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Effect of Hydrochloric Acid (HCl) on Blended Cement (Fly Ash based) and Silica Fume Blended Cement and their Concretes

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ABSTRACT

This paper presents the effect of Hydrochloric acid (HCl) on Blended Cement (Fly ash based(BC)) and Silica Fume Blended Cement(SFBC) and their concretes. The BC and SFBC and their concretes BCC and SFBCC produced with HCl dosage of 100, 150, 300, 500 and 900 mg/l added in deionised water. In addition to this control specimens were prepared with deionised water (without HCl) for comparison. The setting times and compressive strength were evaluated for 28 and 90 days apart from studying Rapid chloride ion permeability. The results show that, as HCl concentration increases, there is retardation in initial and final setting of cements (BC and SFBC). The compressive strength of both BCC and SFBCC has come down with an increase in the concentration of HCl at both 28 and 90 days. Compressive strengths of BCC and SFBCC have decreased in the range of 2 to 19%, at 28 and 90 day age respectively, with an increase in HCl concentration, when compared with the control specimens. It was also observed that Chloride ion permeability has increased with an increase in the concentration of the acid. X-ray diffraction analysis has been carried out for both BCC and SFBCC specimens at HCl concentration of 500 mg/l in deionised water.

Keywords: *HCl, setting time, compression, Chloride Ion Permeability, X-ray diffraction.*

1. INTRODUCTION

Water is an important ingredient of concrete, which is not only actively participates in the hydration of cement but also contributes to the workability of fresh concrete. Cement is a mixture of complex compounds, the reaction of cement with water leads to setting and hardening. All the compounds present in the cement are anhydrous, but when brought in contact with water, they get hydrolyzed, forming hydrated compounds. Since water helps to form the strength giving cement gel, the quality of water is to be critically monitored and controlled during the process of concrete making as the water universally the most abundant and naturally available solvent, can be contain large no of impurities ranging from less to very high concentration of them. In practice, very often, great control on properties of cement and aggregate is exercised but the control on the quality of water is often neglected.

A popular yardstick to the suitability of water for mixing concrete is that, if it is fit for drinking, it is fit for making concrete. This doesn't appear to be a true statement for all condition. Sometimes, water contain a small amount of sugar would be suitable for drinking, but not for making concrete and conversely water suitable for making concrete may not be necessarily be fit for drinking, especially if the water contains pathogenic microbial contaminants. In connection research work has been carried out on effect of polluted/chemical water on hardened concrete strength and durability. The damage impact of various deicing chemicals and exposure conditions on concrete materials was studied and results indicated that the various deicing chemicals penetrated at different rates in to a given paste and concrete resulting in different degree of damages [1]. One study had presented an assessment of the chemical resistance of eight different compositions of polymeric mortars [2]. In one of the studies, the effects of environmental factors on the addition and durability characters, was reported, of epoxy bonded concrete prisms [3]. Some researchers had investigated the resistance of mortars to magnesium sulphate attack and reported that there is a significant change in compressive strength properties [4]. Engineers had also studied the influence of strong alkaline substances (sodium carbonate and bi-carbonate) in mixing water on strength and setting properties of concrete [5]. In many places ground water and surface water contains the impurities, more than that of limits specified by the IS-456-2000. As there is scarcity of potable water in many places, this impure water is being used for mixing as well as curing of concrete in the civil engineering constructions. Hence an attempt is made to study the effect of water containing HCl at various concentrations in cements and their concretes.

2. MATERIALS AND METHODS

Cement: Portland Pozzolana Cement (fly ash based), containing 30% of fly ash was used and Silica fume content of 5% was added to get SFBC used in this investigation. The compositions of major compounds present in the cements are presented in Table 1 and Table 2.

Fine Aggregate: Locally available River sand was used.

Coarse Aggregate: Machine Crushed granite stone of max size 20mm confirming to IS 383 -1970 was used.

