Effect of salts (Na_2SO_4 and $CaCO_3$) in water on properties of natural admixture cements

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ABSTRACT

Water has an important role on application of concrete. This paper presents the experimental results of the effect of neutral salts (Na_2SO_4 and $CaCO_3$) as mixing water on setting times, and compressive strength of admixture cements. In the research PPC plus 10% silica fume was added by weight and cubes were casted with deionised water and deionised water containing neutral salts Na_2SO_4 and $CaCO_3$. The result shows the Na_2SO_4 and $CaCO_3$in deionised water retard the initial as well as final setting processes them at all concentrations. Na_2SO_4 and $CaCO_3$ in deionised water increase the compressive strength of mortar cubes significantly in the early days, i.e., at 3 day, 7 day, 21 day, 28 day,60 day and 90 day age, and decreased in compressive strength in longer periods to higher concentrations except $CaCO_3$. In the present work analysis the hydration characteristics of the admixture cements using the techniques of X-ray diffraction analysis and useful conclusions are obtained regarding the influence of neutral salts.

Key words: PPC, Silica fume, strength development, X-ray diffraction

The presence of neutral salts in water changes the properties of concrete in setting times as well as strength. Water is an essential ingredient of concrete as it effectively participates in the chemical reactions with natural admixture cements like natural pozzolana and other supplementary cementitious materials (Silica fume). The use of pozzolanic materials has gained significant in the wake of the substantial emphasis on the conversion of industrial waste into potential with a waste to wealth are refuse to resource approach. The I.S.Code 456-2000 also specifies the minimum pH-value as 6.0 and also permissible limits for solids in the water to fit for construction purposes. The code has not specified the limits to the individual components like acidic substances. The use of natural and economical materials seems to be one of the possible solutions for the future. The development of an economical cement concrete with interesting properties in the fresh and hardened state will certainly help and encourage the use of this material in the construction industry. Hence, in the present investigation to find the effects and quality of water on setting and strength properties of admixture cement. The effect of neutral salts on setting, hardening and strength development of admixture cement are not known much. Hence, an investigation is carried out on setting time, soundness and strength of admixture cements and the powdered x-ray diffraction techniques.

Materials and Methods

Materials : The details of various materials used in the experimental investigation are presented below.

Cement : The cement used in the present investigation is of 43 grade Pozzolana Portland Cement manufactured by ACC Ltd.

Fine aggregate : The fine aggregate used in this investigation is the river sand obtained from Swarnamukhi river near Tirupati, Chittoor district in Andhra Pradesh.

Silica fume : Silica fume used in the present study was obtained from Elkem India Pvt.Ltd.,Mumbai.

Water : Deionised water spiked with neutral salts (Na_2SO_4 and $CaCO_3$) with different concentration is used in mixing water.

Experimental System : The following equipment is used for casting and testing of specimens: (i)Cube moulds, (ii) 200T U.T.M(Universal Testing Machine) for cube compressive strength determination, (iii)Vicat's apparatus including moulds conforming to IS4031(part-5) - 1988 for setting times, (iv)Le-Chatelier's equipment to determine the soundness of cement and (v) cement cubes prepared with water containing, Na_2SO_4 in the concentration of 1,2,4,10 and 20g/L and $CaCO_3$ in the concentration of 0.05,0.1,0.2g/L in mixing water.

Setting time : Vicat's apparatus confirming IS4031(part-5) 1988 consist of a frame to which a movable rod having an indicator is attached which gives the penetration, weighing 100g and having diameter and length of 10mm and 50mm respectively. Vicat's apparatus included three attachments-square needle for intial setting time, plunger for determining normal consistency and needle with annular collar for final setting time.

Compressive Strength : The test specimens for determination of compressive strength of admixture cement prepared using standard metallic cube moulds adopting IS procedure for the compactions. The cubes were demoulded after 24hours of casting and cured in water having similar quality as used in preparation of mix. The cubes are tested for compressive strength for short term and long term. The compressive strength is computed as the average value of the three samples.

Results and Discussion : The results of the present investigation are presented both in tabular and graphical forms. In order to facilitate the analysis, interpretation of the results is carried out at each phase of the experimental work. This interpretation of the results obtained is based on the current knowledge available in the literature as well as on the nature of result obtained. The significance of the result is assessed with reference to the standards specified by the relevant I S codes;

1. The averages of both the initial and final setting times of three cement samples prepared with mixing water containing typical chemical or biological component of varying concentrations under consideration is compared with those of the cement specimens prepared with deionised water. If the difference is less than 30 minutes, the change is considered to be negligible or insignificant and if it is more than 30 minutes, the change is considered to be significant.

