CORROSION COMBAT

Quarterly Newsletter of NACE International GATEWAY INDIA SECTION

Corrosion of Process Equipment in Chemical Industry affecting the structural stability

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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 publications. To publish your article, submit it to rishikesh@naceindia.org

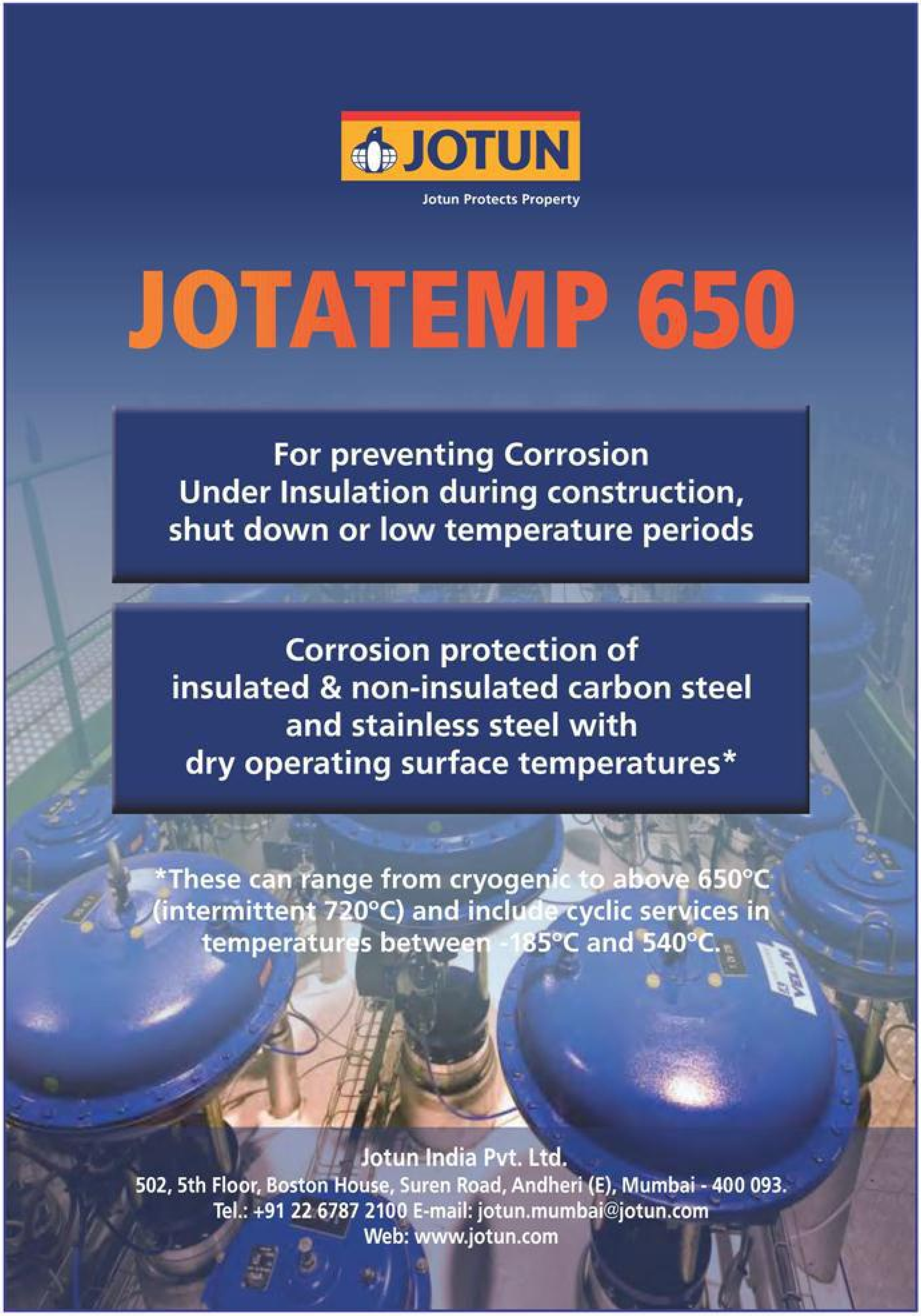
Editorial

Hello Friends,

Greetings for the new year 2019!

During the past few years there is a glut of congregations, trainings and discussions on the Pipeline Integrity Management. Pipelines are lifelines of energy business, economy of a country and global economy. The issue of pipeline integrity arises because of material of construction, which we use for pipelines, i.e. Carbon Steel. This material corrodes even when it gets the slightest corroding environment. This environment can be external or internal to the pipeline. However, carbon steel has its inherent techno-economic advantages. There are substantial investments on pipeline integrity maintenance and management. These investments are on account of various threats and corrosion is one among them. The corrosion threat is handled by various corrosion control, protection and monitoring measures and process control. Detailed plans are drawn to mitigate various threats and those plans are executed to avoid / minimize them. This has resulted in significant improvements in and effectiveness of pipeline integrity management. Various hardware and software contribute to these plans. However, over the life span of a pipeline, there may happen several changes in the external and internal environment that may pose new threats to the integrity of a pipeline. As a result, failures may happen or vulnerability to failure may rise. The result of compromised integrity is not only leak in the pipeline, the reputation and value of a company is also jeopardised. The termination of fluid flow due to pipeline failure may also lead to shut down of process or closing of oil and gas wells. We can learn a lot from failures and take pre-emptive measures to prevent similar failures.

Anil Bhardwaj
Editor – Corrosion Combat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Contamination of Chemical Process Product by Corrosion of Process Vessel: A Case Study

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INTRODUCTION

In general, corrosion phenomenon is considered mostly as a destructive process affecting the structural stability of engineering structures including chemical process equipments in chemical industry. But, one aspect of corrosion is not given its due importance. This aspect is that corrosion of process equipments in the process side affects the quality of the chemical product being manufactured in the equipment. This aspect of corrosion is very important in sensitive industries such as pharmaceuticals, food products, dairy industry etc.

The present case study describes one such incident wherein the white organic chemical product got contaminated with corrosion products of the process equipment and got rejected by the customer.

THE CASE STUDY

The process condition, a batch process, consists of the following:

An Organic Hydrochloride Process Powder from a Pan Crystallizer with about 3.00 % moisture at 50 deg.C enters a Flash Drier through a Lump Crusher and gets increased in temperature to 130 deg.C by mixing with hot air at 130 deg.C coming from a finned hot air heater which heats air through steam heating. The wet powder along with hot air spins in the flash drier by an internal agitator assembly which rotates at 250 RPM. In this process the product powder gets dried and is sent along with hot moist air to cyclone separator. The latter separates the powder and sends it to the packing section and sends the air to the vent.

Within a couple of years of operation, it was observed that the final product, as seen at the outlet of the cyclone separator, was found to be varying color batch to batch, from pure white, off-white, light brown and to full brown as against the specified pure white in color for all batches. This brown product is not acceptable for further processing to a finish consumer product.

Detailed discussion was held and thorough inspection of the wetted parts of the processing vessels was made.

The observed brown contamination of the powder product coming out of the cyclone separator was due to the heavy metal contamination (mostly through iron oxide brown rust) present in the product coming out of the flash drier stage.

This is clear from the chemical analysis results conducted on representative samples from different batches. The "off-white crystalline powder sample supplied showed an e iron content of about 8.00 ppm as compared to typical values of Nil to 1.50 ppm in "white" powder samples, the latter acceptable for further processing, while the former value is not acceptable.

The material of construction (MOC) of all the wetted parts of the process vessels was said to the standard austenitic stainless steel 316L SS, an iron based alloy steel with about 18-20 % Chromium, about 10 % Nickel, 2 to 3 % Molybdenum and Carbon less than 0.03 %.

This contamination is due to heavy corrosion of the 316L SS INTERNAL COMPONENTS of the drier agitator, namely, shaft, plates, spacers, lump-breaking pins etc operating inside the drier.

The stated service condition, namely solution of organic hydrochloride with the associated 3% water, raised to the temperature of 130 deg,C., is highly corrosive to ordinary carbon steels and also standard stainless steels such as 304(L) and 316(L) SS. The corrosion product, almost full brown rust (hydrated iron oxide) with very small amounts of chromium, nickel and molybdenum oxide, comes out in the form of fine rust powder, gets mixed with the organic chloride powder and contaminates the latter to non-acceptable off-white brown powder.









The following forms of corrosion have occurred in the wetted parts of the agitator assembly:

1. General uniform corrosion resulting in uniform overall roughness and reduction in effective wall thinning in general. (See Photographs 1 and 2 below).

Photograph 1

Photograph 2

2. Pitting corrosion in all wetted parts: a form of localized accelerated corrosion resulting in deep pits, either highly localized or throughout the surface, typical of corrosion of stainless steels in chloride solutions well above the atmospheric temperatures (See Photographs 3 and 4 below).

Photograph 3

Photograph 4

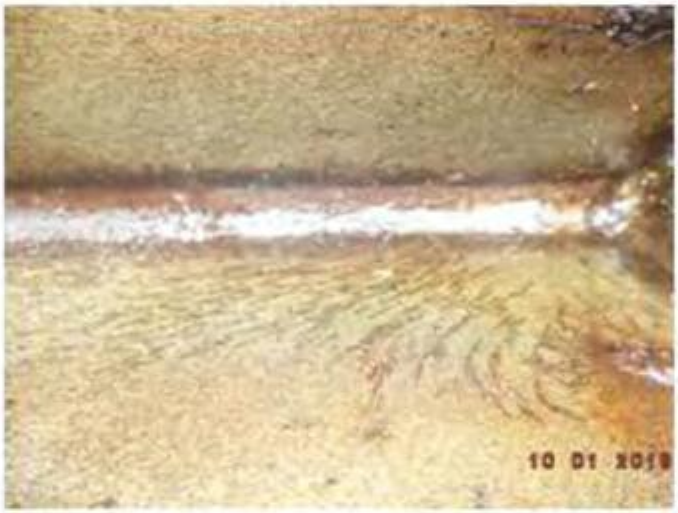
3. Crevice corrosion. A form of highly localized corrosion occurring inside the crevice formed within mechanical joints, like keyways, spacer-shaft areas, gasket grooves etc., also typical of stainless steel corrosion by chloride solutions wherever crevices are present. (See Photographs 5 and 6 below).

Photograph 5

Photograph 6

4. Stress Corrosion Cracking by Chloride (CSCC). This is an intense form of highly localized corrosion occurring in stainless steels in areas where tensile residual stresses are present simultaneously with chloride contact. This form of corrosion, CSCC, shows up in the form of bunches of fine multiple cracks without noticeable corrosion (brown rust formation) in the adjoining areas and without wall thickness reduction. (See Photographs 7 and 8 below for CSCC in areas adjoining welds where residual stresses are present).

Photograph 7



Photograph 8

Thus it is **diagnosed** that the problem of brown contamination of the organic chloride powder is due to corrosion of internal components made of 316L stainless steel making up the agitator assembly.

It was reported by the plant personnel that sometimes the off-white brown coloration was seen only after the white looking powder reaches the overseas customer destination and not before packing at the plant works. The likely reason for this is as follows: The initial corrosion product is iron chloride which is somewhat unstable and colorless. Over a period of time, short or long, depending upon temperature, in the presence of air and moisture, not necessarily in the presence of stainless steel, the iron chloride hydrates, combines with moisture and oxygen and forms hydrated iron oxide (brown rust) which shows up as contamination while the powder packet is unpacked overseas. This is due to the possibility of moisture and air entering the export packing and reaching the powder inside.

