1 2	Synergy of Hydration and Microstructural Properties of Sustainable Cement Mortar Supplemented with Industrial By-Products
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# 44 Highlights

- Fineness of bottom ash along with the occurrence of silica and alumina played a chief role in performance enhancement of bottom ash-based cement mortars.
  - Similarly, the fineness of slag sand along with the availability of additional portlandite generated, assists in undergoing secondary hydration reactions effectively in slag sand-based cement mortars.
  - The ability of the finer fraction of IBPs to undergo secondary hydration reactions was confirmed through advanced characterisation studies.

# 51 Abstract

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52 The present research assists in resolving the issues allied with the disposal of industrial solid wastes/industrial by-53 products (IBPs) by developing sustainable IBPs based cement mortars. The applicability of IBPs as a feasible 54 alternative to river sand in cement mortar has been evaluated by investigating the synergy among the ingredients, 55 resulting engineering properties and microstructural developments at early and late curing ages. The study could 56 effectively substitute 30% volume of river sand with bottom ash and 50% in the case of slag sand mortars. The 57 experimental outcomes disclose that the practice of IBPs as fine aggregate enhances the engineering properties of 58 mortar and the optimum replacement level lies at 10% and 40% usage of bottom ash and slag sand, respectively. 59 The advanced characterization studies and particle packing density illustrate the refinement of pores by void filing 60 action and accumulation of additional hydration products through secondary hydration reactions. The consumption of portlandite followed by increased hydration products formation observed through 61 62 thermogravimetric analysis, X-ray diffraction analysis and energy dispersive X-ray spectroscopy that confirmed 63 the contribution of finer fractions of IBPs to secondary hydration reactions. This constructive development was 64 also observed from the lowering of wavenumber corresponding to Si-O-Si/Al vibration bands in Fourier transform 65 infrared spectroscopy spectra. The improved microstructure resulted in enhancing the compressive strength by 66 9.01% and 18.18% in optimized bottom ash and slag sand mortars, respectively at the curing age of 120 days. Similarly, the water absorption reduced by 1.03% and 1.24% in bottom ash and slag sand mortars, respectively. 67

68 Keywords: Industrial by-products, mortar, hydration, particle packing, microstructure, sustainability.

# 69 1. Introduction

70 Construction industry is one among the leading sectors that greatly contribute to the progress of global economic 71 development [1]. Especially for developing countries, there is a vast scope available for its growth relying on 72 industrialization and urbanization. To achieve these mammoth targets, a huge quantity of construction materials is going to be required. Construction sector being a key for the growth of a country, simultaneously it has also got 73 74 a negative impression towards the ecological balance of nature by depleting the natural resources, polluting the 75 surface, deforestation, carbon footprint etc. As a result of this, many of the resources may run scarce thereby making the construction sector highly expensive. The main reason associated with the aforementioned issues is 76 77 that the construction industry routines cement based composites like concrete, mortar etc. for its activities which 78 consume conventional materials like ordinary Portland cement (OPC) as binder, river sand as fine aggregate and 79 crushed granite rocks as coarse aggregate. The chief ingredient of concrete/mortar is aggregates which account 80 for about 70% of the volume [2]. These aggregates used in the production of concrete/mortar are being mined 81 from sources such as river beds (i.e., for sand as fine aggregate) and rock quarries (for coarse aggregates and also 82 for fine crushed aggregates (i.e., M-sand). Mining of aggregates from river beds leads to serious environmental 83 impacts shattering the ecological balance [3-5] and one of the consequences being mining of sand from the river 84 beds is already being prohibited in several provinces. As of now, fine crushed granite rocks (manufactured sand, 85 i.e., M-Sand) have largely replaced the river sand in the construction industry. Even though M-Sand showed 86 satisfying performance as an alternative to river sand [6, 7], it has certain disadvantages in fulfilling the 87 performance requirements of concrete such as grading requirements, workability [8], surface finishing ability [9– 88 11], compressive strength, density, yield, etc. Thus, the natural resource of aggregate is depleting rapidly due to 89 the high consumption worldwide. As a result of these, scarcity of good quality river sand and ill effects of dredging 90 on the environment, researchers are striving to identify and characterize sustainable alternative materials to 91 substitute river sand.

92 On the other hand, sustainable construction mainly intends to reduce the harmful impacts on the environment 93 caused by the construction industry. Rapid industrialization results in the generation of various kinds of waste 94 which can be hazardous to the environment. Numerous wastes and by-products were being spawned from day-to-95 day activities such as fly ash, silica fume, agricultural wastes, waste paper sludge ash, pulverized fuel ash, waste 96 molecular sieves, volcanic pumice ash, recycled waste water etc. were used by the researchers as an alternative to 97 conventional materials, as the waste management has become one of the most challenging tasks in the world over 98 a period of time [12–16]. Disposal of these wastes/industrial by-products (IBPs) has created serious problems to

99 the surrounding environment in terms of land occupancy, pollution of the surrounding and subsurface area leading

100 to health hazards. Researches have been conducted by implementing these wastes/IBPs in cementitious systems 101 and reported positively in terms of social need, economic feasibility, engineering properties, durability and 102 microstructure to some extent [17-21]. It is also being reported that the global annual waste accumulation of 103 various other IBPs such as glass waste, E-waste, construction and demolition waste (C & D waste), foundry sand and municipal solid waste, accounted for around 130 million tons, 53.6 million tons, 3 billion tons, 13.38 million 104 105 tons and 12 billion tons, respectively. These IBPs have occupied thousands of hectares of land throughout the 106 world and many government bodies are promoting their sustainable utilization by possible recycling and reuse. The implementation of these coarser wastes as an alternative to river sand on the performance of cementitious 107 composites is also restricted to some extent of replacement. However, their usage in cementitious composites has 108 109 shown satisfactory outcomes in terms of hardened properties, but not with respect to the properties at fresh state 110 [22-24].

111 Presently, coal-fired thermal power stations are accountable for producing huge amounts of coal waste in most 112 developing nations. Bottom Ash (BA) is one of the major industrial by-products which is produced at the bottom of the furnace during the process of coal combustion for generating electricity. These thermal power plants 113 114 produce large amounts of bottom ash as a by-product. It is usually treated as a solid waste material and is disposed 115 on surface impoundments or in landfills leading to environmental pollution. Slag sand is another major nonmetallic industrial by-product from metal smelting processes which is manufactured under controlled conditions. 116 117 The granulated slag is obtained by the process of quenching the molten slag of the furnace in water. Therefore, a large quantity of bottom ash and slag wastes is getting accumulated near the industrial locality causing serious 118 119 environmental hazards with time. It is being reported that the global annual waste accumulation of bottom ash and slag sand is about 574 million tons and 300-360 million tons, respectively [25, 26]. However, the effective way 120 121 of regenerating the values from the IBPs in construction industry is not being suitably developed. Thus, there is a 122 potential need to utilize these IBPs in an effective manner. Concrete and mortar are one among the best possible 123 areas where these IBPs can be largely employed as an alternative material to conventional ingredients.

With the view of developing a sustainable solution, the present investigation explores the possibility of utilizing the industrial by-products such as bottom ash and slag sand as construction material by partially substituting the river sand to check their suitability in cement mortar. To check the performance of resulting cement mortar, studies related to engineering properties and microstructural developments were conducted through advanced characterization techniques.

# 129 2. Experimental methodology

# 130 2.1 Material used and their properties

131 Ordinary Portland cement of 53 grade confirming to ASTM C150/C150M-22[27] was used as a binder to produce 132 cement mortar. The fine aggregates used involve 3 kinds of materials namely river sand, bottom ash (BA) and 133 slag sand (SS). River sand confirming to zone II as per IS: 383-2016 was employed and as a partial replacement 134 to river sand, IBPs namely bottom ash and slag sand were used at different replacement levels. For mixing and 135 curing mortars, ordinary potable water confirming to IS 10500:2012 [28] was used. To obtain the desired flow properties in fresh cement mortar, a polycarboxylate ether-based superplasticizer confirming to IS 2645:2003 [29] 136 137 and IS 9103:1999 [30] was used. The preliminary investigations on these raw materials were carried out to 138 investigate the basic properties as per the guidelines mentioned in the standards. Table 1 shows the extracted 139 properties from the preliminary studies on raw materials and Fig. 1 represents their particle size distribution. The 140 morphology of bottom ash and slag sand was observed through scanning electron micrographs which are 141 presented in Fig. 2 and Fig. 3, respectively. The chemical composition of bottom ash and slag sand is presented 142 in Table 2.

