NANOTECHNOLOGY IN CORROSION PREVENTION

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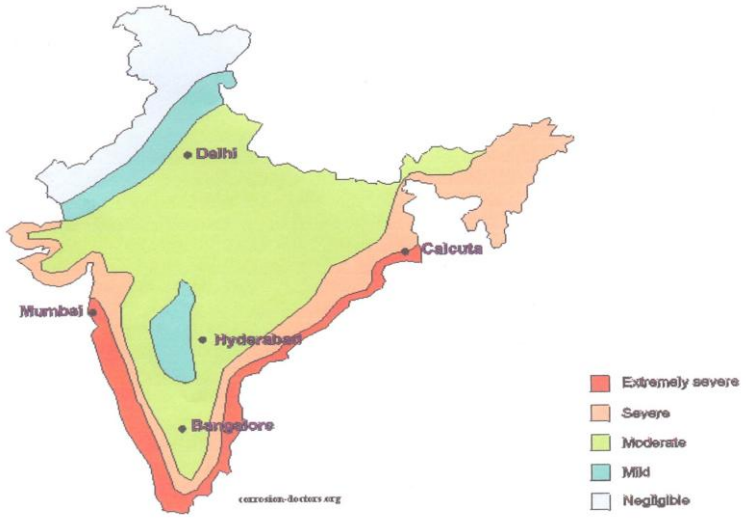
1.0 The International conference- "CORCON 2007" held at Mumbai on September 26-28, organized by NACE International-India Section (National Association of Corrosion Engineers), focused on "Cost of Corrosion to the Nation". Scientists from the U.S.A, Europe and India dealt on the subject at great length. Even a figure was arrived for India vis-a vis world wide, U.S.A. A staggering numerical of Rs. 1,25,000 Crores was justified.

	GDP	**% G.D.P**	**Losses due to Corrosion**
World Wide	$ 30 Trillion	Greater than 3%	$ 930 bn
U.S.A	$ 9 Trillion	Greater than 3.3	$ 300 bn
INDIA	$ 1 Trillion	3 - 4 %	$ 40 bn
			Rs 1,25,000 Crores

Even this figure is considered to be a modest one. More than 3,000 kms of coastline, higher temperature, humid climate justify for higher losses.30% of this loss could be saved if optimum corrosion management practices are employed. 63,000 km rail lines in India, pose a bigger problem for preventive maintenance. Majority of railway accidents are attributed to the corrosion. The cost of replacement of corrosion rails is given a modest figure of Rs. 440 Crores. All these figures of all India losses, do not take into consideration the indirect costs, namely the delay, damage, deaths, production loss, compensation etc. The indirect costs could be much more than the direct losses. The map describing corrosion patterns in India shows macroscopic differences between areas with coastal regions being the most severe.



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Many laboratories all over the world whether defence, national, chemical, metallurgical, naval, electrochemical are working seriously to replicate the conditions, so that the answers to corrosion /erosion can be understood. Thus corrosion protection has attained a subject of National and International interest.

Birla cellulose spends Rs. 2 Crores per year, on painting the sites, so does Bharat Heavy Electricals. What do the two have in common with Bandra-Worli link and the old Vashi Bridge in Mumbai? All face the problem of Corrosion. The process of deterioration is compared with 3 C's.

CORRUPTION-CORROSION-CANCER

Most of the losses, more so in India, have been attributed to the use of sub standard materials (corruption), which accelerates the process of corrosion. This process once started, continues like cancer. Hence corrosion is a silent killer.

A planned, predictive and preventive approach to fight corrosion can save our National assets.

"A stitch in time saves nine."

