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Corrosion Control in Concrete Using an Admixture

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Abstract*-Day by day increase in environmental pollution plays a vital role to cause corrosion in concrete, which necessitate the researchers to focus on this area, to arrive the feasible solutions. Among the various corrosives, chlorides plays an important role by virtue of its high penetrating power, mobility, low activation energy for depassivation and size(among halogens) The present research work was aimed at reduction of free chloride content in the concrete by using 'Lead Oxide' as an admixture. The study was conducted with different proportions of admixture varies from 5 to 20% with an increment of 5% for different curing periods (3 to 28 days) to determine the optimum percentage of reduction of free chloride content in the concrete. From the experimental investigations carried out, it was evident that use of lead oxide as an admixture can be effectively employed in fixing the free chloride which reduces the corrosion in concrete. It was also observed that, there was an increase in the compressive strength of concrete. The outcome of this research work provides a low cost solution for corrosion in concrete structures.

***Index Terms*-Admixture, Concrete, Corrosion, Lead Oxide.**

I. INTRODUCTION

Reinforced concrete is a composite consisting of steel and concrete, which, in itself, is another heterogeneous material consisting of cement and aggregates, with varied shape, size, configuration and orientations. During service, the reinforcements almost invariably undergo rusting, by dint of variable porosity (caused by non-homogeneity), and the principle 'Rust promotes further rusting'. In fact, practically all environments are corrosive to some degree (air, moisture, fresh, industrial atmospheres, steam-Chlorine, Ammonia, fuel-gases, sulphur dioxide, organic-inorganic acids, Alkaline, solvents, vegetable, petroleum oils, and so forth.). In general, inorganic materials (viz, sodium chloride, sulphur, Hydrochloric, and sulphuric acids, water etc) are more corrosive than the organics (viz, oil, naphtha, gasoline etc) and therefore, of late, there has been major interest in developing technology for corrosion control by treating inorganic substances.

Free chloride content in concrete has been found to be one of the major causes of the corrosion in reinforcing steel bars.' In fact, in the marine environment most of the damages of concrete structures can directly be attributed to chloride and chloride content of the concrete. The qualities of chloride that proves its high corrosion potential are[4]:

i) Its repeated use in corrosion reaction,
ii) Its capacity to sustain the corrosion even at a smaller proportion.
iii) Its high penetrating power and aggressiveness due to small size (Ionic radius of chloride is 1.81A in contrast to that of sulphate ion which is 2.3A°
iv) Its high mobility and least activation energy for depassivation.

Thus, intensive studies have been carried out to reduce free chloride content of concrete using various admixtures.' In general, the various admixtures added in concrete are accelerators, retardors, water reducers, super plasticizers, air entraining agents and corrosion inhibitors. The corrosion inhibitors can be of two types: mineral admixtures (fly ash, blast furnace slag, micro silica etc.) and chemical admixtures (normally commercial chemicals). In this work, studies have been carried out for fixation of free chloride in concrete and thereby reduce the corrosion susceptibility by selecting from six commercially available chemicals as admixture, based on their cost and performance studies. During these studies, a threshold percentage of sodium chloride (i.e., 3 % w/w) was deliberately added to the concrete to meet the minimum corrosion initiation requirement (i.e., 0.4 % by the weight of cement, which amounts to 4000 ppm), because the aggregate material used contained 45 ppm of chloride.

II. EXPERIMENTAL WORK

A. *Selection of Admixture*

The chemicals used for selection for the studies were selected based on the following criteria: (i) increase in the degree of chloride fixation in the concrete, (ii) creation of a barrier film on the steel, (iii) increase in the resistance of the passive film on the steel to breakdown by chlorides, (iv) possession of good solubility characteristics (but not leach out from the concrete), (v) ability for moderate to low adsorption by cement paste, so that the major amount of the added admixture is available to inhibit corrosion and (vi) compatibility with other admixtures used in concrete.

The chemicals selected for use as chloride-scavengers are: magnesium oxide, sodium thio-sulphate, titanium oxide, zirconium oxide, lead oxide and sodium alginate. The selection of suitable chloride scavenger was carried out with respect to compressive strength, reduction of chloride content, degree of workability, alkalinity and the market cost of the chemical etc. Table1 gives the detailed analysis of these six scavengers for the above mentioned parameters.