Recommendations for Remedial Measures:

It should be stated here that the shell of the drier is not stainless steel, only the internals are made of stainless steel. The shell is made of FRP, a corrosion resistant engineering plastic material, with good corrosion resistance and good mechanical strength, with the inside surface lined with PVDF, again a corrosion resistant engineering plastic material. There was no corrosion observed on the shell inside surface, only the internals made of stainless steel were affected. Unfortunately all the

internals, the agitator and its associated plates and fittings, are made of Type 316L Stainless Steel which is not at all resistant to the corrosive process conditions inside the drier.

The remedial measures consist of EITHER change of MOC (Material of Construction) OR giving a TEFLON Lining for the interior wetted parts of Agitator assembly since the process side corrosivity cannot be reduced.

There are available certain Super Austenitic Stainless Steels, much better resistant to all forms of chloride corrosion than the Standard Austenitic Stainless Steels such as 304(L) and 316(L) SS. There is also a Nickel Base Alloy which is much more resistant to chloride solution than even the super austenitic stainless steels. These are richer in chromium, nickel and molybdenum content of the stainless steels with or without certain additional alloying elements and hence appreciably more expensive than 316L SS.

The special stainless steels and nickel base alloy, though more expensive than 316L SS, are in use in corrosive applications where 316L SS is not satisfactory with respect to chloride, pH, temperature etc.

Table below gives a comparison of certain corrosion resistant properties of these materials with those of 316L SS.

Material	Critical Pitting Corrosion Temperature as per ASTM G-48 E	Critical Crevice Corrosion Temperature as per ASTM G-48 F	Threshold Stress for CSCC to occur, % of Yield Strength
316L SS	20 deg.C	< 0 deg.C	< 10 %
904L	40 deg C	10 deg C	60 %
254 SMO	65 deg C	35 deg C	80 %
C 276	>100 deg.C	50 deg. C	Fully resistant

Table: Comparison of Certain Corrosion Resistant Properties

One can notice that the mentioned special materials are far superior to the basic 316L SS. Though the mentioned temperatures are much lower than the drier operating temperature of 130 deg, C, the materials would give far better service than 316L SS. The rates of corrosion phenomena experienced by the agitator parts made of these special materials would be much lower than that of 316L SS. By the time appreciable corrosion occurs, the powder process material would have moved out of the region in its continuous movement. Hence the percentage of off-white product would be much smaller than the present level.

Alternative to change of MOC is to go for TEFLON lining (thin layers of organic powder coating) over the exposed surfaces of wetted parts of the agitator assembly. The Teflon coating must be totally pore-free even on crevices and corners and sharp ends.

Author:

Dr. K. ElayaPerumal is a leading Corrosion & Metallurgical Consultant having four decades experience in the industry. He was Research Scientist, Research Guide and Head of the Corrosion & Electro Metallurgy Section of Bhabha Atomic Research Centre, Mumbai. Since 1980 he is acting as a free-lance consultant advising in the areas of corrosion prevention. He has extended his services to various sectors such as oil & gas, oil refineries, petrochemicals, fertilizers, inorganic chemicals, pharmaceuticals & dyes, organic chemicals etc. He is recipient of National Metallurgist Award instituted by Ministry of Iron & Steel, Government of India for contribution in corrosion prevention and failure analysis. He is also recipient of Lifetime Achievement Award by NACE India Section of National Association of Corrosion Engineers, USA for the year 2004.
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CORCON 2018: International Conference & Expo

30th September - 3rd October 2018 in JECC, Jaipur

The contribution of NACE International Gateway India Section (NIGIS) towards generating corrosion awareness and developing corrosion management strategies, over time has been commendable. The annual event CORCON conference & expo on corrosion has earned a name for itself as a unique platform for exchange of knowledge, information and development of solutions on matters pertaining to corrosion and its control.

CORCON 2018 was held in the culturally vibrant, pink city, Jaipur, the capital Rajasthan state, during September 30 – October 3 at Jaipur Exhibition and Convention Centre.

Mr. N Manohar Rao, Chairman NIGIS & CORCON-2018 in his welcome address at the inaugural function highlighted about the significance of the conference expressed that every registered delegate at the conference could have a technical feast of three days in Jaipur.

The conference was inaugurated by Mr. Devendra Bhushan Gupta, IAS, Chief Secretary, Government of Rajasthan. In his inaugural address he said that they at Government of Rajasthan were delighted to be a partner when Mr. N Manohar Rao, Chairman-NIGIS & CORCON-2018 had approached them because the government has a progressive and positive attitude to attract investments in the state of Rajasthan and encourage the visit of specialised professionals from India and abroad, like in the field of corrosion. He appreciated the efforts of NIGIS in providing trainings to industry personal in the area of corrosion control. He emphasised that more efforts are needed to develop green substitutes to control corrosion. He expressed that enhancement of life of aging infrastructure is a matter of great concern and the specialists need to evolve techniques and technologies to take care of them. In the past decades, corrosion professionals focussed primarily on new construction, specifying materials and designing corrosion protection and control systems for buildings, bridges, roads, plants, pipelines, tanks, ships etc. Today when most of the infrastructures reaches end of its design life, the emphasis is on maintaining and extending the life of these valuable assets. The industry should take leverage from R&D to reduce direct and indirect cost of corrosion.

Mr. D. Rajkumar, Chairman and Managing Director, Bharat Petroleum Corporation Ltd., who was the Guest of Honour at the Inaugural function, highlighted that the world is passing through a phase where business revolves around disruptive, innovative and sustainable practices. He observed that this conference on corrosion aims to achieve sustainability, in both, industrial and business environment. He opined that the theme of CORCON 2018, "Uniting the World in Mitigating and Combating Corrosion", has tremendous potential which if explored to the fullest can effectively contribute in enhancing the environment sustainability, optimizing cost, averting infrastructure mishaps and ensuring uninterrupted conduct of business operations. It is said that money saved is more than the money earned, perhaps because of the fact that replacement costs are much higher.

NACE International President, Jeffrey L. Didas, appreciated NIGIS for the great efforts and contributions. He mentioned that India has a big strength of 892 members of NACE International community.

Mr B. Narayan, Group President, Reliance Industries Limited, an ardent supporter of NIGIS for the past several years, mentioned in his address that at this point of time when Industrial Revolution 4.0 is taking off, he expected the corrosion engineers to keep pace with the developments and come up with innovative corrosion prediction models that can predict corrosion under corrosive environment so that effective control measures can be timely adopted.

"CORCON, the annual conference and expo on corrosion science and engineering held in India since last 26 years, is one of the largest event of its kind in Asia. This event offers a powerful platform for information-sharing, knowledge-acquisition, scouting opportunities, market offerings, and networking in the field of corrosion prevention and deployment of materials and components employed in a variety of industries," said

Glimpses of CORCON 2018

Shri N Manohar Rao, Chairman, CORCON 2018
warmly welcoming the fellow delegates

Shri Devendra Bhushan Gupta, IAS,
Chief Secretary Government of Rajasthan
delivering the inaugural speech

Shri D Rajkumar, CMD, BPCL, Guest of Honour
addressing during the Inaugural function

Shri Jeffrey L. Didas, NACE International
President during Lamp Lighting Ceremony

Dignitaries on the Dias releasing the
CORCON 2018 Souvenir

Delegates during the inauguration session

Dr U. Kamachi Mudali, Chairman and Chief Executive, Department of Atomic Energy, Heavy Water Board, Government of India, while speaking on the occasion.

Mr. Tushar Jhaveri, Past President, NACE International congratulated to the entire team consisting of Chairman and the Committee members for such a grand success of CORCON-2018. Mr. Dipen Jhaveri, Secretary, NIGIS proposed the vote of thanks.

A Souvenir of CORCON 2018 was also released during the inaugural session.

The technical sessions of the conference commenced from the morning 1st October. The technical richness of the conference was reflected by the 14 Symposia's in 32 Technical sessions. Four Plenary Talks, 18 Keynote Talks, 184 Oral Papers, 26 Poster Presentations and 6 Technical Interactive Forums were highlight of the conference. This was the biggest ever CORCON in terms of number of delegates, 869. The conference was supported by 01 Platinum Supporter, 09 Gold Supporters, 25 Silver Supporters, 49 Exhibitors with 77 Booths.

The delegates enjoyed a thrilling musical program in the evening, presented by the group Rajasthan Roots. The soulful music, with captivating vocal chord, mesmerising flute and energetic string instruments, refreshed the delegates after a busy day that was packed with heavy weight technical discussions and prepared them for the next day.

There were a few unique features in exhibition area this time. A special arrangement was made for those Supporters / exhibitors who were interested in presenting their products before a larger crowd in one go. The food court was in exhibition area with sitting arrangement. This made technical and business discussions possible during lunch, dinner and tea time. For the first time in expo area, a stall with medical facilities was also arranged. A Portrait Station was also setup for all the participants. This way, the invaluable time of each participant was gainfully utilized.

The four plenary talks, that attracted all the knowledge seekers, focussed on the following topics:

1. "Above Ground Storage Tank Bottom CP - Lessons Learned and What we are doing Today", Jeffrey L. Didas, Senior Technical Specialist, & Corrosion Matcor, USA, President, NACE International.

2. "Corrosion Control and Cathodic Protection of Steel Reinforcement: Past Present and Future", George Sergi, Technical Director, Vector Corrosion Technologies Ltd

3. "Corrosion in The Defence Sector", S.V. Kamat, Distinguished Scientist & Director General, Naval Systems and Materials Defence Research and Development Organisation (DRDO)

4. "Innovative Corrosion Inspection Solutions for Oil & Gas Industries", Krishnan Balasubramanian, Chair Professor, Institute Professor, Dept. of Mechanical Engineering, IIT Madras Chennai

A scintillating Corrosion Awareness Awards function was organized in the evening on 2nd October. On this occasion, Dr V. K. Saraswat, Member, National Institution For Transforming India, NITI Aayog, said, "India loses around US$100 billion annually solely due to corrosion. In this backdrop, the annual edition of CORCON is of special significance. They provide an ideal platform to exchange ideas and views in mitigating this horrendous loss." This year, the award winners were:

Dr T. P. D. Rajan, CSIR-NIIST, Trivandrum for Excellence in Corrosion Science and Technology in Research and Education;

Mr Pankaj Panchal, Corrosion Protection Specialist Pvt Ltd., Ahmedabad, for Excellence in Corrosion Science & Technology in Oil and Gas;

Dr Anita Toppo, Indira Gandhi Centre for Atomic Research, Kalpakkam, for Distinction in Corrosion Science and Technology in Research and Education;

Dr Liju Elias, Indian Institute of Technology Hyderabad, Student Award for PhD;

Mr Bidyut Dutta, IIT Bombay, Student Award for M. Tech;

CSIR-Central Electrochemical Research Institute, Karaikudi, Award for Excellent Laboratory;

Dr V. Saraswathy, CSIR-Central Electrochemical Research Institute, Karaikudi, for Meritorious Contribution to Research and Education.

The Lifetime Achievement Award, nominated by the Section Governing Board-NIGIS, was given to Dr S. L. Kataria, International Certification Services Pvt Ltd., Mumbai.

