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December 2014, Vol. 20 No.2



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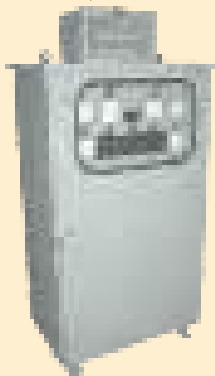


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Corrosion Combat design & layout compiled by Rishikesh Mishra, Manager-Technical Services, NIGIS.

Letters to the editor are always welcome. We invite your suggestion, comments and views on the Newsletter as well as articles for publications. To publish your article, submit it to rishikesh@naceindia.org

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Condolence Message



On behalf of NACE International Gateway India Section and all its esteemed supporters & well-wishers, we extend our sincere and heartfelt condolences to the family and friends of Mr. Ramesh Prasad Nagar, who left all of us for heavenly abode on 4th December 2014.

Mr. Ramesh Prasad Nagar was a MSc, Engineering (Electrical) from Punjab University, Chandigarh. His 43 years' professional experience includes research and teaching, design/engineering of safety earthing, lightning protection and cathodic protection systems.

He was member of NACE International since 1982, Founder Secretary of NIIS and Trustee since July 1, 2012, Mr. Nagar had served the Section Governing Board at all positions since 1992. Mr. Nagar was responsible for the development of local educational/training programs and establishment of policies and guidelines/procedures for the technical programs of CORCON Conferences and NIGIS Corrosion Awareness Awards. He was also a co-author of NIGIS's book 'Corrosion – Case Studies' . During his time as Chairman and Trustee, Student Chapters in Mumbai & Chennai were formed and certification courses of NACE International were introduced.

Recently, he was honoured with 2015 NACE International Distinguished Service Award for the contributions he had made to NACE.

May his soul rest in eternal peace.

Section Governing Board
NIGIS

Message



NACE International Gateway India Section, abbreviated and popularly known as NIGIS was founded in 1992 as NACE International India Section (NIIS). I am privileged to have contributed to the growth and development of the section for last 22 years as a member of section governing board, faculty / coordinator of NIGIS education / training programs, member / chairman of technical committee of CORCON conferences, chairman of NIGIS corrosion awareness awards committee etc. It is a matter of great pride for me and members of the section that:

- NIGIS is well recognized as one of the largest and most active section among 130 worldwide sections of NACE International.
- Our member Shri Tushar Jhaveri is first person from Asia to have had the distinction to serve NACE International as a member of board of directors (2008-11), Vice-President (2012-13) and President (2013-14). Besides, our member Dr. Samir Degan has the distinction to serve NACE International as a member of its board of directors (2011-14) and is poised to take on greater roles at NACE International.
- Our members Prof V S Raja, IIT Bombay and Dr. K M Mudali have been honoured by NACE International with its Fellowship Award for their distinguished contributions to corrosion science and technology.
- NIGIS Corrosion Conference is recognized and certified as a Trade Fair by the concerned authority of the Government of USA

Notwithstanding aforesaid achievements, NIGIS continues to tirelessly contribute to programs for corrosion education / training; corrosion control and mitigation; corrosion awareness; cost of corrosion estimation etc. in India. The level, range and visibility of these activities have substantially increased this year with the signing of memorandum of understanding to carry out certain corrosion related activities jointly with eminent organizations like Federation of Indian Chambers and Industries (FICCI); and US Commercial Services (USCS) department; CHEMTECH Mumbai etc. NIGIS remains grateful to its associates and supporters for their sustaining contributions and invites all individuals/organizations concerned with corrosion control to join us to achieve the NACE mission to protect people, assets and environment from effects of corrosion.

Corrosion professionals understand effects of corrosion and benefits of corrosion control and mitigation. However law makers, officers of union / state government and public / private sector undertakings and others who influence policy and decisions on such matters need to be informed about corrosion and its detrimental effects and convinced that its control and mitigation systems require effective legislation and commitment to patiently monitor and update its performance as corrosion is a natural process that takes place slowly and continuously throughout the service life of metallic object / infrastructure. Corrosion studies conducted in USA and some other countries have indicated that cost of corrosion is equivalent to 3 to 5 percent of country's gross domestic product (GDP) and it can be substantially reduced by well designed, applied and maintained corrosion control and mitigation systems.

Besides Australia, Canada, Europe, Japan, Latin America, the Middle East, the UK, NIGIS India has joined the IMPACT (International Measures of Prevention, Application and Economics of Corrosion Technology) study project that is currently being conducted by NACE International, based on experience of its earlier study, to determine and analyze direct and indirect costs of corrosion, corrosion control and mitigation practices of several industry sectors worldwide to identify best corrosion management practices, opportunities, strategies and techniques to reduce corrosion costs by as much as 30%. The IMPACT study has the potential to be a game-changer for the way corrosion control is handled. NIGIS requests all Indian stakeholders to wholeheartedly contribute to the success of this study to change the scenario of corrosion control and mitigation in India.

Late R P Nagar
Trustee - NIGIS

This message was delivered by Mr. R. P. Nagar for "Corrosion Combat" a few days ago, before he left for heavenly abode.



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Editorial



These days “Cost of Corrosion” is a buzz word in corrosion industry. The studies carried out in the past estimated that this cost hovers around 3 to 3.5% of GDP, with the tag – “Direct Cost of Corrosion”, i.e. the cost incurred by the Asset Owner. This runs into trillions of USD when world GDP is taken into account.

Why this cost on account of corrosion is being talked separately? Perhaps, it does not get recognition as “Process Activity” in most of the companies. And then there is one more basic question – “What is this Cost of Corrosion?”. This is the cost over and above the cost of carbon steel material which is required to protect it against corrosion. The basic premise here is that carbon steel is an excellent and economical structural material but it is not a corrosion resistant material.

According to me, when this cost of corrosion concept is further simplified, then “Direct Cost of Corrosion” will have two components:

Direct Cost of Corrosion = Cost incurred to control corrosion (A) + Losses to the Asset Owner due to Corrosion (B)

Therefore, different techniques such as painting, corrosion inhibitors, alternative materials, CP etc. are used to protect it against the vagaries of corrosion. Depending upon the severity of corrosion, the cost of control measures will vary. This forms component “A”. The component “B” reflects losses when a failure due to corrosion occurs and the various elements of this component are:

- Product loss
- Production loss / deferred production
- Construction material loss
- Damage claims
- Clean-up operations
- Safety & environment risk
- High breakdown repairs & maintenance costs
- Infrastructure collapse

There is a catch in this mathematics. In developed countries, where advanced corrosion control practices are in place, the component “A” may be high but component “B” may be low. The scenario may be opposite in developing and underdeveloped countries.

All the studies on “Cost of Corrosion” estimate that 25 to 30% of annual corrosion costs could be saved if optimum corrosion management practices were employed. By such study, **knowledge and information on corrosion & its control will be pooled and new comers will not have to pass through those segments of learning curve which have already been traversed by several others.**

The savings earned from “Cost of Corrosion” can be used for multitude of gainful purposes. Along with monetary benefit, there is benefit to humanity in terms of reduction in processing of ores and hence reduction in carbon foot print of the industry.

Anil Bhardwaj
Editor - Corrosion Combat



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Effect of Rebar Corrosion on Service Life Reinforced Concrete Bridges

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ABSTRACT

Bridges are very important and expensive component of a road transport network. If a bridge fails, then the traffic in the road network is severely affected. Considering these aspect, the concrete bridges are now being designed for a life of 100 years as per the new IRC: 112-2011. To meet this criterion durability provisions have also been included in this code. Many of the bridges are either exposed to marine environment or built close to industrial areas. In such situation the possibility of the reinforcing steel of the bridges getting corroded due to either chloride attack or carbonation increases, provided the quality of construction is poor or adequate cover has not been provided. Therefore, a study on the various factors influencing the rebar corrosion and its effect on service life of the bridges are discussed. The various remedial measures which hep to delay the initiation of corrosion of steel rebars during the design of a new concrete bridges are also discussed. Also, the effect of implementation of these remedial measures on service life of bridge has been examined.

INTRODUCTION

The durability of concrete bridges has become a serious problem, affecting the national economy, besides influencing the productivity, international competitiveness, and quality of life in a country. Normally, loss of durability occurs gradually, due to various deterioration mechanisms which often remain undetected for quite some time. However, deferment of maintenance and lack of timely action and repair or rehabilitation can result in serious loss of safety and serviceability. Therefore, the engineer must ensure that the loss of performance of the system does not occur during the specified service life of the structure.

Concrete deterioration can range from superficial surface problems to significant disintegration of the concrete within the member, resulting primarily due to presence of moisture (wetting and drying cycles), corrosion

of reinforcing steel, alkali-aggregate reaction, sulphate attack, attack by aggressive chemicals, acid attack other physical, chemical, mechanical and biological causes. The factors influencing durability of concrete bridges are (i) the aggressive environment to which the structure is exposed, (ii)the concrete cover provided to reinforcing steel, (iii)the type and quality of material used for construction, (iv) the cement content and w/c ratio of the concrete, (v) workmanship and (vi) the shape and size of the structural member.

Application of the principles of sustainable development to bridge engineering requires consideration of durability over the entire service life, which involves quantified modelling of the various modes of deterioration and detailed characterization of the environment (macroclimate and microclimate). Ensuring safety and serviceability over the design life of a bridge must also include consideration of its life cycle costs, involving not only the initial cost of design and construction, but also the cost of the future maintenance, repair and rehabilitation, and disposal of the structure at the end of its technical or economic life. The design of a durable and sustainable structural concrete bridge requires optimization of a few alternatives to attain the lowest life cycle cost.

During the last two decades, significant developments have been achieved with respect to construction materials such as high performance concrete and steel, and advanced composites and their applications to bridges. However, this progress has been unmatched by similar developments in design, construction and maintenance techniques. Some of the recent facilities designed for a 100 year service life, such as the Great Belt Link, Denmark, have developed coherent and coordinated requirements for design, construction, maintenance and operation of the structure that have been quantified and incorporated in specifications and the design criteria. These include selection of concrete composition, high quality construction, identification and detailing of the critical parts, and pre-planned operation and maintenance routines.

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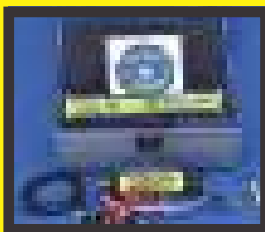
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Durability Considerations in Bridge Design - Past and Present

In earlier days, in India for bridge design, emphasis has been laid on the "strength" criteria. However, after the collapse of Mandovi Bridge, durability issues became a major concern in the bridge design. Thus, the design standard IRC: 21 -2000¹ which was used for reinforced concrete bridge design in India, used to address the durability issue by specifying the minimum concrete grade, minimum cement content and maximum water to cement ratio for structural members of bridge for only two exposure conditions ,i.e., either "moderate" or "severe". The basic steps for designing for durability are (i) to establish the aggressiveness of exposure condition with respect to various deterioration mechanisms, considering the fact that different component of bridge can be exposed to different environment during the service life of the bridge, (ii) to select the type of structure suitable for the aggressiveness of exposure conditions and (iii) to select the materials, mix proportions, workmanship, design and detailing including the minimum cover to the rebars. In IRC:21-2000¹, the design of RC bridges was based on working stress approach, and it specified the minimum grade of concrete to be used for RCC and PSC construction as M30 and M35 in moderate and M35 and M40 for severe condition of exposure. For the construction of RCC culverts, the minimum grade of concrete was specified as M20 and M25 in moderate and severe exposure condition. Also, the minimum cement content and water cement ratio to be adopted were specified for these minimum grades of concrete. Further, the minimum cover depth was specified as 40mm and 50mm for moderate and severe condition of exposure respectively. It is also permitted the reduction in cover depth by 5mm for precast or factory made concrete structural components.

The new IRC: 112 -2011² follows limit state design philosophy for design of concrete bridges and it specifies the design life of bridge as 100 years. Also, to achieve a service life of 100 years, low permeability of concrete has to be achieved, for which durability provisions are stipulated. In comparison to IRC:21-2000¹, the new design code prescribes four service environments for a bridge and accordingly mix proportion and cover thickness to be adopted using normal concrete with maximum aggregate size of 20mm. A comparison of durability provisions applicable for buildings³ and bridges in India is presented in Table 1. It can be seen that for design of bridges more

stringent durability provisions needs to be followed. Apart from this, use of blended cements like Portland pozzolana cement and Portland slag cement, and mineral admixtures like fly ash, GGBS and silica fume are permitted to be used. Also, the use of high performance concrete to enhance the durability has been emphasised.

Table 1 Comparison of durability Provisions for Buildings and Bridges

Exposure conditions	IS : 456-2000 ³			IRC : 112-2011 ²		
	Min Grade of Concrete	Maxm w/c ratio	Min Cement content	Min Grade of Concrete	Maxm w/c ratio	Min Cement content
Moderate	M25	0.50	300	M25	0.45	340
Severe	M30	0.45	320	M30	0.45	360
Very severe	M35	0.45	340	M40	0.40	380
Extreme	M40	0.40	360	M45	0.35	400

Apart from the durability based design of concrete bridges, the additional measures that can be adopted for bridge design as stipulated in IRC: 112-2011² are use of (i) galvanised rebars, (ii) fusion bonded epoxy coated bars, (iii) stainless steel bars, (iv) water proofing membrane over bridge deck, (v) controlled permeability formwork liners, and (vi) cathodic protection. Application of some of these measures can be seen in some of the existing bridges. For example, Confederation Bridge, Canada, Great Belt Link Bridge, Denmark and Bandra - Worli Sea Link, Mumbai have used blended cement, i.e., triple blend of OPC with fly ash and silica fume for construction. Rio Antrio Bridge, Greece and Queen Elizabeth Bridge II, UK have used Portland slag cement. Use of fusion bonded epoxy bars for construction of bridges with in 10km from coastal line is vogue in India since 2000 and many bridges have been built, for example, Bandra -Worli Sea Link, Mumbai. In French Creek Bridge, New York and Broad Meadows Bridge in Ireland Stainless steel has been used to enhance durability. Application of cathodic protection for concrete bridges is in practice since 1970's in USA and Denmark and more than 2 million m² of concrete structures have been cathodically protected worldwide. Different types of waterproofing membranes are available and widely used in bridge construction. Use of controlled permeability liners is also gaining popularity in bridge construction.

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Service Life of Bridge

Service life is the period of time during which the performance of concrete bridge will be kept at a level compatible with the fulfilment of performance requirements of the structure, provided it is properly maintained. In RC structures, generalized cracking of concrete cover indicates the end of service life. The period of time required to crack the concrete element is equal to the period required for deteriorating agents such as chloride /carbonation front to reach the rebar (initiation time for corrosion T_0) plus the time required for the rust to build up around the bar to split the cover (corrosion propagation time, T_1).

