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Letters to the editor are always welcome. We invite your suggestions, comments and views on the Newsletter as well as articles for publication. To publish your article, submit it to nace@mtnl.net.in

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Message

When my parent company in late Sixties was in bad shape, I did not receive salary for almost a year. Ultimately, the company went into liquidation. A job had to be found. No offer was remotely parallel in salary and of course in status to my previous position. One morning Kusum, my wife, cautioned me that our children may get affected by our tension. We had to take drastic decision to start our own business; She would look after administration; I, after technical matters. I had to see my mother for her blessings. She not only consented but advised me "Do not pursue money for money's sake, "Ma Laxshmi" can forsake you, but work as prayers to "Ma Saraswati". In a sense, she was admonishing me that when work is undertaken earnestly, professionally and with unflinching loyalty to customers interest, "Ma Saraswati" will send you inspiration and guidance. Business we started with Rs. 8,000/-, that was an amount of P.F. which theoretically belonged to my wife and children. I had a jest with her that in this gamble if we fail you loose this money also, but if we succeed not only the credit but assets will be yours.

I take this opportunity to thank all those organizations who put trust in me, mostly indulgently, even though the Cathodic Protection system they will have had no precedents for reference and that the equipments will be used for the first time and as such not fully tested for performance. I also wish to thank my associates who were very professional to undertake development without the certainly of market potential. This had to be done with a sense of challenge because economic and industrial progress of the nation depended on safe operations of its infrastructures and their preservation.

It is but apt that I shall be receiving 50 years membership pin when NACE International President will be from our own fraternity. Compliments. Tushar! wish you most successful year.

By this achievement of yours a dream I had all these years is being fulfilled, a dream that corrosion technology and science gets dynamic and momentous momentums in my life time. That is because in those early years "corrosion" was not existant in vocabulary of many engineers. It has been a fascinating journey for our India Section to arrive at this station. My heartfelt thanks and compliments to all past and present Trustees, Chairmen and Board Members, it is because of you all, that India stands proudly in comity of nations.

In conclusion, one looks in wonderment at the recent happening in New-Delhi. The zest and atmosphere was charged with unfathomably vibrant energy. This was as, it was in Aug. 1942 to Aug. 1947 when Nation's energy demanded to take destiny in its own hand. Youths are rising to ampute gangrene part of system of our governance. And to young enterprising entrepreneurs one can only say.

"The Cock crows, The Crow has a call, The call to rise,

The morning sun is rising, The sky, Golden and orange, Young India rise !!
Your destiny is in your hand, None to salvage it.

V T Purohit
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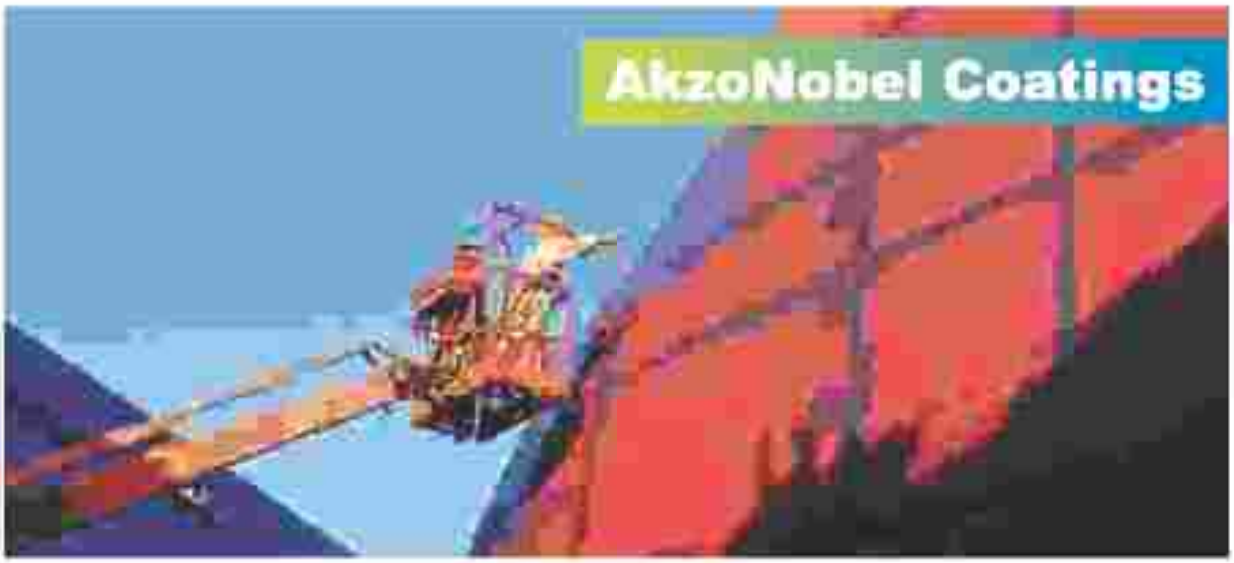

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Editorial

Dear Friends,

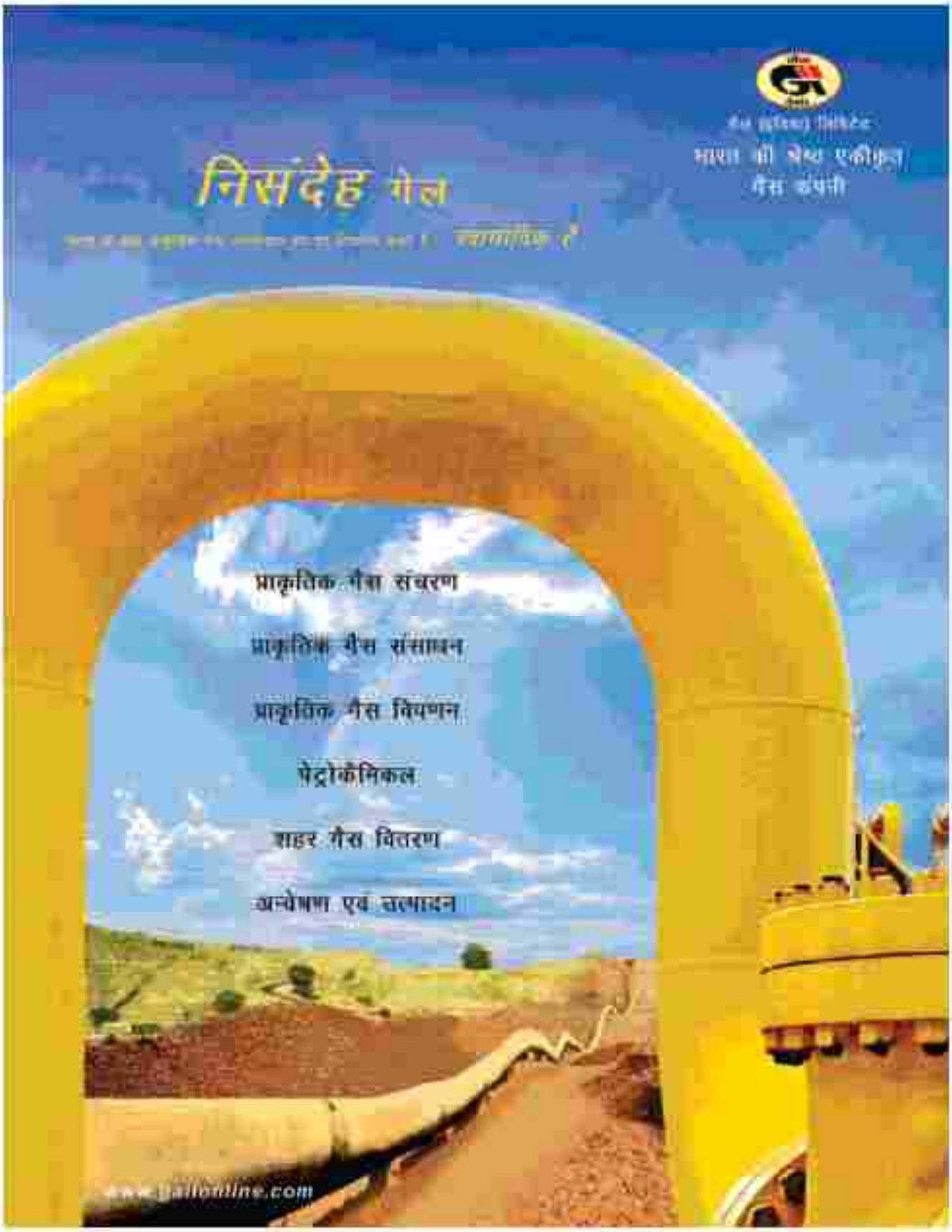
When I recall the discussions at various forums, news paper articles, TV channel reports and the concerns raised by learned people during last one year, it transpires that world has several challenges to face. A few to mention are: sustainable energy resources, water scarcity, pollution, population, poverty (disparity), global warming (climate change), terrorism, urbanization etc. Some call these issues as problems and some call them as challenges. I prefer to call them challenges.

Everyone in the society can contribute in one or other way to overcome these challenges. Corrosion scientists and engineers can definitely play a role in managing energy and global warming challenges.

A lot of steel is required every year to replace corroded steel. As per data collected from internet, one ton of steel turns into rust every 90 seconds and about 50% of the world steel production is consumed in replacement of rusted steel. Production of fresh steel from raw ore needs a significantly large amount of energy. The energy saved by way of protection of steel against corrosion will assist in alleviating global warming by reduced energy consumption and protect the environment by reduced mining.

Today the world is thinking not only in terms of green, renewable and new resources of energy, but is also actively considering conservation and saving of energy. A good deal of effort is being made to utilize every joule of energy. Prevention of loss of low temperature heat by insulation in industry can yield in good savings in energy. Development of affordable paint schemes is in progress which can provide not only protection against corrosion, but can also provide insulation so that the loss of process heat is minimized. The existing practice of insulation not only leaves an opportunity for corrosion under insulation, but also makes NDT cumbersome. A paint scheme with dual feature of corrosion protection and insulation will be a boon for the industry and society. Let's hope that a reasonably priced product with these features becomes readily available in near future.

Anil Bhardwaj
Editor Corrosion Combat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Effect of Surface Working Operations on Electrochemical Corrosion and Susceptibility to Stress Corrosion Cracking of 304L Stainless Steel

Swati Ghosh and Vivekanand Kain
Bhabha Atomic Research Center, Mumbai, India

Abstract

Mechanistic understanding of the effect of surface working techniques like machining and grinding on the electrochemical, oxidation and stress corrosion cracking (SCC) behavior of 304L austenitic stainless steel at ambient and at high temperature (300°C) has been developed in this study. Results show that surface working operations lead to the formation of a highly work hardened surface layer having high density of slip bands, strain induced martensitic transformation and heavily fragmented grains. The depth of the affected layer is a function of the surface working parameters. In the present study the depth of the layer was ~ 100 μm for machined surface and ~ 30 μm for ground surface. The presence of such a highly deformed surface layer drastically increases the electrochemical activity and SCC susceptibility of 304L stainless steel. Moreover, the stainless steel surfaces subjected to machining and grinding condition were exposed to high temperature and high pressure (300°C and 10 MPa) conditions in demineralized water for 360 h. The oxidation of the surfaces was followed by in-situ electrochemical impedance spectroscopy. The oxides produced in each case were characterized by elemental depth profiling and morphological studies. Results show that the high temperature oxides produced in each of the three conditions were distinctly different from each other. The oxide produced over the ground surface has the highest is the most compact layer which is rich in chromium followed by machined condition. This is due to the higher diffusion of chromium in the surface layers at higher temperatures due to the surface strains present in the sample. However the in-situ impedance measurements revealed maximum ionic activity that the metal – oxide interface in case of the ground surface which is indicative of a weak interface which may result in early initiation of damage.

