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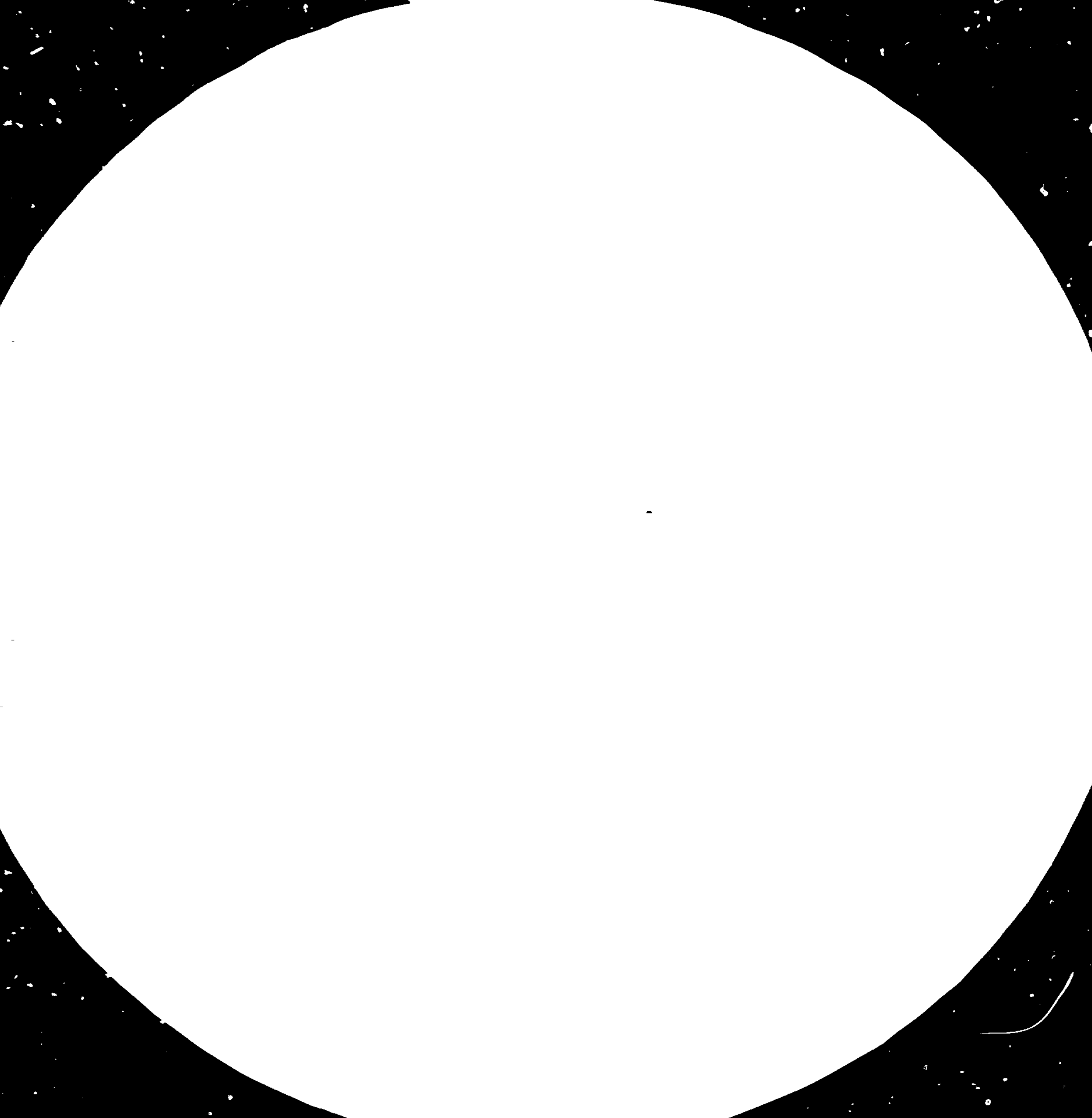

