**3 International Symposium** <u>on Surface Protective Coatings</u>



# November 14-16, 2005

**的第三人称单数** 

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## PROTECTIVE COATINGS FOR STEEL BARS IN REINFORCED STRUCTURES

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The paper incorporates experimental results on comparative performance of various types of coatings normally applied on steel reinforcement bars embedded in chloride contaminated concrete structures. It is observed that a new type of coating based on galvannealing of galvanized coating performs excellently well in comparison to the other coatings.

Uniform and localized corrosion of steel reinforcement bars (rebars) in chloride contaminated concrete is a serious problem that concerns designers, architects as well as to general public. Attempts are being made all over the world to combat this menace by using various types of coatings, inhibitors, steels and other techniques<sup>(1-5)</sup>. Out of these techniques the application of coatings on rebars' surface is most convenient and probably very effective technique to control corrosion. Normally, the following three types of coatings are used to control the corrosion of rebars embedded in chloride contaminated concrete structures.

#### (a) Organic Coatings:

This method of controlling corrosion of rebars is being employed in many countries. There are many merits and demerits associated with this technique. Out of these, the application of fusion bonded epoxy coating (FBEC) on steel bars had been claimed to be quite effective in controlling the corrosion of rebars and are in use at many places since last three decades. The FBECR was developed in United States in 1960s and its use was strongly recommended in coastal areas. It was claimed that FBECR imparted resistance to the permeation of moisture and aggressive anions and functioned as an electrical insulator to provide physical barrier between the steel bars and corrosive electrolytes. It was also proposed that owing to the dielectric property, the coating would not allow the penetration of charged particles such as chloride ions through it. Based on these claims, the FBECR became extremely popular in USA in eighties and a National standard for the application and acceptability of this coating on rebars was formulated <sup>(a)</sup>. Thereafter, the production and use of FBECR also started in many other countries. Unfortunately, the sign of distress of structures having FBECR as reinforcement started appearing within 10 years of their erection (7.6). The findings of the investigation of distressed structures during their service life were so alarming that many experts recommended discontinuing the use of FBECR \*. Many of other findings had also established that FBECR was not a foolproof technique and perhaps more dangerous in causing localized corrosion of reinforcement bars than the uncoated steel bars (16-13). It was reported that in 95% of the cases of bridge decks, the epoxy coating had de-bonded from the steel surface before chloride arrived and did not provide any additional service life ". The investigations revealed that these failures took place either at the defect sites (cracking/mechanical damages caused in coatings prior to/during the erection of the structures) of the coating or at the places where although the coating was intact but corrosion took place under coating. These observations created great concern and had cast doubt on the ability of FBECR to withstand the corrosive attack of chloride contaminated concrete. This led researchers to have a re-look on the performance of FBECR. As a consequence of this, large number of research papers on corrosion resistance performance of FBECR appeared in literature during the last few years and a great deal of disagreement still exists amongst the

