# Failure of Ammonia Synthesis Converter Due to Hydrogen Attack and Its On-Stream Assessment Using ToFD Method

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**Key Words :** Ammonia synthesis converter, Hydrogen attack, 2.25Cr-1Mo steel weldment, ToFD

## Abstract

A failure analysis of ammonia converter which suffered hydrogen attack in two years since its initial operating time was presented. It is constructed from 2.25 Cr–1 Mo steel. Analysis showed that the failure on closing seam weld joint was due to local improper post weld heat treatment (PWHT). Improper PWHT can introduce high residual stresses in thick-walled pressure vessel. High residual stress level in weld joint is very prone to hydrogen attack for any components which are operating in hydrogen gas environment. The repair procedures based on the principle to decrease the residual stress then proposed. The repair was controlled very carefully by applying several nondestructive tests in the each stage of repair. To assure the successful of the proposed repair, after one year since repair time, high temperature ultrasonic and TOFD methods were applied on-stream to this equipment in order to evaluate its post repair condition. The two methods showed good results on the repaired area.

Nomenclature

| | |
|---|---|
| AC | ammonia synthesis converter |
| BHN | brinell hardness number |
| CW | closing seam weld |
| BM | base metal |
| HA | hydrogen attack |
| HAZ | heat-affected zone |
| HTCUT | high temperature conventional ultrasonic testing |
| ID | inside diameter |
| OD | outside diameter |
| PWHT | post weld heat treatment |
| ToFD | time of flight diffraction |
| TWPV | thick-walled pressure vessel |
| VHN | vickers hardness number |
| WM | weld metal |

## 1. Introduction

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### 1.1 Overview

The most generic types of process equipments used in ammonia plant are large TWPV to face the harsh environment such as high pressure, high temperature, and interaction with hydrogen gas as its typical process characteristic. They are usually constructed from low alloy steel materials such as 2.25Cr–1.0Mo steel and fabricated using complex manufacturing stages including fusion welding process. During fusion welding process, residual stresses are induced into the material particularly around the WM. The non uniform and highly localized heat input from welding process, subsequent cooling after welding, and also the non linearity of the material properties are factors that contribute to the creation of residual stresses. These residual stresses may lead to cracking just after welding and sometimes later, during the service time of TWPV.

Although residual stresses can be reduced through PWHT, they are not completely removed. For practical reason, PWHT of TWPV weld joint is performing locally using heating elements attached on OD shell of the TWPV instead of using large furnace. This residual stress level, in case of TWPV, can be introduced into material near to the ID surface of the shell after PWHT as high as the yield stress because the temperature gradient occurs across the wall during PWHT. Heuser (1) modeled this phenomenon and showed that residual stress as high as yield magnitude residual stress can be formed as a result. The existence of high residual stresses in weld has became a primary concern in many welded structures since it increases the crack driving force and reduces resistance to brittle failure. The cracking tendency also increases for TWPVs which are used in hydrogen bearing streams at high temperature and high pressure environment.

Several cracking problems caused by interaction with hydrogen gas in several industries such as petrochemical and oil and gas were outlined by Prescott (2) and Timmins (3). The hydrogen induced cracking susceptibility is usually related to hardness. In the oil industry, cracking in sulfide containing streams is very aggressive on WMs or HAZs at hardnesses above 225 BHN. The maximum recommended hardness of pressure equipment operating in high and low temperature hydrogen service should be 250 VHN (230-240 BHN) according to NACE standard MR-0175 (4) and the limit set in API 942 (5). Thus, it is also normally recommended that all high temperature vessels operating in hydrogen environment should have maximum hardness of WMs of 250 VHN .

### 1.2 Chronology of Failure

One ammonia plant suffered failure on its AC after put it in operation for only two years after plant's commissioning. The failure first was recognized by the operator as leaky indication found by regular explosive gas level measurement that reached 100% explosive level at top portion of this TWPV. It is really very fortune that there was no significant accident happened concerning the explosive nature of hydrogen gas. The ammonia plant then shut down and isolated for further examination and reducing the failure risk. The characteristic of this failure AC is listed in Table 1 below.