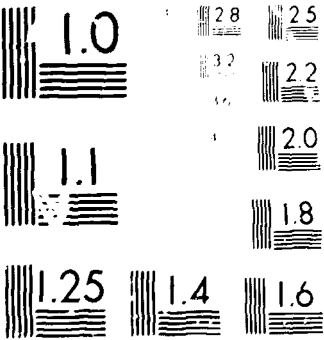

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CORROSION PROBLEMS IN AN AMMONIA PLANT *
(CASE HISTORIES)

by

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Corrosion failures occur in a chemical plant due to several causes. Some case histories on the various types of corrosion failures experienced in Madras Fertilizer's ammonia plant, the remedial and corrosion prevention measures adopted and the success/failure are highlighted in this paper.

INTRODUCTION

Modern large scale process chemical and fertilizer plants handle corrosive fluids at high pressure and temperature and velocity conditions. Higher efficiency and increasing reliability in plant operation have become a necessity as the penalty cost from a shut-down is severe. Demanding conditions of service for the various equipment emphasize the need for more critical selection of materials of construction to meet the high temperature and pressure required for the manufacture.

Development of new corrosion resistant materials and newer corrosion protection systems have, no doubt, kept in pace with the advances in chemical process technology. At the same time new corrosion/material problems continue to occur and may still be envisaged during the plant operation. Frequently plants are shut-down or portions of a process stopped because of unforeseen corrosion failures in large scale fertilizer plants.

This paper deals with the experiences gained in a decade of successful operation of a complex fertilizer unit in Madras Fertilizers Ltd., India. Some case histories of corrosion failures experienced in an ammonia plant, the remedial/corrosion prevention measures adopted and their success/failure are highlighted.

Madras Fertilizers Ltd. operates a 750 MTD ammonia, 880 MTD urea and 1900 MTD NPK complex plants since 1971. During the 10 years of successful operation, corrosion failures due to stress corrosion, pitting, erosion-corrosion, corrosion fatigue, hydrogen attack, high temperature creep were experienced in MFL's ammonia plant equipment. Some of the case histories are discussed here.

CASE-1: Stress Corrosion Cracking - Reformer Components

During pressure testing in 1974, we observed leaks thru the weld areas at the top inlet portions of the reformer. Detailed inspection showed longitudinal and circumferential cracks at the weld areas of the inlet hair-pin tube weld-cap and at the reformer tube stub-ends.(Slide 1) Such cracks at the reformer tube were considered unusual in reformer operating history of many plants in the world.

Metallurgical investigations of both the SS 321 (18-8-Ti) inlet pigtail weld cap and HK-40 (25 Cr. 25 Ni) reformer stub ends were done. The cracks were observed to be transgranular and intergranular in nature in HK-40 reformer stub end and started from the weld and propagated on either side of the heat affected zone areas.(Slides 2, 3) The cracks in the inlet pigtail weld cap were essentially intergranular in nature.(Slide 4) The cracks had a tendency to propagate further when ground. The failures were identified due to stress corrosion cracking. Small traces of chlorides or alkali present in the steam naphtha mixture entering the reformer tube combined with the residual weld stresses were identified as the sources for the large scale stress corrosion cracks observed in the reformer components. We replaced all HK-40 stub ends with Inconel 600 (72 Ni, 16 Cr) alloy and welded the used reformer HK-40 tube with the new Inconel 600 stubs using high nickel electrode. Inconel 600 alloy was considered immune to chloride stress cracking and to a large extent against caustics upto 250°C. The cracked portion of the inlet pigtail weld caps were cut out and repair welding was done with shortened weld caps of the same material.

In 1976, we experienced similar longitudinal and circumferential cracks at the weld areas in both the tube end and inlet pigtail weld cap. But this time we did not observe any cracks in the new replaced Inconel 600 alloy stub ends. The cracks were found only in the HK-40 reformer tube portion. Metallurgical investigation identified these failures, once again. due to stress corrosion cracking. Repair welding was done after cutting out the cracked portions and using Inconel 600 alloy stub ends for the repaired tube. In the case of the inlet pigtail, the weld cap portions were removed and modification to the inlet pigtail arrangement was done.