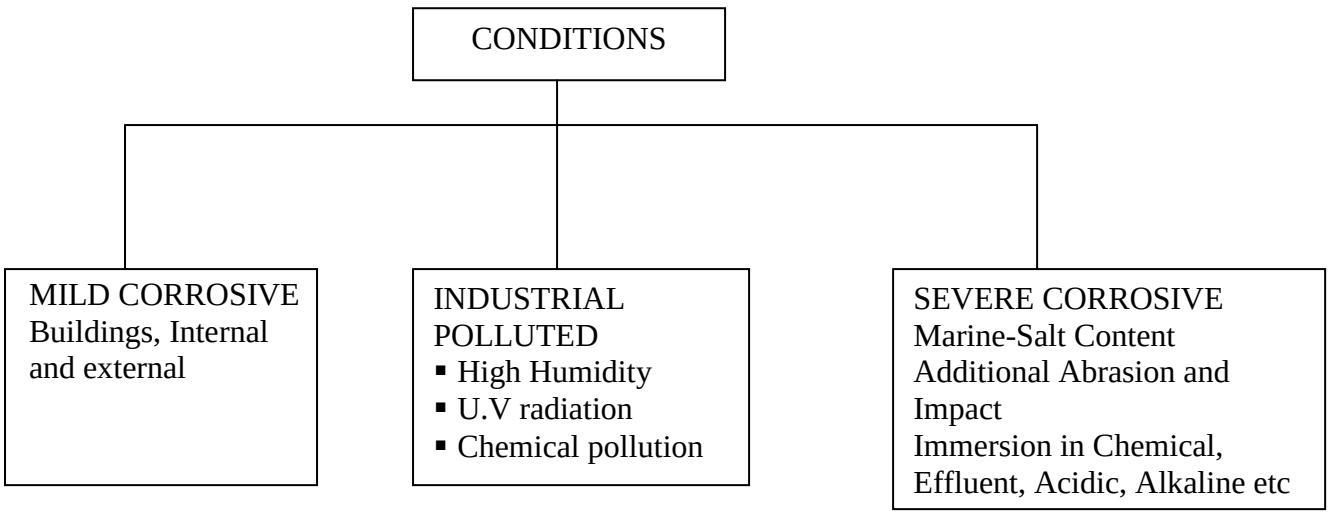
Authors have made efforts in identifying the role of Nanotechnology in corrosion prevention. The R & D experience gained in developing products in protection of concrete through vapor phase, is dealt with. Even our Institute has plans to pursue this work in the years to come.

2.0 METHODS OF CORROSION PROTECTION

There are different ways to protect substrates (metals) from corrosion .A few notable ones are.

- Special alloys
- Galvanizing –Zinc Coating
- Cathodic Protection.
- Alternate materials of construction like Polyethylene, Polypropylene, Polyvinylchloride PTFE; Glass reinforced plastics etc
- Surface Coatings.

This paper mainly deals with corrosion prevention of concrete and metals through Nanotechnology. Before we approach, let us understand the role of high performance coatings in mitigating corrosion. Metal surfaces need application of coatings that possess high passivating properties. The system used, should have a strong tendency towards surface absorption and the ability to form a comparatively strong and stable coating with the metal surface. For a proper selection of a maintenance coating system, the exposure conditions have to be defined.



The performance of any system is directly related to the level of surface preparation. Good systems with poor surface preparation will deteriorate faster than we can imagine. The cost per litre of coating is of little consequence unless it is linked with a long-term protection.

$$C = \frac{M + L}{T}$$

M: Cost of the System
T: Time of Protection (Years)
L: Labour involved in surface preparation and application
C: Cost/Sq meter/mil /Year is considered as a critical yard stick– for selecting a suitable system. Leading surface coating specialists even give a guarantee for more than 10 years under specific environment and conditions.

3.0 CORROSION OF STEEL WITHIN CONCRETE AND ROLE OF NANOTECHNOLOGY IN PREVENTION

3.1

It is well known that mild steel (m.s) embedded in concrete, when rusts, causes severe damage to the structure. The mechanism by which it is attacked, is different from humid atmosphere and marine conditions (refer earlier). In initial stages due to alkalinity of the cement, there is a high pH (Hydrogen ion concentration). Hence steel is in a passive state. With time, due to porosity of concrete, there is ingress of carbon dioxide (CO_2) from the atmosphere. This reacts with lime in cement to form calcium carbonate. This results in lowering of pH and hence loss of passivity as well as increase in porosity of the concrete cover. When atmosphere oxygen and moisture penetrate through this cover, they react with steel to form rust. However at some other site the oxygen will not have access. Then sites rich in oxygen and poor in oxygen form a galvanic couple which initiates corrosion at anode i.e. site where there is oxygen deficiency. In this way the entire steel rod under goes corrosion (rust)