<b>Table 1: Properties</b>	s of	various	materials	used
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Mater	Properties								
1,14001		OPC	RS*	BA	SS	SP*			
Specific g	gravity	3.11	2.66	2.09	2.61	$1.08\pm0.02$			
Initial setting tir	110	-			-				
Final setting tin	170	-			-				
Standard consi	32	-			-				
Fineness (	m²/kg)	300	-			-			
Soundness	s (mm)	2	-			-			
Loss on Ignit	2.30	-			-				
Bulk density	Bulk density Loose		1500	997	1387	-			
$(kg/m^3)$	(kg/m <sup>3</sup> ) Compacted			1075	1465	-			

Γ	% of Voids	Loose		43.07	52.19	46.87	-
70 01 V 01ds	Compacted	-	39.34	48.44	43.87	-	
Γ	Fineness N	-	2.47	2.16	2.67	-	
Γ	Water absorp		0.98	0.83	0.71		
Γ	pH	-	-			$\geq 6$	
	Chloride c	content	-	-			< 0.20 %

144 \*- RS: River sand, \*SP- Superplasticizer





Fig. 1. Particle size distribution of various materials used





Fig. 2 a) Bottom ash, b) scanning electron micrograph of BA at 1500X, c) scanning electron micrograph of BA at 10000X







angular with smooth texture. The particles of slag sand were found to be brighter and whiter which could be due to the presence of excess amounts of calcium-based compounds in them.

Component	<u> </u>						
Component	Bottom ash	Slag sand					
MgO	1.2999	3.9780					
$Al_2O_3$	18.3026	14.6523					
$SiO_2$	46.9721	28.5487					
$P_2O_5$	0.8160	-					
$SO_3$	0.9131	1.4384					
K <sub>2</sub> O	1.7413	0.6182					
CaO	9.6538	45.7530					
MnO	0.1280	1.1584					
$Fe_2O_3$	17.5230	1.8056					
Na <sub>2</sub> O	1.0318	0.1599					
Cl	0.0750	0.0166					
TiO <sub>2</sub>	1.1941	1.3285					
$Rh_2O_3$	-	0.3912					
SrO	0.3080	0.1045					
$ZrO_2$	0.0412	0.0468					

#### Table 2. Chemical compositions of bottom ash and slag sand

#### 158 2.2 Details of cement mortar mixes developed

159 In the present study, three kinds of mortars were developed to check the feasibility of IBPs as fine aggregate in 160 cement mortar. The mortars, entirely produced with river sand as fine aggregates are considered as control mortar (reference mix) designated by CM. The mortar mixes in which the river sand was replaced by bottom ash are 161 designated by alphabet "B" and similarly "S" for the mortar mixes in which the river sand was replaced by slag 162 sand. The numbers following these alphabets depict the extent of fine aggregate replacement in terms of 163 164 percentage volume of river sand. A binder-to-fine aggregate ratio of 1:3 and water-to-binder ratio (w/b) of 0.45 was maintained throughout the study. The required corrections related to water absorption and moisture content 165 166 were taken into consideration while preparing the mortar mixes. A minimum flow value of 150 mm was 167 maintained to ensure better workability using a superplasticizer. Table 3 shows the details of the mixes produced.

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Tał	ole 3.	Details	of the	e mortar	mixes	produced
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		W	_			
Mix designation	OPC	RS	BA	SS	Water	SP (% bwob*)
СМ	777.50	1943.25	-	-	349.88	0.00
		Botto	m ash base	l mortar		
B10	777.50	1795.50	156.38	-	349.88	0.17
B20	777.50	1596.00	312.75	-	349.88	0.40
B30	777.50	1396.50	469.13	-	349.88	1.00
		Slag	sand based	mortar		
S10	777.50	1795.50	-	195.75	349.88	0.05
S20	777.50	1596.00	-	391.50	349.88	0.05
S30	777.50	1396.50	-	587.25	349.88	0.20
S40	777.50	1197.00	-	783.00	349.88	0.20
S50	777.50	997.50	-	978.75	349.88	0.40

169 \*bwob- by weight of binder

170 2.3 Production of cement mortar samples

171 The ingredients of the mortar mix were dry mixed manually and further wet mixing was done using an automatic

172 mortar mixer, designed as per the guidelines mentioned in EN 196-1 [31]. The produced mortars were then cast

in a mould of size 70.6 mm  $\times$  70.6 mm. The cast specimens were further allowed to set under a humid environment (i.e.,  $27 \pm 2^{\circ}$ C and 95% RH). The cast samples were then given time to set in a humid atmosphere

environment (i.e.,  $27 \pm 2^{\circ}$ C and 95% RH). The cast samples were then given time to set in a humid atmosphere (i.e.,  $27 \pm 2^{\circ}$ C and 95% RH) for 24 hours. Later the specimens were demoulded and kept for curing by immersing

175 (i.e.,  $27 \pm 2^{\circ}$ C and 95% RH) for 24 hours. Later the specimens were demoulded and kept for curing by in 176 in normal potable water maintained at  $27 \pm 2^{\circ}$ C till the day of testing. After a curing age of 3, 7, 28, 5

in normal potable water maintained at  $27 \pm 2^{\circ}$ C till the day of testing. After a curing age of 3, 7, 28, 56 and 120 days, samples were taken out, dried and tested to check their performance in a hardened state. Fig. 4 presents a

178 brief overview of the carried-out study.

- 179 2.4 Details of tests performed
- 180 2.4.1 Fresh and hardened properties

181 The workability and setting time of the produced mortars were assessed in the fresh state. Whereas the hardened 182 state properties were extracted by making use of destructive and non-destructive methods. All the properties

183 reported in the present study are calculated by considering the average of results collected from three specimens.

Table 4 shows the details of the tests performed to assess the fresh and hardened properties.

185 2.4.2 Microstructural analysis and characterization techniques used

The microstructure of cement mortar greatly influences their engineering properties and is very crucial to 186 187 comprehend which helps in understanding the chemistry that is contributing to the performance. Thus, the 188 hydrated mortar samples were collected from the core of mortar specimens after 28 and 120 days of curing. 189 Further, these chunks were kept submerged in isopropanol for about 24 hours to prevent further hydration 190 reactions with time [32, 33]. Soon after that, those chunks were oven dried at a temperature range of 40-60 °C till 191 the weight became stabilized. These prepared samples were then preserved in desiccators along with silica gel 192 pellets, and a vacuum environment was maintained to prevent further absorption of moisture by the samples. These preserved samples were further used to conduct various characterization studies. 193

194 The microstructural development in produced mortars was observed by carrying out morphological study using

scanning electron microscopy (SEM) technique in secondary electron mode. Further, the elemental composition

in these samples was examined through energy-dispersive X-ray spectroscopy (EDS). The mortar samples were

197 gold sputtered and taken further for microstructure assessment through SEM-EDS.

198

### Table 4. Details of the tests performed

Туре	Test	Reference	Remarks				
Fresh	Mini flow table	EN 1015-3 [34]	-Workability/flowability measurement -To fix the superplasticizer dosage required for maintaining a minimum flow diameter of 150 mm				
properties	Setting time	ASTM C403/C403 M- 08 [35]	-Initial and final setting time measurement using penetration resistance measurements				
	Compressive Strength	IS 4031-Part 6:1988 [36]	-Using a compressive testing machine at a loading rate of 35 MPa/min				
	Density	BS EN 1015- 10:1999 [37]	-Weight by volume method using weighing balance				
Hardened	Permeable porosity	[38, 39]	-Vacuum water absorption technique using vacuum desiccators				
properties	UPV IS 516 (Part 5/sec 1):2018 [40]		-Using portable ultrasonic non-destructive digital indicating tester (PUNDIT)				
	Water absorption	BS 1881-122 [41]	-By considering the change in weight at saturated surface dried and oven dried condition				

The XRD study was carried out to determine the mineralogical compositions formed in the hydrated cement mortar samples. The preserved samples were ground and sieved through an IS sieve having a mesh size of 75 microns, and the passed fine powdered particles were then used for the study. The XRD tests were carried out in Malvern Panalytical and Jeol-JPX 8P make X-ray diffractometers operated with Cu Ka radiation (40 kV/40 mA) at a scanning rate of 2°/min. The samples were examined at 20 degrees ranging between 4° to 80° and the recorded XRD results were analyzed using X'Pert High Score Plus software.