Introduction

Stress corrosion cracking (SCC) of non-sensitized SS both at ambient temperature and at high temperature and high pressure reactor simulated conditions (HTHP) has been a growing cause of concern [1-10]. Extensive surface cracks have been evidenced on stainless steel components which were in heavily machined and/or ground condition. One of the factors considered to play a key role in causing such extensive attack is the 'nature of the surface' being exposed to the environment i.e. its microstructure, residual stress levels, electrochemical behavior, and the nature of oxide film at HTHP condition. Surface finishing operations like machining and grinding are expected to play a major role in dictating the 'nature of the surface' that finally gets exposed to the environment. The surfaces subjected to machining / grinding have very high residual stresses (~ 1100 MPa for ground and ~600 MPa for machined) [6] but the reason behind such high residual stress levels have not been established by any organized study. The present state of theoretical and experimental knowledge in this direction does not permit any specific predictions to be made about the effect of surface working operations on a) the microstructural characteristics of the surface, b) its electrochemical behavior and c) oxidation behavior at high temperature and pressure (300°C and 10 MPa) of austenitic SS. Hence this study is an organized attempt to understand the effect of surface working techniques like surface machining and grinding on the microstructure, electrochemical behavior, oxidation behavior and susceptibility to stress corrosion cracking of 304L austenitic stainless steel.

Experimental

A solution annealed stainless steel grade 304 L was subjected to three different conditions: a) machining, b) grinding and c) cold rolling followed by detailed microstructural characterization by optical, scanning electron microscopic (SEM), atomic force microscopic (AFM) and characterization of phase transformations by X-ray diffraction (XRD) and electron back scattered diffraction (EBSD) studies were done. The ambient temperature SCC susceptibility was evaluated by exposing

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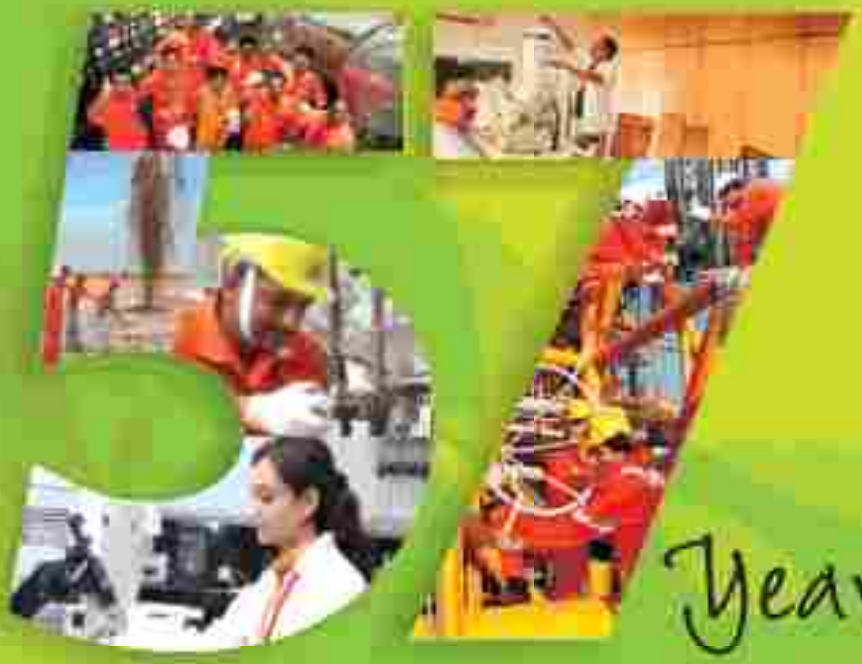

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constant strain samples made from each of the three conditions in 1 M HCl solution at room temperature (26°C). The effect of residual stresses on the SCC susceptibility of industrially fabricated components like tubes, tube to tube sheet roll expansion joints, machined and ground surfaces having different magnitude and nature of residual stresses has been studied as per ASTM G36. The electrochemical nature of the as worked surfaces was studied at ambient temperature by potentiodynamic polarization and scanning electrochemical microscopy (SECM) in a borate buffer solution. The electrochemical nature of the solution annealed, machined and ground stainless steel at 300°C, 10 MPa was studied by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in a borate buffer solution. Oxidation behavior of the material subjected to different surface finishing operations was followed in-situ by contact electric resistance (CER) and EIS measurements using controlled distance electrochemistry (CDE) technique in deaerated high purity water (conductivity < 0.1 μScm^{-1}) at 300°C and 10 MPa in an autoclave connected to a recirculation loop system. The resultant oxide layer produced after 360 h exposure was characterized for a) elemental analyses by glow discharge optical emission spectroscopy (GDOES) and b) morphology by SEM. The following paragraphs discuss the results and the mechanistic understanding derived from the present study on the effect of surface working operations have on the SCC susceptibility of 304L stainless steel.

Results and Discussion

Surface working operations drastically increased the SCC susceptibility of 304L stainless steel in chloride environment [7]. Fig. 1 shows SCC in solution annealed 304L stainless steel after exposure to 1M HCl for 170h. The time for stress corrosion cracking at ambient temperature in 1M HCl environment was minimum for the case of surface working (machined and ground) followed by cold working and solution annealing. However, very shallow cracking took place in case of machined and ground condition as compared to solution annealed condition.

Fig. 1 SCC in constant strained sample in solution annealed condition on exposure to 1M HCl environment for 170 h

The study highlights the distinct difference in the microstructural changes brought about by cold rolling and surface working (machining and grinding) of 304L stainless steel. This in turn helps in understanding the difference in the SCC behavior of 304 L SS in cold rolled and surface worked condition in chloride environment at room temperature. Whereas crack initiation in case of cold worked sample followed the mechanism of pit formation followed by transition from pit to crack after the pit reaches a critical depth, crack propagation was facilitated by the presence of high density of slip bands in the microstructure. AFM studies show that the cracks originally propagating a particular direction got deviated on reaching a set of slip bands along the direction of the slip bands in cold worked 304L stainless steel (Fig. 2). On the other hand, surface working techniques such as machining and grinding resulted in the formation of a highly work hardened layer near the surface having high levels of deformation, sub micron grain size (hence high grain boundary area) and formation of martensite phase in the surface layer (Fig. 3) [8]. The martensite formed in the surface layers propagated further in to the bulk material upto a certain depth along the grain boundaries. The depth of the surface layer was measured to be ~ 100 μm in case of machined sample and ~ 30 μm in case of ground sample. This layer was highly susceptible to SCC in chloride environment and thus crack initiation occurred very early for machined and ground condition as compared to solution annealed 304L stainless steel.

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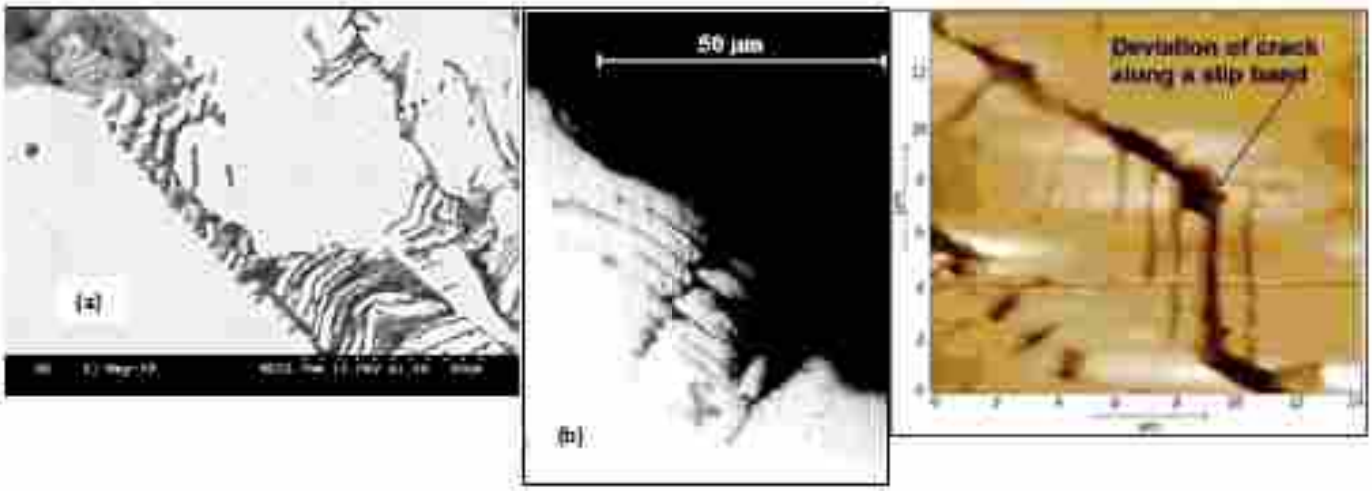

Fig. 2 Micrographs showing cold worked 304L stainless steel after exposure to 1M HCl at room temperature (a) attack along the slip bands resulting in tunnelling effect (b) pit to crack formation with attack along the slip bands and (c) AFM image showing deviation of the crack path along the slip band.

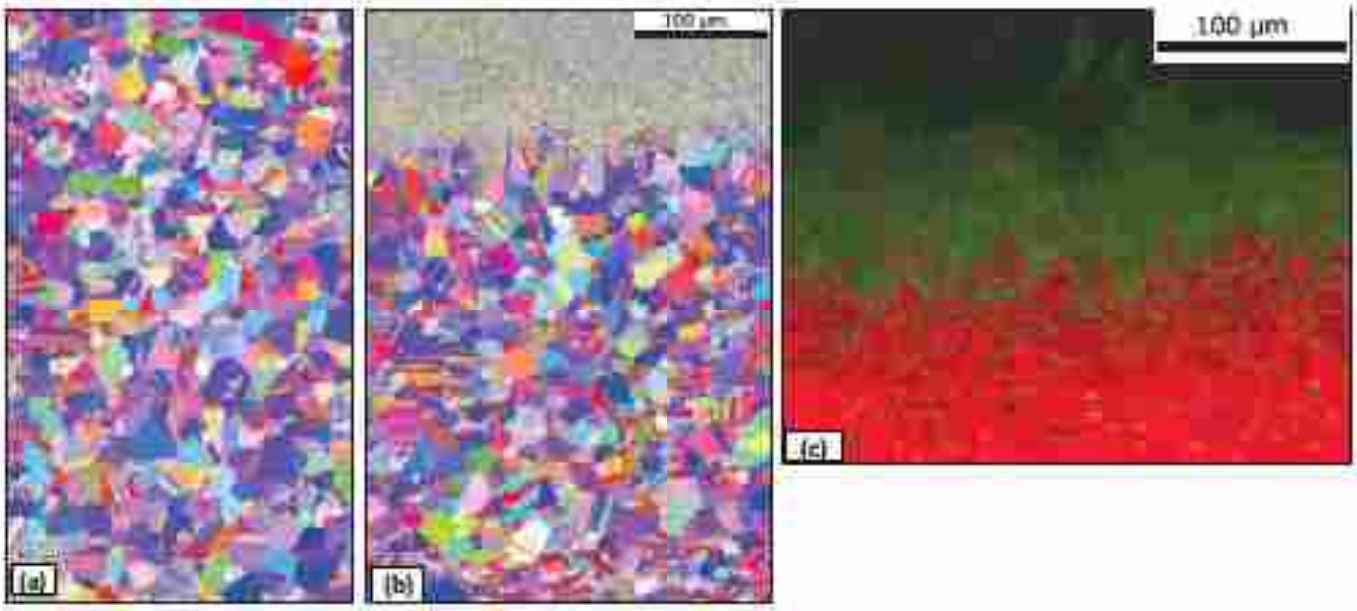

Fig. 3 EBSD of the cross section of 304L stainless steel in (a) solution annealed (b) machined condition showing formation of sub micron sized grains in the surface layers due to machining © phase contrast image showing martensite formation in the surface worked layer.

Machining and grinding operations made the surface of 304L stainless steel electrochemically much more active than in solution annealed condition. The passive current density was higher in case of ground condition followed by machined and solution annealed condition. Potentiodynamic polarization studies at 300˚C revealed that in addition to higher passivation current density, both machined and ground surfaces showed much early onset of transpassivity and hence higher dissolution of chromium from the surface as compared to solution annealed condition. Micro-electrochemical (SECM) studies revealed the cause of higher dissolution from machined and ground surfaces. Results show that higher dissolution of metallic ions takes place along the surface asperities present in machined and ground 304L SS [10]. The overall current from the surface was highest in case of ground sample. The morphologies of high current regions were also observed to be different in case of solution annealed, machined and ground specimens.

