ASSESSMENT OFCORROSION INITIATIONTIME ONCOSTAL CONCRETE STRUCTURE –A CASE STUDY

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Abstract

The durability and serviceability of R.C structures which are located incostal environment are always vulnerable to corrosion of reinforcement. It is impossible to prevent even by providing an additional cover and good construction practice but can be slow down. After construction of concrete structure prediction of corrosion initiation time is very important so as to plan periodic maintenance schedule. The present work aims to determine the chloride diffusion coefficient of the concrete existing in the marine environment of Odisha. For this purpose, Seven concrete samples of demolished structures of known age from Puri and Paradeep are collected. Experiments have been conducted to find the concentration of soluble chloride in different depth by using potentiometric titration. Then the diffusion coefficient is determined by using equation of fick'slaw. The corrosion initiation time have been predicted using again the Fick's 2nd law of diffusion. Lesser corrosion initiation time indicates higher vulnerability towards corrosion of reinforcement and vice versa .Therefore preventive measure scan be taken to slow down the chloride penetration enhance the durability of structure.

Keywords: *Corrosion, Chloride Ingress, Diffusion Coefficient, Carbonation, Reinforcement.*

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1. INTRODUCTION

.Now a days concrete structure have been deteriorating faster than they are expected changing the impression of concrete as the most durable material. Corrosion of reinforcement is the prime cause of failure of most of the concrete structures.As a Consequence the rebuild and repair costs cover a major portion of the current investment in infrastructure. For prevention of failure due to corrosion, timely planning for regular maintenance of structures and monitoring approach is required[1]. In order to prepare maintenance schedule, it is necessaryto predict the corrosion initiation time for the existing structures situated in the coastal environment.

The objective of the study is to obtain diffusion coefficient of concrete which is the key indicator of susceptibility of concrete for chloride ingress and initiation. If the concrete is found to be more prone to be chloride attack and thus corrosion of reinforcement, suitable measures can be taken to slow down the corrosion process and there by enhancing the durability of the R.C structures.

The present work includes experiments to determine total chloride content at different depth from exposed concrete surface of samples collected from partly demolished RC structures situated in sea cost of Bay of Bengal from places of Puri and Paradeep. The chloride diffusion coefficient and corrosion initiation time have been calculated using Fick's law of diffusion. Also, experiments on carbonation have been conducted to conform that corrosion of steel in costal concrete structures are solely due to chloride ingress.

2. CAUSE OF CORROSION

Initially the fresh concrete creates a oxide layer called passive layer on the surface of the steel which protect there inforcement from corrosion. Depassivation can occur due to the penetration of chloride ion orcarbonation. Hence the corrosion of steel is due to:(i) Chloride Ingress and (ii) Carbonation[2].

2.1 Chloride Ingress

The chloride ingress is pre-dominant in coastal areas and in cold countries where structures' exposed to the de-icing salt which contains chloride. Chloride can also penetrate through the admixtures which are used to accelerate curing, contaminated aggregates and/or mixing water, air born salts, salts in ground water, and salts in chemicals that are applied to the concrete surface. The passive layer of the steel bar get destroyed when the chloride concentration at the steel / concrete interface reaches a critical amount known as the chloride threshold[3]. The chloride ingress into the concrete is described by two mechanisms known as absorption and diffusion. Both diffusion and absorption are dependent on moisture content.

2.1.1 Absorption

In absorption mechanism the water containing chloride enters into the capillary pores of unsaturated (dry) concrete through drying and wetting cycles. Chloride building in concrete depends on the permeability and alternate drying and wetting condition. Absorption is dominant if alternate drying and wetting takes place in chloride bearing water.

2.1.2 Diffusion

Diffusion mechanism is most dominant and it takes place due to the concentration gradient *(It is a graduated difference in concentration of the solute within a solution).* The greater the difference in concentration of particles, the steeper is the gradient and migration of chloride takes place through pore water. Researchers have modeled an equation for the chloride ingress using Ficks 2nd law of diffusion using its application to the concrete. [4,5,6].In the Non-Steady state diffusion (Fick's 2nd law), the quantitative treatment of diffusion process is formulated as a partial differential equation and is given as follows

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \quad (1)$$

Where, c= concentration, t= time,
x=distance from boundary and
D= diffusion co-efficient that does not vary with x.