**Table 1** Characteristics of the AC

| Description | Ammonia Synthesis Converter |
|---|---|
| Fluid contained | $H_2$ = 71.41 %wt. and $N_2$ = 27.5 %wt. |
| Design/Operating temperature | 370 $^o$C/270 $^o$C |
| Design/Operating pressure | 155 kg/cm$^2$ G/ 132 kg/cm$^2$ G |
| Shell material/thickness | SA 542 B Cl.4/105.0 mm |

## 2. Failure Analysis Procedures and Results

### 2.1 Procedures

The failure analysis techniques employed consist of visual observation, positive material identification using x-ray fluorescence (XRF) method, dye penetrant testing, hardness testing, and conventional ultrasonic testing. All these techniques performed in field only from OD surface when the AC was shut down after leak found. Before data were taken, the CW joint at OD surface was grinded around 0.5 to 1.00 mm to remove surface corrosion product that can affect the observation's results. Beside those above, there were also performed comprehensive review concerning the AC fabrication's record since the fabrication preparation until its installation and its two years operating condition history such as operating temperature and pressure records.

The visual observation performed together with penetrant testing through the entire CW joint where the leak occurred. These two methods were intended to characterize and found all surface flaw indications.

Positive material identification using portable XRF analyzer was performed for quick chemical analysis of shell's material. This method applied both for BM and WM.

Hardness measurement using brinell portable hardness tester was applied for BM, HAZ and WM. There were 12 testing points for 360 degrees CW where for each point three readings were taken and the average found.

Conventional ultrasonic testing was performed using longitudinal wave normal beam and shear wave angle beam transducers from three orientations, two orientation sides that perpendicular to the WM and one orientation along the WM. For shear wave, two angles were used, 45 and 60 degree angle beam transducers. Ultrasonic testing was intended to find volumetric flaw indications that exist in vessel shell's weld joint.

### 2.2 Results

Visual observation found a leaky transverse crack with 40 mm in length on CW 2 as shown in Fig. 1 below. The crack position was 100 mm in distance after south side thermo well nozzle (180$^o$ orientation). This result agreed with the result from infrared camera observation and explosive gas level measurement that showed the area around the south side thermo well nozzle suffered leakage. By looking the crack characteristic, it is obvious that hoop stress was the major contribution for crack propagation. For TWPV which is applied internal pressure, the maximum hoop stress occurs on ID surface. Then it can be deduced that crack start from ID surface of CW joint. Maximum hoop stress, high temperature and direct contact with hydrogen gas are the major factors for crack initiation and propagation.

Liquid penetrant testing found another crack indication on HAZ of CW2 at 100$^o$ orientation with 20 mm in length. This crack had irregular characteristic and completely different with the leakage one. This indication disappeared after grinding up to 4 mm depth from surface.

Positive material identification using XRF method shows that the WM and BM are made from 2.25Cr–1Mo steel. This result agreed with the vessel's material specification and it is shown in Table 2.

As outlined in introduction above, hardness is the primary indication to assess the WM condition for hydrogen service. The hardness measurement was performed very carefully on shell's vessel because the repair procedure is made based on hardness value. Table 3 lists the average BHN in different zones of the pressure vessel on its OD surface.

**Table 2** Chemical composition analysis of the shell material (wt %)

| Sample | Mn | Cr | Mo | Cu | Ni | V |
|---|---|---|---|---|---|---|
| BM | 0.35 | 2.27 | 1.02 | 0.10 | 0.11 | 0.01 |
| WM | 0.33 | 2.24 | 0.99 | 0.08 | 0.12 | 0.01 |

**Table 3** Average hardness number of different zones of the vessel

| Zone | BM | WM | HAZ |
|---|---|---|---|
| BHN | 140 | 290 | 240 |

Conventional ultrasonic testing found one linear indication around the mid-wall of the shell thickness as shown in Table 4 below. This linear indication amplitude reached 30 % height of standard distance amplitude correction (DAC) curve using basic calibration block with same material and thickness with the vessel's shell. Linear indication sizing performed using 6 dB drop technique.