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researchers on durability of the FBECR exposed to alkaline saline environments (1423). The published research papers attributed the causes of unexpected failures of FBEC either to existence of defects in coating prior to embedding in concrete or to the contaminated surface prior to the application of the coating. The one very vital aspect that has not attracted the attention of researchers is the superb performance of epoxy coatings in preventing the corrosion of pipe lines carrying neutral water that are providing useful service life even after years of their installation. This fact suggests that there exist uncomfortability of epoxy coating in contact with concrete environments. Chloride contaminated concrete pore solution is highly alkaline in nature having plenty of potassium, sodium, calcium and chloride ions. These ions may destabilize the inevitable pinholes existing in the coating and may accelerate the corrosion process. In contrast to the common believe that FBEC resists diffusion of water through it, the work at our laboratory has established that a gradual increase in uptake of water by coating takes place in neutral chloride as well in SPS(simulated concrete pore solution) but at a faster rate in the latter case (Figure 1). These observations indicate that the epoxy coating, when directly exposed to aqueous solution, is not resistant to the penetration of moisture and aggressive ions and presence of alkalinity at the interface accelerates the process of absorption. Park et.al 26 have also reported that the water easily permeates through epoxy coating-metal interface to form cathode because of the presence of hydrophilic groups in epoxy. The presence of chloride ions in SPS has very deleterious effect on the health of FBEC rebars and the corrosion rate increases with increase in concentration of chloride ions(Figure 2). The rebars in contact of neutral chloride solution (3.5% NaCl), show slower corrosion rate even to that of lowest chloride ion added in SPS (0.15%). The above results indicate that in neutral sodium chloride solution, the FBECR exhibit more stable performance in comparison to chloride blended alkaline SPS solution. This was probably the reason that the introduction of FBECR as reinforcement material was strongly recommended during seventies which was based on results recorded for coated rebars exposed in neutral sodium chloride fog tests. Being a dielectric material, the epoxy coating is expected to withstand the diffusion of chloride ions through it. Diffusion of moisture through the coating, especially in alkaline concrete pore solution, which contains considerable amount of potassium ions, was guite fast (Fig. 1). Leidheiser et.al. have shown that K' (Potassium ion) has very high rate of diffusion through the coating in comparison to sodium ions 1271. An unusual increase in absorption of water with passage of time, through the FBECR exposed in SPS. perhaps is caused due to this effect. It is to be noted that in neutral sodium chloride solution, the absorption of water through the coating is considerably less in comparison to SPS having K\* (Fig.1). The presence of moisture and oxygen at the coating-metal interface certainly helps in onset of corrosion but is not the sufficient condition for propagation of corrosion. unless the substrate surface is contaminated with other salts such as chloride, sulphate etc., as stated above. In actual field applications, this condition is fulfilled either due to the presence of contaminants at the metal surface prior to the application of coating or during storage and use at work sites where cracking in coating may develop due to contraction and expansion of coating caused due to temperature fluctuations. Since the coefficient of expansion of epoxy coating is four times higher in comparison to steel, the development of minute cracks in coating is inevitable. These cracks allow settling of ions from the surroundings and later on facilitate the corrosion reactions.



Fig.2 Corrosion rate of FBECR directly exposed in SPS having

different concentrations of chloride ions.

The mechanism of corrosion reaction on the epoxy-coated rebars can be schematically described by considering the diagram shown in Fig.3. This proposed model clearly demonstrates that in the absence of any chloride ion at substratecoating interface, corrosion reaction should either be negligibly small or should decrease with passage of time. In absence of any chloride ion, the alkalinity of pore solution helps in strengthening of already existing passive film at the interface and no corrosion should take place. In certain favourable conditions, where oxygen and water concentration is higher, the normal reaction of stable rust formation, should take place. In the above schematic model it is proposed that migration of chloride underneath of the coating take place through the defects whereas moisture and oxygen can penetrate through the intact coating. Various steps such as water and oxygen diffusion, cationic and anionic transport, development of cathodic and anodic sites, electrochemical reactions, generation of catholytes and anolytes are required to take place prior to blistering, rusting and delamination of coatings. As reported earlier (28-30) the diffusion coefficients of chloride (0.47x10" cm²/S) and sodium (0.3x10 10 cm²/S) ions through epoxy coating are considerably less in comparison to oxygen and water (10\*). This suggests that for an intact defect free epoxy coating, the time required for reaching chloride at the metal surface is about 100 times slower than that for water. In the absence of any chloride present at the interface, the propagation of corrosion on epoxy coated rebars surface therefore has a remorse chance. The pre-requisite for corrosion caused due to chloride at the rebars surface, therefore, is that the coating should either develop cracks during service life or they remain present at the substrate surface prior to the application of the coating. The role of



Fig. 3 (A & B): Schematic Diagram showing (A) Diffusion of moisture and oxygen and (B) Delamination of coating and corrosion of rebars.

Chloride ion in a corrosion process is simply to de-stabilize the stable -Fe<sub>2</sub>O<sub>3</sub> oxide phase by forming a soluble complex salt of iron. These salts are not only acidic in nature, but also act as good ionic conductor owing to their excellent conductivity. This helps in depolarization of the anodic reaction and facilitation of corrosion process. This discussion brings out the fact that if FBECR are completely defects free and no trace of chloride is present on the substrate (steel) prior to the application of the coating, the onset and propagation of corrosion reaction may take a considerable period of time. However, if defects are present, the permeation of chloride ion may take place at an alarming rate and attack will be localized in nature.

