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Liquid Metal Embrittlement in Outlet Pigtails of Reformer of Hydrogen Generation Unit in Digboi Refinery

K K Pandey
Indian Oil Corporation Limited, Digboi Refinery, Tinsukia, India
pandeykk@indianoil.in

Sukla Mistry
Indian Oil Corporation Limited, Digboi Refinery, Tinsukia, India)
mistrys@indianoil.in

S D Chaklader
Indian Oil Corporation Limited, Digboi Refinery, Tinsukia, India)
chakladers@indianoil.in

R Gayen
Indian Oil Corporation Limited, Digboi Refinery, Tinsukia, India)
gayenr@indianoil.in

ABSTRACT

Hydrogen Reformers in Refineries are used to produce Hydrogen which is used in Hydro processing Units like Hydro-treaters and Catalytic Cracking Unit etc. In Digboi Refinery, Hydrogen is produced by reforming natural gas using steam. Hydrogen reformer operates at high temperature in the range of 850-900˚C and has centrifugally cast high nickel - chromium metallurgy tubes to provide high creep strength. The reformer tube assembly at Digboi refinery has pigtails in inlet and outlet. The outlet pigtail tubes are of Alloy 800HT (UNS N08811) and are distributed in two rows having 14 nos. of tubes in each row. The pigtails are externally insulated with preformed calcium silicate, preformed Mineral wool & sheeting of stainless steel as outermost layer. However, Aluminum foil was inadvertently wrapped in direct contact with all pigtail tubes in Row-A before ceramic fiber insulation during Shutdown of the unit. After the start up of the unit, low temperature aluminum foil melted over outlet pigtail tubes, operating at about 825˚C. This caused aluminum Oxide formation by an exothermic reaction and raised the temperature to an extent which subsequently led to the failure of

outlet pigtails and caused huge flash of fire. Such failure caused shutdown of the Hydrogen unit for substantial amount of time. This paper describes about the LME (Liquid Metal Embrittlement) in Alloy 800HT reformer outlet pigtail tubes which finally resulted in fire & property loss.

Keywords: HGU; Reformer; Pigtail, Liquid Metal Embrittlement, Alloy 800 HT, Molten Metal Corrosion

INTRODUCTION

Process Description.

Hydrogen Generation Unit (HGU) is used to produce hydrogen by reforming natural gas. The desulphurised feed gas from Desulphuriser is mixed with steam to ensure the required Steam to Carbon ratio (S/C) and then superheated in the convection section to about 580^{0}C in the Feed / Steam Superheater.

In the tubes of the top Reformer, the mixture of feed and steam reacts over a nickel-based catalyst to produce a mixture of hydrogen, carbon monoxide, carbon dioxide and methane as a result of the following reactions:

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2$$
$$CO + H_2O \Leftrightarrow + CO_2 + H_2$$