The solution of the above equation for a semi - infinite domain with uniform concentration of chloride (Cs) at the surface of the concrete is given as:

$$\frac{C_x - C_i}{C_s - C_i} = 1 - erf[\frac{x}{2\sqrt{Dt}}] \quad (2)$$

Where, C_x= Concentration of chloride at a distance $x$from the boundary and
erf= error function which the Gaussian error function with limiting values as erf (0) =0,
erf (∞) = 1erf (-∞) = -1 , used in present work [7]
C_i= initial chloride content built in at construction stage,

If the depth of cover to the reinforcement $d_c$and amount of chloride concentration at reinforcing steel level isc_c, then above equation takes the form as given below

$$\frac{C_c - C_i}{C_s - C_i} = \left[1 - erf\,\frac{d_c}{2\sqrt{Dt}}\right] \quad (3)$$

The value of Diffusion Coefficient helps to Determine the amount of corrosion that will take place on a structure, the chloride deposition at certain depths and the corrosion initiation time**.** The value of Diffusion Coefficient varies from one place to place [8]. Initially in concrete the chloride present in ingredients and the chloride that ingress in concrete from external sources react with hydration products[9]. Out of total chloride present, some chloride is bound by C-S-H gel which is called chloride binding [9,10].After binding of chlorides by hydration products are over, the remaining chloride remains in pore solution known as free chloride. Free chloride is water soluble and leads to formation of corrosion in reinforcement at initial stage ASTM 1218[11].At low PH, acid-soluble chlorides bound within hydration product get released. At PH value below 11.5, only about 2% of the total chloride on concrete remains as bound chloride.[12]. Diffusion coefficients can be calculated only after determining the chloride content at different depths. Sun G [13] & Zhang J et.al. [14] have calculated the diffusion coefficient for three grades of concrete and found to vary from4.87 x 10 $^{-12}$m^2/s to5.73 x 10 $^{-12}$m^2/s .Nakarai et.al. [15]calculated the diffusion coefficient using Fick'slaw based on free chloride content and total chloride content and found the values varies from 1 x 10^{-12} m^2/sto 2.4 x 10^{-12} m^2/s. The chloride content at which the passivation of steel in concrete is destroyed is known as critical chloride content also known as threshold value[14] and is expressed in terms of total chloride content relative to the weight of the cement[16,17] or weight of concrete [18,19] has found the critical chloride content in term of % weight of cement as 0.17 to 2.5 varying from out door to laboratory condition in concrete.[20]reported the threshold value0.05-0.7 % by weight of cement for the middle east environment.ACI code[16] has specified as follows for different conditions based on free chloride by % weight of cement (i) for prestressed concrete-0.06 (ii)exposed to chloride in service-0.15(iii) Dry or protected room temperature in service-1.0 and (iv) all other constructions -0.3.After determination of diffusion coefficients and the value of critical chloride content for particular environment, corrosion initiation time is calculated.

2.2 Carbonation

One of the principal causes of corrosion in reinforcement is carbonation which is pre-dominant in the industrial areas where the atmosphere contains much of CO_2. Carbon dioxide comes in contact with the moisture present in the atmosphere to forms dilute carbonic acid, which penetrate in to concrete and react with calcium hydroxide resulting in the formation of calcium carbonate

As carbonation proceeds the alkalinity of concrete reduces to making pH below 9 ,there after the calcium hydroxides are converted into calcium carbonate. In such a low pH the depassivation occurs and initiation of corrosion takes place. When low relative humidity exists, the pores are dry and the gaseous CO_2 cannot react with $Ca(OH)_2$ in hydrated cement. Rate of carbonation is higher when relative humidity is between 50-70%.[21] .Optimum is 50 % RH and Optimal range is40-90 % rh[22].Rate of carbonation is less when concrete is strong with low permeability. In this study, experiments have been conducted on carbonation so as to conform that corrosion in costal concrete structures are solely due to chloride ingress.