A longer duration exposure test of FBECR in concrete mortars had established that the undercoating corrosion reactions silently proceed without affecting the outer surface of the coating. To our utter surprise, the coating from out side appeared quite intact except the accumulation of rust at the pinholes (Fig.4). When the coating was removed by a sharp knife, it came out very easily in form of chips. Whole surface of the steel below the coating was covered with loose black rust (Fig.5). The epoxy coating, which was fusion bonded with steel rebars' surface, had lost the bonding with the substrate. The EDXA, SEM and XRD studies supported the view put forward that the undercoating corrosion reaction sets in FBECR. The morphology and EDXA of red rust accumulated at the pinholes' mouth showed nodular structure with strong peaks of chloride. XRD of the red rust confirmed the presence of unstable β-FeOOH rust. The presence of strong peaks of chloride in EDXA suggested that chloride ions play active role in corrosion of FBECR. We have experimentally established that FBEC is more prone to deterioration in chloride contaminated alkaline solution than neutral chloride solution. A defect free coating is very resistant to diffusion of chloride and other ions. Moisture and oxygen, however, can penetrate through the coating but corrosion reaction of substrate is aggravated only when chloride ions are present at coating-metal interface. Propagation of corrosion underneath the coating can proceed silently without any initial indication of bleeding of concrete till the final stage of cracking of concrete occurs.



Fig.4 Photograph showing the condition of FBECR (with defects) after removing cracked mortar Fig.5 Spreading of under film rust at places of pre-existing defects (the defects were originally present in FBECR)

(b) Metallic Coatings: (I) Cathodic / barrier types of coatings:

Another alternative in coatings that appears quite economical and technically feasible, is an electroless nickelphosphorous coating. Although, this coating is cathodic to steel surface and there exists the risk of possibilities of development of cells with large cathode to anode area ratio at defects / cracks sites of the coating, the latest developments in deposition technologies have made it possible to achieve amorphous/microcrystalline, flawless, low, medium and high phosphorous content and ductile nickel-phosphorous coatings. Moreover, only few micron thick of such coatings provide very effective protection and tolerate the chloride attack to an extent which is comparable with expensive materials such as austenitic grades stainless steels and hastealloy<sup>(31,37)</sup>. In alkaline environments, nickel is reported to develop passive film due to the precipitation of Ni (OH)<sub>2</sub> at the metal/electrolyte interface and makes the substrate immune to attack<sup>(33)</sup>.



The results generated in our laboratory have established that medium phosphorus electroless nickel coating (MEPEN, with around 8% Phosphorus) performs excellently well in controlling the corrosion, if steel rebars in chloride contaminated concretes. Some results generated in our lab are shown in Figure 6. It is observed from the plots shown in this figure that the corrosion rate of MEPEN remains in the range of 0.1-1.0  $\mu$ m per year ( $\mu$ mpy) throughout the test period. This indicates that the coating is fairly stable in simulated concrete pore solution having very high level of chloride ion (1M) and attains a stable passivity. Mild Steel (MS), on the other hand, initially (up to 300 hours) exhibits a stable corrosion rate of the order of 15.0  $\mu$ m per year ( $\mu$ mpy) and then gradually increases with time. After 650 hours of exposure, a sharp increase in corrosion rate is

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observed and goes above 30 µmpy, indicating the formation of non-protective corrosion product on its surface. XRD analysis showed that these corrosion products were a mixture of akaganite and hematite, which are unstable phases and do not impart barrier protection to steel surfaces. This type of corrosion products were also observed by many earlier workers on steels exposed in concrete environment<sup>134-36</sup> and does not require detail discussion. The corrosion products accumulated on the surface of the MEPEN electrode exhibited the presence of Ni<sub>2</sub>O<sub>3</sub>, Ni<sub>5</sub>P<sub>2</sub>, NiCl<sub>2</sub> and CaH<sub>2</sub> as confirmed from XRD studies.