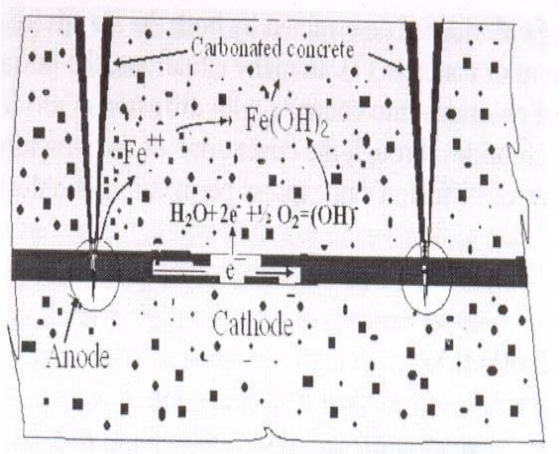
$Fe \rightarrow Fe^{++} + 2e^{-}$

$2e + H_2o + 1/_2O_2 \rightarrow 2OH^{-}$

$Fe + H_2o + 1/_2O_2 \rightarrow Fe^{++} + 2OH^{-}$

$4Fe + 8\ OH^{-} \rightarrow 4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O3\text{-}H_2O + 2H_2O$ – RUSTING

The mechanism is schematically shown in Fig



The corrosion products need more volume, which causes tensile stress on the concrete, leading to cracks, thus paving an easier way for the corrosives and weakening of the

bond between steel and concrete. This results in the separation of concrete from the main structure.

In chloride media (marine atmosphere) the mechanism is different .In the initial stages there is a loss of passivity, but chloride ions also diffuse through the concrete along with oxygen. This oxygen form hydroxyl ion. At oxygen deficient state, this is anode formation leading to Fe^{++}

$$4Fe^{++} + 8cl \rightarrow 4Fecl_2 + 8e^{-}$$

Now the chloride ions and hydroxyl both migrate to the anodic site to neutralize the positive of Fe++. However due to higher mobility, chloride ions react with Fe++ to form the chloride. This salt hydrolyses to generate acid and cause local corrosion. With time, this results in formation of crevice and finally leads to the cleavage. The chloride attack on steel in concrete is catastrophic and needs proper attention.

3.1 Role of Nanotechnology in Corrosion and erosion prevention

The term "Nano" is derived from the Greek word "dwarf". It serves as a prefix, for the dimension on atomic scale. Instead of getting into various definitions, we confine our discussion on the role of nanotechnology in corrosion prevention with respect to embedded reinforced bar in concrete. The reinforced bars are not accessible for protection by external application. Also we touch upon the up gradation of coatings by incorporating monomolecular layer of chemicals for dust and water repellency.

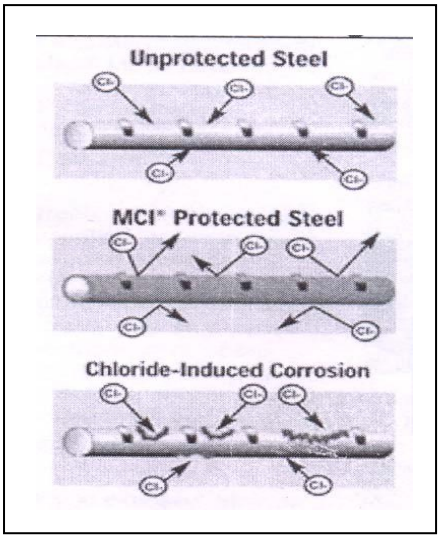
Nano particles are smaller than wavelength of visible light (400-700 nm) and hence are transparent to eye. They are occupied by 5-10 atoms and molecules, stacked in two or three dimensions. Such nano particles when incorporated in a coating or a concrete, physical property of the system gets altered without affecting the clarity. Tiny size of nano particles produces an extra ordinary high surface energy. Later we discuss on the "Lotus effect" in one of the applications that has been commercialized. One more claim made in India is on the use of a four-wheeler lubricant, for protecting the metallic substrate.

