

# Hydrogen Attack of U-Bend Pipe Joint Connecting Heat Exchangers at a Methanol Plant

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**Abstract**— After 13 years of operation, U-bend pipe joint connecting heat exchangers at a methanol plant was failed in a catastrophic manner. Hydrogen attack associated with decarburization was identified as the failure mechanism. Damage or structure degradation was started at the inner surface of a circumferential weld connecting the U-bend pipe joint to the heat exchanger shell' nozzle then, propagated toward outer surface where a catastrophic brittle fracture was occurred. The cause of this failure is related to an improper selection of the material for the subject working conditions. In order to minimize the possibility of such failure in the future and then, increase the lifetime of the concerned equipment, the used ASTM A105 steel was replaced with a higher grade type; ASTM A335 P11 (1Cr-0.5Mo) steel. Periodic inspection was scheduled for the concerned equipment to evaluate its condition in order to be able to make the right decision for its replacement to avoid emergency shutdown. This includes mainly magnetic particle test, ultrasonic test, microstructure examination using replica technique as well as hardness measurements.

**Index Terms**— Microstructure degradation, Hydrogen attack, Catastrophic failure, Material selection, Periodic inspection

## I. INTRODUCTION

Methanol is produced from natural gas by reforming the gas with steam and then converting and distilling the resulting synthesized gas mixture ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ) to create pure methanol. Methanol is a clean-burning, biodegradable fuel. Increasingly, methanol's environmental and economic advantages are making it an attractive alternative fuel for powering vehicles and ships, cooking food and heating homes. It is used to produce other chemical derivatives, which in turn are used to produce everyday products, such as building materials, foams, resins, plastics, paints, polyester and a variety of health and pharmaceutical products.

Among the main facilities of the methanol plant are four heat exchangers; A, B, C, D; each having 450mm shell diameter and 140 vertical tubes with 19.05mm outer diameter, 14.83mm inner diameter and 8000mm length each. Both shell and tubes of the heat exchangers A and B were made from ASTM A105 steel while those of the heat exchangers C and D were made from ASTM A335 P11 (1.5Cr-0.5Mo) steel. The different heat exchangers were connected together using U-bend pipe joints made from ASTM A105 steel pipes except the heat exchangers C and D that were connected using ASTM A335 P11 steel pipe. Dimensions of the connection pipes are 150mm outer diameter, 19mm wall thickness and 1500mm length.

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After 13 years of operation, failure occurred where the U-bend pipe joint connecting the heat exchangers B and C was fractured in a catastrophic manner. The operating temperature of this U-bend pipe joint is  $275^\circ\text{C}/548\text{K}$  and its working pressure is 220 barg. The failed U-bend pipe joint was subjected to detailed failure analysis to identify the root cause of the failure.

## II. INVESTIGATIONS

On site investigation showed that the U-bend pipe joint was fractured and separated from the shell nozzles of both heat exchangers B and C. General view of the fractured U-bend pipe joint after reassembling its segments is shown in Fig. 1. Visual inspection showed that the fracture was occurred at the two ends of the U-bend pipe joint connected to the heat exchangers B and C. However, existence of several segments of the fractured pipe joint on the heat exchanger B side increases the possibility of starting the fracture on this side. Another important point is the absence of bulging of the failed pipe joint.

Enlarged view of the fracture zone on the heat exchanger B side showed thick wall rupture where no indications for corrosion damage or other excessive wastage were observed (Fig. 2-a). Results of wall thickness measurements showed no remarkable reduction in wall thickness of both fractured and non-fractured zones of the failed U-bend pipe joint where wall thickness of 18.7–19.1 mm was obtained compared with 19 mm nominal wall thickness, that in turn indicates brittle fracture. Close up view of the fracture surface of the shell nozzle of the heat exchanger B showed crack propagated from the circumferential weld root toward the outer surface (Fig. 2-b). In other words, beveling the fracture surface increases the possibility that the fracture was initiated at the inner surface of the circumferential weld connecting the U-bend pipe joint to the shell nozzle. Dye penetrant test results showed no indications for surface cracks either around or away from the fracture zones



Fig. 1. General view of the fractured U-bend pipe joint connecting the heat exchanger B (HE-B) to the heat exchanger C (HE-C).