The oxidation studies on 304L stainless steel at high temperature and high pressure (HTHP, 300˚C and 10 MPa) deaerated demineralized

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water together with the ex-situ characterization of the oxide formed for solution annealed, machined and ground condition brought forth the following important points: The oxide film in each case consisted of a typical duplex structure having a chromium rich inner layer and an iron rich upper layer. However, morphology of the upper layer (iron rich particles) was clearly different in all the three cases. The oxide film formed on the machined and ground stainless steel at HTHP at 300°C is much richer in chromium, nickel and oxygen than that formed on the solution annealed stainless steel. This is due to the presence of a highly work hardened surface layer for machined and ground condition having high magnitude of plastic deformation and very higher grain boundary area along with the presence of strain induced martensite. This results in enhanced diffusion of oxygen (from environment) and chromium (from the metal matrix) to the oxide film as compared to that in solution annealed stainless steel. The thickness of the oxide film is highest for solution annealed condition (~ 1.2 μm) followed by machined (~ 0.6 μm) and lowest for ground (~ 0.3 μm). This shows that the oxide formed in surface worked condition and especially in ground condition is most protective in nature as compared to that in solution annealed condition.

The contact electric resistance measurements together with thickness of the oxide film yield the specific resistivity of the oxide film produced over 304L stainless steel in machined, ground and solution annealed condition. The oxide produced over the ground sample has the highest specific resistivity followed by machined and solution annealed stainless steel. The specific resistivity of a film is a measure of the resistance to the diffusion of ions across the film. The higher the specific resistivity of the film, the lower is the permissible diffusion of ions through it. Surface working results in the formation of a chromium rich film having higher protectiveness as compared to solution annealed condition. Hence when the oxide film is formed further diffusion of ions through the film is prevented resulting in the production of a thinner oxide film in case of machined and ground surfaces. The in-situ impedance studies on the oxide revealed the electronic and ionic transport properties of the oxide film formed for surface worked condition vs. the solution annealed condition and has been explained in line with mixed conduction model. The phase angle vs. frequency plot for the solution annealed and the machined steel shows two time constants that are typical of austenitic steels but the presence of an additional time constant for ground condition indicates the presence of a Warburg-type ionic transport process at the metal oxide interface [11]. The possible reason for such behavior is the presence of very high residual stresses on the surface of ground 304L stainless steel which result in higher rate of dissolution of metallic ions at the metal oxide interface. The understanding gained from the HTHP studies is that surface working results in the formation of an oxide film having higher specific resistivity and higher chromium enrichment and hence higher protectiveness due to the increased resistance to the diffusion of ions. However, below the oxide lies the surface which has a) high electrochemical activity, b) high magnitude of residual stresses and c) high plastic deformation. Such conditions prevailing underneath the thin oxide film produced as a result of surface working can make it highly prone to localized rupture and hence crack initiation.

Conclusion

Surface working processes bring about significant changes on the surface of 304L stainless steel in terms of its microstructure, phase transformation and corrosion susceptibility.

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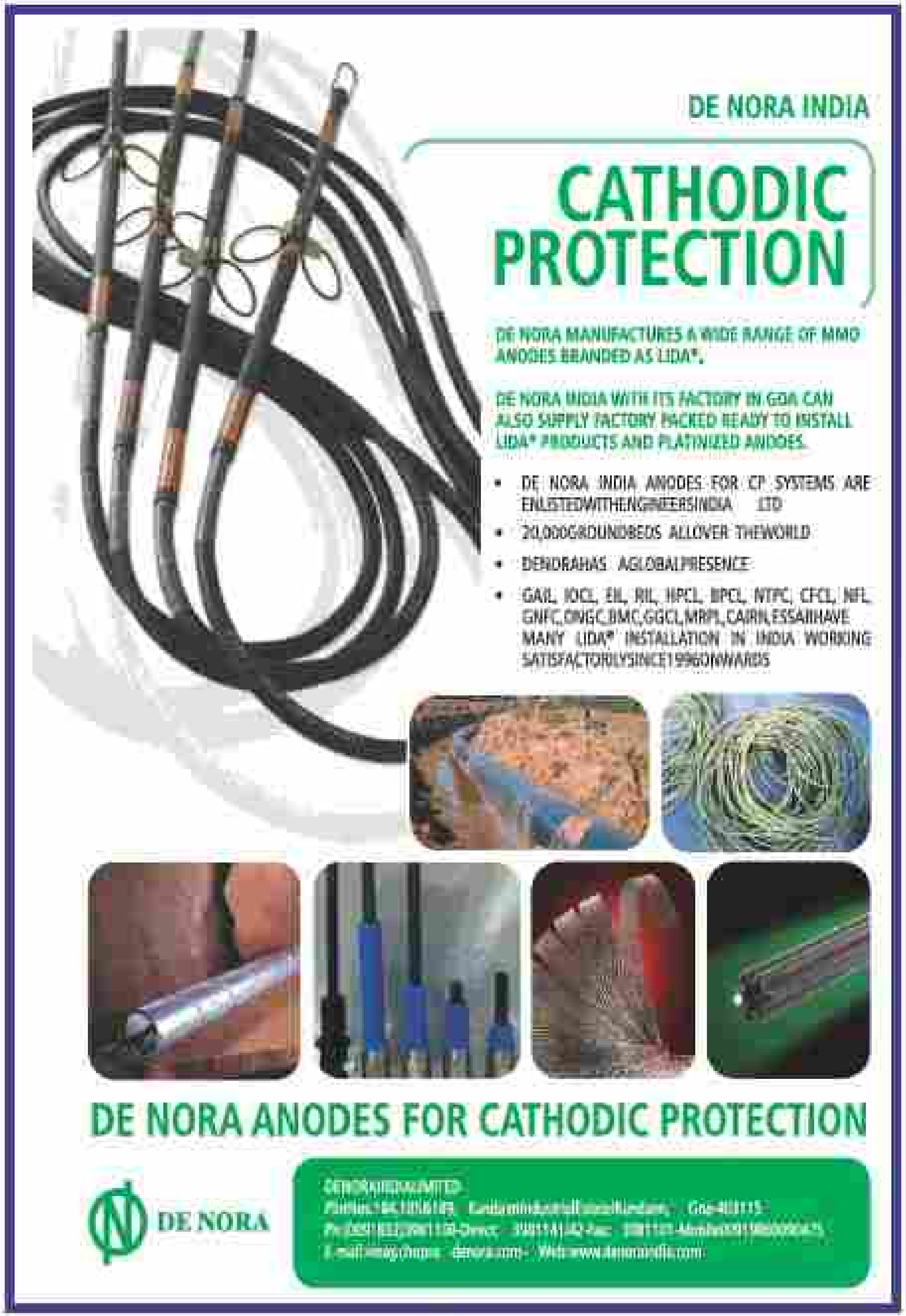
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Authors:

Dr. Swati Ghosh is a scientific officer at Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400085, India, email: ghoshs@barc.gov.in. She is working at this research centre for 5 years. Her areas of research include stress corrosion cracking of stainless steels, surface engineering of stainless steels for improving its corrosion resistance, electrochemical characterization of various phases in stainless steels and failure analysis of different metals and alloys. She has done Ph.D. from Homi Bhabha National Institute and has more than 25 publications in international journals and conference proceedings, and 1 patent.

Vivekanand Kain is a renowned expert in the field of corrosion science. He is the head of the corrosion science section, Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400085, India, email: vivkain@barc.gov.in and is working at this research centre for more than 25 years. He has done Ph.D. from Indian Institute of Technology, Bombay and has more than 200 publications in journals and conference proceedings. He is also the recipient of number of awards in the field of corrosion and materials science. He is a member of NACE International.

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He developed and accomplished procedures for reliable operation and performance of C.P. Systems. This was instrumental in ushering popularity of C.P. Technology in India. The first major I.C.C.P project to be executed in India was for a bunch of submarine pipelines between Butcher Islands (Jawahar Dweep) and Trombay in Mumbai. The system was installed in 1957 and worked efficiently until 2002 when these pipelines were taken out of service.

The unique feature of his career is that he designed and provided C.P. Systems to all types of underground & underwater installations like Onshore and Offshore pipelines, Plant piping, Tank farms, Docks, Jetties, Traveling water screens, Internal Surface of condensers / Heat exchangers / Pipes for cooling water systems, Ships and coastguard vessels & control of stray current corrosion.

It was professional challenge to Mr. Purohit as at that time references were not available. Many of these systems were prototype and most of them are still operational.

To overcome the limitations and constraints, which were being caused by foreign exchange regulation and import policy of the Govt. of India, Mr. Purohit co-operated with M/s Canara Electronics Controls to develop rectifiers and with M/s Metal Founders to manufacture anodes.

He is a member of NACE since 1963, founder Chairman of NACE India Section, member of Institute of Electrical Engineers (U.K.) and many professional and social organizations. He is a first generation pipeline engineer and has wide experience in power distribution, welding technology and radiography.

He is recipient of NACE Lifetime Achievement Award in the year 1999-2000. Even at the age of 85, he is still passionate about the subject of Cathodic Protection and loves to share his experiences with young engineers and scientists.

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Low Temperature Embrittlement of Austenitic Stainless Steel Welds and its Electrochemical Assessment

K. Chandra, Vivekanand Kain and V.S. Raja[1]
Bhabha Atomic Research Centre, Mumbai, India
[1]Indian Institute of Technology, Bombay, Mumbai, India

1. Introduction

Austenitic stainless steels (SSs) are extensively used in light water reactors for in-core components and primary recirculation piping. Although these SSs are fully austenitic in their wrought condition, the weld fusion zones of austenitic SSs have duplex microstructure consisting of an austenite matrix with typically 5 to 12% δ -ferrite. However, the ferrite may transform to various embrittling phases after long service life at reactor operating temperatures of around 300 °C [1]. As a result, the ferrite phase and therefore the weldments may become embrittled. Embrittlement manifests in the form of loss in toughness and increase in hardness of ferrite phase. The primary cause for the aging embrittlement has been attributed to the spinodal decomposition of ferrite into Fe-rich α and Cr-rich α' phases and precipitation of G-phase [1,2]. The formation of Cr-depleted regions around the Cr-rich α' -phase and G-phase precipitates also causes decrease in corrosion resistance of duplex SSs [3,4]. Therefore, the degree of aging embrittlement can be evaluated in terms of changes in electrochemical properties induced by the phase transformations.

The broad objective of the present study is to establish the embrittlement of austenitic SS 304L and 316L welds after long-term aging and develop an electrochemical method to characterize the degree of thermal aging embrittlement. Since duplex stainless steel (DSS) has much higher ferrite content, a similar study was done on this alloy also.

2. Experimental procedures

The study was done on austenitic SS 304L and 316L welds and DSS 2205 (64 wt% ferrite). Welding of SS 304L was carried out using multi-pass gas tungsten arc welding with SS 308L filler wire to achieve two different ferrite contents of average values 10% and 8% in the weld fusion zones of SS 304L. In case of SS 316L weld, ferrite content of an average value of 10% was achieved using SS 316L filler wire. Thermal aging was done at three different temperatures of 335, 365 and 400 °C for up to 20,000 h. Aged samples were examined using transmission electron microscope (TEM) to study the phase transformations. Vickers microhardness and Charpy impact tests were done to establish the degree of embrittlement due to thermal aging. Instrumented microhardness indentation machine with a load of 1 mN was used to measure the Vickers hardness of δ-ferrite and austenite phases. Charpy impact test was conducted at six different temperatures (-196, -100, -50, 0, 25 and 100 °C) for generation of the full impact energy curve.

To measure the degree of sensitization due to Cr-depletion near α' -phase of aged samples, double-loop electrochemical potentiokinetic reactivation (DL-EPR) and single-loop electrochemical potentiokinetic reactivation (SL-EPR) tests of SS 304L and 316L welds were conducted at room temperature in deaerated solutions of 0.5 M H_2SO_4 + 0.01 M KSCN and 1 M H_2SO_4 + 0.1 M KSCN respectively. Anodic polarization test was performed for DSS 2205 in 0.5 M acetic acid solution (deaerated) at room temperature to investigate the effects of aging on the electrochemical behavior.

