1 2	Synergistic Effect of Nano Silica on Carbonation Resistance of Multi-Blended Cementitious Mortar
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## 26 Abstract

Confiscation of alkaline buffer in a blended cementitious system surges the risk of carbonation. 27 28 Understanding the carbonation mechanism and kinetics of multi-blended cementitious systems in correspondence to microstructural properties is the need of the hour. In this context, the change 29 in the microstructure of binary, ternary, and quaternary blended cementitious mortar mix 30 comprising of fly ash or/and ultra-fine fly ash or/and nano-silica upon accelerated carbonation 31 32 (3.5% CO<sub>2</sub>; 70% RH) was studied. All multi-blended mixes were proportioned using modified Andreasen and Andersen particle packing theory. Permeable porosity and carbonation parameters 33 such as carbonation depth, rate of change in compressive strength, and carbonation shrinkage 34 were measured. Further, qualitative/quantitative estimation of carbonation phases was done using 35 characterization techniques such as TGA and FTIR. In control mix with solely OPC, the reaction 36 37 of CO<sub>2</sub> with calcium-bearing phases showed chemo-mechanical changes leading to 18% improvement in strength at 30 days of exposure. The optimized multi-blended cementitious 38 39 systems with nano-silica exhibited higher resistance to carbonation kinetics. Phase assemblages quantified through TGA within depth of carbonation imply a negligible concentration of 40 portlandite (CH). However, mixes without nano-silica exhibited a significant reduction in bound 41 water content associated with C-S-H/AFt/AFm phases and intensified the precipitation of calcium 42 carbonate (CaCO<sub>3</sub>) phase. Asymmetric stretching band of C-O-C at 1424 cm<sup>-1</sup> corresponding to 43 44 calcite phase measured using FTIR validates the outcomes of TGA.

Keywords: Carbonation, particle packing, blended system, FTIR, TGA, nano-silica, phaseassemblage

### 48 1. Introduction

49 The dramatic rise in global greenhouse gas emissions has become an important part of global 50 climatic issues. The production process of ordinary Portland cement (OPC) has a colossal impact 51 on carbon footprint which contributes to about 5-8% of total global anthropogenic CO<sub>2</sub> emission [1-3]. At the same time, a cementitious system is known to be highly alkaline (pH of 12 to 13.8) 52 and porous [4]. The increased concentration of CO<sub>2</sub> in the air exaggerates the carbonation reaction 53 in cementitious systems. Carbonation of concrete is a vital durability property and is considered 54 to be one of the root causes of the deterioration and destruction of concrete over the life cycle [4-55 56 6]. The major detrimental facts in this regard are steel reinforcement corrosion and shrinkage [7-10]. The principal fact here is the drop in pore solution alkalinity to around pH 9 due to the 57 neutralization of solid alkaline phases i.e., Ca(OH)<sub>2</sub> [2]. This phenomenon depreciates the 58 alkaline passive layer of embedded steel reinforcement in concrete. Thus, causing reinforcement 59 corrosion in the presence of oxygen and moisture [2]. However, it is reported that carbonation 60 process in concrete results in the pore refinement of cementitious matrix. Subsequently increases 61 the mechanical and durability properties of hydrated cementitious systems [10]. Carbonation of 62 63 hydrates phases in cementitious system leads to the formation of precipitates of calcium carbonates and amorphous silica gel [11-12]. Houst et al (1997) reported that CaCO<sub>3</sub> crystals 64 formed due to the carbonation reactions are of different sizes that may lead to carbonation 65 shrinkage as a result of water diffusion, reorganization of microstructure, forces developed in the 66 capillary pores, etc [13]. However, the major cause of carbonation shrinkage is the evaporation 67 of water molecules in calcium carbonates formed during the process of carbonation reaction 68 between CO<sub>2</sub> and hydrated phases (CH/C-S-H/Aft/AFm) [13]. Some studies say that the 69 70 formation of calcium carbonate polymorphs during the process of cement paste carbonation leads to an increase in unit cell volume. It is also reported that the dissolution of CH crystals minimizes 71 the crystallization stress resulting in the proliferation of solid skeleton compressibility [14]. Some 72 researchers proposed that the primary cause for carbonation shrinkage is associated with the 73 decalcification of calcium-silicate-hydrate (C-S-H) [15]. The carbonation of cement paste is a 74 complex phenomenon and gets more complicated in the blended cementitious system. This is 75 76 because of the occurrence of fewer species of calcium that are susceptible to carbonation and 77 difference in phase assemblage (includes portlandite, C-S-H, Aft, and AFm) [16]. Upon carbonation, molar volume of C-S-H phase vary with the change in the Ca/Si ratio. Likewise, unit 78

volumes of CaCO<sub>3</sub> phase varies corresponding to its polymorphs [17]. However, the cause for the
volumetric changes induced by carbonation in cement systems is still left unclear and is the focus
of research.

82 The cement and construction industries are well established with the use of supplementary cementitious materials (SCMs) like fly ash, silica fume, and slag to achieve sustainability [1, 18-83 84 21]. Research showed that blended cementitious system comprising of SCMs augmented the resistance to aggressive media such as sulfate, chloride, CO<sub>2</sub>, etc., as a result of reduced permeable 85 porosity [22-23]. Further, the incorporation of SCMs adds several benefits to the properties of 86 cementitious composites such as low heat of hydration, higher freeze-thaw resistance, minimal 87 alkali-aggregate reaction, dense microstructure, volume stability, and also provides 88 89 environmental and economic advantages [20]. In the recent past, nano-silica is considered to be a competent pozzolanic ingredient owing to its extraordinary properties and has been extensively 90 91 studied worldwide [18]. One of the significant advantages of nano-silica against conventional SCMs is the superior early age properties owing to its nucleation, pozzolanic and nano-filler 92 action [21]. Despite its advantages, nano-silica also showed certain disadvantages that include, 93 high heat of hydration, low workability, enhanced chemical shrinkage, and expensive ingredients 94 95 [18]. Physico-chemical properties of SCMs are the prompting parameter for durability and that 96 varies greatly depending on its type, size, source, and proportion. Mix design parameters also 97 have a significant impact on the carbonation process of blended cementitious mix. Hence, it is 98 understood that there is an essential need to use nano-silica in combination with other SCMs to counteract the advantages and disadvantages of both materials [18, 24]. Generally, studies on 99 100 carbonation were focused on single blended cementitious mixtures [8-9, 25]. It is well reported that phase assemblages of cementitious matrix get complex with the incorporation of multiple 101 SCMs [18, 23]. However, carbonation studies related to multi-blended cementitious system 102 103 composed of multiple SCMs of varied particle sizes ranging from micron to nano level is rarely being reported. 104

Evolution in concrete technology from plain to multi-blended cementitious system compels choosing the right proportion of SCMs to achieve better packing density and performance [25]. The trial-and-error method of choosing the suitable proportion of replacement material combinations becomes tedious. Additionally, the type of ingredients and their packing characteristics have a direct impact on the performance of concrete [25]. Therefore, to choose the appropriate proportion of replacement materials from a pool of SCMs, the mixture designer should
be familiar with the particle packing concept [26]. The underlying principle of particle packing is
that the space between the larger particles should be occupied by smaller particles, and then still
smaller particles should occupy the space left by those smaller particles, and so forth [27].