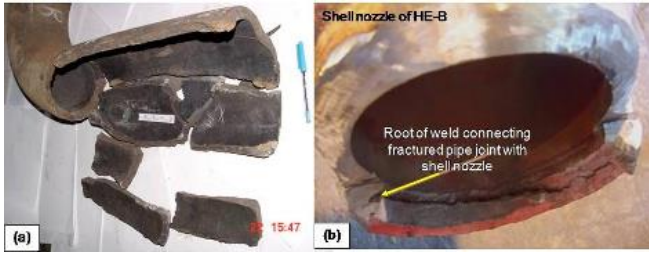


Fig. 2-(a). Enlarged view of the fracture zone on the heat exchanger B side showing thick wall rupture and (b) close up view of the fracture surface of the shell nozzle of the heat exchanger B showing crack propagated from the circumferential weld root toward the outer surface.

Low magnification stereoscopic photograph of the fracture surface on the side of the U-bend pipe joint is shown in Fig. 3-a. It can be seen that the fracture surface showed a brittle appearance with cracks propagated through grain boundaries. Low magnification stereoscopic photograph of the inner surface of the U-bend pipe joint is shown in Fig. 3-b. The important notice is the existence of large amount of surface cracks at the inner surface of the fractured pipe joint. On the other hand, no surface cracks were observed on the outer surface of the failed pipe joint. Scanning electron microscopic examinations of the fracture surface confirmed the brittle fracture mode and disclosed complete decomposition of pearlite into ferrite and spheroidal carbides. Another important finding is the existence of voids in pearlite colonies where fissures and cracks were propagated through such voids (Fig. 4).

Specimens from both fractured and non-fractured zones were taken for chemical analysis, optical and scanning electron microscopic examinations, hardness measurements, tensile and impact tests. Results of chemical analysis of the fractured U-bend pipe joint disclosed that the carbon content of its inner surface (0.05wt%) is much lower than that of its outer surface (0.16). This is most probably related to decarburization at the inner surface. On the other hand, the results of the chemical analysis confirmed that the failed U-bend pipe joint' material is conformed to the nominal composition of ASTM A105 steel.

Optical microscopic photographs of a cross section taken from fracture suspected initiation zone are shown in Fig. 5. The most important notice is the occurrence of decarburization and the existence of voids and fissures at the pipe' inner surface (Fig. 5-a) while normal ferrite-pearlite structure is still existed at the pipe' outer surface (Fig. 5-b). Optical microscopic photographs of a cross section taken from a non-fractured zone, i.e. straight portion of tube, are shown in Fig. 6. It is clear that a microstructure degradation similar to that of the fractured zone (Fig. 5) was observed. In other words, decarburization was occurred and voids as well as fissures were formed at the pipe' inner surface (Fig. 6-a) while normal ferrite-pearlite structure was observed on the outer surface (Fig. 6-b). The microstructure degradation has been confirmed using scanning electron microscopy where decarburization, voids and fissures were clearly observed on the pipe' inner surface (Fig. 7-a, b) while pearlite still has its lamellar morphology on the outer surface (Fig. 7-c, d). The linear fissures observed on the inner surface are along the pipe axis.

The hardness measurements were carried out on the inner surface, the mid-wall thickness, and the outer surface of both

fractured and non-fractured zones and the average of five readings was considered. The inner surface of both fractured and non-fractured zones showed lower hardness values (133-140 HV) than those of the outer surface (182-185 HV). Both the microstructure examinations and the hardness measurements confirmed that the depth of the microstructure degradation at the inner surface is larger in the case of the fractured zone.

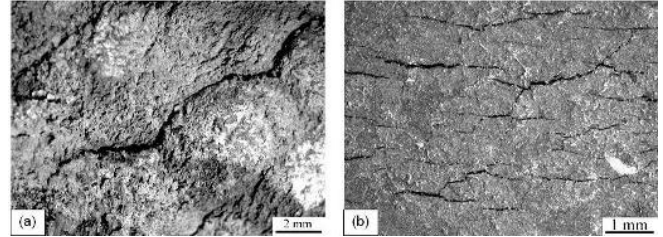


Fig. 3. Low magnification stereoscopic photographs of the fracture surface (a) and the inner surface (b) of the failed U-bend pipe joint.

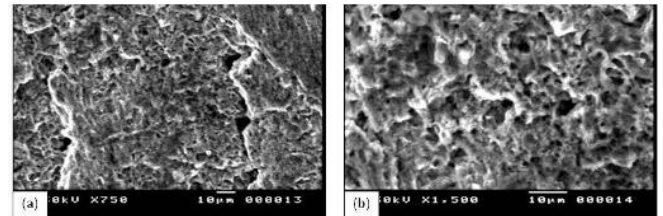


Fig. 4. Scanning electron microscopic photographs of the fracture surface showing brittle fracture mode where fissures were propagated through voids formed in pearlite colonies.

