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Effect of accelerators with waste material on the properties of cement paste and mortar

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Abstract. Accelerators are used to speed up the construction by accelerating the setting time which helps in early removal of formwork thus leading to faster construction rate. Admixtures are used in mortar and concrete during or after mixing to improve certain properties of material which cannot be achieved in conventional cement mortar and concrete. The various industrial by products make nuisance and are hazardous to ecosystem as well. These wastes can be used in the construction industries to reduce the consumption of cement/aggregates, cost; and save the energy and environment by utilising waste and eliminate their disposal problem as well. The effect of calcium nitrate and triethanolamine (TEA) as accelerators and marble powder (MP) as waste material on the various properties of cement paste and mortar has been studied in the present work. The replacement ratio of MP was 0-10% @ 2.5% by weight of cement. The addition of calcium nitrate was 0% and 1%; and variation of addition of TEA was 0-0.1@ 0.025% and 0.1-1.0@ 0.1% by weight of cement. On the basis of setting time, some mix proportions were selected and further investigated. Setting time and soundness of cement paste; compressive strength and microstructure of mortar mix of selected mix proportions were studied experimentally at 3, 7 and 28 days aging. Results showed that use of MP, calcium nitrate, TEA and their combination reduced setting time of cement paste for all the mixes. Addition of calcium nitrate increased the compressive strength at all curing ages while MP and TEA decreased the compressive strength. The mechanism of additives was discussed through scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis of the specimens.

Keywords: calcium nitrate; marble powder; TEA; setting time; compressive strength; SEM; EDS analysis

1. Introduction

Admixtures play an important role in the concrete industry Tang (2010). They are used to improve various properties such as acceleration or retardation of setting time and early age strength of cement paste, flowability and durability of concrete (Saridemir 2017). Accelerators increase the development of early age strength by reducing the setting time. Accelerators are used in fast track construction which requires early removal of formwork, opening to traffic and load applications to the structures. They can also be used to place the concrete where the temperature is low. With the availability of powerful accelerators, concrete can be used for underwater concreting, basement water proofing operations and repair works of the waterfront structures in the tidal zone. With proper proportions these admixtures partly compensate the retardation of strength development due to low temperatures in cold weather concreting. The general action of accelerators is rapid dissolution of cement compound especially tricalcium silicate in water and more rapid hydration of this compound (Gambhir 2013). Initial setting time decreases with increase in belite content and alkali content in cement. The reaction between C_3A and gypsum accelerate in the presence of TEA. TEA accelerates the conversion of ettringite to monosulphate by reacting with C_3A (Myrdal 2007 from SINTEF REPORT). The mechanism behind accelerating is that the increase in rate of hydration of tricalcium silicate C_3S and tricalcium aluminate C_3A increased the heat evolution in early age and also earlier strength development. It behaves as a catalyst in the hydration of C_3S and C_3A (Neville and Brooks 1997). Accelerators are of two types i.e., chloride type and non chloride type accelerators. The calcium chloride is the most commonly used accelerators in the concrete. Calcium chloride has the disadvantage of causing corrosion to steel and decrease the resistance to sulphate attack. To overcome this difficulty, some non chloride type accelerators such as nitrate, nitrite, formate, thiocynate and amines are used by Gambhir (2013). Mineral admixtures, also known as supplementary cementitious materials are also used in concrete. They reduce the cost of the concrete construction and improve fresh, hardened and durability properties of concrete. Marble powder (MP) consists of very fine particles which causes the environmental issue. Marble powder dumped in open areas, forms dust in summer which is dangerous to public health as well as agriculture. To minimise these effects it can be used in various industrial sectors like construction, agriculture, glass and paper industries (Ashish *et al*. 2016). In the present study, MP has been used in mortar with the accelerators i.e., calcium nitrate and triethanolamine to study the effect on properties of mortar.