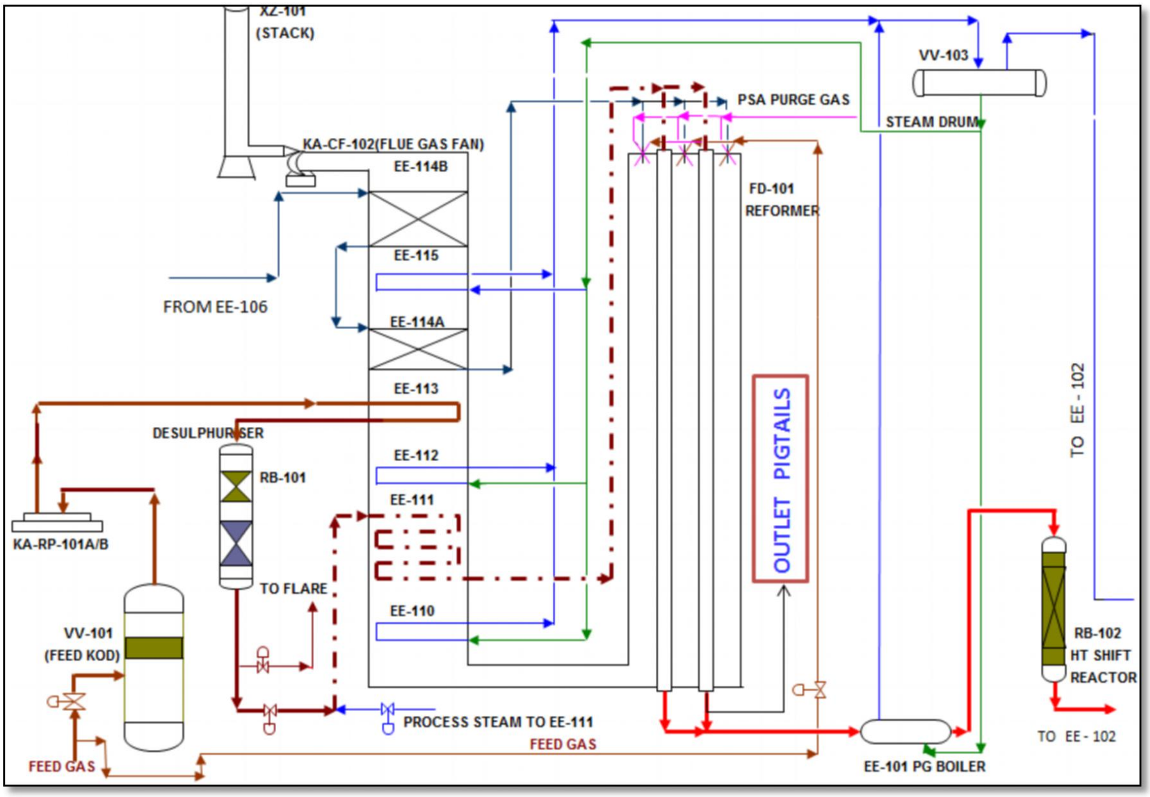

Figure 1 Process Flow Diagram of Hydrogen Reformer Section

The reforming reactions themselves are endothermic and require a substantial heat input. This heat input is supplied by firing PSA (Pressure Swing Adsorber) purge gas and make up fuel in the form of natural gas. The process gas leaves the reformer at a temperature of around 880 ^{0}C.

The heat in the process gas from the Reformer is recovered by generating steam in the Process Gas Boiler. The boiler is equipped with an internal bypass to control the High Temperature (HT) shift Reactor inlet temperature. The shifted effluent gas passed through a steam super heater, superheating the steam to meet the export conditions of 288 ^{0}C at 12 kg/cm^{2}g.

The Reformer catalyst tubes are connected with inlet and outlet pigtail tubes of SS-304H and Alloy 800HT respectively. The pigtails are provided as expansion loops for compensating thermal expansions in different directions of the reformer tubes and headers. The pigtail tubes have a design and metallurgy suitable for reformer gas and endure the thermal cycles due to expansion and high temperature creep. The inlet pigtail tubes operate at 580˚C and 24.8 Kg/cm^{2}g while the outlet pigtail tubes receive the reformed fluid at 825-850˚C and 22.2 Kg/cm^{2}g. The 2 parallel rows (A and B) of catalyst tubes, each row having 14 tubes, are welded to the outlet pigtail tubes. The outlet pigtail tubes have an outer diameter of 42.2 mm and thickness 6.35 mm, and are wrapped with preformed Calcium Silicate followed with preformed mineral wool and Stainless steel sheeting as shown in Figure 2. The further end of the outlet pigtail is connected to a header, which carries the fluid to the Process Gas Boiler.

Alloy 800HT (UNS N08811) is a high Nickel-Iron-Chromium alloy used in liquid and gaseous environments due to its excellent high temperature creep resistance and oxidation resistance properties in both oxidizing and reducing environments. Chromium provides resistance to high temperature oxidization and carburization by the formation of an adherent surface film rich in chromium oxide. Titanium and aluminium, present in the alloy, enhance the stress rupture properties at high temperatures. Addition of titanium controls the grain size and helps in formation of finely dispersed secondary carbides.