Glimpses of CORCON 2018

Dignitaries during the Inauguration of Exhibition

Interaction with Exhibitors in the exhibition premises

Dr. U Kamachi Mudali facilitating
Dr. George Sergi during his Plenary Talk

Delegates during the presentation

Dr. V K Saraswat, Member, NITI Aayog addressing during Corrosion Awareness Award function

Dignitaries with winners of Corrosion Awareness Award 2018

This was followed by a surprise Rajasthan Nite-Chokhi Dhani on the sprawling lawns of the JECC with music, dance, entertainment, puppet shows, pottery makers, bangle makers and even fortune tellers guiding the delegates about their future.

CORCON 2018 had a day with special focus on corrosion in the oil and gas industry including with 'Jung Se Jung' session. 'Jung Se Jung (JSJ)' was organized by GAIL in association with NIGIS on 03 October 2018. The objective of JSJ was to discuss the Prevention Considerations to be taken at the Design and Construction Stage so as to avoid Internal & External Corrosion for Oil & Natural Gas Pipelines, which are one of the important national assets. At the outset of the program, Mr. M K Sogani, GM, GAIL welcomed the participants and briefed about the purpose of JSJ program with a glimpse of journey that has been covered during the past years. The JSJ was inaugurated by Dr. Ashutosh Karnatak, Director (Projects), GAIL (India) Ltd, who was the Chief Guest. In his keynote, he applauded the industries for the steps taken and collaboration in the battle against corrosion as well as appealed to all the industries to participate and share knowledge for prevention and mitigation of corrosion. He stressed on the need of migration from "Reactive" corrosion management to "Proactive" management of corrosion. The eminent keynote speakers and panelists at the JSJ were Dr. Carlos A Palacious, Mr. Hasan Sabri, Dr. Narendra Kumar, ED, O&M-CO, GAIL, Mr. E S Ranganathan, MD-IGL, Mr. A N Pandey, ED (O&M-NR), Mr. A K Tiwari, ED-IOCL (Pipeline), Mr. R Suresh, Business Head – RGTIL. The panelists shared their knowledge and views about corrosion and answered various queries of the participants during Q&A Session. The Interactive panel discussion was co-ordinated by Mr. M K Sogani, GM – GAIL.

The organizing committee of CORCON 2018 also placed on record the overwhelming support from Government of Rajasthan, for providing Jaipur Exhibition and Convention Centre (JECC) for the conducting this conference.

The valedictory function of CORCON-2018 was held on 03 Oct 2018. Ms. Helena Seelinger, Executive Director, NACE International Institute, USA was Chief Guest. She specially applauded of the dedication of NIGIS staff, who worked 24/7 in ensuring grand success of the conference. She had all praise for the NACE Staff in India Mr. Manoj Mishra, Mr. Rishikesh Mishra, Ms Anita D'souza, Mr. T D Sundarakashan and Mr. Maxie Fernandes.

14 best symposia awards and 3 best poster papers, as chosen by eminent experts, were presented during the valedictory session. Awards for two best exhibition stalls and two runner-up exhibition stalls were chosen among the 77 exhibition stalls, were also presented.

CORCON 2018: Best paper awards

1 Materials and Composites - RP Tanks-A Potentioal Alternative Of Rubber Lined Tanks For Acid Storage, Shashank Mishra, Madhusudan Sur and Kumar Sudhir, Indian Oil Corporation Limited, Mathura

2 Cathodic and Anodic Protection - Different Grounding Methods For Mitigation Of AC Induction On Pipelines, Mohammad Shums Abbas and Uma Shanker, GAIL (INDIA) Ltd, NCR

3 Coatings, Linings and Thermal Insulation - Performance Evaluation of a Storage Tank Crossed-linked Two Components Epoxy Coating System at Three Curing Temperatures, M. Dabir, S. Mukadam and A. Al-Hashem, Petroleum Research Center, Kuwait and S. Rajendran, St. Antony's College of Arts and Sciences for Women, Thamaraipady

4 Corrosion in Refineries - Preferential Corrosion-Erosion Of Weldments Of Lean/Rich Amine Piping In Refineries, N Vaartha, Sukant Dev and Rajeev Ranjan Ravi, Indian Oil Corporation Limited, Mathura

5 Internal Corrosion in Pipelines - Qualification of lower-cost CRA clad material for flowlines T. Bos, Shell Technology Centre, Bangalore and M. E. Wilms, J. Smit, Shell Technology Centre Amsterdam

6 Corrosion Monitoring and Testing - ECDA - Indirect Inspection through Combined On ground Survey of Pipeline and its Benefits, Atul Parmar, Indian Oil Corporation Limited, Noida

7 Young Student Scientist Forum - Electrochemical response of embedded steel in carbonated limestone calcined clay (LC3) mortar, Sundar Rathnarajan and Radhakrishna G. Pillai, Indian Institute of Technology Madras, Chennai

Glimpses of CORCON 2018

Rajasthani dance program during the conference

Rajasthan Nite - Chokhi Dani Cultural program during the conference

Dr. Ashutosh Karnatak and other Dignitaries on the Dias releasing the 'Jung Se Jung' booklet

Felicitating the Exhibitors in the exhibition premises

Poster presentation brief highlights of research results

Best Paper awards presented during the Valedictory function

8 Corrosion Control in Water Treatment Utilities - Troubleshooting of Scaling problems in Pressable Waxy Distillate (PWD) product cooler in Crude Distillation Unit (CDU) of Digboi Refinery - A Case Study, K K Pandey, Sukla Mistry , S D Chaklader, C R Rao and R Gayen, Indian Oil Corporation Limited, Digboi Refinery, Tinsukia

9 Microbial Corrosion and Inhibitors - Reduction of toxic thiourea usage by green and abundant guargum for steel corrosion inhibition, Venkata Muralidhar K, Vinay Jain, Beena Rai, Tata Consultancy Services Ltd., Pune

10 Power Plants and Utilities - Self - healing Plasma Spray Coatings on Graphite for High-Temperature Applications, Madhura B, E. Vetrivendan, Ch. Jagadeeswara Rao, S. Ningshen, Indira Gandhi Centre for Atomic Research, Kalpakkam

11 Corrosion in Petrochemical, Chemical and Fertilizer Industries - Significance of Corrosion Assessment in Risk Based Inspection, Viswanathan Venkateswaran, Asset Integrity Services, Lloyd's Register Asia, Mumbai, Maran Periyasamy, Lloyd's Register of Shipping, Kuala Lumpur, Malaysia and Shivakumar Kulkarni, Lloyd's Register Asia, Mumbai

12 Corrosion in RCC Structures - Role Of Renewable Materials in Development of Protective Coatings, P.C. Thapliyal, S.R.Karade, Vibhrant, A. Dixit and R. Kumar, CSIR-Central Building Research Institute, Roorkee

13 Marine Corrosion - Ship Rudder Corrosion – Cause and Concerns, Cdr (Dr) Nitin Agarwala, National Maritime Foundation, New Delhi

14 Direct Assessment Methodology Application - Evaluation of Indirect Inspection Data within ECDA Process, Saleh Al-Sulaiman, Hasan Sabri, Eugene D'Souza, Kuwait Oil Company, Kuwait

Best Poster Awards

15 A Novel chitosan/Ag/GO Composite Coating with Enhanced Antibacterial Activity and Improved Corrosion Resistance, Geetisubhra Jena, B Anandkumar, S.C. Vanithakumari, R. P. George, John Philip and G. Amarendra , Homi Bhabha National Institute, Mumbai & Indira Gandhi Centre for Atomic Research, Kalpakkam

16 High performance green concrete with improved biodeterioration resistance against fungus Fusarium sp., Manu Harilal, , B. Anandkumar, R.P. George, John Philip and G. Amarendra, Bhabha National Institute, Mumbai & Indira Gandhi Centre for Atomic Research, Kalpakkam and Sudha Uthaman, Sathyabama Institute of Science & Technology, Chennai

17 Biocompatibility and electrochemical behavior of sodium incorporated niobium oxide coating on 316L SS for orthopedic applications, K. Saranya and N. Rajendran, Anna University, Chennai

CORCON 2018: Best Stalls

1.	9 Sqm–Winner	B S S Tech CP (I) Pvt. Ltd.
2.	9 Sqm–Runner-up	N D T Global
3.	12 Sqm–Winner	Corrtech Energy Limited
4.	12 Sqm–Runner-up	Sunil Chemical Industries

Mr. Dipen Jhaveri, Secretary, NIGIS proposed the vote of thanks to supporters, exhibitors, speakers, delegates, organization committee, JECC management, Hotel Marriot, Event management, travel management and staff.

The next edition CORCON 2019 will be held during September 22 - 25, 2019, at Kochi, Kerala, popularly known as "God's Own Country".

Burner Tip Failure in a Reformer of a Petrochemical Plant

Dr. Bhupendra Gaur,
Shruti Corrosion Engineering & Management Consultant, Navi Mumbai

ABSTRACT

Paper deals with case study of burner-tip damage at a syngas reformer of a petrochemical plant. A number of burner-tips suffered from premature failure within a short period of about one year from the date of service installation. The construction material of burner tips was a nickel-based alloy namely 'alloy 800' (UNS N08800). In order to explore the root cause of trouble, a few of the affected tips were dismantled from their burner assembly, followed by close inspection and detailed investigation on a severely damaged tip in a well-equipped metallurgical laboratory. The latter consisted of advanced tools and techniques such as optical microscope, scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDEX), X-ray diffraction (XRD), optical emission spectrometer (OES), X-ray fluorescence (XRF), universal (mechanical) testing machine, chemical analysis by instrumental and wet-chemical methods, etc. The study involved unaided and magnified view of affected tip and damage morphology, characterization and analysis of surface and sub - surface metal and products (or deposits), mechanical properties, etc. Subsequently, all factors suspected to lead material degradation, corrosion, scale deposition, coke formation (inside the burner tip), etc., were reviewed and scrutinized. As a result of investigation, oxidation, carburization, carbide precipitation, coking / carbonaceous deposition, etc., were identified as the principal mechanisms of initiation or propagation of the damages, at the burner tip. It is concluded that failure had taken place in the form of "stress rupture cracking" and "bulging". Finally, recommendations have been given to minimize the recurrence of damages (in future) including material upgradation, fuel quality, operating condition, burner tip design, etc.

Keywords: Burner Tip, Cracking, Coke deposition, Carburization, Oxidation, Bulging.

INTRODUCTION

In a petroleum or petrochemical plant, steam reformer (or steam reforming furnace) is used to convert hydrocarbon feed stocks such as natural gas, LNG, LPG, naphtha into hydrogen or hydrogen with carbon monoxide (or syngas). The feed is first desulfurized in upstream units and then mixed with steam followed by charging into the reformer. In a reformer, the feed is passed through a metallic (such as nickel) catalyst at a high temperature (about 800 -900 °C) and pressure (say 20 - 25 bar), resulting in syngas formation at the discharge end. The produced gas is then used for subsequent refinery or petrochemical operations (hydrotreating, hydrocracking, ammonia or methanol generation, etc.).

Reformer in present case included a top fired rectangular box with a number of vertical catalyst tubes (about 4" inner dia. and 30m length). It consisted of about 200 downward facing burners, distributed uniformly (throughout its roof) and installed at the centre of four tubes, thus avoiding flame impingement (localized over heating) at the tube's surface. In a burner, mixture of fuel and air is supplied and ignited, resulting in a controlled flame at the burner tip. It may be fired with a conventional fuel (gas, liquid or solid), gaseous or liquid waste, or any combination of combustibles, etc. Presently, burner fuel was natural gas with occasional use of other fuels (e.g., partial use of tail gas). In view of high temperature acquaintance, burner tips (also called burner head) are generally made of heat resistant stainless steels or nickel based alloys. In present case, used material of construction (MOC) for burner tip was nickel alloy 800 (UNS N08800), which has good resistance to oxidation, carburization, corrosion, creep, etc. at elevated temperatures (say up to 800 °C).