3. Results and discussion

3.1 Microstructure evolution after thermal aging

The results of microstructural characterization indicated that thermal aging of austenitic SS (304L and 316L) welds and DSS 2205 in the temperature range of 335–400 °C led to decomposition of ferrite into Fe-rich α and Cr-rich α' by a spinodal mechanism.No transformation in the austenite phase or carbide precipitation was observed in any of the aged conditions [5,6]. In contrast to the appearance

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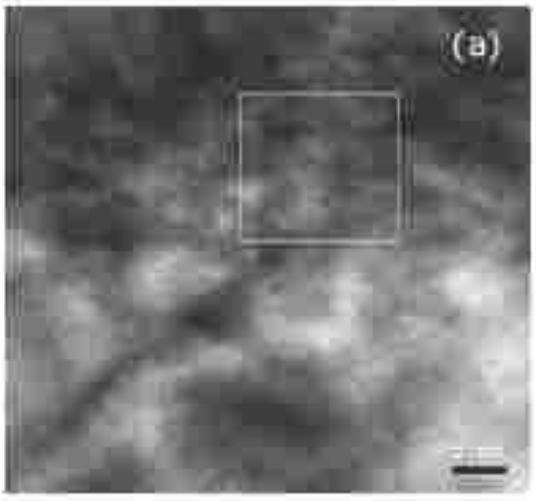
of ferrite phase in as-welded sample, the mottled contrast was observed in the ferrite phase in the aged samples. The mottled contrast in the ferrite phase is attributed to the compositional fluctuation induced by spinodal decomposition into Fe-rich α and Cr-rich α' [1,2].

The lowest Cr concentration as measured using TEM-EDS was about 15 wt% in the decomposed ferrite of SS 316L weld aged at 400°C for 5000 h, while the Cr concentration in the as-welded ferrite phase of SS 316L weld was around 25 wt% [6]. This decrease in Cr concentration or depletion of Cr within the ferrite phase can lead to loss in corrosion resistance of materials, which is discussed later. High resolution electron microscopy (HREM) study showed an additional G-phase precipitation within the ferrite phase for all the materials aged at 400 °C [5-7]. Fig. 1(a) shows one such HREM image in SS 304L weld (10% ferrite) aged at 400 °C for 10,000 h, where the presence of fine precipitates is noticed in the ferrite phase. The Fast Fourier Transforms (FFT) of the precipitate together with the ferrite matrix from a region marked by the solid square (in fig. 1(a)) is shown in fig. 1(b). The key of the FFT corresponding to fig. 1(b) is shown in fig. 1(c) and the precipitate was identified as the G-phase. However, G-phase could not be found in the ferritic phase even after aging for 20,000 h at 335 and 365 °C in the welds of SS 304L and 316L and in DSS 2205.

3.2 Mechanical property changes due to thermal aging

Microhardness of the ferrite phase of the aged specimens was found to be considerably higher than that of the as-welded or as-received ones. This is clearly evident in figs. 2(a) and (b) for SS 304L and 316L welds respectively that show the Vickers microhardness of ferrite and austenite as a function of aging period and temperature. The microhardness of austenite is not affected by the aging process, since, no microstructural changes were observed in the austenite phase. The increase in ferrite hardness results from a hardening mechanism based on α – α' misfit inducing an elastic stress due to spinodal decomposition in the ferrite phase [8].

Table 1 shows the ductile to brittle transition temperature (DBTT) for each aging condition of SS 304L and 316L welds. The Charpy impact toughness data indicated that there were two effects occurring with aging: the DBTT increased (table 1) and the upper-shelf and the lower-shelf energies decreased [5]. This was due to easy fracture in the ferritic regions of the material, as a result of hardening of the ferrite phase. It is noted from the results that the extent of embrittlement in SS 316L weld was considerably higher compared to SS 304L weld as indicated by higher DBTT (table 1) and microhardness of ferrite in SS 316L welds at similar aging conditions (fig. 2). This is due to the presence of Mo in SS 316L, which enhances the rate of embrittlement [2]. In case of DSS 2205, drastic decrease in the impact toughness was observed with aging. The Charpy impact energy at room temperature reduced to a value of 4 J after 5000 h of aging and beyond at each aging temperature from a value of 191 J in the as-received condition [9,10].



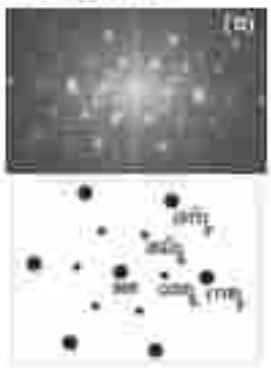


Fig. 1 (a) HREM lattice image of fine precipitates and ferrite matrix along [111] direction in SS 304L weld aged at 400 °C for 10,000 h. (b)The FFT of the solid square region (precipitate and matrix) and (c) the key to the FFT shown in fig. (b). F: ferrite phase, G: G-phase

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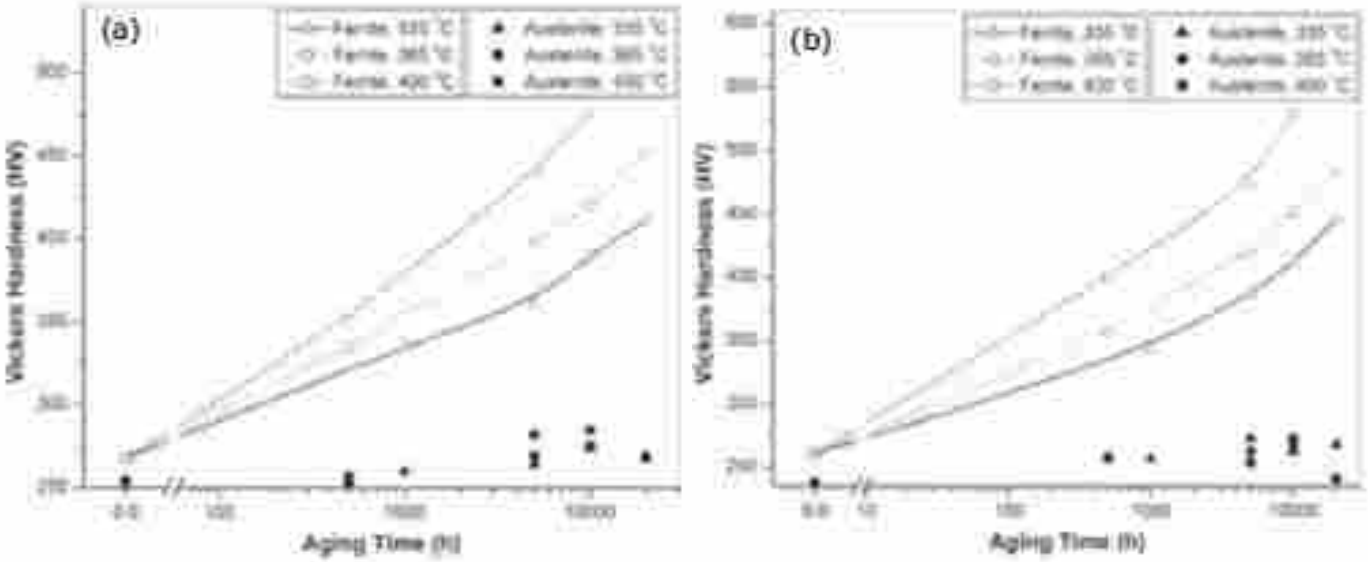

Fig. 2 Effect of aging period on Vickers microhardness of ferrite and austenite phases in (a) SS 304L weld and (b) SS 316L weld (each containing 10% ferrite) aged at 335, 365 and 400 °C.

Table 1 DBTT (°C) of SS 304L and 316L welds in various aging conditions

DBTT in as-welded condition, SS 304L and SS 316L: < -196 °C

Material	Temperature	500 h	1000 h	5000 h	10000 h	20000 h
SS 304L weld	335 °C	NT	-150	-130	-125	-115
	365 °C	-170	NT	-116	-89	-83
	400 °C	-109	NT	-104	-73	NT
SS 316L weld	335 °C	NT	-113	-86	-79	-48
	365 °C	-118	NT	-81	-71	-54
	400 °C	-83	NT	-73	-50	NT

NT: Not Tested

3.3 Effect of thermal aging on electrochemical behavior and its correlation with the degree of embrittlement

DL-EPR results showed increase in reactivation currents with increase in aging period at each aging temperature. The typical DL-EPR curves of SS 304L welds aged at 335 and 400 °C for various aging periods are shown in fig. 3(a) and (b) respectively. Increase in the current in passive region of the DL-EPR curves were also observed with thermal aging, which is clearly evident at higher aging temperatures of 400 °C (fig. 3(a)). DL-EPR values (i.e. $(I_r/I_a) \times 100$) calculated for SS 304L and 316L welds after different aging treatments are shown in table 2, where I_r: peak reactivation current and I_a: peak activation current. SL-EPR test was also done to measure the extent of Cr-depletion due to thermal aging and also to find the locations of corrosion attack due to EPR test. This was done by SEM examination of the sample surface after the SL-EPR test. The typical SL-EPR curves of SS 304L weld samples aged at 400 °C for different aging periods are shown in fig. 4(a). The reactivation current peak for each sample is observed at around -0.2 V_{SCE}, with the only difference being that the reactivation current loop increases with increase in aging time and temperature. The peak current density (i_p) measured during SL-EPR test of as-welded and aged samples is shown in table 3. In general, the DL-EPR value and i_p (during SL-EPR test) increased with increase in aging period/ temperature or the degree of embrittlement. The loss in corrosion resistance due to thermal aging is ascribed to the phase transitions taking place in the ferrite phase.

Formation of Cr-rich α'-phase in ferrite due to spinodal decomposition leads to Cr-depletion in its vicinity and hence higher corrosion was observed during EPR tests [6,11]. This is also confirmed by surface examination after EPR tests showing dissolution of ferrite (fig. 4(b)) and corrosion attack at ferrite–austenite interface.

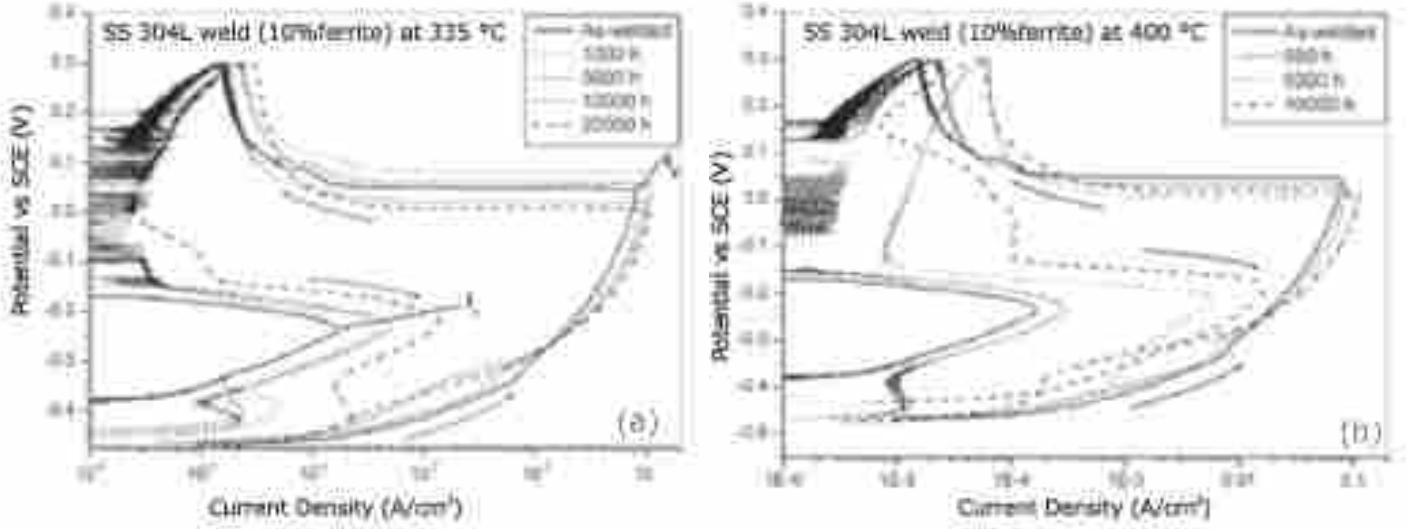

Fig. 3 DL-EPR curves of SS 304L welds aged at (a) 335 °C and (b) 400 °C for different aging periods.