205 The decomposition of various phases associated to hydration products with the temperature was investigated 206 through thermogravimetric analysis (TGA), with the aid of RIGAKU TG-DTA 8112 thermogravimetric analyzer. 207 Further, the hydration products formed in different types of mortars were quantified using the obtained TGA data. 208 The sample preparation method followed for TGA was similar to that followed for XRD study and testing was 209 carried out in a nitrogen purge atmosphere where the temperature varied from room temperature to 875°C. During 210 the course of test, the temperature was increased at a rate of 10°C/min and nitrogen purge rate was kept at 20 211 ml/min. The quantification of hydration products was done based on their decomposition at particular temperature 212 boundaries in terms of weight loss. The endothermic peaks formed in derivative thermogravimetric curve (DTG) 213 as a result of compound decomposition (in the form of weight loss) determine the temperature boundaries. In the

present study, the endothermic peak observed in the temperature range of 400-500°C is considered as the mass

loss from the decomposition of calcium hydroxide (CH) [32, 42–45]. Similarly, the temperature boundary associated with the decomposition of calcium carbonate was taken in the temperature boundary of 600-800°C [32, 46]. Further, the amount of water associated with other hydration products (WH) was quantified by considering the weight loss associated with the temperature range of 35-600°C, excluding the decomposition of CH[32, 46].

Fourier transform infrared spectroscopy (FTIR)studies were carried out with Bruker Alpha II make equipment and the data were extracted from the OPUS software. The sample preparation method used is similar to that followed for XRD and TGA analysis. The FTIR spectra were collected in transmittance mode between the wavelengths ranging from 600 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> using ATR method. The different hydration phases that are formed during the course of hydration such as portlandite (Ca (OH)<sub>2</sub>), C-S-H, C-A-S-H, sulfates and carbonate phases (such as ettringite, monosulfoaluminate, sulfoaluminate, calcium carbonate) etc., were studied based on

recorded peaks with intensities and their wavenumber shifts over the age of curing.





Fig. 4. Flowchart showing the details of the study

# 228 3. Analysis of results and discussions

229 3.1 Particle packing in the developed cement mortars

230 Modified Andreasen and Andersen packing model was employed in the present study using "EMMA" software 231 to check the degree of particle packing achieved in the produced mortars[47]. A distribution coefficient (q) of 232 0.30 suitable for attaining medium workability was chosen for the analysis[32]. The particle packing curves of BA based and SS based mortars are presented in Fig. 5. The obtained particle packing curves depict that the 233 234 particle packing density is enhanced with the implementation of IBPs as a partial alternative to river sand. The 235 improvement in the extent of fitting  $(R^2)$  of IBPs based mortars particle packing curves, calculated with respect 236 to the target curve (fixed by the modified Andreasen and Andersen packing model) confirms the increment of 237 particle packing density[48].





Fig. 5. Particle packing curves for a) Bottom ash based mortars and b) Slag sand based mortars

240 3.2 Fresh properties

241 3.2.1 Workability

- Workability of produced cement mortar mixes with varying dosages of BA and SS is presented in Fig. 6 a) (BA based mortar) and Fig. 6 b) (SS based mortar) which consists of flow diameter, flow value and their corresponding
- based mortar) and Fig. 6 b) (SS based modosage of superplasticizer consumption.

245 By observing the results obtained, it can be noted that the addition of BA into the mortar mix as a substitute to 246 river sand reduces the flow characteristics. This behavior can be observed through the increased dosage of 247 superplasticizer consumption with the percentage usage of BA. The control mortar (CM) produced entirely with 248 river sand as fine aggregate achieved the required minimum flow diameter of 150 mm without consuming any 249 superplasticizer. With the percentage usage of BA, the flow characteristics were observed to become poorer due 250 to the intrinsic properties of BA. The rough textured BA particles (which can be observed through SEM images 251 in Fig. 2 c)) increase the friction between the particles, thereby resisting the movement of particles over one 252 another. Also, the fine nature of BA particles as compared to river sand (which can be observed from Fig.1) 253 demands more water for particle surface wetting. Thus, dry and harsh mortar mixes were formed at high volume 254 usage of bottom ash which requires more superplasticizer to achieve the required flow.

- 255 Similarly, by observing the superplasticizer dosage requirement and their corresponding flow values in SS based
- 256 mortars, it can be concluded that the workability of produced mortars tends to reduce with the increasing volume
- of slag sand. The possible reasons for this reduced workability are, a) the irregularly shaped particles of slag sand (seen in Fig. 3b) restrict the movement of particles over one another, and b) the calcium rich particles of slag sand increase the degree and heat of hydration which makes the mortar mix harsh due to the increased water demand.
- 255 Increase the degree and heat of hydration which makes the mortal mix harsh due to the increased water dem

It is also important to notice the sudden declination of flowability characteristics and increased superplasticizer consumption in bottom ash and slag sand mortars at a replacement level of 30% and above. This could be due to the formation of harsh mortar under the influence of excessive amounts of fines, due to the increased proportion of IBPs. The fine particles of IBPs tend to fill the void spaces and form cohesive mortar at lower proportions till 20% replacement volume. The occurrence of fines in relatively higher volume at higher replacement levels (30%)

- and above) enhances the water demand and reactivity which affects the overall flow characteristics.
- 266 3.2.2 Setting time

The influence of using IBPs such as BA and SS on the setting time of cement mortar is presented in this section.
Fig. 6c) and Fig. 6d) depict the graphical representation of setting times recorded for different BA and SS based
cement mortars respectively.

270 By observing the results shown in Fig. 6c), it can be seen that the bottom ash addition in the cement mortar as a 271 partial substitute to river sand retards the hydration process which can be seen from the increased setting time 272 values. This could be due to increased concentration of silica and alumina in the cement mortar by the usage of 273 bottom ash, which reduces the heat of hydration and further prolongs the hydration mechanism. Whereas, in case 274 of SS based cement mortar mixes, both initial and final setting time was found reducing with the increasing 275 replacement level of river sand. This can be attributed to the increased amount of calcium oxide in the cement 276 mortar formed by the addition of slag sand, which intensifies the degree and heat of hydration, resulting in the 277 fast setting of mortar mixes. Also, there could be a possibility of variation in the amount of heat accumulation generated from the hydration reaction in cement mortar mix depending on the heat absorbing capacity of 278 279 replacement material compared to that of river sand. Thus, the heat absorbing property of bottom ash and slag 280 sand has also influenced the initial and final setting time.



Fig. 6. Flow characteristics of a) bottom ash based cement mortar and b) slag sand based cement mortar;
 setting time of c) bottom ash based cement mortar and d) slag sand based cement mortar

**284** 3.3 Hardened properties

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**285** 3.3.1 Compressive strength

Compressive strength development in control (CM), BA and SS based mortars were measured at the curing age
of 3, 7, 28, 56 and 120 days. Fig. 7a) and Fig. 7d) shows the compressive strength of BA based and SS based
cement mortars, respectively.

289 The compressive strength results obtained from the BA based mortars exhibited a decreasing trend with the 290 increasing replacement level of river sand in the initial days of curing (i.e., till 28 days). This could be attributed 291 to the increased concentration of silica and alumina with the usage of bottom ash in cement mortar which reduces 292 the heat of hydration and further prolongs the hydration mechanism. However, there observed a comparable performance by B10 mortar against CM at almost all the curing ages, owing to the enhanced particle density 293 fashioned by void filling action and possible secondary hydration activity (after 28 days of curing) undergone by 294 295 finer bottom ash particles. Similarly, the positive influence on using slag sand as a partial replacement material to 296 river sand can be seen through the compressive strength results after 28 days of curing. The improvised particle 297 packing density with the increasing slag sand content (which can be seen in Fig. 5) helped the ingredients of 298 mortar to undergo primary and possible secondary hydration reactions more effectively. Since the slag sand is 299 rich in calcium oxide, siliceous and aluminous compounds, the finer particles of slag sand undergone 300 supplementary hydration reactions (secondary hydration reaction/ pozzolanic reaction) after 7 days of curing, 301 resulting in the formation of additional hydration products. These actions helped in refining the pore structure of 302 mortar mixes in an effective manner leading to the formation of dense microstructure which enhances the hardened 303 mechanical properties such as compressive strength.