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Ground granulated blast furnace slag (GGBS) is one of the commonly used mineral admixtures in concrete to improve the performance and quality of the concrete. Increasing laterite content in GGBS-blended-concrete showed decreasing trends in the strength parameters (Karra *et al*. 2016). Application of AP2RC and P1RB additives provided proper workability during construction and led to increased tensile, compressive and flexural strength values for the concrete (Zahrai *et al*. 2016). Maximum and optimum usage amount of marble dust as filler material was 200 kg/m^3, in order to obtain best performance for both of fresh and hardened properties of SCC (Topcu *et al.* 2009). Calcium nitrate and combination of calcium nitrate with TEA or Triisopropanol amine (TIPA) decreased setting time in comparison to control mix. Workability of self compacting concrete (SCC) improved with use of pozzolana and MP. Compressive strength of binary and ternary SCC decreased with increase in natural pozzolana and marble dust content (Belaidi *et al.* 2012). Modified TEA significantly optimized particle size distribution, improved strength of cement, had excellent dispersing and grinding effect (Zhao *et al.* 2015). TEA accelerated C_3A reaction and retarded hydration process of C_3S and these effects increased with dosage of TEA. TEA at low dosage optimized pore size distribution and at high dosage injured pore size distribution. TEA accelerated setting time; but, reduced early age strength (Han *et al.* 2015). MP up to 10% had beneficial effect; but, at larger replacement of cement by MP were detrimental to the mechanical properties (Vardhan *et al.* 2015).

In the present study MP, calcium nitrate and TEA have been used to study the effect on initial and final setting time and soundness of the cement paste, compressive strength and micro-structural analysis of mortar. Scanning electron microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) techniques have been used for micro-structural analysis of mortar.

2. Experimental programme

Ordinary portland cement of 43 grade (Fineness - 3%, soundness - 7 mm, consistency - 27.5% with initial setting time - 210 min. and final setting time - 330 min. and 3, 7 and 28 days compressive strength as 26.64 MPa, 35.9 MPa and 44.26 MPa respectively; chemical compounds of cement obtained through EDS analysis has been shown in Fig. 1 were CaO: 64.28%, SiO_2: 14.33%, Al_2O_3: 6.10%, FeO: 6.66%, MgO: 1.40%, Na_2O: 0.11% and K_2O: 2.33%) and natural coarse sand (Fineness modulus - 3.17, specific gravity - 2.62, bulk density in loose condition - 1646 kg/m^3 and in compacted condition 1824 kg/m^3) as fine aggregates have been used. Calcium nitrate tetra-hydrate purified {$Ca(N0_3).4H_20$} having minimum assay (ex. Ca) 98.0% and maximum limit of impurities for chloride 0.005%, sulphate 0.04%, magnesium 0.05% iron 0.01% and lead 0.01% has been used. Tri-ethanolamine with chemical formula $C_6H_{15}NO_3$ (minimum assay 98.0% and refractive index 1.484 - 1.488) and MP from the local sources has been used. Calcium nitrate, TEA and MP have been used in different proportions to study their effect on various

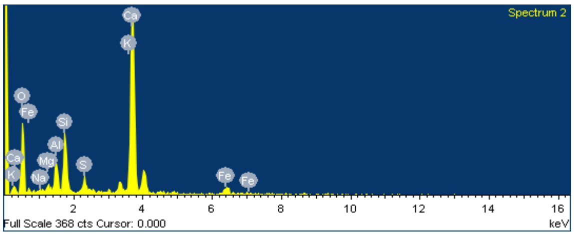


Fig. 1 Energy dispersive X-ray spectroscopy analysis of cement

properties of cement and mortar mix. Calcium nitrate and TEA have been used as accelerator. MP has been incorporated at percentage of 0%, 2.5%, 5.0%, 7.5% and 10% as partial replacement of cement. Calcium nitrate in proportion of 0% and 1% and dosages of tri-ethanolamine in proportion of 0%, 0.025%, 0.050%, 0.075%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9% and 1% by weight of cement.

Different mix proportion of cement paste i.e., 94 in number with different combination of MP, calcium nitrate and TEA (designated as M1, M2, M3,.....,M94) were prepared to study their effect on the setting time and soundness of cement. The setting time of cement paste by Vicat apparatus and soundness by Le-Chatelier was determined. On the basis of results obtained from the setting time; mixes were classified into three categories: High accelerators (HA) (initial setting time varies from 0-45 min.), Medium accelerators (MA) (initial setting time varies from 46 -90 min.) and Low accelerators (LA) (initial setting time varies from 91-145 min.). The setting time and soundness of the cement paste; and compressive strength of cement mortar cubes of size 70.6 mm×70.6 mm×70.6 mm were studied experimentally for the selected mix proportions. The specimens were water cured and tested after 3, 7 and 28 days. The samples (broken pieces of mortar cubes) were collected from the compressive strength test and then gold coating of the sample was done to make it electrical conductive before SEM and EDS analysis. Micro-structural analysis of mortar specimens was done by SEM and EDS.