3. EXPERIMENTAL INVESTIGATION

3.1 Materials

The prime objective is to determine chloride diffusion coefficient and corrosion initiation time of concrete in chloride laden costal environment. Also experiments on carbonation of concrete has been conducted to clarify about the type of corrosion. Concrete samples were collected from demolished structures exposed to marine environment situated in two cities of Orissa, named Puri and Paradeep on the coast of Bay of Bangle.

Concrete debris pieces of known ages having part of exposed surface were collected and sealed in plastic bags. Table - 1 describes the sample details which includes location, age and corrosion level from visual inspection. In above two town ground water is the main source for preparation of concrete and curing. Hence water samples from three bore wells of Paradeep and three bore wells of Puri have been collected to know the initial chloride content in mixing water. The chemicals used in the experiments were of Fisher Scientific certified brand. Deionized (DI) Water was produced in a Millipore deionizing unit and was used for solution preparation. Kimax Kimble laboratory glassware assortment were utilized for titration and other chemical experiments.

Table 1 Details of samples collectedfor experiments.

Sample No	Location	Approximate age in years	Corrosion level from visual inspection
1	Puri	10	None
2	Puri	15	Mild
3	Puri	25	Mild
4	Puri	35	Moderate
5	Paradeep	45	Severe
6	Paradeep	55	Extreme
7	Paradeep	65	Extreme

3.2 Experimental Methods& Test Results

Concrete powders i.e samples are extracted from the depth of 5,10,20,30,40,50 mm from the collected debris by drilling as shown in Figure - 1. Figure – 2 shows the holes left after collecting samples from the concrete pieces. The dust was used to determine the water soluble chloride (WSC) content and the acid soluble chloride (ASC) content in the concrete as per ASTM C 1218/C 1218M – 99 [11] and 1152/C 1152M-04 [23] test procedure respectively. The bound chloride (BC) was determined by deducting WSC from ASC. The corresponding results of ASC,WSC and BC values are presented in Table 2. The plot of WSC i.e. free chloride versus depth is shown in Figure-3.

Figure -4 shows variation of ASC i.e. total chloride with respect to depth of concrete. The variation of BC i.e chemically bonded chloride with depth of concrete is shown in Figure – 5. The relation between surface chloride and age of concrete is presented in Figure – 6.

The initial chloride content in ground water sources of Puri and Paradeep were also determined following same procedure. The results are produced in Table – 3. Density of the concrete samples were determined using buoyancy balance method. The density values are provided in Table - 2. Carbonation tests have been conducted on the collected samples and the colour changes are shown in Figure – 8.

Fig – 1: Extraction of concrete powder for sample preparation

Fig – 2: Holes left in the concrete debris after sample collection

Table 2 Chloride contents at various depths of the samples

Samples / Age	Density kN/m^3	Chloride types	Chloride contents in % by weight of concrete					
Depth in mm			0-5	5-10	10-20	20-30	30-40	40-50
Sampe-1 10 years	2420	WSC	0.178	0.108	0.050	0.0145	0.00	0.00
		ASC	0.2	0.13	0.071	0.035	0.02	0.0155
		BC	0.022	0.022	0.021	0.0205	0.02	0.0156
Sample-2 15 years	2450	WSC	0.229	0.155	0.089	0.04	0.0125	0.00
		ASC	0.26	0.176	0.109	0.06	0.032	0.02
		BC	0.021	0.021	0.02	0.02	0.0195	0.02
Sample-3 25years	2410	WSC	0.27	0.202	0.135	0.0795	0.039	0.015
		ASC	0.29	0.223	0.157	0.101	0.061	0.037
		BC	0.02	0.021	0.022	.0215	0.022	0.022