Corrosion rate in carbonated concrete is high at high humidity level and the arrival of carbonation front at the rebar is shortly followed by spalling of concrete. Therefore, time for initiation of corrosion can be considered with good approximation as the minimum service life of concrete bridge structure. Propagation time starts when the passive film is destroyed as a result of falling pH due to carbonation. Corrosion propagation is governed by the corrosion rate which will be decided by the availability of water and oxygen at the steel surface and is function of concrete quality and cover. The corrosion rate is affected by electrical resistivity of the concrete when the relative humidity is low and by the oxygen availability at the cathode when the relative humidity is high. In the coastal region of India, the relative humidity is quite high and hence corrosion rate is governed by the availability of oxygen at the steel surface. The oxygen availability depends on the concrete quality, w/c ratio, cover and environmental factors like temperature and relative humidity. Effect of rebar corrosion on RC structures is depicted in Fig. 1

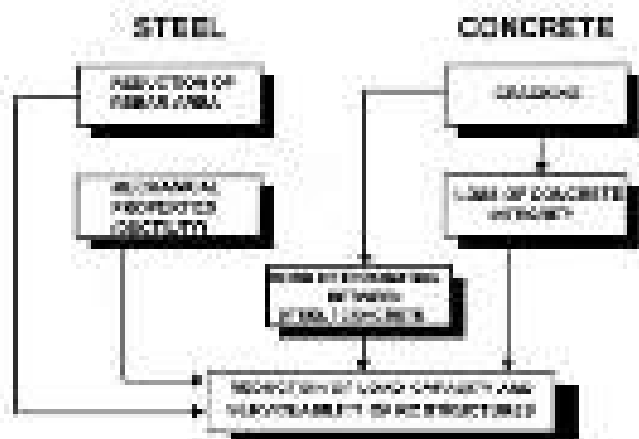


Fig. 1 Effects of steel corrosion on reinforced concrete structures

Effect of Carbonation

Concrete is a porous material and when CO_2 in the air penetrate via the pores to the interior of concrete, chemical reaction takes place with hydrated minerals in concrete leading to lowering of alkalinity and thereby pH value of concrete below 9 in carbonated zone. Corrosion is initiated when the carbonation front reaches reinforcement and time to initiation of corrosion is a function of deterioration rate. The deterioration rate of concrete due to carbonation depends on the thickness and permeability of concrete cover, type of binder, curing, density, water cement ratio, environmental effects such as temperature, relative humidity and the details are discussed⁴.

Deterioration rate of concrete cover due to carbonation is expressed mathematically as follows^{5,6}:

$$\mu (d) = K_c t^{1/2} \quad (1)$$

The initiation time of corrosion (t_0) due to carbonation can be expressed as

$$t_0 = c / K_c \quad (2)$$

The carbonation rate factor depends on the strength and composition of the concrete and suggested as

$$K_c = c_{env} c_{air} a (f_{ck} + 8)^b \quad (3)$$

The values of environmental coefficient (C_{env}) are 1 and 0.5 for structures sheltered from rain and structures exposed to rain respectively. The air content coefficient (c_{air}) is 1 and 0.7 in non-air entrained and air entrained concrete. The constants a and b are 1800, -1.7 for Portland cement binder (Type 1) and 360 and -1.2 for Portland cement +28% fly ash or Portland Cement +70% blast furnace slag (Type 2) binder.

Using Eqs 1-3, the time for initiation of carbonation induced corrosion of rebars have been studied for concrete made of Binder (Type1) and Binder (Type 2) for the durability criteria specified in IRC:112-2011 and the results are presented in Table 2.

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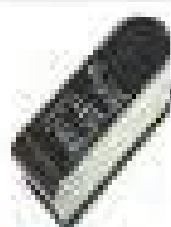
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Table 2 Estimated Time for Initiation of Carbonation Induced Corrosion in RC Bridges

Grade of concrete	Minimum Cover (mm)	Time for Initiation of carbonation induced corrosion			
		Binder (Type1)		Binder (Type2)	
		Non-air entrained	air entrained	Non-air entrained	air entrained
M25	40	72	147	54	111
M30	45	147	237	97	197
M40	50	401	819	209	427
M45	75	>1102	>2250	>510	>1060

From Table 2, it is seen that addition of fly ash in concrete shows higher rate of deterioration of concrete due to carbonation, lowering the time for initiation of carbonation induced corrosion. In case the Portland cement +fly ash (28%) is used as binder, then either the minimum grade needs to be specified as M30 with a minimum cover of 45mm to withstand the carbonation attack and make the bridge structure durable for at least 100 years. Air entrainment is beneficial in enhancing the time required for carbonation front to reach the reinforcement level.

Effect of Chloride Attack

Chloride is the main cause for breakdown of the passive film formed around the reinforcement bars leading to initiation of corrosion of reinforcement. Chloride may diffuse through the protective concrete cover and corrosion is initiated once the chloride concentration exceeds a critical threshold value, which is generally taken as 0.4% of content of cement in concrete. The length of the initiation of corrosion due to chloride ingress (T_0) depends on the rate of ingress of chlorides into concrete, surface chloride concentration, depth of concrete cover, and the value of threshold chloride level. It may be noted that the IRC: 112-2011² has specified the limiting value of total acid soluble chloride content expressed as chloride ions as 0.1%, 0.2% and 0.3% of mass of cement for prestressed concrete, reinforced concrete in severe, very severe and extreme exposure conditions and reinforced concrete in moderate conditions respectively.

The ingress of chlorides into concrete occurs with the help of the complex combination of several transport processes like diffusion, capillary sorption (absorption of water containing chlorides into unsaturated concrete) and permeation (water flow in concrete due to a pressure gradient). The time-dependent distribution of chloride over the depth of the

bridge deck can be obtained from the solution of Fick's second law of diffusion assuming concrete deck as a homogeneous isotropic semi infinite medium.

For initial condition $C(x,t=0)$ and boundary condition $C(x=0,t)=C_s$ the chloride distribution at depth x and time t is given by Eq. 4.

$$C(x,t)=C_s[1-\text{erf}(\frac{x}{\sqrt{Dt}})] \quad (4)$$

where, C_s is the chloride concentration at the exposed surface (Kg/m^3), D is diffusion coefficient of chlorides into concrete (cm^2/s) and 'erf' is the error function.

Using the Eq.(4) and assuming the same initial and boundary conditions, the time to initiation corrosion T_0 (in seconds) is given by Eq.(5)

$$T_0 = (d_c^2/4D)*[\text{erf}^{-1}(1-C_{th}/C_s)]^2 \quad (5)$$

where, d_c is the depth of concrete cover (cm), C_{th} is the threshold level of chloride concentration(Kg/m^3).

Also, initiation corrosion time T_0 (in seconds) can be expressed in parabolic form as

$$T_0 = (1/12D)*[d_c/\{1-(C_{th}/C_s)^{0.5}\}]^2 \quad (6)$$

Diffusion coefficient of chloride (D in cm^2/s) is primarily influenced by water/cement ratio (w/c) because an increase in water/cement ratio increases capillary porosity and for a given water/cement ratio, the diffusion coefficient is given by Eq.(7)

$$D \approx 10^{-10+4.66(\frac{w}{c})} \quad (7)$$

Using Eq. 6 and 7, the time for initiation for chloride attack has been estimated as 500 years and 113 years for durability provisions given IRC: 112 -2011² for "extreme" and very severe exposure condition for an assumed C_s of $2.925(\text{Kg}/\text{m}^3)$ and threshold chloride concentration, $C_{th}=0.4\%$ by weight of cement in the concrete.

Conclusion

In this paper an attempt has been made to emphasize the importance of durability provision for design of RC bridges. The influence of carbonation and chloride induced corrosion on rebars and how these aspects affect the time for initiation of corrosion which reflects the minimum service life of bridge. Also, the factors influencing the propagation time of corrosion have been discussed. Additional measures available to achieve the design life of 100 years for concrete bridges have been discussed in brief. Again, it is emphasized that ensuring appropriate cover depth and quality of construction plays a vital role in enhancing the durability.

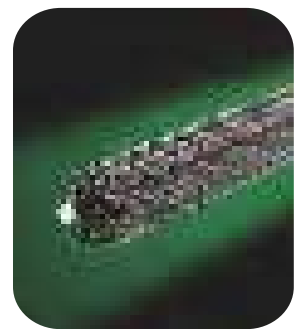
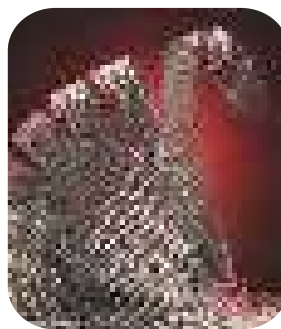
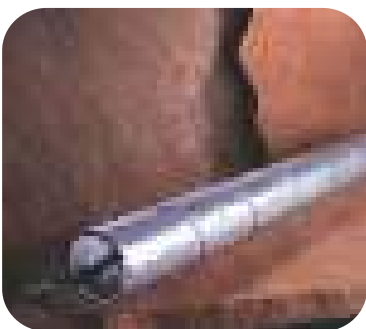
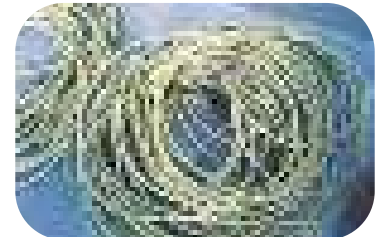
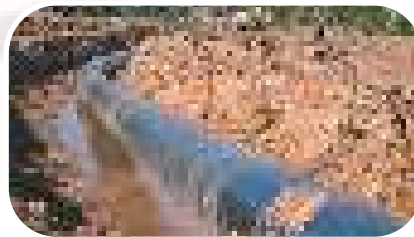
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Propagation Time of Corrosion

The formulae for estimating the propagation time of corrosion (T_1) on the basis of cracking of concrete cover (d_c) are given by Eq. 9⁸:

$$T_1 = 80 \frac{d_c}{d \dot{u} n} \quad (8)$$

The rate of corrosion (r) in concrete depends on the ambient atmospheric conditions such as humidity and temperature. Also, the rate of corrosion is dependent on relative humidity of the environment, at 100% humidity $< 10 \mu\text{m}/\text{year}$, for 80 to 95% humidity it varies from 50 to 1000 $\mu\text{m}/\text{year}$. For various mean rate of corrosion of the propagation time has been computed using Eq. 8 and the variation of propagation time for rebars of different diameter (d) is given in Table 3

Table 3 Effect of Concrete Cover and Rebar Diameter on Propagation Time

Concrete Cover (d_c) in mm	Rebar Diameter (d) in mm	Propagation Time in Years		
		Rate of Corrosion $r(\mu\text{m}/\text{year})$		
		10	50	100
40	12	26.67	5.33	2.67
	16	20.0	4.0	2.0
	20	16.0	3.2	1.60
	25	12.80	2.56	1.28
45	12	30.0	6.0	3.0
	16	22.5	4.5	2.25
	20	18.0	3.6	1.80
	25	14.40	2.88	1.44
50	12	33.30	6.67	3.33
	16	25.0	5.0	2.5
	20	18.0	4.0	1.8
	25	14.4	3.2	1.44
75	12	5.0	10.0	50.0
	16	3.75	7.5	37.5
	50	3.0	6.0	30.0
	75	2.4	4.8	24.0

It is seen from Table 3 that propagation time of corrosion is more in small diameter reinforcing bar.

Acknowledgement: The paper is published with the kind permission of Director, CSIR-CRRI, New Delhi.

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Author :

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Corrosion Basics : Factors Affecting Atmospheric Corrosion*

Various methods have been developed for measuring many of the factors that influence atmospheric corrosion. The quantity and composition of pollutants in the atmosphere, the amount collected on surfaces under a variety of conditions, and the variation of these with time have been determined. Temperature, relative humidity, wind direction and velocity, solar radiation, and amount of rainfall are easily recorded. Not so easily determined are dwelling time of wetness, and the quantity of sulfur dioxide and chloride contamination. However, methods for these determinations have been developed and are in use at various test stations.

The most important factor in atmospheric corrosion, overriding pollution or lack of it, is moisture, either in the form of rain, dew, condensation, or high relative humidity. In the absence of moisture, most contaminants would have little or no corrosive effect. Rain may have a beneficial effect in washing away atmospheric pollutants that have settled on exposure surfaces.

Dew and condensation are undesirable from a corrosion standpoint if not accompanied by frequent rain washing which dilutes or eliminates contamination. A film of dew, saturated with sea salt or acid sulfates, and acid chlorides of an industrial atmosphere provides an aggressive electrolyte for the promotion of corrosion. Also, in the humid Tropics where nightly condensation appears on many surfaces, the stagnant moisture film either becomes alkaline from reaction with metal surfaces, or picks up carbon dioxide and becomes aggressive as a dilute acid.

Temperature plays an important role in atmospheric corrosion in two ways. First, there is the normal increase in corrosion activity, which can theoretically double for each ten-degree increase in temperature. Secondly, a little-recognized effect is the temperature lag of metallic objects, due to their heat capacity, behind changes in the ambient temperature.

As the ambient temperature drops during the evening, metallic surfaces tend to remain warmer than the humid air surrounding them and do not begin to collect condensation until sometime after the dew point has been reached. As the temperature begins to rise in the surrounding air, the lagging temperature of the metal structures will tend to make them act as condensers, maintaining a film of moisture on their surfaces.

The period of wetness is often much longer than the time the ambient air is at or below the dew point and varies with the section thickness of the metal structure, air currents, relative humidity, and direct radiation from the sun.

Cyclic temperature has produced severe corrosion on metal objects in the Tropics, in unheated warehouses, and on metal tools etc. stored in plastic bags. Also, the dew point of an atmosphere is the equilibrium condition of condensation and evaporation from a surface. To ensure that no corrosion will occur by condensation on a surface, the temperature should be maintained some 10 to 15°C above the dew point.

Some metals, particularly steel, are corroded in high relative humidity in the absence of cyclic temperature. There is said to be a critical relative humidity at which corrosion rates suddenly increase. This is probably a function of the hygroscopicity of the corrosion products and of contaminants present. The danger of corrosion appears to increase rapidly as relative humidity passes 60%.

* Adapted from Corrosion Basics – An introduction, National Association of Corrosion Engineers

Stress on skill development, research and development to reduce \$2.5 trillion global cost of corrosion, at CORCON 2014

"It's time to adopt a zero tolerance approach to corrosion, in the same seriousness we should be attacking cancer or corruption," said Mr Ananth Kumar, Union Minister for Chemicals and Fertilizers, Government of India, speaking at the Special Plenary Session at CORCON-2014 in Mumbai recently. "In fact, I was surprised when I learnt about the enormity and economics of corrosion!" he said.

According to a recent report of the World Corrosion Organization, the annual corrosion cost is approximately \$2.5 trillion or 3 - 4 percent of the global GDP. In India alone, the loss on account of corrosion is estimated at around \$ 67 billion (over Rs 4 lakh crore). "Even if we save 10 percent of that amount we lose because of corrosion, the figure would be enormous."

Mr Ananth Kumar said, "Our Prime Minister has laid great emphasis on 'Make In India' with 'Zero Defect' and 'Zero Effect' on environment. Keeping this in mind, we should work towards manufacturing products, and infrastructure that are corrosion-free."

He said, it is important we should make corrosion planning compulsory in all infrastructure projects and just as we say a product is 'energy efficient,' 'fuel efficient,' we should also be able to say the product is 'corrosion control efficient.'" "Corrosion management will facilitate the manufacturing sector to enhance its competitive edge in the global market. Corrosion control should become an integral part of 'good manufacturing practices."

The need for standardization and set parameters for corrosion control; the need to make corrosion audit a mandatory requirement for industry, and the need for coordination between the operation and maintenance departments towards corrosion mitigation were some of the issues he highlighted. He said, with use of right materials and proper maintenance, for example, a pipeline with three-year longevity, can extend to 15 years. "This is what we need to achieve," he emphasized laying stress on renewed research and development in inventing environmentally sustainable corrosion control techniques.