304 It is also important to notice from the results that the bottom ash based and slag sand-based mortars showed 305 optimum performance at about 10% and 40% volume replacement of river sand, respectively. The reduction in 306 the compressive strength beyond the optimized dosage of BA is due to poorer gradational characteristics that 307 caused bleeding and further affected the matrix of the produced mortar. Also, the enhancement in the silica-308 alumina content by using the BA at higher levels restrains the degree of hydration reactions. Whereas in the case 309 of slag sand-based mortars, the excessive amount of calcium hydroxide generated from the calcium rich slag sand particles caused leaching and also accelerated the early hydration reactions with greater heat of hydration which 310 311 altogether makes the cement system weak due to the formation of microcracks. At the curing age of 28, 56 and 312 120 days, S40 mortar recorded 45.36%, 14.40% and 29.83% higher compressive strength than the control mortar respectively. Similarly, B10 mortar showed 2.94% and 9.01% at the end of 56 and 120 days of curing respectively. 313

**314** 3.3.2 Dry density

The dry density of control (CM), BA and SS based mortars were measured at a curing age of 3, 7, 28, 56 and 120
days. Fig. 7 b) and Fig. 7 e). represents the dry density of BA based and SS based mortars, respectively.

The obtained results showed an increasing trend of dry density with the progress in curing age due to continued 317 318 formation of hydration products which refine the mortar pore structure. It is also important to notice that the dry 319 density of produced mortars reduces with the increasing proportion of BA and SS. This is attributed to lower 320 specific gravity of replacement material (i.e., BA and SS) than that of river sand. The lower specific gravity of a 321 material causes a reduction in the unit weight of the resulting mortar. Even though the fine particles of IBPs 322 increase the particle packing density by filling the void spaces, there observed a reduction in the dry density with 323 the increasing percentage of IBPs, as the variation in the dry density is highly reliant on the specific gravity of the 324 IBPs.

325 3.3.3 Ultrasonic pulse velocity (UPV)

The uniformity and quality of mortars produced using IBPs were investigated by conducting UPV tests after the curing age of 3, 7, 28, 56 and 120 days. Fig. 7 c) and Fig. 7 f) represents the UPV results of BA based and SS

328 based mortars, respectively.

329 From the measured values of UPV, there observed an improvement to UPV with the progress in curing age for all 330 types of produced mortars, due to densification of microstructure by hydraulic and pozzolanic reactions. The UPV 331 of control mortar was observed to be higher than any other IBPs based mortars at early ages of curing (i.e., till 7 332 days). The UPV tends to reduce with the increasing proportion of river sand replacement by IBPs. This could be 333 attributed to the lack of uniformity formed in the mortar by the usage of IBPs, consisting a wide number of 334 minerals. However, the UPV tends to increase with the increasing proportion of slag sand beyond 7 days of curing 335 which could be due to the influence of secondary hydration reactions imparted by slag sand particles that refined 336 the mortars pore structure. It is also important to notice that there observed a gradual fall in the UPV values beyond 337 40% usage of slag sand at all the curing ages. The generation of cracks due to higher heat of hydration and 338 reduction in the uniformity of the mix at higher proportions of slag sand were the causes for reduced UPV. All 339 the mortars produced recorded a UPV value ranging between 3700 m/s and 4700 m/s by the end of 120 days of 340 curing. Hence the produced mortars were in the category of good to excellent grade quality as per IS 13311:1992 341 – Part 1 [49].

**342** 3.3.4 Water absorption and Permeable porosity

The water absorption and permeable porosity of control and IBPs based mortars were assessed at the end of 3, 7,
28, 56 and 120 days of curing. Fig. 8 a) and Fig. 8 b) presents the water absorption and permeable porosity of BA
based mortars, respectively. Similarly, Fig. 8 c) and Fig. 8 d) represents the water absorption and permeable
porosity of SS based mortars, respectively.

From the obtained results it can be observed that the water absorption and permeability porosity followed a quite similar trend with the usage of IBPs at all the curing ages. This could be due to the fact that the absorbed water predominantly accumulates in the permeable void spaces or pores present in the mortar mixes and these pore volumes are regarded as porosity. The water absorption and permeable porosity were found reducing with the progress in curing age which is due to the refinement caused to the pore structure of mortar by the generation and accumulation of hydration products.

353 The utilization of IBPs in mortars as a partial replacement to river sand showed a positive influence on water 354 absorption and permeable porosity. The general trend of water absorption and permeable porosity was found 355 reducing with the increasing proportion of IBPs till the optimum replacement level (i.e., 10% of BA and 40% of 356 SS) and thereafter found increasing. This behavior can be ascribed to the synergetic influence from the improved 357 particle packing and effective secondary hydration reactions with the increasing proportion of IBPs. In addition 358 to these, the lower water absorbing property of BA and SS in comparison with river sand also contributes in 359 reducing the water absorption and permeable porosity of mortar. However, exceeding the dosage of IBPs beyond 360 the optimum percentage caused an increment in the values of water absorption and permeable porosity. This 361 development is due to the increased finer particles in the mortar mix at higher volume of IBPs, which lowers the water availability in mortar for undergoing hydration reactions effectively. The increased composition of silica, 362 363 and alumina by the usage of BA and increased calcium composition by the usage of SS beyond the optimum 364 requirement also affects the hydration mechanisms leading to the development of weak microstructures in mortar, 365 which increases the water absorption and permeable porosity.





Fig. 7 a) Compressive strength, b) Dry density, c) UPV of bottom ash based cement mortar; and d) Compressive strength, e) Dry density, f) UPV of slag sand based cement mortar



Fig. 8 a) Water absorption, b) Permeable porosity of bottom ash based cement mortar; and c) Water
 absorption, d) Permeable porosity of slag sand based cement mortar

- 372 3.4 Microstructure and characterization studies
- **373** 3.4.1 Mineralogical characterization

The mineralogical characteristics of hydrated samples of control, BA and SS based cement mortars at a curing age of 28 days and 120 days were investigated with the aid of XRD technique. The XRD analysis was carried out for control mortar and IBPs based mortars till one replacement level beyond the optimum replacement percentage for river sand (i.e., till B20 and S50). The chemical name, empirical formula and peak assignment designations corresponding to various mineralogical compounds detected were tabulated in Table 5.

379 The XRD patterns of BA based mortar at 28 days and 120 days of curing are depicted in Fig. 9 a) and Fig. 9 b), 380 respectively. Similarly, the XRD patterns of SS based mortar at 28 days and 120 days of curing are presented in 381 Fig. 10 a) and Fig. 10 b), respectively. By observing the XRD patterns of 28 days cured mortar samples, it can be 382 noticeable that the occurrence of portlandite (CH) peaks are more and prominent in BA based mortars. This is due 383 to the delay in hydration process caused by the increased concentration of silica and alumina with the usage of 384 bottom ash. The addition of calcium from the IBPs to the mortar composition also enhances the portlandite 385 formation. However, there observed a preferential formation of additional calcium silicate hydrates and calcium 386 silicate aluminium hydrates through the effective conversion of portlandite into stable hydration products such as 387 CSH and CASH phases in IBPs based mortars. The mineralogical compounds related to CSH and CASH phases 388 such as Gismondine, Chabazite, Tobermorite and Kamaishilite have additionally formed in BA based mortars. 389 Similarly, Gismondine, Kamaishilite, and Hillebrandite were observed in the case of SS based mortar. While in 390 the control mortar (CM), in addition to Xonotlite (CSH), the portlandite (calcium hydroxide; CH) generated were 391 rapidly converted into various other hydration products such as carbonates and sulfate hydrates (Gypsum, 392 Yeelimite etc.) that implement a comparatively weaker microstructure in mortar.

