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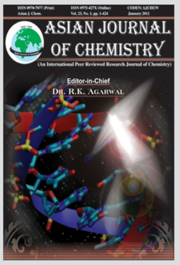

Chemical Reaction of Waterproofing Admixtures on the Corrosion Behaviour of Reinforced Cement Concrete

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This paper deals about the corrosion behaviour of reinforced cement concrete using waterproofing admixtures. This addition of waterproofing admixtures turns concrete into a construction material in harmony with sustainable building development. The addition of waterproofing chemicals also increases the various strength of concrete. These studies were carried out by conducting accelerated corrosion test over the concrete specimen with and without chemicals for various dosages and curing period of 28 days. The cubical specimens of size 150 mm × 150 mm × 150 mm have been taken for this test. The contribution of waterproofing admixtures was found more in the corrosion behaviour of reinforced cement concrete since it reduces the permeability and improves the corrosion resistance.

Key Words: Admixtures, Concrete, Corrosion, Durability, Permeability, Waterproofing.

INTRODUCTION

Physical adsorption, chemical adsorption and chemical reactions may occur between the admixtures and the hydrating components of cements. Physical and chemical changes occur when admixtures such as accelerators, retarders[1], waterproofing admixtures, water reducers and superplasticizers are added to the cement-water system. Mechanisms of the action of admixtures, changes in water demand, viscosity, setting, slump loss and shrinkage, kinetics of hydration, microstructure, strength and durability of fresh and hardened cement pastes can be explained by the interaction effects. Concrete has traditionally been regarded as a durable material requiring little or no maintenance[2]. However experience shows that this is not the case, many concrete structures are now showing signs of deterioration despite being only 20-30 years old. The major cause of deterioration is the chloride contamination of concrete and hence reinforcement corrosion.

Chemical admixtures confer certain beneficial effects on concrete, including reduced water requirement, increased workability, controlled setting and hardening, improved strength and better durability. Many approaches have been adopted to investigate the role of chemical admixtures. One approach is to determine the state of the admixture in concrete at different times of curing. The admixture may remain in a free state as a solid or in solution, or interact at the surface or chemically combine with the constituents of cement or cement paste[3]. The type and extent of the interaction may influence the physico-chemical and mechanical properties of cement paste. In this paper an attempt is made to discuss the possible interactions of different types of chemical admixtures in the cement-water system, with particular reference to the changes in physico-mechanical properties.

The permeability of concrete determines the ease with which gases, liquids and dissolved deleterious substances such as carbon-dioxide or oxygen or chloride ions penetrate the concrete. If the corrosion process has started the rate of corrosion is still dependent on the supply of oxygen[4]. The permeability of concrete is a major factor affecting the service life of reinforced components. Addition of waterproofing admixtures reduces the permeability of concrete and thus protects the reinforcement for corrosion.

Corrosion of reinforcement: Due to the high alkalinity of concrete a protective oxide film is present on the surface of steel reinforcement[5]. The protective passivity layer can be lost due to carbonation. This protective layer can also be lost due to the presence of chloride in the presence of water and oxygen. In reality, the action of chloride in inducing corrosion of reinforcement is more serious than any other reasons[6].

Mode of action: The reinforced steel in concrete is in highly alkaline environment due to the formation of calcium hydroxide, formed by the hydration of cement. At this environment of higher alkalinity, reinforcement is protected by the passivate layer of ferric oxide, it is not initiate any corrosion. If the passivate layer is destroyed by any corrosion influencing factor, that the ferric oxide is reduced in to ferrous oxide, it initiate corrosion.

Reinforced steel is manufactured and exposed to the atmosphere; sufficient oxygen and moisture are available to react with steel[7]. Oxidation of iron molecules naturally occurs. Corrosion of steel in concrete is an electrochemical process. When there is a difference in electrical potential along the steel reinforcement in concrete, electrochemical cell is setup. Steel becomes active or passive. In the steel one part becomes anode and other part becomes cathode. They connected by electrolyte in the form of pore water in the hardened cement paste.

If the steel is active (more negative potential), the solid steel surface dissolves and goes into the solution as ferrous ions. This is called anodic reaction.

$$\text{Fe (solid)} \rightarrow \text{Fe}^{2+} \text{ (ions)} + 2e^- \rightarrow \text{to cathode}$$

Since the reaction releases electron, these electrons are simultaneously accepted in cathode, where oxygen reduction occurs. This is called cathodic reaction[8].