Cyclic polarization experiments also confirmed that MEPEN was almost immune to the pitting attack by chloride ions present in SPS (Figure 7). This fact was further corroborated from its breakdown potential. The deposited coating did not exhibit any pitting tendency even up to 1.0 V anodic to its corrosion potential. XRD studies of corrosion products formed on MEPEN exhibited the presence of Ni<sub>2</sub>O<sub>3</sub> and Ni<sub>5</sub>P<sub>2</sub> phases with small peaks of NiCl<sub>2</sub> and CaH<sub>2</sub>. We have shown that the phosphorus present in the coating forms insoluble Ni<sub>5</sub>P<sub>2</sub> compound and blocks the defects present in passive oxide of the metal. Siconolfi and Frankenthal<sup>(3n</sup> have also reported that the presence of phosphorous in Ni(OH)<sub>2</sub> may alter its defect structure. The insignificant role of chloride in destabilizing the coating as noted in the above results is attributed to observed dense passive film of Ni<sub>2</sub>O<sub>3</sub> embedded with Ni<sub>5</sub>P<sub>2</sub>.



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#### (c) Galvanic Coatings:

Galvanizing appears to be quite effective technique in controlling the corrosion of steel rebars. Many research papers and reports have appeared in literature where it is claimed that hot dip galvanized coatings (HDG) perform superior than the bare steel rebars in contact with chloride contaminated alkali environments<sup>(36-43)</sup>. This is attributed to the formation of passive layer of calcium hydroxyzincate (CHZ) during the corrosion of zinc<sup>45)</sup> in these environments. The greatest disadvantage with this layer, however, is its pH sensitivity. This coating provides best results in the pH range of 12 to 13.4<sup>450</sup>. Above and below this pH, the CHZ formed on galvanized surface is

unstable and dissolves quickly in concrete environments. A of the concrete is controlled by many factors such as type of cement used, type of additives blended in the concrete, guality of water used and also the penetration and neutralisation effect of corrosive gases on concrete pore solution. Maintainance of pH of concrete in the protective range (12.0 to 13.4), therefore, is impractical in real life situation. To offset this negative aspect (pH sensitivity) associated with the galvanized coatings, their alloying with other elements appears very promising solution. Leidheiser and Suzuki<sup>47</sup> have proposed that the corrosion products formed at HDG surface can be made more resistant to oxygen reduction reaction by doping of coating with suitable elements. These elements not only strongly act as negative catalyst for reduction reaction of corrosion but may also dissolve with galvanized zinc and form intermetallic corrosion products having wide tolerance towards pH variations. Cheng et al<sup>(46)</sup> have studied Galfan (5% Al Zn) and Galvalume (55% Al-Zn) coating in saturated lime solution (which is considered as the simulated composition of concrete environments) and have reported that both these coatings are more prone to corrosive attack than Zinc coatings in saturated lime solution. These observations of the authors were quite expected in view of the fact that aluminium metal, like zinc, is amphoteric in nature and violently reacts in acidic as well as in alkali solutions. The corrosion products of galvanized coating having aluminium are expected to posses the same corrosion characteristics as zinc. Short et.al" have studied the effect of cathodic alloying elements in HDG and electroplated zinc coated steel in alkaline environments They have also reported that except zinc-cobalt alloy coatings, others showed very disappointing results in alkaline environments.

Alloying of zinc coating with other elements having their sufficient concentration is possible only by electroplating routs. This makes the coated rebars not only uneconomical but also suffers from the drawbacks of entrapment of hydrogen in the coating, which may introduce further problem such as hydrogen embrittlement. Due to technological, economical and operational difficulties, it is extremely difficult to maintain higher concentration of cathodic elements in hot dip galvanized (HDG) coatings. Another type of zinc coating employing the principle of cathodic alloying is Galvanneal coating (GA). This coating now a days is very much popular in auto and other industries. GA is obtained by post coating heat treatment where inter diffusion of zinc and iron takes place to form alloy coating. This inter metallic zinc-iron alloy layer attains higher potential (more positive than the zinc potential) and reduces the driving force of potential for propagation of corrosion reaction. The normal GA coating where iron in the coating remains in the order of 10% of the total zinc, posses improved cosmetic and brown rust corrosion resistance and weldability (reduced welding current and longer life of welding electrodes) and better

