

CHEMICAL CHARACTERIZATION OF DETERIORATED CONCRETE IN AGGRESSIVE MEDIA

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The loss due to deterioration of concrete and subsequent corrosion of reinforcement has been reported to be very high. A systematic study of deterioration of concrete in highly aggressive industrial and marine environments has been reported in this paper. Samples were allowed to deteriorate in acid and neutral media namely, HCl, HNO₃, H₂SO₄, H₃PO₄, MgCl₂, NH₄Cl and (NH₄)₂SO₄. Various parameters such as percentage of deterioration in terms of loss in compressive strength, change in pH and corrosion constituents such as chloride and sulphate have been studied. The thermogravimetric analysis of deteriorated samples have also been carried out. The deterioration in acid media was found to be in the following order : HNO₃ > HCl > H₂SO₄ > H₃PO₄. In the case of neutral media, the deterioration was found to be in the following order. MgCl₂ > NH₄Cl > (NH₄)₂SO₄. The thermogravimetric analysis has thrown much light on the formation of various complex compounds formed between constituents of cement in the aggressive media.

Keywords: Deterioration of concrete, percentage of deterioration, thermogravimetric analysis

INTRODUCTION

Corrosion of concrete and reinforced concrete have been drawing the attention of scientists and engineers for the past few decades as they have caused extensive damage to structures, even within a short period [1-3]. This has led to the various investigations in the direction of analysing the behaviour of concrete in different industrial and marine environments [4-7]. Coastal structures are subjected to marine environments. Industrial structures are exposed to different environmental conditions during and after the construction. These conditions deteriorate the concrete as well as corrode the steel. Deterioration to concrete occurs in terms of loss in strength and appearance. Depending upon the severity of the environment the damage to the concrete occurs in a shorter or longer period. Deterioration of concrete occurs mainly by physical, mechanical and chemical actions of aggressive environments. Physical action is exemplified by extremes of temperature and humidity in the atmosphere. Mechanical action is due to the running water flowing with high velocities around the concrete face, i.e., cavitation damage or erosion corrosion. Damage by chemical action takes place in concrete either by leaching of lime or

crystallization of salts in pores causing expansion and bursting of concrete [8].

Aggressive liquids such as acids, bases, solutions of salts or aggressive gases penetrate the concrete and cause deterioration. A good concrete is resistant to a wide variety of chemical attack and high durable. Physical action develops fine cracks opening up path ways for the penetration of aggressive solutions and gases. The chemical corrosion of concrete is also caused by the internal transformation of hardened cement paste and the recrystallization of hydrates formed during the setting of cement. Acceleration of this process is caused by diffusion of gases and liquids through open pores in the concrete.

In order to understand the deterioration of concrete, it is necessary to identify the various reactive products formed within the concrete. Some investigators have shown that sufficient loss of free "CaO" originally present as Ca(OH)₂ in cement resulting in the formation of the reaction products which partially get leached out and the rest remaining in the concrete mass would result in cracking and 20 to 40 per cent loss in flexural strength of concrete could occur in solutions of acids [9,10]. Dinesh Mohan and Mohan Rai have made use of DTA of deteriorated concrete samples collected from

various compounds formed [11]. Papayianni has also made use of DTA to find out the pozzolanivity and hydraulic reactivity of high lime fly ash [12]. In view of the above, an attempt has been made to predict the mechanism of deterioration of concrete in various aggressive media used in the experiments. Different aggressive media such as HCl, HNO₃, H₂SO₄, MgCl₂, NH₄Cl, (NH₄)₂SO₄ were simulated and deterioration of concrete samples in these media were evaluated in terms of percentage reduction in strength, change in pH, etc., are reported in the present work. In addition to the above, thermogravimetric analysis was carried out on the deteriorated concrete samples to find out the various complex compounds formed during the deterioration process.