As indicated by Table I, lead oxide, zirconium oxide and titanium oxide give approximately the same compressive strength and chloride-sorption. However, since lead oxide is cheaper than zirconium oxide and titanium oxide, the former is selected for the studies. In fact, lead oxide is an industrial waste from thermal processes, and therefore utilization of this compound as concrete admixture would be useful not only as a chloride scavenger in concrete, but as an environmental control measure as well.

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TABLE I. Chemical and strength analysis of chloride Scavengers

S. No	Admixture	Chemical Symbol	7-Days compressive strength N/mm^2	Free-chloride ppm	Reduction in chloride level%	Cost/ 500g Rs	Degree of workability	Alkalinity pH	Comments
1	Cement grout+3%Nacl (C)	-	20	8300	0	-	Low	12.3	-
2	C+ sodium thiosulphate (10%)	$Na_2S_2O_3$	14.44	Confusing result	-	150	Low	-	Reduce compressive strength sulphate attack
3	C+ magnesium oxide (10%)	MgO	17.77	-	-	225	Very low	-	Reduce compressive strength require 26% increase in W/C
4	C+Zirconium oxide (10%)	ZrO	23	6123.75	26.2	800	Medium	12.1	Compressive strength increased,chloride level Reduced
5	C+Titanium oxide (10%)	TiO	22.22	5900	28.9	500	Medium	12.2	
6	C+ lead oxide (10%)	PbO	22.67	6035	27.3	130	Medium	12.2	
7	C+ sodium alginate (10%)	$C_6H_7O_6Na$	-	-	-	650	Very low	-	Not set

B. *Material Characterization*

The constituent and the details of the materials used for the concrete used in this work are presented in Tables 2 and 3.

TABLE II. List of the Constituent materials

	Description
	OPC-Dalmia(43grade)
	Local river sand(Zone III of IS 383-1970);Fineness modulus 2.7,Specific Gravity 2.5
Coarse Aggregate	20mm normal size aggregate; Fineness modulus 7.6,Specific gravity 2.8
Chemicals used	Lead Oxide, Sodium Chloride
Water	Potable water

TABLE III. Detail of the specimen

Samples	Tests	Remark
Concrete Cube (150 x150 x150mm)	Compressive strength	Curing time:3,7,14,21& 28 days for each proportion No of Specimen: 3 each proportion and curing time
	Chloride test	Interval: 7,14,21 &28 days Sampling: from crushed cubes
	Alkalinity	
	Workability, Consistency & Setting Time	Studies on fresh Concrete Mix
Cement grout	Chloride test	Sampling: from crushed cement grout cubes(after 21 days of atmospheric exposure)
	Alkalinity	

[Mix proportion=1:1.9:4.1 by weight, water cement ratio=0.58]

The sample was made with four proportions of admixture (viz 5%, 10%, 15% and 20% by weight of cement) in addition to the control.

C. *Preparations and Study of Various Parameters Of Cement Grout And Concrete Cubes.*

The 43 Grade Ordinary Portland Cement (100gm), water (200m1), analar grade sodium chloride (3gm) and the various proportion (namely, 0%, 5%, 10%, 15% and 20% by weight of cement) of lead oxide were added as separate sets. The mixture (i.e. admixed cement grout), thus obtained, was crushed mechanically, and the powder was tested for free chloride (using the silver nitrate titration method) and alkalinity (in terms of pH by digital pH meter) and as prescribed by APHA (2000).

To study the characteristics of the admixed concrete, the water: cement ratio was kept as 0.58 and the proportion of ingredients was maintained to be 1: 1.9: 4.1. After 24 hours of setting the cubes (150mm X 150mm X 150mm) were remolded and cured by complete immersion in water for 7, 14, 21 and 28 days. The setting time and workability were also studied in addition to the study of compressive strength, using Vicat's Apparatus, Slump-Cone. Test and Compression Testing Machine (capacity = 1000KN), respectively. The free chloride content of the crushed concrete cubes were studied for each of the above mentioned curing time, using the method employed for cement grout.

III. Results and Discussion

Since the analysis of various ingredients of concrete such as cement, fine aggregate, coarse aggregate and water are

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found to have very low chloride content (viz. 8 mg/I, 14 mg/I, 23 mg/I, respectively), as discussed in preceding paragraphs, an extra chloride has been added and their effects were studied with respect to various parameters.

A. Study on Cement Grout

The effect of lead oxide admixture on the chloride content of the cement grout is presented in Table IV.