Mr Ananth Kumar said he was ready for an in-house task force on corrosion control in his ministry. Skill development was another area he emphasized on. "For example, painters

should know why they are doing a particular job. The skilled and semi-skilled labor who are part of this should be aware that what they are doing is part of corrosion control." He also said, the government will be mandating an institution, the CIPET - Central Institute of Plastic Engineering and Technology to be part of this skill development program.

"Yes! We have to work hard towards what our minister has said," noted Dr Samir Degan, Chairman, CORCON 2014, while speaking about the highlights of the event. Dr Degan said this conference was unique and unparalleled in many ways. "In fact, this was the first time that CORCON has been associated with the Ministry of Heavy Industries, Ministry of Chemical and Fertilizers, Federation of Indian Chambers of Commerce and Industry (FICCI), the United States Department of Commercial Services and others in various ways."

Besides plenary talks, key note lectures, invited lectures, there were around 200 contributory oral and poster presentations in 15 technical symposia attended by over 800 delegates from across the globe, noted Dr Samir. "This year too, we had an exclusive student session and besides the technical symposia, eight technical interactive forums were also organized on relevant issues."

Organized by the NACE International Gateway India Section, CORCON 2014, now into its 21st edition, was held at Hotel Grand Hyatt, Mumbai, November 12 - 15, 2014. An exclusive exhibition area featured over 60 participants showcasing their latest products and included FRP (fiber reinforced polymer) and US pavilions.

Earlier, at the inaugural function, Chief Guest Mr Sekhar Basu, Director, Bhabha Atomic Research Centre, Mumbai, said: "With improved corrosion management techniques, it is important that we extend the life of aging assets. For example, the cost to generate one kW of power works out to Rs 5 at a new nuclear energy plant, whereas at old ones like at Tarapur, it works out to only 90 paise per kW. So, the more we extend the life of an asset, the more we save." Dr Basu was also emphatic that corrosion management must start at the design stage. Guest of Honor Mr B. Narayan, Group President, Reliance Industries Ltd, felt that a subject on corrosion must be introduced as basic education in schools.

In addition, as part of the India USA commercial dialogue on corrosion, NIGIS hosted Mr. Arun

Kumar, Assistant Secretary of Commerce, Government of USA and Mrs. Mugdha Sinha, Director, Ministry of Commerce, Government of India, This dialogue focuses on strategies, standards and regulation to enhance cooperation between the two nations to reduce the cost due to corrosion in both economies. Towards this effort, NIGIS along with FICCI will be drafting a white paper in the next 30 days to take the dialogue forward.

The CORCON 2014 Expo had around 65 booths including a USA pavilion with several new participants. Delegates from Australia, China, Denmark, Japan, Switzerland, the United Kingdom, and the United States also attended the conference and expo.

Every year, NACE International Gateway India Section (NIGIS) Corrosion Awareness Awards are presented to honor and respect individuals / institutions for their contribution to corrosion awareness and developments in the field of corrosion science and technology in India.

This year, the awards were as follows: Excellence in Corrosion Science and Technology in Research and Education, Dr R. Vedalakshmi, CSIR – Central Electrochemical Research Institute, Karaikudi; Distinction in Corrosion Science and Technology in Industrial Organization, Dr P. Saravanan, Steel Authority of India Ltd, Ranchi; Distinction in Corrosion Science and Technology in Research and

Education, Mr Sunil Kumar Dayarambhai Kahar, M. S. University of Baroda, Vadodara; the Student Award for PhD Degree to Dr K. Rajesh Kumar, Indian Institute of Technology - Bombay, Mumbai; and Mr Jagadeesh Sure, Indira Gandhi Centre for Atomic Research, Kalpakkam; Student Award for M Tech, Mr Dinesh Bapurao Balgude, Institute of Chemical Technology, Mumbai; Meritorious Contribution in Industrial Organization, Dr Sunil Kumar Chaudhary, Road Construction Dept, Dharbhanga; Meritorious Contribution in Research and Education, Mr Indranil Chatteraj, National Metallurgical Laboratory, Jamshedpur; and Prof S. Rajendran, RVS School of Engineering and Technology, Dindigul; and the Excellent Laboratory Award, CSIR – Structural Engineering Research Centre, Chennai, and Welspun Corp Ltd, Bharuch.

The Lifetime Achievement Award was conferred on Mr S. P. Rao, who served as Chairman and Managing Director of Gail (India) Ltd, the largest gas transmission company in India, for his exemplary efforts in supporting the development of NIGIS and for his vision that has contributed to outstanding growth of the oil and gas industry, including corrosion-control and mitigation technologies in India.

On the last day, 15th November, best technical oral and poster papers, best stalls at the expo were honoured and winners of these awards were :

Technical Sessions	Paper and Author
Cathodic Protection	Electrical Resistivity of Soil for Calculating Resistance of CP Anodes Ramesh Prasad Nagar, AFCONS Corrosion Protection Pvt Ltd, Mumbai
Microbial Corrosion and Inhibitors	Application of Electrochemical Impedance Spectroscopy (EIS) for the Selection of Corrosion Inhibitor Packages for West Kuwait Oil Fields S. Mukadam, Abdulhameed Al-Hashem and M. Dabir, Kuwait Institute for Scientific Research
Corrosion in Petrochemicals, Chemicals & Fertiliser Industries	Failure Analysis of Reactor Recirculation Pump Impellers M Y Joshi and K N Amin, GNFC, Bharuch
Corrosion in Refineries	Damage Mechanisms in Hydroprocessing Units Anil Singh, Pasadena, California, USA & Digvijay Charan, Fluor Daniel India Pvt Limited, Delhi & Cathleen Shargay, Fluor Corporation, USA
Coatings & Linings	Innovative Zinc rich epoxy primers with excellent corrosion and outstanding mechanical properties Santiago Arias Codolar, Pinturas Hempel, Spain
Internal Corrosion of Pipelines	A case study on repair of corrosion defects in bridge attachment river crossing section of in-service petroleum pipeline - challenges and learnings S.D. Pande, Indian Oil Corporation Limited, Panipat and Lalit Kumar Thakur, Indian Oil Corporation Limited, Abu Road

Technical Sessions	Paper and Author
Marine and Offshore Corrosion	Influence of Sea Water on the Mechanical Properties of Glass Fibre Reinforced Polyester Composites Ranjeet S Banthiya, Ajit Bhandakkar , R C Prasad, IIT Bombay, Ashish Jain, IIT (BHU) Varanasi and N. Girish, Indian register of Shipping, Mumbai
Materials and Composites	Long Term Durability of Composite Sleeve Repairs – Historic Literature Vs Real World Removals James Knights, Shawn Laughlin and Andrew Patrick, Clock Spring Company, USA
Power Plants and Utilities	Enhancement of stress corrosion cracking resistance of machined type 304L stainless steel through laser surface treatment Ram Kishor Gupta, P. Ganesh, R. Sundar, R Kaul, K. Ranaganathan, D C Nagpure, K S Bindra, S. M. Oak and L M Kukreja, RRCAT, Indore & B Sunil Kumar & Vivekanand Kain, BARC, Mumbai
Corrosion in RCC	Installation of Cathodic Protection System for Concrete Seawater Structure Rod Callon, Corrosion & Technical Services, Bahrain
Student Symposium	Optimization of Process Parameters for Preparation of Linseed Oil Based Microcapsules for Self Healing Coatings Karan Thanawala, IITB-Monash Research Academy, Mumbai, A S Khanna, IIT Bombay and R K Singh Raman, Monash University, Australia
Structural Integrity and Reliability Assessment	Steam Reformer Tube Life: A Case Study Utilising Advanced Inspection Techniques and Remaining Life Calculations for Bharat Petroleum Corporation Limited (BPCL) Barry R Fisher, Quest Integrity Group, LLC, England and Mahesh S., Bharat Petroleum Corporation Limited, Kerala
Corrosion in Defence Equipment and Facilities	Development of Intumescent fire retardant coating for wooden and metallic structure of the Naval ships Sushil S Pawar and V R More, Naval Materials Research Laboratory, Thane

The following posters were awarded:

Winner	Corrosion Behaviour of Novel Lean Duplex Stainless Steels S Srikanth and P Saravanan, Steel Authority of India Limited, Ranchi
1 st Runner up	Removal iron from glycol water in LNG industries by effective (birm media + charcoal) filtration Sandip Modi, S B Singh & Sanjay Kumar, Petronet LNG Ltd., Bharuch
2 nd Runner up	Electrophoretic deposition of Yttria stabilized Zirconia for detection of Hydrogen sulphide S. Suresh Kumar, L. Sujatha and B. Venkatachalapathy, Rajalakshmi Engineering College, Chennai & T. Subba Rao, BARCF, Kalpakkam and T.M. Sridhar, University of Madras, Chennai

The following exhibition stalls were adjudged as best in various categories:

12 Sqm – Winner	Tinker & Rasor
12 Sqm – Runner	Jotun India Pvt. Ltd.
9 Sqm – Winner	Metal Samples
9Sqm – Runner	Blastline India Pvt. Ltd.

CORCON-2015 is scheduled to be held in Chennai, dates for which will be announced soon.

Glimpses of CORCON 2014



Chief Guest Sekhar Basu, Director, BARC lighting the lamp to inaugurate the conference



Honourable Union Minister for Chemicals and Fertilizers, Shri Ananth Kumar, speaking at the Special Plenary Session



Tushar Jhaveri, Past President, NACE International addressing the delegates during his inaugural address



NIGIS hosted a meeting between Secretary of Commerce, Govt. of USA and Director, Ministry of Commerce, Govt. of India.



Dignitaries in the Dias releasing the CORCON 2014 Technical Proceeding



Delegates during the inauguration session

Glimpses of CORCON 2014



R P Nagar addressing the delegates during Corrosion Awareness Award



Harvey P Hack, President, NACE International delivering Keynote talk



NACE President Harvey P Hack (right) presents the Lifetime Achievement Award for 2014 to S P Rao on behalf of NIGIS



Panel Members during Technical Interactive Forum: Pipeline Integrity and Management



CORCON 2014 Exhibition Area



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High temperature oxidation behavior of Alloy 800 during hot conditioning

Geogy J. Abraham, V. Kain, G. K. Dey and V.S. Raja[#]

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[#]Indian Institute of Technology Bombay, Mumbai, India

Abstract

The iron base alloys are susceptible to localized corrosion attack and the major contributing factor in all these corrosion mechanisms are the properties of oxide film formed on the alloy. The defects in the oxide film such as chemical inhomogeneity, pores and grain boundaries are the main cause of localized attack. The localized attack such as pitting and IGA act as precursors for the initiation of SCC in the material. The present study was aimed at optimizing the hot conditioning parameter by varying the temperature of oxide formation for minimum ion release rate during reactor operation. The characterization of oxide film formed at high temperature in lithiated environment on Alloy 800 was carried out using micro laser Raman spectrometer (MLRS) and glow discharge quadruple mass spectrometer (GDQMS) to identify the oxides formed on the surface and elemental variation along the oxide thickness respectively. The defect density of oxide films were studied using electrochemical impedance spectroscopy (EIS).

1. Introduction

Alloy 800 has been in service for more than 25 years in Canadian Deuterium Uranium (CANDU) reactors and in Indian PHWR's and German PWR nuclear power plants [1]. It's known to be more resistant than Alloy 600 to stress corrosion cracking (SCC) and intergranular attack (IGA) in chlorides as well as primary water stress corrosion cracking (PWSCC) [2]. Alloy 800 is a fully austenitic alloy and maintains a stable, austenitic structure during prolonged exposure to high temperatures. It was developed in the 1940's as a low nickel substitute for Alloy 600 at a time when nickel was in short supply. The recent occurrences of Alloy 800 intergranular stress corrosion cracking (IGSCC) within the tube-sheet region of some German steam generator (SG) is attributed to the unusual conditions, pre-existing exposure to phosphate and to the different early fabrication methods used compared to following SG designs in Germany and Canada. However, some minor and shallow under-deposit corrosion indications have been observed recently in Alloy 800 tubing in some CANDU SGs, which leads to concerns over the long term behavior of this material. The Fe-Cr-Ni alloys are susceptible to localized

corrosion attack [3-4] and major contributing factor in all these corrosion mechanisms are the properties of oxide film formed on the alloy. The defects in the oxide film such as pores and grain boundaries are the main cause of localized attack. The localized attack such as pitting and IGA act as precursors for the initiation of SCC in the material.

The present study was aimed at optimizing the hot conditioning parameter by varying the temperature of oxide formation for minimum ion release rate during reactor operation. The characterization of oxide film formed at high temperature in lithiated environment on Alloy 800 was carried out using MLRS and GDQMS to identify the oxides formed on the surface and elemental variation along the oxide thickness respectively. The defect density of oxide films were studied using EIS.

2. Experimental Procedure

The Alloy 800 was solution annealed and rectangular coupons having dimensions of 15 mm x 10 mm x 1.5 mm were prepared. The coupons were then ground to 600 grit emery finish, subjected to ultrasonic cleaning and then degreased with acetone. The chemical composition of the alloy is tabulated in Table 1.

Table 1: Chemical composition of Alloy 800 used

Elements (wt %)							
Alloy	Ni	Cr	Fe	C	Mn	Si	Ti
800	27.2	21.6	45.49	0.05	2.31	0.14	0.38

The hot conditioning environment of demineralized water with 1 ppm lithium hydroxide (LiOH), maintaining a pH of 10.5 at room temperature was simulated in a static autoclave made of nickel alloy. The samples were exposed at three different temperatures of 250, 275 and 300 °C for 72 h in separate exposures at 10 MPa pressure. The initial and final weights of the samples were measured to six decimal value for each experiment. The autoclaved samples were examined under a scanning electron microscope (SEM) to assess the extent of coverage of oxide. The characterization of the oxide film was carried out by GDQMS technique, MLRS technique and EIS technique.



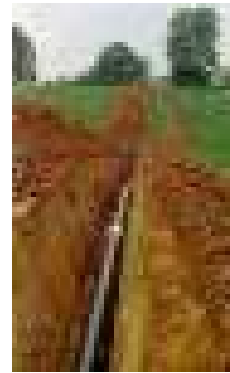
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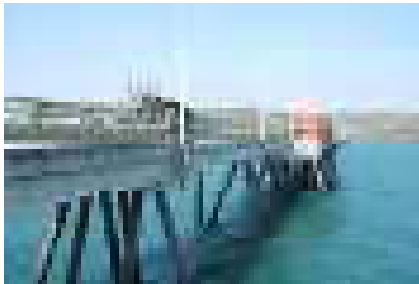


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3. Results and Discussion

The weight gain measurements of Alloy 800 in lithiated environment with varying temperature showed an initial increase in the weight and subsequent decrease at 300 °C. The dissolution of metal ions such as Ni²⁺ and the oxygen diffusion were enhanced at a higher temperature. Thus, the nickel-ferrite spinel layer and the inner Cr-rich layer will grow with increasing exposure temperature. At certain temperature Cr₂O₃ dominates the barrier layer of alloy thereby acting as an impediment to the further interaction of the alloy with the environment. Alloy 800 showed a decrease in weight gain at 300 °C indicating a stable oxide film on the surface. This is further reiterated by the GDQMS results which show increased chromium content in the oxide film with temperature. Figure 1 shows the variation of weight gain with temperature.