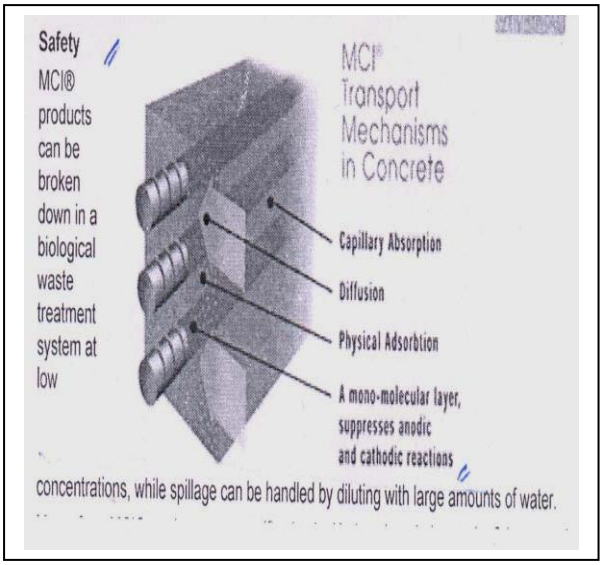
3.2 FUNDAMENTAL PRINCIPLES OF CORROSION PROTECTION THROUGH NANO VAPOUR PHASE INHIBITORS

The spirit of innovation has been extended to the field of corrosion prevention where the substrate is not accessible for application. In this case, nano particles travel to the substrate through vapour phase and protect the rebar from corrosion. Such materials are also known as vapour phase corrosion inhibitors or penetrating type. In designing a volatile corrosion-inhibiting compound, we have to observe ourselves that the compound will have an appreciable vapour pressure as well as the capability of forming a stable bond with the metal surface. Therefore the chemical compounds used as a volatile inhibitor, must not have a too high or too low vapour pressure but an optimum one.

3.3 NANOTECHNOLOGY IN REINFORCED BAR PROTECTION IN EMBEDDED CONCRETE.

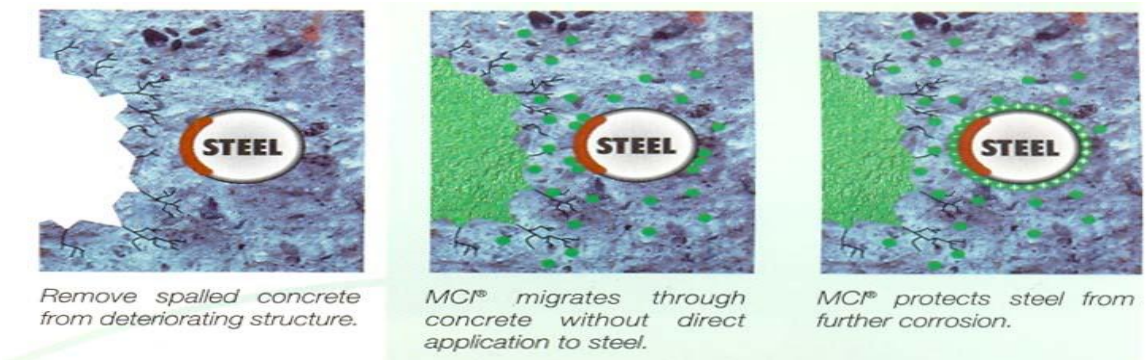
Steel becomes conducive to corrosion after chlorides and carbonation breakdown its natural passivating protection. When volatile, migrating corrosion inhibitor travels to the steel substrate it forms a layer of protection. Using X-rays this protective layer has been measured (20-100nm) thick at the molecular level.