2. The average compressive strength of at least three cubes prepared with water under consideration is compared with that of three similar cubes prepared with deionised water. If the difference in the strength is less than 10%, it is considered to be insignificant and if it is greater than 10%, it is considered to be significant.

SETTING TIME

Sodium Sulphate (Na_2SO_4): The effect of Na_2SO_4 on initial and final setting times is shown in the Fig 3. Both initial and final setting times got retarded with an increase of sodium sulphate content in the deionised water. The retardation for initial and final setting times is significant (i.e., more than 30 minutes), when the sodium sulphate concentration exceeds 4 g/L, the initial setting time is about 190 minutes and final setting time about 312 minutes, which are respectively 62 and 35 minutes more than that of deionised mixing water Fig 3.

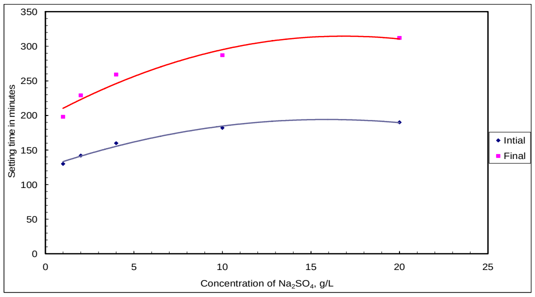


Fig.3. *Variation of Setting times of admixture cement (PPC + 10% Silica fume) corresponding to various concentrations of Na_2SO_4 in deionised water.*

Calcium Carbonate ($CaCO_3$)

The effect of $CaCO_3$ on initial and final setting times is shown in the Fig 4. Both, initial and final setting got retarded with an increase of calcium carbonate concentration in deionised water. Notably, there is a significant change in the initial setting time at the maximum concentration, 0.2 g/L, and in the intial setting time and the time is 160min i.e., 32 min greater than that of control mix. The final setting time is about 328 minutes, which is 19 minutes less than that of the control mix.

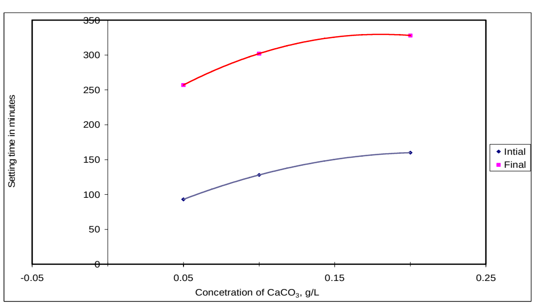


Fig.4. *Variation of Setting times of admixture cement (PPC + 10% Silica fume) corresponding to various concentrations of $CaCo_3$ in deionised water.*

COMPRESSIVE STRENGTH

The effect of Na_2SO_4 concentration on compressive strength of cement mortar is presented in Fig.5. As the concentration of Na_2SO_4 increases, the compressive strength of the cement mortar cubes decreases even up to 20 g/L.

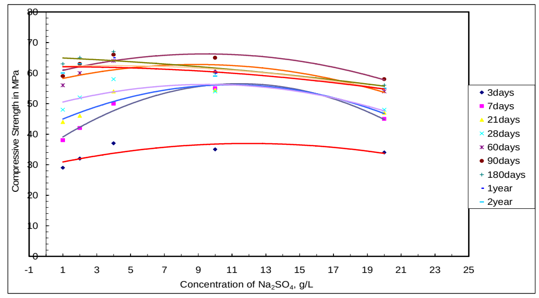


Fig.5. *Variation of compressive strength of admixture cement (PPC + 10% Silica fume) mortar cubes at different ages corresponding to various concentrations of $Na_2\,So_4$ in deionised water.*

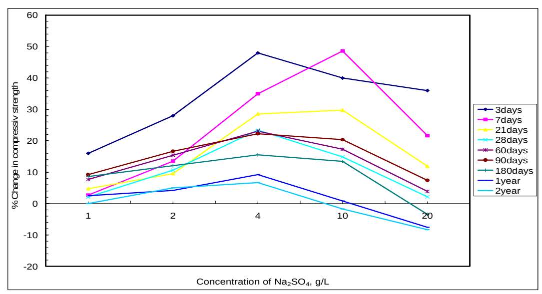


Fig.6. *Shows the Percent variation of compressive strength of admixture cement (PPC cement + 10% Silica fume) mortar cubes at different ages corresponding to various concentrations of Na_2So_4 in deionised water.*