Table 2 DL-EPR values of SS 304L and 316L welds in various aging conditions

DL-EPR value in as-welded condition, SS 304L: 0.21 and SS 316L: 0

Material	Temperature	500 h	1000 h	5000 h	10,000 h	20000 h
SS 304L weld	335 °C	NT	0.15	0.40	0.48	0.86
	365 °C	0.20	NT	0.72	0.87	1.25
	400 °C	0.33	NT	5.49	14.52	NT
SS 316L weld	335 °C	NT	0.022	0.036	0.086	0.028
	365 °C	0.014	NT	0.04	0.085	0.031
	400 °C	0.048	NT	7.59	6.56	NT

NT: Not Tested

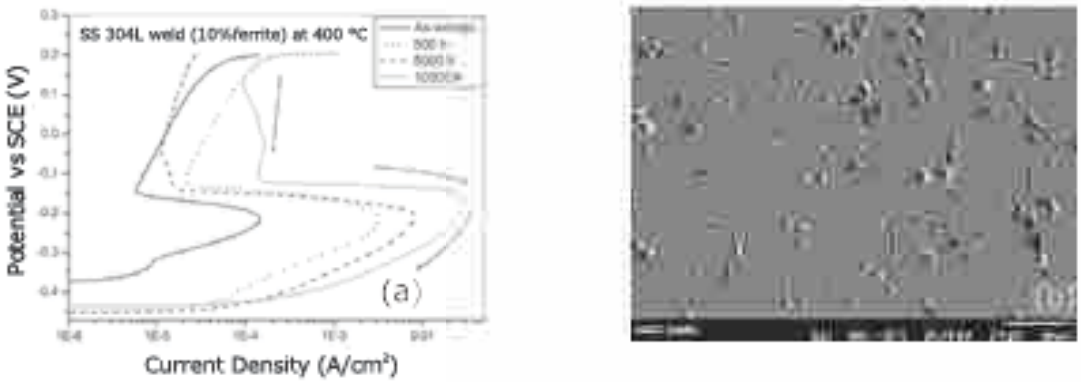

Fig. 4 (a) SL-EPR curves of SS 304L weld aged at 400 °C for different aging periods (b) SEM micrograph showing the surface appearance of SS 304L weld aged at 400 °C for 5000 h after SL-EPR test.

Table 3 Peak current density, i_p, (x 10^{-3} A/cm^2) during SL-EPR test of SS 304L and 316L welds in various aging conditions

Value of i_p in as-welded condition, SS 304L: 0.14 and SS 316L: 0.85

Material	Temperature	500 h	1000 h	5000 h	10,000 h	20000 h
SS 304L weld	335 °C	NT	1.30	1.41	3.04	7.86
	365 °C	2.30	NT	2.59	3.50	17.6
	400 °C	3.16	NT	8.06	30	NT
SS 316L weld	335 °C	NT	0.95	1.80	5.12	2.02
	365 °C	1.36	NT	5.34	6.02	4.13
	400 °C	1.60	NT	17.70	16	NT

NT: Not Tested

Specimens aged at 400 °C showed major loss in corrosion resistance (as indicated by large reactivation peak (fig. 3(b) and fig. 4(a)) and very high DL-EPR values and i_p in tables 2 and 3 respectively) compared to specimens aged at 335 or 365 °C. The reason for observing such a behavior is precipitation of G-phase along with spinodal decomposition in the ferrite phase at 400 °C. However, G-phase was not observed after aging up to 20,000 h at 335 and 365 °C. G-phase contains much higher Cr, Ni, Mo (if present) and Si content than the matrix [2,4]. It has been reported [4] that there is high Cr depletion adjacent to the G-phase precipitates. In case of SS 316L weld, after longer aging period to 20,000 h at 335 and 365 °C and 10,000 h at 400 °C, the DL-EPR values (table 2) and peak current density (i_p) during SL-EPR test (table 3) were found to decrease. This can be attributed to the desensitization or the "healing" effect at longer aging periods, whereby, the Cr diffusion reduces or completely eliminates the concentration gradient of Cr [12].

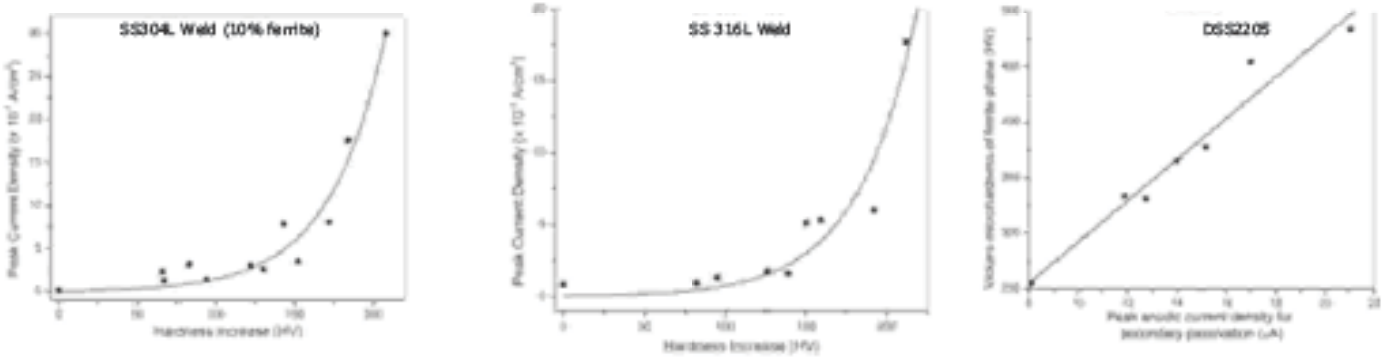

Fig. 5 A relationship between the peak current density (i_p) during the SL-EPR test and the hardness increase of ferrite phase after thermal aging in (a) SS 304L weld and (b) SS 316L weld. (c) A relationship between the peak anodic current density for secondary passivation in 0.5 M acetic acid and microhardness of ferrite phase in aged DSS 2205.

For correlation of electrochemical properties with the degree of embrittlement, the i_p values obtained during the SL-EPR tests of SS 304L and 316L welds were compared with the increase in microhardness of ferrite phase. For DSS 2205, the value of peak anodic current density for secondary passivation during the anodic polarization in 0.5 M acetic acid was taken to correlate with the hardness of ferrite. Fig. 5(a) shows the relation between ip and the increase in Vickers hardness of ferrite (as compared to the as-welded condition) in SS 304L welds. This figure shows that the i_p increases exponentially with the increase in the microhardness of ferrite phase. Similar relationship was obtained for SS 316L weld samples (fig. 5(b)). For DSS, a good linear correlation was observed (fig. 5(c)) between the peak anodic current density for secondary passivation in 0.5 M acetic acid and the microhardness of the ferrite phase. Based on these results, it is indicated that the extent of thermal aging embrittlement in austenitic SS welds is possible to be predicted by electrochemical measurements. Conclusively, these electrochemical tests can be used in-situ in plants to determine the thermal aging embrittlement of components made up of austenitic SS

welds. However, the electrochemical methods to evaluate the aging embrittlment must be used with caution due to uncertainty if densensitization or chromium replenishment occurs in ferrite due to over-aging.

4. Conclusions

Thermal aging of austenitic SS welds and DSS at 400 °C leads to both spinodal decomposition and G-phase precipitation in the ferrite phase. However, aging at 335 and 365 °C showed only spinodal decomposition. Aging embrittlement manifests in the form of increase in the hardness of δ-ferrite phase and decrease in upper-shelf and lower-shelf energy together with an increase in DBTT during impact toughness tests. There was drastic decrease in the impact toughness of aged DSS 2205 and the Charpy impact energy at room temperature saturated to a value of 4 J after aging to 5,000 h and beyond at each aging temperature. The embrittlement rate was considerably higher in SS 316L weld as compared to SS 304L weld. Decrease in the corrosion resistance after thermal aging was noticed due to Cr depleted regions formed in the ferrite phase due to phase transformations. In general, DL-EPR value measured during the DL-EPR test and the peak current density during the SL-EPR test increased with the increase in the degree of embrittlement. Precipitation of G-phase leads to higher loss in corrosion resistance of the aged materials. SL-EPR and DL-EPR tests for austenitic SS welds and anodic polarization in 0.5 M acetic acid for DSS have the potential to be used as non-destructive methods to characterize thermal aging embrittlement in the operating plants.

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Authors

K. Chandra is a scientific officer at Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400085, India, email: kchandra@barc.gov.in. He is working at this research centre for 10 years. His areas of research include low temperature embrittlement of stainless steels, electrochemical characterization of various phases in stainless steels, corrosion behavior of austenitic stainless steels in nitric acid environment and failure analysis of different metals and alloys. He has done Ph.D. from Indian Institute of Technology, Bombay and has more than 40 publications in journals and conference proceedings.

Vivekanand Kain is a renowned expert in the field of corrosion science. He is the head of the corrosion science section, Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400085, India, email: vivkain@barc.gov.in and is working at this research centre for more than 25 years. He has done Ph.D. from Indian Institute of Technology, Bombay and has more than 200 publications in journals and conference proceedings. He is also the recipient of number of awards in the field of corrosion and materials science. He is a member of NACE International.

V. S. Raja is a professor in Indian Institute of Technology Bombay, Mumbai 400076, India, email: vsraja@iitb.ac.in. His areas of research include passivity of metals and alloys, stress corrosion cracking, high temperature and high pressure aqueous corrosion and failure analysis. He has guided a number of Ph.D. and M.Tech students. He is a member of NACE International.

Report On

CORCON 2012- Corrosion Conference and Expo

26th – 29th Sept 2012 at Hotel Grand Hyatt, Goa

NACE International Gateway India Section (NIGIS) organized "CORCON 2012" International Conference and Expo during 26th – 29th Sept 2012 at Hotel Grand Hyatt, Goa. CORCON 2012 provided an excellent opportunity for exchange of information on matters concerning corrosion problems and solutions. It provided an excellent networking platform for interaction amongst experts, academicians, professionals from large PSUs or Governmental agencies and the private industries.

Around 550 delegates attended the conference, including 55 from overseas. In order to encourage participation of young students, NIGIS waived the registration fees and paid for accommodation for all presenting authors in student category.

The conference started with a very high note for expanding the horizons of corrosion studies. On the morning of 26th September, a workshop, "Research Techniques in Corrosion", was organized by Student Chapter of NIGIS.

On the evening of 26th, the conference was inaugurated by CMD of ONGC. The inaugural function was also attended by Patron-in-Chief Dr. Srikumar Banerjee, Former Chairman Atomic Energy Commission & Secretary Dept. of Atomic Energy, Govt. of India along with Mr. Kevin Garrity, President NACE International. The other present on dais were Mr. Bob Chalker, Executive Director NACE International; Mr. Tushar Jhaveri, Vice President NACE International, Mr. K L Batra, Chairman NIGIS & Chairman CORCON 2011 and Dr. Samir Degan, Area Director, NACE International, East Asia and Pacific Area; Mr Anand Kulkarni, Treasurer and Head Technical Committee CORCON 2012; Mr. Michelle Lau, Area Chair, East Asia and Pacific Area; Mr. Astley Pung, Manager, East Asia and Pacific Area and Mr. R. Radhakrishnan, Secretary, NIGIS.

In the inaugural address the chief guest Mr. Sudhir Vasudeva talked about corrosion issues in upstream oil & gas industry and necessity more research for enabling production in high temperature, high pressure and sour conditions. He mentioned about the corrosion challenges in deepwater oil & gas production. He expressed that collaborative efforts among users and research institutes can play a big role in advancement of corrosion control and monitoring. He congratulated NACE India section for organizing CORCON 2012 which provided an excellent opportunity for sharing knowledge and experiences related to the science of corrosion and the technologies to control it.

Oil and Natural Gas Corporation Limited and GAIL (India) Limited were Platinum Sponsors of the conference. In addition, there were 32 gold and silver sponsors of the event. 27 companies exhibited their products and services. The main highlights of CORCON-2012 were Technical symposia for the presentation of technical papers including keynote talks, Open sessions for discussions of corrosion related issues, Talks by eminent scientists and professionals, Expo for display of products and services, and Celebration of Corrosion Awareness Day and presentation of 18th Corrosion Awareness Awards - 2012 (an annual event) to individuals and organizations for their contributions in the field of corrosion and its control.