In 1978, we observed similar longitudinal and circumferential cracks. But this time cracks were seen only at the Inconel 600 alloy stub ends. (Slide 5) The HK-40 reformer tube portions did not develop any cracking. Also no cracks were observed at the inlet pigtail stub. Stress corrosion cracking due to caustics/chloride present in steam naphtha mixture was identified the cause for the failures observed in the Inconel 600 alloy. In our experience, both design and material changes did not prove to be a success as on every occasion the problem faced was different and independent of the changes made. Such repeat problems were also unheard in the history of reformer operation in India and other countries.

To overcome this stress corrosion cracking problem we considered several proposals. Of these we attempted stress relieving the welds at 860°C (HK-40 to Inconel 600 or HK-40 - HK-40) for 45 minutes on an experimental basis in 1978. All the experimentally stress relieved welds did not develop any further cracking in seven months. Encouraged by this success, we stress relieved at 860°C/mill annealed at 980°C for one hour all the other stub end welds during the two shutdowns in 1978 and 1980. All the stress relieved stub ends did not develop any cracks.

In our experience, this approach of stress relieving/mill annealing the weld areas has been a success. The repeated stress corrosion cracking problem at the reformer top HK-40 stub end welds has been practically minimised/eliminated. The occurence was due to a combination of stress and corrosion of which the left over stress seemed to be dominant especially in view of the repeated cutting and welding done during 1974-78.

CASE-2: Stress Corrosion Failure - Syn Gas Turbine Condenser Tube

In our single stream ammonia plant, all the four drive units of the compressors - Process air, Synthesis gas, Carbon-dioxide, Refrigeration (ammonia) are steam turbines. We experienced frequent tube failures in the surface condenser of the synthesis gas turbine during 1974-76. In this heat exchanger cooling water flows thru the tube and steam is condensed under vacuum on the shell side. The tube material is inhibited Admiralty brass (70 cu, 29 zn, 1 Sn).

Metallurgical analysis of the failures indicated two mechanisms of stress corrosion cracking. In one case, a local dissolution (de-zincification) plus intergranular stress cracks were observed.(Slide 6) Cracks were initiated at the dezincified areas and started from the ID surface. These indicated that the de-zincified areas could have acted as stress raisers.

In a second case, circumferential cracks at the middle of the baffle supports were observed. Intergranular stress cracks were found to propagate from external to internal surface.(Slide 7) In the sound portions of the tube, the micro-structure was found to be normal, fine grained alpha phase.

In both the failures, a noticeable corrosion product was observed. An accelerated stress corrosion test, per ASTM B 154, using Mercurous-nitrate solution was done to determine the sensitivity of the good portions of the tubes for stress cracking. Fine intergranular cracks developed in this test indicating high residual stresses were left over in the good tubes which were supplied in half-hard condition.

We considered several preventive approaches for solving the stress corrosion problems experienced in the surface condenser Admiralty tubes. Three replacement materials were considered viz. (a) cupro-nickel alloy, (b). austenitic stainless steel and (c) titanium. Ultimately we decided to use the same inhibited Admiralty Brass material in annealed condition instead of half-hard condition. The exchanger after the retubing and except for two isolated failures is in service without further problems during the last 6 years.

CASE-3: Stress Corrosion Cracking - Heat Exchanger SS Bellow

A third case of stress corrosion cracking was experienced in the stainless steel 321 (18-8 Ti) expansion bellow of our methanator heat exchanger.(Slide 8) Synthesis gas exchanges heat on both the shell and the tubes in this exchanger before entering the methanator. The first year of operation, we experienced cracks in the SS 321 expansion bellow given for the shell. The cracks were identified as caustic stress corrosion cracks due to small carryover K_2CO_3 and moisture along with the synthesis gas at the outlet of our CO_2 absorber.

Local repair welding was done in the cracked bellow. Replacements with new bellow design and materials of Inconel 600 and SS 321 were considered. Replacement was done with SS 321 and new design in 1974. Along with this, design improvements were made to the saddle supports for the overhang portions of the shell. This bellow is in service from 1974 without further problem.