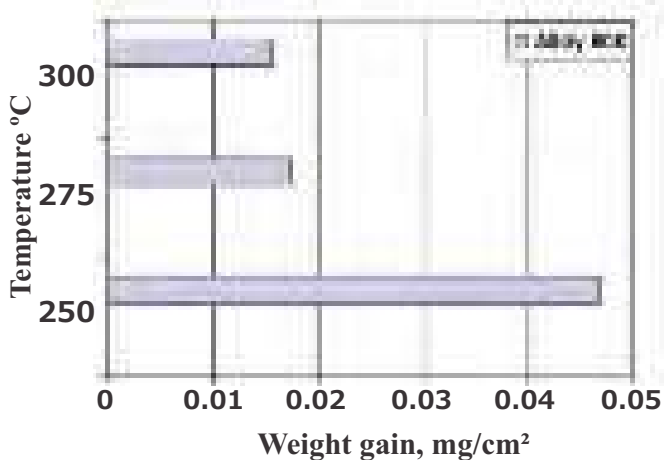


Figure 1: Weight gain measurements for Alloy 800 at different temperatures exposed in autoclave for 72 hours in lithiated environment [5].

The SEM micrographs (fig. 2) for the autoclaved Alloy 800 for increasing temperature showed a clear increase in density of oxide platelet and the coverage of these oxides is more as temperature increases. The porosity in the top layer (dissolution and precipitation layer) of oxide film also reduces with increase in temperature. The observation of porous oxides is based on morphology of the oxide film as seen in SEM micrographs (fig. 2 (a-c)).

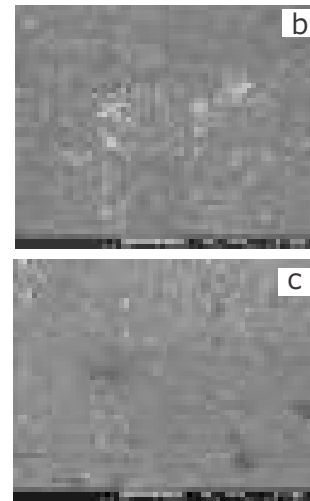
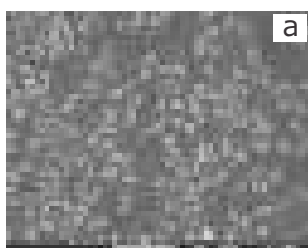
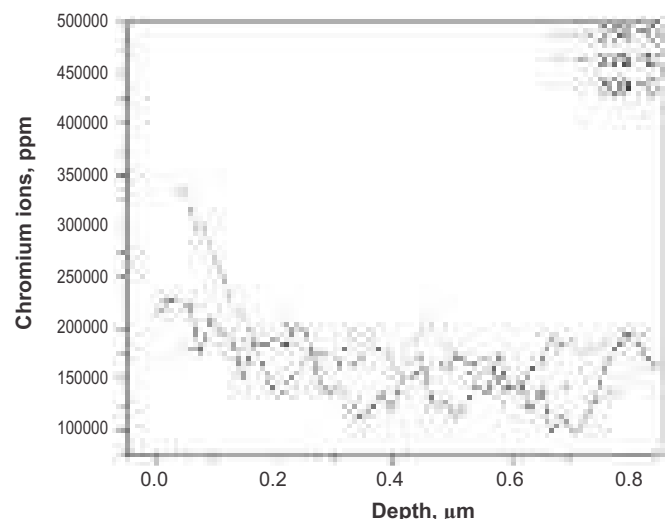


Figure 2: SEM micrograph of Alloy 800 at (a) 250 °C (b) 275 °C and (c) 300 °C for 72 hours autoclave exposure showing lateral spreading of oxide with temperature [5].

GDQMS results show chromium concentration for 250 °C and 275 °C is almost the same with the chromium content falling beyond 0.1 μm in figure 3(a). This fall in chromium concentration indicates the interface between the oxide film and the metal surface since at this thickness oxygen concentration becomes 50 % (fig. 3 (b)). In 250 °C exposure the chromium build up is not that significant in the oxide film which constitutes other elemental oxides such as NiO, FeO, Fe₂O₃ and Fe₃O₄ and spinel oxides (fig. 3). As the temperature increases to 300°C the chromium content is the highest but the oxygen content reduces considerably indicating the lesser presence of Fe and Ni oxides and the predominant oxide present is spinel in nature.

This can be reiterated by the Raman spectra for Alloy 800 (fig.4). The hydrated compound of chromium is present in higher amount at 300°C which is depicted as a plateau across the oxide thickness which is assumed to be 0.1 μm in the GDQMS plot (fig.3 (a)). The structure of the interface of oxide and metal plays a very



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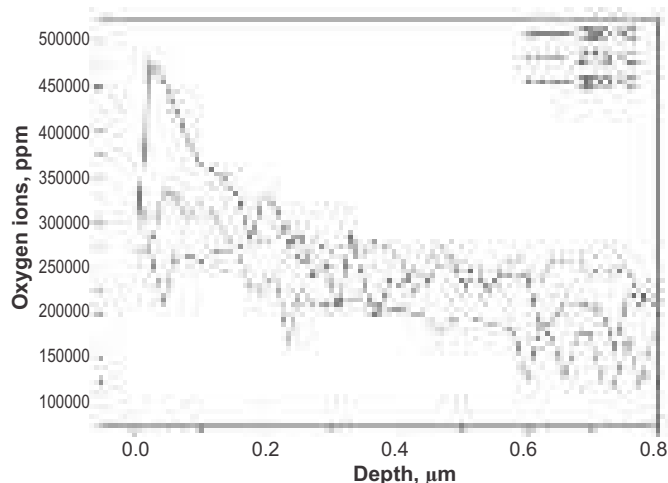


Figure 3: Chromium and oxygen profile from GDQMS analysis of autoclaved Alloy 800 with increased chromium presence and decreased oxygen content at higher temperatures [5].

crucial role in the electrochemical behavior and the oxidation rate of the nickel containing alloys. The nickel has a blocking effect on the diffusion of chromium from the alloy to the film during the initial stages of oxidation of Alloy 600 in PWR water [6]. Raman spectra obtained for Alloy 800 autoclaved at three different temperatures are shown in fig. 4. The peaks of the spinels NiFe_2O_4 at 701 cm^{-1} [7] and oxides such as Cr_2O_3 ($340\text{-}360\text{ cm}^{-1}$) and ($520\text{-}560\text{ cm}^{-1}$) [8, 9], Fe_3O_4 (676 cm^{-1}) [10] and NiO (532 cm^{-1}) [11] are present in all the cases. Among the three conditions of autoclaving, 250 °C treated conditions showed the highest intensity peaks in the Raman spectra (fig. 4). As the temperature increases at 275 °C

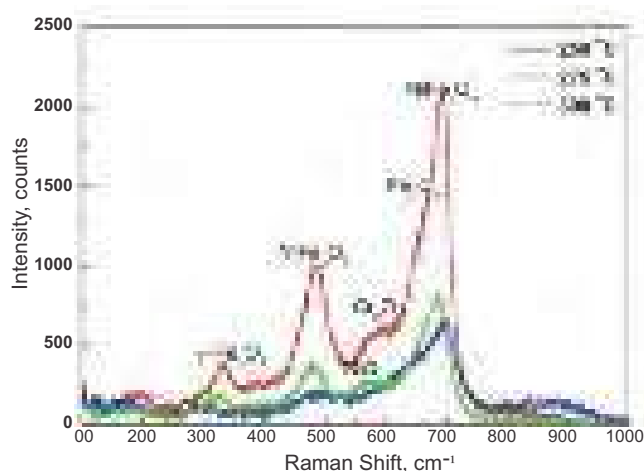


Figure 4: Raman spectra of the oxide layer on autoclaved Alloy 800 in lithiated environment showing prominent peaks of nickel-ferrite spinel[5].

there is lesser formation of $\gamma\text{-Fe}_2\text{O}_3$. At 300 °C the major peaks for NiFe_2O_4 is observed while the other oxide peaks are not predominant. The intensities of the oxide peaks are the highest for the oxide film formed at 250 °C compared to those formed at 275 and 300 °C. This can be correlated to the higher weight gain seen for this alloy after autoclaving at 250 °C resulting in a thicker oxide.

The electrochemical impedance studies for Alloy 800 were done in room temperature lithiated water in deaerated condition having a pH of 10.5. The capacitance values calculated after the fitting obtained over a potential range in Nyquist and Bode plots were plotted. The Mott-Schottky (M-S) plots for $1/C^2$ Vs. potential is plotted. The positive and negative slope of the curve in M-S plot gives defect density values for n-type and p-type defects respectively [12-14]. In case of nickel base alloys the defects are associated with spinel structure of oxides formed on these materials. Thus M-S plot would reflect the various acceptor and donor types available in the spinel structure. There are two acceptor types, A and B cation vacancies, which would give rise to a negative slope in the M-S plot and there is one donor type, O anion vacancies, which would give rise to a positive slope [15]. The defect density values for n-type and p-type defects present in the surface film formed on autoclaved samples at different temperature are tabulated in Table 2. With increase in temperature, Alloy 800 first shows an increase in defect density and then a decrease in defect density.

Table 2: Defect density of p-type and n-type defects in the oxide film formed on autoclaved Alloy 800 at different temperatures for 72 hours [5].

Temp.	Alloy 800	
	Defect density (n type)	Defect density (p type)
250°C	1.0×10^{23}	7.3×10^{22}
275°C	4.2×10^{23}	2.8×10^{23}
300°C	6.8×10^{22}	3.0×10^{22}

The change in slope in the M-S plot can be related to the existence of second donor level formed by Fe^{+2} ions placed in the octahedral sites of the unit cell of the spinel [16, 17]. The increase in defect densities is more characteristic of electronic properties of iron oxide and the decrease is due to the dominance of nickel oxide in the film formed [18].

4.0 Conclusions

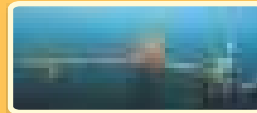
1. Alloy 800 showed decreased weight gain and increased lateral oxide distribution, Raman and GDOES analysis showed increased presence of nickel ferrite content and chromium content within the oxide film after autoclaving at 300 °C.
2. The best oxide film characteristics in terms of lowered defect densities, increased chromium content was observed at 300 °C.
3. Optimal temperature for hot conditioning of Alloy 800 in lithiated environment is 300 °C.



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NIGIS organized following certification course during the period May – Nov 2014 in India.

Course No.	Course	Period	Venue	No. of Participants
1	CIP Level 1	12 – 17 May 2014	Kochi	26
2	CIP Level 1	19 – 24 May 2014	Mumbai	7
3	CIP Level 1	26 – 31 May 2014	Mumbai	18
4	CIP Level 2	2 – 7 June 2014	Mumbai	21
5	CIP Level 1	30 June – 5 July 2014	Bengaluru	15
6	CIP Level 1	7 – 12 July 2014	Mumbai	19
7	PCS – 2	10 – 14 July 2014	Mumbai	12
8	CIP Level 1	1 – 6 Sept 2014	Kolkata	15
9	CIP Level 1	8 – 13 Sept 2014	Mumbai	27
10	Basic Corrosion	8 – 12 Sept 2014	Mumbai	13
11	CIP Level 2	15 – 20 Sept 2014	Mumbai	28
12	CIP Level 1	12 – 17 Nov 2014	Mumbai	30
13	CIP Level 2	24 – 29 Nov 2014	Mumbai	25

Photographs of CIP Courses



CIP Level 1 participants during 30 June – 5 July 2014



CIP Level 1 participants during 8 – 13 Sept 2014



PCS – 2 participants during 10 – 14 July 2014



Basic Corrosion participants during 8 – 12 Sept 2014

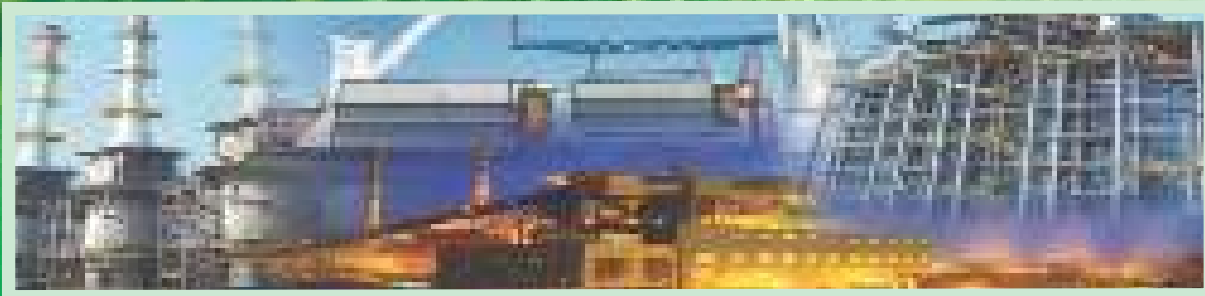


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Critical Review of Duplex Stainless Steel for Offshore Oil and Gas Applications: Metallurgy, Engineering Codes and Welding Practice

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Welding and Metallurgical Specialist Ontario, Canada

Abstract

Duplex stainless steels are high grade engineering alloys combining extremely good corrosion resistance with high strength and ease of fabrication. The corrosion resistance of these steels encompasses both resistance to general corrosion, pitting corrosion and stress corrosion cracking. By virtue of the above attributes these steels are common materials of choice in the upstream oil and gas production environments, for various critical components such as process piping, valves, manifolds, risers and many more.

Superior mechanical properties of DSS & SDSS's steels (as compared to standard austenitic stainless steels such as Type 304 or 316), allows thinner sections to be used for many critical components. The overall benefits and the Life Cycle Analysis (LCA) causes DSS and SDSS to be the outright winners providing significant cost benefits in many instances.

Duplex alloys cannot be used at elevated temperatures. Formation of various brittle intermetallic phases reduces toughness of these steels significantly. ASME B-31.3, the piping code often followed in offshore process piping; restrict the service temperature of all DSS and SDSS grades to 600°F (315°C).

Duplex alloys could be broadly divided into three main groups: lean duplex, 22% Cr duplex and 25% Cr super duplex; with hyper duplex grade being an addition in the family. The metallurgy of the duplex stainless steel family is complex and requires very close control of weld metal composition and heat treatment regimes to ensure that mechanical properties and / or corrosion resistance would not be adversely affected. To produce the optimum mechanical properties and corrosion resistance, the microstructure or phase balance of both the parent and weld metal should be approximately 50% ferrite and 50% austenite. This precise value is impossible to achieve with accuracy, but a range of phase balances between 35 - 60% ferrite and the rest austenite is acceptable in the various industry standards.

This paper illustrates the various grades of DSS/SDSS, their pros and cons, requirements of design Codes/specifications, metallurgical & weldability issues.

Keywords: Duplex Stainless Steels, Design Codes/Industry Standards, Corrosion Resistance, Metallurgy.