EXPERIMENTAL

Particulars of concrete mix design and media used in the studies are as follows:

Size of the specimen	: 100 x 100 x 100 mm
Mix ratio of concrete	: 1 : 1.7 : 2.09 by weight of concrete
Water cement ratio	: 0.5
Compressive strength	: 20 N/mm ² (after 28 days curing)
Acid media	: HCl, HNO ₃ , H ₂ SO ₄ , H ₃ PO ₄
Neutral media	: MgCl ₂ , (NH ₄) ₂ SO ₄ , NH ₄ Cl
Grade of chemicals:	: AR
Duration of immersion	: 3, 6 and 12 months

After curing, the specimens in triplicate were immersed in the respective solutions, as per standard atmospheric conditions at 301 ± 2K. The solutions were replaced once in two weeks to accelerate the deterioration process and any loss due to evaporation was also made up.

After the period of immersion was over, the specimens were taken out from the solutions and air dried. The compressive strength tests were carried out on these specimens using AIMIL concrete compressive strength testing machine of 200 tonnes capacity. The different compressive strengths were compared with the compressive strength of control specimens which were kept in distilled water for the same period. The percentage of deterioration was then calculated with respect to the compressive strength of the control specimens.

The concrete specimens subjected to compressive strength were taken out and powdered so as to pass through No.300 mesh sieve. The powdered samples were dried in an air oven at 383K for four hours. It was then cooled in desiccator. 100 g of powdered mass was shaken with 100 cc of distilled water in a MICROID flask shaker for one hour. The extract was then filtered through No.1 whatman filter paper. The

following constituents were analysed in the extracts: (1) pH, (2) lime (CaO) (3) Chloride, (4) sulphate.

The pH of the extract was measured using ELICO pH meter model 1400 P. A combined glass, calomel electrode type TL-42 was used for making measurements. Lime was estimated as per analysis of water sample using murexide (ammonium purpurate) as indicator and titrating against standard EDTA solution. Chloride was determined by Mohr's method by titrating with standard AgNO₃ solution using K₂CrO₄ as indicator in neutral medium [13]. Sulphate was determined gravimetrically in HCl medium by precipitating with BaCl₂ solution as BaSO₄. The precipitated barium sulphate was ignited at 1173K and expressed as SO₄. Differential thermal analysis (DTA) of concrete samples were also carried out using Stanton Thermo Balance Model STA-780. The samples were heated upto a temperature of 1073K and heating rate was 273K per minute. The chart speed was 200 mm per hour. From the DTA curves the formation of different complex compounds of cement in the deterioration process viz., calcium hydroxide, gypsum, chloro aluminate, sulpho aluminate and nitro aluminate were found out.

RESULTS AND DISCUSSION

The various parameters studied to identify the deterioration of concrete in various aggressive media, such as HNO₃, HCl, H₂SO₄, H₃PO₄, MgCl₂, NH₄Cl and (NH₄)₂SO₄ are given in Table I. It is interesting to see that the percentage of deterioration varies from as low as 12% in the case of (NH₄)₂SO₄ to a maximum of 29% in the case of HNO₃. It can be seen that the maximum percentage of deterioration was found in the case of HNO₃ followed by MgCl₂, HCl, H₂SO₄, NH₄Cl, H₃PO₄ and the least in the case of (NH₄)₂SO₄. It can be observed that in all the media, the deterioration increases with increase in exposure period. This may be attributed to the complex reaction formed between the media and the constituents of cement. In the case of chloride media, the complex formation is taking place between chlorides with the formation of chloroaluminate complex.

It can also be seen from Table I that the pH of the concrete falls to around 11.00 at the end of 12 months. Thus the fall in pH is about 1.5 which is considerable for a short duration of 12 months for low concentrations. Generally for 3 months exposure, the pH of the concrete was not much altered in all the media. In the case of free chloride a maximum value of 1700 ppm was obtained in HCl medium whereas in MgCl₂ 1550 ppm of chloride was found at the end of 12 months. In the case of sulphate, a maximum value of 2160 ppm was found in H₂SO₄ medium at the end of 12 months. In (NH₄)₂SO₄ medium, 2060 ppm of free sulphate was observed.