The percent change in compressive strength of mortar cubes prepared with various concentrations of Na_2SO_4 solution in deionised water is shown in Fig 6. Significant increase in early days and gradually decreases the compressive strengths of cement mortar cubes of all concentrations, and the rate of decrease also gradually increases with an increase in the concentration of the Na_2SO_4. The 2 year sample showed the nominal decrease in compressive strength with an increasing in concentrations of Na_2SO_4 tested. When the concentration is 20 g/L, the decrease in compressive strength is as much as 8.33% when compared with that of control mix.

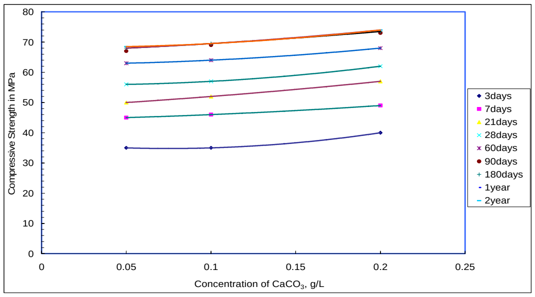


Fig.7. *Variation of compressive strength of admixture cement (PPC + 10% Silica fume) mortar cubes at different ages corresponding to various concentrations of $CaCo_3$ in deionised water.*

The effect of $CaCo_3$ concentration on the compressive strength of cement mortar is presented in the Fig .7. Increase in compressive strength of the cement mortar cubes prepared with $CaCO_3$ solution is observed as the calcium carbonate concentration increases, whereas there is practically significant change in compressive strength for 3-day sample at any concentration. The maximum concentration considered for experimentation is 0.2 g/L.

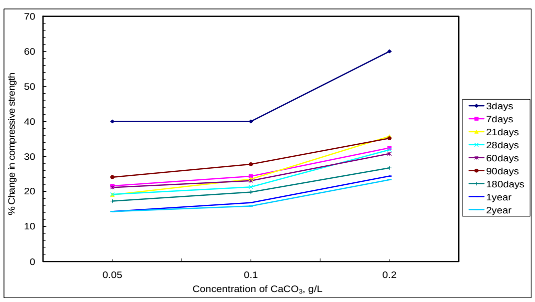
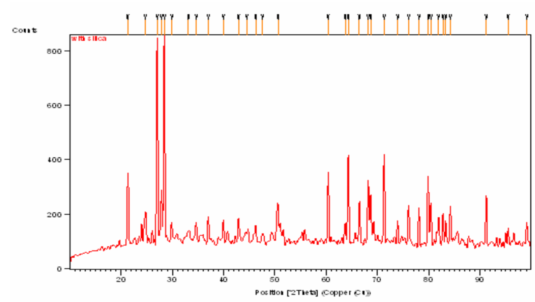


Fig.8. *Percent variation of compressive strength of admixture cement (PPC cement + 10% Silica fume) mortar cubes at different ages corresponding to various concentrations of $CaCo_3$ in deionised water.*

The percent change in the compressive strength of mortar cubes prepared with various concentrations of $CaCO_3$ solution in deionised water is shown in Fig .8. The effect of $CaCO_3$ in the water at any concentration (up to 0.2g/L) is significant on long-term basis, which is evident from the 2 year sample.

