase change materials on hydration and microstructure properties of nano-silica admixed cementitious mortar, J. Mater. Civ. Eng. 32 (6) (2020) 04020108.

[7] M. Frigione, M. Lettieri, A. Sarcinella, Phase change materials for energy efficiency in buildings and their use in mortars, Materials (Basel). 12(8) (2019) 1260.

742 [8] M. Gandhi, A. Kumar, R. Elangovan, C. S. Meena, K. S. Kulkarni, A. Kumar, G.
743 Bhanot, N. R. Kapoor, A Review on shape-stabilized phase change materials for latent
744 energy storage in buildings, Sustainability. 12(22) (2020) 9481.
745 [9] B. Sharma, Incorporation of phase change materials into cementitious systems, Thesis,
746 Arizona state university, USA, 2013.
747 [10] S. Drissi, T. C. Ling, K. H. Mo, A. Eddhahak, A review of microencapsulated and
748 composite phase change materials: Alteration of strength and thermal properties of
749 cement-based materials, Renew. Sust. Energ. Rev. 110 (2019) 467-484.
750 [11] B. Šavija, Smart crack control in concrete through use of phase change materials
751 (pcms): a review, Materials. 11 (2018) 654
752 [12] A. Matthew, D. Sumanta, C. Cesar, K. Nihat, S. Gaurav, N. Narayanan, Porous
753 inclusions as hosts for phase change materials in cementitious composites:
754 Characterization, thermal performance, and analytical models, Constr. Build. Mater.
755 134 (2017) 574 - 584.
756 [13] W. C Choi,1 B. S. Khil, Y. S. Chae, Q. B. Liang, H. D. Yun, Feasibility of using phase
757 change materials to control the heat of hydration in massive concrete structures, Sci.
758 World J. (2014).
759 [14] S. Ramakrishnan, Enhancement of thermal performance of buildings using
760 cementitious composites containing phase change material, Thesis, Swinburne
761 University of Technology Melbourne, Australia, 2017.
762 [15] V. D. Cao, S. Pilehvar, C. S. Bringas, A. M. Szczotok, J. F. Rodriguez, M. Carmona,
763 N. Al-Manasir, A. L. Kjoniksen, Microencapsulated phase change materials for
764 enhancing the thermal performance of Portland cement concrete and geopolymer
765 concrete for passive building applications, Energy Convers. Manag. 133 (2017) 56–66.
766 [16] M. Hunger, A. G. Entrop, I. Mandilaras, H. J. H. Brouwers, M. Founti, M. The
767 behavior of self-compacting concrete containing micro-encapsulated Phase Change
768 Materials, Cem. Concr. Compos. 31 (2009) 731–743.
769 [17] A. R. Sakulich, D. Bentz, Incorporation of phase change materials in cementitious
770 systems via fine lightweight aggregate, Constr. Build. Mater. 35 (2012) 483–490.
771 [18] Z. Zhang, G. Shi, S. Wang, X. Fang, X. Liu. Thermal energy storage cement mortar
772 containing n-octadecane/expanded graphite composite phase change material, Renew.
773 Energy. 50 (2013) 670-675.

774 [19] K. Snehal, B. B. Das, Acid, alkali and chloride resistance of binary, ternary and
775 quaternary blended cementitious mortar integrated with nano-silica particles, Cem.
776 Concr. Compos. 2021 104214.
777 [20] S. Sahoo, B. B. Das, S. Mustakim, Acid, alkali, and chloride resistance of concrete
778 composed of low-carbonated fly ash, J. Mater. Civ. Eng. 29 (3) (2017), 04016242.
779 [21] Z. Wei, G. Falzone, B. Wang, A. Thiele, G. Puerta-Falla, I. Pilon, N. Neithalath, G.
780 Sant, The durability of cementitious composites containing microencapsulated phase
781 change materials Cem. Concr. Compos. 81 (2017) 66-76.
782 [22] A. K. Suryavanshi, J. D. Scantlebury, S. B. Lyon, Mechanism of Friedel's salt
783 formation in cements rich in tri-calcium aluminate, Cem. Concr. Res. 26 (5) (1996)
784 717–727.
785 [23] K. Snehal, B.B. Das, M. Akanksha, Early age, hydration, mechanical and
786 microstructure properties of nano-silica blended cementitious composites, Construct.
787 Build. Mater. 233 (2020) 117212.
788 [24] S. Chithra, S.R.R.S. Kumar, K. Chinnaraju, The effect of colloidal nano-silica on
789 workability, mechanical and durability properties of high-performance concrete with
790 copper slag as partial fine aggregate, Construct. Build. Mater. 113 (2016) 794–804.
791 [25] H. Sattawa, T. Pulngern, S. Chucheepsakul, Effect of nanosilica particle size on the
792 water permeability, abrasion resistance, drying shrinkage, and repair work properties
793 of cement mortar containing nano-SiO_2, Ann. Mater. Sci. Eng. (2017).
794 [26] B. B Das, A. Mitra, Nanomaterials for construction engineering-A review, Int. J. of
795 Mater. Mech. Manuf. 2 (1) (2014) 41–46.
796 [27] H. Du, S. Du, X. Liu. Durability performance of concrete with Nano silica. Constr.
797 Build. Mater. 73 (2014) 705-712.
798 [28] ASTM C150/C150M - 15 Standard Specification for Portland Cement, ASTM
799 International, 2015.
800 [29] IS 383:2016 Coarse and Fine Aggregate for Concrete – Specification, Bureau of
801 Indian Standards, New Delhi, India.
802 [30] IS 4031 (Part 6) -1988, Determination of Compressive Strength of Hydraulic Cement
803 Other than Masonry Cement, Bureau of Indian Standards, New Delhi, India.
804 [31] M. Albitar, M. Mohamed Ali, P. Visintin, M. Drechsler, Durability evaluation of
805 geopolymer and conventional concretes Constr, Build. Mater. 136 (2017) 374–385.