The curves obtained from Differential Thermal Analysis (DTA) on deteriorated concrete samples are given in Figs. 1

TABLE I: Results of deteriorated concrete samples

Sl. No.	Medium	Deterioration			pH	Free $\text{Cl}^-/\text{SO}_4^{2-}$				
		3	6	12		3	6	12		
1.	0.1 N HNO_3	18.5	22.0	29.0	12.0	11.6	11.0	40	80	120
2.	0.1 N HCl	16.0	20.5	25.0	12.4	11.8	11.2	1000	1400	1700
3.	0.1 N H_2SO_4	15.4	17.4	21.0	12.3	12.0	11.3	975*	1650*	2160
4.	0.1 N H_3PO_4	10.3	12.0	15.2	12.4	12.2	11.5	40	80	120
5.	1% MgCl_2	21.2	24.0	27.0	12.5	12.2	11.5	600	920	1550
6.	1% $(\text{NH}_4)\text{Cl}$	8.0	14.4	18.0	12.5	12.0	11.6	600	920	1520
7.	1% $(\text{NH}_4)_2\text{SO}_4$	7.0	10.0	12.0	12.4	12.0	11.5	840*	1520*	2060*

to 4. The results are summarised in Table II. From the curves and Table II it can be seen that chloroaluminate, sulfoaluminate, nitroaluminate formation are taking place in HCl , H_2SO_4 and HNO_3 respectively. The formation of chloroaluminate, sulfoaluminate and nitroaluminate is the important factor in causing the disintegration of concrete. From the endothermic peaks, it can be seen that calcium hydroxide formed is undergoing decomposition at temperature around 823 K. It is very interesting to note that no endothermic peaks are formed in the case of H_3PO_4 showing thereby calcium hydroxide formation is not taking place. Intense reaction and loss of calcium hydroxide, result in the penetration of large amounts of chloride, sulphate and corresponding formation of chloroaluminate and sulfoaluminate. It can also be seen from Table II that chloroaluminate and $\text{Ca}(\text{OH})_2$ are formed during the deterioration in MgCl_2 medium. In the case of ammonium sulphate, calcium sulfoaluminate formation is taking place and gypsum formed is getting decomposed at 738K. Here also endothermic peaks are formed around temperature 823K showing thereby that the $\text{Ca}(\text{OH})_2$ formed during the deterioration process is getting decomposed and that the deterioration is due to leaching of lime. In the case of NH_4Cl ,

$\text{Ca}(\text{OH})_2$ is formed. It is clear, from the above results that the DTA curves indicate the formation of various compounds formed between calcium hydroxide of cement and the aggressive medium under investigation. Thus there is a good correlation with the various parameters studied which is also supported by DTA studies.