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \rightarrow \text{to anode}$$

$$4Fe(OH)_2^- + 2H_2O + O_2 \rightarrow 4Fe(OH)_3 \text{ (Ferric oxide)}$$

$$4e^- + O_2 + H_2O \rightarrow 4(OH)^-$$

Thus one can see that oxygen (O_2) and water (H_2O) are required to the cathode reaction, of the overall corrosion process. When concrete is dry, oxygen is able to diffuse and reach the steel[9] and when the concrete is wet, water is able to reach the steel. Corrosion is usually accompanied by the formation of solid corrosion debris from the reactions between anodic and cathodic products.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \text{ (Ferrous hydroxide)}$$

Pure Ferrous hydroxide is white but the material initially produced by corrosion is normally a greenish colour due to partial oxidation in air.

$$H_2O + \tfrac{1}{2}O_2 \rightarrow Fe(OH)_3 \text{ (Ferric hydroxide)}$$

Further hydration and oxidation reactions can occur and the reddish rust that eventually forms is a complex mixture whose exact constitution will depend on other trace elements which are present.

Chloride ingress: The best known and most damaging factor leading to corrosion is the chloride ingress. The chloride ingress can be by diffusion, capillary suction as well as by permeation. Diffusion of chloride ions occurs through slow moments through pores and capillaries in paste. Dry concrete, through simple absorption can suck in large amount of chloride-laden water, several hundred times faster than the chlorides, which can travel by diffusion. Chloride ions that diffuse to the steel surface can disrupt the passivate layer and induce corrosion[10].

$$Fe^{2+} + 2Cl_2 \rightarrow FeCl_2$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2Cl^-$$

$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3$$

Integral waterproofing admixture increase resistance to capillary absorption. When they are mixed with concrete, it has two distinct waterproofing actions. The first is the reaction of hydrophobic component with concrete mix, which fundamentally changing its surface tension, producing a concrete, which is inherently water repellent and non absorptive throughout its entire mass. It means that an increase in the contact angle between the walls of the capillary pores and water, so that water is pushed out of the pores. In the second action polymer globules moving with the bleed water during hydration collect in the capillaries. When the hardened concrete is subjected to water pressure, these globules are compacted together to form a physical plug blocking the capillaries and preventing water entry.

Chemicals such as stearates (RCOOH) are reacted with calcium hydroxide [$Ca(OH)_2$] and formed insoluble calcium stearate (Ca^+COOR^-). It coats the capillary pores.

$$Ca(OH)_2 + RCOOH \rightarrow Ca^+COOR^- + H_2O$$

Corrosion of steel in concrete is an electrochemical process, when there is a difference in electrical potential along the steel, one part becomes anode other part becomes cathode connected by electrolyte in the form of pore water in the hardened cement paste. The positively charged ferrous ions Fe^{2+} at the anode pass into solution while negatively charged free electrons e^- pass through the steel into cathode where they are absorbed by the constituents of the electrolyte and combine with water and oxygen to form hydroxyl ions $(OH)^-$. These travel through the electrolyte and combine with the ferrous ions to form ferric hydroxide which is converted by further oxidation to rust[11].

Ordinary concrete even of high quality contains capillaries and micro cracks. This allows water to pass through its structure by an action similar to tree drawing water to its canopy. Concrete absorbs water because surface tension in capillary pores in the hydrated cement paste pulls in water by capillary suction. It is called capillary absorption. An integral waterproofing admixture increases resistance to capillary absorption. When they are mixed with concrete, it has two distinct waterproofing actions.

EXPERIMENTAL

Ordinary portland cement of 53 grade is used in this investigation. The physical properties of the cement, fine and coarse aggregates are shown in Table-1.

TABLE-1
PHYSICAL PROPERTIES OF CEMENT, FINE AGGREGATE AND COARSE AGGREGATES

S. No.	Tests	Cement	Fine aggregate	Coarse aggregates
1.	Specific gravity	3.15	2.6	2.5
2.	Fineness	2 %	-	-
3	Fineness modulus	-	2.2	5.73
4.	Standard consistency	31 %	-	-
5.	Compressive strength			
	7 days	34 N/mm^2	-	-
	28 days	54 N/mm^2		
6.	Setting time			
	Initial	30 min	-	-
	Final	585 min		

According to IS 2645-1975 integral waterproofing chemicals are used. The chemicals used, properties and their dosages are given in Table-2.

For the entire test, M20 designed mix (1:1.55:3.1) was taken. The water -cement ratio is 0.55 by mass.

