

Studies on the aspects of chloride ion determination in different types of concrete under macro-cell corrosion conditions

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Abstract

In the present investigation various extraction methods have been carried out for the estimation of free chloride and total chloride contents in different types of concretes, namely ordinary Portland cement (OPC), Pozzolana Portland cement (PPC) and Portland slag cement (PSC). Macro-cell concrete specimens were cast and subjected to severe alternate wetting and drying cycles of 10-months exposure. Concrete core samples were collected from the above specimens under different depths, namely 20, 40 and 60 mm. Six extraction methods for determination of free chloride and two extraction methods for determination of total chlorides in concrete have been carried out. Boiling water method was found to be a suitable for the determination of free chloride contents in concrete. As the depth increases the amount of chloride ion decreases. Filtration method is found to be not suitable for the determination of chloride ion in concrete. There is no quick method for determining the chloride concentration in concrete either in the field or in laboratory. Water-soluble chloride alone is a good indicator of the concentration of chloride ion in concrete. ISE method appears to be most convenient but it requires lot of calibration before analysis.

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1. Introduction

The reinforcement corrosion is the most destructive form of damage affecting serviceability and strength of concrete structures [1]. There are number of external and internal factors viz. carbonation, pH, deterioration, chloride ingress, etc., that create conditions favourable for reinforcement corrosion in concrete [2]. Of all these factors, chloride contamination is probably the most critical as it is observed to initiate the form of corrosion that is much more severe and detrimental to the integrity of concrete structure [3]. The assessment of corrosion risk in chloride containing reinforced concrete is uncertain. Chloride ion penetration arises from a variety

of sources from chloride bearing mix, from marine environments or indirectly by surface water or traffic spray. The critical content of chloride was studied by several authors [4,5]. Chloride acquires different forms in concrete: chemically bound, physically adsorbed and free chloride. Only free chloride is responsible for rebar corrosion in concrete [6]. If the free chloride to hydroxide ratio exceeds 0.6 loss of passivity occurs and pitting progresses.

Syed Hussain et al. reported that the importance of determination of chloride threshold for corrosion of reinforcement in concrete [7]. Attempts can be made by various investigations to quantify the value of threshold Cl^-/OH^- ratio using corrosion test, and steel in alkaline solution as well as in concrete. Hausmann and Gouda have shown that the passivity is broken and Cl^-/OH^- ratio exceeds a particular value [8,9]. ASTM specifies the

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importance of determination of water-soluble chloride in mortar and concrete [10]. ASTM C 1152 specifies the determination of acid-soluble chloride in mortar and concrete [11]. The code of practice for structural concrete BS 8110 in the UK limits the total chloride in concrete with the limit varying with the type of cement used and vulnerability of the steel [12]. The code recommends the total chloride content in concrete can be calculated from the mix proportion and measured chloride content in each concrete material, i.e., the total chloride means the summation of the individual chloride contents of the constituent materials. Contrary to UK, American practice [13] places the limits of water-soluble chloride in concrete for both constituent materials and hardened concrete. As it is considered that only these chloride ions can contribute under normal conditions to reinforce corrosion. Extensive research has been done to establish the relation between chloride ion content and onset of corrosion.

Berman standardized the determination of total chloride content in concrete [14]. This method involves quite accurate chemical analysis and careful specimen preparation. However, two other types of chloride ion contents have come into use recently: free chloride and water-soluble chloride ion content. As the name implies, the water-soluble chloride readily dissolves in water. A standard test for the identification of these types of chlorides in concrete exists [15,16]. It is, however an issue that is not as clear as that of total chloride. This is because the amount of chloride ions released into the solution depends on the testing method adopted, which involves factors such as fineness of concrete samples, the amount of water added, temperature, the agitation method and time allowed [17]. In fact it has been claimed that given enough time and water, all chlorides can be reclaimed from the solution [18].