**Table 4** Linear indication characteristic found by ultrasonic test

| Position | Length (mm) | Height (mm) | Depth from surface (mm) |
|---|---|---|---|
| 30$^o$ | 30 | 5 | 43 |

The manufacturing records indicated that the CW2 was subjected to local PWHT using heating elements around the OD of the vessel. The local PWHT was performed for 5 hours at 595$^o$C.

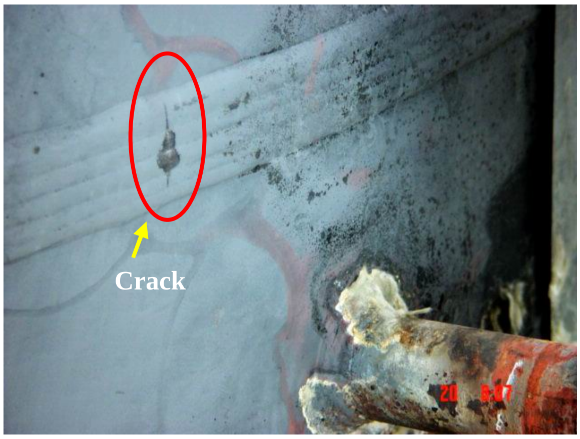



**Fig. 1** A leaky transverse crack position on CW 2

## 3. Repair Procedures and Results

### 3.1 Procedures

The repair procedure flow chart is shown in Fig. 2 below.

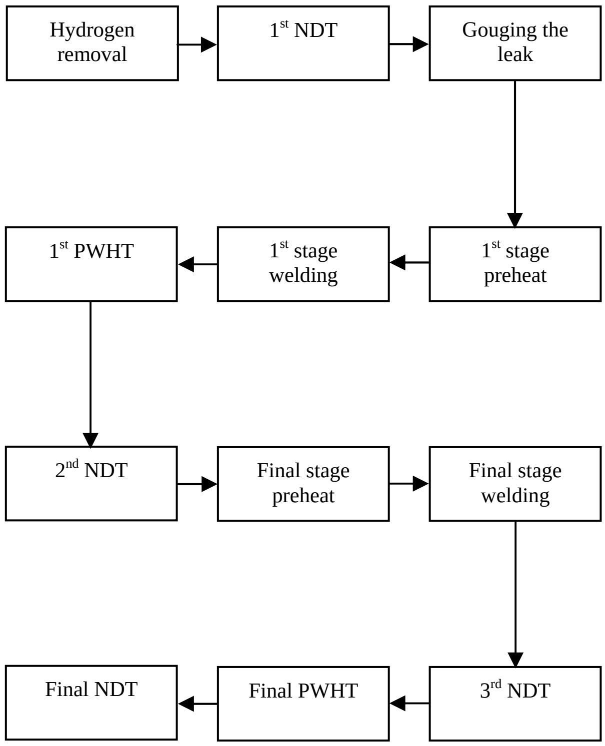



**Fig. 2** Flow chart of repair procedure

### 3.2 Results

Hydrogen removal is intended to remove absorbed hydrogen atoms in CW 2. This is done by using heating elements which were attached from OD surface of the vessel. The CW 2 temperature then increased into 400 $^o$C and held in this temperature for 5 hours and finally decreased into 200 °C. In this temperature, leak's gouging was conducted and to assure there was no crack left during leak's gouging, high temperature penetrant testing was applied.

The 1st preheat was performed by increasing the temperature of CW 2 into 225 °C ± 10 °C. The 1st stage welding was conducted using SMAW and fill the leak's gouging result up to 50 mm height of weld deposit (half the shell thickness). After that PWHT was applied to this repair zone by increasing temperature into 450 °C ± 10 °C and held for 4 hours, then into 720 °C ± 10 °C and held for 3 hours, finally the temperature decreased into 200 °C. In order to attain the uniform temperature distribution on repair zone, 4 thermocouples were installed on it.