Water: Deionised water spiked with HCl at different concentrations i.e. 100, 150, 300, 500 and 900 mg/l

Table 1: Chemical Composition of Blended Cement (Fly Ash Based)

S.No	Parameter	Result
1.	Insoluble Material (% by mass)	18.90
2.	Magnesia (% by mass)	0.99
3.	Sulphuric Anhydride (% by mass)	2.67
4.	Loss on Ignition (% by mass)	2.04
5.	Total Chlorides (% by mass)	0.001

Table 2: Characteristics of Silica Fume

S.No	Constituent	Percent content
1	SiO_2	95.65
2	Al_2O_3	0.23
3	Fe_2O_3	0.07
4	CaO	0.31
5	MgO	0.04
6	SO_3	0.17
7	Na_2O	0.15
8	K_2O	0.56
9	LOI	2.27
10	Specific surface area m^2/g	16.7

Experimental Programme

The influence of HCl at different concentrations (100, 150, 300, 500 and 900 mg/l) was studied when the HCl is spiked with deionised water. Test samples are compared with the control samples. This comparison is may not be possible in case of control samples made with locally available potable water since it varies in chemical composition from place to place. With the above reason, HCl is mixed with deionised water in the dosage of 100, 150, 300, 500 and 900 mg/l. This water is used for preparation of samples for setting times (initial & final) of BC and SFBC and their concretes namely BCC and SFBCC. The IS mix design is adopted for concrete mix. For determining the initial and final setting times of cement, Vicat apparatus is used and to assess the compressive strength, 30 cubes of size 150x150x150mm for each concrete were cast and tested. To determine the chloride ion permeability, RCPT was used, for which 15 specimens for each concrete were cast and tested.

3. RESULTS AND DISCUSSION

3.1 Effect on setting times of Blended Cement (BC)

The effect of HCl on initial and final setting times is shown in Table 3. From the table, it is observed that both initial and final setting times got retarded with increase in hydrochloric acid concentration in deionised water. IS 456-2000 (Clause 5.4.1.3) stipulates that, when the difference in setting time(s) 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. The retardation for initial and final setting times is significant (i.e., more than 30 minutes), when the hydrochloric acid content exceeds 500 mg/l. When the acid content is 900 mg/l (Maximum concentration) , the initial setting time is about 180 minutes, which is 47 minutes more than that of the control mix. Similarly the difference of 70 minutes is observed in case of final setting time.

Table 3: Variation of Setting Times Of BC Corresponding to HCl Concentrations

S.No	Water sample	Setting time in minutes & Percentage change			
		Initial	% change	Final	% change
1	Deionised water (Control)	133	--	361	--
2	100 mg/l	138	3.42	375	3.74
3	150 mg/l	140	5.4	381	5.67
4	300 mg/l	152	14.52	388	7.56
5	**500 mg/l**	**166***	**24.72**	**395***	**9.46**
6	900 mg/l	180	35.02	431	19.49

*- Significant

3.2 Effect on setting times of SFBC

The effect of HCl on initial and final setting times is shown in Table 4. From the table, it is observed that both initial and final setting times got retarded with increase in hydrochloric acid concentration in deionised water. The retardation for initial and final setting times is significant (i.e., more than 30 minutes), when the hydrochloric acid content exceeds 500 mg/l. When the acid content is 900 mg/l (Maximum concentration) , the initial setting time is about 193 minutes, which is 51 minutes more than that of the control mix. Similarly the difference of 72 minutes is observed in case of final setting time.

Table 4:Variation Of Setting Times Of SFBC Corresponding To HCl Concentrations

S.No	Water sample	Setting time in minutes & Percentage change			
		Initial	% change	Final	% change
1	Deionised water (Control)	142	--	368	--
2	100 mg/l	147	3.68	382	3.78
3	150 mg/l	151	6.24	391	6.17
4	300 mg/l	164	15.31	395	7.26
5	500 mg/l	178*	25.36	406*	10.41
6	900 mg/l	193	35.87	440	19.43

*- Significant

3.3 Effect on Compressive Strength of Blended Cement Concrete (BCC)

The effect of HCl concentration on the compressive strength of BCC is presented in Table 5. Continuous decrease in compressive strength BCC specimens prepared with HCl acid solution is observed as the acid concentration increases till the maximum concentration (900 mg/l) tested. Although there is decrease in the compressive strength of concrete cubes of all samples, significant decrease is observed only from concentration of 500 mg/l. The rate of decrease in compressive strength also gradually increases with the increase in the concentration of the HCl. When HCl concentration is maximum, i.e., 900 mg/l, the decrease in compressive strength is 15.72% for 28 day) concrete and 18.64% for 90 day concrete, when compared with that of cubes prepared with the deionised water (control test sample).

