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ALTERNATE APPROACH FOR LIMITING CHLORIDES IN CONCRETE MIX

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ABSTRACT

Chloride is considered as an important parameter in concrete as it accelerates corrosion of reinforcement, which is one of the main causes of deterioration of reinforced concrete structures. Different Codes describe different limits for either one or more constituents of concrete. The Indian Standard 269 – 2013 "Ordinary Portland cement, 33 grade – fifth revision" prescribes a limit of total chloride content in cement used in prestressed concrete structures and long span reinforced concrete structures, while Indian Standard 456- 2000 "Code of practice for plain & reinforced concrete – fourth revision" imposes a limit of total amount of chloride (as Cl) in the concrete at the time of placing, without any mention about the methodology of determining the total amount of chloride (acid soluble or water soluble). Further, Italian standard prescribes limit for aggregates. American Concrete Institute (ACI) publication has given a new direction to the study of chloride induced corrosion by taking limit of water soluble chloride in concrete mix as the criteria for evaluation of risk of corrosion. This novel & improved approach which avoids confusion in interpreting specifications and results, was applied to some concrete ingredients samples received from a Nuclear Power Project of coastal region of India. The alternate approach suggested in this Paper does away with te laborious process of casting cubes and and waiting for twenty eight days before test could be carried out. Where different quarries of coarse and fine aggregates have been identified, the alternate approach can at the initial stage itself rule out of the possibility of casting cubes of different grades of concrete mixes, resulting in time saving and economy.

1. INTRODUCTION

Portland cement concrete generally provides adequate protection of embedded materials against surface corrosion. However, the degree of protection of reinforcement depends upon the alkalinity around reinforcement and relatively high electrical resistivity on atmospheric exposure. The degree to which the concrete provide satisfactory protection in most instances is the function of the quality of the concrete, the depth of concrete cover and the degree to which the good practices are followed throughout entire construction operation. The damage of concrete structures from corrosion of embedded steel manifests in the form of expansion, cracking and spalling of the concrete cover.

2. MECHANISM OF STEEL CORROSION OF REINFORCEMENT:

The mechanism of corrosion of reinforcement is essentially due to either in stand alone or in combination of factors such as carbonation of concrete, chloride attack and sulphates diffusing into the body of concrete and subsequently coming into contact with reinforcing steel. These factors substantially reduce the alkalinity around steel component & facilitate corrosion process. Chloride attack on reinforcing steel in concrete has been well documented. Chloride ion in mixing and curing water or water soluble chlorides from the atmosphere or ground water or from concrete ingredients, reaches the reinforcing steel.[1]

As the water permeability of concrete varies in a given section, there will always be different ionic concentration at the interface of concrete and the embedded steel. Corrosion cells form anode and cathode at the higher and relatively lower chloride ion concentration regions respectively. Formation of corrosion cell results in pitting corrosion. As chloride attack is an electro- chemical process, it changes the chemistry of steel affecting the ductility properties of the bars too. [6]

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Without oxygen at anode

$Fe + 2Cl^- \rightarrow Fe^{+2} + 2Cl^- + 2e^-$

$Fe^{+2} + 2Cl^- + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2Cl^-$

In presence of oxygen at anode

$6(Fe^{+2}+2Cl^-)+O_2+6H_2O \rightarrow 2Fe_3O_4+12H^+ +12Cl^-$

Chloride acts as catalyst in corrosion of steel and becomes free to take part in corrosion reaction again.

Attack on hydrated paste

$Ca(OH)_2+MgCl_2 \rightarrow CaCl_2+Mg(OH)_2$

$3CaO.Al_2O_3.6H_2O + CaCl_2 + 4H_2O \rightarrow 3CaO.\ Al_2O_3.CaCl_2\ .10H_2O$

3. LIMITS OF CHLORIDE

Chloride content as water soluble state in concrete in combination with oxygen and moisture can cause corrosion of embedded metals in concrete. Unfortunately, chlorides are among the most abundant materials on earth. Therefore, it is not practical to specify a maximum chloride content of "zero" for a concrete mixture. Because of this fact, the American Concrete Institute (ACI) has established some practical limits for chloride ions in concrete based on service conditions. Tables 1 reproduces the recommendations of ACI 222R, "Protection of Metals in Concrete against Corrosion. [4]