The final preheat was performed by increasing the temperature of CW 2 into 250 °C ± 10 °C. The final stage welding was performed up to full thickness of the shell. Then, the final PWHT was applied to this repair zone by increasing temperature into 740 °C ± 10 °C (for WM) and 650 °C ± 10 °C (for BM) for 4 hours, and finally the temperature decreased into 200 °C.

Non destructive testing such as hardness testing, high temperature penetrant testing, magnetic particle testing, conventional ultrasonic testing, and TOFD were applied during and after weld repair.

Final hardness test result is presented in Table 5 while the non destructive test results in Table 6. Fig. 3 shows the shell repair after weld up to 50 mm and its ToFD result respectively.

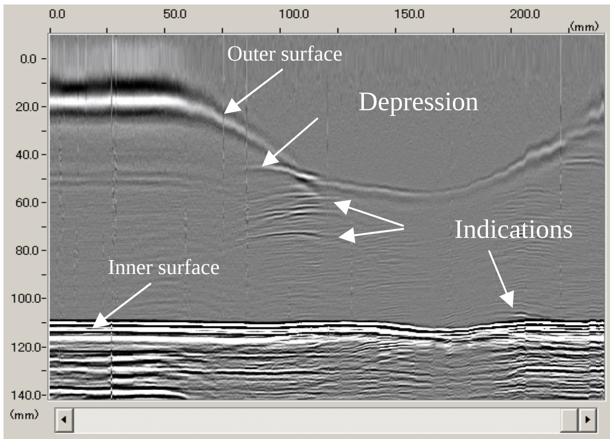
**Table 5** Average hardness number of different zones of the vessel after repair

| Zone | BM | WM | HAZ |
|---|---|---|---|
| BHN | 140 | 170 | 175 |

**Table 6** Non destructive result during vessel repair

| Stage | PT | MT | UT | ToFD |
|---|---|---|---|---|
| 1st NDT | --- | --- | Accepted | --- |
| 2nd NDT | Accepted | Accepted | --- | Accepted |
| 3rd NDT | Accepted | --- | Accepted | Accepted |


(a)




(b)

**Fig. 3** (a). Shell repair (b) ToFD result after 1st PWHT stage

## 4. On-Stream Assessment

HTCUT performed after one year since the repair time. This testing conducted on-stream to vessel with outer surface temperature reach 240 °C. The gain setting for this testing was 80-85 dB. In this gain range, this testing is not suitable for detection of defects that may occur within the outer 0-25 mm range due to high level noise during testing. The accuracy of the defect's depth measurement is likely within ± 10% accurate meanwhile the height of defect is greater than actual height.

High temperature ultrasonic ToFD was also performed in order to solve the weaknesses of HTCUT for estimating the defect's height. Same as conventional one, high temperature ToFD is also not suitable for detection of subsurface defect and give high level noise up to 20 mm due to gain adjustment as shown in Fig. 5 below.

HTCUT and high temperature ToFD results are shown that all indications found were acceptable and showed that CW2 in good condition. The results are shown in Fig. 4 and 5 respectively. The indication found from HTCUT is summarized in Table 7.