Particle packing of concrete is assessed using its packing density. It is calculated by dividing 114 volume of solids by the total volume of particles. The basic concept of particle packing is that the 115 space between the larger particles is to be occupied by smaller particles and space between smaller 116 117 particles by further smaller particles and so on. To achieve optimal filling, several particle packing 118 models were established by the researchers [28]. Modified Andreasen and Andersen particle packing model proposed by Dinger and Funk are found to be the most preferred and relevant model 119 for designing a multi-blended cementitious system [26-27]. According to the literature, blended 120 cement mortar designed using modified Andreasen and Andersen model displayed promising 121 122 qualities like improved hydration, compressive strength, filler effect, and dense microstructure that helps for better material durability [25, 29-30]. 123

At this point of time, there is a need to comprehend the effect of multi-sized pozzolanic 124 ingredients blended with OPC in the form of binary, ternary, and quaternary systems on the 125 126 magnitude of carbonation when proportioned optimally using Andreasen and Andersen particle packing approach. The extent of carbonation was measured in terms of carbonation depth, 127 128 carbonation coefficient, change in compressive strength, and carbonation shrinkage at accelerated 129 carbonation conditions (3.5% CO<sub>2</sub>; 70% RH). Further, variations in phase assemblages such as Ca(OH)<sub>2</sub>, water associated with hydration phases i.e., C-S-H/AFt/AFm and CaCO<sub>3</sub> during the 130 carbonation process until the long-term exposure period of 180 days were quantified for various 131 combinations of pozzolanic ingredients (micron to submicron to nano-sized particles) using the 132 TGA and FTIR techniques. 133

### 134 **2.** Experimental investigation

135 2.1 Materials and material properties

136 Mortar mixes were prepared using ordinary Portland cement (OPC) confirming to ASTM type 1

- 137 [31], class F fly ash (FA, ASTM C 618) [32], ultra-fine fly ash (UFFA), and colloidal nano-silica
- 138 (CNS) having a specific surface area of 300 m<sup>2</sup>/kg, 265 m<sup>2</sup>/kg, 670 m<sup>2</sup>/kg and 200000 m<sup>2</sup>/kg,

respectively. Zone II river sand confirming to IS 383-2016 [33] was used as a fine aggregate. To maintain the required workability of the mortar mixes polycarboxylate ether-based superplasticizer was used. Table 1 summarises the oxide composition and physical properties of the materials used. The oxide composition of raw materials except nano-silica was determined through the X-ray fluorescence (XRF) technique. The physical properties of OPC and FA/UFFA were determined as per IS-12269 [34] and IS3812: part 1 [35], respectively. Fig. 1 presents the particle size distribution curve of the materials used in this study.

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Table 1 Oxide composition and physical properties of materials used in this study

		Oxid	e Composition	1		
Oxide		OPC	FA	UFFA	CNS*	Sand
SiO <sub>2</sub>		20.5	60.6	63	99.9	-
Al <sub>2</sub> O <sub>3</sub>		4.0	28.6	29.2	-	-
CaO		64.2	1.5	1.3	-	-
Fe <sub>2</sub> O <sub>3</sub>		4.96	3.9	3.2	-	-
K <sub>2</sub> O		-	0.1	0.12	-	-
MgO		1.2	1.8	1.4	-	-
Na <sub>2</sub> O		-	0.4	0.28	-	-
SO <sub>3</sub>		1.8	1.2	1	-	-
LOI		2.11	1.6	1.5	-	-
Compressive	3 days	22.1	-	-	-	-
Strength (MPa)	7 days	36.5	-	-	-	-
	28 days	48	-	-	-	-
			Physical P	roperties		
Specific gra	wity	3.15	2.2	2.2	2.2-2.4	2.56
Initial setting tin	me (min)	110	-	-	-	-
Final setting tin	ne (min)	170	-	-	-	-
Bulk density (	kg/m <sup>3</sup> )	-	-	-	-	1780
Loose density	(kg/m <sup>3</sup> )	-	-	-	-	1524
Solid conten	t (%)	-	-	-	40 (w/v)	-
Dispersion m	edium	-	-	-	water	-
pН		-	-	-	9	-

147 \*Provided by the manufacture



# 148



Fig. 1 Particle size distribution curve of materials used in the present study

# 150 3.2 Mix Recipe

In this study control and three sets of multi-blended (i.e., binary, ternary, and quaternary blends) 151 mixes were designed using the principle of particle packing theory. Modified Andreasen and 152 Andersen particle packing model (with a software tool: "EMMA") was used in designing the 153 multi-blended mortar mixes. A detailed explanation of the working principles of EMMA software 154 and the steps involved in the generation of mix recipes is given in the EMMA manual [36] and 155 elsewhere [27]. Particle size distribution curve (actual particle packing curve) of binary, ternary, 156 and quaternary blended mortar mixes were made to relate with the modified Andreasen and 157 158 Andersen model curve (ideal curve) for achieving better packing density. This was done by altering the material quantity inputs of mixes through the trial-and-error method until the actual curve of 159 the mix fit the ideal curve. On this basis, material proportions such as 'F', 'U', and 'N' are fixed 160 for a particular mix. To maintain the homogeneity, in this study constant distribution coefficient 161 162 value of 0.3 (represents the medium workability), water/sand ratio of 1:3, and water/binder ratio of 0.5 was used for all the mixes designed. Table 2 represents the mix recipe generated through 163 164 "EMMA" software.

The study began with seven binary blended CNS mixes (i.e., 0.5 % to 3.5 % at intervals of 0.5%)and three mixes (total replacement level of 15%, 25%, and 35%) each for other binary (FA and UFFA mixes), ternary (FA+UFFA, FA+CNS, UFFA+CNS), and quaternary (FA+UFFA+CNS) blends. Mix recipes were prepared by using modified Andreasen and Andersen particle packing model (which can be found in the previously published article, [18]). In this research, the best-

- performing mixes with respect to compressive strength from each set (i.e., CNS-3, F-25, U-25,
- 171 FU-25, FN-25, UN-25, and FUN-25) were used for conducting carbonation studies.

	D.66	0/ 0	3.41	OBC	<b>F</b> 4		CNIC	C 1	***	<b>XX</b> /D	CD
Blends	Different	% Of	Mix	OPC	FA	UFFA	CNS	Sand	Water	W/B	SP
	combination	SCMs	designation							ratio	(%
		(bwoc)				<b>(kg</b> /i	m <sup>3</sup> )			-	bwob)
Control	OPC	100	С	568.35	-	-	-	1705.1	284.2	0.5	-
Dinowy	OPC + CNS	97+3	CNS-3	551.30	-	-	17.1	1705.1	284.2	0.5	0.25
blinary blonda	OPC+FA	75+25	F-25	426.35	142.1	-	-	1705.1	284.2	0.5	-
biends	OPC+UFFA	75+25	U-25	426.35	-	142.1	-	1705.1	284.2	0.5	-
	OPC+FA+	75+15+10	FU-25	426.35	85.3	56.8	-	1705.1	284.2	0.5	-
	UFFA										
Ternary	OPC+FA+	75+23+2	FN-25	426.35	130.7	-	11.4	1705.1	284.2	0.5	-
blends	CNS										
	OPC+UFFA	75+23+2	UN-25	426.35	-	130.7	11.4	1705.1	284.2	0.5	-
	+CNS										
Quaternary	OPC+FA+	75+16+7+2	FUN-25	426.35	90.9	39.8	11.4	1705.1	284.2	0.5	-
blends	UFFA+CNS										