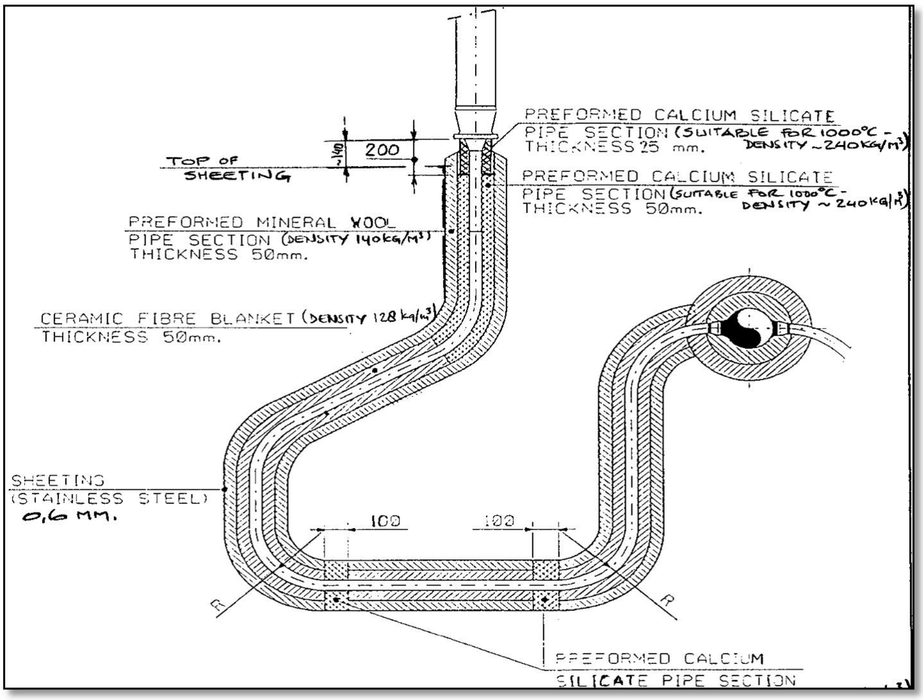

Figure 2 Design and Insulation Details of Outlet Pigtail

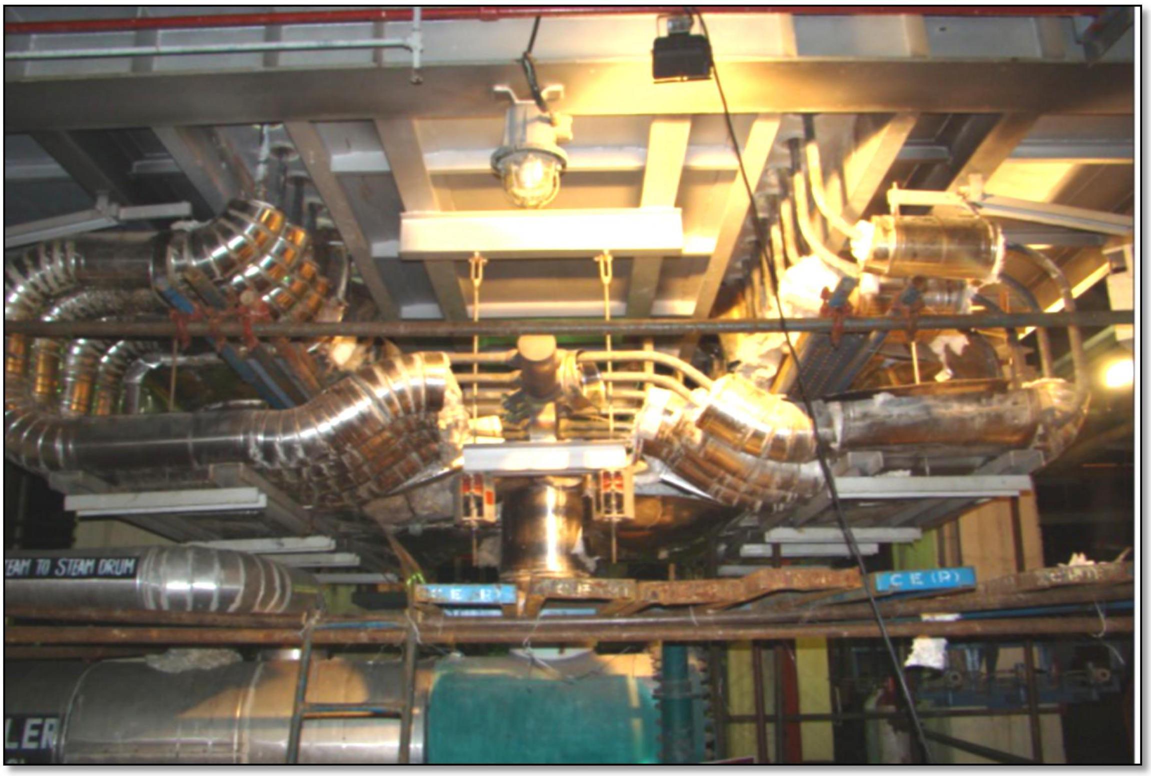

Figure 3 Outlet Pigtail Tube Arrangement (Row-A and Row-B)

Background

The Unit was commissioned in the year 2003. In April 2009 turnaround, rectification of the insulation of the outlet pigtails in Row-A was carried out as per original specification (refer Figure 2). However, the outlet pigtail tubes (20Cr-33Ni) were inadvertently wrapped with Aluminium foil. After completion of the maintenance job, the unit was commissioned on May 07, 2009. After 3 days of operation, on 10th May 2009, in the morning shift, huge flashes of fire was reported at 2 nos. outlet pigtail tubes. Subsequently, the unit was brought down.