Preparation and casting of test specimens: Concrete specimens were cast using the cubical mould of size 150 mm

TABLE-2
CHEMICAL ADMIXTURES, DOSAGES AND PROPERTIES

S. No.	Name of the admixture	Supply form	Colour	Chloride content	Specific gravity @27 ºC	Density Kg/m^3	Dosage of admixture		
							Dosage 1	Dosage 2	Dosage 3
1.	Naphtha based	Powder	White	Nil	1.20-1.25	1225	0.8 kg/50 kg of cement	1.0 kg/50 kg of cement	1.2 kg/50 kg of cement
2.	Polymer based	liquid	Dark yellow	Nil	1.30-1.35	1320	0.1 L/100 kg of cement	0.2 L/100 kg of cement	0.3 L/100 kg of cement
3.	Melamine based	liquid	Light brown	<0.005 %	1.28-1.31	1300	0.22 L/100 kg of cement	0.33 L/100 kg of cement	0.40 L/100 kg of cement
4.	Ligno sulphonate based	liquid	Light brown	Nil	1.125	1125	0.35 L/100 kg of cement	0.4 L/100 kg of cement	0.5 L/100 kg of cement
5.	Stearate based	liquid	Dark brown	Nil	1.350	1350	0.18 L/50 kg of cement	0.20 L/50 kg of cement	0.22 L/50 kg of cement

× 150 mm × 150 mm. A reinforcement steel bar of 20 mm diameter and 300 mm long is weighed and is noted down. A cube of 150 mm × 150 mm is used for preparing the specimen. The steel bar, explained earlier is held in position and concreting is done. Care should be taken so that the rod stays in position while compacting. After 24 h, the specimens were demolded and cured in a water tank until the time of test was reached. The specimen is allowed to cure for 28 days. The specimens were cast with and without admixtures of various dosages.

Test procedure: The test setup that essentially measures resistivity of concrete consists of a constant DC supply providing constant voltage of 60 V through a shunt in a constant voltage mode and 80 million ampere in constant current mode. The test was carried out in a 6 % NaCl solution with an embedded reinforcement bar as a working electrode and a copper bar as a counter electrode. The variable parameter voltage was recorded at every 15 min interval for 6 h in constant current study. The set up is kept for 15 days without disrupting the power supply. The solution turns to reddish brown in colour due to the formation of rust. Then the specimens are removed from the set up, dried in air, visually inspected and carefully split open to access the corroded steel bar. The reinforcement bar was then cleaned as per ASTM G1 of 1981 by dipping it in Clark's solution (HCl of specific gravity 1019 L + antimony trioxide 20 g + stannous chloride 50 g) for 25 min. Each bar was weighed again to the accuracy of 0.1 mg to find out the change in weight. Fig. 1 shows the schematic view of test setup.

RESULTS AND DISCUSSION

The expected amount of corrosion in terms of mass loss of the reinforcing bar due to corrosion can be estimated by the following eqn. 1.

$$C_R = [(W_0 - W) / W_0] \times 100 \qquad (1)$$

where, C_R -expected amount of rebar corrosion; W_0 - the initial weight of the bonded length of rebar; W -the weight of the bonded length of rebar after removal of corrosion products.

The results are tabulated in the Tables 2-4. The loss of weight of rod in conventional concrete is estimated as 3.3 %. By adding the naphtha based admixture for dosage 1 of 0.8 kg/50 kg of cement, the loss of weight is estimated as 2.81 %, for the dosage 2 of 1.00 kg/50 kg of cement, the loss of weight of rod is 2.62 % and for the dosage 3 of the admixture by 1.2 kg /50 kg of cement it is decreased further by 2.35 %. While comparing with the conventional concrete, it is decreased for dosage 1 by 14.85 %, for dosage 2 it is decreased by 20.61 % and for dosage 3 by 28.78 %.

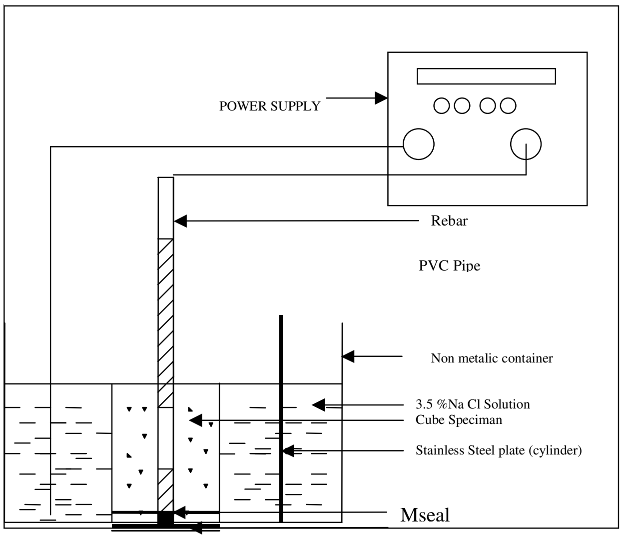

Fig. 1. Accelerated corrosion test setup.