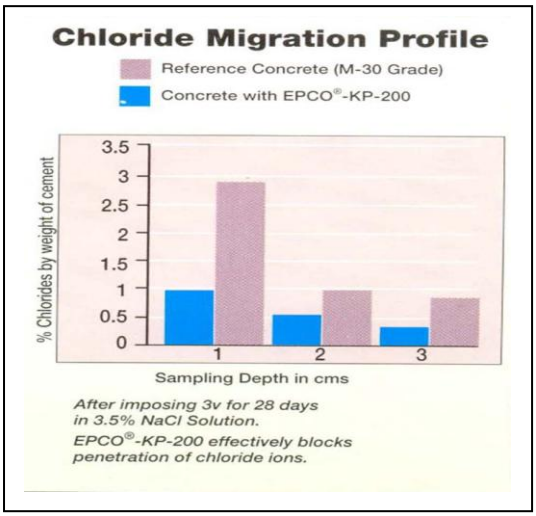


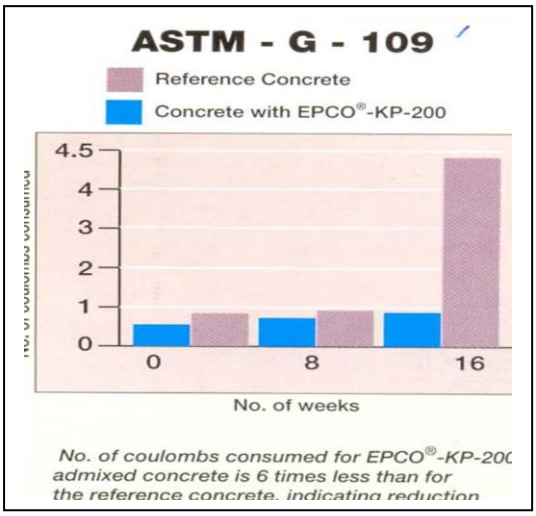
- Vaporises and migrates to all reused areas and cavities.
- Vapour condenses on all metal surfaces.
- Ions dissolve in moisture water layer.
- Protective ions are attracted to metal surfaces.
- Ions form a thin molecular protective layer at the metal surface.

Thus penetrating type inhibitor is used in concrete mixture during construction of new structures and during the rehabilitation of old structures. It migrates through the old concrete and seeks any ferrous metal in the structure. The thin layer of inhibitor prohibits chemical reaction between chlorides and steel in the structure.



At a reputed industrial laboratory the R&D work on such type of chemical compounds was initiated, as the imports were prohibitive and the Indian construction industry were not ready to accept the high price. The result can be summarized as follows.





The conclusions drawn from the paper published are as follows

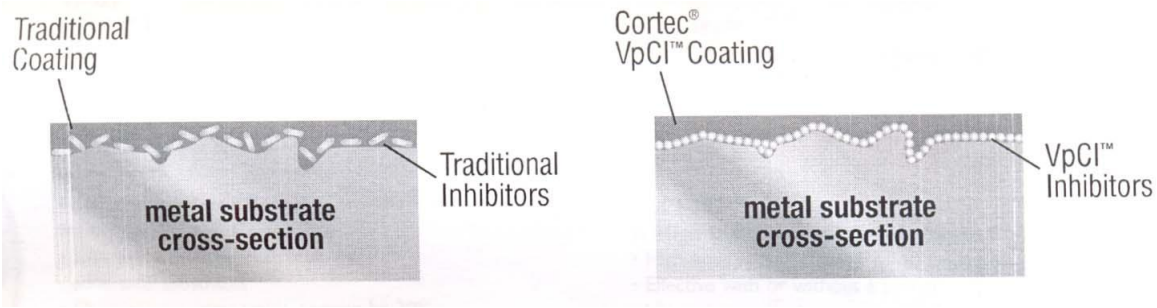
i) The incorporation of penetrating corrosion inhibitor as an admixture in concrete does not impair any mechanical properties.

ii) The electro chemical studies reveal that there is a significant advantage in incorporating penetrating type inhibitor, as it dramatically reduces the rate of corrosion. This effect is more pronounced in weak porous concrete as compared to dense ones.

iii) Admixture produces better results as compared to coating on the concrete surface. Quite likely the efficacy of the coating is reduced as most of the inhibitor lost because of evaporation.

iv) The efficacy of the penetrating inhibitor did not deteriorate even at higher temperatures (60°C). This is significantly important in a tropical country like ours.