Sample-4 35 years	2440	WSC	0.28	0.219	0.1595	0.107	0.065	0.034
		ASC	0.30	0.24	0.181	0.126	0.085	0.055
		BC	0.017	0.017	0.018	0.019	0.02	0.021
Sample-5 45 years	2400	WSC	0.250	0.249	0.191	0.1365	0.082	0.057
		ASC	0.32	0.265	0.208	0.154	0.11	0.076
		BC	0.016	0.016	0.017	0.0175	0.018	0.019
Sample-6 55years	2380	WSC	0.258	0.273	0.2174	0.161	0.113	0.077
		ASC	0.34	0.284	0.228	0.173	0.126	0.09
		BC	0.01	0.01	0.0106	0.012	0.013	0.013
Sample7 65years	2350	WSC	0.249	0.292	0.239	0.181	0.132	0.093
		ASC	0.36	0.30	0.247	0.19	0.142	0.103
		BC	0.008	0.008	0.008	0.009	0.01	0.01

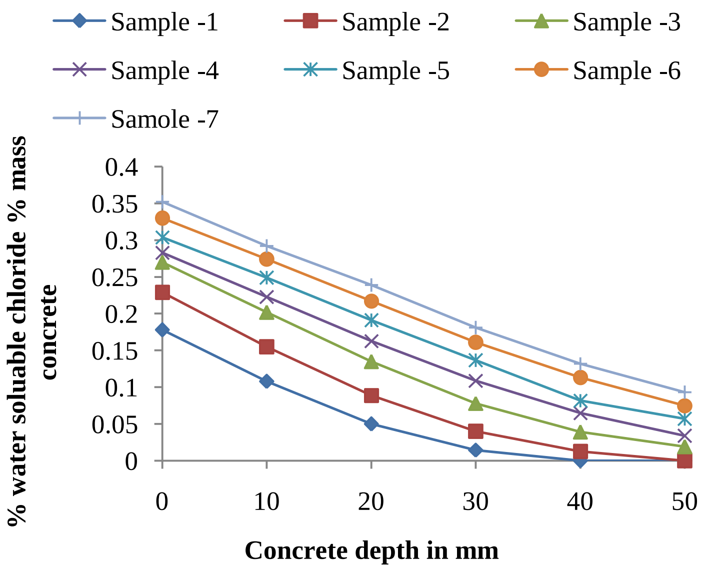

Fig – 3: Relation between WSC and depth of concrete

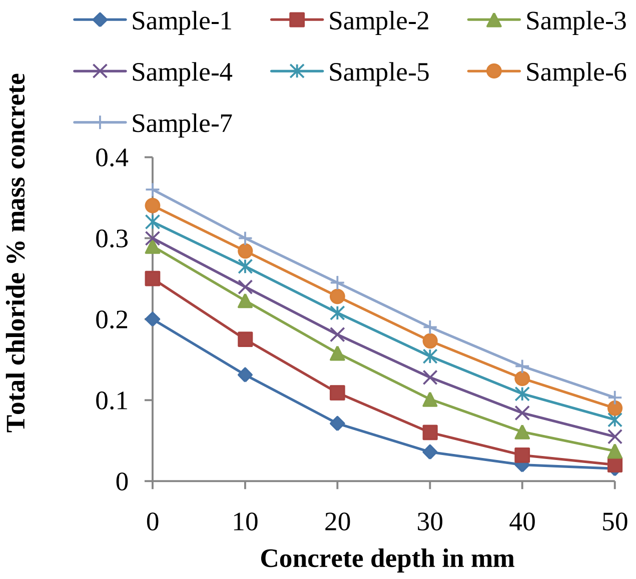

Fig – 4: Relation between ASC and depth of concrete

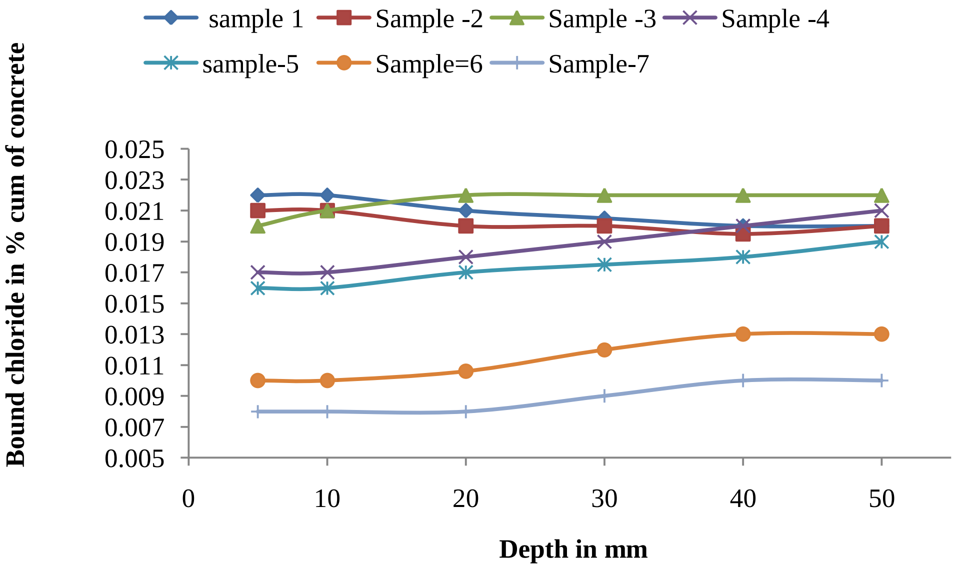

Fig -5: Relation between BC and depth of concrete

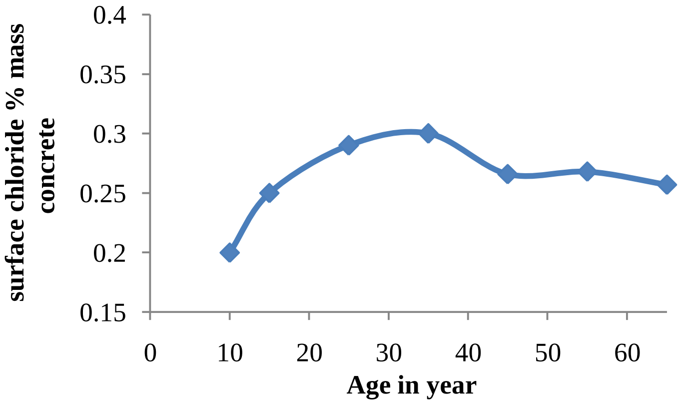

Fig -6: Surface chloride vs age of concrete

Table-3: Chloride content in mixing and curing water

Location	Paradeep			Puri		
Chloride content in mg/lit	164.0	168.0	166.0	162.0	167.0	163
Averagein mg/lit	165					

4. ANALYTICAL INVESTIGATION

4.1 Calculation of Diffusion Coefficient

For the calculation of diffusion coefficient fick's second law (equation-3) has been used.

Where C_s= Chloride concentration at the surface of the concrete at 0-5 mm depth.
C_c = Chloride concentration at the desired depth of concrete such as 10 mm,20 mm,30 mm 40 mm, and 50 mm,
C_i = initial chloride concentration present in the concrete.

From field survey, It is found that the buildings at that time were built with nominal mix concrete with mix proportion (1:2:4). Ordinary Portland cement (OPC) of 33 grade was used in the concrete. The concrete mix have cement content and w/c as 333 kg /m^3 and 0.58 respectively. Those concrete have density equivalent to normal weight concrete 24 kN/m^3 . Chloride content in OPC is 0.1% , which is equal to 0. 01396 % [24] by weight of concrete. The average chloride content in mixing water is 165 mg/lit and is equal to 0.00229 % by weight of concrete . So c_i initial chloride in concrete has been calculated to be 0.01425 % by weight of concrete . Corrosion of steel get initiated when the free chloride get deposited on surface of steel up to threshold level, but free chloride changes as PH value of concrete changes. Hence in real structures in natural condition actual free chloride changes and assessment is difficult. Therefore, total chloride which is sum of free chloride and bound chloride is used for calculation of Chloride diffusion coefficient. Diffusion coefficients calculated are presented in table -4. The plot of diffusion coefficient with that of depth of concrete is shown in Figure – 7.