adhesion to organic paints and coatings in comparison to normal HDG coating<sup>50</sup>. However, in alkaline environments, Molina et.al<sup>(5)</sup> and sergi et.al<sup>(52)</sup> have reported that the zeta phase of the coating corrodes at a higher rate than the pure zinc. Zeta phase normally contains about 7.00% of iron in the coating. During one of our studies, we noticed that the corrosion behaviour of HDG varied considerably with the type and time of heat treatment provided to the galvanized coating. We have also noticed that the behaviour of the coating having other alloying elements such as nickel, changed drastically after heat treatment was given to the HDG<sup>15355</sup>. It was further observed that unlike HDG coatings, the corrosion products formed on coating having higher iron content were extremely stable in low; as well as higher pH solutions. The work on HDG and GA coatings' properties evaluated in contact with cement slurry, SPS and solid cast mortars, at our lab has established that GA performs far superior than HDG under all the test conditions. The gist of results incorporating these studies are shown in Figures 9-10. In all cases GA is observed to perform superior than HDG.

The visual observations of the corroded interface of the two coatings exhibited a localised deposition of corrosion product at HDG surface. The GA surface on the other hand, had no such deposition. Such localised deposition of corrosion products are not desired on reinforcement bars as they may create localised stresses on concretes that may result in its cracking. This corrosion product was analysed by XRD that confirmed ZnH<sub>2</sub>.





Fig.9 Variation in Corrosion rate of coatings in SPS + 1M CI with time

In addition to reducing the corrosion rate, GA was also observed to be more resistant to chloride than HDG. The results shown in Figure 10 exhibit that GA attains a stable corrosion rate above the concentration of 0.45 M of chloride ions. The HDG coating, on the other hand, shows a steep rise in corrosion rate with increase in concentrations of chloride ions.

The XRD spectra recorded for the corrosion products of the two coatings exhibited the presence of dominant phases of ZnH<sub>2</sub> for both the coatings. Few peaks of other than ZnH<sub>2</sub> phase were also observed in corrosion products of GA coating. These peaks corresponded to Zn-Fe compounds (Figure 11). Scanning Electron Microscopy and Energy Dispersive X-ray Analysis (EDXA) of corrosion product of GA coatings revealed platelet type of structure (Figure 12). However, when these platelets were further resolved at higher magnifications (X 3000), acicular type of structures were found to be embedded in between the major corrosion products (Figure 13). The microstructure of corrosion

product of HDG revealed porous structures (Figure 14). These results confirmed that the corrosion products formed on GA surface was more compact and protective in comparison to the corrosion products of HDG surface under identical test conditions.



Fig 11 XRD Spectra of corrosion product of HDG



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verated at the surface of GA coating after exposing in SPS + 1M chloride ion.

Fig.12 SEM phot



Fig.13 Microphotograph of GA after

exposing in SPS +1(M) CI for 15 days.



Fig.14 Microphotograph of HDG after exposing in SPS + 1 (M) CI for 15 days

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#### Conclusions

Most of the present data available on corrosion of reinforcing steel pertains to their study in simulated concrete pore solution environments. The actual field conditions, however, are entirely different than the simulated conditions. The understanding of corrosion of steel rebars in contact of chloride contaminated concrete needs more attention. The researches should be directed for insitu study of the mechanism of deterioration of rebars embedded in concrete. The latest available instrumentation techniques can help to achieve this goal. The present system of FBEC being used to protect steel rebars from chloride induced corrosion appears not to be a foolproof technique and needs serious attention to look into its demerits. Researches should be directed to develop metallic coatings, both galvanic as well as cathodic types, to control corrosion of rebars. Extensive studies carried out at National Metallurgical Laboratory, Jamshedpur and in other laboratories of India and abroad, show that metallic coatings might be a technologically feasible and economically viable method to control the corrosion of chloride induced corrosion of rebars.

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Acknowledgement: The authors are thankful to Council of Scientific and Industrial Research, New Delhi for financial helps provided through net work project programme, to accomplish this work. And to the Director, National Metallurgical Laboratory, Jamshedpur for permission to publish this work.

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