Arya and Newman distinguished between water-soluble chloride and free chloride contents in concrete [19]. They define free chloride an ion in the pore solution. So this can be determined by the pore solution expressing technique that has already been used by many researchers, but this method has only limited applications for the determination of chloride ions in concrete from actual structures. Accordingly leaching and other techniques have been proposed to estimate the chloride ion concentration in paste and mortars [20–22]. The leaching technique offers a most practical method for determining free chloride. However, several leaching techniques that are sufficiently accurate over the range of chloride additions investigated have been proposed [22]. The estimation and determination of chloride in different types of cement also varies with respect to the composition of cement, reaction involved etc. Hence, the determination of chloride contents in concrete is extremely important to take a suitable remedial measure for the corrosion of steel in concrete structures.

The scope of the present investigations includes evolving suitable extraction methods for the determination of free chloride and total chloride contents in different types of concretes, namely ordinary Portland cement (OPC), Pozzolana Portland cement (PPC) and Portland cement (PSC), by accelerated corrosion studies [23–26]. The effect of temperature on chloride ion determination and the comparison of the chloride ion determination by filtration and decantation methods with ion selective electrode method are also carried out.

2. Experimental details

2.1. Materials used

- (a) OPC.
- (b) PPC.
- (c) PSC.

The following materials were used in the present study:

OPC:	Conforming to IS: 811-1989 (equivalent to ASTM C 150-type I).
Fine aggregates:	Local clean river sand (fineness modulus of medium sand equal to 2.6) conforming to grading zone III of IS: 383-1970.

The specific gravity of fine aggregates is 2.4. The water absorption of fine aggregates is 0.5%. The composition of OPC, PPC and PSC are given below:

Constituents	OPC (%)	PPC (%)	PSC (%)
Silicon dioxide (SiO ₂)	20–21	28–32	26–30
Aluminium oxide (Al ₂ O ₃)	5.2–5.6	7–10	9–11
Ferric oxide (Fe ₂ O ₃)	4.4–4.8	4.9–6	2.5–3.0
Calcium oxide (CaO)	62–63	41–43	44–46
Magnesium oxide (MgO)	0.5–0.7	1–2	3.5–4
Sulphur-tri-oxide (SO ₃)	2.4–2.8	2.4–2.8	2.0–2.4
Loss on ignition (LOI)	1.5–2.5	3.0–3.5	1.5–2.5

2.2. Mix design used

The details of design proportion used are given as follows:

Strength	Type of cement	w/c	Cement (kg/m ³)	Fine aggregates (kg/m ³)	Coarse aggregates (kg/m ³)	28 day compressive strength (MPa)	Slump (mm)
20 MPa	OPC	0.67	284	770	1026	27	50
	PPC	0.67	284	770	1026	23	60
	PSC	0.67	284	770	1026	28	10

2.3. Macro-cell specimen preparation and method of exposure

A rectangular concrete specimen of size 400 mm × 250 mm × 150 mm was designed as per ASTM G109-92 for macro-cell corrosion studies. A cold twisted deformed (CTD) rod with 16 mm diameter and 320 mm length was used as cathode, and 320 mm length was used as an anode and electrical connection was taken by screwing 100 mm long bar on the anode and the edges were properly insulated from the aggressive environments. The top mat of rebar acts as an anode and the bottom mat of rebar acts as cathode. The anode to cathode ratio was maintained as 1:2 in order to induce accelerated corrosion.

Concrete specimens were prepared as per the designed mix. The specimens were mechanically vibrated. After 24 h of setting the specimens were demoulded and cured in distilled water for 28 days. After the curing period is over, all the concrete specimens were removed from the curing tank.

Then all the specimens were subjected to alternate wetting and drying test by ponding with 3% NaCl solution at the top of the specimen for 4 days followed by 3 days drying and thus 7 days constituted one cycle of alternated wetting and drying. During exposure to salt solution, chloride ions tend to diffuse through the cover concrete and depassivate the steel positioned at the top level. After 10 months of exposure the core samples of size 60 cm long were taken near the anode. The core samples were sized for every 20 mm depth using a diamond cutter. These cylindrical concrete specimens under various depths, namely 20, 40 and 60 mm were subjected to free and total chloride estimations.

2.4. Chemicals used

Silver nitrate (AR—Loba chemie).
 Phenolphthalein (AR—Qualigen's INDIKROM).
 Sulphuric acid (AR—FISCHER).
 Nitric acid (AR—FISCHER).
 Potassium chromate (AR—Qualigen's).
 Ferric alum indicator (AR—Qualigen's).
 Potassium thiocyanate (AR—Qualigen's).