Introduction

Duplex Stainless Steels are two-phase alloys based on the iron-chromium-nickel (Fe-Cr-Ni) system, comprising of approximately equal amounts of Body-Centered Cubic (BCC) ferrite(α -phase), and Face-Centered Cubic (FCC) austenite(γ -phase), in their microstructure. Over last 30 years duplex stainless steels have seen extremely widespread application in the offshore oil, gas industries. Lately this material is considered to be an excellent choice for downstream refining and petrochemical industries. An attractive combination of high strength and excellent resistance to general corrosion & various forms of stress corrosion cracking and good weldability makes Duplex and Super Duplex Alloys as candidate materials for applications as stated above.

Corrosion resistance (both against pitting, chloride) and other forms of Stress Corrosion Cracking (SCC) is the result of the presence of ferrite and austenite phases in the microstructure. In the 'sweet' and 'sour' corrosive environments for upstream oil and gas environments, duplex stainless steels are the standard design basis materials. In regards to the downstream side for many engineering applications in the petroleum and refining industry, Duplex Stainless Steels (DSS) are currently the preferred material over conventional austenitic stainless steels.

Metallurgy of Duplex Stainless Steels

Figure 1 shows a schematic isoplethal section of the Fe-Cr-Ni diagram for an iron content of 68%. As shown in this figure, DSS solidify as a fully ferritic structure, which partly transforms to austenite as the temperature falls to approximately 1000° C (1832°F) depending on the composition of the alloys. Throughout the transformation there is little change in the **equilibrium ferrite–austenite balance** even at lower temperatures. This allows the desired phase balance and the diffusion of all elements closer to their preferred equilibrium positions during initial solidification. Nitrogen promotes austenite formation from the ferrite at a higher temperature. However, as cooling proceeds to lower temperatures, carbides, nitrides, sigma and other intermetallic phases are all possible as micro structural constituents.

The **austenite/ferrite ratio** depends on the chemical composition of the alloy and the heat treatment. Too fast cooling rates during solidification may reduce this α - γ retransformation process. Small changes in the nickel and chromium content have a large influence on the amount of austenite and ferrite in duplex stainless steels.

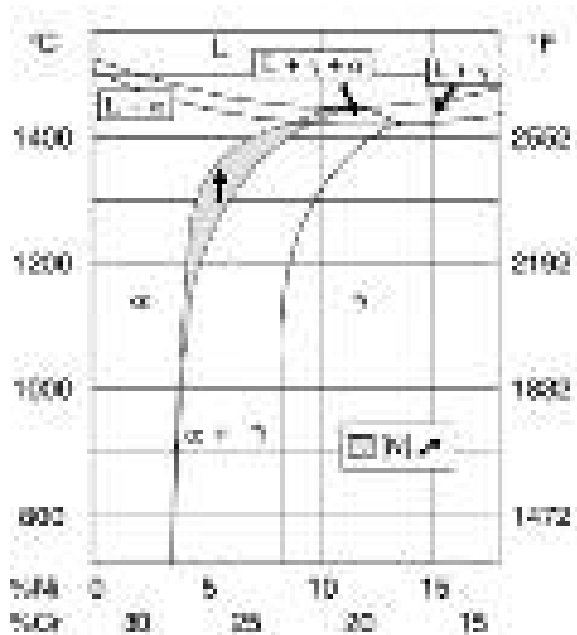


Figure 1 : Solidification diagram of duplex stainless steels Fe-Cr-Ni system at 68% iron ⁽³⁾

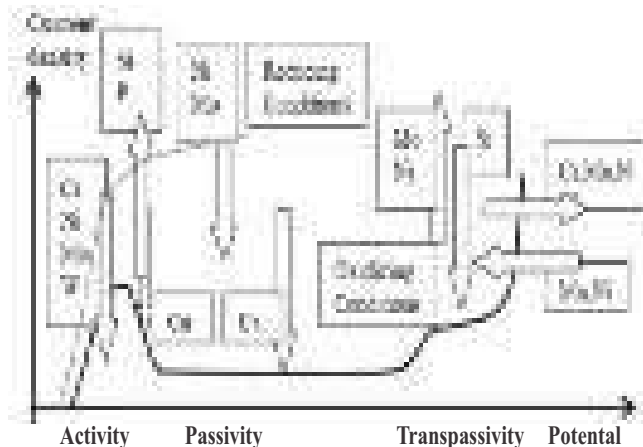


Figure 2: Influence of alloying elements on the corrosion resistance ⁽²⁾

Table-1, explains the roles of various alloying elements in duplex stainless steels. Alloying elements in DSS/SDSS are categorized as ferrite stabilizer and austenite stabilizers. Individual effects of these alloying elements are explained at great length in this table.

Higher alloyed Super Duplex Stainless Steels (SDSS) developed typically in the late 1980's are designed to withstand more aggressive environments, but also bear a higher risk of precipitation unfavourable phases due to the higher alloying element content. Super DSSs are usually characterized by having a PREN greater than 40. The higher the PREN, the better the predicted corrosion properties of a DSS are. This is an increasingly common specification for certain offshore applications. However, PREN numbers only provide an approximate grading of alloys and do not account for the microstructure of the material. An acceptance corrosion test on material in the supply condition is much more meaningful and a necessity in many offshore applications. The most common way of ranking stainless steels for their PREN according to the relation between the amount of the essential elements and the corrosion properties can be formulated by using this relation.

$$\text{PREN} = (\%Cr) + (3.3 \times \%Mo) + (16 \times \%N)$$

Or

$$\text{PREW} = (\%Cr) + (3.3 \%Mo) + (0.5 \%W) + (16 \%N)$$

Table-1
Role of the Alloying Elements in Duplex Stainless Steels

Alloying Elements	Role	Effects on Duplex S.S Metallurgy
Chromium	Ferrite stabilizer	<ul style="list-style-type: none"> ● Increase corrosion resistance. ● The duplex grades are designed for superior corrosion resistance than ferritic or 304/316 austenitic grades
Molybdenum	Ferrite stabilizer	<ul style="list-style-type: none"> ● Together with Cr improves chloride corrosion resistance to stainless steels. ● With at least 18%, chromium content, additions of molybdenum become approximately three times as effective as chromium additions against pitting and crevice corrosion in chloride-containing environments. ● Molybdenum increases the tendency DSS to form detrimental intermetallic phases. Typically restricted to 4% in duplex stainless steels
Nickel	Austenite stabilizer	<ul style="list-style-type: none"> ● DSS/SDSS contain an intermediate amount of nickel such as 4 to 7%. ● Prevents formation of detrimental intermetallic phases in austenitic stainless steels ● Increases notch-toughness of the austenitic stainless steels. ● Balances the austenite Ferrite Ratio
Nitrogen	Austenite stabilizer	<ul style="list-style-type: none"> ● Nitrogen is added to offset the effects of chromium and molybdenum contents to form <u>sigma phase</u>. ● Increases pitting and crevice corrosion resistance ● Substantially increases strength (mechanical properties) and toughness. ● The most effective solid solution strengthening element. ● Delays formation of intermetallic phases during welding and fabrication.
Manganese	Austenite stabilizer	<ul style="list-style-type: none"> ● The addition of manganese has a controversial effect; they are known to increase the nitrogen solubility and in some respect to stabilize the austenitic phase directly or indirectly. ● On the contrary, most of the localized, mainly pitting corrosion resistance investigations have underlined a negative effect of manganese additions.
Sulphur		<ul style="list-style-type: none"> ● Among the detrimental alloying elements, Sulphur likely has the worst effect. Sulphur is generally combined with manganese or several oxides to form precipitates. The worst case is a large oxide inclusion surrounded by sulphur species. ● Locally, the passive film is unable to resist and severe local corrosion may start.

Corrosion Resistance

Stainless steels with at least 12% Chromium are corrosion resistant due to formation of an invisible passive film that is established in oxidizing environments. This is equally true with duplex and super duplex stainless steels. The relatively high chromium, molybdenum and nitrogen also give them very good resistance to chloride pitting and crevice corrosion. These steels exhibit a high level of corrosion resistance in most environments. DSS are often used in lieu of austenitic SS in service environments where the common austenitic grades would have problems with chloride pitting or Chloride SCC.

Their duplex structure is an advantage in potential CSCC environments. If the microstructure contains at least 25 or 30% ferrite, DSS are far more resistant to CSCC than Types 304 or 316. Ferrite is, however, susceptible to hydrogen embrittlement; thus, the DSS do not have high resistance in environments or applications where hydrogen may be charged into the metal.

Pitting and Crevice Corrosion Resistance

Each grade stainless steel can be characterized by a temperature above which pitting corrosion will initiate and propagate within approximately 24 hours to a visibly detectable extent. Pitting initiation below this temperature will not occur in indefinitely long times. This temperature is known as the Critical Pitting Temperature (CPT). It is a characteristic of the particular type of stainless steel and specific service environment and may occur over range of temperatures. This is true, as pit initiation is random, and the CPT is sensitive to minor within product / grade variations. However, with a new research tool described in ASTM G 150, CPT can now be accurately and reliably measured by electro potential measurements.

Similar critical temperature for initiation of crevice corrosion is called the Critical Crevice Temperature (CCT). The CCT is dependent on the individual sample of stainless steel, chloride environment and nature (i.e. tightness, length, etc.) of the crevice. This geometrical factor of the crevices causes more scatter for the measurement of CCT than for the CPT. Typically, the CCT could be 15 to 20°C (27 to 36°F) lower

than the CPT for the same steel and corrosion environment.

DSS and SDSS are generally designed with higher Cr levels than the austenitic stainless grades; since the duplex grades readily accept alloying with molybdenum and nitrogen, most DSS grades have significantly better chloride pitting and crevice corrosion resistance than the standard austenitic SS, such as 304L and 316L (UNS S30403 and S31603). Depending on the alloy content, some duplex grades are among the best performing stainless steels. The most common tools for predicting the chloride pitting resistance of corrosion resistant alloys are the PREN and CPT (as narrated below). A comparison of pitting and crevice corrosion resistance for a number of stainless steels in the solution annealed condition as measured by the ASTM G 48 procedures (10% ferric chloride) is given in Figure 3.

Generally, higher critical pitting or crevice corrosion temperatures indicate greater resistance to the initiation of these forms of corrosion. Due to the welding heat input cycle, CPT and CCT in as-welded or stress relieved conditions would be expected to be somewhat lower than the equivalent base metal.

The CPT and CCT of 2205 and all other grades of DSS are well above those of Type 316 (refer to Figure 3). This makes 2205 and other DSS / SDSS a versatile preferred material for applications involving chlorides / salinity, such as backish waters and deaerated brines. However, for critical seawater applications involving superior corrosion resistance, the super duplex grades are extremely popular and highly competitive against higher alloyed austenitic steels and Nickel base alloys

$$\text{CPT} = \text{constant} + \%Cr + 3.3x\%Mo + 16x\%N$$

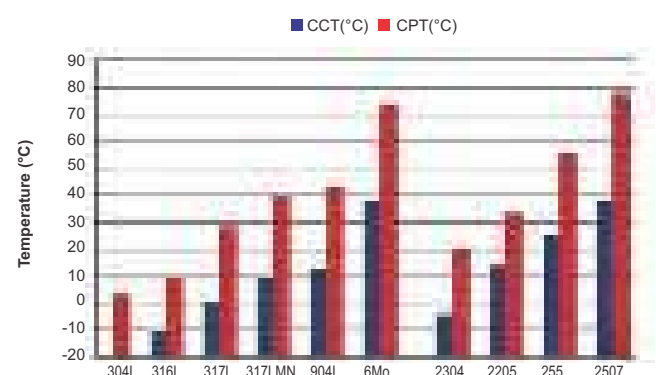


Figure 3: Various CCT and CPT temperatures (°C) ⁽³⁾

Resistance to Stress Corrosion Cracking

Initial applications of DSS for offshore oil and gas industries were based heavily on their resistance to CSCC, which is significantly better than austenitic stainless steels with similar chloride pitting and crevice corrosion resistance. In many lower refining, petrochemical process

industries, DSS are replacements for austenitic grades in applications with a significantly risk of SCC (both CSCC and sulphide SCC). However, DSS may be susceptible to stress corrosion cracking under certain conditions such as in high temperature, chloride-containing environments, or when conditions favour hydrogen-induced cracking.

Some information with respect to SCC in various media are provided in Table-2.

Table 2
Examples of environments which SCC of duplex stainless steels may be expected ⁽³⁾

Alloy Type	42% MgCl ₂ Boiling 154°C U-Bend	35% MgCl ₂ Boiling 125°C U-Bend	40% CaCl ₂ 100°C 0.9xY.S.	25-28% NaCl Boiling 106°C U-Bend	26% NaCl Auto-clave 200°C U-Bend	600 ppm Cl (NaCl) Auto-clave 300°C U-Bend	100 ppm Cl (Sea Salt +O ₂) Auto-clave 230°C U-Bend
S.S 304L/316L*	Cracking anticipated	Cracking anticipated	Cracking anticipated	Cracking anticipated	Cracking anticipated	Cracking anticipated	Cracking anticipated
Sandvik 3RE60*	Cracking anticipated	Cracking anticipated	Cracking not anticipated	Cracking not anticipated	Cracking anticipated	Insufficient data	Cracking anticipated
Duplex 2205	Cracking anticipated	Cracking anticipated	Cracking not anticipated	Cracking not anticipated	Cracking anticipated	Insufficient data	Cracking anticipated
25 Cr Duplex	Cracking anticipated	Cracking anticipated	Cracking not anticipated	Cracking not anticipated	Cracking anticipated	Insufficient data	Insufficient data
Super Duplex	Cracking anticipated	Cracking anticipated	Cracking not anticipated	Cracking not anticipated	Cracking not anticipated	Insufficient data	Insufficient data

Cracking anticipated
 Cracking not anticipated
 Insufficient data

*- Information on these materials are provided for information.