It was suspected that the failure occurred in assistance of Liquid Metal Embrittlement (LME) or Liquid Metal Induced Embrittlement (LMIE). LMIE occurs catastrophically resulting in brittle failure by a thin film of molten metal (usually a metal with lower melting point). This form of failure is predominant in embrittling couples with low or no solid solubility. The presence of liquid metal in direct contact with the surface and at crack tip is of utmost importance for the occurrence of brittle fracture.[1]

On further analysis, other mechanisms assisting the failure came to light. One of these mechanisms resembled molten metal corrosion which occurs due to dissolution of an alloy surface. The mechanism of this attack may be intergranular in nature or by leeching. Literature [2] available on this subject shows that molten Aluminium is detrimental for Nickel-Chromium alloys.

OBSERVATIONS

Following the unit shutdown, the reformer tubes were pneumatically tested with nitrogen at 5.5 Kg/cm^{2}g. Leaks were detected at six locations in Row-A outlet pigtails. At the outlet pigtail of tube 2, leaks at two locations were found while one leak each at outlet pigtail of tubes 01, 11, 12 and A13 was observed. No leak found in outlet pigtails of Row B tubes.

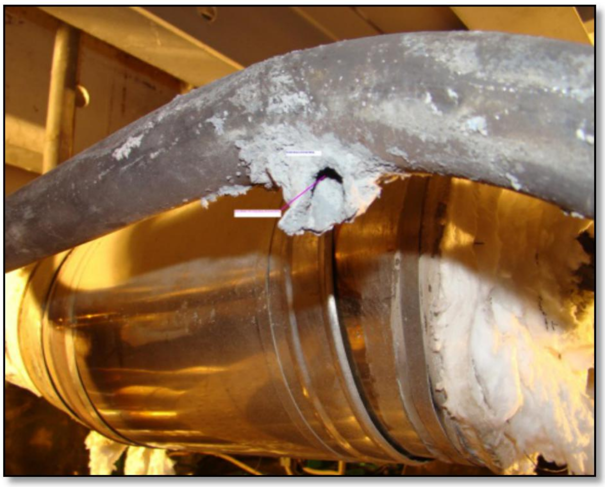

Figure 4 Failed Tube

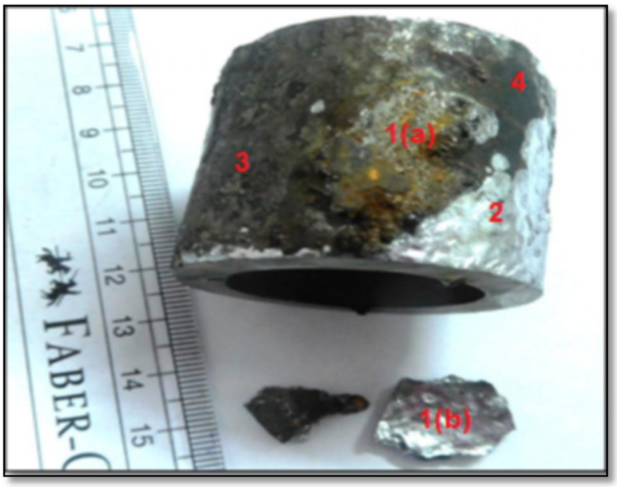

Figure 5 Cut Sample piece of the Outlet Pigtail Tube (1(a) &(b)- Adherent Oxide Layer; 2-Chipped Surface; 3-Greyish Tube surface; 4- Greyish-black oxide layer)

On close observation of the outlet pigtail tubes, various surface features were observed. As seen in Figure 5, an adherent oxide layer having rough texture with uneven profile was observed on the outer surface of the outlet pigtail tubes at many locations. The surface of the cut section of one of the tube was exposed by chipping away the oxide layer. A shiny silver-like uneven surface was observed with pit-like localized, closely spaced metal loss. A shiny dark grayish uneven surface adjacent to the adherent oxide layer was also observed. The rest surface of the tube had thin grayish-black oxide layer with smooth profile indicating in-service oxidation of the tubes. All the surfaces were checked using XRF based Positive Material Identification (PMI) to establish the composition of the observed surfaces.