In the reformer under concern, the tip of a few burners suffered from pre-matured failure (within a year of installation into the service), through cracking and bulging at their outer peripheries. Too early failure of burner tips, made of a nickel based alloy (UNS N08800) which was considered adequate for the intended service application, necessitated detailed exploration for the root cause of trouble and the remedial measures. Accordingly, detailed investigation was undertaken on a severely damaged burner tip. During study, numerous aspects were reviewed and analysed that could have an impact on burner tip integrity, e.g., material, process and operating conditions, design, etc.

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For nearly three decades, Raychem RPG has been internationally recognized for designing and providing effective cathodic protection systems. Our team shares a high level of expertise about cathodic protection systems. We can offer superior technical support and assistance from the design stage through manufacturing and installation of CP system.

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TESTING AND EXAMINATION

During a plant shutdown, affected burners were removed from the service and dismantled. Burner tips were then visually inspected to identify the type of distortion, extent of damage, surface appearance and nature of scale, inside deposits, etc., as a preliminary examination. A severely affected burner tip was subjected to detailed investigation involving normal and magnified visualization; analysis and characterization of surface/sub-surface material, film, structure and corrosion products; defects, damage morphology and deposits; chemical and mechanical properties of MOC, etc., using a well-equipped metallurgical laboratory. The latter consisted of the advanced tools and techniques along with conventional test facility, such as optical microscope, scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDEX), X-ray diffraction (XRD), optical emission spectrometer (OES), X-ray fluorescence (XRF), universal testing machine (for mechanical properties), hardness tester, instrumental and wet-chemical analysis, etc. On the other hand, process, operational and design aspects, e.g., fuel gas constituents, operating parameters/ flow-pattern, design configuration, etc. were reviewed as these could also influence the performance/ integrity of material, corrosion and scaling, internal deposition, etc. Moreover, metallurgy of burner tip was revisited for assessing its continuance or need of an upgrade, to get rid of the problem in future.

RESULTS, ANALYSIS AND DISCUSSION

During visual inspection of the burner tips, following were mainly observed:

- No visible damage in the inner (central) zone of the burner tip, though some tight (moderately adherent) scale formation took place . (Fig. 1)
- Cracking took place at the peripheral edges, mainly. (Fig. 2)
- Significant scale (oxides) formation occurred at the entire surface. (Fig. 3)
- Appreciable bulging has taken place at the peripheral zone . (Fig.3)
- Some dark grey/ blackish powder deposited inside of the burner tip

The forthcoming sections will deal with the assessment and review of various aspects those could perhaps contribute to the present case of burner tip failure.

Chemical analysis of burner tip material, made with the help of inductively coupled plasma spectroscopy (ICP), confirmed it to be in compliance with the design(i.e., nickel alloy 800). Mechanical properties (tested on an undamaged section) were also found to be within the nominal range of alloy specification. Hence, there was no any role of material quality or metallurgical condition to result in the current burner tip failure.

SEM photographs of the burner tip surface indicated excessive oxide/scale formation, particularly in the peripheral or ruptured zone (Fig.4). Due to heavy layer of oxide/ scale, dominant mode of fracture (such as brittle or ductile) as well as grain orientation could not be distinguished. However, cracking is suspected to a brittle fracture because of the natural characteristic of the oxides which prevailed at the damaged surface [4-6].

Cross sectional micro structure, of the damaged tip part, also showed a heavy layer of oxide (corrosion product) and scale at the top side surface (Fig. 5a, 5b and Fig. 6a). Localized thinning (irregular outer surface) of the base material, caused by metal deterioration at the external surface of the burner tip, could be attributed to the occurrence of high temperature corrosion (oxidation) as shown in Fig.5. [7-8].The EDAX analysis of oxide/ scale, at the upper surface of burner tip, indicated the presence of non-metallic species also (e.g., sulphur, calcium, silica, etc.), along with the metallic oxides (oxidation product of alloy constituents). The surface layer; however, is dominated by metallic oxides those preferentially form in presence of ample oxygen (available in combustion air) as well as oxidation of primarily formed carbides, at high temperatures. Source of non-metallic species deposits, at the burner tip surfaces, might be the presence of sulphur (up to 100 ppm) in the fuel gas and traces of refractory dust (carrying calcium, silicon, etc.) inside the reformer.

Beneath oxide or scale layer discussed above, cross sectional micro structure (of damaged part of the burner tip) of base metal indicated oxidation-carburization followed by heavy carburization (from middle to innermost surface). To check elemental distribution (metallurgy) herein, energy dispersive X-ray (EDX) analysis was carried out. Chemical analysis of base material indicated

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In alloy 800 also, intermetallic phases (dominated by chromium carbide) precipitate in temperature range of about 540-760 °C (called sensitization range) similar to other austenitic stainless steels, thus it can be become susceptible to intergranular corrosion when exposed to certain environments(3,9-10) Sensitization susceptibility of nickel alloy 800 may exist due to appreciable presence of carbon (about 0.1%) as its alloying constituent, though certain proprietary products manage it by addition of stabilizer (such as titanium) but it was found in presently used MOC. Further, intermetallic phases (carbides), formed in sensitized material (discussed earlier) may also undergo oxidation (in sufficient presence of oxygen in combustion air as well as high temperature at tip), in due course(11). This may be cause of observed presence of carburization - oxidation phase in affected material as shown in Fig. 5a.

As mentioned earlier, metallic matrix of the damaged material is found with carburization (in an increasing order from upper to lower thickness of the burner plate), as shown in Fig.7. This section will throw some light on the probable cause of heavy carburization of the burner tip material, which particularly dominated at its fluid side thickness. In context of reformer under subject, fuel gas and combustion air are jointly discharged (and ignited) at the burner tip with a downward flame of high temperature (say about 1500 °C), causing heating up of the reformer tubes to about 900 °C. The fuel gas consisted of mainly methane and ethane gas (say about 93% methane and 6% ethane) with about 100 ppm sulphur, while, combustion air contained about 20% oxygen and 74% nitrogen. It is an established fact that burner tip material is susceptible to heavy carburization in presence of active carbon (at high temperature) [7-8]. The latter can form during low (or no) firing rate of burners (due to an operational excursion) while reformer is under normal operation[12]. The overheating of burner tip can cause the carbon in the fuel to thermally crack, giving rise to coking inside the tip with adverse consequences on burner's performance and tip integrity (plugging of holes, carburization and other degradations of metal at high temperature, etc.). However, in case of normal firing, cool fuel gas discharged at the burner tip doesn't permit overheating of the burners.

The effect of gas flow rate on coke formation is also reported elsewhere [13]. Occurrence of coking, in current case, is partly supported by some deposition of a carbonaceous material inside the burner tips, which was latter on confirmed (through chemical analysis) to be coke. Thus, some role of coking in present case of burner tip failure should be considered. Based on above discussion and literature information, it is emphasized that effort should be made to minimize coking inside the tip, with proper control of fuel quality (process) and operating conditions (temperature, pressure, flow rate, etc.).

In addition, some nitride inclusions were also detected in the severely carburized metal matrix of the affected burner tip(Fig.7a.), which are also intermetallic compound and may contribute to embrittlement of the metallic matrix (MOC) because of their high hardness. Now possible source of nitride formation will be reviewed. Generally, the diffusion of carbon from outside carburizing atmosphere forces migration of nitrogen in metallic lattice towards metallic surface.

However, in present case, presence of nitrides in metallic matrix indicates inward diffusion of both carbon and nitrogen. This could be due to a significance presence of nitrogen in the combustion air (about 74%). Such cases have been reported in literature (11). Nitride formation in material matrix should be carefully attended, in consultation with a burner manufacturer. For this, a design modification such as number, size and angle of holes, etc., may be required to minimize NOx emissions.

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CONCLUSIONS AND RECOMMENDATIONS

Based on above analyses and discussions, damage mechanisms and role of different factors to result in burner tip failure along with suitable remedial measures, are summarized below:

Different metallurgical degradation processes {e.g., metal carburization, metal oxidation, intermetallic (carbides) precipitation, carbide's oxidation, etc.} have collectively attributed to create voluminous change in the metal matrix, causing high metal loss, internal stresses, metal-embrittlement, etc., in the construction material. Because of high internal stresses and material embrittlement, burner tip underwent appreciable bulging (deformation) as well as cracking, leading its failure via "stress-rupture cracking" mode.

Out of different factors, process ingredients and excursions in operating conditions, could have played a leading role in creating unfavourable circumstances which latter on initiated and propagated the different mechanisms of degradation, both at surface and structure of the material. High temperature corrosion (oxidation) environment and inside coke formation could be the culprits from this side.

To some extent, metallurgy of construction material could also have contributed to the current failure, because of limited resistance of nickel alloy 800 to conquer the actually prevailing service conditions(more aggressive than anticipated).

There is little possibility (which can't be completely ruled out) of the effect of burner tip design configuration, as it may also affect coke deposition inside the burner tip as well as NOx emissions.

In current scenario (severe service conditions), it is advisable to consider replacement of the existing MOC (nickel alloy 800) with a superior one which has better resistance to corrosion (oxidation), carburization, creep, sensitization, etc. Inconel 600 is one of the most common candidate materials for high temperature applications, inside furnaces. However, Inconel 601 may be a better alternate due to lower carbon, more chromium and addition of aluminium, and therefore, overall superior corrosion and metallurgical properties with formation of strong protective film at high temperature (when exposed to burner environment).

Design review of burner tip configuration (number, size and angle of ports) should be conducted, to minimize the possibility of coke formation (inside the tip) and NOx emissions. Alternately, burners with different design can be tested in real service conditions, having same material of construction.

