Influence of neutral salts (NaCl and KCl) in water on properties of natural admixture cements

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ABSTRACT

The study is aimed at investigating the effect of neutral salts 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 NaCl and KCl. The result shows the NaCl in deionised water accelerates the initial as well as final setting processes whereas the other salt KCl retard them at all concentrations. NaCl and KCl 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 KCl. 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 deterioration of cement structures due to 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 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 (NaCl and KCl) 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, NaCl in the concentration of 1,2,4,10 and 20g/L, and KCl in the concentration of 0.05,1,3 and 5g/L.

Setting time : Vicat's apparatus confirm-ing 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 speci-mens 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 24 hours 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 Chloride (NaCl): The effect of NaCl on initial and final setting times are shown in Fig 1.From the figure; it is observed that both initial setting and final setting got accelerated with the increase in concentration of NaCl in deionised water. Initial setting and final setting time at1, 2, 4 and above 10 g/L of concentration of test blocks, differed significantly when compared with the experimental results obtained with deionised water. When the concentration of NaCl is 20 g/L (maximum), the differences in initial and final setting times are 80 minutes and 141 minutes respectively when compared with those of the control mix.

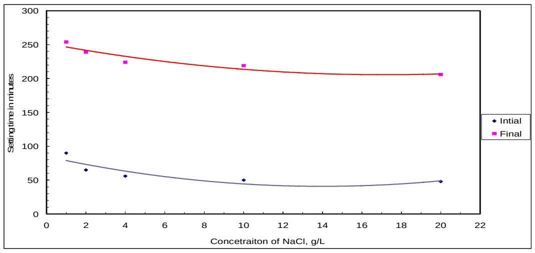


Fig.1. *Variation of Setting times of (PPC + 10% Silica fume) corresponding to various concentrations of NaCl in deionised water.*

Potassium Chloride (KCl): The effect of KCl on initial and final setting times is shown in Fig 2. both initial and final setting times got retarded with an increase in potassium chloride concentration in deionised water. Notably, there was no significant change in the initial setting time at all concentrations except 0.5 g/L. There is no significant change in final setting time at all concentrations except 0.5 g/L. The final setting time is about 349 minutes when potassium chloride content is 5 g/L, which is 2 minutes more than that of control water sample shown in the Fig 2.

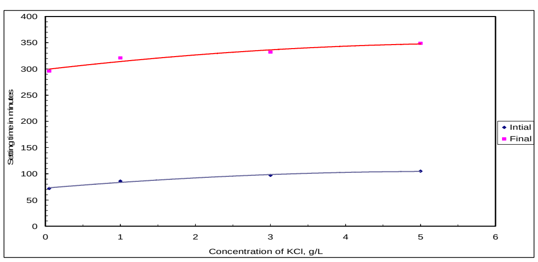


Fig.2. *Variation of Setting times of admixture cement (PPC + 10% Silica fume) corresponding to various concentrations of KCl in deionised water.*

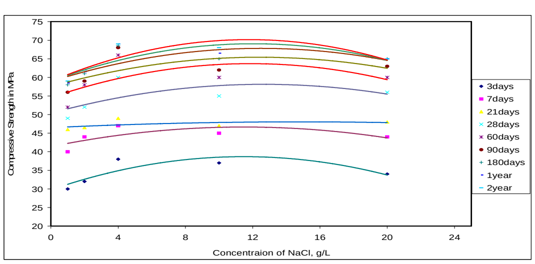


Fig.3 *Variation of compressive strength of admixture cement (PPC + 10% Silica fume) mortar cubes at different ages corresponding to various concentrations of NaCl in deionised water.*

The effect of NaCl concentration on the compressive strength of cement mortar is presented in Fig 3. The results indicate that there is an early gain in compressive strength of the cement mortar irrespective of NaCl concentration.