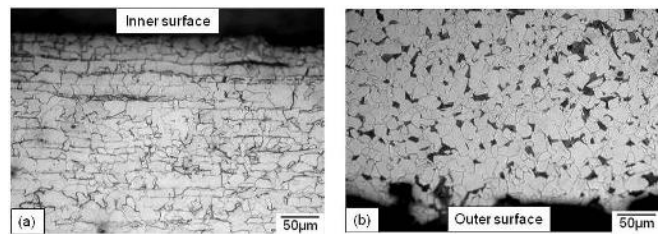


Fig. 5. Optical microscopic photographs of a cross section taken from fracture suspected initiation zone showing decarburization and fissures on the inner surface (a) and normal ferrite-pearlite structure on the outer surface (b).

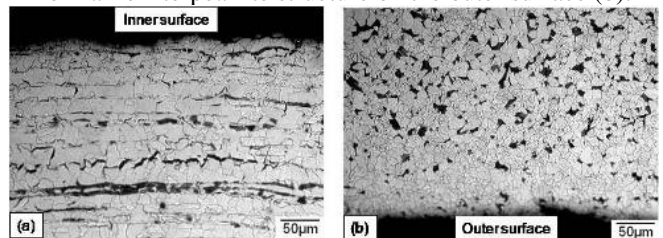


Fig. 6. Optical microscopic photographs of a cross section taken from non-fractured zone showing decarburization and fissures on the inner surface (a) and normal ferrite-pearlite structure on the outer surface (b).

Tensile and Charpy impact tests were carried out for both the used/fractured and unused U-bend pipe joints. It should be mentioned that the specimens made out of the fractured U-bend pipe joint, for both tensile and impact tests, did not have linear cracks on its inner surface after machining. Results of the tensile test indicated severe deterioration in the tensile properties of the used/fractured pipe joint where

its tensile strength and elongation were sharply decreased to 180 MPa and 5 %, respectively in comparison with 485 MPa and 30 % for the unused pipe joint (Table 1). Results of the Charpy impact test at 25°C (298K) showed that the impact absorbed energy of the used/fractured pipe joint was remarkably reduced to 15 J compared with 135 J for the unused joint (Table 1). The considerable loss in the mechanical properties of the fractured pipe joint is attributed to microstructure degradation including decarburization occurrence as well as formation of voids and fissures at the inner surface.

The used/fractured U-bend pipe joint was checked for hydrogen attack using ultrasonic testing technique based on wave velocity change and attenuation. Both longitudinal-wave (VL) and shear-wave (VS) measurements were carried out at an ultrasonic frequency of 5 MHz and its results are shown in Table 2. Longitudinal-wave velocity decreased by 17.52 % relative to the velocity in the unused joint while the shear wave velocity decreased by 8.58 % relative to the corresponding velocity of unused specimen. The ratio of VS/VL for the used/fractured joint is 0.589 while it is 0.531 for the unused joint. These results are in good agreement with other research studies in which it is pointed out that the decrease in the longitudinal wave velocity is remarkable in comparison with that of the shear wave [1], [2]. Attenuation in the used/fractured and unused specimens are 0.850 and 0.185 dB/mm, respectively (Table 2). These results are in good agreement with the work of Sorell, et al. where they showed that a loss in attenuation greater than 0.42 dB/mm is an indication of hydrogen damage [3].

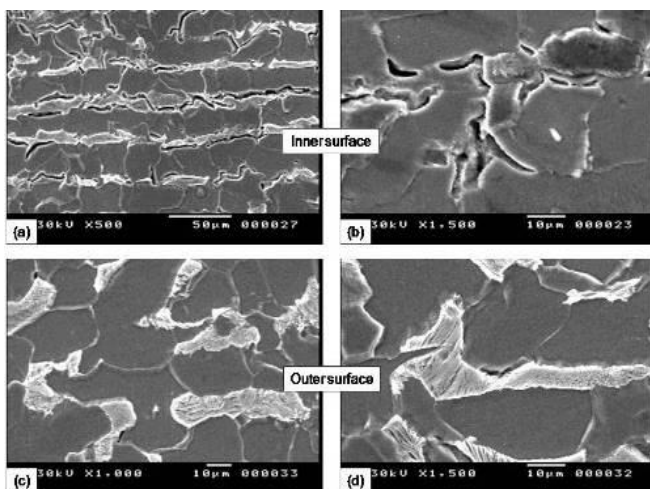


Fig. 7. Scanning electron microscopic photographs of a cross section taken from fracture suspected initiation zone. Note decarburization, voids and fissures on the pipe inner surface (a, b) while pearlite lamellar morphology still existed on the outer surface (c, d).