1.1 Traditional coatings vs. vapour corrosion penetrating type inhibitor



These inhibitors protect the metal substrate with a tight bonding molecular structure. The system eliminates the gaps which occur with traditional inhibitors and prevent corrosion from starting.

4.0 Lotus Effect:

As late as nineties, Scientists even in Europe were unable to identify the cause of water repellency in lotus leaves. The explanation of low surface tension does not identify the cause. Daimler Chrysler research is applying the lotus effect to develop self-cleaning dust repellent properties. The extremely fine structure on the lotus leaf, enables water and dirt roll off without leaving a trace. These self-cleaning, dust repellent characteristics have been incorporated through nano particles. Now it is successfully commercialized by a leading paint manufacturer.

4.1 Additive for oils and lubricants:

Oil based corrosion inhibitor for lubricating oils for gasoline and diesel protects the base metal. A leading lubricant manufacturer advertises, as magnetic engineered molecule that is more than oil.

5.0 What future looks like?

Thus Nanotechnology is playing a constructive role in corrosion prevention. However the "CORCON 2007" International Conference highlighted multi-thronged approach to fight menace of corrosion. The National Bridge Inventory database maintained by the Federal High way Administration, a division of the USA's development of transportation confirmed that the average age of the bridge without maintenance is 40 years. Out of 600000 bridges 14% were structurally deficient and the primary cause of the deficiency was corrosion of reinforcing steel. In the USA, they are looking for a life span of approximately 100 years if possible. Hence an approach of "Fusion bonded Epoxy Rebar" with engineered concrete, using corrosion inhibitors are being explored and the work is in progress. Since India is on the take off on the infrastructure, there is a lot to pick up and put them into practice to protect our national assets.

Our "Innovation Centre" is toying with the idea of R& D coupled with testing and training. It can hope to play a constructive role in the years to come. Time alone can say!!! Every thing is possible if we have a burning desire.

References

i) Souvenir –"CORCON 2007"

ii) Corrosion of iron & Steel – Prof R.D. Angal
Seminar proceedings "organic coatings in Corrosion prevention" September 2/3-2002.

iii) High Performance functional coatings seminar 2002 paper. Prof V.S. Bhakre. September 2/3 2002.

iv) CORTEC CORPORATION. INSTUCTION SHEETS ON VpCI®/MCI® Technologies.

v) DATA-SHEET ON EPCO-KP-200-Concrete penetrating corrosion Inhibiting Admixture.

vi) Corrosion map of India-National Metallurgical laboratory book. Jamshedpur.

vii) Controlled Permeability form work (CPF) liner reduces corrosion of Reinforcement in concrete AK. Mvelick & Kumar
CORCON 2007 Seminar

viii) Nanotechnology –coating industry perspective
Nilesh Desai and Avinash Sardesai-Asian Paints
Paint India-March 2007

ix) Corrosion Protection Systems for reinforced concrete CORCON 2007-
Paul Viramani.
Office of Infrastructure R & D. FHWA.TFHRC.USA

x) Service Life Modelling for reinforced concrete structures –Ali Akbar Sohangh Purwala
CONCORR, Inc- USA.

xi) Micro particle to Nano particle- the technology of tomorrow –Debarta Pal-Berger Paints (I) Ltd, Paint India, January 2007.

xii) Fundamental Principles of Corrosion protection with vapour phase inhibitors.
B.A Miksic and R.H Miller-Cortec Corporation published September 1980.
5th European Symposium on Corrosion Inhibitors European Federation of Corrosion, Italy.

xiii) Concrete coatings and Rebar coatings from Advanced corrosion Technologies –LLC 50 Indiana polis In 46222

xiv) Nanotechnology –Wikipedia
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