172 **Table 2** Mix designation and mix recipe of multi-blended mixes used in the present study

\*Eg: Mix designation for CNS-3 indicates the replacement of OPC by 3% CNS; F-25 represents the replacement of
OPC by 25% fly ash; FU-25 indicates the total 25% replacement of OPC by fly ash + ultrafine fly ash; FUN-25
indicates the total 25% replacement of OPC by fly ash + ultrafine fly ash + nano-silica etc.,

## 176 **4. Methodology**

#### 177 4.1 Sample preparation

- Mortar mixes were prepared using an automatic mortar mixer (works on the EN 196-1 [37] based
  mixing procedure). To measure compressive strength and carbonation depth, the prepared mortar
  mixtures were cast in 70.6 mm × 70.6 mm × 70.6 mm cubes. Prisms with the dimensions of 25
  mm × 25 mm × 285 mm were cast to measure the length change related to carbonation shrinkage.
  After placing the mixture in respective moulds, mixtures are compacted using vibrators and then
  kept for moist curing for 24 hrs at 27±2 °C. Consecutively, samples were demolded and subjected
  to submerged water curing for 28 days.
- For conducting thermogravimetric analysis (TG-DTG) and Fourier transform infrared spectroscopy (FTIR) samples were crushed, ground, and passed through a 75  $\mu$ m sieve. Further, ground samples passing through a 75  $\mu$ m IS sieve were oven dried at 40-60 °C for few minutes (15 to 20 minutes) without altering the hydrate phases significantly [38]. After cooling the

powdered samples were stored in air-tight desiccators composed of silica gel (to evade themoisture contact) till the day of testing.

### 191 4.2 Permeable porosity

The vacuum water absorption method was adopted to determine the permeable porosity of mortar
mixes [39]. Permeability porosity of each mix after 28 days of curing was assessed using Eq. 1.

194 Permeable porosity 
$$= \frac{V_v}{V_T} = \frac{W_s - W_d}{V_T}$$
 (1)

195 Where,  $V_{v}$ ,  $V_{T}$ ,  $W_{d}$ , and  $W_{s}$  represents the volume of voids, the total volume of mortar, dry weight 196 of mortar, and the saturated weight of mortar, respectively.

197 4.3 Carbonation studies

198 4.3.1 Change in compressive strength and carbonation depth

Accelerated carbonation test was carried out by assessing the change in compressive strength and 199 carbonation depth of mortar specimens. Cubical mortar specimens of size 70.6 mm  $\times$  70.6 mm  $\times$ 200 70.6 mm after attaining the curing age of 28 days, were taken out of the water-submerged 201 202 condition and allowed to attain saturated dry state for 14 days in ambient condition 203 (preconditioning) [40]. Subsequently, the compressive strength of all the specimens was 204 measured and that is recorded as the initial compressive strength value before CO<sub>2</sub> exposure. Then, all the specimens were kept in a carbonation chamber at accelerated carbonation conditions. 205 206 Carbonation chamber was set for 3.5% CO<sub>2</sub>, 70% humidity, and 27°C temperature. Carbonation chamber conditions were periodically checked and maintained throughout the days of exposure. 207 Specimens were stored in a carbonation chamber for the duration 30, 60, 90, 120, and 180 days. 208 209 After the required days of accelerated CO<sub>2</sub> exposure specimens were taken out of the carbonation 210 chamber. Next, the final compressive strength of the specific mortar mix at a specific period of exposure was measured. The compressive strength test was conducted according to IS 4031 (part-211 6) – 1988 [41] using a compressive strength testing machine of the capacity 2000 kN (at a loading 212 rate of 35 N/mm<sup>2</sup>/min). Percentage change in compressive strength was calculated using Eq. 2. 213

214 Change in compressive strength (%) = 
$$\frac{(initial strength - final strength)}{initial strength} \times 100$$
 (2)

To measure the carbonation depth, phenolphthalein test was conducted as per RILEM CPC-18 [42]. Phenolphthalein indicator solution (95% by volume in ethanol) was sprayed on the thoroughly cleaned surface of the split cubical specimens exposed to accelerated carbonation. The non-carbonated area appears to be pink (pH >9.5, alkaline), while the carbonated area tends to be colourless (pH <9.5). Further, carbonation depth was assessed by measuring the depth of the colourless area at eight different points (D1 to D8) as shown in Fig. 2. The average value was recorded as the final carbonation depth (D, Eq. 3).

222 
$$D = \frac{D1+D2+D3+D4+D5+D6+D7+D8}{8}$$
 (3)



223

224

Fig. 2 Typical plot of carbonation depth measurement

225 Several models have been proposed by various researchers to describe the relationship between 226 carbonation depth (D) and exposure period (t). The most commonly used relationship in this regard is 227 the one that resulted from Fick's law based on the uni-directional diffusion [43] i.e.,

228 
$$D = K\sqrt{t}$$
  
229 i.e.,  $K = \frac{D}{\sqrt{t}}$  (4)

230 Where K is the carbonation coefficient (mm/ $\sqrt{y}$ ear), D is carbonation depth in mm and t is the 231 exposure period in years.

- The average of three specimens for each mix at particular exposure periods was taken as the final carbonation coefficient value.
- 4.3.2 Carbonation shrinkage

A carbonation shrinkage test was carried out for mortar prism specimens of size 25 mm  $\times$  25 mm 235 × 285 mm using a length comparator device (ASTM C490 / C490M) [44]. After the curing age 236 237 of 28 days, initial comparator readings (Li) were recorded at surface dry conditions. Subsequently, prism specimens were exposed to accelerated CO<sub>2</sub> conditions (3.5% CO<sub>2</sub>; 70% RH and 27°C 238 temperature) for the duration of 1, 3, 7, 14, 30, 60, 90, 120, and 180 days. Length comparator 239 readings at a particular period of exposure  $(L_x)$  for all the prism specimens were recorded. Length 240 change associated with carbonation was measured as per ASTM C157 / C157M [45]. Carbonation 241 shrinkage in terms of micro strain for all blended cementitious mortar specimens was measured 242 using Eq. 5. 243

$$\Delta L_x = \frac{L_x - L_i}{G} \ge 10^6 \tag{5}$$

245 Where,  $\Delta L_x$ : change in length at the exposure period "x" (micro strain);  $L_x$ : comparator reading at 246 particular exposure period "x";  $L_i$ : initial comparator reading and G: gauge length (250 mm).

- 247 4.4 Characterization studies
- 248 4.4.1 Thermogravimetric analysis (TG-DTG)

Thermogravimetric analysis (TG-DTG) was carried out for the powder samples (passing through a 75  $\mu$ m sieve) before and after the long-term exposure (180 days) to accelerated CO<sub>2</sub> using TG/DTA analyser (EXSTAR 6000 TG/DTA 6300). TG-DTG test was performed under a nitrogen environment with a flow rate of 20 ml/min and the temperature was raised from 50 °C to 900 °C at the heating rate of 10 °C/min.