3. Results and discussions

3.1 Setting time

In the present study, 94 mix proportions of the cement paste containing MP, calcium nitrate and TEA separately and their combination were studied experimentally. It has been observed from Fig. 2 that addition of CN decreased the initial setting time and final setting time by 53.33% and 41.52% respectively with respect to control mix. The addition of TEA reduced the initial and final setting time of cement paste by 94.29% to 72.38% and 95.76% to 78.79% respectively with reference to control mix. The inclusion of marble powder in cement paste decreased the setting time from 49.95% to 37.14% and 34.24% to 21.21% with reference to control mix. The combination of CN and TEA, CN+MP and MP+TEA decreased the initial and final setting

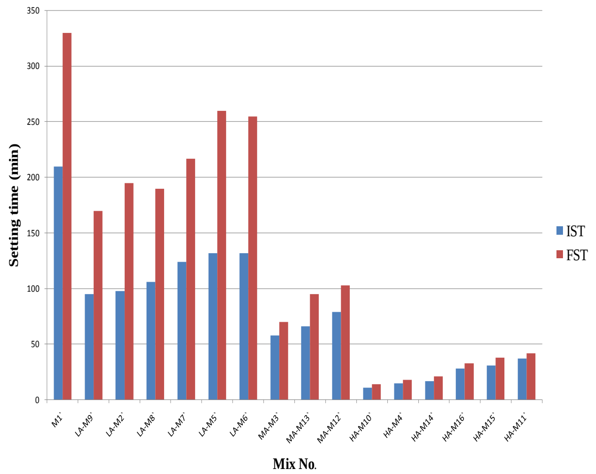


Fig. 2 Setting time of various mix proportions

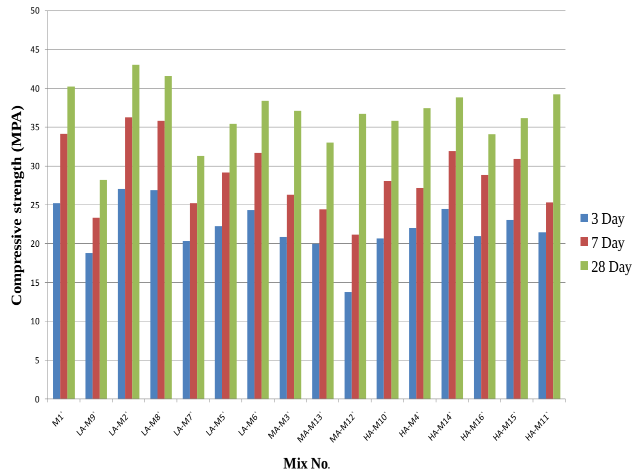


Fig. 3 Compressive strength of various mix proportions

time from 85.71% to 96.67%, 49.05% to 54.76% and 95.24% to 98.57%; and 76.36% to 96.97%, 41.52% to 48.48% and 94.55% to 98.48% respectively with reference to control mix. The reduction in initial and final setting time due to combination of CN, TEA and MP was varied from 67.62% to 93.81% and 71.21% to 97.88% respectively in comparison to control mix. CN reduced the setting time of cement paste which may be due to increase in concentration of calcium cations (Kičaitė *et al*. 2017). TEA reduced the setting time of cement paste (Ramachandran 1976)**.** Marble powder decreased the setting time of cement paste due to higher fineness of marble powder which had higher total surface area and larger area contact with water which consequently increased hydration process.

In the present study, three different categories of the accelerators i.e., high range accelerators (HA) (0-45 minutes), medium range accelerators (MA) (46-90 minutes) and low range accelerators (LA) (91-145 minutes) were defined based on initial setting time of the cement paste. These three categories of the accelerators were further subdivided into three categories high, medium and low. HA were subdivided into high (H-H) (0-15 min.), medium (H-M) (16-30 min.) and low (H-L) (31-45 min.) categories, MA was subdivided into high (M-H) (46-60 min.), medium (M-M) (61-75 min.) and low (M-L) (76-90 min.) categories, LA was subdivided into high (L-H) (91-105 min.), medium (L-M) (106-120 min.) and low (L-L) (121-145 min.) categories.

