Cracking of a Closing Weld in a Secondary Autothermal Reformer in a Mega Methanol Plant

After six years of operation a major leak was detected in May 2010 in a very large water jacketed Autothermal Secondary Reformer (ATR) made to ASME Section VIII Div1 in the Atlas 5000 MT/d methanol plant in Trinidad. The cracked weld was a “closing weld” that had been locally post weld heat treated. Inspection revealed that the cracking was present around the entire circumference of the vessel on the inside. Metallurgical examination revealed that the cracking had initiated at the inside of the vessel as a result of CO-CO$_2$-H stress corrosion cracking, primarily in the heat affected zone and weld. This case is the first known ATR or secondary reformer to crack as a result of stress corrosion cracking at a locally post weld heat treated closing weld.

D M Firth, Q Rowson, A Saunders-Tack, C Thomas, K Lichti and J Soltis
Quest Integrity NZL Limited

P Tait
Methanex Global

M Wei, R Dookran, S Ramjattan and W Boodram
Methanex Trinidad

Introduction

A significant leak at a 686 mm (27 in) through wall crack was detected in a circumferential shell to head weld of the Autothermal Secondary Reformer (ATR) in the 5000 MT/d Methanex Atlas methanol plant in Trinidad in May 2010. The Atlas plant was commissioned in 2004 and the ATR has run since that time, apart from planned and unplanned plant outages.

The ATR operates in a similar manner to a secondary reformer in an ammonia plant, except that oxygen is used rather than air. It is refractory lined and water cooled. The ATR is shown in Figure 1 and schematically in Figure 2. It was designed and built to ASME Section VIII Div 1 [1].

The leak in the shell/head circumferential weld occurred within the water jacket. Luckily a fire did not occur. Three other leaks had previously occurred at thermowell nozzles. The first after two years of operation, the second after four years of operation, and the third after one of operation. A fourth leak occurred at a pressure tapping after three years of operation. In each of these cases cracking occurred at a either a branch connection weld or a pipe to flange weld in the 50 mm (2 in) Sch80 piping. One event resulted in a significant fire.
A detailed investigation was carried out in 2010 to determine the following:

1. How extensive was the cracking?
2. What was the cause of cracking?
3. Was the cracking related to the operation of the vessel?
4. Could the cracking have been predicted and detected by risk based inspection?
5. How close was the vessel to catastrophic failure?
6. Was the vessel designed and made in accordance with ASME Section VIII Div 1?
7. If the vessel was made to code; is the code adequate for the vessel?

The findings are discussed in this paper. The repair and inspection strategies and the post-repair operation of the vessel post repairs are NOT covered in this paper.

The ATR is 22 m (72 ft) tall, has an internal diameter of 5.58 m (18 ft) a shell wall thickness of 82 mm (3¼ in) and a head thickness of 92 mm (3¾ in). It is internally insulted with 3 layers of brick refractory of differing grades, for a total thickness of 270 mm (10½ in). The vessel shell was made in three major pieces. The closing weld locations which were locally post weld heat treated (PWHT) are shown in Figure 2. Seven thermo wells (T1-T7) are present to monitor the temperature of the top of the bed. One thermo well (T8) is in the bottom of the catalyst bed, as shown in Figure 2.

The ATR was made from 1 ¼ Cr ½ Mo steel (Grade 11) [2]. This was used to ensure high temperature hydrogen and creep damage would not occur if the vessel was operated without water
cooling. A Brinell hardness of <233 HB was specified for the vessel, presumably, to prevent the risk of hydrogen embrittlement (HE). The Vickers hardness of <250 HV (<235HB) is the maximum limit in NACE standard MR-0175 to prevent HE [3].

Syngas from the primary reformer and the oxygen enter a burner in the top of the ATR vessel. The gas, at 1300°C (2370°F), passes through a catalyst bed and a support bed of alumina balls, passes through a refractory support cone before exiting via two transfer lines to waste heat boilers. The exiting gas is nominally 27% H₂O, 16% CO, 5.7% CO₂, 1.5% CH₄ and 49% H₂ at 34 barg (490 psig) and 985°C (1800°F). The dew point for this gas mixture is approximately 177°C (350°F).

A review indicated that there had been no significant cycling or abnormal conditions in the operation conditions over the six years of service, other than the cycling associated with shutdowns which are very infrequent.