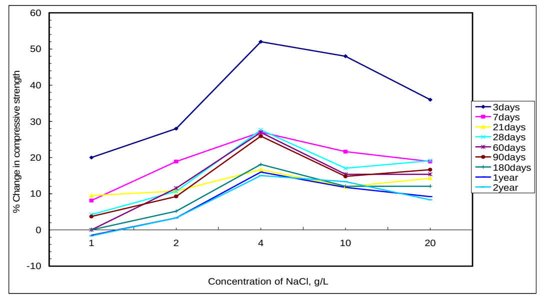


Fig.4 *Shows the Percent variation of compressive strength of admixture cement (PPC + 10% Silica fume) mortar cubes at different ages corresponding to various concentrations of NaCl in deionised water.*

For 3-day test cubes, marked increase in compressive strength is observed with increase in concentration of NaCl and it is significant. When the NaCl concentration is maximum i.e., 20 g/L, the increase in compressive strength is 36% (Fig 4) and also surprisingly when the concentration is 4g/L at the early age it reached the maximum percent change in compressive strength of 52%. At greater age (2 year), there is a significant increase in strength irrespective of concentration of NaCl in deionised water even up to 20g/L.

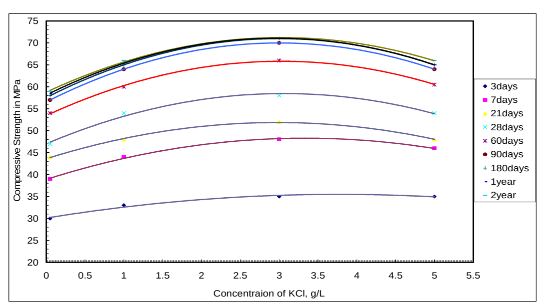


Fig.5 *Variation of compressive strength of admixture cement mortar cubes at different ages corresponding to various concentrations of KCl in deionised water.*

The effect of KCl concentration on compressive strength of cement mortar is presented in Fig 5. As concentration increases there is an increase in compressive strength of the cement mortar prepared with KCl solution up to a maximum concentration of 5 g/L.

At the early age, there is an increase in compressive strength is observed with the increase in concentration of KCl. From fig.6. The change in compressive strength is significant up to 180-days and slightly marginal over longer periods (at 2 years), except when the KCl concentration is at 3g/L.

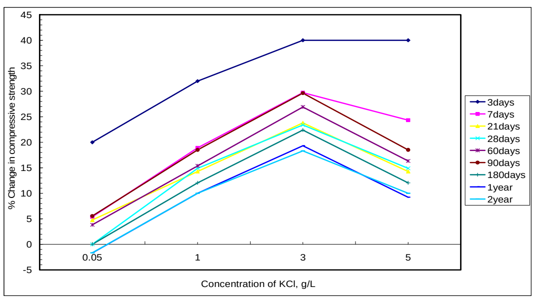
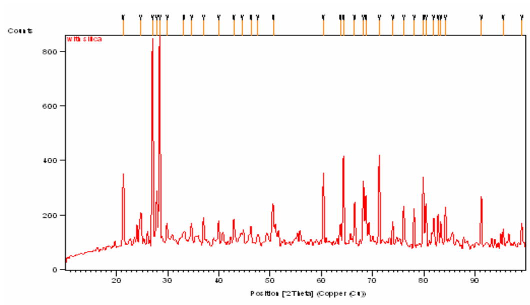


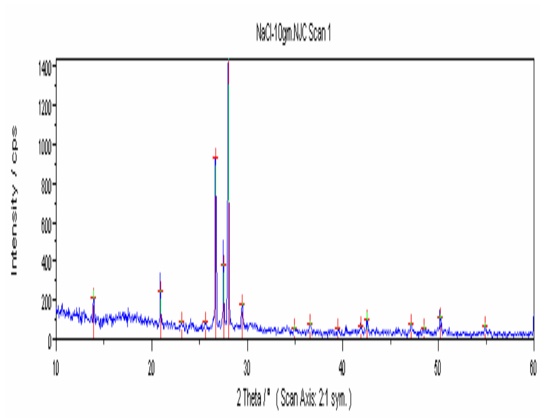
Fig.6 *Shows the Percent variation of compressive strength of admixture cement (PPC + 10% Silica fume) mortar cubes at different ages corresponding to various concentrations of KCl in deionised water.*