Variations in phase assemblages before and after carbonation were identified by means of differential thermogravimetric (DTG) curves. Temperature boundaries of phase decomposition were determined based on endothermic peaks in DTG curves. Amount of calcium hydroxide (CH) and calcium carbonate (CC) was quantified using thermogravimetric (TG) mass loss data (Eqs. 6 and 7) [46-47], respectively for both non-exposed and 180 days CO<sub>2</sub> exposed samples.

259 
$$CH\% = \frac{m_{CH_1} - m_{CH_2}}{m_{900}} \times \frac{M_{CH}}{M_{H_2O}}$$
 (6)

260 
$$CC\% = \frac{m_{CC_1} - m_{CC_2}}{m_{900}} \times \frac{M_{CC}}{M_{CO_2}}$$
 (7)

where, m<sub>CH1</sub> and m<sub>CH2</sub> are the mass losses at onset and end temperature of CH decomposition, respectively. m<sub>CC1</sub> and m<sub>CC2</sub> are the mass losses at onset and end temperature of CC decomposition, respectively and m<sub>900</sub> is the total mass losses that occurred at the designated temperatures of 900
°C. M<sub>CH</sub>, M<sub>H2O</sub>, M<sub>CC</sub>, and M<sub>CO2</sub> are the molecular weight of calcium hydroxide (74 g/mol), water
(18 g/mol), calcium carbonate (100 g/mol), and carbon-di-oxide (44 g/mol), respectively.

The onset and end temperature range of CH decomposition for non-carbonated samples were found 266 to be 400 °C and 500 °C, respectively. However, no endothermic peak representing CH 267 decomposition was noticed for samples taken within the carbonation depth indicated by 268 phenolphthalein solution. The onset and end temperature of CC decomposition is considered as 269 600 °C and 720 °C for un-carbonated samples. Same for the carbonated samples decomposition of 270 CC takes place at broad range of temperatures i.e., 550 °C to 770 °C. However, < 600 °C is 271 associated with poorly crystalline carbonate phases [48]. Therefore, the temperature range 272 considered for the quantification of CC in this study for carbonated samples was between 600 °C 273 to 770 °C. 274

Further, the amount of water related to hydration products excluding CH content was determinedusing Eq. 8 [18, 42].

277 
$$WH\% = \frac{m_{35} - m_{600}}{m_{900}} - \frac{m_{400} - m_{500}}{m_{900}}$$
 (8)

where,  $m_{35}$ ,  $m_{600}$ ,  $m_{400}$ ,  $m_{500}$ , and  $m_{900}$  are the mass losses at the designated temperatures of 35 °C, 600 °C, 400 °C, 500 °C and 900 °C, respectively.

# 280 4.4.2 Fourier transform infrared spectrophotometry (FTIR)

Fourier transform infrared spectra (FTIR) from Bruker (Alpha II) was used to obtain FTIR spectra 281 of powdered cementitious samples (passing through a 75 µm sieve) before and after 180 days of 282 carbonation in the attenuated total reflection mode (ATR). Samples were analysed at the 283 wavenumber range of 500 to 4000  $cm^{-1}$  with a resolution of 2  $cm^{-1}$  and at 32 scans. Changes in 284 functional groups were identified using FTIR spectrum and qualitatively analysed according to the 285 286 position and shape of the transmittance peaks. Quantitative analysis of FTIR spectrum was done by measuring the area under the characteristic band of calcite i.e., at the wavenumber of 1424 cm<sup>-</sup> 287 <sup>1</sup> for estimating the formation of calcite throughout the carbonation period of 180 days. 288

### 289 **4. Results and discussion**

290 4.1 Modified Andreasen and Andersen particle packing model



#### 291

Fig. 3 Actual gradation curve for binary, ternary, and quaternary blended mortar optimized using
 modified Andreasen and Andersen particle packing model

294 The modified Andreasen and Andersen model equation is given as

295 
$$CPFT = \left[\frac{(d-d_0)}{(D-d_0)}\right]^q$$
 (9)

296 Where, CPFT = cumulative percent finer than, d = particle size, d<sub>o</sub> = particle size distribution of 297 smaller particles, D = the maximum particle size, and q = distribution exponent.

EMMA software specifies that distribution modulus (q) in Andreasen and Andersen model/ modified Andreasen and Andersen model equation varies from 0.21 to 0.37 depending on the need for workability [28]. Higher the value of q factor lowers the degree of workability [27, 36].

301 According to EMMA manual and SP3 handbook, the relative value of the compaction factor for distribution modulus "q= 0.3" is 0.9 which specifies the medium workability [36]. Actual particle 302 packing curves for all blended mixes are therefore made to fit with the ideal curve (target curve) 303 with distribution modulus value "q=0.3" (medium workability). Based on this, optimized particle 304 305 packing curves were identified by varying the quantity of mortar mix ingredients. Fig. 3 presents the optimized actual particle packing curves for all multi-blended cementitious mortar mixes. The 306 307 procedure involved in attaining an optimized particle packing using EMMA software tool which 308 works on the principle of modified Andreasen and Andersen particle packing model is demonstrated in EMMA guide manual [27, 36] and also can be found elsewhere [18, 23]. All the 309

- 310 obtained actual gradation curves were found to fit well exponentially with a coefficient of
- determination " $R^2$ " value > 0.9. It is to be noted that FUN-25 mix made up of micron-submicron-
- nano sized particles exhibited the finest fit with the ideal curve with an  $R^2$  value of 0.976 indicating
- the better-quality particle packing density of the mix.
- 314 4.2 Carbonation studies
- 4.2.1 Carbonation depth and rate of carbonation

316 The carbonation mechanism is not only dependent on the binding capacity of CO<sub>2</sub> with cement

317 hydration product but also relies on the pore size distribution and permeable porosity of the

cementitious system [8, 49]. It is for that reason permeable porosity of all the mixes at the curing
age of 28 days before CO<sub>2</sub> exposure was measured and presented in Fig. 4.



320

Fig. 4 Permeable porosity values of multi-blended cement mortar at the curing age of 28 days

Fig. 4 depicts that at the curing age of 28 days, the permeable porosity values for F-25, U-25, and 322 FU-25 mixes were higher by 11%, 3%, and 5%, respectively in correspondence to that of control 323 mix. This is ascribed to the slow reactivity of fly ash particles. However, ultrafine fly ash mix (U-324 325 25) showed minimal variation in permeable porosity compared to that of control owing to its size effect. In contrast, blended mortar mixes integrated with nano-silica showed a significant drop in 326 the percentage of permeable porosity. Binary (CNS-3), ternary (FN-25, UN-25), and quaternary 327 (FUN-25) blended mortar mixes with nano-silica showed 74%, 28%, 48%, and 70% reduction in 328 329 permeable porosity, respectively in correspondence to the control mix. This is because of the

intensified chemical (nucleation and pozzolanic) and physical (nano-filler) activity of nano-silica
 particles in cementitious systems [50]. Further, improved particle packing of quaternary blended
 FUN-25 mix is attributed to the synergetic act of multi-sized pozzolanic particles.

Fig. 5a represents the measured carbonation depth (D) values for all the mixes exposed to accelerated carbonation for different exposure periods. Carbonation coefficient (mm/ $\sqrt{Yr}$ ) value determined using Eq. 4, based on the carbonation depth (mm) measurement with respect to the exposure age of specimens ( $\sqrt{Yr}$ ) is shown in Fig. 5b.