2.5. Determination of free chloride contents

The determination of free chloride was carried out by different extraction methods, namely decantation method, boiling method and filtration method.

2.5.1. Decantation method

2.5.1.1. Twenty-four hours method (W_1). The cylindrical specimens were crushed and sieved through a 600 μ m sieve. A known quantity of the sieved powder and triple distilled water was mixed and stirred well and then sealed and stored for 24 h. A ratio of powder and water of 1:3

was used for this preparation. After 24 h, the solution was carefully decanted. 5 ml of decanted solution was taken and one drop of phenolphthalein indicator was added. A pink-colour solution was obtained. This shows that the pH of the decanted solution was alkaline. This was then neutralized with 0.1 N sulphuric acid by decolourizing the pink colour. Then add few drops of 10% potassium chromate indicator and titrated against 0.1 N silver nitrate solution. The end point is the appearance of yellowish red colour. The titration was repeated till the concordant values were obtained.

2.5.1.2. Thirty-six hours method (W_2). The cylindrical specimens were crushed and sieved through a 600 μ m sieve. A known quantity of the sieved powder and triple distilled water was mixed and stirred well and then sealed and stored for 36 h. A ratio of powder and water of 1:3 was used for this preparation. After 36 h, the solution was carefully decanted. The decanted solution was taken and the titration was carried out as per the procedure given above.

2.5.1.3. Forty-eight hours method (W_3). The cylindrical specimens were crushed and sieved through a 600 μ m sieve. A known quantity of the sieved powder and triple-distilled water was mixed and stirred well and then sealed and stored for 48 h. A ratio of powder and water of 1:3 was used for this preparation. After 48 h, the solution was carefully decanted. The decanted solution was taken and the titration was carried out as per the procedure given above.

2.5.2. Boiling method (W_4 and W_5)

(a) The cylindrical specimens were crushed and sieved through a 600 μ m sieve. A known quantity of the sieved powder and triple-distilled boiling water was mixed and stirred well and then sealed and stored for 24 h. A ratio of powder and water of 1:3 was used for this preparation. After 24 h, the mixture was carefully decanted. The decanted solution was taken and the titration was carried out as per the procedure given above.

(b) The cylindrical specimens were crushed and sieved through a 600 μ m sieve. A known quantity of the sieved powder and triple-distilled water was mixed and stirred, then boiled for few minutes (not to evaporate) and then sealed and stored for 24 h. A ratio of powder and water of 1:3 was used for this preparation. After 24 h, the solution was carefully decanted. The decanted solution was taken and the titration was carried out as per the procedure given above.

2.5.3. Filtration method

The cylindrical specimens were crushed and sieved through a 600 μ m sieve. A known quantity of the sieved

powder and triple-distilled water was mixed and shaken for 1 h by using microid mechanical shaker. Then it is filtered through a Whatmann filter paper. The filtrate was then used for chloride determination and the titration was carried out as per the procedure given above.

2.6. Determination of total chloride

Weigh 10 g of the crushed and sieved sample by using 600 μm sieve in a 250 ml beaker. Disperse the sample with 75 ml of the distilled water. Without delay slowly add 25 ml of 1:1 nitric acid, breaking up any lumps with a glass rod. Cover the beaker with a watch glass. For PPC and PSC, if the smell of hydrogen sulphide is strongly evident at this point, add 3 ml of hydrogen peroxide. Heat the covered beaker rapidly to boiling. Do not allow boiling for more than a few seconds (In another method the beaker was digested for 4 h on a water bath.) Then it is filtered in a 250 ml standard flask. From this 50 ml of the extract was taken. Then 25 ml of 0.1 M silver nitrate was added. When silver nitrate was added the free chloride present in the solution gets precipitated as silver chloride. Then add 5 ml of distilled and pure nitrobenzene. The purpose of this is to ensure that silver chloride which was probably surrounded by a film of nitrobenzene did not interfere in the titration. Few drops of ferric alum indicator are then added and titrated against 0.1 N potassium thiocyanate. The end point is the appearance of red colour. The titration was repeated till the concordant values were obtained.