Table 1: Chloride Limits for New Construction

Category	Chloride Limit for New Construction (% by Weight of Cement)		
	Test method		
	Acid soluble	Water soluble	
	ASTM C 1152	ASTM C 1218	ASTM C 1524 (Soxhlet)
Prestressed concrete	0.08	0.06	0.06
Reinforced concrete in wet conditions	0.10	0.08	0.08
Reinforced concrete in dry conditions	0.20	0.15	0.15

1 Taken from Table 3.1 in ACI 222R-11

2 The Soxhlet test method is described in ACI 222.1

On hydration of cement, 90% of chlorides react with aluminium and ferrites to give solid tricalcium chloroaluminate and tetra calcium chloroferrite. Thus only 10% of the chloride which remains in the pore fluid of concrete and chloride present in aggregate interstices is responsible for corrosion. Safe limit of chloride in cement is 0.05% for prestressed concrete as per Indian Standard [2] and no limit has been given for aggregates. IS 456-2000[3] prescribes a limit of chloride content as 0.15% by wt. of cement in concrete. However, no distinction has been made whether the limit is for water soluble or acid soluble chlorides. Moreover, no limit has been specified for other types of concrete such as prestressed concrete or reinforced concrete. Whenever there is chloride in concrete there is an increased risk of corrosion of embedded metal. The higher the chloride content, the greater is the risk of corrosion. All constituents may contain chlorides and concrete may be contaminated by chlorides from the external environment. To minimize the chances of deterioration of concrete from harmful chemical salts, the levels of such harmful salts in concrete coming from concrete materials, that is, cement, aggregates water and admixtures as well as by diffusion from the environment should be limited.

3.2 The limits of chloride ion content to be taken for different types of concrete under different environment have been sorted out in ACI publication ACI 318-95/318R-95 [5]. Limits of water soluble chlorides given are reproduced in Table-2.

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Table 2: Maximum chloride ion content for corrosion protection of reinforcement

Type of member	Maximum water soluble chloride ion (Cr) in concrete, percent by weight of cement
Prestressed concrete	0.06
Reinforced concrete exposed to chloride in service	0.15
Reinforced concrete that will be dry or protected from moisture in service	1.00
Other reinforced concrete construction	0.30

For corrosion protection of reinforcement in concrete, maximum water soluble chloride ion concentrations in hardened concrete at ages from 28 to 42 days contributed from the ingredients including water, aggregates, cementitious materials, and admixtures shall not exceed the limits given in Table 2. When concretes are tested for soluble chloride ion content, the tests should be made at an age of 28 to 42 days. The limits in Table 2 are to be applied to chlorides contributed from the concrete ingredients, not those from the environment surrounding the concrete. The chloride ion limits in Table 2 slightly differ from those recommended in ACI 222R (Table 1).

For reinforced concrete that will be dry in service, a limit of one percent has been included to control total soluble chlorides. Table 2 includes limits of 0.15 and 0.30 percent for reinforced concrete that will be exposed to chlorides or will be damp in service, respectively. These limits compare to 0.10 and 0.15 recommended in ACI 201.2R. ACI 222R recommends limits of 0.08 and 0.20 percent by weight of cement for chlorides in prestressed and reinforced concrete, respectively, based on tests for acid soluble chlorides, not the test for water soluble chlorides required here. The total acid soluble chloride content should be calculated from the mix proportions and the measured chloride contents of each of the constituents. Wherever possible, the total chloride content of the concrete should be determined,

4. NOVEL TECHNIQUE FOR DETERMINATION OF TRACES OF CHLORIDE

It is evident from Table 1 that the limit of water soluble chloride in concrete is very low. Conventional volumetric method has limitations for estimating chloride in concrete ingredients as it cannot estimate very low levels of chloride ion content. A method using Atomic Absorption Spectrophotometer (AAS) found useful to determine trace level of chloride ion. It involves precipitation of chloride as silver chloride by adding known amount of silver nitrate solution in water or acid extract od the sample. The precipitate of silver chloride is removed either by filtration or centrifugation technique. The concentration of excess silver in solution is determined by AAS. This method gives accurate and reproducible results as compared to the conventional methods.