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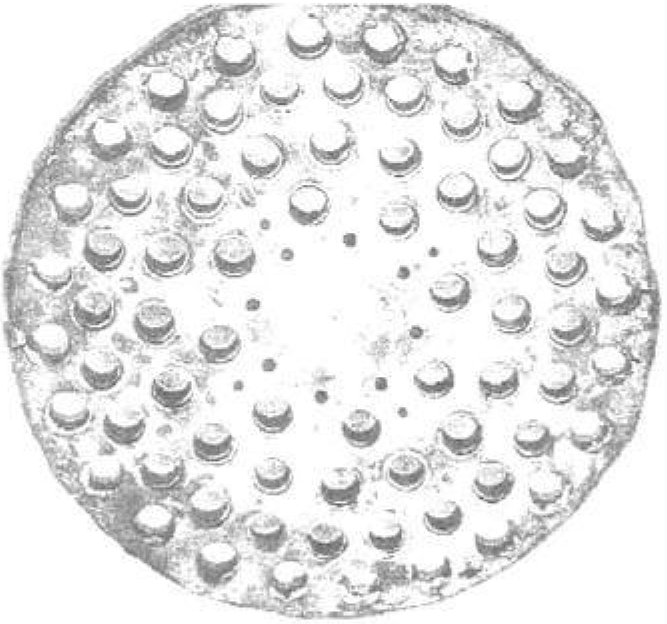

Figure 1 Reformer burner tip

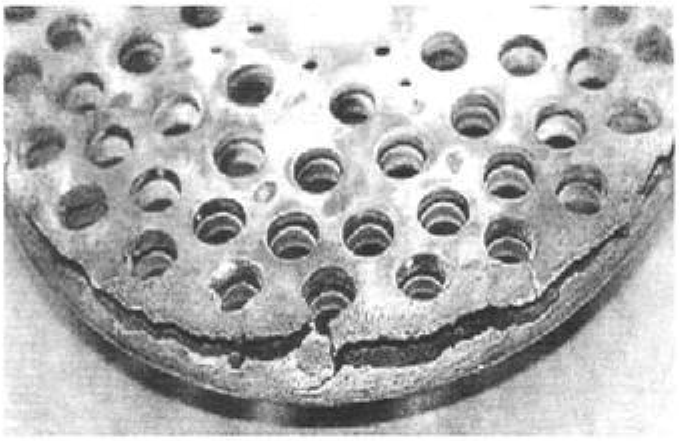

Figure 2 Close up view of failed section of burner tip

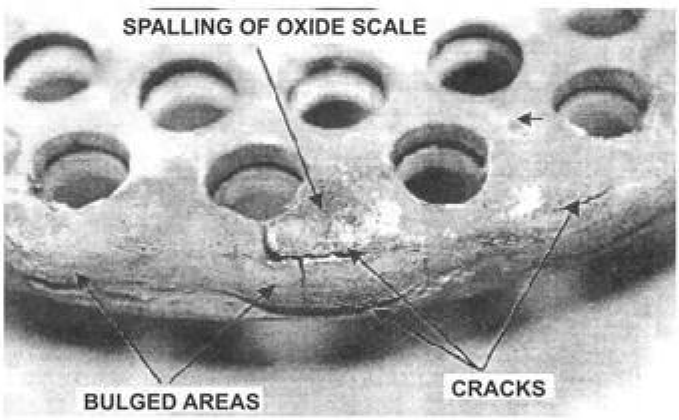

Figure 3 Close up view of burner tip identifying spalling of oxide scale, bulging and rupture

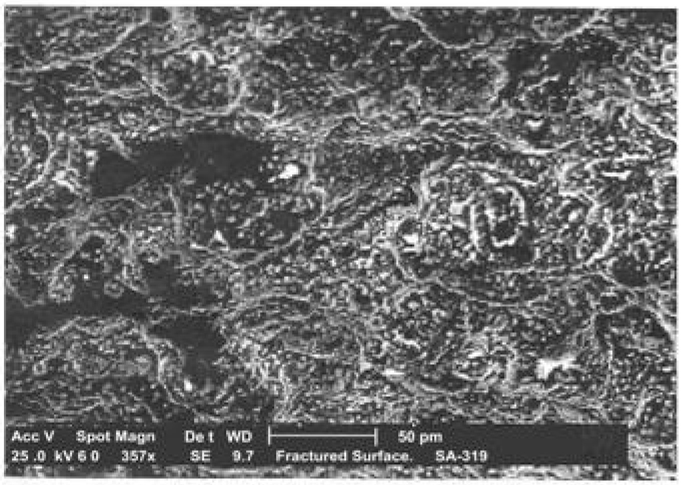

Figure 4 SEM photograph of the fractured surface

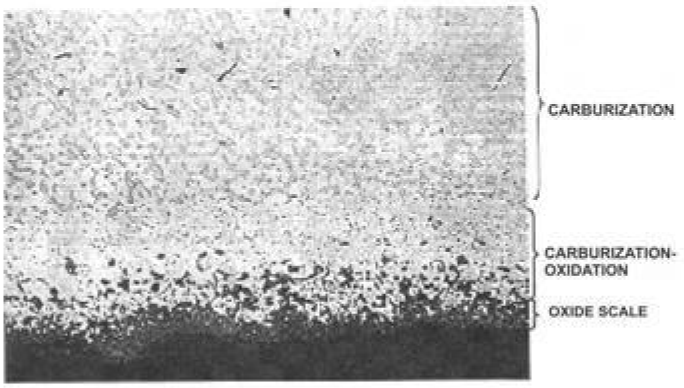

Figure.5. Optical microphotograph of the cross section of failed burner tip. (a) oxidation oxidation-carburization and carburization matrix (b) uneven outer surface after metal loss, x200

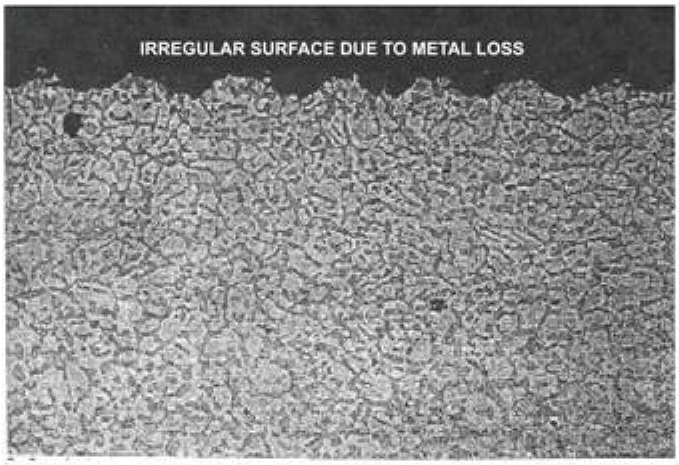

Fig. 6 Irregular Surface Due To Metal Loss

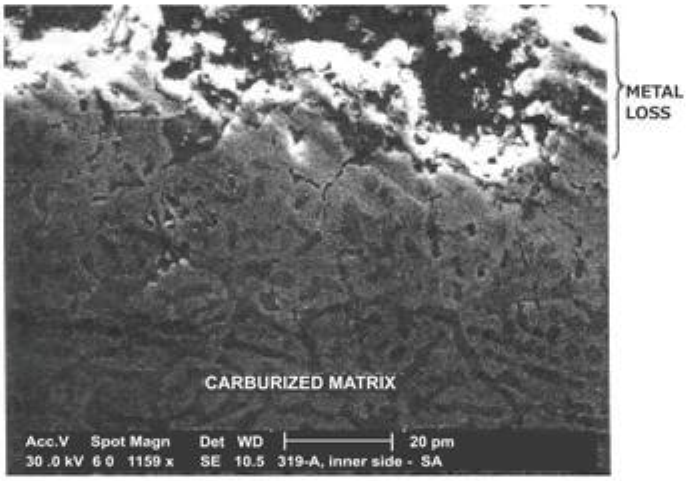

Figure 6a SEM photograph of failed burner tip

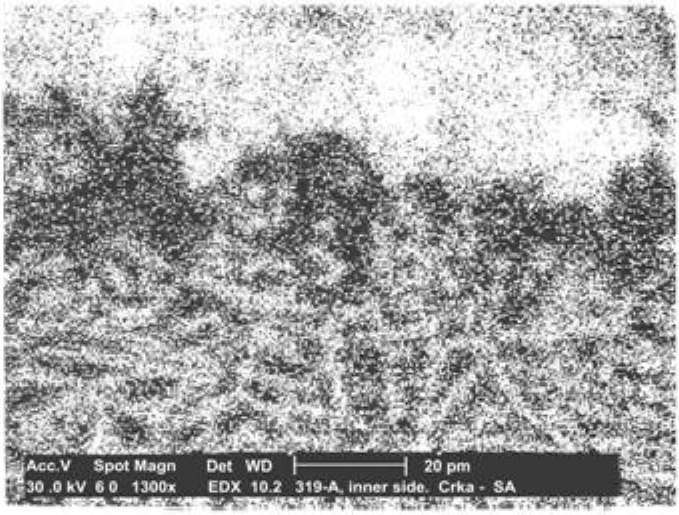

Figure 6b EDX picture depicting elemental distribution of chromium in cross section of the failed tip. Note chromium depletion with in the grains

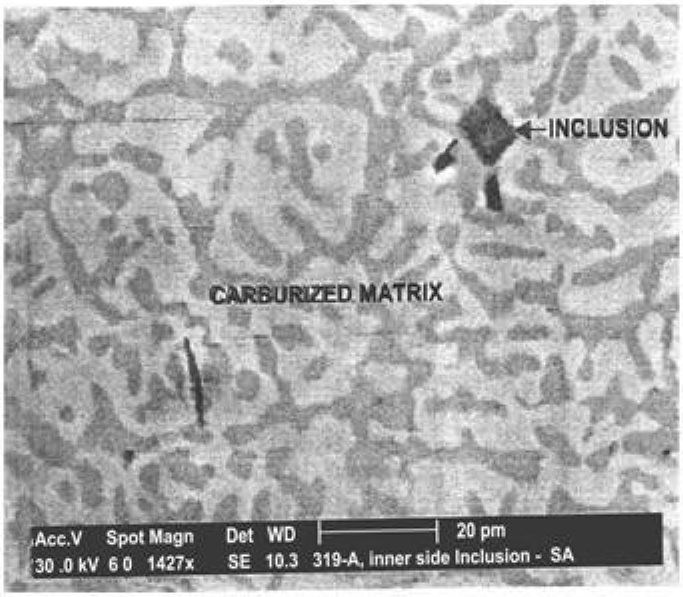

Figure 7 a SEM photograph of the cross section of the failed material of burner tip. Note the carburization of entire matrix and nitride inclusions

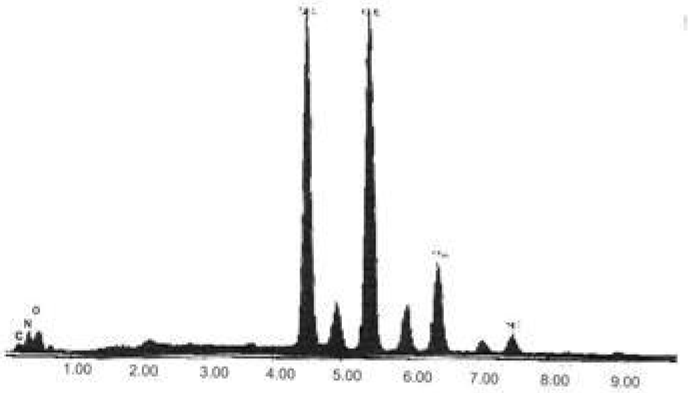

Figure 7b EDX mapping (line profile) showing elemental distribution in the inclusions.

Corrosion Basics : Coating Concrete *

There are some physical and chemical properties of concrete that have a direct bearing on coatings. Concrete performs best when under compression, and it has a relatively high compressive strength, i.e. 2000 to 6000 psi. In this state, it resists cracking and checking, and the surface does not appreciably change, even with time. This makes a good, constant surface over which to apply coatings. Unfortunately, the opposite property tensile strength is low, so that concrete in tension can crack, making the surface difficult to protect. Cracks can occur as a result of foundation setting, earth movement (as in the case of concrete pipe), the vibration of machinery, and other reasons. Whenever concrete changes from a state of compression to one of tension, cracks appear. Concrete is also brittle, which adds to the cracking problem and often causes spalling.

One of the ways in which cracking is reduced is to prestress concrete or place it in permanent compression. Many concrete tanks, both above and below ground, are of a prestress design, which means that the reinforcing is in sufficient tension to maintain the concrete under compression. Cracking, however, is not completely eliminated, as some prestressed cylindrical tanks that are wound with high tensile wire may develop a few cracks parallel to the reinforcing wire. Much concrete pressure pipe is also made using a prestress design. Each of these physical conditions can create coating problems where concrete is used under corrosive conditions.