393 Similarly, by investigating the XRD patterns of 120 days cured mortar samples, it is clear that the peaks 394 corresponding to portlandite are found to be more and prominent which indicates the formation of portlandite 395 content (CH) with curing age. The produced CH in control mortar remains mostly unutilized after 28 days of 396 curing. However, the portlandite produced in the IBPs based mortars was consumed for secondary hydration 397 reactions, leading to the formation of additional hydration products that were detected in the form of mineralogical 398 compounds associated to CSH and CASH. The mineralogical compounds associated to CSH and CASH phases 399 such as Gismondine, Chabazite, Wairakite and Tobermorite were additionally formed in BA based mortars. 400 Similarly, Gismondine, Wairakite, Rosenhahnite, Hillebrandite and Katoite are the compounds that were 401 additionally formed in SS based mortars. It is also important to notice that the XRD pattern of 120 days cured 402 samples appeared less crystalline than that of 28 days cured ones, owing to the effective conversion of 403 mineralogical compounds from crystalline phase to amorphous CSH and CASH phase.

404 Overall, by analyzing the XRD patterns, it can be concluded that a significantly higher number of mineralogical
 405 compounds associated to calcium silicates and calcium aluminium silicates were formed by the application of
 406 IBPs in cement mortar with lesser formation of carbonates and sulfates. This development in IBPs mortars
 407 facilitated to perform better than control mortar which can be seen through the measured engineering properties
 408 such as compressive strength, water absorption and permeable porosity.



# Table 5. Details of the mineralogical compounds and their peak assignment

	Peak assignment of bottom ash based mortar						Peak assignment of slag sand based mortar									
Compound	28	28 days curing		120	days cur	ing		28	days curi	ng			120	days cu	ıring	
	СМ	B10	B20	СМ	B10	B20	<b>S10</b>	S20	S30	<b>S40</b>	<b>S50</b>	S10	<b>S20</b>	<b>S30</b>	<b>S40</b>	S50
Quartz (Silicon Oxide) (SiO <sub>2</sub> )	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q
Portlandite (Calcium Hydroxide) (Ca $(OH)_2$ )	Р	Р	Р	Р		Р	Р	Р	Р	Р	Р	Р	Р	Р	Р	Р
Rosenhahnite (Calcium Silicate Hydroxide) (Ca <sub>3</sub> (Si <sub>3</sub> O <sub>8</sub> (OH) <sub>2</sub> )													1			
Hillebrandite (Calcium Silicate Hydroxide) (Ca <sub>2</sub> (SiO <sub>3</sub> ) (OH) <sub>2</sub> )									2			2			2	
Kamaishilite (Calcium Aluminium Silicate Hydroxide) (Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>6</sub> (OH) <sub>2</sub> )			3					3								
Katoite, Silicatian, (Ca <sub>3</sub> Al <sub>2</sub> (SiO) <sub>4</sub> (OH) <sub>8</sub> ) (Calcium Aluminium Silicate Hydroxide)															4	
Tobermorite (Calcium Silicate Hydroxide Hydrate) (Ca <sub>5</sub> (OH) <sub>2</sub> Si <sub>6</sub> O <sub>16</sub> ·4H <sub>2</sub> O)		Т			Т											
Calcium Silicate Hydroxide (Ca <sub>4</sub> Si <sub>5</sub> O <sub>13.5</sub> (OH) <sub>2</sub> )				5												
Xonotlite (Calcium Silicate Hydrate) (Ca <sub>6</sub> Si <sub>6</sub> O <sub>17</sub> (OH) <sub>2</sub> )												Х				
Calcium Silicate Hydrate (Ca <sub>2</sub> SiO <sub>4</sub> ·H <sub>2</sub> O)						6	6							6		
Chabazite (Calcium Aluminium Silicate Hydrate) (Ca <sub>2</sub> Al <sub>4</sub> Si <sub>8</sub> O <sub>24</sub> ·12H <sub>2</sub> O)		7			7											
Wairakite (Calcium Aluminium Silicate Hydrate) (CaAl <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> ·2H <sub>2</sub> O)					W									W		
Gismondine (Calcium Aluminum Silicate Hydrate) (CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> .4H <sub>2</sub> O)			8			8	8		8	8	8	8	8		8	8
Calcium Aluminium Carbonate Silicate (Ca4Al6Si6O24·CO3)	9															
Calcite (Calcium Carbonate) (CaCO <sub>3</sub> )			С			С	С	С		С	С	С	С		С	С
Aragonite (Calcium Carbonate) (CaCO <sub>3</sub> )	А	А		А												
Dolomite (Ca Mg $(CO_3)_2$ )					D											
(Calcium Magnesium Carbonate)					D											
Thaumasite (CaSiO <sub>3</sub> .CaCO <sub>3</sub> .CaSO <sub>4</sub> .15H2O) Calcium Carbonate Silicate Sulfate Hydroxide Hydrate																а
Gypsum (Calcium Sulphate Hydrate) (CaSO <sub>4</sub> .2H <sub>2</sub> O)	G			G		G	G		G		G			G		
Yeelimite (Calcium Aluminium Oxide Sulphate) (Ca <sub>3</sub> Al <sub>6</sub> O <sub>12</sub> .CaSO <sub>4</sub> )	Y	Y	Y	Y	Y			Y								

415 3.4.2 Thermo gravimetric analysis (TGA)

416 The weight loss of the mortar samples with the increasing temperature was recorded through TGA and further 417 TG/DTG curves were plotted. Fig. 11 a) and Fig. 11 b) presents the TG/DTG curves of 28 days and 120 days 418 cured BA based mortar samples, respectively. Similarly, Fig. 11 c) and Fig. 11 d) shows the TG/DTG curves of 419 28 days and 120 days cured SS based mortar samples, respectively.





Fig. 11. TG and DTG curves of a) 28 days cured bottom ash based cement mortar, b) 120 days cured
 bottom ash based cement mortar, c) 28 days cured slag sand based cement mortar and d) 120 days cured
 slag sand based cement mortar

In the present study, the hydration products such as calcium hydroxide (CH), calcium carbonate (CC) and the
water associated with other hydration products (WH) were quantified on the basis of their decomposition by
weight loss at their specific temperature boundaries. The hydration products such as gypsum, ettringite, CSH,
CASH, Friedel's salts, etc., were not calculated individually in this investigation due to overlapping temperature
boundaries [32, 50, 51]. The measured values of CH, WH and CC are graphically presented in Fig. 12.

429 The quantified values of hydration products in the case of 28 days cured BA and SS based mortar samples 430 exhibited an increasing CH content with the increasing percentage replacement of river sand by IBPs. This 431 behavior confirmed the hindrance occurred to the hydration process caused by the excessive silica and alumina present in bottom ash. The additional calcium oxide obtained from the bottom ash particles and calcium rich slag 432 433 sand particles causes an additional formation of portlandite, which is also responsible for the increasing trend of 434 CH. On the other hand, the CH produced in control mortar (CM) readily takes part in hydration reaction and forms 435 various other hydration products such as gypsum, ettringites and carbonates along with CSH. As a consequence, 436 the quantified values of CH in CM recorded lowest at the curing age of 28 days.

It is also important to notice the variation of WH found to be in line with the consumption of CH. The control mortar showed the highest value of WH and BA based mortar samples recorded comparatively lesser WH due to the delayed hydration process. Whereas, the excessive calcium reserve in slag sand based mortars accelerates the hydration reactions to a greater extent which leads to the augmentation of WH with the increasing content of slag sand. This increment in the values of WH was observed till the optimum dosage of slag sand (S40) and is evident for the extensive formation of CSH/CASH gel which contributes to the performance enhancement of mortar.

The observed values of CC signify that the usage of IBPs (i.e., bottom ash and slag sand) drastically reduced the content of CC in the mortar which can be seen in Fig. 12. The preferential formation of gypsum and ettringite in the control mortar can also be observed through an intensive endothermic peak existing in DTG curve within 150°C. Whereas, the IBPs based mortar showed relatively broader endothermic peaks which signifies the development of additional CSH and CASH with a limited amount of gypsum and ettringite.