Table 4 Diffusion Coefficient of Collected Samples

Depth in mm		10	20	30	40	50
Samplewith Agein years	Density kg/m^3	Diffusion coefficients in m^2/s				
Sample-1 ,10	2420	6.558X 10^{-13}	6.02X 10^{-13}	5.603 X 10^{-13}	5.39X 10^{-13}	5.26 x10^{-13}
Sample-2, 15	2450	6.458X 10^{-13}	6.008X 10^{-13}	5.627X 10^{-13}	5.305 X 10^{-13}	5.172X 10^{-13}
Sample-3 , 25	2410	6.612X 10^{-13}	6.053X 10^{-13}	5.633X 10^{-13}	5.363X 10^{-13}	5.225X 10^{-13}
Sample-435	2440	6.379X 10^{-13}	5.888X 10^{-13}	5.535X 10^{-13}	5.329X 10^{-13}	5.235X 10^{-13}
Sample-5, 45	2400	6.803X 10^{-13}	6.196X 10^{-13}	5.721X 10^{-13}	5.523X 10^{-13}	5.404X 10^{-13}
Sample-6,55	2380	6.107X 10^{-13}	5.697X 10^{-13}	5.371X 10^{-13}	5.12X 10^{-13}	5.049X 10^{-13}
Sample-7, 65	2350	6.018X 10^{-13}	5.622X 10^{-13}	5.20X 10^{-13}	4.947X 10^{-13}	4.867X 10^{-13}

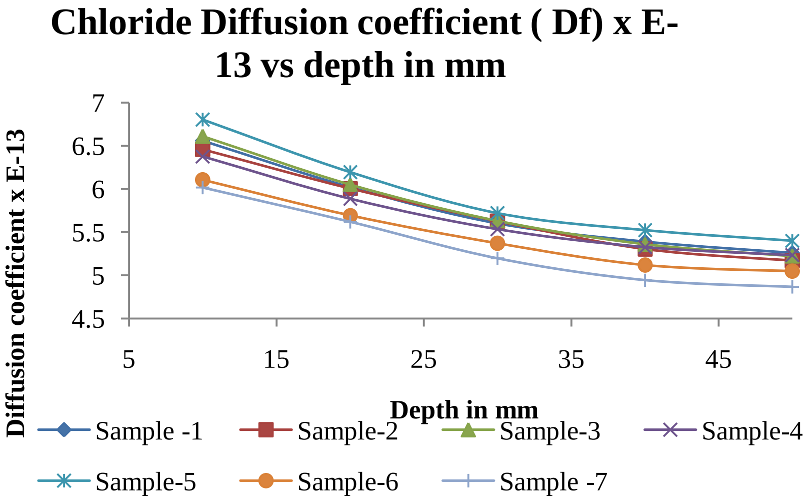

Fig-7 Diffusion coefficient vs depth of concrete

Fig – 8: Carbonation test and change of colour

4.2 Calculation of Corrosion Initiation Time

Corrosion initiation times for different samples have been calculated based on some assumption considering the local environmental conditions. Puri and Paradeep are exposed to rainy season about 3 -4 months in a year and rest 8-9 months remain dry with occasional rain . On the other hand most of the structures are protected by painting , distempering or colour washing to the exposed surface. For calculation purpose, the values of the mix proportion, water content and cement content were taken same as that had been used while determining diffusion coefficients. Average threshold chloride content was obtained from ACI[16] i.e, 1.0% free chloride , for dry or protected room moisture in service. The amount is equivalent to 0.13958 % by weight of concrete . Taking average bound chloride to be 0.02 % by weight of concrete, threshold value becomes 0.15958 % based on total chloride. The values of corrosion initiation time for different depth are calculated as per equation -5 and tabulated in table- 5. For use of equation - 5 the values of erf (z) have been taken from the Mathematical Tables Project, "Table of Probability Functions" Vol. 1, Federal Works Agency, Works Projects Administration, New York 1941 [7].