The following brain storming Key Note Talks energized thought process level of all the delegates:

- "Corrosion and its Control in Nuclear Power Reactors", by Dr. Srikumar Banerjee, DAE Homi Bhabha Chair Professor, BARC and Former Chairman, AEC
- "Corrosion and Punishment", by Kevin Garrity, President, NACE International
- "Aging Offshore Oil and Gas Infrastructure – Effective Management of Subsea Corrosion", by Jim Britton, Deepwater Corrosion , USA
- "Operating Windows for the Safe Use of Titanium and Zirconium in Corrosive Environments", by Brian J. Saldanha, DuET Materials Engineering, USA

- "Biological and Chemical Reactions within DWDS that Determine Drinking Water Quality", by T. L. Gerkea, University of Cincinnati, USA
- "Anti-Corrosion Measures Concerning Spent Fuel Pools of Fukushima Daiichi Nuclear Power Plant after the Accident", by Yutaka Watanabe, Graduate School of Engineering, Tohoku University, Japan
- "AC interference – contemporary issues, Henrik Rosenberg and Lars Vendelbo Nielsen", by Balslev Consulting Engineers A/S, Denmark
- "MIC and Inhibitors", by Rolf Gubner, Curtin University, Australia
- "Proactive Pipeline Integrity Management: Safety, Reliability and Economic Benefits Realized at an Indian Producing Offshore and Onshore Asset", by Patrick J. Teevens, Broadsword Corrosion Engineering Ltd, Canada

The technical topics covered in the symposia of the conference were on Cathodic Protection, Corrosion Inhibitors & MIC, Corrosion Research in Progress, Corrosion Testing, Monitoring & Inspection, Failure Analysis, Materials & Composites, Protective Coatings, Paints & Linings and RCC and Infrastructure which provided an unique opportunity to upgrade and improve the participants knowledge about the subject with comprehensive information on protection of assets from the menace of corrosion.

22 Technical Symposia comprised on technical lectures. 2 Plenary talks, 7 Keynote Addresses, 11 Invited Lectures, 111 Contributory Oral Papers and 22 poster presentations. At the sidelines of the conference there was a good technical interaction between experts in the fields and the delegates on various corrosion problems faced by them. Six Technical Interactive Sessions were held on the issues of NACE International TCC Activities, Electric Power Plants and Utilities, Industrial Water Treatment, Corrosion Monitoring, Regulations & Standards in Pipeline Industry and Cathodic Protection: Specific issues for pipelines.

NIGIS presented Corrosion Awareness Awards every year to Scientists, Engineers and Professionals to recognize their contributions in corrosion science and technology which were distributed during the CORCON-2012. The awards were distributed by H.E. Bharat Vir Wanchoo, Governor of Goa. The award winners were honoured by His Excellency. The winners were:

For Excellence in Corrosion Science & Technology in Research & Education:	Raghuvir Singh,
Excellence in Corrosion Science & Technology in Oil & Gas:	Bhupendra Gaur
Distinction in Corrosion Science & Technology in Industrial Organisation:	Dr. Deepashri D. Nage
Distinction in Corrosion Science & Technology in Research & Education:	Dr. Supratik Roychowdhury
Student Award for PhD Degree:	Dr. Swati Ghosh
Student Award for PhD Degree:	Dr. Kamlesh Chandra
Student Award for MTech Degree:	Rajan Bhambroo

The Life Time Achievement Award was awarded to most deserving candidate and who was none other than Mr. Rajan Bahri. He has relentlessly and insistently fighting for the cause of fight against corrosion since 1994 by way of organizing this event. He has held the office of Chairman and Trustee of NIGIS in the past.

A cultural bonanza was organized on 28th September to mentally rejuvenate the delegates for the next and last day's technical proceedings. The event presented trip to India through dance, drama and songs.

On the last day, 30th September, best technical oral and poster papers, best stalls at the expo were honoured and winners of these awards were:

Technical Session	**Paper and Author**
Paint Coating and Lining:	NACE SPO198 and Corrosion Prevention Under Insulation. Michael MeLampy, Hi-Temp Coatings Technology, Inc., USA.
Offshore Corrosion:	Offshore Coating Maintenance - Cost Affect by Choice of New Building Specification and Ability of The Applicator. Nis-Peter Taekker and Soeren Nyborg Rasmussen, Hempel A/S, Denmark.
Materials and Composites:	The Stress-Corrosion Cracking Susceptibility of Alloy IMI 834 at 350°C. Mangesh D Pustode and V S Raja, IIT Bombay And Neeta Paulose, GTRE, Bangalore.
Failure Analysis:	Investigation into The Incidence of Delayed Catastrophic Cracking in Low Nickel Austenitic Stainless Steel Coils. S Srikanth, P Saravanan and K Ravi, SAIL, Ranchi and S, Sisodia, Salem Steel Plant, Salem.
RCC and Infrastructure:	Early Detection of Corrosion in RC Structures Using EMI Technique. Talakokula Visalakshi and Suresh Bhalla, IIT New Delhi.
Electric Power Plants and Utilities:	Effect of Surface Finishing Operations on High Temperature Oxidation behaviour of Alloy 800. Geogy J. Abraham, Sunil Kumar B and Vivekanand Kain, BARC, Mumbai and Kushal Singla, PEC University Of Technology, Chandigarh.
Cathodic Protection:	Wireless and Remote Monitoring of PSP I.E. Cathodic Protection Thru CTSU Data Loggers. Manoj Kumar Chauhan, HPCL, Gujarat.
Inspecting and Testing:	Steps Taken for Mitigation of Corrosion Under Insulation (CUI) at Haldia Refinery. S. K. De, Debashis Dutta, Kaushik Boral and Bhaskar Sharma, IOCL, Haldia Refinery, Haldia.
MIC and Inhibitors:	Microbiologically Influenced Corrosion in Gas Compression Plants Operating in Lakwa, Geleki and Rudrasagar Oil Fields of Assam Asset of ONGC and its Control. Veena Kothe, ONGC, Panvel and V Banerjie, ONGC Academy, Dehradun
Student Session:	Effect of Incorporation of Surface Treated Zinc Oxide on Corrosion Protection of Non-Isocyanate Polyurethane Coatings. Mukesh Kathalewar, Nilesh Shinde, Dr. Anagha Sabnis, ICT, Mumbai.

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The following posters were awarded:

Winner	High Temperature Oxidation of NiCrAlY Coatings in Presence of Air and Vanadium Salts with Special Reference to Formation of Alumina. Nidhi Rana, R.Jayaganthan and Satya Prakash, Indian Institute of Technology Roorkee.
1st Runner up	Active Nano Zinc Oxide Coating on Titanium for Bio-fouling Resistance in Sea Water. K R Rasmi and U Kamachi Mudali, IGCAR Kalpakkam.
2nd Runner up	Corrosion Protection by Multilayered Zn-Ni-ZrO2 Coating. Yathish Ullal and A Chitharanjan Hegde, National Institute of Technology Karnataka Surathkal.

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

12 Sqm – Winner	3M India Ltd.
12 Sqm – Runner	West Coast Polychem Pvt. Ltd.
9 Sqm – Winner	Airblast Equipment India Pvt Ltd
9 Sqm – Runner	Honeywell Process Solutions India

The efforts of Mr. K.L. Batra, Chairman, Organizing Committee, CORCON 2012, Mr Anand Kulkarni, Head Technical Committee, Mr. Manohar Rao, Mr. Radhakrishnan and Mr. Dipen Zhaveri were lauded by one and all for their superb efforts in making this conference and expo a grand success.

Mr. Kevin C. Garrity, P.E. , NACE International President 2012-2013 commented, "The technical content, the pageantry, the fellowship and the camaraderie was really unparalleled in our industry".

The conference ended with a gigantic round of applause for the entire organizing committee and governing board of NIGIS, with special mention of NIGIS administration and staff, viz. Manoj Mishra, Manager - Administration, Rishikesh Mishra, Manager – Technical Services , Anita D' Souza, Executive and Kim Shah, Manager - Conference & Training course who always put their best effort whether it is conference or training.

The dates and venue of next Conference, CORCON 2013, were announced as 30th September – 3rd October, 2013 at New Delhi.

Glimpses of CORCON 2012

Mr. K L Batra, Chairman, CORCON 2012 lighting the lamp to inaugurate the conference.

Dr. Srikumar Banerjee, Former Chairman, AECI inaugurating the CORCON 2012 exhibition.

Mr. Sudhir Vasudeva, CMD, ONGC addressing the delegates during his inaugural address

H.E. Bharat Vir Wanchoo, Governor of Goa visiting the exhibition premises of the conference.

Dignitaries in the Dias releasing the CORCON 2012 Souvenir

Delegates during the inauguration session

Glimpses of CORCON 2012

Jim Britton President & CEO, Deepwater Corrosion Services Inc delivering Keynote address

Panel Members during Technical Interactive open Discussions

17th NIGIS Lifetime Achievement Award being presented to Mr. Rajan Bahri by H.E. Bharat Vir Wanchoo, Governor of Goa

Mr. V G Kulkarni, Founder Trustee, NACE India Section felicitating the sponsors

Cultural programme during the conference

Certificates for best paper awards being presented by Mr. Kevin C. Garrity, President, NACE International during valedictory function

NACE INTERNATIONAL CERTIFICATION COURSES

NACE International Gateway India Section (NIGIS) so far has successfully organized 75 NACE International certification courses during last 5 years.

NACE International Gateway India Section regularly organises certification courses "Coating Inspector Program" Level I, II & Peer Review of NACE International. NACE CIP training programs are the best and most comprehensive training programs in the industrial coating business. NIGIS organized following certification course during the period July 2012 – January 2013 in India.

Course No.	Course	Period	Venue	No. of Participants
1	CIP Level 1	2 - 7 July, 2012	Bengaluru	11
2	CIP Level 1	9 - 14 July, 2012	Mumbai	24
3	CIP Level 2	16 - 21 July, 2012	Mumbai	26
4	CIP Peer Review	1 – 3 October, 2012	Mumbai	19
5	CIP Level 1	1 – 6 October, 2012	Mumbai	22
6	CIP Level 2	8 – 13 October 2012	Mumbai	21
7	CIP Level 1	26 Nov – 1 Dec 2012	Mumbai	23
8	CIP Level 2	3 – 8 Dec 2012	Mumbai	13
9	CIP Level 1	14 – 19 Jan 2013	Mumbai	9
10	CIP Level 2	21 – 26 Jan 2013	Mumbai	9
11	CIP Level 1	28 Jan – 2 Feb 2013	Vadodara	17

CIP level 1 course describes an inspector who has been taught the fundamentals of non-destructive coatings inspection for the surface preparation and application of coatings on steel substrates.

CIP Level 2 course focuses on advanced inspection techniques and specialized application for both steel and non-steel substrates. The course includes in-depth coverage of surface preparation, coating types, inspection criteria, and failure modes for various coatings including specialized coatings and linings.

CIP Level 3 (Peer Review) candidates must demonstrate that they can apply the practical and theoretical knowledge of coatings they have learned throughout the CIP Level – 1 and Level 2 courses and from experiences faced on the job in real-life situations.

First time in CIP history, NACE HQ along with NACE International Gateway India Section conducted CIP Peer Review course with video conference facilities.

NIGIS is also organising Offshore Corrosion Assessment Training (O-CAT) training program during 20 -24 May 2013. O-CAT course is a five-day intensive program addressing the elements of in-service inspection and maintenance planning for fixed offshore structures. The course also addresses the Minerals Management Services (MMS) A-B-C facility evaluation grading system requirements for Level I inspection reporting.

Photographs of CIP Courses

CIP Level 1 participants during 2 - 7 July, 2012

CIP Level 1 participants during 1 – 6 October, 2012

CIP Level 1 participants during 9 - 14 July, 2012

CIP Level 1 participants during 26 Nov – 1 Dec 2012

CIP Level 2 participants during 16 - 21 July, 2012

CIP Level 2 participants during 21 – 26 Jan 2013

Stress-tolerant Polymer and Online Polymer Monitoring for Cooling Water Systems

Dr. Rajendra P Kalakodimi, Kubal Chandrshekhar and Ritesh Saxena
GE India Industrial Pvt. Ltd., Bangalore India.

Abstract

With water scarcity and environmental concerns leading to increasing conservation efforts and water discharge restrictions, cooling towers are facing the challenge of operating at higher cycles. Since increased cycles bring elevated stresses in the form of higher levels of salts and a broad range of contaminants, cooling water treatment programs must be more robust to resist problems associated with such elevated stresses. This paper presents advanced technology designed to treat cooling towers under stressed water conditions. The paper will demonstrate the superior performance of this technology in controlling the formation and deposition of mineral deposits and in inhibiting corrosion over a broad range of application and high stressed conditions relative to industry benchmarks. Case-study is also discussed.