5. ALTERNATE APPROACH

Determination of water soluble chloride in concrete as required in Table 1 is time consuming process. It requires casting of concrete cubes and curing for 28 days before taking up the analysis work. In order to avoid confusion in interpreting specification and test results, ACI-318 Building Code[5] suggests that each ingredient of concrete to be tested individually for total or acid soluble chloride content. Then, if the calculated total chloride content of concrete is below the applicable limit, further test would not be required. If the total chloride content in the ingredients is higher than the applicable limit, concrete samples would have to be made and ground up samples tested by water soluble method after curing for 28 days. This approach is less time consuming and interpretation of chloride limit becomes easy for corrosion point of view. By taking into consideration individual chloride ion contributions for assessing its potential contribution towards corrosion, a more in-depth approach is being adopted.

6. EXPERIMENTAL WORK

Few cement, coarse aggregate and fine aggregate samples received from Nuclear Power Project of coastal region of India were analysed in this laboratory for acid soluble chloride content. Results obtained are presented in Table 3 &4.

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Table 3 : Observations of chloride ion in concrete ingredients

Sl No	Acid soluble chloride, % by wt. of sample			Chloride in water, %
	Cement	Coarse aggregate	Fine aggregate	
1.	0.080	0.000922	0.000489	0.0023
2.	0.017	0.000896	0.000883	-
3.	-	0.000472	0.000814	-
4.	-	0.000879	0.000336	-
5.	-	0.000901	-	-
6.	-	0.000514	-	-
7.	-	0.000523	-	-
8.	-	0.000923	-	-
9.	-	0.000510	-	-

Table 4: Chloride ion in concrete grades

Sl No	Concrete Ingredients↓	Concrete Mix			
		M 20	M 30	M40	A40M25
1.	Cement, Kg/M^3	336	472	531	500
2.	Coarse aggregate, Kg/M^3	1155	1115	1250	1050
3.	Fine aggregate, Kg/M^3	831	550	425	450
4.	Water, Kg/M^3	179	219	195	230
5.	Admixture, Kg/M^3	-	-	-	1.5
		Acid soluble chlorides, % by wt.			
6.	Acid soluble chloride in cement, %	0.080	0.080	0.080	0.080
7.	Acid soluble chloride in Coarse aggregate, %	0.000923	0.000923	0.000923	0.000923
8.	Acid soluble chloride in Fine aggregate, %	0.000883	0.000883	0.000883	0.000883
9.	Acid soluble chloride in Water, %	0.0023	0.0023	0.0023	0.0023
10.	Acid soluble chloride in admixture, %	0.00249	-	-	0.0068
11.	**Total (Acid soluble) chloride in Concrete, %**	**0.0866**	**0.0841**	**0.0841**	**0.0909**

It is evident from the above table that acid soluble chloride in all the four concrete mixes are within the limit prescribed in ACI document and the least corrosion is to be expected. Based on the above, it is also possible to infer for all the coarse and fine aggregate samples from different quarries. Necessarily, all of them are within safe limits from corrosion point of view. This approach is simple and lot of time was saved. Conventional approach of casting cubes and waiting for 28 days was done away.

7. CONCLUSION

Determination of chloride content in concrete/ingredients is a must to understand corrosion of the reinforcement. The effect of water soluble chloride portion (about 90% of of total chloride content) is detrimental on the corrosion of reinforcement.

At present, ACI Code gives better understanding of chloride limits specifically in RCC.

The alternate approach suggested in this Paper does away with the laborious process of casting cubes and waiting for 28 days before test could be done. Where different quarries of coarse and fine aggregates have been identified, the alternate approach can be adopted at an initial stage itself. This approach can rule out the possibility of casting cubes in different permutation and combination of concrete mixes.

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