TABLE IV. Percentage of chloride removed in pure cement grout

S. No	Cement grout formulations	Free chloride content (ppm)	Free chloride level Reduction percent(FCLR)
1	Cement grout + 3% Nacl (C)	8520	0.00
2	C + 5% Pbo	8340	02.11
3.	C +10% Pbo	7630	10.50
4	C + 15% Pbo	7460	12.50
5	C + 20% Pbo	7498	11.99

The degrees of alkalinity of the various cement grout formulations do not show any significant variation irrespective of the lead oxide proportion. In fact, the maximum alkalinity variation in all samples is less than 1% (which is less than maximum experimental error for alkalinity determination, i.e. 2.5 °/0). Thus, alkalinity of the grout is not affected by the admixture content.

The reduction in chloride percentage, however, varied from 0% (for cement grout without admixture) to 12.5°/0(for cement grout with 15% lead oxide). Since the variation between percentage free chloride level reduction (FCLR) for cement grout with 10% lead oxide and that with 15% lead oxide (i.e. 2%) is less than the experimental error (or chloride determination, maximum 3%), the former is found to be optimum proportion of lead oxide for FCLR. Note: The FCLR for cement grout with 5 % lead oxide (i.e. 12.1%) and for that with 10% lead oxide (i.e. 10.5%) is significant (8.5%). The reduction in chloride percentage varied from 0°/0 (for cement grout without admixture) to 12.5% (for cement grout with 15% lead oxide).As mentioned before 3% sodium chloride has been added with the cement grout in each of the cases to attain the threshold free chloride content for initiation of corrosion. The experimental error was found to be less than 3%. Since the variation between percentages free chlorides level reduction (FCLR) for cement grout with 10% lead oxide and that with 15% lead oxide (i.e. 2%)is less than the experimental error(3°/0) . The former is found to be optimum proportion of lead oxide for FCLR. [Note: The FCLR for cement grout with 5% lead oxide (i.e. 12.1%) and for that with 10% lead oxide (i.e. 10.5%) is significant (8.5%)].

B. Study on Concrete

The study of consistency showed almost constant (31 %to 33 %) and standard values for both the control and the blended concrete indicating its constancy in relation to the admixture used. However initial setting time as well as final setting time given in Table V and show the distinct rise with increasing lead oxide content in the concrete as per BI standard for OPC recommends.(i.e., the initial setting time to not less than 30 minutes and the final setting time to not more than 600 minutes). Thus, the maximum allowable content of lead oxide should be less that 20% (in which case final setting time is more than 600 minutes).

TABLE V. Setting time of the Concrete Formulations

S. No	Mix	Consistency %	Initial Setting Time(min)	Final setting Time (min)
1	Cement (c)	31	30	300
2	C+3%Nacl	32	150	400
3	C+35Nacl+5%PBO	31	165	480
4	C+35Nacl+10%PBO	32	180	540
5	C+35Nacl+15%PBO	33	210	570
6	C+35Nacl+20%PBO	35	248	620

The study of workability for the specimens (i.e. control and concrete with different percentage of lead oxide) indicates the decrease in slump with increase in amount of lead oxide in the concrete is given in Table VI. It is also observed that the initial addition of sodium chloride makes a significant improvement in the workability of the concrete formulation. Since control of corrosion is applicable for concrete with reinforcement and RCC necessitates medium to high workability, initial addition of sodium chloride is further justified. The require range of workability in terms of slump for normal RCC construction is 50 to 100 and therefore based on this studies all the concrete formulations with 5% to 20% lead oxide are found to be suitable.

TABLE VI. Workability of the concrete Formulations

S. No	Concrete Formulations	Slump in mm	Degree of workability
1	Cement (c)	27	Low
2	C+3%Nacl	120	High
3.	C+3%Nacl+5%PBO	20	Low
4	C+3%Nacl+10%PBO	80	Medium
5	C+3%Nacl+15%PBO	75	Medium
6	C+3%Nacl+20%PBO	50	Medium

The alkalinity of all the concrete formulation display a strikingly the constant value (PH 13) for both cement grout and the concrete irrespective of the amount of admixture as well as the duration of curing. This means, the alkalinity of the concrete is not affected because of addition of lead oxide this finding is in consonance with studies on use of lead of oxide other chlorine scavenging admixture such as aluminum oxide. In fact the high alkalinity of all the concrete formulations studied may be expected to affect the microstructure and the hydration of the cement paste.