X-RAY DIFFRACTION

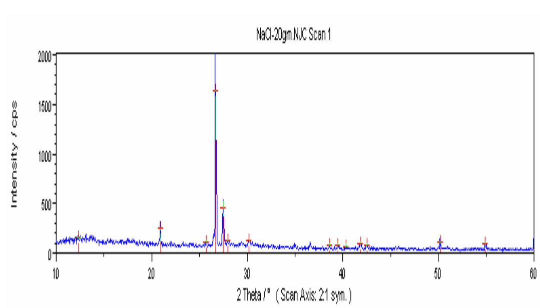


Pos [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel.Int. [%]
21.2999	284.22	0.2854	4.1681	34.84
24.6774	108.28	0.4955	3.60474	13.27
27.044	808.37	0.2522	3.29443	99.08
27.8776	207.59	0.2099	3.19779	25.45
28.4259	815.83	0.2414	3.13734	100
29.8629	61.46	0.017	2.98956	7.53
33.171	21.87	1.773	2.69859	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.7. *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	FWHM	2-Theta
1	6.36	13.9	13.9	10.1	20.8	216	245	0.2	13.9
2	4.25	20.9	20.9	14	23.1	251	46.2	0.13	20.9
3	3.85	23.1	23.1	21.1	23.9	91.6	35.2	0.74	23.1
4	3.47	25.6	25.6	23.7	26.4	84.4	29.6	1.63	25.6
5	3.34	26.7	26.7	26.5	26.9	930	27.7	0.14	26.7
6	3.24	27.5	27.5	26.9	27.8	379	26.3	0.12	27.5
7	3.18	28	28	27.8	28.2	1458	25.4	0.15	28
8	3.03	29.5	29.5	28.4	31.7	176	23.2	0.28	29.5
9	2.57	34.9	34.9	34.3	36.1	58.2	16.8	0.83	34.9
10	2.45	36.6	36.6	36.2	37.5	79.1	15.5	0.3	36.6
11	2.28	39.5	39.5	38.4	40	54.6	13.7	0.33	39.5
12	2.16	41.9	41.9	40.4	42.4	69.9	12.7	0.38	41.9
13	2.12	42.5	42.5	42	43.4	100	12.5	0.22	42.5
14	1.93	47.2	47.1	46.8	47.8	79.8	11.5	0.43	47.2
15	1.88	48.5	48.5	48	49.9	54.1	11.4	0.79	48.5
16	1.82	50.2	50.2	49.8	50.5	118	11.3	0.24	50.2
17	1.67	54.9	54.9	54.5	55.2	70.4	11.2	0.3	54.9



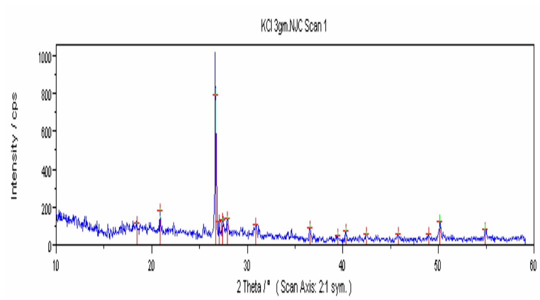
``	d_Fit (A1)	Ang-parab	Ang-COG	Low Limit	Upp. Limit	I-net	I-bgr	FWHM	2-Theta
1	7.21	12.3	12.4	10.1	20.8	160	160	4.47	12.3
2	4.25	20.9	20.9	10.1	24	253	30.6	0.18	20.9
3	3.46	25.7	25.7	24.4	26.3	109	9.86	26.5	25.7
4	3.36	26.5	0	25.8	26.5	171	7.93	0.43	26.5
5	3.34	26.7	26.7	26.5	26.9	1634	7.13	0.15	26.7
6	3.24	27.5	27.5	26.9	27.9	464	5.09	0.19	27.5
7	3.19	28	28	27.7	30.1	129	4	1.66	28
8	2.96	30.2	30.2	28.1	34.8	123	0	2.39	30.2
9	2.33	38.6	38.6	36.7	39.4	76	0	0.46	38.6
10	2.28	39.5	39.5	38.7	40.2	76.9	0	0.52	39.5
11	2.24	40.3	40.3	39.7	41.6	69.3	0	1.32	40.3
12	2.16	41.9	41.8	40.4	42.4	97.6	0	0.41	41.9
13	2.13	42.5	42.5	42	45.8	84	0	0.41	42.5
14	1.82	50.2	50.2	42.6	52.3	106	0	0.26	50.2
15	1.67	54.9	54.9	51.1	55.8	92	0	0.27	54.9