Concrete is porous, and it also contains a permanent amount of free moisture that can evaporate or be absorbed, depending on the humidity to which the concrete is exposed. Concrete is saturated when immersed in water, while the moisture content goes down when exposed to low humidity and increases rapidly when the humidity rises above 80%. Concrete can be formed in such a way that it will not transmit liquid water; on the other hand, concrete is not impervious to moisture vapour or moisture vapour transfer, as indicated by its change in moisture content resulting from humidity.

The fact that water, in the form of vapour, can readily pass through the concrete structure is extremely important to a coating that is applied. For example, in a coated concrete vault that is kept at a constant humidity of 50%, if there is no waterproofing on the exterior and the earth around the vault is damp, there is a constant positive vapour pressure on the concrete side of the coating. Unless the coating has excellent adhesion, blistering and coating failure will occur. This is not an isolated example. Subterranean structures, basements, subways, and electrical vaults all have problem of this sort. The cause is the vapour pressure going through the concrete and constantly pushing on the back of the coating. This may be the most important problem encountered in obtaining a proper coating over a concrete surface.

It is difficult to apply a coating on the interior of a concrete surface, when the exterior is subject to moisture conditions, and to maintain the interior of the structure free of moisture. During World War II, there were literally hundreds of large underground tanks built to contain petroleum products. Most were of a prestressed design to reduce cracking; however, most did not have any exterior water barrier. They were coated on the interior with a petroleum resistant coating, and many coating blistering problems as well as actual leaks developed. Wherever coatings are to be applied to underground concrete structures, there should be an exterior waterproofing membrane applied.

The alkalinity of concrete also comes into play under such conditions in which the moisture is being transferred from the exterior of a structure to the interior. The alkaline salts within the cement can be brought to the concrete surface where calcium oxide then reacts with carbon dioxide in the air to form rather voluminous white crystalline deposits. In many cases in which somewhat porous coatings are applied, these are actually pushed off to the surface by the formation of the calcium salts which are brought to the cement surface from the interior of the wall. Any time that moisture conditions such as these exist, it is very difficult, without the very penetration and adhesion, to obtain coatings that will satisfactorily adhere to concrete over long periods of time.

* Taken from C.G. Munger, Corrosion Prevention by Protective Coatings, NACE

A Report - NIGIS Foundation Day 2018

The NACE International Gateway India Section (NIGIS) marking its **'Foundation Day'** was held on 18th July 2018 at Hotel Meluha, Powai, Mumbai.

The program stated by Mr. Sumeet Kataria, NIGIS-member executive committee welcoming invitees and participants to the Foundation Day.

Dr. U Kamachi Mudali, Vice-chairman, NIGIS marked the commencement of the annual foundation day, by welcoming all the members, eminent personalities of the industry and academia present, during the opening address of the evening which was largely applauded.

Mr. Dipen Jhaveri, Secretary, NIGIS presented a holistic report of the India Section for the period 2017-2018, which was well received.

On the momentous 26th foundation day Mr. Anand Kulkarni, India Section Trustee welcomed to past Trustees for their untiring and selfless services to the India Section of Mr. V G Kulkarni, Mr. O P Degan, Mr. Tushar Jhaveri and Dr. Samir Degan.

The NIGIS and CORCON 2018 Chairman Mr. N Manohar Rao provided a holistic view of the oncoming CORCON 2018 conference and what the conference and the expo is to offer. The Chairman also felicitated the outstanding personalities who made their mark in the industry and academia by the significant difference in the area of corrosion. Mr. Vivek Natu past Treasurer for the 2016-17 and 2017-18 was honored with a memento for his reliable services as a Treasurer of the India Section. Dr. Rani George, Prof. V S Raja and Mr. Ajay Krishnan was honored with a memento. The Chairman appreciated Osnar Paints and Contracts Pvt Ltd, Jotun India Pvt Ltd, Berger Paints India Ltd, Jimco Exim and Trade Pvt Ltd for their support NACE certifications programs.

The Chief Guest for the event Mr. Tushar Jhaveri, Past President, NACE International, addressed the invitees sharing his perspective of NACE India Section of the past, the times ahead and the overall evolving India Section over the years.

The occasion was completed with vote of thanks by Treasurer Dr. Narendra Kumar. The event was followed by gala Dinner through the rest of the evening.

Dipen Jhaveri, Secretary, NIGIS briefing the members and guests.

NIGIS SGB, EC Committee and staff members

N Manohar Rao felicitating Dr. Rani P. George for being NACE Fellow 2018

Member and dignitaries during the foundation day

A Report - NACE International Certification Courses

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NIGIS organized CIP 1, CIP 2, CIP Peer Review, PCS 2 Advanced, CP 1, CP 2, CP 3, Direct Assessment certification course during the year of 2018 in India.

CIP Level 1 covers the technical and practical fundamentals of coating inspection work. Students will be prepared to perform basic coating inspections using non-destructive techniques and instrumentation. This course provides students with knowledge and application of coating materials, along with techniques for surface preparation.

CIP Level 2 focuses on advanced inspection techniques and specialized application methods for both steel and non-steel substrates, including concrete using both nondestructive and destructive techniques. Surface preparation, coating types, inspection criteria, lab testing, and failure modes for various coatings, including specialized coatings and linings are also covered. Students will also participate in case studies based on real-life situations and practices of a coatings inspector.

CIP Peer Review is the Coating Inspector Level 3 oral exam is designed to assess whether a candidate has the requisite knowledge and skills that a minimally qualified Level 3 Coating Inspector must possess. The CIP Level 3 Peer Review is an intensive, detailed oral examination that is given in front of a three-member review board and is based on the Coating Inspector body of knowledge. A candidate should have "expert knowledge" of all corrosion, surface preparation, cleanliness, environmental conditions, test instruments, coating mixtures, and safety. They should also be able to perform unsupervised non-destructive inspections of liquid and non-liquid coatings to any substrate and demonstrate technical knowledge, problem solving ability regarding issues that may arise on site and is capable of supervising basic (CIP level 1) and intermediate (CIP level 2) coating inspectors.

The **PCS 2 Advanced** course provides advanced level technology topics related to protective coatings. Highlights include an in-depth discussion of coatings, their basic chemical properties, and any unique considerations for their surface preparation, application and inspection. Testing coating properties and performance, common coating defects, substrates, selecting coating systems, the specification, and surveys and maintenance planning are also covered.

The **CP 1 - Cathodic Protection Tester** course provides both theoretical knowledge and practical techniques for testing and evaluating data to determine the effectiveness of both galvanic and impressed current CP systems and to gather design data.

The **CP 2 - Cathodic Protection Technician** course provides intermediate-level training in both theoretical knowledge and practical techniques for testing and evaluating data to determine the effectiveness of both galvanic and impressed current CP systems and to gather design data.

The **CP 3 - Cathodic Protection Technologist** Course builds on the technology presented in the CP2 course with a strong focus on interpretation of CP Data, trouble shooting and migration of problems that arise in both galvanic and impressed current systems, including design calculations for these systems.

The **Direct Assessment** course concentrates on internal, external, and stress corrosion cracking direct assessment, along with pre- and post-assessment, quality assurance, data analysis and integration, and remediation and mitigation activities. The course will also cover the benefits and limitations of Direct Assessment, its relationship to an overall integrity assessment program and industry standards, regulations, and best practices.

Photographs of Certification Courses

Direct Assessment participants
during 19 - 23 March 2018

CIP Level 1 participants
during 14 - 19 May 2018

CP 2 participants during
29 May - 02 June 2018

CIP Level 1 participants
during 25 - 30 June 2018

CIP Level 2 participants during
02 - 07 July 2018

CIP Level 1 participants during
26 Nov - 1 Dec 2018

Study of sour gas resistance and hydrogen embrittlement susceptibility of Cu-Mo and Cr bearing commercial grades of API X65 steel

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Steel Authority of India Limited, Ranchi - India

INTRODUCTION

High strength line pipe steels used for transporting crude oil or natural gas, containing hydrogen sulfide, are required to posses "sour-resistance" comprises hydrogen induced cracking (HIC) resistance and resistance to stress corrosion crack (SCC) resistance, in addition to adding to strength, toughness, and weldability [1-2]. The phenomenon of hydrogen-induced cracking (HIC) of steel is based on a process in which hydrogen ions generated by corrosion reaction are adsorbed on the surface of steel, penetrate into steel as atomic hydrogen, and diffuse and accumulate around non-metallic inclusions such as manganese sulohide (MnS) and hard second phase of steel, thus triggering crack initiation by an increase in internal pressure. Hence, research has been focused to control the morphology and distribution of MnS inclusions in steel and also to reduce to sulphur (S) level <0.002 wt% in steel. Reducing S to <0.002 wt% in industrial level is very difficult task for steel makers [2]. Diffusion of hydrogen occurs through autocatalytic regeneration of hydrogen ions from the adsorption film formed on the steel when exposed to sour gas environment [3-4]. Altering the film will be viable route to control HIC. Therefore the present work was focused to evolve an alloying addition, which can change the film characteristics and resist for HIC and SSC failure.

EXPERIMENTAL WORK

The microalloyed with varying Cr, Cu and Mo added API X65 hot rolled coils were collected from RSP, for comparison hot rolled Cu added API X70 hot rolled coil from BSL was also collected for studies. Their chemical composition is given in the Table-1. Microstructural and mechanical characterizations were carried out for all the steels. Electrochemical corrosion studies both polarization and EIS studies were performed in 7N H_2SO_4 + 1 g 1/l thiocarbamide solution equivalent to NACE solution (as per kovel et al. 1974) [10] and also in NACE solution (5% NaCl + 0.5% acetic acid, without purging of H_2S gas) HIC test was carried out for both hot rolled and pipe samples of API steel as per the NACE TM-0284 standard procedure in the NACE solution A and SSC studies were carried out as per NACE TM 0 177 Method A. In order to characterize the failure behavior the slow strain rate tensile test (SSRT) studies were carried out in stimulated NACE solution. Fractured samples were analyzed in SEM to relate the failure with micro structure and chemical composition of the material.

RESULTS AND DISCUSSION

Microstructural and mechanical characterizations were carried out for all the steels. The steels under investigation showed typical ferrite-pearlite microstructure with grain size around 9 to 11 µm (Fig. 1). Steel cleanliness were evaluated for its inclusions content and found within the range of specified level as per the API 5LX specification. The steel were also found to conform to API 5LX specification in terms of yield strength (Table 2). In order to investigate the corrosion behaviour of these steels in sour gas media, various studies were conducted.

HIC studies were conducted as per NACE TM0284 [5] and HIC parameters like, crack length ratio (CLR) and crack thickness ratio (CTR) and crack sensitivity ratio (CSR) were evaluated for all the steels. From the study it was observed that Cr added API X65 steel found to be within the acceptable level specified for sour gas application [(Class III material should have CSR ≤ 2 %, CLR ≤ 15 % and CTR ≤ 5% as per BS EN 10229] (Table 3). However Cu added both X65 and X70 steel of RSP and Bokaro showed a drastic improvement in HIC performance with CLR, CTR and CSR are within the limits of Class I specification required for sour gas application [Class I class material should have CSR ≤ 0.5%, CLR ≤ 5.0% and CTR ≤ 1.5% as per BS EN 10229]. HIC behaviour of Cr added and Cu added API X65 steel were evaluated after pipe making. The HIC parameters for Cr added API X65 steel pipe found to significantly higher than that of the class III level specified for sour gas application, Where as Cu added API X65 pipe qualifies class II specification acceptable for sour gas application.