2.7. Ion selective electrode (ISE)

A chloride ion-sensing electrode together with a double-junction reference electrode (calomel) and a precision digital mV metre, was used to measure directly the chloride content in various test solutions.

Initially, the system was calibrated using aqueous solutions of known chloride concentrations. A linear relationship was obtained between the measured mV reading and chloride concentration. The test solutions prepared from different types of concrete samples under different covers were subjected to ISE analysis.

3. Results and discussion

3.1. Determination of total chloride

The determination of total chloride contents by two different methods under different depths, namely 20, 40 and 60 mm for OPC, PPC and PSC concretes, are given in Table 1. Between the two methods, digested method showed higher amount of chloride when compared to boiling method. It is interesting to note that, the total

Table 1

Total chloride contents for OPC, PPC and PSC concretes under different depths

Type of concrete	Depth (mm)	Total chloride (%)	
		Boiling method	Digested method
OPC	20	0.216	0.220
	40	0.202	0.210
	60	0.184	0.188
PPC	20	0.156	0.159
	40	0.151	0.155
	60	0.137	0.139
PSC	20	0.119	0.121
	40	0.115	0.117
	60	0.113	0.115

chloride contents decreases as the depth increases from 20 to 60 mm. This is to be observed in all the three types of concretes used. For example the total chloride content in OPC concrete under different depths are 0.216%, 0.202% and 0.184%. PSC concrete showed lesser chloride contents when compared to OPC and PPC concretes. PPC concrete showed lesser chloride content than OPC concrete. Among three types of cement used for the study, PSC concrete is able to resist the chloride to the maximum extent. The same observation was reported by several authors. PPC and PSC concretes contain mineral admixtures like fly ash (upto 20%) and slag (50–60%), respectively. The fineness of these mineral admixtures after several treatments became finer than cement particles. Blending of these finer materials with Portland cement results PPC and PSCs. The specimens used in this study are core samples collected after 10 months exposure period under severe alternate wetting and drying cycles with 3% NaCl solution. Even under these aggressive conditions, PPC and PSC concretes reduced the chloride penetration into the concrete. This is due to the fact that in PPC and PSC concretes, the reduced permeability, enhanced pore size distribution, lesser capillary pores and required strength do not allow the chloride to ingress into the concrete.

3.2. Determination of free chloride contents

The free chloride contents estimated for macro-cell concrete specimens under different depths were reported in Table 2. Six different extraction methods are adopted in this study. It is observed from the table that, the free chloride contents decreases as the depths increases. This fact is observed almost in all the extraction methods studied. Among the six different extraction methods, boiling water method (both W_4 and W_5) showed more chloride contents. But in 24, 36 and 48 h methods, the chloride concentration was found to be in the range 4000–4400 ppm under 20 mm depth. The corresponding

Table 2
Free chloride contents (ppm) for OPC, PPC and PSC concretes under different depths

Types of concrete	Depth (mm)	Extraction methods					
		W_1	W_2	W_3	W_4	W_5	W_6
OPC	20	4020	4440	4200	5400	5220	2200
	40	2760	2520	2640	3120	3600	1500
	60	1980	1920	2040	2100	2040	1000
PPC	20	4500	4860	4860	6780	5880	3000
	40	300	300	240	300	240	180
	60	240	180	180	240	240	100
PSC	20	1860	2460	2460	2520	2520	1000
	40	240	180	240	240	180	100
	60	120	180	240	180	120	90

$W_1 = 24$ h: $W_2 = 36$ h: $W_3 = 48$ h: W_4 and $W_5 =$ Boiling water method: $W_6 = 1$ h.

value by boiling water methods is 5000–5400 ppm. A difference of more than 1000 ppm was observed between these two methods of analysis. On the other hand, a simple 1 h method (W_6) yields only 2200 ppm under 20 mm depth. Here, a difference of more than 2000 ppm was observed, when compared to the other methods.