448 By investigating the TGA results of 120 days cured mortars, the formation of CH was found to be continuing with the curing age. Whereas a higher consumption of CH for the primary and secondary hydration reactions was found 449 450 in IBPs based mortars, owing to the formation of supplementary CSH/CASH gels. This development can also be 451 noticed through the increased value of WH along with broadened endothermic peaks observed in the temperature range of 110 °C-300 °C. Similar to 28 days results, the formation of WH at 120 days curing was found to be 452 453 slightly higher for optimized IBPs based mortar (i.e., B10 and S40) which is due to the optimized content of IBPs 454 favorable for undergoing reactions efficiently. In addition to these, the quantified values of CC in 120 days cured 455 IBPs based mortar samples were also found to be significantly lower than the control mortar.





457 Fig. 12. Phase compounds formed in bottom ash based mortar [(a) CH; (b) WH; c) CC] and slag sand
458 based mortar [(d) CH; (e) WH; (f) CC] after 28 days and 120 days of curing



Fig. 13 a) and Fig. 13 b) presents the FTIR spectra of BA based cement mortar after 28 days and 120 days of
curing, respectively. Further, Fig. 14 a) and Fig. 14 b) presents the FTIR spectra of SS based cement mortar at a
curing age of 28 days and 120 days, respectively. The details regarding the functional group assignment associated
to different wavenumbers are tabulated in Table 6.

464 The major functional groups visible in all types of mortars were found to be similar in the obtained FTIR spectra. 465 The vibration band associated to Si-O-Si asymmetric stretching visible in the wavenumber range of 900-1000 cm<sup>-</sup> 466 <sup>1</sup> is more prominent and consistent in all types of mortars produced. This Si-O-Si asymmetric stretching band showed a significant shift towards a lower wavenumber by the usage of IBPs such as bottom ash and slag sand in 467 468 cement mortar. The BA based mortar showed a shift from 1001.69 cm<sup>-1</sup> to 954.48 cm<sup>-1</sup> and from 993.48 cm<sup>-1</sup> to 469 960.63 cm<sup>-1</sup> by the end of 28 days and 120 days of curing, respectively. Similarly, the SS based mortar records a 470 shift from 1001.69 cm<sup>-1</sup> to 956.63 cm<sup>-1</sup> and from 993.48 cm<sup>-1</sup> to 942.16 cm<sup>-1</sup> by the end of 28 days and 120 days 471 of curing, respectively. This reduction in the wavenumber associated to Si-O-Si asymmetric stretching band 472 signifies the formation of stronger bonds which is attributed to the synergetic effect of improved particle packing 473 and secondary hydration reactions imparted by the usage of IBPs. The enhanced degree of particle packing eases 474 the reactivity of minerals, leading to the formation of additional hydration products. The pozzolanic reactivity 475 offered by the particles of IBPs enables secondary hydration reactions which produce additional C-S-H and C-A-476 S-H phases.





Fig. 13. FTIR spectra of control and BA based mortars at a curing age of a) 28 days and b) 120 days



480 Fig. 14. FTIR spectra of control and SS based mortars at a curing age of a) 28 days and b) 120 days

The vibration band corresponding to Si-O-Si/Al symmetric stretching was also prominently observed in the produced mortars at a wavenumber range of 675-800 cm<sup>-1</sup>. These vibration bands are found slightly broad and intense in the case of IBPs based mortars both at 28 days and 120 days of curing. This development is due to the extensive formation of CSH and CASH phases by the action of secondary hydration reactions facilitated by IBPs particles which create stronger bonds and hence better microstructure. However, there is no considerable shift observed in the vibration bands associated to Si-O-Si/Al symmetric stretching by the implementation of IBPs. All these findings are found in line with the XRD analysis data.

488 It is also important to notice the significant reduction in the intensities of vibration bands related to O-C-O asymmetric stretching and O-C-O bending with the usage of IBPs in both 28 and 120 days cured mortars. This feature assisted the IBPs based mortars to have a quality microstructure irrespective of delayed hydration lag in the early stages of curing. These findings are in good alignment with the TGA and SEM results presented.

Notation	Age of			Wavenumbe		Functional group assignment					
No	curing	СМ	B10	B20	S10	S20	S30	S40	S50	Functional group assignment	
1	28	3304.94	3296.05	3368.38	3397.44	3462.80	3403.27	3323.22	3411.48	O II agreementais stratching	
1	120	3513.32	3339.49	3456.64	3466.96	3442.27	3411.48	3403.27	3614.71	O-H asymmetric stretching	
2	28	1601.34	1673.76	1633.21	1653.48	1650.59	1596.95	1629.79	1604.24	O II agummatnia handing	
2	120	1650.59	1647.69	1687.27	1653.48	1589.75	1619.53	1665.07	1699.83	O-n asymmetric bending	
3	28	1416.32	1418.37	1428.64	1414.27	1428.63	1408.11	1412.22	1414.27	0 C 0 asymmetric stratching	
3	120	1410.16	1414.27	1412.21	1408.11	1422.48	1408.10	1416.32	1395.79	0-C-O asymmetric stretching	
1	28	1085.85	1098.16	1096.11	1104.32	1106.37	1100.21	1089.95	1098.16	S O stratching	
4	120	1088.58	1088.58	1106.37	1106.37	1098.16	1104.32	1085.85	-	5-0 stretching	
	28	1001.69	954.48	968.85	960.63	964.74	962.69	956.53	960.63		
5	120	-	-	-	-	-	999.63	1024.27	-	Si-O-Si asymmetric stretching	
		993.48	966.79	960.63	954.48	964.74	958.58	942.16	958.58		
6	28	872.37	872.37	872.37	872.37	874.42	870.32	870.32	874.42	$O \subset O$ handing	
0	120	874.42	-	868.27	870.32	880.58	862.11	864.16	-	O-C-O bending	
	26	773.84	769.74	775.90	788.21	777.95	775.89	749.22	792.32		
	20	691.74	-	704.05	710.21	-	695.84	-	700.28		
7		777.95	773.84	782.06	782.06	788.21	790.27	792.32	777.95	Si-O-Si/Al symmetric stretch	
	120	-	-	736.90	726.63	-	747.16	749.21	722.53		
		685.58	681.48	-	681.48	-	-	-	679.42		
	20	632.21	644.53	642.48	650.69	638.37	665.05	667.11	646.58		
	20	-	626.05	-	-	-	628.1	624	624		
8	120	634.27	640.42	652.73	626.05	624	624	624	640.42	S-O bending	
		-	-	-	-	673.27	650.69	669.16	-		

 Table 6: Particulars of the functional group assignment at different wavenumbers

494 3.4.4 Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS)

The microstructural development and the morphology of hydrated control and optimized IBPs mortars (i.e., CM,

B10 and S40) were examined through SEM. The scanning electron micrographs of 28 days and 120 days cured

mortar samples are presented in Fig. 15 and Fig. 16, respectively. The compounds in the micrographs were visually

identified based on their structure, shape, color and texture [52]. Further, the EDS analysis results highlighting
the elemental composition of these mortar samples are tabulated in Table 7. Fig. 17 shows a typical image on
which EDS analysis was conducted.

501 The Ca/Si atomic ratio was extracted from the obtained EDS results and used to study the extent of hydration

502 products formation such as calcium hydroxide (CH) and CSH. Since the development of CSH phases highly relies

503 on calcium (Ca) and silicate (Si) ions present in pore solution, the Ca/Si atomic ratio signifies the extent of calcium

- 504 hydroxide (CH) and CSH formation[53]. The cement matrix with lesser Ca/Si atomic ratio indicates a dense
- 505 microstructure, owing to the formation of greater and stronger CSH network [54].

506 The SEM micrographs of 28 days cured IBPs based mortar samples appear to have a dense microstructure with 507 reduced number of voids in comparison with the control mortar. This could be due to the improved particle 508 packing achieved with the usage of IBPs, which contributes to the effective hydration reactions which eases the 509 process of pore refinement. The occurrence of CSH gels in substantial amounts with lesser Ca/Si atomic ratio 510 confirms this development. However there also observed a significant amount of unutilized CH in IBPs based 511 mortars which is possibly due to decelerated hydration reaction caused by the excessive silica and alumina content in BA based mortars. In contrast, the presence of excessive CH in SS based mortars is attributed to the additional 512 513 calcium oxide particles added from the slag sand particles. It is also important to observe that the SEM micrographs of control mortar shows higher formation of CC and ettringites in comparison to that of IBPs based 514 515 mortars.