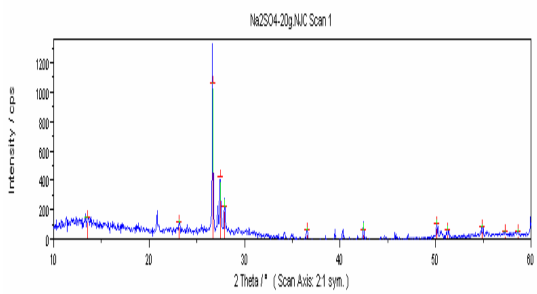
X-RAY DIFFRACTION



Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel.Int. [%]
21.2999	284.22	0.2854	4.1681	34.84
24.6774	108.28	0.4955	3.60474	13.27
27.044	808.37	0.2522	3.29443	99.08
27.8776	207.59	0.2099	3.19779	25.45
28.4259	815.83	0.2414	3.13734	100
29.8629	61.46	0.017	2.98956	7.53
33.171	21.87	1.773	2.69859	2.68
34.6229	69.14	0.3235	2.58867	8.48
36.999	95.41	0.3082	2.42769	11.69
39.9368	86.14	0.2457	2.25562	10.56
42.9052	94.01	0.2153	2.10619	11.52
44.5205	26.66	1.9653	2.03345	3.27
46.209	62.09	0.3433	1.963	7.61
47.5966	1.82	0.0013	1.90896	0.22
50.5851	112.53	0.5774	1.80296	13.79
60.3873	271.37	0.2481	1.53164	33.26
63.6841	71.39	0.2107	1.46006	8.75
64.2899	349.65	0.2524	1.44776	42.86
66.4734	167.42	0.2302	1.4054	20.52
68.16	278.63	0.1668	1.37467	34.15
68.6174	127.28	0.8095	1.36662	15.6
71.3241	356.41	0.2348	1.32126	43.69
73.9238	51.08	0.6812	1.28109	6.26
76.0972	158.41	0.2823	1.24982	19.42
78.0615	135.48	0.2351	1.22321	16.61
79.882	266.63	0.2495	1.19985	32.68
80.4209	154.97	0.2624	1.19316	18.99

81.8855	95.91	0.3066	1.17548	11.76
82.7426	103.41	0.2265	1.16547	12.68
83.3019	89.55	0.202	1.15906	10.98
84.2383	135.62	0.2587	1.14854	16.62
91.1915	195.95	0.2402	1.07822	24.02
95.4305	30.71	0.952	1.04121	3.76
99.0816	87.25	0.2877	1.0124	10.69

Fig.9. *X-ray diffraction pattern of powdered admixture cement (PPC +10% silica fume) mortar cube prepared with deionised water.*



No	d_Fit (A1)	Ang-parab	Ang-COG	Low Limit	Upp. Limit	I-net	I-bgr	FW HM	2-Theta
1	6.5	14	14	10	21	149	245	3	14
2	3.8	23	23	21	26	112	43	0.5	23
3	3.3	27	27	26	27	1058	30	0.1	27
4	3.2	27	27	27	28	424	32	0.2	27
5	3.2	28	28	28	29	222	33	0.2	28
6	2.5	37	37	36	37	61.8	56	0.1	37
7	2.1	42	42	42	43	68.2	52	0.1	42
8	1.8	50	50	50	50	106	31	0.1	50
9	1.8	51	51	51	51	63.1	27	0.4	51
10	1.7	55	55	55	55	82.8	13	0.2	55
11	1.6	57	57	55	58	48.2	2.7	0.8	57
12	1.6	59	59	57	60	49.1	0	0.6	59

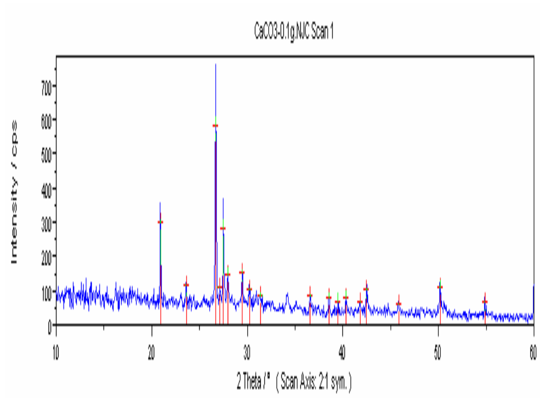
Fig. 10. *Powder X-Ray Diffraction pattern for the cement mortar cubes prepared with Na_2SO_4 (20g/L) in deionised water.*

Powder X-Ray Diffraction pattern for the admixture cement (PPC cement + 10% Silica fume) mortar cubes prepared with Na_2SO_4 (20g/L) in deionised water shown in fig.5.14. The comparison of the present pattern with that of deionised water indicates the formation of $Ca_6\ Al_2\ (OH)_{12}\ (SO_4)_3\ 26H_2O)$ (Ettringite) compound which is evident by the presence of d-spacing's 3.342, 3.246 Å and 2.456 Å in fig 10, which are absent in the Fig 9.