Fig.8.*Powder X-Ray Diffraction patterns for the admixture cement(PPC cement + 10% Silica fume) mortar cubes prepared with deionised water and with NaCl (10 g/L,20 g/L) in deionised water.*

The comparison of the two patterns clearly indicates the formation of paragonite $Na_2 Al_2 (Si_6 Al_4 O_{20}) (OH)_4$ contents. This is characterized by the presence of d-spacing's 4.247Å, 3.337 Å, 2.277Å in Fig 5.6 and these peaks being absent in Fig 7. and Fig.8. The probable chemical reaction upon the hydration of cement with mixing waters containing different NaCl concentrations is as follows:

$$2NaCl + 3Al_2O_3 + 6SiO_2 + 2H_2O + CaO \rightarrow Na_2Al_2(Si_6Al_4O_{20})(OH)_4 + CaCl_2$$

Initially, when NaCl added to the cement, the formation of sodium alumino silicate hydrates (paragonite-complex) is responsible for the acceleration of setting times of cement. Significant increase in strength of early age samples is due to intrusion of sodium ions into the alumino silicate structure. The significant increase in compressive strength during the early days is attributed to the chloride ion charge; later there is no significant increase in strength due to saturation except 4g/L and 10g/L. During the early age, the soluble salts ($CaCl_2$) are involved in hydration process. At early stages of crystallization, the salts are trapped in the pores leading to strength gain. Later on, the internal stress in crystallization develops negative effect by disrupting the cement mortar and hence, the increase in strength is nullified slowly.



No	d_Fit (A1)	Ang-parab	Ang-COG	Low Limit	Upp. Limit	I-net	I-bgr	FW HM	2-Theta
1	4.818	18.399	18.423	15.9	20.8	116.7	118.4	1.438	18.399
2	4.248	20.894	20.869	10.1	25.2	177.4	58.66	0.177	20.894
3	3.34	26.672	26.659	26.5	26.9	791.9	38.11	0.16	26.672
4	3.293	27.059	27.065	26.9	27.3	125.8	37.7	0.215	27.059
5	3.247	27.449	27.433	27.2	27.8	134.5	37.29	0.504	27.449
6	3.192	27.931	27.924	27.6	29.3	137.9	36.78	0.308	27.931
7	2.893	30.888	30.854	29.4	31.2	110.9	33.72	0.441	30.888
8	2.456	36.556	36.556	36.4	36.8	86.77	27.78	0.253	36.556
9	2.282	39.462	39.461	38.3	39.9	52.37	24.69	0.381	39.462
10	2.236	40.297	40.306	40.2	40.6	71.1	23.78	0.294	40.297
11	2.126	42.497	42.471	42.2	43.1	61.43	21.42	0.6	42.497
12	1.98	45.792	45.805	45.4	46.7	53.96	17.87	0.802	45.792
13	1.858	48.997	48.998	48.3	50	55.77	14.43	0.422	48.997
14	1.817	50.155	50.156	49.9	50.8	127.2	13.19	0.3	50.155
15	1.671	54.899	54.906	54.7	55.9	84.91	8.1	0.323	54.899