CASE-4: EROSION/CORROSION - PROCESS AIR COMPRESSOR LABYRINTH SEALS

In our ammonia plant, we have four high speed centrifugal compressors. This problem relates to the Labyrinth seals of the process air compressor. Process air compressor is operating at 9400 rpm. Seals form an important part of high speed centrifugal compressors. Labyrinth seals with a series of circumferential knife edges are provided for these compressors and are used as shaft seals for interstage shaft and impeller eye sealing. For an optimum compressor performance, the sealing between the labyrinth seal and the rotor should not be damaged due to rubbing, erosion and corrosion. Close labyrinth seal clearances are usually maintained to permit operation with minimum seal leakage and for high compressor performance. The life of the labyrinth seals, thus, is critical for the compressor performance and efficiency.

Labyrinth seals are affected due to wear or rubbing when rotor vibration is increased and also due to corrodents present in the atmosphere. Erosion, due to high velocity of air, is aggravated further by carry-over water particles in air. Due to this the labyrinth seal knife points get eroded and the water particles containing traces of CO_2, NH_3, SO_2, H_2S, O_2 etc. corrode the seals.(Slide 9) Labyrinth seals originally supplied were made of cast aluminium alloy (92 Al, 6 Sn, 1 Cu, 0.6-1.0 Fe, 1 Si) with hardness ∠100 BHN. New replacements of the same material lasted only a few months. Heavy seal leak occurred again resulting in some loss of compressor performance efficiency. Installing air moisture separators and knockout drum at the suction side minimized the frequency of erosion corrosion to some extent.

To solve this we considered use of Nickel silver (67% Cu, 19% Sn, 12% Ni) and Aluminium Bronze (Al - 11%, Fe-4%, Ni-4%, Mn-3.5%, Cu-81%). Both materials offer excellent erosion and corrosion resistance to high velocity air and water particles containing traces of CO_2, NH_3, SO_2, O_2 vapours. We used Aluminium Bronze to ASTM B 140 Alloy 9D in place of the aluminium alloy at the end seals of L.P. Compressor which performed well for 16 months. Seal leakage was considerably reduced from 7% to 3%. An improved seal with changed design made of S.S. 304 was available in 1978 and we started using this for the shaft end seals which worked in a similar way like aluminium bronze.

CASE-5: Erosion-Corrosion - CO_2 Absorber

Reformed gases (H_2, N_2, CO_2, CO, CH_4, Ar, etc.) leaving the shift converters have to be free of all impurity gases before compression in the synthesis compressor. 'Catacarb Process' of CO_2 removal is employed in our CO_2 Absorber where the reformed gas at 25 kg/cm^2 and 150°C is sent from the bottom and catacarb solution (24 to 28% K_2CO_3 and inhibitors) is circulated from the top three distribution packing columns.

Gas channelling was suspected in 1979 at the bottom bed portions of the absorber. Detailed visual and ultrasonic thickness examination in '80 revealed severe corrosion and erosion signs at the bottom bed.(Slide 10) As a preventive measure, we repair built the affected portion (250 ft^2) by overlaying using austenitic SS electrodes. The repair overlay built up SS areas were stress-relieved in-situ using special infra red heater pads.(Slide 11) Although the gas channelling continues, on-stream thickness measurements indicated no further corrosion in the repair overlay portion of the shell.

CASE-6: CORROSION FATIGUE - PROCESS AIR COMPRESSOR. IMPELLER SPACER RINGS AND SLEEVES

Impeller spacer rings and sleeves, shrunkfit on the rotor, of process air compressor, broke into two pieces in service after three years. The broken spacer rings and sleeves were between the 4th and 5th stage impeller of the low pressure stage rotor. (Slide 12) A similar failure occurred in the CO_2 compressor rotor. We observed cracks in the spare rotors, in storage, all in the spacer rings and sleeves.

Visual examination of the broken spacer rings showed chevron shape markings, typical of a rapid brittle fracture.(Slide 13) In addition to the fracture there was a transverse fatigue crack at a severely worn out area that probably occurred after the spacer rings and sleeve broke into two pieces.