Table 1 PMI Results of the Sample Piece

Sr. No	Element	Observed Composition (%)					
		Cross-section of tube	1(a) Adherent oxide layer	1(b) Adherent oxide layer	2 Bright Surface	3 Greyish surface	4 Greyish-black oxide layer
1	Ni	31.8	4.35	3.83	37.625	32.53	14.03
2	Fe	46.2	12.51	11.67	48.9	50.45	34.43
3	Cr	19.5	4.87	3.74	11.71	15.03	41.78
4	Ti	0.9	-	-	0.4	0.11	0.76
5	Al	0.4	77.7	80.52	0.4	0.4	0.4

PMI of the sample piece was done at locations as marked in figure-5 and the results are as tabulated in Table 1. At cross section of the tube i.e. in middle portion, PMI revealed Alloy 800 HT and no deviation was observed. The composition of the inner side of the chipped out oxide layer (1(a) & 1 (b)) predominantly had Aluminium, which implies the melting of the Al-foil over the tubes. The bright shiny surface (2) shows that Chromium has depleted at the surface. At the greyish-black oxide layer, chromium was found in excess.

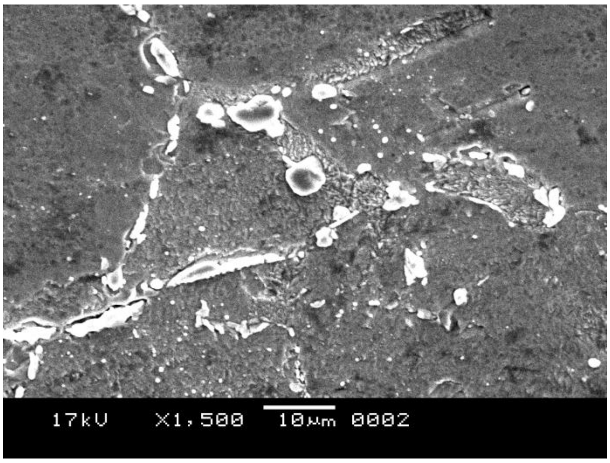

Figure 6 Microstructure of Cross-Section near Outer Surface showing carbide precipitation and micro-cracks at Mag-1500x