**Fig. 5** a) Carbonation depth (mm) v/s exposure period ( $\sqrt{Yr}$ ) and b) calculated carbonation coefficient values (K, mm/ $\sqrt{Yr}$ ) for multi-blended cementitious mortar

337

340 It can be observed from Fig. 5a that carbonation depth for F-25, U-25, and FU-25 mixes was found to be 12%, 5%, and 8% higher than that of control mix. Theoretically, results were expected 341 342 to be in converse as the incorporation of fly ash and ultra-fine fly ash particles in cementitious mix would react with CH which is susceptible to carbonation reaction [11, 24]. However, it is a 343 well-known fact that the pozzolanic reaction of fly ash particles are a slow process. In addition to 344 that dilution effect and insufficient curing age (i.e., 28 days) resulted in higher permeable porosity 345 and less solid primary C-S-H in the matrix (can be found in the previous articles [18, 23]). Further, 346 347 a significant drop in carbonation was observed for cementitious mortar mixes comprising of nanosilica in the form of binary (CNS-3), ternary (FN-25, UN-25), and quaternary (FUN-25) blends. 348 349 This is attributed to the densified microstructure of the mortar mix formed due to the presence of miniature particles of silica. The specific surface area and atom count on the surface of nano-350

silica is significantly high compared to conventional mineral admixtures such as fly ash. Since 351 352 the surface of nano-sized particles have large number of free/unsaturated bonds the particles tend 353 to be in an unstable thermodynamic state. As a result, nano-silica attains high surface energy and possess highly active atoms on its surface [51]. Nano-silica has the potential to promote 354 nucleation reaction in the cementitious system and acts as a C-S-H seed complimenting to the 355 topo-chemical reaction of cement grains in addition to pozzolanic activity [51]. Further, the 356 inclusion of nano-silica can act as a filler for material pores (both harmful as well as less harmful 357 pores). This phenomenon also produces discontinuities in capillary pores by causing the 358 production of additional C-S-H gel in the nano-silica based cement system. Therefore, makes the 359 360 cementitious system denser and less susceptible to aggressive agents such as CO2 [52]. Carbonation depth for CNS-3, FN-25, UN-25, and FUN-25 mixes was found to be reduced by 361 81%, 62%, 70%, and 80%, respectively in correspondence to control mix. The reduction rate was 362 363 found to be immense in the case of CNS-3 mix. It is also important to note that FUN-25 mix comprising of FA+UFFA+CNS also showed significant reduction in carbonation depth as like 364 CNS-3 mix owing to the increased packing density offered by the synergetic action of multiple-365 sized (micro-sub-micron-nano scale) filler ingredients. 366

Carbonation coefficient relating to the rate of CO<sub>2</sub> ingression is also considered as the indicator
to measure the extent of carbonation [50, 53-56]. The rate of carbonation (carbonation coefficient,
K) value-was measured considering the slope of roughly linear carbonation depth v/s exposure
time plot (Fig. 5a). The carbonation coefficient results are presented in Fig. 5b.

Fig 5b demonstrates the significant variation in carbonation coefficient value from the control 371 372 mortar system to the blended mortar systems. However, a huge difference was noticed between 373 the mixes with nano-silica and without nano-silica. It is important to note that the carbonation 374 coefficient value for binary blended CNS-3 mix and quaternary blended FUN-25 was found to be reduced by  $\approx$ 70% and that is followed by ternary blended UN-25 and FN-25 mix i.e., 65% and 375 60%, respectively. This can be attributed to the significant reduction in permeable porosity of 376 blended mortar composed of nano-silica as a result of the superior physio-chemical action of 377 nano-sized silica particles. In case of binary (F and U mixes) and ternary (FU mix) blended mortar 378 379 systems without nano-silica, the value of carbonation coefficient was seen to be intensified 380 compared to other mixes. This is because of the following facts such as i) FA and UFFA particles undergo a slow rate of pozzolanic reaction resulting in increased permeable porosity (Fig. 4) and 381

ii) lower availability of CH content owing to the dilution effect as well as the small amount of
pozzolanic reactivity. All these associated reason causes higher rate of C-S-H /C-A-S-H
carbonation for fly ash mixes and this may also lead to a deviation in Fick's law and similar
observations are made by the researchers [9].

386 4.2.2 Compressive strength

387 Variation in compressive strength observed for all multi-blended cementitious mixes exposed to

accelerated carbonation for the periods of 30, 60, 90, 120, and 180 days is presented in Fig. 6.



389

Fig. 6 a) Compressive strength development b) representative plot of 56 days water cured and 28
 days water cured + 30 days CO<sub>2</sub> exposed mortar specimens c) rate of change in compressive
 strength of CO<sub>2</sub> exposed multi-blended cementitious mortar

It can be inferred from the figure that the initial compressive strength value at the curing age of 394 28 days before subjecting to carbonation was seen to be highest for binary blended CNS-3 mix, 395 396 followed by FUN-25 (quaternary blend), UN-25 and FN-25 (ternary blend) mixes composed of nano-silica. The results indicate that the incorporation of a small percentage of nano-silica into 397 cementitious mortar has a great influence in enhancing the compressive strength due to its pore 398 399 refinement properties. Nano-silica has the potential to refine the pores at the nano-scale owing to its superior ability to react (hydraulic/pozzolanic) as well as to fill the nano-sizes pores physically 400 [11]. It is to be noted from the Fig. 6a that all other blended mixes without nano-silica showed 401 402 lower compressive strength compared to the mixes with nano-silica.

403 On exposing mortar mixes to accelerated carbonation conditions, compressive strength was found 404 to be increased with the increase in exposure period for all the mixes. The enhancement in compressive strength observed could be due to the progress of hydration/pozzolanic reactivity 405 406 and also due to the ingress of accelerated CO<sub>2</sub> (3.5% at 70% relative humidity). For instance, to understand the independent influence of hydration and combine influence of hydration and 407 carbonation a typical plot showing the compressive strength results of 56 days water cured and 408 28 days water cured + 30 days CO<sub>2</sub> exposed mortar specimens are shown in Fig. 6b. For example, 409 the compressive strength of 56 days water cured CNS-3 mix was determined to be 66 MPa. 410 411 However, the compressive strength of 28 days water cured + 30 days CO<sub>2</sub> exposed CNS-3 mix was shown to be raised by 4% (i.e., 68.5 MPa). This is attributed to the formation of calcium 412 carbonate phase as a result of CO<sub>2</sub> ingression. Hence, strength development observed after 413 carbonation is not solely dependent on carbonation action, it is associated to the combined action 414 of hydration and carbonation. However, the rate of change in compressive strength with exposure 415 to 3.5% CO<sub>2</sub> was found to be more significant in control mix (C), especially at initial exposure 416 periods of 30 to 90 days (Fig.6c). This is because of the progress in the reaction of cement grains 417 418 and also due to the formation of calcium carbonate (CaCO<sub>3</sub>) phases caused by the ingression and reaction of CO<sub>2</sub> with hydrated phases (CH/C-S-H) [18, 56]. Decrement in the rate of strength 419 420 development in later exposure periods of 120-180 days could be attributed to the reduced rate of hydration as well as pore blockage caused due to the presence of CaCO<sub>3</sub> crystals which obstructs 421 422 the further CO<sub>2</sub> diffusion.