Table 3: Chemical composition of commonly used DDS and other alloys ⁽¹⁾

UNS #	Type ^b	Cr	Mo	Ni	N	Cu	C	Mn	P	S	Si	Min PREN ^d	Other
First Generation DSS													
S32900	Type 329	23.0 - 28.0	1.0 - 2.0	2.5 - 5.0	-	-	0.080	1.00	0.040	0.030	0.75	26.3	-
S31500	"3RE6 0"	18.0 - 19.0	2.5 - 3.0	4.25 - 5.25	0.05 - 0.10	-	0.030	1.20 - 2.00	0.030	0.030	1.40 - 2.00	27.1	-
Lean and Semi-lean DSS													
S32304	2304 ^c	21.5 - 24.5	0.05 - 0.60	3.0 - 5.5	0.05 - 0.20	0.05 - 0.60	0.030	2.50	0.040	0.030	1.00	22.5	-
S32101	2101	21.0 - 22.0	0.10 - 0.80	1.35 - 1.70	0.20 - 0.25	0.10 - 0.80	0.040	4.0 - 6.0	0.040	0.030	1.00	24.5	-
S32003	2003	19.5 - 22.5	1.50 - 2.00	3.0 - 4.0	0.14 - 0.20	-	0.030	2.00	0.030	0.020	1.00	26.7	-
25% Cr and Super DSS													
S31200	-	24.0 - 26.0	1.2 to 2.0	5.5 to 6.5	0.14 - 0.20	-	0.030	2.00	0.045	0.030	1.00	30.2	-
S31260	-	24.0 - 26.0	2.5 to 3.5	5.5 to 7.5	0.10 - 0.30	0.20 - 0.80	0.030	1.00	0.030	0.030	0.75	34.0	W: 0.1 - 0.5
S32520	-	24.0 - 26.0	3.0 to 5.0	5.5 to 8.0	0.20 - 0.35	0.50 - 3.00	0.030	1.50	0.035	0.020	0.80	37.1	-
S32550	255 ^c	24.0 - 27.0	2.9 to 3.9	4.5 to 6.5	0.10 - 0.25	1.50 - 2.50	0.040	1.50	0.040	0.030	1.00	35.2	-
S32750	2507 ^c	24.0 - 26.0	3.0 to 5.0	6.0 to 8.0	0.24 - 0.32	0.50	0.030	1.20	0.035	0.020	0.80	37.7	-
S32760	-	24.0 - 26.0	3.0 to 4.0	6.0 to 8.0	0.20 - 0.30	0.50 - 1.00	0.030	1.00	0.030	0.010	1.00	37.9 ^d	W: 0.5 - 1.0
S32950	-	24.0 - 29.0	1.0 to 2.5	3.5 to 5.2	0.15 - 0.35	-	0.030	2.00	0.035	0.010	0.60	31.7	-
S39274	-	24.0 - 26.0	2.5 to 3.5	6.0 to 8.0	0.24 - 0.32	0.20 - 0.80	0.030	1.00	0.030	0.020	0.80	38.6	W: 1.5 - 2.5
S39277	-	24.0 - 26.0	3.0 to 4.0	6.5 to 8.0	0.23 - 0.33	1.20 - 2.00	0.025	0.80	0.025	0.002	0.80	38.9	W: 0.8 - 1.2

a) Single values indicate maximum content unless otherwise specified. The number of significant figures reflects the ASTM recommended practices as shown in ASTM A959 and in ASTM A240, but these rules have not yet been universally adopted for all product forms and all specifications systems.

b) Unless otherwise indicated, a grade designation originally assigned by the American Iron and Steel Institute (AISI). Names shown in quotation marks are not listed in ASTM specifications.

c) As listed by ASTM, a widely-used common

name (not a trademark and not associated with any one producer).

d) Minimum PREN is calculated based on the minimum chemistry requirements. Note that UNS S32760 which has a minimum PREN of 40 required by the ASTM / ASME material specifications.

e) The chemistry may vary slightly between product forms and the specifications often change with time. Hence, for the latest chemistry requirements, the product specifications should be reviewed.

Table 4: ASME and ASTM specifications for DSS ⁽¹⁾

Product Form	ASME or ASTM Specifications
Plate, Sheet	SA-240
Bar Products	SA-479, A276
Pipe	SA-790, A928
Tubing	SA-789
Fittings	SA-815
Forgings	SA-182
Castings	SA-351, A890, A995
Testing	ASTM A923

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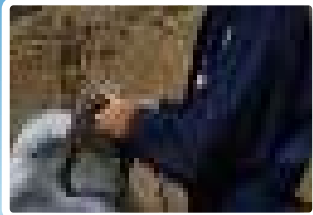
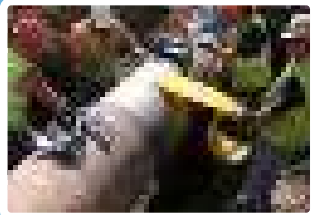
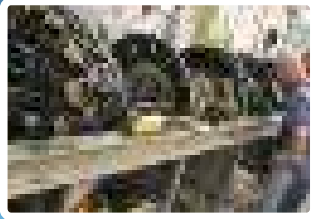
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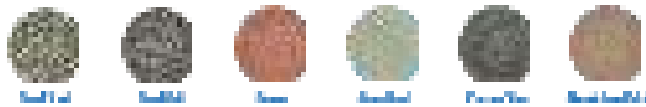
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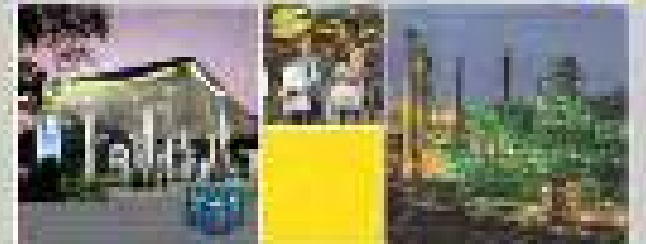
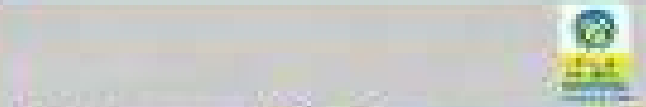
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Fiber Bragg Grating Sensors to monitor corrosion of structural steel

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CSIR-Structural Engineering Research Centre, Chennai

ABSTRACT

Corrosion detection and monitoring are essential diagnostic measures for preserving material health and reducing economic loss of civil engineering infrastructures, life line structures, transmission and telecommunication towers, bridges, water tanks, silos, offshore platforms etc. Thus improving the effective sensor technology for corrosion detection can reduce the economic loss and provide safe structures with long service. In this paper, Fiber Bragg Grating (FBG) sensors are used to monitor the progress in corrosion process of structural steel coupons under stressed and unstressed condition in a laboratory environment. The durability of steel structures and easy maintenance in severe environments such as marine is extremely important and is considered for the study. The accelerated corrosion process is carried out by keeping the test specimen as anode and a similar parent material as cathode, immersed in 3.5%NaCl solution (electrolyte). During the progress in corrosion process, the strains are monitored with electrical resistance strain gauges and FBG sensors. It is observed that the pH and temperature of the electrolyte changes with the progress in corrosion process. Strain in coupons under stressed and unstressed condition are measured and difference in strain behaviour is brought out and reliability of measurements in adverse environment is noticed. Experimental results showed that the FBG sensor is capable to monitor the occurrence of corrosion in steel structures in aggressive environment.

Keywords: Fiber bragg grating (FBG) sensor, electrolyte, accelerated corrosion, stress, electrical resistance strain gauge.

INTRODUCTION

Optical fiber technology is currently generating considerable interest, particularly with respect to its use in civil engineering applications or in remote health monitoring. These optical sensors, which are superior in durability, corrosion resistance, water proof and explosion proof, provide numerous advantages over conventional electrical resistance sensors such

as their small size, their low weight or their immunity to electromagnetic interference. Fiber Bragg Gratings (FBG) sensor are one of the advanced devices in this technology, especially to measure strain and deformations in severe environments. FBG based sensors are capable to measure the physical parameters such as strain, pressure, temperature. [1-3] had reviewed advances in Fiber Bragg sensors technologies]. Fiber gratings are intrinsically sensing elements as their resonant wavelengths vary with the perturbation induced change of the grating period and the fiber effective index. Although the conventional electric resistance based sensors were well established and are still under continuous development, fiber grating sensors have exhibited their distinct advantages and competitiveness in developing e.g. sensor array multiplexed in serial, remote sensors for harsh environment monitoring, and ultrasensitive miniature optical sensors, besides their well known merits including electrically passive operation, immunity to electromagnetic interference, self-referencing and high sensitivity. [4] demonstrated simultaneous measurement of strain and temperature using FBG sensors. The corrosion phenomena of structural steel involve mainly two elements: the material and its environment. In particular, corrosion is defined as the deterioration of a material, usually a metal, which results from a reaction with its environment, causing the degradation of both. The local pH and temperature influence corroding chemical reactions and affects the rate of corrosion. In the present study comparative measures of laboratory simulated corroded coupons bonded with FBG and conventional electrical resistance sensors are carried out. Corrosion is induced by galvanostatic method on structural steel coupons. The variation in temperature and pH of electrolyte are monitored with WTW probes. The experiments are conducted under two conditions, Case 1: unstressed and Case 2: stressed and the results are discussed.

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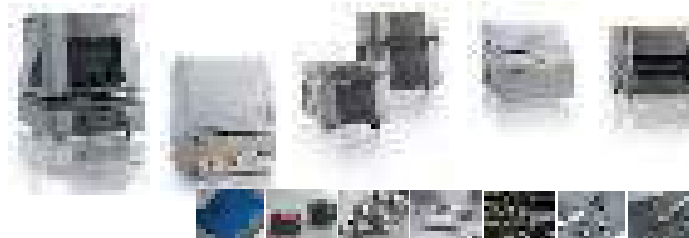
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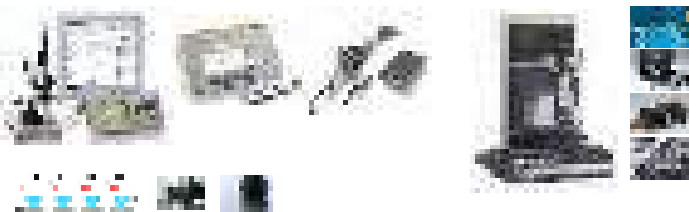


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FIBER BRAGG GRATING (FBG) SENSORS

The FBGs used are fabricated by creating a periodic modulation of the refractive index along a photosensitive silica fiber, reflectivity of more than 95% and a bandwidth of 0.2nm. Fiber bragg gratings are used as strain or temperature, pH sensors in which variations of those parameters are transformed to a shift of the Bragg wavelength reflected back as a Gaussian profile signal. In general, fiber bragg gratings are periodic structures that are imprinted directly into the core of glass optical fiber by powerful ultraviolet radiation. Such structure consists of a periodically varying refractive index over typically several millimetres of the fiber core. The specific characteristic of FBG for sensing applications is that their periodicity causes them to act as wavelength sensitive reflectors. During imprinting process, the intensity of the ultraviolet illumination is made to occur in a periodic fashion along the fiber core. At a sufficiently high power level, local defects are created with in the core, which then give rise to a periodic change in the local refractive index. This change in refractive index (RI) created is permanent and sensitive to a number of physical parameters, such as pressure, temperature, strain and vibration. Thus by monitoring the resultant changes in reflected wavelength FBG can be used for sensing applications to measure various physical quantities. Fiber Bragg grating sensor the response arises from two sources, namely the induced change in pitch length (Λ) of the grating and the perturbation of the effective core refractive index (n). The wavelength of the reflected spectrum band is defined by the bragg condition [5], given by the expression

$$\lambda_B = 2n\Lambda \quad (1)$$

Where n is effective refractive index of the core and Λ is the grating pitch.

Λ fiber bragg grating consists of a longitudinal, periodic variation in the refractive index of the core of an optical fiber as shown in Fig.1.

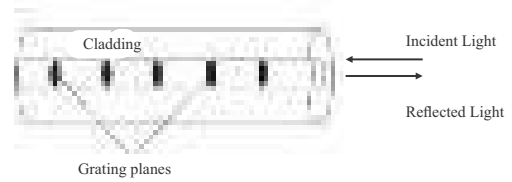


Fig.1 Schematic of the in-fiber grating structure of a Fiber Bragg Sensor

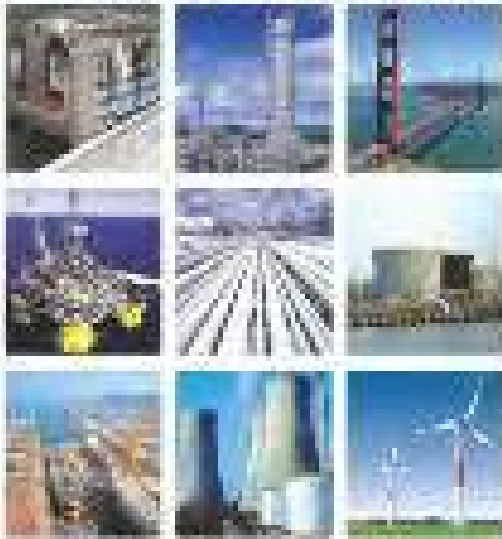
FIBER BRAGG GRATING SENSING TECHNIQUE

Fiber Bragg grating (FBG) is a passive optical component obtained by recording a local, longitudinal period modulation of the refractive index in the optical fiber core, as depicted in Fig.2(a). Due to the local change of the refractive index, any light propagating along the fiber core suffers partial reflection at each of the grating layers. As a consequence of the periodicity of the index modulation, constructive interference of the reflected light takes place for those wave vectors that satisfy the Bragg condition given in Eq.1. This implies that part of the incident spectrum is not transmitted, but reflected, by grating as shown in Fig.2(a). The technical details of the FBG used for the present study is given in Table.1. Since the wavelength reflected by the grating is a function of n and Λ , variations of the temperature ΔT , variations of the pH, ΔpH , or of the strain to which the grating is submitted, $\Delta \epsilon$, give rise to appreciable wavelength change, which can be considered as $\Delta \lambda_B = \lambda_B (\alpha \Delta T + \beta \Delta pH + \gamma \Delta \epsilon)$ as indicated in Fig.2 (b). Where α, β, γ are constant coefficients and $\Delta T, \Delta pH, \Delta \epsilon$ are incremental increase in temperature, pH and strain respectively. The principle of operation of FBG sensing consists of monitoring the Bragg wavelength and correlating wavelength change, $\Delta \lambda_B$, to the variations on the measured value.

Table.1 Technical details of FBG

Centre wave length	CW tolerance	Reflectivity	3dB bandwidth	Fiber Type	Grating Length
1540nm	+/- 1nm	0.70%	0.25+/- 0.05nm	SMF28-C Polyimide	10mm

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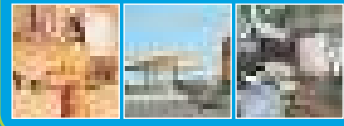
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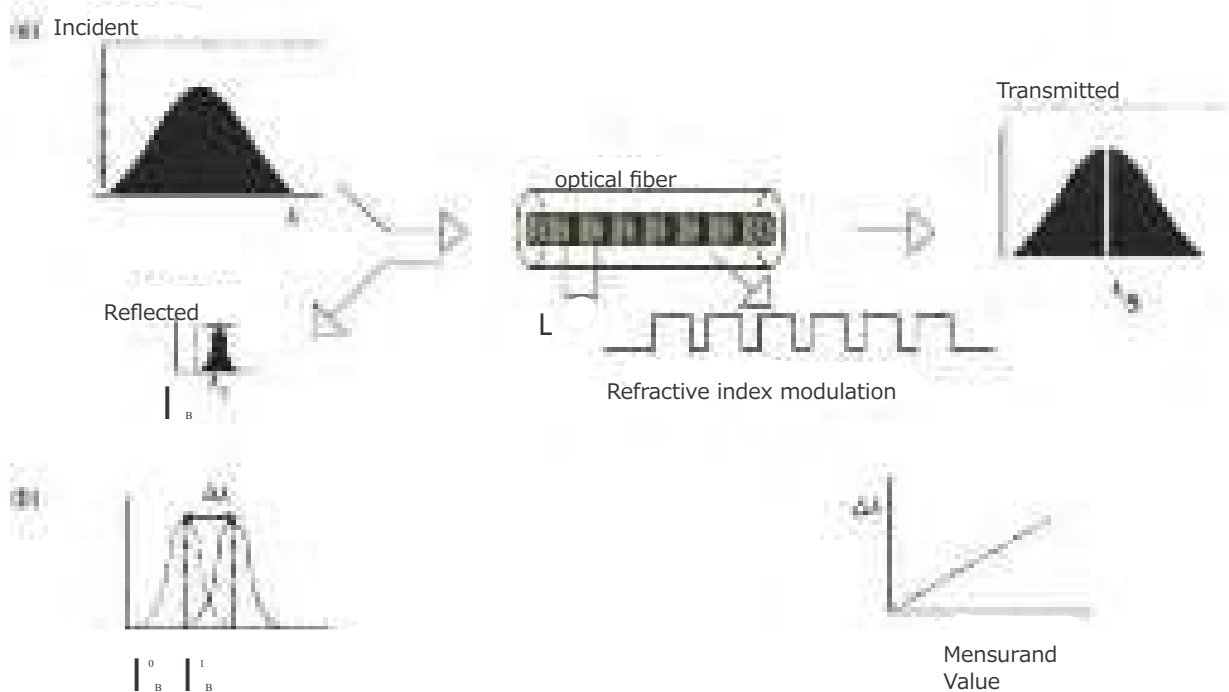


Fig.2 Scheme of Fiber Bragg grating operation.