From the above classification based on setting time, 16 mix proportions were selected to study the effect of CN, TEA and MP on setting time and have been illustrated in Fig. 2

3.2 Compressive strength

The influence of CN, TEA and MP on the compressive strength of the cement mortar has been illustrated in Fig. 3. The compressive strength of the cement mortar varied from 13.79 MPa to 27.07 MPa, 21.21 MPa to 36.28 MPa and 28.23 MPa to 43.07 MPa at 3, 7 and 28 days. The compressive strength increased with the addition of calcium nitrate separately and in combination of marble powder (5%). The use of TEA and marble powder decreased the compressive strength of mortar. Increase in content of MP decreased the strength due to lack of binding of marble powder but replacement upto 7.5% strength increased beyond that it start to decrease because lesser quantity of cement was available to bind the mortar constituents and strength increased with the curing age (Rana *et al*. 2015). CN increased the compressive strength due to high content of lime as suggested by Neville (1997). TEA reduced the compressive strength at all curing ages as corresponds to (Ramachandran 1976). The compressive strength of the mortar at 3, 7 and 28 days have been shown in Fig. 3.

3.3 High accelerator

In the present study, HA were defined as those mixes for which initial setting time varied from 0 to 45 minutes. Six mix proportions (Table 1) were selected for HA category and compared with control mix. HA decreased the initial and final setting time from 82% to 95% and 87% to 95% respectively in comparison to control mix as shown in Fig. 2. The initial and final setting time decreased by 93% and 94% for HA-M4`, 95% and 96% for HA-M10`, 92% and 94% for HA-M14`, 86% and 90% for HA-M16`,82% and 87% for HA-M11`, 85% and 88% for HA-M15` respectively. Soundness of the cement paste was within the permissible limit except for mix HA-M11` as depicted in Table 1. The compressive strength decreased by 13%, 18%, 2.89%, 16.88%, 14.89% and 8.51% at 3 days; 20.46%, 17.83%, 6.47%, 15.52%, 25.79% and 9.43% at 7 days; 7.03%, 10.94%, 3.56%, 15.32%, 2.58% and 10.10% at 28 days for HA-M4`, HA-M10`, HA-M14`, HA-M16`, HA-M11` and HA-M15` respectively as shown in Fig. 3. The optimum mix proportion for compressive strength was found to be HA-M14`.

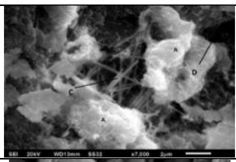
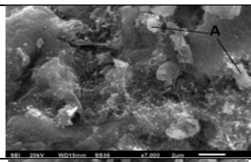
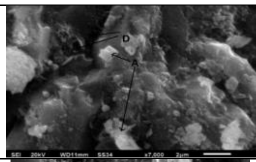
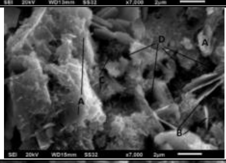
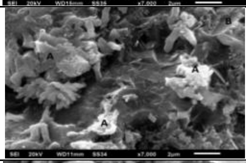
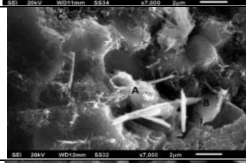
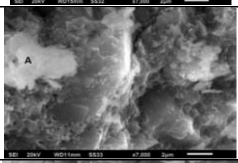
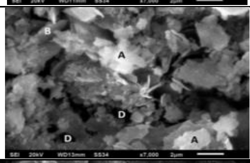
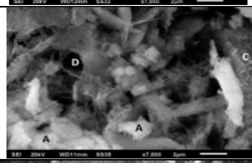
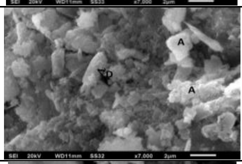
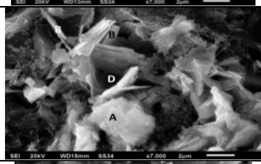
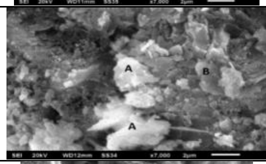
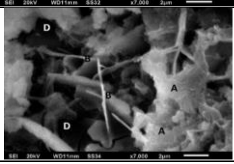
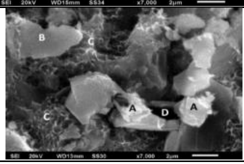
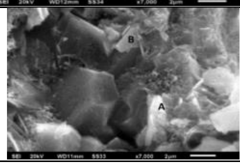
3.4 Medium accelerators