Table 2 also gives the free chloride contents for PPC concrete under different depths. The free chloride contents under 20 mm depth are found to be more when compared to corresponding OPC system. But under 40 and 60 mm depths, the free chloride contents are drastically reduced when compared to OPC system. Again, boiling water method (W_4 and W_5) yields better results when compared to other methods. After 36 h (W_2) and at 48 h (W_3), the same value is obtained indicating the saturation of chloride contents after 36 h. These data showed that, for PPC concrete a minimum of 36 h is required to release more chloride ions into the solution. As already observed, 1 h (W_6) method fails to release chloride ions into solution.

The free chloride contents of PSC concrete under 20, 40 and 60 mm depths extracted by different methods are given in Table 2. The free chloride contents estimated for PSC concrete is very less when compared to PPC and OPC concretes. The same observation was already observed in the estimation of total chloride also. Here again, the boiling water method (W_4 and W_5) is able to release more chloride ions into the solution when compared to other methods. The values of W_1 , W_2 and W_3 indicate that a minimum of 36 h is required for the free chloride estimation in PSC concretes. The 1 h filtration method (W_6) yielded a very less amount of chloride into the solution.

Decantation methods, namely W_1 , W_2 and W_3 dissociate chloride ions considerably into the solution. The boiling water methods (W_4 and W_5) released more

chlorides into the solution, indicating that either addition of boiling water or the boiling of total contents influence the release of more free chlorides into the solution. On the other hand, the filtration method, namely W_6 (1 h), released a very less amount of chloride ions into a solution. Since in this method not only is the contact time with concrete powder less, but also most of the chlorides are adsorbed on the cement paste itself during filtration.

From the above results, it should be clearly understood that, in different extraction methods, temperature and contact time with the concrete powder would appear to influence the amount of chlorides brought into solution. Buenfield reported that by given enough contact time and temperatures only brought sufficient chloride into the solution [27]. All the test methods used in this study are suitable for the determination of chlorides in a concrete, which is obtained by water extraction methods. The concentration of chlorides obtained into solution from hardened concrete appears to be independent of the method of extraction provided the extraction time is equal to or greater than 24 h.

The reduction in free chloride contents by various concretes follows the order: PSC > PPC > OPC. The better performance of the PSC and PPC concretes may be due to the fact that the presence of alumina contents in both the concretes are more than that of OPC concrete. The alumina content in cement is most responsible for binding of free chloride ions available in the concrete. Vanikar and Mullarky [28] reported that mineral admixtures like fly ash and slag improved the binding of chlorides in paste and, therefore, there was reduction in available chlorides for the attack of embedded steel in concrete.

3.3. Ion selective electrode method

The free chloride contents estimated using chloride ISE for OPC, PPC and PSC concretes are reported in Table 3. The boiling water method is used for this study. In ISE method also, the free chloride contents decreased as the depth increased. The free chloride contents under 20 mm depth are 4600 ppm for OPC, 3200 ppm for PPC and 1320 ppm for PSC. In general, the free chloride contents determined from the ISE method are lower than volumetric methods. However, ISE technique requires lot of calibration, which should be carried out with the additional presence of soluble ions obtained from chloride-free hardened concrete by the extraction method to be used for test samples.

4. Conclusions

The following conclusions were drawn from the present investigation:

Table 3
Free chloride contents for OPC, PPC and PSC concretes under different depths by ISE method

Type of cement	Depth (mm)	Free chloride (ppm)
OPC	20	4600
	40	2200
	60	1800
PPC	20	3200
	40	120
	60	62
PSC	20	1320
	40	900
	60	104

- (1) As the depth of concrete increased, the amount of chloride ions decreased. The amount of free chloride contents in OPC concrete is more when compared to PPC and PSC concretes.
- (2) Among the various extraction methods used decantation method is found suitable for determining chloride ion in concrete. Boiling water method yield better results when compared to other methods. Filtration method is not found suitable for determining chloride concentration in concrete.
- (3) The ISE appears to be the most convenient method for measuring chlorides in solution. However, this technique requires lot of calibration.
- (4) The total chloride content observed in PPC and PSC concretes are less than the OPC concretes. This may be due to the reduced permeability, enhanced pore size distribution; lesser capillary pores and required strength resist the chloride ingress into the concrete.
- (5) Finally, the single most important conclusion of this study is that there is no “quick method” of determining the chloride concentration in the field or laboratory. Free chloride contents seem to be good indicator of the concentration of chloride in a concrete.

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