Table 5: Compressive Strength of Blended Cement Concrete Corresponding To HCl Concentrations

S.No	Water Sample	Blended Cement Concrete			
		Compressive Strength		% variation	
		28 days	90 days	28 days	90 days
1	Deionised Water (Control)	23.89	27.47	--	--
2	100 mg/l	23.24	26.68	-2.74	-2.86
3	150 mg/l	23.06	26.44	-3.46	-3.76
4	300 mg/l	22.73	25.58	-4.87	-6.88
5	**500 mg/l**	**21.39**	**24.23**	**-10.46**	**-11.79**
6	900 mg/l	20.13	22.35	-15.72	-18.64

Through an experimental work, similar behavior in compressive strength was observed for different grades of concretes. During the acidic attack on concrete, dissolving of bases and atmospheric oxides caused increase in porosity, which leads to the movement of chemical substances into and out of the concrete, consequently affecting the strength and durability properties of the concrete [6].

3.4 Effect on Strength of SFBCC

The effect of HCl concentration on the compressive strength of SFBCC is presented in Table 6. Continuous decrease in compressive strength of the SFBCC specimens prepared with HCl acid solution is observed as the acid concentration increases till the maximum concentration (900 mg/l) tested. Although there is decrease in the compressive strength of concrete cubes of all samples, significant decrease in compressive strength is observed when the concentration of HCl is equal 500 mg/l. When HCl concentration is maximum, i.e., 900 mg/l, the decrease in compressive strength is 16.24% 28 day concrete and 18.23% for 90 day concrete respectively, when compared with that of cubes prepared with the deionised water (control test sample).

One scientist had studied acidic resistance effect on cement based materials prepared with chemically modified silica fume. The results have shown significantly increased acid resistance of the composites that are based on the combination of Portland cement and blast furnace slag. A significant change in compressive strength was also observed in the present investigation when compared with BCC. During hydration process, the silica fume content affects the decomposition of hydration products in the cement matrix followed by decrease of ignition loss, bound water and CaO content [7]. This may be a reason to obtain a significant change in compressive strength in SFBCC compared with BCC.

Table 6: Compressive Strength of SFBCC Corresponding To HCl Concentrations

S.No	Water Sample	SFBCC			
		Compressive Strength		% variation	
		28 days	90 days	28 days	90 days
1	Deionised Water (Control)	26.09	29.8	--	--
2	100 mg/l	25.41	28.71	-2.62	-3.67
3	150 mg/l	25.34	28.53	-2.89	-4.26
4	300 mg/l	24.68	27.72	-5.42	-6.98
5	**500 mg/l**	**23.29**	**26.34**	**-10.72**	**-11.62**
6	900 mg/l	21.85	24.37	-16.24	-18.23

3.5 Effect of HCl on Chloride ion Permeability

The rapid chloride permeability levels in terms of coulombs passed through OPCC, BCC and SFBCC observed are tabulated and listed in the Tables 7 to 9. By comparing the coulombs passed, which gives chloride ion permeability, it is observed that the chloride ion permeability of OPCC is very at both 28 and 90 days age against BCC and then SFBCC. A glance at the said results establishes that the chloride ion permeability of all the three concretes studies has increased with the increase in the concentration of HCl up to 900 mg/l which is the maximum experimented concentration. Quantum of variation in coulombs passed is 17.24% at 90 days for SFBCC when compared with the control sample.