In the present study, medium accelerators are those mix, whose initial setting time varies from 46 to 90 minutes (Table 1). For this classification three mix proportions had been selected and results have been compared with M1`

Table 1 Selected mix proportions for cement paste and mortar

Accelerator type	Mix No.	Sub category of accelerators	Calcium Nitrate (%)	Marble Powder (%)	TEA (%)	Soundness (mm)
Control mix	M1`		0	0	0	7
High accelerator (0-45 min.)	HA-M10`	H-H	1	0	0.1	4
	HA-M4`		0	0	0.1	4
	HA-M14`	H-M	1	5	0.1	4
	HA-M16`		1	10	0.1	2
	HA-M15`	H-L	1	7.5	0.1	10
	HA-M11`		1	5	0.025	13
Medium accelerator (45-90 min.)	MA-M3`	M-H	0	0	0.025	11
	MA-M13`	M-M	1	10	0.025	10
	MA-M12`	M-L	1	7.5	0.025	4
Low accelerator (90-145 min.)	LA-M9`	L-H	1	10	0	8
	LA-M2`		1	0	0	5
	LA-M8`	L-M	1	5	0	12
	LA-M7`	L-L	0	10	0	9
	LA-M5`		0	5	0	5
	LA-M6`		0	7.5	0	5

Table 2 SEM images of different mix proportion at 3, 7 and 28 days

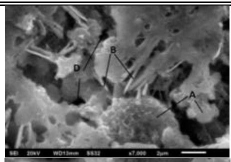
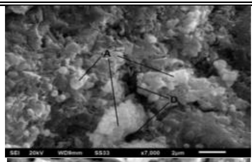
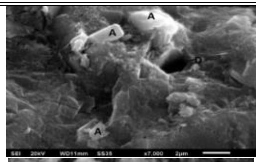
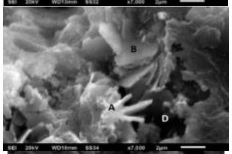
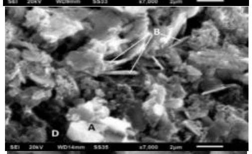
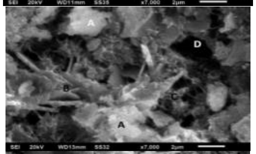
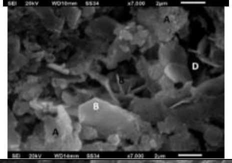
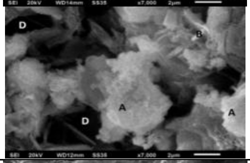
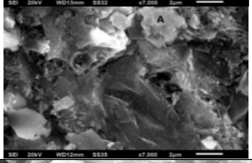
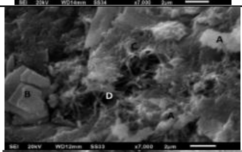
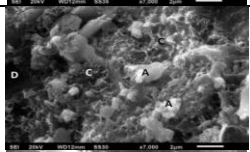
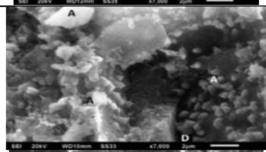
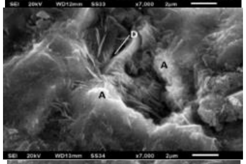
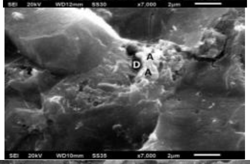
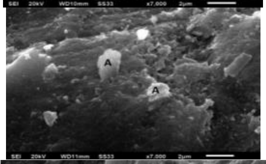
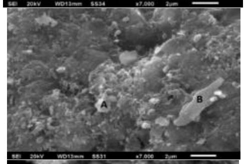
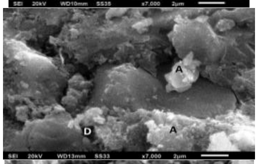
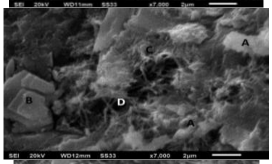
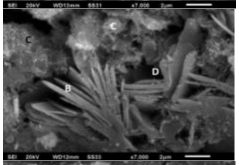
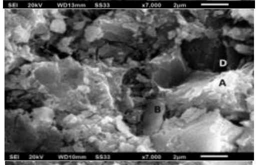
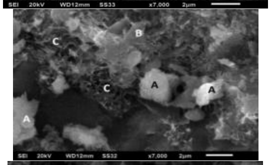
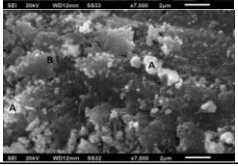
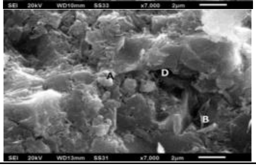
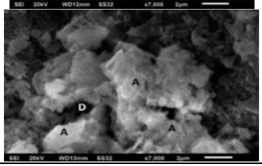
Accelerator type	Mix no.	3 days compressive strength	7 days compressive strength	28 days compressive strength
High accelerator	HA-M1`			
	HA-M10`			
	HA-M14`			
	HA-M16`			
	HA-M15`			