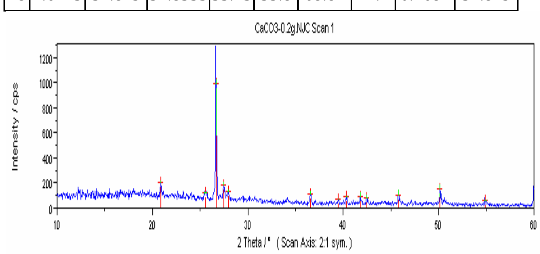
The probable chemical reaction upon the hydration of cement with mixing water containing Na_2SO_4 is

$$6CaO + 2Al(OH)_3 + 3\ Na_2SO_4 + 32H_2O \rightarrow Ca_6Al_2(OH)_{12}(SO_4)_3 26H_2O + 6NaOH$$

One of the reasons for the retardation of initial and final setting of cement is attributed to the formation of ettringite. Continuous decrease in compressive strength for samples of all ages and significant decrease form 21-day sample onwards is due to the formation of ettringite. Calcium hydroxide and alumina-bearing phases of hydrated Portland cement are more vulnerable to the attack of sulphate ions. The water-possessing sulphate ions penetrate into the hardened cement paste and damage the cement mortar due to the formation of voluminous water-rich calcium sulpho-aluminates. It is evident that sulphate-related expansions in concrete are associated with ettringite. This is due to the exertion of pressure generated by growing ettringite crystals and swelling due to adsorption of water in alkaline environment. The deterioration in the cohesiveness of the cement hydration products is caused by the sulphate attack leading to a progressive loss of strength and loss of mass.



No	d_Fit (A1)	Ang-parab	Ang-COG	Low Limit	Upp. Limit	I-net	I-bgr	FWHM	2-Theta
1	4.2456	20.9066	20.9043	19.75	23.25	301.79	60.48	0.1316	20.9066
2	3.7671	23.598	23.6211	23.15	24.35	114.84	32.32	0.3157	23.598
3	3.3366	26.6956	26.7068	26.3	26.9	580.3	21.8	0.1304	26.6956
4	3.2818	27.15	27.1363	26.85	27.35	111.56	20.73	1.0105	27.15
5	3.2405	27.503	27.5059	27.25	27.85	279.81	19.92	0.1695	27.503
6	3.1881	27.964	27.9696	27.65	29.35	149.66	18.93	0.3461	27.964
7	3.0265	29.4896	29.481	28.1	30.1	150.69	15.81	0.2383	29.4896
8	2.9525	30.2461	30.2208	29.6	31.25	102.24	14.56	0.4892	30.2461
9	2.8526	31.3323	31.3436	30.35	35.05	88.07	12.7	0.6263	31.3323
10	2.4555	36.5644	36.5751	34.4	38.15	83.02	7.09	0.3953	36.5644
11	2.333	38.5588	38.5469	38.25	39.4	79.75	6.02	0.2486	38.5588
12	2.2793	39.5051	39.5055	38.7	40.25	69.11	5.69	0.3327	39.5051
13	2.2334	40.3507	40.3388	39.6	41.75	80.23	5.49	0.2586	40.3507
14	2.1587	41.8111	41.8016	40.45	42.35	66.51	5.33	0.9173	41.8111
15	2.1249	42.5098	42.4904	41.85	45.75	102.22	5.34	0.2655	42.5098
16	1.9777	45.8456	45.8332	44.8	49.5	59.39	5.98	1.3435	45.8456
17	1.8161	50.1943	50.1877	49.8	50.95	108.35	8.03	0.3091	50.1943
18	1.6725	54.849	54.8553	53.45	55.8	68.82	11.1	0.1684	54.849



No	d_Fit (A1)	Ang-parab	Ang-COG	Low Limit	Upp. Limit	I-net	I-bgr	FWHM	2-Theta
1	4.2497	20.8861	20.8792	10.1000	23.1500	201.20	33.82	0.4327	20.8861
2	3.4847	25.5413	25.5717	24.3500	26.3500	121.70	14.17	8.4023	25.5413
3	3.3409	26.6605	26.6581	26.3000	26.8500	993.56	17.30	0.1310	26.6605
4	3.2422	27.4881	27.4846	26.8500	27.8500	182.55	19.78	0.2819	27.4881
5	3.1913	27.9350	27.9368	27.6000	34.7000	137.81	20.90	0.3841	27.9350
6	2.4555	36.5653	36.5471	36.1500	36.8500	112.98	14.84	0.2314	36.5653
7	2.2795	39.5013	39.4897	36.7500	40.2000	70.74	9.41	0.4462	39.5013
8	2.2342	40.3361	40.3461	39.6000	41.7000	90.72	8.32	0.2630	40.3361
9	2.1587	41.8108	41.8065	40.5000	42.3500	93.24	6.97	0.2970	41.8108
10	2.1252	42.5029	42.4903	41.9500	45.7000	79.31	6.54	0.2687	42.5029
11	1.9790	45.8131	45.8068	45.0500	46.4500	100.65	6.06	0.2467	45.8131
12	1.8175	50.1527	50.1547	49.8500	51.0500	148.78	8.23	0.1756	50.1527
13	1.6721	54.8616	54.8574	54.1000	55.5500	64.45	11.91	0.1424	54.8616