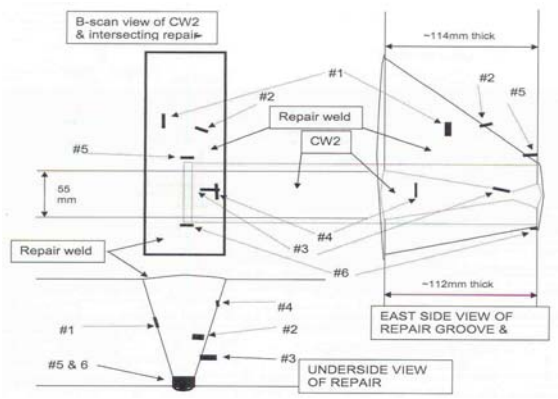



**Fig. 4** Indications found by high temperature conventional ultrasonic

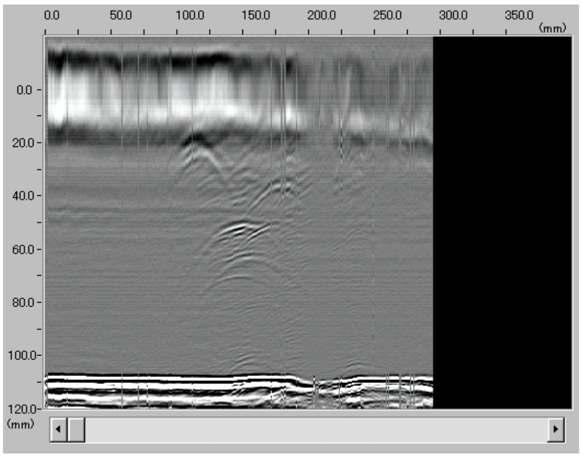



**Fig. 5** Indications found by high temperature ToFD

**Table 7** Detail of indications found by HTCUT

| Indication no. | Depth (mm) | Height (mm) |
|---|---|---|
| #1 | 50 | 2 |
| #2 | 60 | 4 |
| #3 | 75 | 10 |
| #4 | 24 | 3 |
| #5 | ID Surface | < 3 |
| #6 | ID Surface | < 6 |

## 5. Discussion

AC had failed after 2 years in operation. The failure occurred was a leaky transverse crack on CW2 which had applied local PWHT during vessel fabrication. The similar failure with short operating time after put in service also happen in ammonia related facilities such as in heat exchanger. The repair had also been done using temper bead welding techniques combined with local PWHT such as outlined by Firt (6).

Hardness test from OD surface shown that CW2 around the leakage zone have hardness value above the maximum value after PWHT i.e. more than 250 VHN according to NACE standard MR0175 and API 942 (4, 5). This is most caused by improper local PWHT during fabrication, such as:

1. Local PWHT using heating elements only applied from one shell surface (usually from OD surface).
2. Lack of thermocouple amount to control uniformity of temperature during PWHT.
3. Insufficient temperature and or insufficient holding time during PWHT.

The synthesis gas contained in this TWPV is rich with hydrogen gas with operating temperature around 300 $^{o}$C. With improper local PWHT applied, not all bainite structure transformed into tempered bainite and residual stress reduce significantly as shown by hardness results. This makes the vessel still has high sensitivity to high temperature HA and failure occurred in two years operating time of this vessel.

During repair, re-PWHT had applied on CW2 in order to decrease the sensitivity to high temperature HA by transformed all bainite structure into tempered bainite and also decrease the residual stress. For leakage zone, two times PWHT had applied, those were after weld up to 50 mm and after weld into full thickness 110 mm. The PWHT temperature 740 $^{o}$C ± 10 $^{o}$C was higher than ASME recommendation on 677 $^{o}$C (7). This is because from simulation using carbon steel plate 100 mm thickness found the different temperature of 100 $^{o}$C–120 $^{o}$C between two contact and non contact surfaces with heating elements. Because the repair only attach the heating elements from OD surface of shell, higher temperature with two stages PWHT was intended to reach the ID surface of shell because this surface has direct contact with synthetic gas and decrease its sensitivity to high temperature HA.

## 6. Conclusion

The failure of this TWPV is caused by HA. WM is critical location due to various microstructures and high level of residual stresses that created during welding. The tendency for failure caused by HA can be decreased with PWHT if it is done properly. Proper

PWHT can decrease the residual stress level inside weldment. Repair procedure that had been performed is based on this principle. From the on-stream vessel's assessment after one year since its repairing time using HTCUT and high temperature ToFD showed the CW2 in good condition. This successful repair procedure is very dependent on very controlled and careful step during repair stage.

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