(control mix). Medium accelerator reduced initial setting time by 72%, 68% and 62% and final setting time by 79%, 71% and 69% for MA-M3`, MA-M13` and MA-M12` respectively as shown in Fig. 2. Soundness of the cement paste of medium accelerator was within the allowable limit except MA-3` as depicted in Table 1. The compressive strength decreased by 17.12%, 20.68% and 45.36% at 3 days; 22.83%, 28.45% and 37.91% at 7 days; 7.75%, 17.89% and 8.76% at 28 days for MA-M3`, MA-M13` and MA-M12` respectively as shown in Fig. 3. The optimum mix proportion for compressive strength was MA-M3` in case of medium accelerator.

3.5 Low accelerators

In the present study, the low accelerators were defined as those mixes, for which initial setting time varies from 91 to 145 minutes (Table 1**)**. Low accelerators reduced initial

Table 2 Continued

Medium Accelerator	MA-M3`			
	MA-M13`			
	MA-M12`			
Low Accelerators	MA-M9`			
	LA-M2`			
	LA-M8`			
	LA-M7`			
	LA-M5`			

Notation of Table 2 Scanning electron microscope images showing A-Calcium Silicate Hydrate (CSH), B-Calcium Hydroxide (CH), C-Ettringites and D-Voids

and final setting time by 37% to 54% and 21% to 48% respectively as shown in Fig. 2. Low accelerators decreased initial setting time by 53%, 55%, 50%, 37%, 37% and 41% and final setting time by 41%, 48%, 42%, 21%, 23% and 34% for LA-M2`, LA-M9`, LA-M8`, LA-M5`, LA-M6` and LA-M7` respectively. The soundness of the cement paste was within the permissible limit except LA-M8`. The compressive strength decreased by 32%, 8.5%, 2.2% and 20.3% at 3 days; 35.34%, 19.33%, 12.36% and 30.23% at 7 days; 34.8%, 18.1%, 11.23% and 27.6% at 28 days for LA-M9`, LA-M5`, LA-M6` and LA-M7` respectively. The compressive strength increased by 6.76%, 5.84% and 6.48% for LA-M2`; 6.14%, 4.69% and 3.17% at 3, 7 and 28 days for LA-M8` respectively as shown in Fig. 3. The optimum mix proportion for the compressive strength was found to be LA-M2` for low accelerator.

4. Micro-structural analysis

The micro-structural analysis of different mix proportions has been studied using SEM and EDS techniques.

4.1 Scanning electron microscopy

SEM uses a focused beam of electron to generate a variety of signal at surface of solid specimens and reveal information about external morphology, chemical composition, crystalline structure and orientation of the material. SEM plays an important role in revealing the microstructure of the concrete.

The microstructure of the concrete has the hydrated cement paste, interfacial transition zone and aggregates

Table 3 Values of Ca/Si ratio, (Al+Fe)/Ca ratio and S/Ca ratio

Sr. No.	Hydration product	Ca/Si	(Al + Fe)/Ca	S/Ca
1	CSH	0.8-2.5	$\leqslant$ 0.2	-
2	CH	$\geqslant$10	$\leqslant$ 0.04	$\leqslant$ 0.04
3	AFm	$\geqslant$4.0	> 0.4	> 0.15

phase. The strength of the concrete depends on its microstructure. The factors on which the microstructure of the concrete depends are the type of cement, admixtures, water cement ratio and duration of hydration. In the present study, SEM images of various mix proportions of mortar mix with the use of MP, calcium nitrate and TEA and their combination have been shown in Table 3. The broken sample of mortar cubes were collected from the compressive strength test and golden plating was done before mounting the sample in the SEM stub.