Table IV shows chloride removal in the concrete. In case of concrete, however, the FCLR shows increase of more than 30% for concrete with 15% lead oxide (Table4.4). In fact the optimum FCLR corresponds to the concrete with higher % of lead oxide (15%) than that of the cement grout (10%). However it is observed that the percentage increase in FCLR

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from 5% lead oxide mixed concrete to 10% still remains the highest (12.6%) like that of cement grout. It is also noted that the FCLR does not show much variation with respect to the curing time especially for higher percentage of lead oxide mixer i.e., for more than 10%.

Table VII also shows improvement with increasing curing time. The maximum percentage of FCLR is observed for the concrete with 15% lead oxide (35.2%).Fig 1 shows the variation of FCLR with curing time. The rate of chloride removal shows less variation with respect to time for higher % of lead oxide (15 — 20 %). The concrete with 15 and 20% lead oxide behave almost the same way with respect to FCLR. Fig 2 shows that the FCLR percentage is higher in case of concrete than in cement grout. This may be because of higher level of porosity available in concrete that the cement grout allowing the better participation of chloride in the bonding leading to less free chloride availability. Here also concrete with 15% lead oxide showed better or equal performance with respect to FCLR both in the case of cement grout and concrete.

TABLE VII. Compressive strength of concrete

S. No	Concrete Formula - tions	Curing time in days							
		7		14		21		28	
		FC (ppm)	RC (%)	FC (ppm)	RC (%)	FC (ppm)	RC (%)	FC (ppm)	RC (%)
1	Concrete + 3% Na Cl (c)	2840	0.0	2660	0.0	1775	0.0	1595	0.0
2	C+5% Pbo	2800	1.4	2310	13.2	1680	9.4	1420	11
3	C+10% Pbo	2130	25	1950	26.7	1365	23.1	1240	2.3
4	C+15% Pbo	1900	33.1	1775	33.3	1150	35.2	1050	34.2
5	C+20% Pbo	1915	32.6	1756	33.9	1151	35.1	1057	33.7

The compressive strength of the different concrete formulation is presented in Table VIII. There is distinct improvement in the compressive strength of the concrete with the increasing the lead oxide content as indicated in Fig 3 we find the concrete with 15% lead oxide showed the maximum improvement in compressive strength in entire curing duration (Viz:3,7,14,21 &28 days). It is interesting to note that (Fig 4) the concrete with 20% lead oxide behaves very much similar to the concrete with 10% lead oxide. The optimum strength improvement is observed for the concrete with 15% lead oxide. The study on incremental improvement of compressive strength (C,,) with curing time for each of the concrete formulation studied showed that the maximum rate of improvement is observed between 7 — 14 days than that after 14 days and this variation (7 — 14 days and 14 — 28 days) reduces with higher percentage of lead oxide content. This means, although the rate of hydration is faster in the first 14 days than the rest, yet increase in lead oxide content lowers the hydration rate. Thus, the addition of lead oxide causes distinct improvement in early compressive strength.

TABLE VIII. Compressive Strength of concrete

S. No	Cement grout formulation	Curing time days Compressive strength N/mm^2				
2	C (W/C =0.58)	12.90	20.00	22.22	25.77	26.67
3	C + 3% Nacl	16.6	23.55	26.44	27.55	29.33
4	C+ 5% Pbo	18.11	23.11	28.89	31.11	35.15
5	C+3%Nacl+5%PBO	19.11	31.55	34.67	35.11	35.55
6	C+3%Nacl+10%PBO	28.22	34.22	35.33	37.77	40.44
7	C+3%Nacl+15%PBO	30.22	35.55	36.44	38.40	41.33
	C+3%Nacl+20%PBO	28	34.20	36	38.21	40.12

Note: C = Control 1:1.9:4.1 with W/C 0.58
Cube size 150mm x 150ifirn x 150rnm
[Note: FC = Free chloride contents
RD = Reduction in chloride level
C = Control]

IV. CONCLUSION

The studies presented a novel method of chloride reduction in concrete using lead oxide, as a chemical admixture. Although lead oxide marginally delays the setting time with respect to the OPC, yet the improvement of workability, invariability of alkalinity, better compressive strength, free chloride removal, certainly, proves its viability and robustness in concrete formulation. In fact, the optimum percentage of chloride removal was found to be more than 35 % and the maximum compressive strength obtained was 41.3 N/mm2 (showing an improvement of 60 to 140%). In fact, the admixed concrete show early high strength compared to OPC. The studies also provide an optimization of lead oxide admixture content with respect to various parameters, which was found to be 15 % of the weight of cement. A further study of the effect of reduction of gypsum content in the cement (to improve the setting time) on the chloride removal and compressive strength improvement can be helpful.

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