Rate of development in compressive strength especially for mixes comprising of nano-silica with
 respect to CO<sub>2</sub> exposure was seen to be significantly lower than that of control mortar. Rate of

compressive strength development for CNS-3, FN-25, UN-25, and FUN-25 mixes from 30 to 180 425 days ranges from 4%-2%, 5%-3%, 7%-4%, and 8%-5%, respectively (Fig. 6c). This can be 426 427 attributed to the occurrence of significant variation in pore solution and phase assemblages in the blended cementitious system comprising of SCMs [15]. The presence of active filler particles 428 rich in siliceous/ Aluminicious components tends to react chemically with CH to produce dense, 429 stable compounds such as C-S-H and C-A-H/C-A-S-H making the mortar more compact and less 430 porous [18]. The highest compressive strength was observed for the CNS-3 mix followed by the 431 FUN-25 mix. However, all blended mortar showed higher compressive strength compared to that 432 of control mix. 433

The carbonation depth value of all the blended mixes used in this study was made to relate with the compressive strength of blended mortar specimens at various periods of exposure and plotted in Fig. 7.





438

**Fig.** 7 Relationship between compressive strength and carbonation depth

The figure depicts the linear relationship with an  $R^2$  value of 0.91. Eq. 9 presents the linear equation between the carbonation depth (D) and compressive strength of blended mortar specimens with SCMs (FA, UFFA, and CNS) at the replacement level of 25% exposed to 3.5% CO<sub>2</sub> ( $\sigma_{CO2}$ ). However, the relationship may vary with different SCMs and extent of replacement level [57]

#### 444 $\sigma_{CO2} = 26.05 + 2.85D$

### 445 4.2.3 Carbonation shrinkage

446 Measured carbonation shrinkage values for all the mixes exposed to 3.5% CO<sub>2</sub> for the long-term
447 exposure period of 180 days are presented in Fig. 8.



448

449 Fig. 8 Carbonation shrinkage values of multi-blended cementitious mixes exposed to CO<sub>2</sub>

The data in Fig. 8 show that the carbonation shrinkage values of all the mixes increased as the 450 amount of time exposed to CO<sub>2</sub> increased. At 180 days of exposure, the measured carbonation 451 shrinkage value for the control mortar was 820 micro strains. This can be attributed to the quicker 452 formation of calcium carbonates and water due to the increased availability of CH content in the 453 454 pore solution to react with CO<sub>2</sub>. In this case, the resulting shrinkage is caused by the evaporation of water released during the carbonation process. According to the measured carbonation 455 shrinkage values, binary blended F-25 (937 micro strains) experienced the highest carbonation 456 shrinkage at a long-term exposure period of 180 days. Followed by U-25 and FU-25 mixes with 457 carbonation shrinkage values of 900, and 848 micro strains, respectively at 180 days of exposure. 458 The carbonation-induced shrinkage was more pronounced in blended mixes containing FA and 459

UFFA particles. Carbonation shrinkage is highly dependent on the pore system of the 460 cementitious matrix. The presence of fly ash particles in the mortar system led to an increase in 461 total porosity making the system more susceptible to carbonation and associated shrinkage. It is 462 463 also to be noted that these blended mortar specimens were subjected to only 28 days of curing, which is not sufficient enough for fly ash particles to undergo pozzolanic reaction. However, it is 464 465 reported that the actual cause for carbonation shrinkage is difficult to differentiate which may 466 either be due to a) carbonation-induced physical adsorption of water on the pore walls or b) 467 evaporation of carbonation-formed water [14, 50, 58].

468 In case of nano-silica blended mortar results related to carbonation shrinkage were found to be converse. The intensity of reduction in carbonation shrinkage was seen to be high for mortar 469 mixes composed of nano-silica. The highest reduction in carbonation shrinkage value was noticed 470 for the binary blended CNS-3 mix. The maximum value of carbonation shrinkage at the long-471 term exposure of 180 days for CNS-3 mix was seen to be 98 micro strains i.e., 90% lower than 472 473 that of control mortar. This reduction in shrinkage is attributed to the minimized percentage of porosity (Fig. 4) which is responsible for the permeation of CO<sub>2</sub> gas and CH content in the pore 474 solution as well as the lower availability of moisture content within the mortar as a result of 475 densification. Quaternary blended FUN-25 mix was the next mix which showed lower 476 carbonation shrinkage with a value of 115 micro strains (i.e., 88% lower than control mortar) at 477 478 the exposure period of 180 days. It can be ascribed to the improved particle packing and associated 479 reduction in permeable porosity. Further, the synergetic action of Pozzolans in triplet scale contributed to the lowering of the CH concentration owing to its chemical reaction and also helped 480 physically by blocking the micron to nano-scale pores [59]. Other ternary blended mortar with 481 nano-silica (FN-25 and UN-25) also showed >75% reduction in carbonation shrinkage compared 482 483 to that of control mix. This indicates that nano-silica presence in the cementitious system can resist the vulnerability to carbonation shrinkage. 484

485 4.3 Characterization

486 4.3.1 Thermogravimetric analysis

TG-DTG results of multi-blended cementitious mortar cured for 28 days (before exposure to an
 accelerated CO<sub>2</sub> environment) are presented in Fig 9.



Fig. 9 TG- DTG plot of non-CO2 exposed blended cementitious samples

TG curves specify the percentage of mass loss corresponding to the decomposition of multiple 492 phases at specified temperature ranges (Fig. 9a). DTG curves (Fig 9b) of the hydrated 493 494 cementitious system show three distinct endothermic peaks at different zones of temperature. The first major endothermic peak observed at 50-300 °C is very complicated as it relates to the 495 decomposition of multiple phases such as free water molecules (up to 105 °C), and bound water 496 in C-S-H phase/Aft/AFm/gypsum [23, 58]. Water loss associated with C-S-H inter layer occurs 497 at the broad temperature range of 50-600 °C, dehydroxylation of AFt/AFm phases happens 498 between 50 °C to 180 °C and 50 and 200 °C, respectively and gypsum loses water at around 100-499 140 °C [47]. The second prominent endothermic peak was seen at the temperature range of 400-500 501 500 °C, which was due to the dehydroxylation of the portlandite (calcium hydroxide, CH) phase. The third endothermic peak at 600-700 °C corresponds to the decarbonation of calcium carbonate 502 503 (CC) phases [23, 47].

504 TG-DTG plots of multi-blended cementitious mortars that have undergone 180 days of 505 carbonation are presented in Fig. 10.



506





508

Fig. 10 TG- DTG plot of 180 days CO<sub>2</sub> exposed blended cementitious samples

It is to be noted that in the case of carbonated mortar specimens, samples for TG-DTG analysis 509 were collected within the carbonation depth region (i.e., 4 mm). It can be perceived from Fig. 10b 510 511 that an endothermic peak relating to the dehydroxylation of CH at the temperature boundary of 400-500 °C was seen to be absent after being subjected to carbonation. Whereas the endothermic 512 peak corresponding to CC was found to be broadened compared to that of unexposed hydrated 513 samples i.e., the peak initiates from 500 °C and ends at 750 °C (Fig. 10b). Further, it is also 514 important to note that the endothermic peak relating to the dehydration of CSH/AFt/AFm phases 515 at the temperature range of 50-300 °C was found to be diminished in the case of carbonated 516 samples. This is attributed to the associated carbonation reaction between hydrated phases (CH/C-517 518 S-H/Aft/AFm) and CO<sub>2</sub> to form CaCO<sub>3</sub> phases.