The length of the FBG, which is an integral part of the fiber, is normally few millimetres. When light from a broadband source is launched in the fiber, the FBG reflects wavelength intensity that satisfies Eq.1 while the rest of the wavelengths get transmitted. The reflected wavelength is called Bragg wavelength λ_B and is determined by the period of the grating (L). The bragg wavelength is sensitive to changes in either the fiber-core refractive index or the period of the grating. This makes it an excellent sensor for measurement of mechanical or thermal perturbations. Unlike intensity modulated sensors which need a very stable light source and interferometric sensors which need a highly coherent laser, fiber bragg grating based sensors generally require a broadband source and a high resolution wavelength shift detection system. Fiber Bragg gratings have been reported for the measurements of strain temperature, dynamic magnetic field etc. The sensing principle is that the Bragg wavelength will vary with the change of these parameters experienced by the fiber. In the case of load induced strain, both physical elongation of the optical fiber (and the corresponding change in the grating pitch) and the change in the refractive index of the fiber due to photo elastic effects takes place. As a result the shift in Bragg wavelength occurs. The shift in Bragg wavelength with strain can be expressed as

$$\Delta \lambda_B = (1 - p_e) \lambda_{BT} \quad (2)$$

Where e the applied strain and p_e is an effective photo elastic coefficient term, for the present study it has been taken as 0.2.

The sensing of strain and temperature due to physical elongation of the sensor and change in fiber index due to photo elastic effect is expressed [1] as

$$\Delta \lambda_B = 2nL \left(\left\{ 1 - \left(\frac{n^2}{2} \right) [P_{12} - n(P_{11} + P_{12})] \right\} e + \left[a + \frac{dn}{dT} \right] \Delta T \right) \quad (3)$$

Where ϵ is the applied strain, P_{ij} coefficients are the Pockel's coefficients of the stress-optic tensor, ν is Poisson's ratio, and a is the coefficient of thermal expansion of the fiber material and ΔT is the temperature change.

The factor $\left(\frac{n^2}{2} \right) [P_{12} - n(P_{11} + P_{12})]$

has a numerical value of ≈ 0.2 .

However there is not much studies are carried out to sense the change in fiber index due to combine effect of change in strain, temperature and pH.

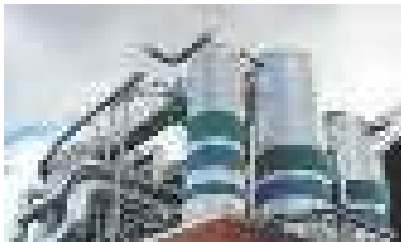
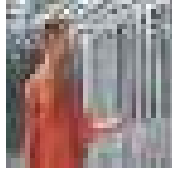
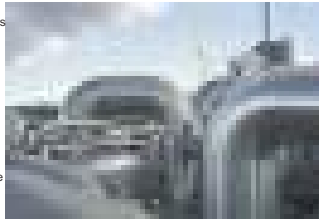
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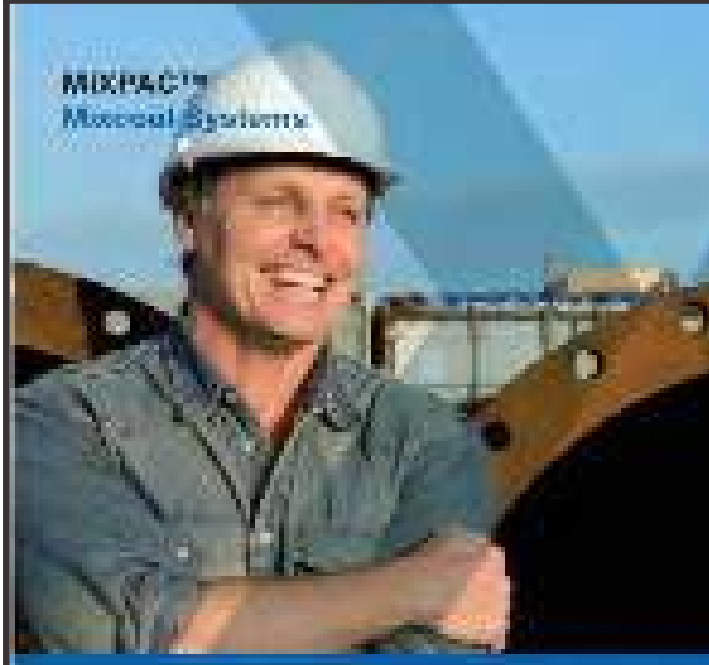
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ELECTRICAL RESISTANCE STRAIN GAUGE

The electrical resistance strain gauge is a physically simple device, which can be easily applied in a straightforward manner for elementary measurements of surface strains. In the present study electrical foil strain gauge of gauge length 2mm is fixed to the coupon using cyano acrylate adhesive. The foil gauge, Fig.3 is essentially a small printed circuit on photographic plate. The details of the foil gauge used for the present study are shown in Table. 2. The gauge factor is 2.0. In order to use such a gauge for detecting a strain of $1\mu\epsilon$ (which corresponds to that produced by a 206.84kN/m^2 stress in steel for a simple uniaxial loading), a change of resistance ΔR of $240\mu\Omega$ need to be measured with an indicator.

Table.2 Details of Foil strain gauge

Gauge Length (mm)	Gauge Width (mm)	Backing Length (mm)	Backing Width (mm)	Resistance (Ω)
2	1.5	6.5	3	120

Note: The present gauge backing is made of epoxy resin with thickness 0.03mm which exhibits excellent electrical insulation performance. The backing has self-temperature compensation for steel ranging from 0°C to 80°C .

The all electric strain gauges transfer the extensional strain of the surface of a metallic surface into proportional strain in the element of a resistive strain gauge. Thus the strain changes can be measured as

$$R = r \frac{L}{A} \quad (4)$$

Where A is uniform cross section of the wire, and r is resistivity and L is length of the wire, R is the resistance.

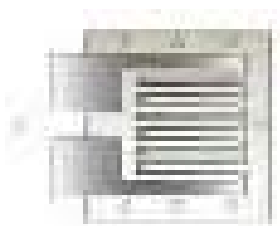


Fig.3 Typical foil strain gauge

The strain sensitivity can be defined as a basic bulk property of the strain-sensitive alloy used in a strain gauge. When this metal is formed into a grid, and provided with attachment points for lead wires, the gauge will exhibit a different relationship between resistance change and applied strain. The term 'gauge factor' (GF) [6] is used to quantify this relationship, and is defined as

$$GF = \frac{\Delta R/R_o}{\Delta L/L_o} = \frac{\Delta R/R_o}{\epsilon} \quad (5)$$

Where ΔR is resistance change in the gauge in ohms, R_o is original or unstrained gauge resistance, ϵ is unit engineering strain in the specimen surface under the gauge grid $\Delta L/L_o$. However the use of electric strain gauges in harsh environment is not advisable due to their low sensitivity to respond against variation in temperature and pH.

EXPERIMENTAL SET-UP

Experiments are carried out with fiber bragg grating-based sensors and conventional electrical resistance strain gauges to monitor strains induced during simulated corrosion of a stressed coupon under galvanic method. The tension coupons are cut from tubes of dia 76.1 mm and are corroded by using accelerated corrosion process. The corrosion process is carried out by keeping the test specimen as anode and steel plate cut from the same parent metal as cathode. They are placed in the electrolyte of 3.5% NaCl solution. The specimen (coupons are 250 mm long with a mid gauge length of 60 mm and width as 12.5mm, as per ASTM E8M specifications, Fig.4) to be corroded is treated as anode and a structural steel specimen of slightly large area of exposure than anode ($80\text{mm} \times 75\text{mm}$) is considered as cathode. Anode is connected to the +ve terminal. A specimen cut from the same parent metal was used as cathode and connected to the -ve terminal. Calomel electrode is used to measure the initial and final potential under zero current condition. The width of the gripping edge is 75 mm and width of the gauge length area is 12.5 mm. The galvanic corrosion of the

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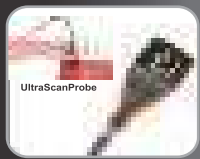
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gauge portion is completely achieved by passing current of 3.4Amps for duration of 300 minutes. The gauge length of the coupon is bonded with FBG sensor of centre wavelength 1540nm and grating length 10mm and conventional electrical resistance strain gauge of 2mm gauge length on the opposite face of corrosion. The corrosion is carried out by two methods, case1 is unstressed condition, Fig.5 and case2 is stressed condition, Fig.6. Under stressed condition, the tension coupon specimen is gripped in a 25 ton UTM and applied 10% of the ultimate load to generate stress under the test condition.

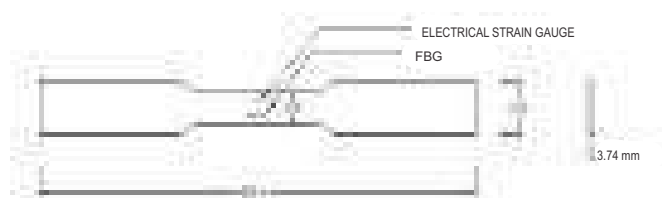


Fig.4 Structural steel coupons glued with FBG and Electrical resistance strain gauge.

The sensing capability of FBG sensor in the corrosive environment to sense strains generated due to irregular changes on the surface, variation in pH and temperature depend on refractive index and pitch of grating. While the performance of ordinary strain gauge used is guaranteed till 23°C with 50% relative humidity and apparent strain is guaranteed for a range of 0-80°C. And influence of variation in pH is unknown. During the accelerated corrosion process, it is observed that temperature as well as pH of the electrolyte varies. The temperature and pH characteristics of the electrolyte during corrosion process are also measured with WTW probes.

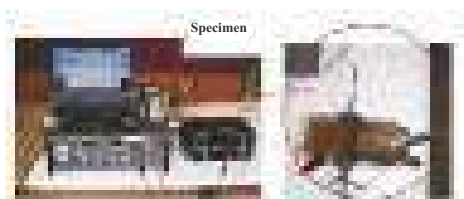


Fig.5 Experimental set-up for unstressed condition

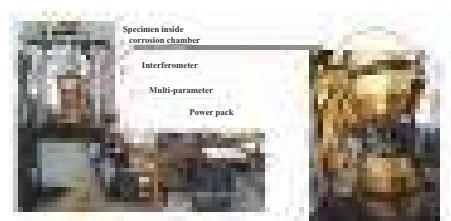


Fig.6 Experimental set-up for stressed condition

RESULTS AND DISCUSSION

The observed strain vs time behaviour of FBG sensors and electrical resistance strain gauge under induced corrosion process under stressed and unstressed condition are shown in Figs. 7-9. From the experimental investigations, it is observed that the strain sensed by the electrical resistance strain gauge varies from $-28 \mu\epsilon$ to $500 \mu\epsilon$ and strain sensed by FBG sensors varies from 0 to $655 \mu\epsilon$ for duration of 5hrs. The observed strain measurements confirm that there is no physical damage due to applied load to the specimen. The detected strains in all cases by sensors are due to metal loss from the corroding surface along with variation in pH and temperature. The entire gauge region of the specimen is expected to be completely corroded within 5hrs (ie 300 minutes). Initially under unstressed condition both FBG and electrical resistance strain gauge were initialised, where as under stressed condition both FBG and electrical resistance strain gauge shows initially a strain value of $283 \mu\epsilon$ due to applied load and initialised. As the corrosion process progress, the electrical resistance strain gauge shows apparent strain, i.e compensation for temperature component during unstressed condition (case1), where as under stressed condition, it is capable to sense strain induced due to combine effect of abrupt reduction in cross sectional area and temperature. Compared to electrical resistance strain gauges, FBG sensors shows its versatility to sense strains induced due to abrupt changes in cross sectional area, variation in pH and temperature in a severe corrosive environment. The strain sensed by FBG sensor consist of three components, the induced strain due to stress (i.e strain induced due to abrupt change in cross sectional area under stressed condition), the strain induced due to change in temperature, the strain induced due to corrosion (in a varying pH environment). Under unstressed condition the strain sensed by FBG is due to change in temperature and due to corrosion (in a varying pH environment). The sensed strain by FBG sensor for stressed condition (case2) is found to be higher than unstressed condition (case1), this may be due to higher rate of corrosion in a stressed condition. After 130minutes (2.17hrs) of test FBG sensors under case1 shows dropping

behaviour under unstressed condition, this indicates the depletion of sensor from surface of the specimen. Half the initial weight of the metal from surface of anode is expected to be removed due to electrochemical process within 2.5hrs, then after the formation of irregularities on the surface of anode observed to be high and this may be correctly sensed by the FBG. The typical variation in temperature and pH observed during the test is shown in Fig.10 and Fig.11 respectively.