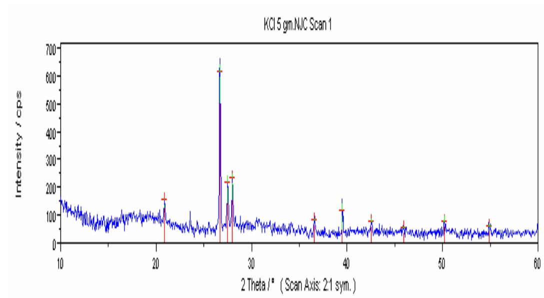


Fig.9 *Powder X-Ray Diffraction patterns for the cement mortar cubes prepared with deionised water and with KCl (3 g/L, 5 g/L) in deionised water.*

No	d_ Fit (A1)	Ang-parab	Ang-COG	Low Limit	Upp. Limit	I-net	I-bgr	FW HM	2-Theta
1	4.25	20.9	20.9	10.1	22.7	156	60.7	0.34	20.9
2	3.34	26.7	26.7	26.5	26.9	618	54.1	0.15	26.7
3	3.24	27.5	27.5	26.9	27.9	221	53.5	0.19	27.5
4	3.18	28	28	27.7	30.5	236	53.1	0.18	28
5	2.45	36.6	36.6	36.4	37.2	86	44.2	0.27	36.6
6	2.28	39.5	39.5	39.4	39.8	115	40.5	0.18	39.5
7	2.12	42.6	42.5	42.2	47	79.5	36.4	0.52	42.6
8	1.98	45.9	45.9	42.7	47.4	58.6	31.6	0.28	45.9
9	1.82	50.2	50.2	48.5	51.5	76.7	25.3	0.63	50.2
10	1.67	54.9	54.9	53.1	57	64.4	18.3	0.31	54.9

The comparison of the present pattern with that of deionised water indicates the formation of $K_2\ Al_2\ Si_6\ Al_4\ O_{20}\ (OH)_4$ (muscovite) compound which is evident due to the presence of d-spacing's 4.248Å, 2.453 Å and 1.671 Å in Fig 5.10, which are absent in the pattern for the control mix in fig.7 and fig. 9. The probable chemical reaction upon the hydration of cement with mixing water containing KCl concentration is

$$2KCl + 3AL_2O_3 + 7SiO_2 + 2H_2O \rightarrow K_2Al_2Si_6Al_4O_{20}(OH)_4 + SiOCl_2$$

The reason for the retardation of setting of cement is attributed to the formation of muscovite and also the larger size of potassium ions involved in the crystallization of muscovite leading to increase in voids. Considerable increase in compressive strength during the early days may be attributed to chloride ion charge; later there is no significant increase in strength. During the early days, the soluble salts ($SiOCl_2$) might have been produced in hydration. Crystallization of these salts might have taken place in the pores at early stage. Later on the internal stress due to crystallization could have produced negative effect by disrupting the cement mortar and consequently, the strength gain is reduced slowly.

Effect of Neutral Salts:

The neutral salts that are generally present in water are NaCl and KCl. 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: NaCl in deionised water accelerates the initial as well as final setting processes whereas the other salt KCl retard them (Fig 1and Fig 2) at all concentrations.

NaCl and KCl 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 KCl

The prominent effect of NaCl and KCl 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. By comparing these two neutral salts, it is evident that NaCl and KCl affect the compressive strength only positively.

CONCLUSIONS

1. Presence of NaCl in water accelerates the intial and final setting times of admixture cements mortar cubes significantly when the concentrations 2, 4 and above 10 g/L of concentrations respectively, Further For 3-day test cubes, marked increase in compressive strength is observed with increase in concentration of NaCl and it is significant. At greater age (2 year), there is a significant increase in strength irrespective of concentration of NaCl in deionised water even up to 20g/L.

2. Presence of KCl in water retards the both initial and final setting times got retarded with an increase in potassium chloride concentration in deionised water. Notably, there was no significant change in the initial setting time at all concentrations except 0.5 g/L.

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