One study had reported similar behavior with respect to chloride permeability on cement mortars[6]. Based on their studies, it was noticed that the chloride permeability (electric charge (coulombs)) was more in OPC than PPC. The permeability results reflect the interconnected pores network of concrete in which ions migrate. The use of porous concrete would not lead to lower permeability of concrete.

If the interfacial between aggregate and cement is intact then the lesser pores are formed which will lead minimal migration of ions, ultimately resulting in lower permeability [8]. This mechanism may be one of the reasons to get lower chloride permeability in BCC.

Table 7: Chloride Ion Permeability In Terms Of Coulombs Passed In OPCC Corresponding To HCl Concentrations

Sl. No	Water sample	Coulombs passed			
		28 days	% change	90 days	% change
1	Deionised water(Control)	2265		1418	
2	100 mg/l	2330	2.89	1466	3.41
3	150 mg/l	2362	4.27	1486	4.81
4	300 mg/l	2385	5.32	1526	7.64
5	500 mg/l	2523	11.41	1587	11.89
6	900 mg/l	2590	14.34	1622	14.36

Table 8: Chloride Ion Permeability In Terms Of Coulombs Passed In BCC Corresponding To HCl Concentrations

Sl. No	Water sample	Coulombs passed			
		28 days	% change	90 days	% change
1	Deionised water(Control)	2036		1187	
2	100 mg/l	2094	2.87	1231	3.71
3	150 mg/l	2114	3.84	1242	4.67
4	300 mg/l	2163	6.24	1273	7.28
5	500 mg/l	2265	11.24	1329	11.94
6	900 mg/l	2359	15.87	1399	17.82

Table 9: Chloride Ion Permeability In Terms Of Coulombs Passed In SFBCC Corresponding To HCl Concentrations

Sl. No	Water sample	Coulombs passed			
		28 days	% change	90 days	% change
1	Deionised water(Control)	1959		1026	
2	100 mg/l	2011	2.64	1052	2.57
3	150 mg/l	2032	3.71	1062	3.49
4	300 mg/l	2082	6.28	1100	7.24
5	500 mg/l	2179	11.21	1146	11.69
6	900 mg/l	2240	14.36	1203	17.24

Some of the scientists had conducted experimentation on chloride ion permeability in ternary concrete containing silica fume and blast furnace slag. Herein the authors had reported that the permeability has decreased considerably [9]. The same trend has been observed in the present investigation for concrete containing silica fume and BCC (Fly ash based). This is probably due to the fact that the total pore volume of concrete is not reduced by the pozzolanic reaction, but the pore structure becomes more discrete. The use of PPC and silica fume dilutes the pore solution and increases the binding of different ions, leading to lower permeability for concrete.

In one of the studies, researchers had observed similar trend of increased porosities i.e increase in chloride ion permeability for different grades of concretes [6]. The permeability of concrete is mainly attributed to the diffusivities of aggressive ions in concrete, which depends on material microstructure and fluid properties. However, in general, chemical reactions are much faster than the diffusion rate, and thus, the overall rate of the degradation processes will be governed by the slower diffusion of one of the species (reactant or product).

3.6 Powder X-ray Diffraction Analysis

Powder X-ray diffraction patterns, presented in Fig. 1 and Fig. 2, are for the BCC and SFBCC cubes prepared with HCl (500 mg/l) in deionised water. Upper portion of the said graph indicates the XRD pattern of the control sample prepared with deionised water. Perusal of the said graphs establishes that the compounds such as $3CaO.Al_2O_3.CaCl_2.10H_2O$ (Friedel's salt), C2S, C3S, Calcium Hydroxie (CH), CaCl2 and C-H-S are found at 11.9^0, $16^{0,}$ 17^0, $21^{0,}$ 44.7^0 and 55^0 respectively. Comparing with control sample, the sample of HCl additionally consists of Friedel's salt and Calcium Chloride.

Setting times of the BC were observed to get retarded with the increase in HCl concentration in the mixing water. Chemical equations when HCl is added in mixing water with cement are given below.