806 [32] ASTM C490/C490M-17 Standard Practice for Use of Apparatus for the Determination
807 of Length Change of Hardened Cement Paste, Mortar, and Concrete, ASTM
808 International, 2017.
809 [33] ASTM C157/C157M-17 Standard Test Method for Length Change of Hardened
810 Hydraulic-Cement Mortar and Concrete, ASTM International, 2017.
811 [34] ASTM C1012/C1012M-18b Standard Test Method for Length Change of Hydraulic-
812 Cement Mortars Exposed to a Sulfate Solution, ASTM International, 2018.
813 [35] ASTM C596-18, Standard Test Method for Drying Shrinkage of Mortar Containing
814 Hydraulic Cement, ASTM International, 2018.
815 [36] W. Chen, B. Huang, Y. Yuan, M. Deng, Deterioration process of concrete exposed to
816 internal sulfate attack, Materials. 13 (2000) 1336.
817 [37] Z. Shi, M.R. Geiker, B. Lothenbach, K. De Weerdt, S.F. Garzon d, K.E. Rasmussen,
818 J. Skibsted, Friedel's salt profiles from thermogravimetric analysis and thermodynamic
819 modelling of Portland cement-based mortars exposed to sodium chloride solution,
820 Cement Concr. Compos. 78 (2017) 73–83.
821 [38] S. Barbhuiya, D. Kumala, D, Behaviour of a Sustainable Concrete in Acidic
822 Environment. Sustainability. 9 (2017) 1556.
823 [39] B. Tian, M. D. Cohen, Does gypsum formation during sulfate attack on concrete lead
824 to expansion? Cem. Concr. Res. 30(1) (2000) 117-123.
825 [40] A. M. Ramezanianpour, Sulfate Resistance and Properties of Portland-Limestone
826 Cements, Thesis, University of Toronto, 2012.
827 [41] E. F. Irassar, A. Di Maio, O. R. Batic, O. R. Sulfate attack on concrete with mineral
828 admixtures. Cem. Concr. Res. 26(1) (1995) 113-123.
829 [42] F. Kontoleontos, P.E. Tsakiridis, A. Marinos, V. Kaloidas, M. Katsioti,, influence of
830 colloidal nanosilica on ultrafine cement hydration: physicochemical and
831 microstructural characterization, Constr. Build. Mater. 35 (2012) 347–360.
832 [43] M. Drábik, L. Gáliková, E. Scholtzová, E. Hadzimová, Thermoanalytical events and
833 enthalpies of selected phases and systems of the chemistry and technology of concrete
834 part I. calcium-silicate-aluminate-sulfate hydrates, Ceramics – Silikáty 58 (3) (2014)
835 184-187.

836 [44] Black, L., Breen, C., Yarwood, J., Deng, C.-S., Phipps, J. Maitland, In situ Raman
837 analysis of hydrating C_3A and C_4AF pastes in presence and absence of sulfate. Adv.
838 Appl. Ceram. 1005 (4) (2006) 209-216.
839 [45] W. Kurdowski The protective layer and decalcification of c-s-h in the mechanism of
840 chloride corrosion of cement paste, Cem. Concr. Res. 34(9) (2004) 1555-155.
841 [46] A. Jayalath, R. Nicolas, M. Sofi, R. Shanks, T. Ngo, L. Ayea, P. Mendis, P. Properties
842 of cementitious mortar and concrete containing micro-encapsulated phase change
843 materials. Constr. Build. Mater. 120 (2016) 408–417.

844

Highlights:

- Formation of deleterious compounds such as AFt, Gy and Fs (due to the action of SO_4^{2-} and Cl^- ions) amplified for PCM based cementitious mortar.
- Nano-silica (3%) modified PCM based cementitious mortar significantly reduced the vulnerability to aggressive ions.
- Existence of endothermic peak at 250º C-300 °C indicates the presence of PCM (n-octadecane) in nano-silica admixed mixes.
- Cross-linking action of PCM with tobermorite like C-S-H shifts the endothermic peak from 80º C-300 °C to 250º C-300 °C.