Laboratory Screening & Polymer Development

The advanced scale control chemistry, referred as stress tolerant polymer (STP), was comprehensively tested in laboratories and compared with a sulfonated acrylic acid copolymer (SAA) and other commercial sulfonated copolymers and terpolymers, designated polymer A, B, C, and D. The SAA polymer is one of the most widely used cooling water dispersants, based on total volume.The tests were conducted using static beaker test protocol and dynamic Bench Top Unit (BTU) protocol. The BTU is a recirculating system with a heat transfer surface installed. Both testing methods have been described in prior papers (1, 2).

Static beaker tests are designed to be a screening tool that can quantify inhibition efficacy of the chemistry for calcium phosphate, zinc phosphate and other mineral deposits. BTU tests are designed to simulate cooling tower operation. Bulk water and heat transfer surface temperatures are controlled, pH is monitored and controlled, and corrosion rates of low carbon steel (LCS) and admiralty (Adm) are also measured online. Test results using those two methods are discussed in details in the paper.

1. Static Beaker Tests

A. Calcium Phosphate & Zinc Inhibition Testing

Figures 1 & 2 shows that STP polymer is highly effective for PO4 inhibition and Zn inhibition even at lower dosages compared to the industry standard polymers.

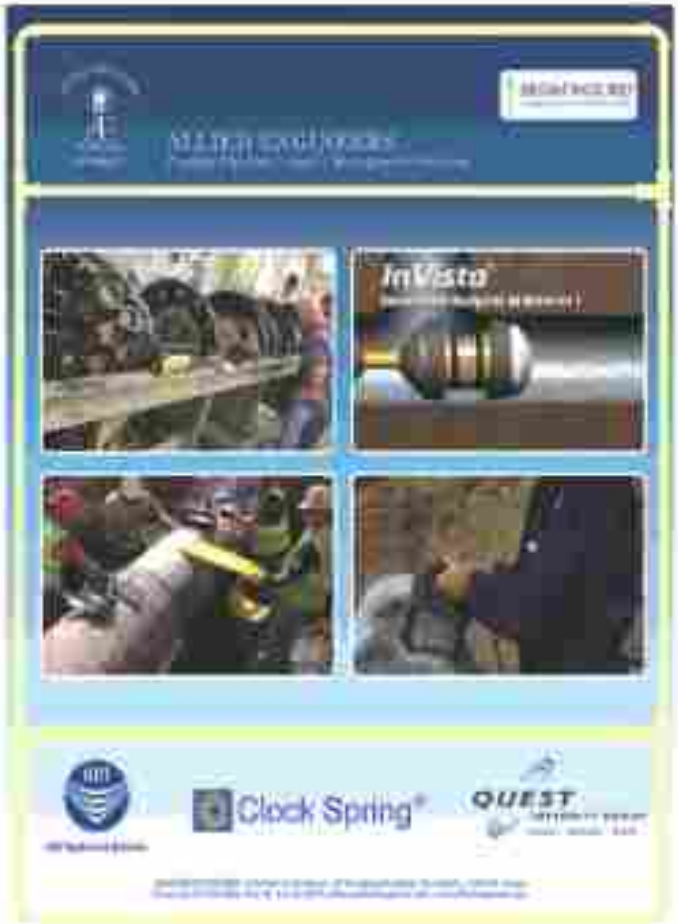
2. Bench Top Unit (BTU) Development

The standard BTU water composition and operating parameters are shown in Table 1.The cooling treatment contained 15 ppm orthophosphate, 3 ppm pyrophosphate, and 1.2 ppm Halogen Resistant Azole (HRA) unless specified otherwise. Polymer dosages were varied based on test conditions and polymers used. During a 7 day BTU test, samples were taken from the sump daily for water chemistry characterization including turbidity, ortho-PO4 and ICP analysis of both filtered (F) and un-filtered (UF) samples.

Corrosion rate of LCS and Adm was monitored using LCS and Admprobes connected to a Corrator. At the end of each BTU run, coupons and tubes were visually inspected for cleanliness of metal surfaces. The coupons were also cleaned and weighed to determine corrosion rate using the weight of coupons before and after BTU tests to calculate mils per year (mpy).

A. Standard Conditions

As shown in Table 2, a minimum of 4 ppm for the SAA polymer was required to provide a clean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heat transfer surface and to maintain good bulk water control and low corrosion rates. Under the same test conditions, the STP polymer achieved excellent performance at 2 ppm, half of the SAA dose required. High efficacy of the STP polymer was demonstrated in the standard water condition.

B. High hardness

The STP polymer was further evaluated under high hardness conditions, up to 1600 ppm Ca and 2400 ppm total hardness. The test water condition, treatment program and BTU test results were summarized in Table 2. At 1200 ppm Ca and 600 ppm Mg, 4 ppm STP polymer effectively inhibited deposition on the surfaces of the heat transfer tube and coupons.

Turbidity was less than 0.5 NTU and delta PO4 was 0.12 ppm. The corrosion rate was zero at the end of testing and no corrosion was observed on the heat transfer tube and coupons. To achieve the same performance under the water condition, the minimum dose of the SAA polymer required was 8 ppm, two times that of the STP polymer.When the hardness level was increased to 1600 ppm Ca and 800 ppm Mg, 5 ppm STP polymer was required to keep the heat transfer surface clean of any deposit while maintaining good water quality. Low corrosion rate was achieved, 0.10 mpy for LCS and 0.1 for Adm.

C. Soluble Iron contamination

The effect of ferrous iron on polymer performance was evaluated by feeding ferrous irons (prepared from FeCl2 prior to its addition and daily) directly to the BTU sump. This test was designed to simulate ferrous iron (Fe2+) released from LCS surfaces. The ferrous iron stock solution was shot fed to the sump to generate 0.5 ppm Fe, and then was continuously fed 24 hrs after test initiation. The 3 ppm target iron concentration was achieved after 2 days. As shown in Table 3, at 14 ppm SAA polymer, bulk water chemistry was maintained stable, 2.46 ppm Fe was kept as soluble Fe, and corrosion rate of LCS was 0.265 mpy. A light deposit was observed on the heat transfer surface. In contrast, at 7 ppm STP polymer, 2.63 ppm Fe was kept soluble and bulk water chemistry was well under controlled. Most importantly, the heat transfer surface was clean of any deposit and corrosion.

D. Aluminum contamination

Effect of Al on polymer performance was examined following the procedures similar to those used for the iron contamination study. An aluminum stock solution was prepared from AlCl3.6H2O and was shot fed to the sump to a dosage of 0.5 ppm. Then, it was continuously fed to target 2 ppm Al concentration 24 hours after test being initiated.

At 5 ppm STP polymer, 0.95 ppm Al was detected in the filtered sample and a total of 1.91 ppm of Al, 95% of the aluminum fed, was kept in the unfiltered solution phase. The average delta PO4 was 3.3 ppm after Al reached to 2 ppm. The surface of the heat transfer tube and all coupons was maintained clean, indicating that the polymer effectively kept the Al and PO4 containing species off the surfaces.

At 7 ppm SAA polymer, 0.76 ppm Al was found in the filtered sample and a total of 1.75 ppm, 85% Al fed, was maintained in un-filtered sample. The delta PO4 and turbidity were higher than in the STP BTU run. A light deposit was observed on the heat transfer surface (Table 4).
The form of Al species under this condition may not be the same as that typically found in cooling tower since in the BTU tests, Al was fed to the sump as unhydrolyzed Al which may interact immediately with polymer and PO4. In cooling towers, the majority of Al may result from water clarification processes in which the pH is about 7, and thus the dominant Al species is hydrolyzed Al, such as insoluble Al(OH)3.

E. Clay Contamination

Since clay and silt are the most common solids in a cooling water loop, BTU tests in the presence of clay were conducted using a mix of Kaolin and Montmorillonite clay at a 1 to 1 ratio under standard BTU water and test condition (Table 1). The clay in the makeup water tank was agitated continuously with a stirrer to keep solids suspended in the solution.The particle size of the clay mixture used in the BTU test was analyzed using an AccuSizer (Model 770). The analytical results are summarized in Table 5. The clay particle used in the tests was extremely fine, 85% of the particles were less than 1 micron or 97% less than 2 micron.


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For a BTU conducted with 2 ppm STP polymer in the presence of 75 ppm clay, the average turbidity was about 35 NTU. Delta PO4 was less than 0.5 ppm.The surface of the heat transfer tube and allcoupons was clean of deposits and was well protected from corrosion as indicated by the low corrosion rate.

The SAA polymer also provided good corrosion and deposition protection for the surface of all metals and good water quality, but needed twice the amount of the polymer compared to the STP polymer (Table 6). Highly stressed water condition was created by increasing clay concentration to 200 ppm (1:1 mix of kaolin and montmorillonite). The turbidity of this stressed water was about 100 NTU. Under this water condition, the demand for the SAA polymer increased significantly from 4 to 14 ppm (10 ppm additional polymer), in order to maintain good control of water chemistry and a clean heat transfer surface. However, only 7 ppm additional STP polymer was required to handle the same stress level. These BTU tests clearly demonstrated that the STP polymer was not only superior for Po4 inhibition, but also highly effective to disperse very fine clay particles (Table 6).

All the results presented in this paper demonstrate the robustness of the STP polymer to normal and high stress cooling tower waters. The STP polymer based cooling treatment programs are being evaluated under field conditions in order to validate laboratory observations. These results may be presented in a future paper after compilation and analysis.

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Conclusions:

Stress Tolerant Polymer (STP) provides unparalleled corrosion, scale/deposit control, and biological control protection in the presence of halogens. Online Technology's CoreAnalytes Module (CAM) directly measures the functional chemistry of all three key elements of a treatment program including:

Orthophosphate for steel corrosion control

Polymer for the prevention of deposits from mineral scales and dispersion of suspended solids

Free Halogen for the cost-effective control of microbiological growth.

References

(1) S. M. Kessler, K. M. Given, "Halogen Compatible Treatment Programs For Open Recirculating Cooling Water Systems," Corrosion/99, Paper #300, 1999

(2) S. M. Kessler, N. T. Le, "Performance of a New Paper Mill Supply Treatment Program," Materials Performance, Vol. 36, No. 8, 1997, pp. 35-41

(3) Caroline Sui, Gary Geiger, "Improved Calcium Phosphate Control for Stressed Systems", Cooling technology institute annual conference, Houston, TX, 2008.

A successful experience in handling low quality water with STP-based Program: Case Study

Challenge

One of leading metal processing unit in India have set up a 160 MW TPP. This power plant was set up to cater to their smelter units. The geographical location where this plant was set up is a water scarce area and the water available as a makeup to the cooling system is very low quality. Customer's expectation is to use this water as a makeup to the cooling tower and also operate the cooling tower at higher Cycles of concentration. Achieving and maintaining good performance with low quality and quantity of the makeup water was a challenge. The makeup water quality and the cooling tower details are:

With the full load of operation of cooling water system, the expected cooling water velocity was 1-1.2 m/sec. However, during the first three months of operation, the plant had run at 50% of load due to the plant commissioning activities. The circulation rate during that time was 12500 m3/hr. This reduced the water velocity and made the operation further challenging.

pH	8-8.5
Turbidity	3-20 NTU
Conductivity	1500-2500 umhos/cm
Total Alkalinity	200-375 ppm
Total Hardness	300-575 ppm
Ca Hardness	180-320 ppm
Chlorides	380-520 ppm
Total Iron	0.2-0.5 ppm

Circulation Rate	25000 m3/hr
System Volume	10000 m3
Temperature Difference deg C	7-8
CoC	3-4

Solution:

To meet the expected performance and stringent customer requirements, GE has proposed a STP polymer Technology based solution. The proposed program also contains an oxidizing biocide along with a slug feed of non-oxidizing biocide. The program also has a halogen resistant azole as the consider tube metallurgy was admiralty brass. The proposed CoC was 3-4 depending on the stress on the treatment program. Acid dosing was maintained to maintain the necessary pH and alkalinity.

Results:

Even with the highly demanding and stressed water quality, the program has achieved excellent scale control and very good heat transfer along with excellent corrosion rates on both mild steel and yellow metallurgy. The system was successfully operated at a CoC of 4 which results in good water savings to the customer. An average corrosion rate of 1.0 mpy on mild steel and an average corrosion rate of 0.25 mpy on brass metallurgy were obtained over a period of more than 1 year.