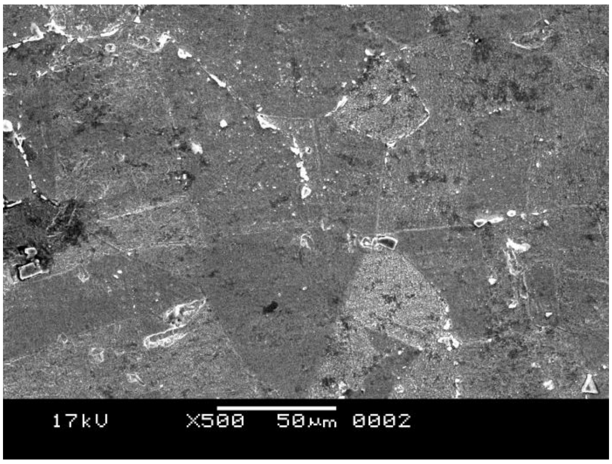

Figure 7 Microstructure of Cross-Section near Outer Surface at Mag-500x

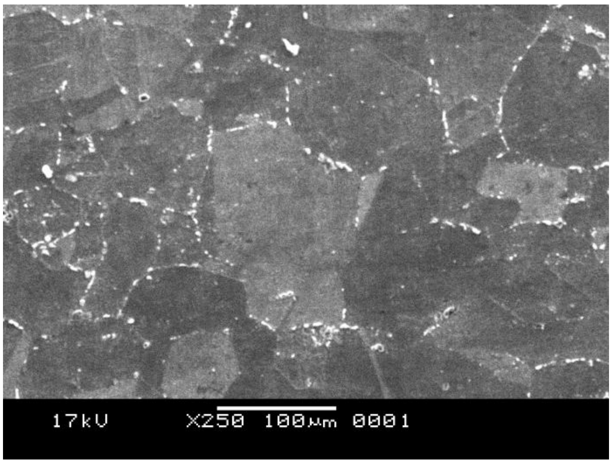

Figure 8 Microstructure of Cross-Section in the Middle at Mag-250x

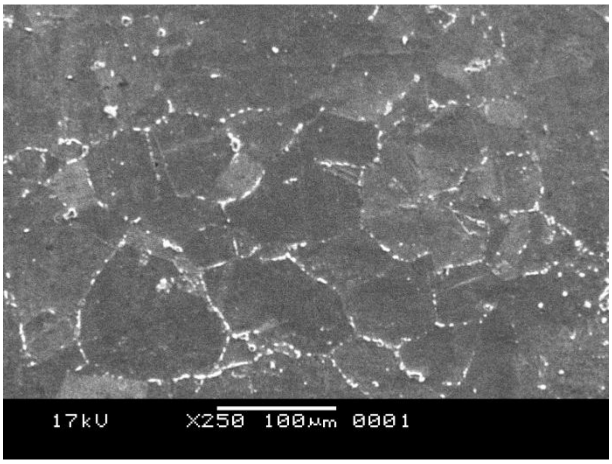

Figure 9 Microstructure of Cross-Section in the Middle showing secondary carbides at Mag-250x

The microstructure of the tube cross-section was developed from a sample piece extending from inner diameter of the tube to the exposed outer diameter. The obtained micrographs are given in Figure 6-9 at magnification ranging from 250x to 1500x. In figure 6, the segregation of secondary carbides at grain boundary in an austenitic matrix is visible. The secondary carbides is accompanied with foreign particle deposition. This phenomenon was observed throughout the cross-section. Also, micro-cracks are observed adjacent to the secondary carbide bodies, primarily at the locations towards the outer periphery of the tube.

INFERENCES

Aluminium foil was wrapped around the outlet pigtail tubes. At the operating temperature range 825 ˚C-850˚C, prevailing at the outlet pigtail tubes of the reformer, Aluminium foil started melting, due to the low melting point of 662˚C. At temperatures as high as 850˚C, the Aluminothermic reduction of chromium oxide (Equation 1) takes place which is highly exothermic.

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3 \quad \text{.................................Equation 1}$$

As a result of the above reaction at the tube outer surface and Aluminium foil interface, a high amount of energy was released leading to localized rise in temperature. Further, due to the reaction, chromium may also have leeched out of the metal to the surface. This is also established by the PMI results (Table 1) of the area 2 in figure 5. The oxides of Aluminium so formed are present as adherent layer over the tube surface. Due to the above reaction (Equation 1) and presence of liquid Aluminium at surface, conditions suitable for molten metal corrosion were formed. Dissolution of the tube outer surface took place, leaving behind highly irregular surface profile. These might have been the initiators of the cracks.

The outlet pigtail tubes of the reformer are in continuous exposure to high temperature. Alloy 800HT is used due to its superior creep strength. However, after long hours of continuous service, changes in various metallurgical properties begin to occur. Evolution and progression of grain boundary cavity nucleation, coalescence of carbides and microcrack formation are among the various metallurgical changes that affects the long-term creep properties. The micrographs in Figure 6-9, show formation of secondary carbides at the grain boundaries of an austenitic matrix. In the improper form or morphology, the presence of carbides at grain boundaries may behave as weak links[3]. Further, voids and micro-cracks were observed along with foreign particles at the grain boundary. The presence of voids and micro-cracks at the grain boundaries near the surface were affected by the presence of liquid Aluminium. In presence of the embrittling species (liquid Aluminium in this case), critical crack was initiated at the surface. The adsorption of liquid metal at regions of stress intensity (like micro-cracks) accelerates the crack growth and propagation. This crack propagated by intergranular attack, which was assisted by low grain boundary strength. The high grain boundary energy, due to segregation of carbides and formation of micro-cracks, is the reason for weakening of the grain boundaries and making the intergranular region critical for attack. This form of failure is typical in liquid metal emrittlement.

CONCLUSIONS

The outlet pigtail tubes of the reformer are exposed to temperatures in the range 825-850˚C. The tubes suffered catastrophic failure within very short span of operation after inadvertent application of aluminium foil over the tubes. Melting of aluminium and further, heat generated by the exothermic reaction of aluminium and chromium oxide, provided a conducive environment for the failure of the tubes, predominantly by intergranular attack. The segregation of secondary carbides and formation of microcracks were favourable factors leading to crack propagation. In view of the the observations, a single mechanism does not explain the occurrence of the failure under the given circumstances. Both molten metal corrosion and liquid metal Embrittlement might have worked in synergy leading to the formation of crack and subsequent failure of the tube.

Consequently, application of stainless steel foil has been made mandatory for all high temperature piping and other applications. The system was further strengthened with three-stage (i.e. before-during-after application) PMI check.

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