Hydrated phases of blended cementitious samples such as CH, CC, and WH (i.e., water associated
with hydration products like C-S-H/Aft/AFm excluding CH content), were quantified using Eqs,
5, 6, and 7, respectively. Fig. 11 shows the histogram plot of the same.



522



The quantified percentage of CH (Fig. 11a) was seen to be higher before the action of carbonation. 525 526 The percentage of CH for all the mixes within the carbonation depth indicated by phenolphthalein solution was found to be negligible. At the same time, Fig. 11b indicates the increase in the 527 calcium carbonate phase for the carbonated samples compared to that of the initial carbonate 528 529 phase present in the hydrated samples. This is attributed to the absorption of CH and other 530 hydration phases (C-S-H/AFt/AFm) by dissolved carbonates in the pore solution, which was formed due to the diffusion of CO<sub>2</sub> in accelerated conditions. The percentage of CH recorded for 531 the unexposed hydrated binary blended CNS-3 mix was found to be the lowest among all the 532 mixes. It is also important to noted that the percentage of CH involved in the formation calcium 533

carbonate was found to be <1% i.e., CH% before carbonation (2.2%) - CH% after carbonation</li>
(3%). Reduced CC content in CNS-3 mix is ascribed to the densified microstructure of the mix
formed due to the intensified reactivity of nano-silica particles [18, 21], which blocked the
pathway for CO<sub>2</sub> diffusion into the cementitious matrix.

Other binary/ternary blended mixes composed of fly ash or/and ultra-fine fly ash mixes such as 538 539 F-25, U-25, and FU-25 mixes showed a marginal reduction in CH content (i.e., 8%-15%) at the curing age of 28 days. It is for that reason no much decrement in CC% was detected for these 540 mixes at their carbonated segment. The small addition of nano-silica particles in conjunction with 541 542 fly ash or/and ultra-fine fly ash particles (i.e., FN-25, UN-25, and FUN-25) significantly reduced the concentration of CH% at the curing age of 28 days. This can be attributed to the action of 543 544 nano-silica particles as well as due to the synergetic action of microns-to-nano sized particles indicating the dense matrix. Reduction in CH% and improved microstructure would be the 545 546 possible reason associated with the drop in the formation of the CC content. It is interesting to note that the quaternary blended FUN-25 mix showed comparable results to the CNS-3 mix. 547

548 Fig 11c shows the variation in the quantified amount of WH% before and after the action of 549 carbonation. It can be noticed from the figure that on carbonation percentage of WH showed decreasing trend irrespective of mix type. However, the percentage of reduction in WH% was 550 found to be high in control mix (i.e., 65%) and blended mixes without nano silica such as F-25, 551 U-25, and FU-25. Quantified amount of WH% for the blended mixes without nano-silica at the 552 curing age of 28 days was found to be 40-50% less than control mix. This is mainly linked to the 553 554 dilution effect of the mix and slow pozzolanic reactivity. Further reduction in WH% after 555 carbonation can be attributed to the carbonation reaction that happened between dissolved CO<sub>2</sub> 556 and hydrated phases such as calcium silicate hydrates (CSH)/ettringite/un-hydrated calcium silicate phases to form precipitates of calcium carbonates (CC) and amorphous silica gel. While 557 other ternary and quaternary blended mixes with a small percentage of nano-silica exhibited 558 higher percentage of WH compared to that control mix both before as well as after the carbonation 559 560 reaction.

561 Based on TG-DTG analysis it is possible to quantify the amount of calcium carbonate formed 562 considering the characteristic temperature range. Calcium carbonate is found in three 563 polymorphic forms i.e., calcite, aragonite, and vaterite. It is well reported that calcite decomposes

at the temperature boundaries of 600-800 °C. Other polymorphs of CC such as aragonite and 564 vaterite, recrystallizes to calcite at the temperature of ~ 450 °C without any indication of weight 565 change during TGA measurement [60]. The weight loss peak associated with decarbonation 566 process is typically detected at 700-720 °C that specifies the presence of coarser calcite. The 567 weight loss peak at 600-650 °C indicates the occurrence of hemi/mono carbonates and CH/C-S-568 H converted calcium carbonate. Even though CH and CC can be quantified through TGA, it is 569 difficult to classify the polymorphs of CC formed [60]. It is for that reason one of the 570 characterization techniques which detects the various phases of carbonates formed based on the 571 function group identification technique known as Fourier transform infrared spectroscopic (FTIR) 572 573 analysis [61-62] was employed.

- 4.2.2 Fourier transform infrared spectroscopic (FTIR) analysis
- 575 FTIR spectra of multi-blended cementitious mixes at the curing age of 28 days (i.e., uncarbonated
- samples) are presented in Fig. 12.





578 Fig. 12. FTIR spectra of hydrated multi-blended samples before exposure to accelerated CO<sub>2</sub>

Different phase assemblages of a hydrated cementitious composite system were identified 579 through FTIR spectra based on various functional groups at its characteristic wavenumbers. The 580 highlighted fine peaks at a wavenumber range of 3640-3652 cm<sup>-1</sup> signifies the stretching vibration 581 of the hydroxyl group (-OH) bound within the Ca(OH)<sub>2</sub> phase indicating the presence of 582 portlandite [59-61]. Fig. 12 depicts that band corresponding to portlandite at 3640 cm<sup>-1</sup> for the 583 control mix is found to be intense compared to all other blended mixes. While CNS-3 mix and 584 585 other blended mixes integrated with nano-silica particles (FN, UN, and FUN- mixes) showed a less significant band of CH. The next prominent vibration band was observed at the wave number 586 of 3409 cm<sup>-1</sup>. It is reported that the broad vibration band at 3300 cm<sup>-1</sup> to 3600 cm<sup>-1</sup> in hydrated 587 cementitious systems links to the stretching vibration of bound water in C-S-H gel [62-63]. This 588

band is found to be strong for blended cementitious mixes especially for mixes incorporated with 589 nano-silica. The vibration band at 1424 cm<sup>-1</sup> corresponds to asymmetric C-O-C stretching bonds 590 that signifies the presence of carbonate phase such as calcite resulted due to CO<sub>2</sub> absorption 591 during the hydration process [62, 64]. The intense vibration band observed at 1000  $\text{cm}^{-1}$ 592 corresponds to the asymmetric stretching band of T-O-Si (T represents tetrahedral Si or Al) 593 594 indicating the occurrence of C-S-H/ Aft/ AFm phases [45]. The shift in peak towards the left in case of blended cementitious system (1050 cm<sup>-1</sup>) is due to the formation of additional C-S-H 595 through the occurrence of supplementary reaction. 596

FTIR spectrum of multi-blended cementitious composites exposed to accelerated carbonation for180 days is shown in Fig. 13.