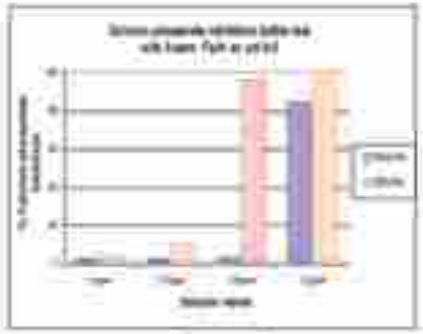

Figure 1
Calcium phosphate inhibition test in presence of 3ppm ferrous irons

400 ppm Ca, 100 ppm Mg, 35 ppm M-alkalinity (all as CaCO3), 10 ppm o-PO4, and the polymer under evaluation

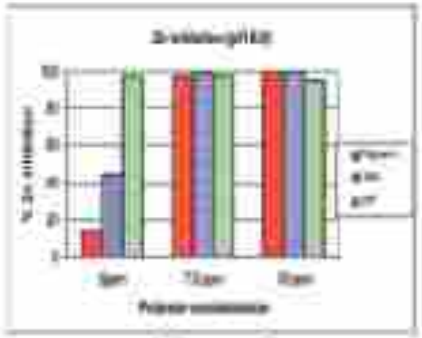

Figure 2
Zn Inhibition

300 ppm Ca, 10 ppm PO4, 5 ppm Zn, a polymer under evaluation and 20.5 ppm M-alkalinity

Water Chemistry		
	Ca as CaCO3	600 ppm
	Mg as CaCO3	300 ppm
	M-Alkalinity as CaCO3	50 ppm
	pH	7.2
Treatment Chemistry		
	Ortho as PO4	15 ppm
	Pyro as PO4	3 ppm
	HRA	1.2 ppm
	Polymer Under Evaluation	
Operating Parameters		
	System Volume	11 L
	Bulk Temperature	48.9 oC
	Test Duration	7 Days
	Heat Flux	2.17 kCal/cm^{2}hr
	Water Velocity	0.87 m/s
Metallurgy	Coupons	4 LCS Coupons and 4 ADM coupons
	Heat Transfer Tube	1 LCS

Tabel 1. BTU Test conditions

ppm as CaCO3		ppm as PO4		Treatment	ppm	Turbidity	Delta PO4	Corrosion Rate (mpy)		Heat transfer surface
Ca	Mg	Ortho	Pyro			(NTU)	(ppm)	LCS	ADM	Clean-no deposit
600	300	15	3	SAA	4	0.39	0.05	0.45	0.5	Clean-no deposit
600	300	15	3	STP	2	0.37	0.22	0.43	0.37	Clean-no deposit
1200	600	15	3	SAA	8	0.36	0.18	1.2	0.65	Clean-no deposit
1200	600	15	3	STP	4	0.40	0.12	0.48	0.5	Clean-no deposit
1600	800	10	3	STP	5	0.35	0.17	048	0.18	Clean-no deposit

Table 2. BTU test results: Standard and high calcium water conditions

Treatment	Ppm	Turbidity (NTU)	Delta	Fe (F)	Delta Fe	Corrosion LCS(mpy)	Corrosion ADM(mpy)	Heat transfer surface
SAA	14	3.66	0.27	2.47	0.09	1.71	0.48	Light deposit
STP	7	4.00	0.25	2.63	0.04	0.2	0	Clean-no deposit

Table 3. BTU test results: Standard water condition in the presence of 3ppm ferrous ions.

Treatment	Ppm	Turbidity (NTU)	Delta	Fe (F)	Delta Fe	Corrosion LCS(mpy)	Corrosion ADM(mpy)	Heat transfer surface
SAA	7	7.46	3.87	1.75	0.993	0.5	0.45	Light deposit
STP	5	5.19	3.27	1.91	0.96	0.56	0.33	Clean-no deposit

Table 4. BTU test results: Standard water condition in the presence of 2ppm Al ions.

Particle size (microns)	Particles per mL	% of total particles	Volume ppm	% of total volume	Particle volume
0.5-1.0	23750665.8	85.4%	3.8564	0.81%	57855721
1.0-2.0	3199333.2	11.5%	4.1202	0.87%	61813628
2.0-4.0	558666.6	2.0%	6.7351	1.42%	1.01E+08
4.0-6.0	116666.7	0.4%	7.6153	1.60%	1.14E+08
6.0-8.0	65333.3	0.2%	10.6018	2.23%	1.59E+08
8.0-10.0	39333.3	0.1%	14.8117	3.12%	2.22E+08
10.0-15.0	38000.0	0.1%	36.9940	7.78%	5.55E+08
15.0-20.0	18000.0	0.1%	49.8421	10.49%	7.48E+08
20.0-30.0	15333.3	0.1%	115.7404	24.36%	1.74E+09
30.0-40.0	2000.0	0.0%	40.8220	8.59%	6.12E+08
40.0-50.0	1333.3	0.0%	65.6902	13/82%	9.86E+08
50-100	666.7	0.0%	118.3781	24.91%	1.78E+09
100-200	0.0	0.0%	0.0000	0.00%	0
Total	27805332.3	100.0%	475.2073	100%	

Table 5. Particle size analysis of a mix of kaolin and montmorillonite clays

Authors

Dr. Rajendra Prasad Kalakodimi is a Product Manager with GE Water & Process Technologies, Bangalore. Email: rajendra.kalakodimi@ge.com Prior to this, he was a Lead Scientist and Engineering Technical Leader at GE India Technology Centre, John F. Welch Technology Centre, Bangalore, India. His research interests were development of proprietary, organic corrosion/scale inhibitors for utilities and refinery applications. His expertise is also in the areas of high temperature corrosion testing and material selection for various applications. He holds a Ph.D. in the areas of material electrochemistry, corrosion science and energy-storage devices. He has authored more than 20 publications in reputed international journals and has 6 patent filings.

Chandrashekhar Kubal is a Regional Technical Manager, Product Applications Group at GE Water & Process technologies. Email: Chandrashekhar.kubal@ge.com. He has more than 27 years of professional experience in handling cooling water treatment programs in Hydrocarbon Processing Industries and Chemical Processing Industries.

Dr. Ritesh Saxena is working as Regional Sales Manager – North India for GE Water & Process Technologies, E-mail: ritesh1.saxena@ge.com. He has 10 years' professional experience in Sales, Service, Technical Support and Key Account Management for water treatment. He has core competence in boiler water chemistry management & industrial Dust Control applications. He is the TrueSense (Online polymer monitoring & control device for water chemistry) champion for GE Water in India. He has Ph.D. in Environmental Chemistry. He has 08 publications in reputed international/national journals.

Corrosion Basics

Why Metals Corrode

The driving force that causes metals to corrode is a natural consequence of their temporary existence in metallic form. To reach this metallic state from their occurrence in nature in the form of various chemical compounds (ores), it is necessary for them to absorb and store the energy required to release the metals from their original compounds for later return by corrosion. The amount of energy required varies from metal to metal. It is relatively high for metals such as copper and silver. Table below lists some metals in order of diminishing amounts of energy required to convert them from their ores to metal.

A typical cycle is illustrated by iron. The most common iron ore, hematite, is an oxide of iron (Fe_2O_3). The most common product of the corrosion of iron, rust, has the same chemical composition. The energy required to convert iron ore to metallic iron is returned when the iron corrodes to form the same compound. Only the rate of energy change is different. Destruction by corrosion takes many forms, depending on the nature of the metal or alloy; the presence of inclusions or other foreign matter at the surface; the homogeneity of its structure; the nature of corrosive medium; the incidental environmental factors such as the presence of oxygen and its uniformity, temperature, and velocity of movement ; and other factors such as stress (residual or applied, steady or cyclic); oxide scales (continuous or broken); porous or semiporous deposits on surfaces, built-in crevices; galvanic effects between dissimilar metals; and the occasional presence of stray electrical currents from external sources.

Except in rare cases of a grossly improper choice of materials for a particular service, or an unanticipated drastic change in the corrosive nature of the environment or complete misunderstanding of its nature, failures of metals by rapid general attack (wasting away) are not often encountered. Corrosion failures are more often localized in the form of pits, intergranular corrosion, attack within crevices, etc.

TABLE – Positions of Some Metals in the Order of Energy Required to Convert Their Ores to Metal

Most Energy Required	**Potassium**
	Magnesium
	Beryllium
	Aluminum
	Zinc
	Chromium
	Iron
	Nickel
	Tin
	Copper
Least Energy Required	**Silver**
	Platinum
	Gold

Adapted from Corrosion Basics - An Introduction, National Association of Corrosion Engineers.

One-day workshop on Experimental Techniques for Corrosion Research
26th September 2012
Grand Hyatt, Bambolim, Goa.

The workshop was organised under the aegis of NACE International Gateway India Student Section mainly for the purpose of training young researchers from universities and R & D institutions. This workshop was convened by Prof. V. S. Raja from Indian Institute of Technology, Bombay. The workshop was inaugurated by Dr. Kevin Garrity, President of NACE International and Tushar Javeri, Vice President of NACE International. Also Robert H. Chalker, Executive Director of NACE International graced the occasion.

Eminent speakers delivered the talks on a wide variety of experimental techniques for corrosion research. The topics which were discussed during the workshop were

1. "Polarization Techniques for Corrosion Research" by Prof. V. S. Raja from Indian Institute of Technology, Bombay
2. "Micro-Electrochemical Techniques" by Dr. Geogy J. Abraham, BARC Mumbai
3. "Application of Electrochemical Impedance Spectroscopy for Study of Organic Coatings" by Prof. V. S. Raja from Indian Institute of Technology, Bombay
4. "Electrochemical Techniques Applied to Microbiologically Influenced Corrosion" by Dr. Brenda Little, Sr. Scientist, Naval Research laboratory
5. "Corrosion as a Professional Career" by Prof. Rolf Gubner from Curtin University, Australia

The response to the workshop was good with the number of delegates exceeding 40. Participation from students and faculties from various reputed educational institutions spread over India was heartening. They were joined by several industrial experts. The feedback for this workshop was positive and it proved to be beneficial especially for the student delegates, getting to learn from the veterans in their respective fields of expertise.

Bring on the Heat – INDIA

18 – 19 April 2012
Mirage Hotel, Mumbai

NACE International Gateway India Section in association of NACE International is organizing a conference "Bring on the HEAT" (BOTH) from 18 - 19 April 2013 at Hotel Mirage, Mumbai.

The objective of this conference is to provide you with an ideal opportunity to discuss on the hottest coatings, fire proofing solutions, high-temperature and other protective coatings in the industry. BOTH would cover :-

- Passive Fire Protection
- Corrosion Under Insulation
- Corrosion Under Passive Fire Protection
- High-Temperature Coatings
- Thermal Spray Aluminium (TSA)
- Epoxy Intumescent Fireproofing
- Cementitous Fireproofing

The conference will combine the best of India hospitality with an exciting technical program and a social networking session to make the event a truly memorable experience. The Conference is expected to attract over 150 leading practicing coating professionals, upper management, engineers and inspectors that are responsible for the topic in their specific industries. For more information please contact technical@corcon.org or visit www.nace.org/bothindia.

NACE International Certification Cathodic Protection (CP) Program

NACE International Gateway India Section conducted the first CP -1 Tester Training program during 4 – 9 June 2012 and 17 participants from across the globe attended the program and CP - 2 Technician Programme was held on June 11 – 16, 2012 at Mumbai. 26 participants attend CP – 2 programme.

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.

The CP 1- Cathodic Protection Tester course presents CP technology to students entering the cathodic protection industry.

The CP – 2 Cathodic Protection Technician course provides intermediate-level training in Corrosion Theory and CP concepts, Types of CP Systems, AC and DC stray current interference, Field measurement techniques and CP Recordkeeping

The CP 3-Cathodic Protection Technologist Course builds on the technology presented in the CP 2-Cathodic Protection Technician course.

The CP 4-Cathodic Protection Specialist Course focuses on the principles and procedures for CP design on a variety of structures for both galvanic and impressed current systems.

CP 1 Participants during 4-9 June 2012

CP 2 Participants during 11- 16 June 2012

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India:
Vasu Chemicals: Vasu Centre, Military Road, Marol, Andheri (E), Mumbai - 400 059
Tel: +91-22-61449600 Fax: +91-22-28209804, 66959101, Email: info@vasuchemicals.com

Middle East:
VasuChem Technologies FZC: A-642, P.O. Box No.8446, SAIF Zone, Sharjah UAE
Tel.: + 9716-5570068 Fax: + 9716-5574068, Email : info@vasuchem.com

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