516 Similar kind of advancements were observed in the microstructure of 120 days cured mortar samples. However,

517 the microstructure of mortars appeared denser than 28 days cured ones due to the continuation of hydration process 518 with the curing age. In addition to these, IBPs based mortars showed a much denser microstructure with well-

developed CSH/CASH network and minimal amount of ettringites and CC. The reduction in Ca/Si atomic ratio

520 of IBPs based mortars from 28 days to 120 days also confirms the effective conversion of CH into CSH/CASH

521 phases. The additional formation of CSH and CASH phases in IBPs based mortars observed in the SEM

micrographs helped in improving the microstructure. The bottom ash based mortar showed an extensive formation
 of CSH and CASH phases in the form of globular, spongy, fibrous and amorphous network. Similarly, fibrous

and amorphous structured CSH and CASH phases were predominantly formed in slag sand based mortars. These

525 distinctly formed CSH and CASH phases beyond 28 days of curing in IBPs based mortars are evident for the

526 formation of additional hydration products through secondary hydration reactions, facilitated by the reactive finer

527 fractions present in IBPs. This constructive development densified the IBPs mortar microstructure and helped to

528 perform superior than conventional mortar.



530Fig. 15. Scanning electron micrograph of control (CM) [a), b)], B10 [c), d)] and S40 [e), f)] mortar at 28531days of curing



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Fig. 16. Scanning electron micrograph of control (CM) [a), b)], B10 [c), d)] and S40 [e), f)] mortar at 120 days of curing





Fig. 17. Typical image showing the EDS analysis of mortar sample

Element	Atomic v	veight (%) o cured morta	
	СМ	B10	
С	15.43	22.84	
Ca	14.99	14.49	
0	58.2	55.37	
A 1	5 22	0.5	ľ

Table 7: EDS elemental analysis of produced mortars at 28 days and 120 days of curing

Element	Atomic v	veight (%) o sured morte	of 28 days	Atomic weight (%) of 120 days						
Element	СМ	B10	S40	СМ	B10	S40				
С	15.43	22.84	18.32	16.00	19.10	19.10				
Са	14.99	14.49	17.98	9.85	12.975	16.175				
0	58.2	55.37	56.58	54.60	55.55	54.11				
Al	5.22	0.5	0.74	2.55	1.40	1.05				
Si	5.29	6.03	5.43	4.05	5.75	5.10				
Mg	0.16	-	0.38	-	0.10	0.167				
S	0.28	0.28	0.23	10.65	0.80	0.90				
Cl	0.03	0.11	-	-	-	-				
K	0.11	0.1	0.03	0.3	0.10	0.05				
Fe	0.3	0.28	0.22	1.75	0.30	0.10				
Na	-	-	0.09	0.25	0.05	-				
Ti	-	-	-	-	0.45	0.35				
Mn	-	-	-	-	2.20	1.60				
Zr	-	-	-	-	1.25	1.30				
Ca/Si	2.836	2.402	3.311	2.432	2.256	3.171				

#### 538 4. Conclusions

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539 The conclusions drawn from the present investigation are presented as follows,

- 540 The primary investigations on the bottom ash and slag sand showed comparable properties with river 541 sand and hence could be utilized as a partial substitute to river sand in developing cementitious 542 composites.
  - The mortar produced with IBPs presented lower workability characteristics and the study confirms the flowability of about 15 cm can be easily achieved with the aid of superplasticizers.
- 545 The usage of IBPs as fine aggregate found influencing the setting of mortars. The experiments revealed that the inclusion of BA retards the setting process by around 2 hours at their optimum level usage. 546 547 Whereas, the inclusion of SS accelerated the setting process by an hour approximately at optimum level 548 usage. Thus, the usage of these mortars can be made as per the required application suitably or a 549 compatible retarder/ accelerator can be equipped to regulate the setting time. 550
  - The inclusion of IBPs as fine aggregates in mortar enhanced the degree of particle packing and secondary hydration activity. This further assists in enhancing the performance, observed in terms of compressive strength, water absorption and permeable porosity. The performance increment of slag sand based mortar is quite significant when compared with the bottom ash based mortars. Hence, these IBPs improve the service life of structure by encasing the load bearing structure effectively from surrounding exposures that affect the durability of structure.
  - The experimental findings confirm that, in conjunction with the degree of particle packing and the hydration mechanism, the dry density of produced mortars greatly relies on the specific gravity of ingredients and the UPV highly depends on the extent of homogeneity in the mix. The reduced dry density and improved UPV at optimised proportion of IBPs confirms the reduction in density is due to lower specific gravity associated with the alternative used for river sand. Further, the reduced dry density contributes in reducing the dead load of the structure.
- The advanced characterization studies such as SEM-EDS, XRD, TGA and FTIR analysis confirms the 562 • 563 performance enhancement seen in IBPs based mortars. The lowering Ca/Si ratio through EDS, formation of additional CSH and CASH phases through XRD, increased consumption of CH along with augmented 564 565 values of WH through TGA and occurrence of additional Si-O-Si/Al stretching bands with considerable 566 shifts towards the lower wavenumber through FTIR confirms the occurrence of secondary hydration reactions by the IBPs particles that helped in improving the microstructure (observed through SEM) and 567 568 overall performance of engineered cement mortar further.

569 The conclusions drawn from the experimental findings recommend the usage of bottom ash up to 10% and slag 570 sand up to 40% as a feasible alternative to river sand without compromising the performance of cement mortar.

#### 571 Declaration of Competing Interest

572 The authors declare that they have no conflict of interest, financial interests or personal relationships that could573 have appeared to influence the research work reported in this article.

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#### 579 References

- Hussin JM, Rahman IA, Memon AH (2013) The way forward in sustainable construction: issues and challenges. International Journal of Advances in Applied Sciences 2:15–24
- 582 [2] Oktay H, Yumrutas R, Akpolat A (2015) Mechanical and thermophysical properties of lightweight aggregate concretes. Construction and Building Materials 96:217–225
- 584[3]Dhir RK, de Brito J, Silva R V., Lye CQ (2019) Processing of Recycled Aggregates. Sustainable585Construction Materials: 57–88. https://doi.org/10.1016/b978-0-08-100985-7.00004-2
- 586 [4] Drew LJ, Langer WH, Sachs JS (2002) Environmentalism and natural aggregate mining. Natural Resources Research 11:19–28. https://doi.org/10.1023/A:1014283519471
- 588 [5] Dan Gavriletea M (2017) Environmental impacts of sand exploitation. Analysis of sand market.
   589 Sustainability (Switzerland) 9:. https://doi.org/10.3390/su9071118
- 590 [6] Suresh S, Revathi J (2016) Effect of M-Sand on Setting Time of High Performance Concrete. Asian
  591 Journal of Research in Social Sciences and Humanities 6:1648. https://doi.org/10.5958/2249592 7315.2016.01118.7
- 593 [7] Jayswal S, Mungule M (2018) Assessment of M-Sand As Potential Substitute for Natural Sand in Concrete. In: International Conference on 2019, pp 7-8.
- 595 [8] Sudha C, Kottuppillil AK, Ravichandran PT, Divya Krishnan K (2016) Study on Mechanical Properties
  596 of Concrete with Manufactured Sand and Bagasse Ash. Indian Journal of Science and Technology 9: 1597 6. https://doi.org/10.17485/ijst/2016/v9i34/95867
- 598 [9] Pilegis M, Gardner D, Lark R (2016) An investigation into the use of manufactured sand as a 100% replacement for fine aggregate in concrete. Materials 9:440. https://doi.org/10.3390/ma9060440
- Li B, Ke G, Zhou M (2011) Influence of manufactured sand characteristics on strength and abrasion resistance of pavement cement concrete. Construction and Building Materials 25:3849–3853.
   https://doi.org/10.1016/j.conbuildmat.2011.04.004
- Elavenil S, Engg C (2013) Manufactured Sand, A Solution And An Alternative To River Sand And In
   Concrete Manufacturing. 2:20–24
- 605 [12] Alyami M, Hakeem IY, Amin M, Zeyad AM, Tayeh BA, Agwa IS (2023) Effect of agricultural olive, rice
   606 husk and sugarcane leaf waste ashes on sustainable ultra-high-performance concrete. Journal of Building
   607 Engineering 72:106689
- 608 [13] Alyami M, Mydin MAO, Zeyad AM, Majeed SS, Tayeh BA (2023) Influence of wastepaper sludge ash
   609 as partial cement replacement on the properties of lightweight foamed concrete. Journal of Building
   610 Engineering 79:107893
- 611 [14] Golewski GL (2023) Mechanical properties and brittleness of concrete made by combined fly ash, silica
   612 fume and nanosilica with ordinary Portland cement. AIMS Mater Sci 10:390–404
- [15] Zeyad AM, Shubaili M, Abutaleb A (2023) Using volcanic pumice dust to produce high-strength self curing concrete in hot weather regions. Case Studies in Construction Materials 18:e01927