599

**Fig. 13.** FTIR spectra of hydrated multi-blended samples exposed to accelerated CO<sub>2</sub> for 180

601

days

The chief product of carbonation reaction is calcium carbonate (CaCO<sub>3</sub>). Three crystalline 602 polymorphs of calcium carbonate (CaCO<sub>3</sub>) are calcite, aragonite, and vaterite [58]. It is reported 603 604 that the formation of calcium carbonate polymorphs depends on various internal factors such as pH, temperature, supersaturation, additives, and impurities [60]. FTIR techniques is one of the 605 prominent techniques adopted to analyse polymorphs of carbonation product. The fundamental 606 vibration bands of calcium carbonates can be found at the wavenumbers of 1400-1500  $\text{cm}^{-1}$  and 607 700-800 cm<sup>-1</sup> representing the asymmetric stretching and in-plane bending of C-O-C bonds of 608 carbonates. Two major bands of C-O-C observed after the action of carbonation are at the 609 wavenumbers of 1424 cm<sup>-1</sup> and 734 cm<sup>-1</sup> that correspond to the two polymorphic forms of CaCO<sub>3</sub> 610 i.e., calcite and vaterite, respectively. It can be noticed from the figure that the height and width of 611 the bands corresponding to C-O-C stretching at 1424 cm<sup>-1</sup> and 734 cm<sup>-1</sup> are found to be increased 612 after the long-term CO<sub>2</sub> exposure of 180 days. It is important to note that the intensity of C-O-C 613 stretching bond at 1424 cm<sup>-1</sup> for CNS-3 and FUN-25 mix was found to be less significant. 614 However, other blended mixes with nano-silica also showed a lower height peak at 1424 cm<sup>-1</sup> as 615 well as at 734 cm<sup>-1</sup> compared to other mixes without nano-silica. These results are found to be in 616 617 alignment with TGA data.

For having a quantitative estimate of calcite formation area under the asymmetric stretching band
of C-O-C at 1424 cm<sup>-1</sup> was determined for both uncarbonated and carbonated mixes and presented
in the form of a histogram (refer Fig. 14).





Fig. 14. Quantitative estimate of calcite phase measure for both uncarbonated and carbonated
 mixes using FTIR spectrum

625 Fig. 14 demonstrates that carbonation area under the asymmetric C-O-C band at a wavenumber of 1424 cm<sup>-1</sup> relating to the calcite phase increased on carbonation irrespective of mix type. The 626 highest rise in the C-O-C band area was noticed for control mix (C) i.e., approximately 70% to 627 that of initial carbonates formed during the hydration mechanism. This is attributed to the larger 628 concentration of hydration phases (CH/C-S-H) in the 100% OPC mix as well as due to the 629 increased level of porosity. The quantified area under the curve of the C-O-C band for CNS-3 630 mix exposed to 180 days of CO<sub>2</sub> exposure remained almost the same as that of unexposed 631 hydrated sample. This specifies the potentiality of CNS-3 mix in curtailing the diffusion of CO<sub>2</sub> 632 gas owing to its densified microstructure at the nano-scale. Further, ternary and quaternary 633 blended mixes embedded with nano-silica such as FN-25, UN-25, and FUN-25 mix also showed 634 a tremendous reduction in the formation of secondary calcite associated to carbonation. This is 635 ascribed to the presence of nano-sized silica particles as well as the modified packing density in 636 the mix due to the physicochemical action of multi-grained particles. However, other blended 637 638 mixes without nano-silica did not show significant improvement in resisting the formation of 639 calcite, unlike the mixes with nano-silica.

To have an understanding of the relationship between the quantified amount of CC (crystalline calcite phase decomposed in the temperature range of 600 °C to 770 °C) determined through the thermogravimetric technique and the calculated area under the curve of asymmetric stretching of C-O-C band at a wavenumber of 1424 cm<sup>-1</sup> relating to the functional group of carbonates (calcite palynomorph) measured through FTIR technique were related to one another. Fig. 15 shows the relationship plot for the same.



646

**Fig. 15** Relationship between CC% (measured through TGA) and A<sub>coc</sub> (measured through FTIR)

648 Calcium carbonate values measured through TGA (CC%) and FTIR ( $A_{c-o-c}$ ) was seen to be related 649 linearly. The obtained coefficient of correlation " $R^{2}$ " value was 0.9091. This relationship gives the 650 information that quantification of carbonation extent in terms of calcite formation through two 651 different characterization techniques such as TGA and FTIR holds good with one another.

### 652 **5.** Conclusions

On the basis of the carbonation studies conducted on binary, ternary, and quaternary blended cementitious mortar composed of micron to nano-sized pozzolanic ingredients designed using modified Andreasen and Andersen particle packing tool, following conclusions can be drawn.

The synergetic act of nano-silica in multi-blended cementitious system significantly reduced
the rate of carbonation.

Carbonation mechanism in the multi-blended cementitious system varies significantly from that
 of sole OPC system. It is well understood that particle packing density, and portlandite
 concentration in the pore solution differs from binary to ternary to the quaternary blended
 system with and without nano-silica particles that has great influence on the rate of carbonation.
 Progressive increase in compressive strength for control mix with 100% OPC is associated with

- the blocking of meso-macro sized pores in the cementitious mortar caused due to the formation of the precipitates of CaCO<sub>3</sub> due to the carbonation of the portlandite (Ca(OH)<sub>2</sub>) phase. Therefore, eventually controls the rate of strength gain in the specimens caused by the action of carbonation.
- In the case of blended mortar strength development is not solely dependent on carbonation
   action, it is also caused due to the hydraulic and pozzolanic activity of Pozzolans.
- The resulted carbonation shrinkage is instigated due to the evaporation of water released during
   the process of carbonation process. Blended cementitious mixes without nano-silica amplified
   the susceptibility to carbonation associated shrinkage. the converse scenario was identified for
   the blended mixes comprising of nano-silica even in the presence of FA or/and UFFA.
- Small incorporation nano-silica in conjunction with FA and UFFA particle (i.e., quaternary
   blended FUN-25 mix) showed significant improvement in the reduction of carbonation depth,
   carbonation coefficient and carbonation shrinkage without having any impeding effect on
   compressive strength.
- It can be concluded from TGA results that the endothermic peak corresponding to CC was found to be broadened i.e., the peak initiates from 500 °C and ends up at 750 °C for carbonated samples compared to that of unexposed hydrated samples. It is important to note that diminished endothermic peak relating to the dehydration of CSH/AFt/AFm phases at the temperature range of 50-300 °C in carbonated samples signifies the formation of calcium carbonate phase.
- The unidentified polymorphic forms of precipitated CaCO<sub>3</sub> such as aragonite and vaterite other
   than calcite from TGA can be identified through FTIR. Characterization performed through
   FTIR specifies the formation of two polymorphic CaCO<sub>3</sub> phases i.e., calcite and vaterite at its
   characteristic wavenumbers of 1424 cm<sup>-1</sup> and 734.55 cm<sup>-1</sup>, respectively.
- The quantitative estimation of calcium carbonate phase and the carbonate phase through two
   different characterization methods, i.e., TGA and FTIR, respectively found to have a linearly
   correlated.

# **Declaration of competing interest**

690 The authors declare that they have no known competing financial interests or personal 691 relationships that could have appeared to influence the work reported in this paper.

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