From Table 2, it can be concluded that HA-M10` mix has the hexagonal shape, CH present in larger amount in comparison to M1` at all curing periods which lead to decrease in compressive strength. HA-M14` was dense and showed a high content of CSH gel at 3 days curing and few voids were also presented at 7 and 28 days. CSH gel can be seen spread over the mix and this mix shows the minimum reduction in the compressive strength. In HA-M16`, fewer voids were present at 3 and 28 days curing; but, at 7 days the images showed both CH and voids in the large amount. In case of HA-M15`, the formation of ettringite can be seen along with CSH, CH and voids. In case of medium accelerator, MA-M3` showed the presence of CH along with CSH and voids at 3, 7 and 28 days. Due to the presence of CSH, reduction in the compressive strength is less in comparison to other mix proportion of medium accelerator type. From the image of MA-M13`, it can be seen that the hexagonal shape of CH present with CSH and voids shows the formation of ettringites. Mix MA-M12` consists of large voids at 7 days and also developed the hydration product like CSH, CH with voids at 3 and 28 days. The CSH was spread over the images in case of mix LA-M2` and had higher strength due to dense and compact microstructure in comparison to control mix. Presence of ettringite could be seen with other hydration product formation in LA-M9`. In case of LA-M8`, CSH gel was present and at 28 days the ettringite was also formed. CSH gel and few voids were present in LA-M5`. The hydration product such as CSH and CH and ettringite formed with the development of hydration process for LA-M7`.

4.2 Energy Dispersive X-ray Spectroscopy (EDS)

EDS is an analytical technique that can be coupled with SEM. EDS analysis is used to determine the elemental composition of the individual points or to map out the lateral distribution of elements from the imaged area. EDS spectrum portrays the plot between the *X*-rays and energy. The energy peaks corresponds to various elements present in the sample. To evaluate the hydrate phase of CSH, CH and AFm, the following criteria shown in Table 3, has been used which was reported by (Mohammed *et al.* 2013). In the present study, taking into consideration the atomic

Table 4 Ca/Si ratio, (Al+Fe)/Ca ratio and S/Ca ratio for different mix proportions

Accelerator type	Mix No.	Ca/Si			(Al+Fe)/Ca			S/Ca			Hydration product formation
		3 Days	7 Days	28 Days	3 Days	7 Days	28 Days	3 Days	7 Days	28 Days	
High Accelerator	M1`	1.1068 (CSH)	0.0206	0.5726	0.1807 (CSH)	7.4560 (AFm)	-	-	-	-	CSH+AFm
	HA-M10`	1.8716 (CSH)	0.02647	0.47805	0.2427 (CSH)	9.1476 (AFm)	-	-	-	-	CSH+AFm
	HA-M14`	1.4328 (CSH)	2.3539 (CSH)	1.5163 (CSH)	1.4034 (AFm)	0.4035 (AFm)	0.2720 (CSH)	0.02372 (CH)	-	-	CSH+CH+AFm
	HA-M16`	1.3082 (CSH)	2.1533 (CSH)	2.3672 (CSH)	0.4483 (AFm)	0.5566 (AFm)	0.2222 (CSH)	-	0.03954 (CH)	-	CSH+CH+AFm
	HA-M15`	2.4503 (CSH)	0.2803	1.4078 (CSH)	0.2026 (CSH)	2.5287 (AFm)	0.1764 (CSH)	-	-	-	CSH+AFm
Medium Accelerator	M1`	1.1068 (CSH)	0.0206	0.5726	0.1807 (CSH)	7.4560 (AFm)	-	-	-	-	CSH+AFm
	MA-M3`	1.1400 (CSH)	0.5036	1.4675 (CSH)	0.2863 (CSH)	1.6970 (AFm)	0.06845 (CH)	-	-	-	CSH+CH+AFm
	MA-M13	1.3928 (CSH)	1.01480 (CSH)	0.6616	0.5058 (AFm)	0.4915 (AFm)	0.7337 (AFm)	0.0571 (CH)	0.0853 (CH)	-	CSH+CH+AFm
	MA-M12`	0.9978 (CSH)	0.80575 (CSH)	2.0570 (CSH)	0.5818 (AFm)	0.6805 (AFm)	0.1892 (CSH)	-	-	-	CSH+AFm
Low accelerator	M1`	1.1068 (CSH)	0.0206	0.5726	0.1807 (CSH)	7.4560 (AFm)	-	-	-	-	CSH+AFm
	LA-M2`	1.7876 (CSH)	1.9204 (CSH)	0.0537	0.1091 (CSH)	0.2188 (CSH)	9.6773 (AFm)	-	-	0.03975 (CH)	CSH+CH+AFm
	LA-M9`	1.6461 (CSH)	1.62070 (CSH)	1.0084 (CSH)	0.1741 (CSH)	0.2527 (CSH)	0.2485 (CSH)	0.0509 (CH)	0.0385 (CH)	0.03906 (CH)	CSH+CH+AFm
	LA-M8`	0.03502	0.02647	0.47805	4.6757 (AFm)	9.1476 (AFm)	-	-	-	-	AFm
	LA-M5`	1.4627 (CSH)	1.4009 (CSH)	0.09656	0.4461 (AFm)	0.4456 (AFm)	4.9246 (AFm)	0.1200 (AFm)	0.0645 (CH)	-	CSH+CH+AFm
	LA-M7`	4.3406	1.5038 (CSH)	0.3574	0.5619 (AFm)	0.4583 (AFm)	2.2654 (AFm)	0.03693 (CH)	-	-	CSH+CH+AFm