TABLE-3
SPECIMENS WITHOUT CHEMICALS

Specimen	Initial weight of bar (g)	Final weight of bar (g)	Loss in weight (%)
Without chemical	738.35	714.58	3.22
	740.31	714.99	3.42
	736.36	712.35	3.26
		Average	3.30

TABLE-4
SPECIMENS WITH NAPHTHA BASED CHEMICALS

Specimen	Initial weight of the bar (g)	Final weight of the bar (g)	Loss in weight (%)	Average Percentage loss in weight
Dosage I	736.36	715.25	2.87	2.81
	738.37	717.47	2.83	
	739.65	719.55	2.72	
Dosage 2	735.25	715.95	2.62	2.62
	738.45	718.47	2.71	
	739.38	720.64	2.53	
Dosage 3	738.53	720.12	2.49	2.35
	736.65	720.34	2.21	
	735.35	717.85	2.37	

By the addition of polymer based admixture of dosage 1 the loss of weight is estimated as 3.12 %, for the dosage 2, the loss of weight of rod is 2.85 % and for the dosage 3 of the admixture by 2.32 %. While comparing with the conventional concrete, it is decreased for dosage 1 by 5.45 %, for dosage 2 it is decreased by 13.64 % and for dosage 3 by 29.69 %.

By the addition of ligno based admixture of dosage 1 the loss of weight is estimated as 2.88 %, for the dosage 2, the loss of weight of rod is 2.76 % and for the dosage 3 of the admixture by 2.51 %. While comparing with the conventional concrete, it is decreased by 12.73 % for dosage 1, it is decreased by 16.36 % for dosage 2 and for dosage 3 by 23.94 %.

By the addition of melamine based admixture for dosage 1 the loss of weight is estimated as 3.37 % and for the dosage 2, the loss of weight of rod is 2.95 % and for the dosage 3 of the admixture by 2.61 %. While comparing with the conventional concrete, it is decreased for dosage 1 by 6.06 %, for dosage 2 it is decreased by 10.61 % and for dosage 3 by 20.91 %.

By the addition of stearate based admixture for dosage 1 the loss of weight is estimated as 2.77 % and for the dosage 2, the loss of weight of rod is 2.57 % and for the dosage 3 of the admixture by 2.41 %. While comparing with the conventional concrete, it is decreased for dosage 1 by 16.06 %, for dosage 2 it is decreased by 22.12 % and for dosage 3 by 26.97 %.

Out of all chemicals polymer based admixtures gives better result by 2.32 % which is obtained by adding dosage 3. This is 28.78 % more than that of controlled concrete (Table-5).

Conclusion

Since the pores presented in the concrete are blocked due to the addition of waterproofing admixtures, it reduces the loss of weight in the embedded bar and thus reduces the corrosion. Increasing the dosage of admixtures reduces the permeability and thus reduces the corrosion to the reinforcement. Thus the impermeability of concrete is improved by the addition of these types of admixtures, the life of reinforced concrete structure is improved. Due to the seepage in building, not only the structure gets weakened and results in higher maintenance cost, but also causes a lot of inconvenience to the uses. By the addition of admixtures at the pre & post construction stages of buildings the problem of seepage of buildings can be minimized and controlled, and also concrete with waterproofing admixtures can be used for the structures contructed in the marine environment and under water construction. Out of all the chemicals, polymer based admixtures gives better result and hence it is recommended for field use.

TABLE-5
COMPARISON TABLE FOR % VARIATION IN LOSS OF WEIGHT WITH AND WITHOUT CHEMICAL

Specimen	Loss of weight (%)	% Variation with and without chemicals
Conventional concrete (Without chemical)	3.30	-
Naphtha Based Chemicals		
Dosage 1	2.81	14.85
Dosage 2	2.62	20.61
Dosage 3	2.35	28.78
Polymer based Chemicals		
Dosage 1	3.12	5.45
Dosage 2	2.85	13.64
Dosage 3	2.32	29.69
Ligno Based Chemicals		
Dosage 1	2.88	12.73
Dosage 2	2.76	16.36
Dosage 3	2.51	23.94
Melamine Based Chemicals		
Dosage 1	3.37	6.06
Dosage 2	2.95	10.61
Dosage 3	2.61	20.91
Stearate Based Chemicals		
Dosage 1	2.77	16.06
Dosage 2	2.57	22.12
Dosage 3	2.41	26.97

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