Microscopic examination of the failed LP stage spacer and sleeve showed consistent grain size and tempered martensite expected of a heat treated [illegible] % Cr stainless steel material.(Slide 14) The broken spacer ring and sleeve contained considerable amount of corrosion deposit, numerous pitting and some fretting on the inner diameter. Pitting was more extensive on the OD surface. Examination showed the origin of the brittle fracture was from a relatively large corrosion pit. The shear lip observed at the brittle fracture area indicated that stresses responsible for the fracture were tensile in nature and in a peripheral direction. These stresses could have developed during shrink fit installation on the rotor.

Hardness measurements of the failed parts gave values of 340 to 450 BHN. Manufacturer's hardness specification was 210 to 240 BHN and spacer ring and sleeve material to Din x 32 Cr 13 (equivalent to 420 SS). X-ray diffraction and electron diffraction of the surface corrosion product disclosed them to be essentially iron oxides and moisture particles could have initiated the corrosion pits. These pits could have occurred when the compressor was idle. The fracture appearance of the failure was conclusive of corrosion fatigue originating from a corrosion pit (Slide 15) High stress resulting from the shrunkfit application was a factor for the crack initiation and propagation. High hardness values indicated that tempering was done in the range of 450-500°C producing this material highly notch sensitive. Failure was therefore concluded due to corrosion fatigue and delayed hydrogen stress cracking.

To overcome this problem, new impeller spacer rings and sleeves were made of the same material to DIN x 32 Cr 13 (SS 420) but with hardness in the range of 210 to 240 BHN. Since 1975 the problem of cracks in the spacer rings and sleeves due to embrittlement and corrosion pitting was not experienced. All spacers and sleeves in the spare rotors of both air compressor and CO_2 compressor were replaced with hardness 210-240 BHN. Both the rotors are used without any further problem.

CASE-7: Crevice Corrosion - Carbondioxide Inter Cooler

CO_2 regeneration is done in the ammonia plant for urea manufacture. We use a booster CO_2 centrifugal compressor operating at 8000 rpm and developing 13 kg/cm^2 pressure. The compressed CO_2 gas from this is sent to the urea plant for further compression in a reciprocating compressor. This booster CO_2 compressor has inter and after coolers for cooling the gas.

We experienced small leaks at the bottom of the CO_2 inter cooler in the first year of operation. Initially the leak was patched up. Later we provided a 24" wide carbon steel patch at the bottom of the shell. During a periodic inspection, we observed a peculiar corrosion pattern. Severe corrosion was noticed only in a local band and this was in line with the internal baffle support plate area. Some liquid entrainment (moist CO_2 vapours) had occurred in the crevices between the baffle and the shell at the cold end of the exchanger. The width of the corroded band was only 0.50" (13.0 mm) and this was observed on all the 8 baffle support areas. (Slide 16) In all other areas of the CS shell on-stream thickness measurement did not indicate any corrosion. (Slide 17)

To overcome this peculiar crevice corrosion, at the baffle supports, we provided SS strip pads on-stream at the localized areas without shutting down the ammonia plant. Exchanger was in service till 1975 before we replaced with new SS 304 shell. This SS exchanger shell installed in 1976 has been working well since then.

CASE-8: PITTING CORROSION - OVERHEAD CONDENSER AMMONIA

Overhead condensers A & B in the CO_2 removal section are heat exchangers where hot CO_2 gas from the regenerator flows on the shell side and coolingwater flows on the tube side. After 3 years in service, we observed pin hole leaks on the shell at areas adjacent to the vapour outlet nozzle in both the condensers.

The corrosion pattern observed was not uniform throughout the vapour outlet nozzle. Localized impingement and pitting corrosion, due to moisture laden CO_2 vapours, was observed on the shell around the outlet nozzle pipe. Detailed thickness measurements on both the exchangers confirmed that the pitting and impingement was restricted only to a local portion around the vapour outlet nozzle. We provided SS 304 reinforcement pads(Slide 18) around the affected and corroded areas and these exchangers are in service for the last 6 years without any further problem.