Steels	C	Mn	S	P	Si	Al	Nb	V	Ti	Cu	Cr	Mo
API X65 – 45 (0.2% Cr added) steel	0.06	0.98	0.0035	0.009	0.41	0.058	0.06	0.05	0.014	---	0.26	---
API X65 – 47 (0.1% Cr-Cu-Mo added) steel	0.068	1.00	0.0038	0.01	0.41	0.06	0.057	0.05	0.013	0.1	0.1	0.1
API X65 – 48 (0.2% Cu-Mo added) steel	0.065	0.90	0.004	0.01	0.43	0.06	0.052	0.05	0.013	0.21	---	0.2
API X70 (0.2% Cr-Cu added) steel	0.10	1.33	0.004	0.014	0.24	0.031	0.045	0.044	0.011	0.23	0.26	---

Table 1 Chemical Composition of the collected API Steels

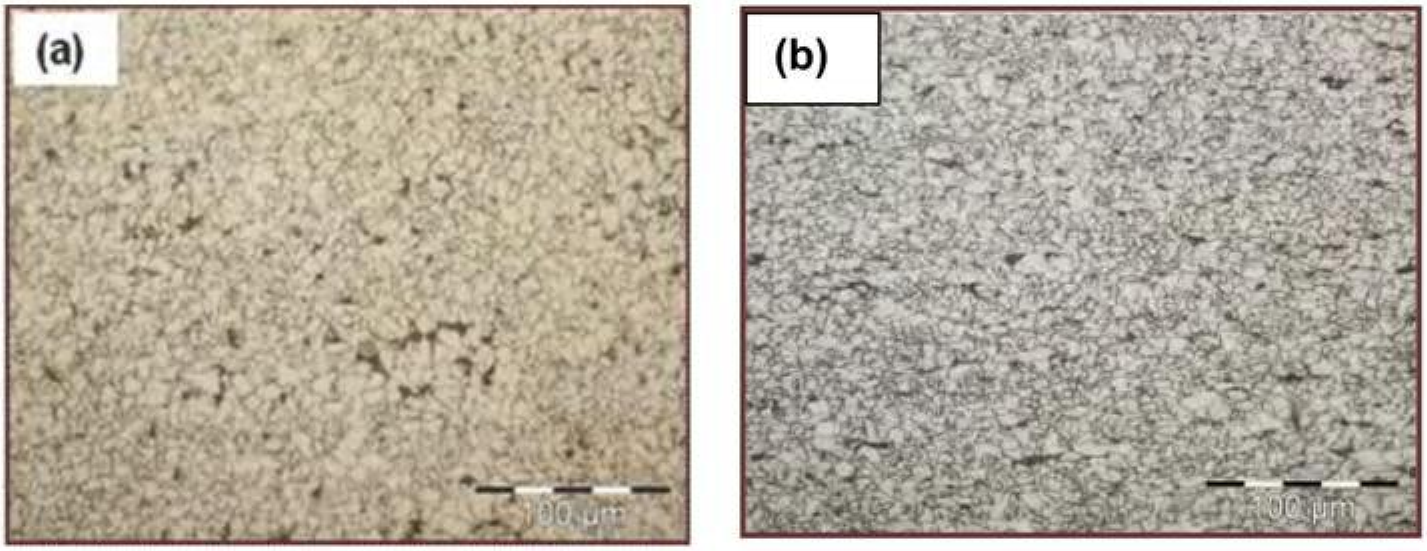

Figure 1 Typical Microstructure of the (a) Cr added API steel and (b) Cu added API steel

Steels	YS Mpa	UTS Mpa	% Elongation	YS/UTS	CIE, J	
					0° C	-20° C
API X65 – 45 (0.2% Cr added) steel	520	613	34.1	0.85	144	116
API X65 – 47 (0.1% Cr-Cu-Mo added) steel	524	620	36.6	0.85	150	118
API X65 – 48 (0.2% Cu-Mo added) steel	528	628	38.2	0.84	154	120
API X70 (0.2% Cr-Cu added) steel	530	630	35.4	0.84	243	---

Table 2 Mechanical Properties

	Hot rolled coils (%)				Pipe (%)		Acceptable limit for sour gas application [Type 1, Type 2 & Type 3 class] (%)
	API X65 – 45 (0.2% Cr added) steel	API X65 – 47 (0.1% Cr-Cu-Mo added) steel	API X65 – 48 (0.2% Cu-Mo added) steel	API X70 (0.2% Cr-Cu added) steel	0.2% Cr added API X65 steel	0.2% Cu-Mo added API X65 steel	
CSR	1.84	0.3	0.06	0.12	2.7	0.8	≤0.5, ≤ 1, ≤2
CTR	3.7	1.9	0.41	1.43	5.3	1.64	≤1.5, ≤ 3, ≤5
CLR	10.43	6.25	1.2	4.13	16.04	5.8	≤5.0, ≤ 10, ≤15

Table: 3 Hydrogen induced corrosion (HIC) studies as per NACE TM 0284

The SSC test were conducted as per NACE TM 0177 Method A [6] (Fig. 2), the threshold stress were evaluated to be 51% and 65% of the yield stress for Cr added API X65 and Cu added API X65 steel respectively. SSC for pipe samples were also evaluated and it was observed that Cr added pipe API X65 steel pipe showed poor in SSC resistance as that of the Cu added API X65 steel pipe. The SCC studies [7] (Fig. 3a) were also conducted to understand the qualitative nature of the failure. From the studies it was observed that addition Cu has increased the elongation and UTS value. Fracture surface observed under SEM showed that brittle kind of failure for Cr contacting API steel and mixed mode of failure for Cu containing API steel (Fig 3b and c).

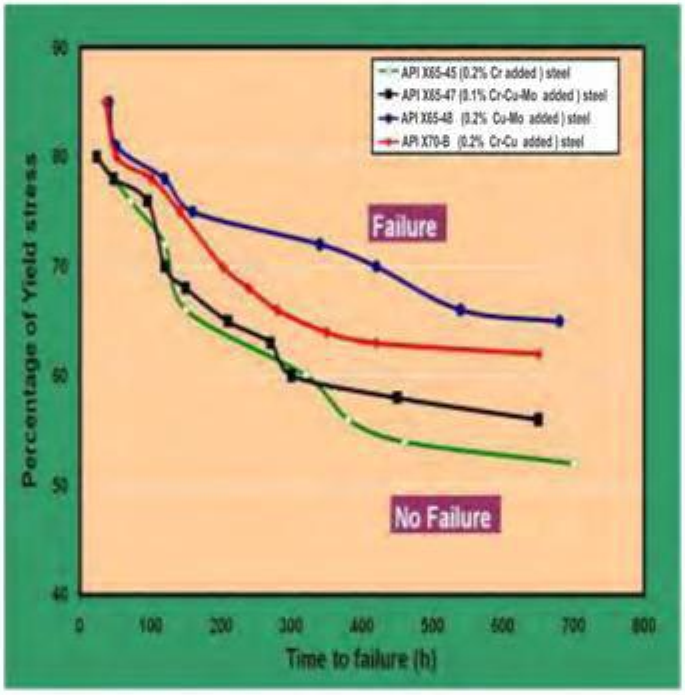

Figure 2 Sulphide stress corrosion cracking (SSC) studies of API steels as per NACE TM O177 Method A

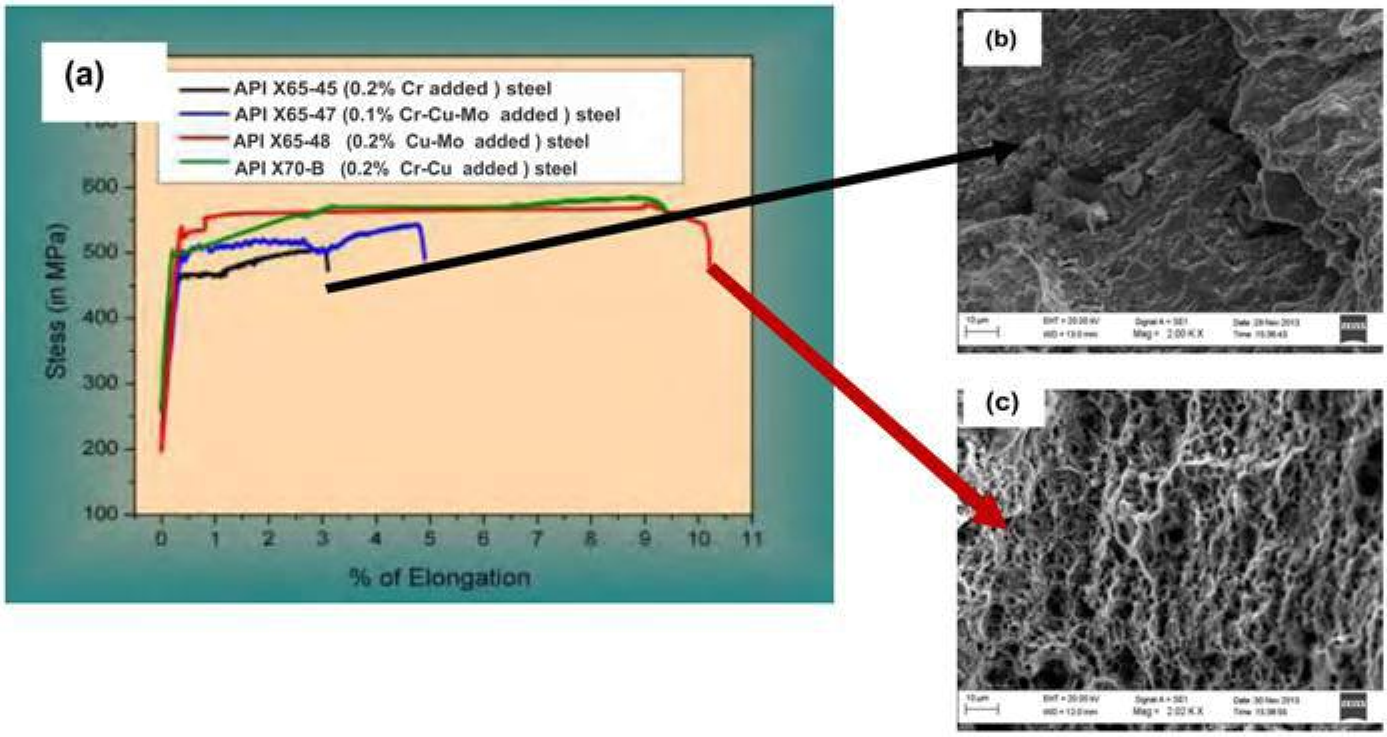

Figure 3 Stress corrosion cracking (SCC) studies (a) Graph showing cu addition has increased ductility of the material in sour gas environment (b) and (c) Fractographs of fractured surface of API steels in SEM showing Cu addition has changed the morphology of cracking from intergranular brittle failure to mixed mode (brittle for river like pattern and ductile for dimple) failure

To understand the mechanism electrochemical corrosion studies (polarisation and electrochemical impedance spectroscopy [EIS]) were conducted in two media namely, 7N H2SO4 + 1 g 1/l thiocarbamide [8] and NACE solution (without purging of H2S gas). Cu containing API steel showed a passive film characteristics) in NACE solution (without purging of H2S gas), where as, Cr containing API steel showed a anodic dissolution characteristics (Fig. 4a). This was confirmed by EIS (Fig. 4b), where Cr containing steel showed a negative loop in the Nyquist plot correspond to inductance behaviour or chemisorption film (FeHS-ads) [9]. The Cu containing API steel showed absence of negative loop which corresponds to absence of chemisorption film (FeHS-ads). Hence, it can be concluded that Cu alters the surface reaction (avoiding the formation of adsorption film) and restricts the hydrogen ingress into steel, thereby increasing the corrosion resistance, HIC and SSC performance.