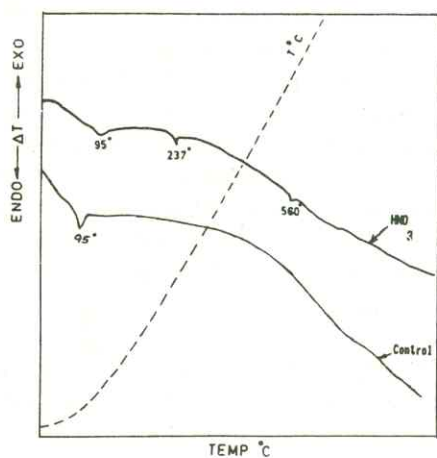
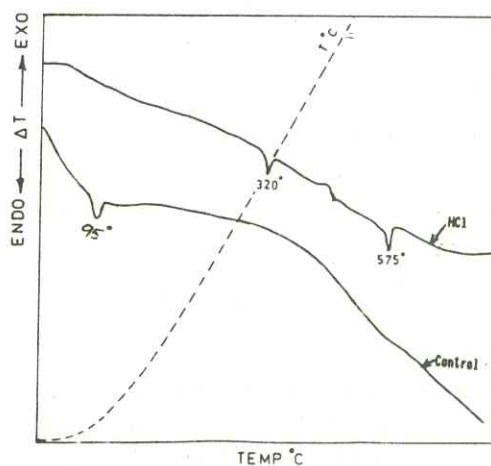
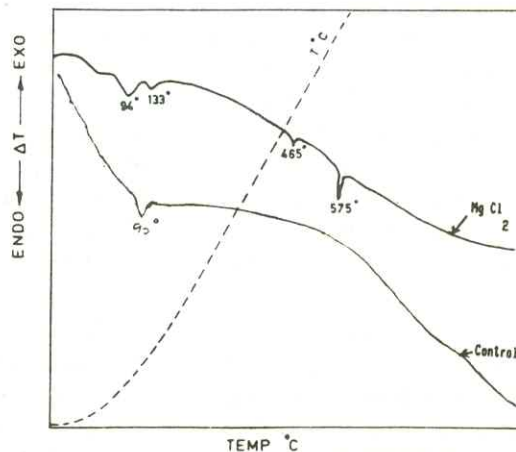
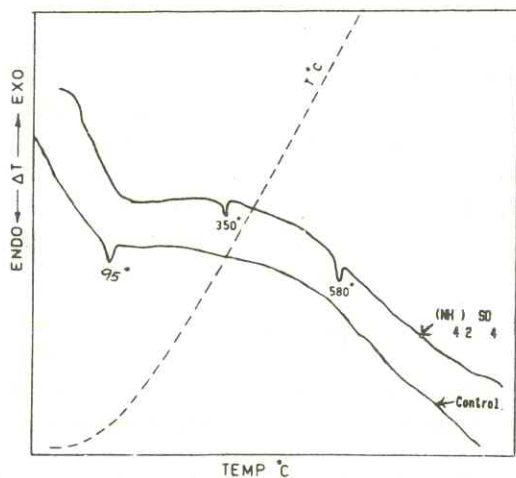
Fig. 1: DTA curve of concrete exposed to HNO_3 Fig. 2: DTA curve of concrete exposed to HCl Fig. 3: DTA curve of concrete exposed to MgCl_2

TABLE II: DTA analysis of deteriorated concrete samples

System	Temperature at which endothermic peaks are formed (from DTA curve °C)	Probable compound formed
0.1 N HNO ₃	a. 95	Dehydration
	b. 237	Dehydration of calcium nitroaluminate
	c. 560	Ca(OH) ₂ The decomposition of calcium hydroxide
0.1 N HCl	a. 320	Partial dehydration of chloro aluminate
	b. 525	Ca(OH) ₂ The decomposition of calcium hydroxide
0.1 N H ₂ SO ₄	a. 157	Tricalcium sulpho aluminate hydrate
	b. 484	Decomposition of gypsum (CaSO ₄)
	c. 575	Ca(OH) ₂ The decomposition of calcium hydroxide
0.1 N H ₃ PO ₄	No peaks	No peaks are formed
1% MgCl ₂	a. 350	Partial dehydration of chloro aluminate hydrate
1% (NH ₄)Cl	a. 565	Ca(OH) ₂ The decomposition of calcium hydroxide
1% (NH ₄) ₂ SO ₄	a. 94, 133	Calcium sulpho - aluminate hydrate
	b. 465	Inversion of gypsum (CaSO ₄) ₂ H ₂ O
	c. 575	Ca(OH) ₂ The decomposition of calcium hydroxide

CONCLUSION

1. The percentage of deterioration of concrete in the aggressive media at the end of 12 months is found to be in the following order: HNO₃ > MgCl₂ > HCl > H₂SO₄ > NH₄Cl > H₃PO₄ > (NH₄)₂SO₄. The change in parameters such as pH, free chloride and free sulphate also clearly reflect the above order.
2. Differential Thermal Analysis on deteriorated concrete samples has also clearly shown the formation of various compounds formed during the deterioration process. The endothermic peaks obtained around 823K corresponds to the Ca(OH)₂ formed during deterioration.

Fig. 4: DTA curve of concrete exposed to (NH₄)₂SO₄

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