Table 1 Mechanical properties at room temperature (25°C/298K) of both used/fractured and unused U-bend pipe joints.

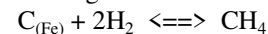
Specimen	Tensile strength (MPa)	Elongation (%)	Impact absorbed energy (J)
Used/Fractured	180	5	15
Unused	485	30	135

Table 2 Ultrasonic longitudinal and shear wave velocities and attenuation measurements taken at 5MHz of both used and unused specimens.

Specimen	Velocity, msec	VL/VS	Attenuation dB/mm
	VL VS		
Fractured	4860.6	0.589	0.85
	2861.9		
Unused	5893.3	0.531	0.185
	3130.6		

### III. DISCUSSION

Chemical analysis of the failed U-bend pipe joint showed that its material was conformed to the nominal composition of ASTM A105 steel. Visual investigation showed brittle fracture with no bulging or corrosion around the fracture zone where almost no reduction in wall thickness was observed. Visual and stereoscopic examinations of both fractured and non-fractured U-bend pipe joints disclosed large amount of surface cracks on the inner surface. Optical and scanning electron microscopic examinations of both fractured and non-fractured U-bend pipe joints showed decarburization, voids, and fissures on the inner surface while almost normal ferrite-pearlite structure was observed on the outer surface. It is believed that fracture was started on the inner surface of circumferential weld connecting the U-bend pipe joint to the heat exchanger shell' nozzle then, rapidly propagated toward the outer surface where catastrophic brittle fracture was occurred. It is clear that microstructure degradation due to decarburization, voids and fissuring have resulted in a considerable loss in the hardness, tensile strength, elongation and Charpy impact absorbed energy. They have resulted also in higher VS/VL ratio and attenuation value. These findings strongly support hydrogen attack associated with decarburization as a mechanism of the current catastrophic failure [4]-[6]. The cause of this failure was related to an improper selection of the material for the subject application or working conditions. Generally, a hydrogen gas in contact with a steel at high temperatures can result in decarburization and the subsequent formation of hydrocarbons as following:



Surface decarburization is the formation of hydrocarbons at the metal surface, which causes a migration of carbon atoms to the surface. Both hardness and room-temperature strength of a steel decreases due to surface decarburization. Regarding internal decarburization, hydrogen permeated into the steel can react with carbon, resulting in the formation of methane which will accumulate in voids in the metal matrix. The gas pressure in these voids can generate an internal stress high enough to fissure, crack or blister the steel. As the reaction that forms methane consumes the carbon that is present in the steel, hydrogen attack is also called "internal decarburization" [7]-[9]. Decarburization was confined to the pipe inner surface since its temperature is higher than that of the outer surface. Hydrogen attack and decarburization will result in degradation of mechanical properties, as tensile strength and ductility drop dramatically, and finally will lead to catastrophic brittle failure.

## IV. CONCLUSIONS

Based on the results obtained in this investigation, it can be concluded that failure mechanism of the subject U-bend pipe joint is attributed mainly to hydrogen attack associated with decarburization. The cause of this failure type is related to an improper selection of the material for the subject working conditions. Steel suffers from high temperature hydrogen attack when the hydrogen from the flow stream (hydrocarbons) seeps into steel at high temperatures. Hydrogen reacts with the carbides in the steel, decarburizing the steel and forming methane gas or bubbles at the grain boundaries with no loss of thickness. The methane gas bubbles grow with time and result in voids and micro-cracking and lower the toughness of the steel. In other words, combination of decarburization and micro-cracking reduces the fracture toughness of steels and lead to major failures with no thickness reduction or corrosion associated with it.

## V. ACTION TAKEN

Hydrogen attack of steel can be avoided by following the operating limits on temperature, partial pressure of hydrogen, and alloy composition set forth by the API Standard 941 [10]. Therefore, the used low carbon steel ASTM A105 was replaced with a higher grade type; ASTM A335P11 (1Cr-0.5Mo) steel for a longer lifetime of the subject equipment. It is recommended that the heat exchangers and its connecting U-bend pipe joints to be periodically subjected to non-destructive inspection to evaluate its condition to be able to make the right decision for its replacement in order to avoid sudden failure and unexpected shutdown. This includes dye penetrant test, magnetic particle test, ultrasonic test, SUMP or microstructure examination using replica technique, and hardness measurements.

## ACKNOWLEDGMENT

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