- [16] Zeyad AM (2023) Sustainable Concrete Production: Incorporating recycled wastewater as a green building material. Construction and Building Materials 407:133522
- 617 [17] Golewski GL (2023) Assessing of water absorption on concrete composites containing fly ash up to 30%
   618 in regards to structures completely immersed in water. Case Studies in Construction Materials 19:e02337
- [18] Wang L, Zhang P, Golewski G, Guan J (2023) Fabrication and properties of concrete containing industrial
   waste. Frontiers in Materials 10:1169715
- [19] Elbasri OMM, Nser S, Shubaili M, Abdullah GMS, Zeyad AM (2022) Performance of self-compacting concrete incorporating wastepaper sludge ash and pulverized fuel ash as partial substitutes. Case Studies in Construction Materials 17:e01459
- 624 [20] Golewski GL (2023) Concrete Composites Based on Quaternary Blended Cements with a Reduced Width
   625 of Initial Microcracks. Applied Sciences 13:7338
- 626 [21] Golewski GL (2023) The effect of the addition of coal fly ash (CFA) on the control of water movement within the structure of the concrete. Materials 16:5218
- Juric B, Hanzic L, Ilic R, Samec N (2006) Utilization of municipal solid waste bottom ash and recycled aggregate in concrete. Waste Management 26:1436–1442
- Fatil AR, Sathe SB (2021) Feasibility of sustainable construction materials for concrete paving blocks: A review on waste foundry sand and other materials. Materials Today: Proceedings 43:1552–1561
- [24] Yoshizawa S, Tanaka M, Shekdar AV (2004) Global Trends in Waste Generation. In: Recycling, Waste
   Treatment and Clean Technology, TMS Mineral, Metals and Materials Publishers:1541-1552.
- 634 [25] Yin K, Ahamed A, Lisak G (2018) Environmental perspectives of recycling various combustion ashes in cement production–A review. Waste Management 78:401–416
- 636 [26] Rashad AM (2018) An overview on rheology, mechanical properties and durability of high-volume slag
  637 used as a cement replacement in paste, mortar and concrete. Construction and Building Materials 187:89–
  638 117
- 639 [27] ASTM C150/C150M-22 (2022) Standard specification for portland cement. West Conshohocken, PA:
  640 ASTM International, approved July 1, 2022, Published July 2022,
  641 https://doi.org/10.1520/C0150 C0150M-22.
- 642 [28] BIS (2012) Indian Standard Drinking Water Specification (Second Revision). Bureau of Indian Standards
   643 IS 10500:1–11
- 644 [29] Bureau of Indian Standards (2003) IS 2645: 2003 Integral Waterproofing Compounds for Cement Mortar and Concrete -Specification. 16
- 646 [30] Bureau of Indian Standards (1993) IS 9103: 1999 Indian standard concrete admixtures-specifications
- 647 [31] EN BS (2005) 1052-3. BS EN 196-1: Methods of testing cement. Determination of strength. https://doi.org/10.3403/30291447U
- [32] Snehal K, Das BB, Akanksha M (2020) Early age, hydration, mechanical and microstructure properties of nano-silica blended cementitious composites. Construction and Building Materials 233:117212
- [33] Zhang J, Scherer GW (2011) Comparison of methods for arresting hydration of cement. Cement and
   Concrete Research 41:1024–1036
- [34] EN BS (1999) 1015-3. Methods of Test for Mortar for Masonry—Part 3: Determination of Consistence
   of Fresh Mortar (by Flow Table). NBN, Bureau for Standardisation: Brussels, Belgium
- [35] ASTM C403 (2005) ASTM C 403, "Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance," ASTM C 403-95, Annual Book of ASTM Standards, American Society for Testing and Materials, Pennsylvania, 1998. ASTM. 1–7. https://doi.org/10.1520/C0403
- [36] BIS (2005) Indian Standard IS: 4031 (Part 6)-1988 (Reaffirmed 2005). Methods Of Physical Tests For
   Hydraulic Cement-Part 6: Determination of compressive strength of hydraulic cement other than masonry
   cement (First Revision).

- 661 [37] EN BS (1999) 1015-10, 1999. Methods of test for mortar for masonry—Part 10: Determination of dry bulk density of hardened mortar. Br Stand[29] BS EN 1011–1015
- [38] Safiuddin M, Hearn N (2005) Comparison of ASTM saturation techniques for measuring the permeable
   porosity of concrete. Cement and Concrete Research 35:1008–1013
- 665 [39] Das BB, Singh DN, Pandey SP (2010) A comparative study for determining pore volume of concrete.
  666 Indian Concrete Journal 84:7
- [40] Bureau of Indian Standards (2018) IS 516: Part 5/Sec 1-2018 Hardened Concrete Methods of Test,
   Non-destructive Testing of Concrete, Section 1, Ultrasonic Pulse Velocity Testing, First Revision.
- 669 [41] BS 1881-122 BS (2011) Testing concrete-Method for determination of water absorption.
- [42] Singh LP, Goel A, Bhattacharyya SK, Sharma U, Mishra G (2015) Hydration studies of cementitious material using silica nanoparticles. Journal of Advanced Concrete Technology 13:345–354
- [43] Jain J, Neithalath N (2009) Analysis of calcium leaching behavior of plain and modified cement pastes in pure water. Cement and Concrete Composites 31:176–185
- [44] Singh LP, Bhattacharyya SK, Mishra G, Ahalawat S (2012) Reduction of calcium leaching in cement hydration process using nanomaterials. Materials Technology 27:233–238
- 676 [45] Singh LP, Bhattacharyya SK, Ahalawat S (2012) Preparation of size controlled silica nano particles and its functional role in cementitious system. Journal of Advanced Concrete Technology 10:345–352
- [46] Jayalath A, San Nicolas R, Sofi M, Shanks R, Ngo T, Aye L, Mendis P (2016) Properties of cementitious mortar and concrete containing micro-encapsulated phase change materials. Construction and Building Materials 120:408–417
- [47] Dinger DR, Funk JE (1997) Particle-packing phenomena and their application in materials processing.
   Mrs Bulletin 22:19–23
- 683 [48] User Guide Elkem Materials Mixture Analyser-EMMA, Version-1.
- [49] IS 13311: Part 1-1992 Method of Non-destructive testing of concrete, Part-1: Ultrasonic pulse velocity.
  Bureau of Indian Standards: 1–7
- Snehal K, Das BB (2022) Pozzolanic reactivity and drying shrinkage characteristics of optimized blended
   cementitious composites comprising of Nano-Silica particles. Construction and Building Materials
   316:125796
- 689 [51] Snehal K, Das BB (2021) Acid, alkali and chloride resistance of binary, ternary and quaternary blended
   690 cementitious mortar integrated with nano-silica particles. Cement and Concrete Composites 123:104214
- 691 [52] Patil AY, Banapurmath NR, EP S, Chitawadagi M V, Khan TMY, Badruddin IA, Kamangar S (2020)
  692 Multi-scale study on mechanical property and strength of new green sand (Poly Lactic Acid) as
  693 replacement of fine aggregate in concrete mix. Symmetry 12:1823
- Hu Q, Aboustait M, Kim T, Ley MT, Hanan JC, Bullard J, Winarski R, Rose V (2016) Direct threedimensional observation of the microstructure and chemistry of C3S hydration. Cement and concrete research 88:157–169
- 697 [54] Goudar SK, Sumukh EP, Das BB (2023) Implication of high-volume mineral admixture on mechanical
   698 properties and microstructure at steel-concrete interface. The Indian Concrete Journal 97:17-27.
- 699