Fig.11. *Powder X-ray Diffraction pattern for the cement mortar cubes prepared with $CaCO_3$ (0.10g/L and 0.20g/L) in deionised water*

The Powder X-ray Diffraction pattern for the cement mortar cubes prepared with $CaCO_3$ (0.10g/L and 0.20g/L) in deionised water is shown in fig.11. The comparison of the present pattern with that of deionised water indicates the formation of Ca_5 (Si_6 O_{18} H_2) $4H_2O$ (11-Å Tobermorite) compound, which is evident from the presence of d-spacing's 1.979Å, 1.672 Å which are absent in Fig 5.1. and 5.2. And due to the presence of hydrated silicates , which is evident from the presence of d-spacing's 2.455Å, 2.279 Å , which are absent in control mix.

The possible chemical reaction upon the hydration of cement with mixing water containing $CaCO_3$ is

$$4CaO + 6\ SiO_2 + 6H_2O + CaCO_3 \rightarrow Ca_5(Si_6O_{18}H_2)4H_2O + H_2CO_3$$

One of the reasons for the retardation of the setting of cement could be the formation of Tobermorite gel and weak acid like carbonic acid. But surprisingly the increase in compressive strength at early age and gradually decreases to a significant level i.e. 23.33% at0.2g/L for longer periods(2years). Calcium hydroxide and silica-bearing phases of hydrated Portland cement are only slightly vulnerable to attack by carbonate ions.

Effect of Neutral Salts:

The neutral salts that are generally present in water are Na_2SO_4 and $CaCO_3$. The effect of each of these neutral salts at various concentrations in deionised water on the initial and final setting times of cement and on the compressive strength of cement mortar cubes has been already discussed in the above subsections. The behavior of neutral salts is elucidated in a comprehensive manner as follows: Na_2SO_4 and $CaCO_3$ in deionised water the retard initial as well as final setting processes at all concentrations.

Na_2SO_4 and $CaCO_3$ in deionised water increase the compressive strength of mortar cubes significantly in the early days, i.e., at 3 day, 7 day, 21 day, 28 day,60 day and 90 day age, and decreased in compressive strength in longer periods to higher concentrations except $CaCO_3$

The prominent effect of $CaCO_3$ on the compressive strength of mortar cubes slowly decreases as time advances and the total effect during the longer period's decreases and on very long periods, i.e., 2-year age the increase in compressive strength becomes insignificant. In the case of the other salt Na_2SO_4, the trend in the variation of the compressive strength is exactly opposite. As time elapses, i.e., at 180-day,1 year and 2 year, the decrease in the compressive strength is observed in the case of Na_2SO_4.

By comparing all these two neutral category salts, it is evident that $CaCO_3$ affect the compressive strength only positively, whereas, Na_2SO_4 affect it negatively and their negative effect goes on increasing with age. The salt, Na_2SO_4 is the more dangerous one; hence a lot of care should be taken if it exists in the mixing water and its concentration should not be more than 7.5 g/L.

CONCLUSIONS

1. Presence of Na_2SO_4 and $CaCO_3$ in deionised water the retard initial as well as final setting processes at all concentrations.

2. Presence of $CaCO_3$ on the compressive strength of mortar cubes slowly decreases as time advances and the total effect during the longer period's decreases and on very long periods, i.e., 2-year age the increase in compressive strength becomes insignificant.

3. Presence of Na_2SO_4, in water the trend in the variation of the compressive strength is exactly opposite. As time elapses, i.e., at 180-day,1 year and 2 year, the decrease in the compressive strength is observed in the case of Na_2SO_4.

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