Following step by step procedure can be undertaken to calculate corrosion initiation time.

(a). Surface chloride contents(C_s)(acid soluble) can be found by laboratory test taking 10 mg of powdered samples from a depth 0-5 mm in term of % of weight of concrete .
(b). Cover depth(d_c) is to be selected
(c). Chloride threshold value (C_t) which can initiate the corrosion by destroying passive layer is selected.
(d). Initial chloride contents (C_i) can be selected considering the initial chloride in cement, mixing and curing water etc.
(e). Diffusion coefficients at required depth can be selected from table -4 depending on the age and density of concrete and depth of concrete cover.
(f). Equation to be used is taken by rewriting the equation-3given as as

$$1-\frac{C_t-C_i}{C_s-C}=erf[z] \qquad (4)$$

Where$z=\frac{dc}{2\sqrt{D\ \ t}}$

Left hand side parameters of equation x are known and can be calculated . For different values of $erf[z]$ the values of‘z’ can be calculate from table of error function [7]

Now using the equation - 5 , corrosion initiation time (t) can be calculated as

$$t=\left[\frac{dc}{2z\sqrt{D}}\right]^2 - \qquad (5)$$

4.3 Examples for Case Study for Prediction of Corrosion Initiation Time on Field

For prediction of corrosion initiation time 4 nos of samples were studied. Chloride diffusion coefficient and initial chloride content and chloride threshold can be taken as per present research work and only data to be collected from the samples are surface chloride contents(Cs).Calculation of corrosion initiation time for one sample is shown in example below and same procedure is followed for other samples. Values of corrosion initiation time of samples are presented in table -5.

Cover depth(d_c)=15 mm, Threshold value(C_t) = 0.15958 % wt. of concrete, Surface chloride (Cs) =0.26 % wt . of concrete. Initial chloride content(C_i) = 0.01425 % wt of concrete and density of concrete =2450 Kg/m^3. D_{ava}=6.233 x10^{-13}which is taken from table -4

$erf[z]$ = 1- (C_t- C_i)/(C_s-C_i) = 1-(0.15958-.01425)/(0.26 -0.01425)=0.40879

From table of error function err(z) =0.4243z =0.4 and For err(z) = 0.3794,z=0.35

By interpolation for erf(z) =0.40879 , z=0.38339773

$$\text{Now} t = \left[\frac{15}{1000\ \times 2\times 0.38339773\sqrt{6.233\ \times 10^{-13}}}\right]^2 \frac{1}{365\times 24\times 60\times 60} = 19.467 years$$

Table5 Estimated Time of Corrosion Initiation at Different Depth

Depth in mm	15	25	35	45
Density of concrete in kg/m^3	2450	2450	2450	2450
Threshold value (Cc) % by wt. of concrete	0.15958	0.15958	0.15958	0.15958
Diffusion coefficientm^2/s	6.233 x10^{-13}	5.814x10^{-13}	5.4915 x10^{-13}	5.2385 x10^{-13}
Surface chloride(Cs) % by wt. of concrete	0.26	0.3	0.34	0.36
Initial chloride content (% wt of concrete)	0.01435	0.01435	0.01435	0.01435
Initiation time in years	19.467	38.93	60.83	94.2

4.4 Carbonation Test for Concrete

The use of phenolphthalein indicator helps in determining the amount of carbonation in the concrete sample. Samples were cut perpendicular to the exposed surface and phenolphthalein indicator was poured on the freshly cut surface[24]. If the color changes from pink to colorless, then the concrete is affected by carbonation. Figure - 3 shows no change in the colour of specimens in the carbonation test.