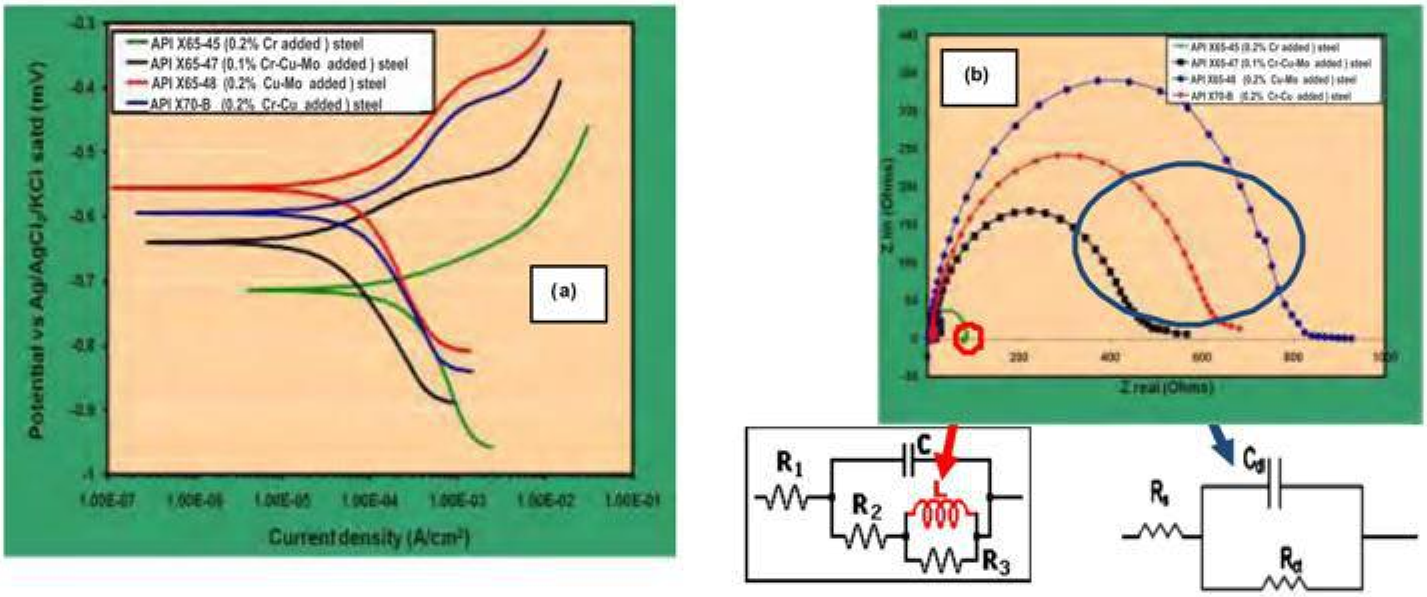

Figure 4 Electrochemical Corrosion studies plots of Cu-added API X 65 steels in sour gas environment (a) Polarization plots showing shift in corrosion potential towards noble potential and lowering corrosion current with addition of Cu (b) Electrochemical impedance spectra showing Cu addition has improved in impedance of the passive film and changed film characteristics

CONCLUSIONS

From Electrochemical corrosion studies it is was found that the Cr added API X65 steel, the effect of H_2S on the anodic reaction was likely caused by H_2S chemisorbtion on the metal surface. Cr added API X65 steel show poor resistant to Hydrogen induced cracking (HIC) and Sulphide stress corrosion cracking (SSC). The addition of Cu to API X65 steel has improved the corrosion resistant of the steel by alters the surface film and restricts the hydrogen diffusion. Also the Cu has improved the HIC resistance with CSR = 0.06%, CTR = 0.41, CLR = 1.2% and also SSC performance of the API steel because of low diffusion of hydrogen.

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Dr. P. Saravanan is a renowned Corrosion Scientist having 12 years experience in the steel industry. He has created corrosion facility at RDCIS for undertaking corrosion studies under sour gas environment as per NACE testing procedure. This includes Hydrogen Induced cracking (HIC) and Sulphide Stress Corrosion cracking (SSC) tests in accordance with NACE standards. Dr. Saravanan is instrumental in the development of HIC free API steel even with higher sulphur content (0.01 wt%). He has also developed a number of other products, like next generation high nitrogen steel (HNS) with improved corrosion resistance for structural applications, Lean Duplex Stainless Steel, environmental friendly passivator for zinc coated sheet as well as development of process technology for manufacture of 301LN grade with higher UTS (> 1000 MPa) and YS/UTS ratio < 0.80 for metro coaches. Also developed low cost stainless steel for elevator application, Fuel cell application and developed an unbelievable combination of high strength (>1GPa) and ductility (66%) of duplex stainless steel. He is recipient of Distinction in Corrosion Science & Technology in Industrial Organization - NACE International Gateway India section for the year 2014. He is also recipient of Meritorious Award for the year by National Corrosion Council of India, (NCCI), for the year 2018 and also has 10 more national awards to his credit.

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A Report - NIGIS Participation in various Corrosion Events

NACE International Gateway India Section (NIGIS) had participated various technical conference to exchange knowledge and connect with the entire corrosion-fighting continuum: scientists, researchers, engineers, technicians, contractors, students, business executives and organisation having latest technology and corrosion solutions. Some of the industry's top leaders and organisation also participated in these corrosion prevention conferences.

Surface Coating Expo -2018" was held from 31 Aug – 2 Sept 2018 at CTC, Chennai, Tamil Nadu. The Exhibition and Conference on Surface Engineering, Preparation, Coating, Finishing, Corrosion Protection, Environment & Technologies.

19th NCCI organised national conference on corrosion was held during 05-07 December at Bhubaneswar. The aim of the conference Analyze various industrial corrosion problems and provide a platform for interaction between industrialists, scientists and professionals to enhance the state of art knowledge on "Corrosion Science and Engineering"

CII – SIDM in Association with INS Vishwakarma, Indian Navy had organized a Symposium and Exhibition, titled "Symposium on Corrosion Management" on 6th & 7th December 2018 at INS Vishwakarma, Visakhapatnam. The discussion point was corrosion issue of warships and submarines and difficult access for maintenance.

RIL had organised 8th conference on "Safety and Integrity of Onshore & Offshore Petroleum Pipelines " during 13 - 14 Dec 2018 at Reliance Corporate Park, Navi Mumbai. The theme of the forum- "Harnessing new technology for managing pipeline integrity."

The participants showed their interest in to participate in CORCON conference, courses and NACE membership. The efforts of NIGIS in spreading corrosion awareness: A safer world, protected from the effects of corrosion.

NIGIS Section Vice Chairman Dr. U Kamachi Mudali visited NIGIS stall in SCE-2018.

Shri Dharmendra Pradhan, Hon'ble Minister of Petroleum and Natural Gas; Minister of Skill Development and Entrepreneurship during his visit to NIGIS stall in 19 NCCI conference

Indian Navy's officers & NIGIS participants in INS Viskhwakarma

Participants of R-Pipeline Integrity Forum-2018

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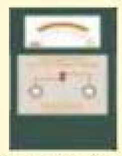
 Automatic Pull Off Athesion Tester	 Rebar Locator	 Concrete Moisture Meter

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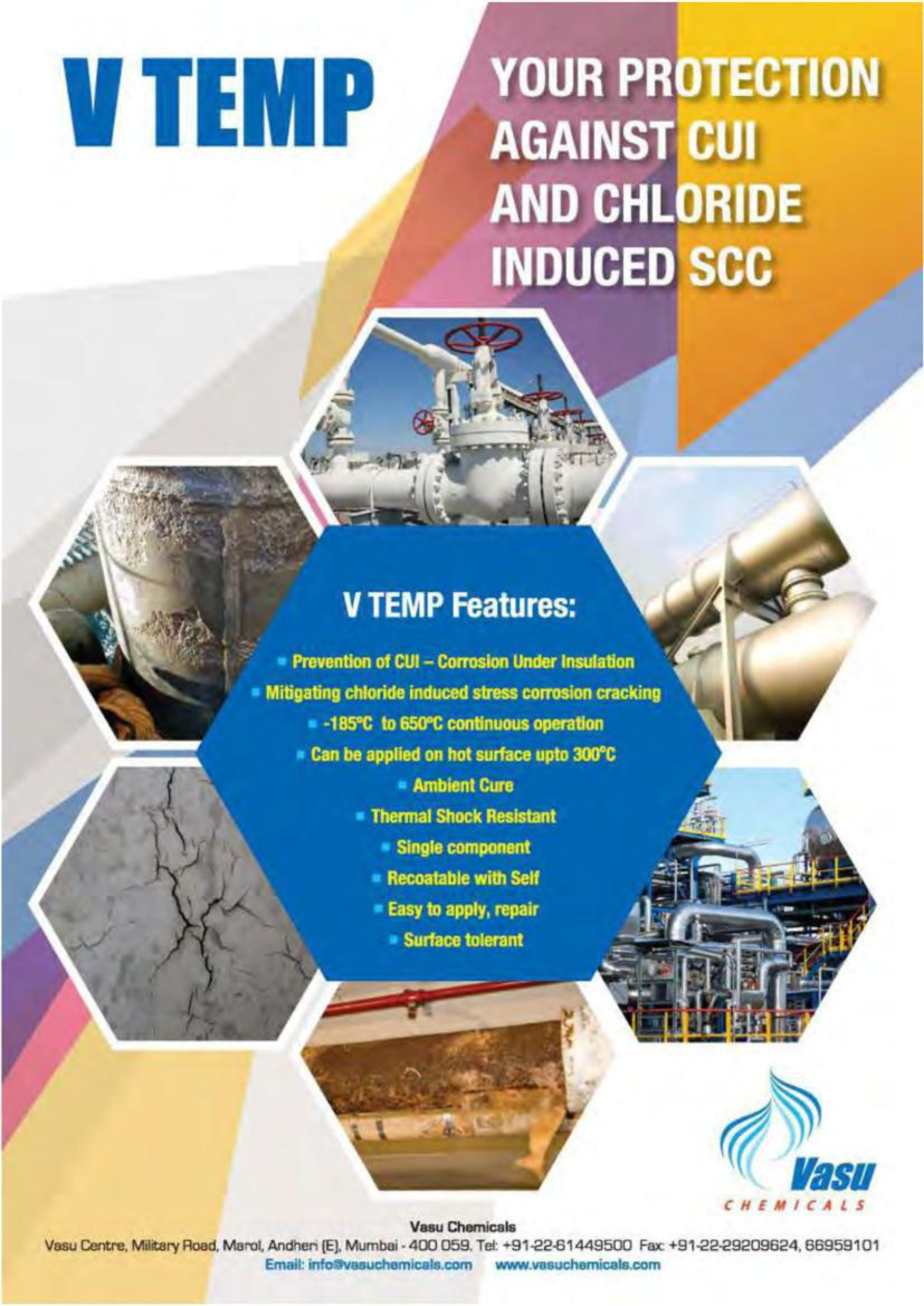
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