weight, percentage values of Ca, Si, Al, Fe and S were computed and it was observed that the values of Ca/Si ratio, (Al+Fe)/Ca ratio and S/Ca ratio varies from 0.0154 to 8.4001, 0.06845 to 9.6773 and 0.00199 to 0.1200.

The values of Ca/Si ratio, (Al+Fe)/Ca ratio and S/Ca ratio from the EDS results at 3, 7 and 28 days curing have been shown in Table 4. From Table 4 it can be concluded that in all the mix proportions, CSH formed during all the curing days. In most of the mix proportions, the CSH gel formed during the hydration process except LA-M8 at 3 days; M1`, MA-M3`, LA-M8`, HA-M10`, HA-M15` at 7 days and LA-M2`, LA-M5`, LA-M7` at 28 days and these mix proportions formed AFm in the hydration process with CSH. CH formed the mix proportions of LA-M7`, MA-M13`, HA-M14` at 3 days; LA-M5`, MA-M13`, HA-M16` at 7 days and MA-M3` at 28 days along with CSH and AFm. In LA-M2`, there was a majority of CSH and that`s why the compressive strength was higher than control mix and it can also be seen from SEM images. In case of high accelerator mix HA-M14`, there was CSH along with CH and AFm (from SEM images and EDS) and therefore compressive strength decreased; but, reduction was less as compared to other mix proportions.

5. Conclusions

The effect of addition of calcium nitrate and triethanolamine and partial replacement of cement by marble powder in the cement paste and mortar mix was studied. The following points have been concluded from the study.

• The initial and final setting time of the cement paste reduced with the addition of the calcium nitrate and TEA in comparison to control mix. The cement replaced with MP also showed decrease in setting time as compared to the control mix. Combination of these admixtures accelerated setting time.
High accelerators decreased the initial and final setting time by 82% to 95%, 87% to 95% and also reduced compressive strength of mortar by 24%, 20%, 21% for mix HA-M16` and 7%, 11%, 10% at 3, 7 and 28 days for mix HA-M14`.

• Medium accelerators reduced initial and final setting time by 62% to 72% and from 69% to 79% and low accelerators by 37% to 54% and 21% to 48 % respectively.

• The compressive strength decreased by 2.89%-18% at 3 days, 6.47%-25.79% at 7 days and 2.58%-15.32% at 28 days for high accelerator mix proportions respectively.

• The compressive strength decreased by 17.12%-45.36% at 3 days, 22.83%-37.91% at 7 days and 7.75%-17.89% at 28 days for medium accelerator mix. The compressive strength decreased by 2.2-32% at 3 days, 12.36-35.34% at 7 days and 11.23%-34.8% at 28 days for low accelerator mix proportions.

• The compressive strength increased by 6.76%, 5.84% and 6.48% for LA-M2` and 6.14%, 4.69% and 3.17% at 3, 7 and 28 days for LA-M8` respectively.

• From the analysis of results obtained from the samples of different mix proportions it can be concluded that the optimum mix proportions for the compressive strength was HA-M14`, MA-M3` and LA-M2` for high, medium and low accelerator respectively. LA-M2` and LA-M8` increased the compressive strength of the mortar mix. Both initial and final setting time decreased in all the mix proportions.

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