Compressive strength also has decreased with an increase in the concentration of HCl. Chemical equations when HCl is added in mixing water with cement are given below. The XRD pattern indicates that the lower peaks of CH which is responsible in decrease of compressive strength when compared with the control sample.

$$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$$

$$CaCl_2 + 3\ CaO.Al_2O_3 + 10H_2O \rightarrow 3CaO.Al_2O_3.CaCl_2.10H_2$$

In case of SFBCC also, compressive strength has decreased with an increase in the concentration of HCl. The XRD pattern of SFBCC with mixing water containing 500 mg/l is presented at Fig. 2. Apart from the above it can be seen that the compressive strength of the SFBCC is more than the BCC because of the presence of silica fume.

4. CONCLUSIONS

The following observations were made from the experimental work.

1. Both initial and final setting times of BC and SFBC got retarded with an increase in hydrochloric acid concentration in deionised water. The retardation for initial and final setting times is significant (i.e., more than 30 minutes), when the hydrochloric acid content exceeds 500 mg/l.
2. Continuous decrease in compressive strength BCC and SFBCC specimens prepared with HCl acid solution is observed as the acid concentration increases till the maximum concentration (900 mg/l) tested.
3. Although there is decrease in the compressive strength of concrete cubes of all samples, significant decrease is observed only from concentration of 500 mg/l. The rate of

decrease in compressive strength also gradually increases with the increase in the concentration of the HCl.

4. Results indicated that the chloride ion permeability of BCC and SFBCC has increased with the increase in the concentration of HCl up to 900 mg/l which is the maximum concentration.

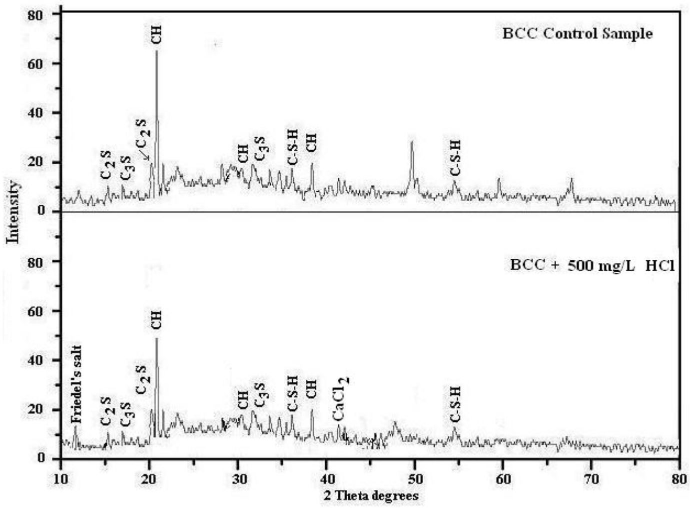

Figure 1. X-Ray diffraction pattern of powdered BCC sample prepared with HCl (500 mg/l) in deionised water.

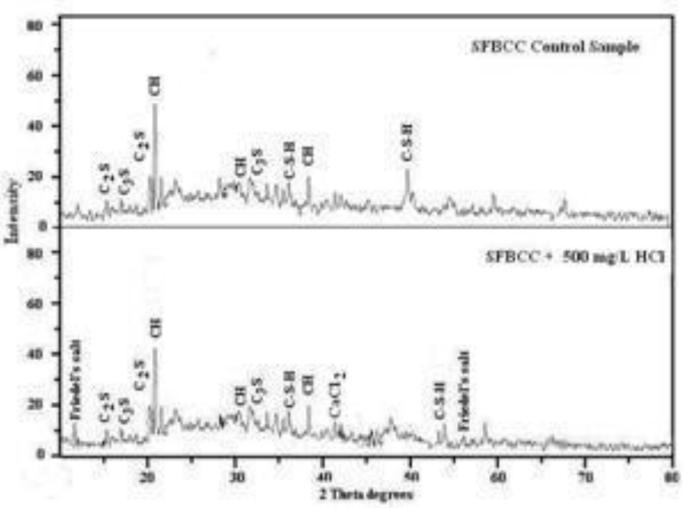

Figure 2. X-Ray diffraction pattern of powdered SFBCC sample prepared with HCl (500 mg/l) in deionised water

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