CASE-9: HYDROGEN ATTACK - BOILER FEED WATER - PREHEATER EXCHANGER TUBES

Boiler feed water preheater exchanger is located at the down stream of the ammonia converter where heat exchange takes place. Synthesis gas at 240 kg/cm^2 and 300°C flows on the tube side and heat is exchanged to produce steam on the shell side. Alloy steel tubes (2¼ Cr-0.5 moly) are used against high temperature hydrogen attack and creep. In the design of this exchanger strength welding between the tube and the tube sheet was given in addition to strength rolling.(Slide 19)

We experienced tube failures after 3 years in service. Close examination of the failed tubes revealed small cracks at the HAZ zone of the tube and the tube sheet weld. High hardness was observed which could be the cause for the high temperature hydrogen attack seen in these tubes. Low chrome alloy materials are air-hardenable type and high hardness observed in the HAZ of tube was due to leaving the tube without stress relieving after the strength welding.

A new exchanger was installed in 1976 with the same design and material but care was taken to stress relieve all the tube to tube sheet strength welds, after the welding. Heat affected zone hardness of the low chrome steel tube (2¼ Cr - 0.5 Mo) was reduced to lower than 240 BHN against any possibility of delayed high temperature hydrogen attack. The exchanger is in service for the last 5 years without any further problem.

CASE-10: HYDROGEN ATTACK-CARBON STEEL FORGING: AMMONIA CONVERTER

We observed surface decarburization and intergranular penetration due to permeation of high temperature hydrogen gas in the top carbon steel forging of the ammonia converter.(Slide 20) Carbon steel used in high temperature hydrogen service is susceptible for hydrogen attack. API 941 gives the 'Nelson Curve Limit' for different materials in this service. In our case, 'Nelson Curve' limit is 232°C for hydrogen partial pressure of 134 kg/cm^2 (1900 psi) for carbon steel.

To protect the medium carbon steel forgings, the earlier designs of 1960s provided special insulation canisters against any direct impingement or contact of synthesis gas entering the converter at 200-240 kg/cm^2 and at 450°C. In our case the top forging could have occasionally seen higher temperature. To protect against hydrogen attack, an improved insulation canister was provided and also a continuous external steam quenching arrangement to maintain the forging temperatures below the 'Nelson curve limit'.

CASE-11: NITRIDING - CONVERTER EXCHANGER TUBES

Converter exchanger located down stream of the ammonia converter handles lean syn gas on the shell side at 240 kg/cm^2 and 420°C and converted syn gas at 240 kg/cm^2 and 490°C on the tube side. Shell and the tube materials were originally made of alloy steel 3 Cr - 0.9 Mo. Low alloy steels, operating above 450°C and 200-500 kg/cm^2 in synthesis service are susceptible for nitriding after 5-8 years (40,000 to 60,000 hrs) period. We experienced frequent tube failures during 1976-78. Examination of the failed tubes indicated depth of nitriding and in some of the tubes the depth was of the order of 0.5 to 0.6 mm. Nitriding gives rise to a high hardness of 450-550 BHN embrittling the tubes

The tube bundle was changed in 1978 with SS 304 tubes. SS 304 or SS 310 materials have appreciably lower nitriding rate in this service temperature and pressure compared to low chrome alloy steels. This exchanger has been performing well after the retubing with SS 304 in 1978.

CONCLUSION

Considerable experience has been gained from the different failures in the 'Case Histories' presented and discussed in this paper. Direct and indirect cost due to corrosion failures and equipment down-time is enormous. Unforeseen corrosion problems/failures can occur inspite of good design and material selection. Corrosion failure could be effectively reduced, in the event of an occurence, by a proper and systematic diagnosis of the problem. Similarly an evaluation of all the corrosion prevention measures/ remedial measures (design change, material improvement, heat treatment, protection system) will help and is required to prevent any recurrence of the same problem.

MFL's experiences in solving some of these corrosion failures may be useful to those who experience similar problems in the ammonia plant equipment.

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