5. DISCUSSIONS ON RESULTS

5.1 Chloride Profile

Water soluble chloride (WSC), acid soluble chloride(ASC) and bound chloride (BC) are determined from the experiments and are presented in Table –2. WSC represents the free chloride and ASC denotes the total chloride present in the concrete. BC corresponds to chemically bounded chloride to concrete. From Table-2 and Figure-3 and Figure-4, it is found that chloride contents for ASC and WSC decrease as depth of concrete increases from exposed surface. The results shows good agreement with the profile presented by Matthew and Pritzl [23] The outcome may be due to the fact that concrete is denser towards interior. Also interior concrete is less exposed to moist condition, which is mostly responsible for diffusion process.

It was also noted that bound chloride (BC) content (Figure – 5) in surface zone and those of in interior zone are more or less same without much variation. BC is the difference between ASC and WSC, and both ASC & WSC are decreasing uniformly towards interior from surface.As a result, BC remains almost constant from surface towards interior.

Figure - 6 represents the variation of surface chloride with age of concrete. Surface chloride increases up to 35 years of age and then decreases. This may be attributed to the leaching of chloride from the surface zone on long period of exposure and the results are similar to those found by Weerdt et.al.[25]

5.2 Diffusion Coefficients

Diffusion coefficients for different depths are presented inTable-4. Diffusion coefficients found to very from 6.8 x10^{-13} m^2/sec to4.867 x10^{-13} m^2/sec. Other researchers have found to be1x$10^{-7}$$m^2$/sec to5.73 x 10^{-12} m^2/sec [14,15] .Most of them adopted rapid chloride penetration or adopted continuous chloride diffusion in natural marine environment .Therefore actual period of corrosion process are known and reflected in calculation of corrosion initiation time. The diffusion coefficients calculated in present study may be accepted as average annual diffusion coefficient (D_{ava}).Figure –7shows the variation of those diffusion coefficients with depth of concrete. The diffusion coefficient decreases with increase in depth of concrete. As the impermeability of concrete increases with the depth, the diffusion coefficient decreases. From Table-4, it is found that chloride diffusion coefficient decreases with age of concrete. Therefore, chloride diffusion coefficient values obtained for concrete of age group 35 to 45 years is important and should be used for calculation of corrosion initiation time.

5.3 Corrosion Initiation Time

The corrosion initiation time also calculated using Fick's law (Equation - 5)for different cover depths such as 15 mm, 25 mm,35 mm and 45 mm at threshold level based on total chloride . Details of values of parameters considered in this calculation are presented in Table –5.It basically depends on surface chloride contents. It is found that corrosion initiation time for 15 mm,25 mm 35 mm and45 mm thick cover are 19.467 years , 38.93 years , 60.83 years and 94.2 years respectively which seems to be relevant to real structures .

5.4 Carbonation

Figure-8 shows the colour change of specimens after spraying phenolapthylene indicator. Pink colour developed in entire cut section which represents that the concrete samples have been least affected by carbonation. This indicates that in coastal areas principal reason for corrosion of steel in concrete is chloride diffusion.

6. CONCLUSION

Based on the above experimental results and discussions thereafter, following conclusions may be drawn.

1. The case studies show that the corrosion initiation takes place to therein for cement in normal weight concrete of age group 35 to 40 years.
2. It is difficult to ascertain the actual time for which corrosion process continues inside the concrete depending wetting and drying period in a year in actual structures. Therefore chloride diffusion coefficient computed in this study is in annual average basis (D_{ava}) .This value seems to provide good convergence towards actual value of corrosion initiation time in real structures.
3. Chloride diffusion coefficient decreases with age of concrete. Therefore chloride diffusion coefficient values obtained concrete of age group 35 to 45 years is important and should be used for calculation of corrosion initiation time.
4. Health monitoring of the reinforced concrete structures of age group 15 years and more should be donein term of corrosion initiation time as proposed in this study. If the structure is found to be more vulnerable to chloride attack, precautions should be taken to check the chloride migration in to the concrete by adopting proper maintenance.
5. The values of chloride threshold, initial chloride content and chloride diffusion coefficient decided in present study can be utilized for determination of corrosion initiation time for costal concrete structures on East coast region of west bangle, Orissa and Andrapradesh.

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