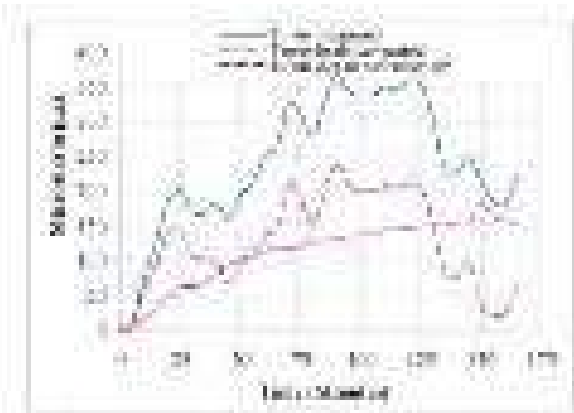


Fig.7 Strain vs Time from FBG sensor under unstressed condition

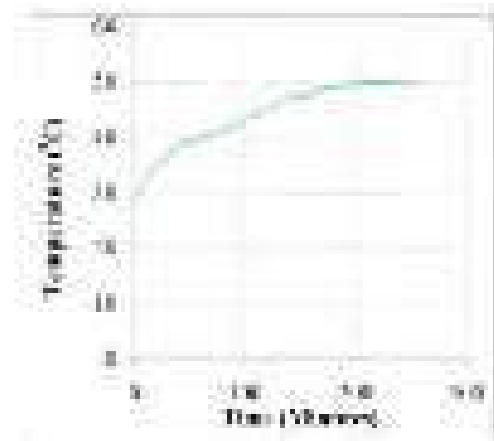


Fig.10 Typical temperature vs time

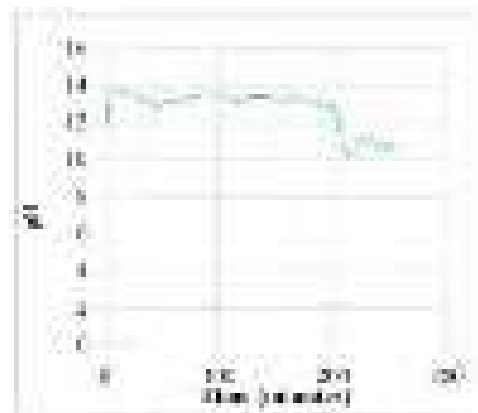


Fig.11 Typical pH vs time

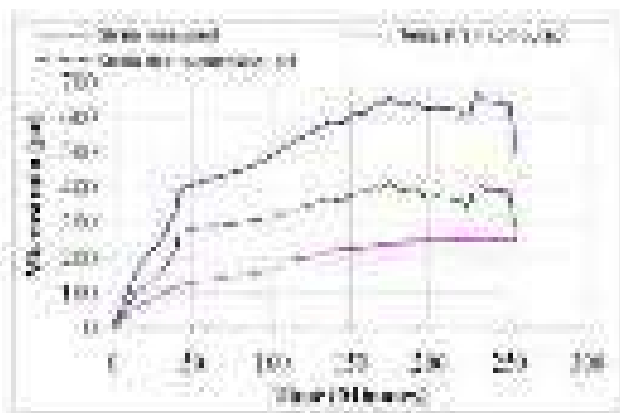


Fig.8 Strain vs Time from FBG sensor under stressed condition

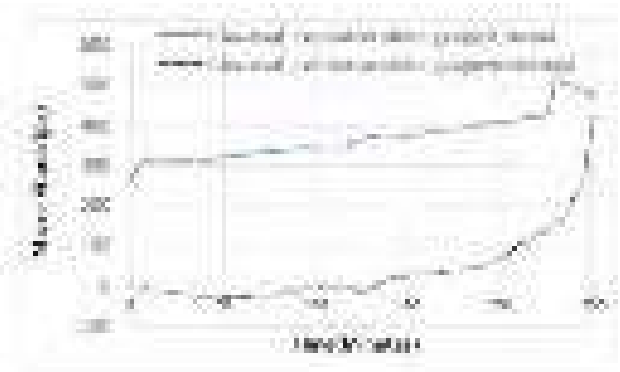


Fig.9 Strain vs Time electrical strain gauge under stressed and unstressed condition

CONCLUSION

In the present study, experiments are carried out by inducing galvanic corrosion on structural steel coupons. The coupons are corroded under two conditions, viz. unstressed (case1) and stressed (case2). The strain measurements in coupons under stressed and unstressed conditions are monitored with FBG sensors and electrical resistance strain gauges. From the studies, it is concluded that FBG are suitable to measure strain due to corrosion, since it is capable to measure strains due temperature (0°C -50°C) and other interference (variation in pH from 11.4 to 14). The electrical resistance strain gauge are incapable to sense the induced strain on a metal surface exposed to corrosive environment with varying temperature and pH. From the FBG measures it is concluded that the strain induced during unstressed condition is combined effect of temperature and variation in corrosion rate due to changing in pH. While the resultant strain in stressed condition is combined effect of strain due to stress, temperature strain and variation in corrosion rate due to changing in pH. Thus it can be established that FBG based sensors sensitivity is comparatively better than other conventional electrical resistance based strain gauges. Therefore, it can be established that FBG's can be used to indicate the onset of the corrosion before major impairment in the surface of the metal specimen.

ACKNOWLEDGEMENT

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A Report Training Programme on Pipeline Corrosion

NACE International Gateway India Section (NIGIS) organized an educational & training programme on "Pipeline Corrosion" during the period 07 – 10 May, 2014 and 23 – 26 July, 2014 at Hotel Rodas, Powai, Mumbai.

Pipeline Corrosion Training Programme covers various aspects of corrosion of pipelines and methods for prevention and control of their corrosion. The topics covered during the programme were Pipeline Integrity & Corrosion – An overview, Pipeline Corrosion & its Prevention / Control, Galvanic Anode & Impressed Current Cathodic Protection

Systems, Pipeline Internal Corrosion and Prevention, Intelligent Pigging, Pipeline Risk Analysis / Assessment, Pipeline Installation, Security Management, Maintenance and Repairs, External Pipeline Corrosion Protection Monitoring & Health Assessment Surveys, Selection & Application of Corrosion Protection Coatings, Case Studies: Coating / Cathodic Protection / Electrical Interferences, Plant pipe Corrosion Case Studies.

Faculty included eminent professionals from industry and academia and faculty as well as course content received appreciation from participants.



Pipeline Corrosion participants from 7 – 10 May 2014



Pipeline Corrosion participants from 23 – 26 July 2014

Coating Applicators Training Programme - A Report

NACE International Gateway India Section (NIGIS) organized an Educational & Training Programme on "Coating Applicators" during 17 – 18 October 2014 at Hotel Rodas, Powai, Mumbai.

Coating Applicators training programme covers various aspects of Protective Coatings. Protective Coatings are the most widely used method to control and/or mitigate Corrosion. This course thoroughly trains coating professionals to properly understand the technical aspects of surface preparation and application of a protective coatings system on a variety of structures in any industry and the basics of NACE Standards & matters referring to coatings & their applications. The different topics covered during the training were: Principles of corrosion, Environmental effects on Corrosion and Monitoring, Instruments used by Inspectors, Coating Inspectors responsibilities, Surface Preparation Standards, Surface Preparation Process, Coating Types and Recommendations of usage, Coating Defect

and its causes, Paint Application & Good practices, Paint Measuring Equipments, Paint Data sheets and its importance, Safety and its importance and Practical with airless applications and videos.

The participants were from various industries and Institutes like Manipal University Jaipur, Bharat Petroleum Corporation Limited, App Pumps & Engineering Co., Heliflex Hydraulics & Engg Co. , Duflon Industries Pvt. Ltd., Shreya Engg Works, Petronet CCK Limited, Stanford Engineers, NTPC Limited, Indian Oil Corporation Limited, Blastline India Pvt. Ltd., Reliance Industries Limited, IOT Infrastructure & Energy Services Ltd., Petronet LNG Limited, Cairn India Limited, Saipem India Projects Ltd., Berger Paints India Limited, IMCO Alloys Pvt. Ltd, Mahanagar Gas Limited , Bhawani Enterprises. The program ended with great applause from the participants.



Coating Applicator participants during 17 – 18 October 2014



U.S.-India Trade and Economic Cooperation

Fact Sheet
Office of the Spokesperson
Washington, DC
September 30, 2014

The growing economic relationship between the United States and India has been a foundational element of the U.S.-India relationship and strategic partnership. Our bilateral trade expanded fivefold from \$19 billion in 2000 to \$97 billion in 2013. The United States and India have committed to working together to facilitate greater investment in both directions, to open new Indian sectors to private investment, and to address impediments to growth that will enable trade between our countries to grow another fivefold.

- Smart Cities: The United States welcomes India's offer for U.S. industry to be lead partner in developing smart cities in Ajmer (Rajasthan), Vishakhapatnam (Andhra Pradesh) and Allahabad (Uttar Pradesh) ...
Digital India Initiative: The U.S. Department of Commerce and the Indian Ministry of Communications Technology and Electronics, the United States Agency for International Trade Administration, and the U.S. Department of State are supporting digital infrastructure, deploying e-government, and U.S.-India Information and Technology Summit in November 2014.
Infrastructure: The U.S. Department of Commerce and the Indian Ministry of Commerce and Industry agreed to establish an Indo-U.S. Commercial Dialogue with a pair of public-private roundtables on new areas of discussion that address key U.S. and Indian concerns with regard to manufacturing and infrastructure. One roundtable will be on market friendly approaches to innovation in advanced manufacturing. The other will be on corrosion prevention technologies and standards.
Bilateral Trade: U.S. Commerce looks forward to a visit to the U.S. by Indian Commerce Minister N. Chandrababu Naidu to discuss ways to grow through trade.
Cross-Sectoral: The United States and India have a partnership, investment and create jobs in India.
Private Investment: U.S. Commerce has committed over \$500 million and more in U.S. investment in India.
Intra-regional: U.S. Commerce and the Indian Ministry of Commerce and Industry agreed to identify and advance economic corridors that will foster connectivity, increased trade and greater investment opportunities for U.S. business collaboration.
Financing Infrastructure Development: U.S. Trade and Development Administration (USTDA) plans to invest over \$15 million in infrastructure planning activities in India.
Aviation and Energy Cooperation: Recognizing the importance of growing U.S. - India cooperation in the critical aviation and energy sectors, the U.S. - India Aviation Cooperation Program and the U.S. - India Energy Cooperation Program have provided platforms for the public and private sectors of both countries to identify cooperation opportunities and establish commercial ties that are mutually beneficial.
Indo-U.S. Investment Initiative: The Ministry of Finance and the U.S. Department of the Treasury agreed to establish an Indo-U.S. Investment Initiative to facilitate investment in India by institutional investors and corporate entities. As part of the U.S. India Economic and Financial Partnership, the investment initiative will focus on deepening capital markets, especially debt markets, to support the long-term financing of infrastructure in India.

The U.S. Department of Commerce and the Indian Ministry of Commerce and Industry agreed to inaugurate the 2014-2016 term of the Commercial Dialogue with a pair of public-private roundtables on new areas of discussion that address key U.S. and Indian concerns with regard to manufacturing and infrastructure. One roundtable will be on market friendly approaches to innovation in advanced manufacturing. The other will be on corrosion prevention technologies and standards.

Collaborative Dialogues

- U.S.-India Commercial Dialogue: The U.S. Department of Commerce and the Indian Ministry of Commerce and Industry agreed to inaugurate the 2014-2016 term of the Commercial Dialogue with a pair of public-private roundtables on new areas of discussion that address key U.S. and Indian concerns with regard to manufacturing and infrastructure. One roundtable will be on market friendly approaches to innovation in advanced manufacturing. The other will be on corrosion prevention technologies and standards.
U.S.-India CEO Forum: The U.S.-India CEO Forum was designed to enable a forthright conversation both about immediate policy issues to encourage greater trade and investment as well as the longer term path for economic and business ties between our two countries. A reinvigorated Forum will serve as a platform for business leaders to highlight their needs, interests, and desired policy reforms for government consideration and action.
Trade Policy Forum: Recognizing the tremendous potential in our bilateral trade relationship, the Office of the U.S. Trade Representative and the Indian Ministry of Commerce and Industry look forward to convening a Trade Policy Forum (TPF) to renew bilateral discussions on trade and investment policy issues of interest to the two countries such as intellectual property, investing in manufacturing, services and agriculture. Work under the TPF will encourage trade-related policies that promote investment and manufacturing in both countries through a regularized dialogue. As part of an ongoing commitment to strengthen engagement, both governments also agreed to establish a high-level working group on intellectual property under the TPF that will meet at the senior official and expert level to discuss the range of intellectual property issues of concern and interest to both sides.
U.S.-India Agriculture Dialogue: With participants from the public and private sectors, the U.S.-India Agriculture Dialogue promotes bilateral cooperation through a comprehensive approach to agricultural capacity building that is of practical and immediate benefit to the Indian farm sector. USDA's Foreign Agricultural Service has been working with India's National Institute of Plant Health Management to monitor and control pests and strengthen quarantine facilities.

NIGIS organises Fight Corrosion @ Vizag Sept 26th 2014 at the ITC Grand Bay,Vizag

NACE International Gateway India Section organised a workshop on Corrosion Management work named "FIGHT CORROSION AT VIZAG" at the ITC Grand Bay on 26th September 2014.

The program was attended by over 80 delegates from industries around Vizag, including HPCL, NTPC, BHEL, VCTPL, VEDANTA, AKZO NOBEL, OWENS CORNING, ONGC, INDIAN OIL, MARITIME UNIVERSITY and EASTERN NAVAL COMMAND to name a few.

The inaugural function was attended by guests from the US Embassy –

- Consul General Michael Mullins US Consulate General, Hyderabad,
- Minister Counselor for Commercial Affairs John McCaslin from US Commercial Service, US Embassy New Delhi
- Dr Samir Degan, Chairman, NIGIS
- B.Ramakrishnan, MD Protective Coatings Akzo Nobel India
- Commodore Hemant Khatri, Head Quarters Eastern Naval Command.



Also present were Mr Sankaran, Head BHPV-BHEL, Mr Sushil Mulchandani, CEO VCTPL, Mr Sandeep Saxena, Country Development Manager NIGIS, Mr Ramesh S, Head Indian Maritime University, Vizag Campus and Mr John Fleming, Ms Sathya Prabha, Ms Malarvizhi Parimel from the US Commercial Services Office, Mr Sabharwal Vizag Industrial Scan.

The program included a back ground to corrosion, cost of corrosion, a brief on NACE International and its activities in India, and a comprehensive background to corrosion protection using coatings and a detailed background to ISO 12944. The technical program ended with a presentation on the use of glass fibre composites in the marine and oil & gas industry. The speakers for the program were Dr. Samir Degan (NIGIS and Osnar Paints), Mr. B. Ramakrishan, Mr. Kaushik Duttagupta, Mr. Venu (All from Akzo Nobel) and Mr. Rajesh Khisty (Owens Corning).

Congratulations!



NACE International Gateway India Section congratulates Mr. Ajay Krishnan who has been awarded the prestigious Prime Minister's' Scholarship for doctoral research for the year 2014.

Ajay Krishnan, Research Scholar, working under Prof. V.S. Raja at Indian Institute of Technology, Bombay. He is one among 38 recipients of the scholarship selected by a high level Apex council consisting of members from academia, industry and government. This is a joint initiative of Science & Engineering Research Board (SERB), Department of Science & Technology (DST) and Confederation of Indian Industry (CII) to build future leaders in Industrial Research & Development.

Ajay will be co-mentored by Mr. S.M. Vaidya, Vice President & Business head of Godrej & Boyce Manufacturing Co Ltd., Mumbai, India. He will be working on stress corrosion cracking behavior of high strength aluminum alloys. Ajay is also the chairman of NACE International Gateway India Students' Section. We congratulate him and wish him all the very best for his endeavors.

Cathodic Protection Certification Program – A Report

Cathodic Protection (CP) Program of NACE is the most recognized CP training and certification in the world. This program provides students with the theoretical and practical fundamentals for testing, evaluating, and designing both galvanic and impressed current cathodic protection systems.

NACE International Gateway India Section organised certification courses on Cathodic Protection Tester, Cathodic Protection Technician and Cathodic Protection Technologist.

The CP program includes four certification courses and moves from entry level (CP 1) to the most knowledgeable and experienced specialist level (CP 4). Each CP course is an independent component of the program and has a different skill and education level for entry, taking into account the student's work experience, and mathematics and science background. The NACE Cathodic Protection (CP) Training and Certification Program is a comprehensive program designed for individuals working in the field of cathodic protection from the beginner to the specialist.

NIGIS organized following certification course during the period May - Nov 2014 in India.

Course No.	Course	Period	Venue	No. Of Participants
1	CP Level 1	19 – 24 May 2014	Mumbai	13
2	CP Level 2	26 – 31 May 2014	Mumbai	22
3	CP Level 2	15 – 20 Sept 2014	Mumbai	22
4	CP Level 3	22 – 27 Sept 2014	Mumbai	17
5	CP Level 2	27 Oct – 1 Nov 2014	New Delhi	28



CP Level 1 participants from 19 – 24 May 2014



CP Level 2 participants from 15 – 20 Sept 2014



CP Level 2 participants from 26 – 31 May 2014



CP Level 3 participants from 22 – 27 Sept 2014



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