Although the vessel was designed to be able to operate without cooling, a water jacket is present around the bottom head and up the parallel walls to the start of the top domed head. Cooling water, at about 60°C (140°F), enters at the bottom of this jacket and is also sprayed over the unjacketed top head of the vessel. The bottom water inlet is designed to induce circular flow to prevent the formation of deposits in the bottom of the jacket. As a result the vessel wall is cooler at the bottom than at the top.

Condensation will occur on the inside of the shell. To prevent corrosion from carbonic acid condensate the inside wall of the vessel was designed and specified to be coated with an acid resistant coating.

**Cracking Seen**

Major cracking was detected when gas was rapidly blowing out water from the water jacket. A window was cut in the jacket, and a 686 mm (27 in) long through-wall crack was found at the edge of the circumferential weld at lower head to shell as shown in Figure 3.

Additional windows were cut in the water jacket to determine the extent of the cracks. Initial manual ultrasonic (UT) inspection indicated that cracks, typically ½ the wall thickness deep, were present in a number of locations around the ID circumference. Some areas were free of cracking.

A complete ring was removed from the water jacket to allow access to the bottom closing weld and a detailed time of flight diffraction (TOFD) and phased array UT inspection was carried out. Cracks were present, parallel to the weld, around the entire circumference. The average depth of cracking was approximately ½ wall thickness, 40 mm (1⅝ in) with a minimum depth of 17 mm (⅝ in). Cracks were present in both shell and head side heat affected zones (HAZ) of the weld. The extent of cracks is shown schematically in Figure 4. In addition, intermittent transverse weld cracks initiating at the ID were detected. The advanced UT inspection showed that the manual shear wave testing carried out did not accurately size the defect present.

![Figure 3 - Outside of the crack at the edge of the lower closing weld.](image)

Samples were removed to determine the extent of cracks and to carry out a metallurgical assessment. Examination of the samples revealed that cracks had initiated at both the shell side and the head side toe of the circumferential weld on the ID. These cracks had initially propagated into the HAZ and then nearly perpendicularly to the
surface in the weld, shown in Figure 5. In addition, transverse cracks were present in the weld. No significant cracking was present in the parent material outside of the HAZ.

The cracks were all typical of transgranular stress corrosion cracking, see Figure 6. The microstructure of the weld HAZ etched readily and was typical of untempered martensite. The hardness of the HAZ varied up to 380 HV, which is significantly harder than the maximum specification of 233 HB (250 HV). Hardness values in this range promote very high residual stresses.

Investigations a couple of years earlier of the two leaks at that time – one at a thermowell and the other at a pressure tapping also indicated that the cracking was typical of CO-CO₂ stress corrosion at welds that had not been adequately PWHT.

Numerous welds on the vessel, including sections of longitudinal welds within the water jacketed area, were inspected by manual UT and UT phased array. Particular attention was paid to the top closing weld. Crack like defect indications were reported to be present in the following areas:

- The bottom head segment welds. These were subsequently found to be refractory bracket anchors.

The inner surface of the vessel was uniformly pitted due to corrosion. Corrosion had occurred in the weld region with a classic “Messa” morphology. This corrosion is typical of CO/CO₂ corrosion. No evidence was found of any acid resistant coating having been applied to the inner wall of the vessel. In addition, analysis of the corrosion products on a crack revealed the presence of iron carbonate.

![Figure 4 - Cross section of shell at the bottom closing weld showing the proportion of cracking (red) in the 82mm wall thickness](image1)

![Figure 5 - Schematic diagram of the crack cross section](image2)

![Figure 6 - Cracks initiated at the ID of the vessel in the HAZ](image3)
In the top head segment weld to top closing weld in two locations. These were subsequently monitored and re-inspected. The defects were found to be minor welding defects.

The lack of accuracy of the results of the initial inspections indicated the need to have detailed procedures, very skilled and experienced NDT operators and to carry out repeat inspections to ensure a high total confidence in results.

**Cracking Mechanism**

The cracking observed is consistent with CO/CO₂ stress corrosion cracking (SCC) [4]. CO/CO₂ SCC is known to affect carbon steel and occurs when there is a sufficient quantity of CO and CO₂ present with a free water phase. Like all SCC processes, cracking only occurs when the combination of environment, material susceptibility, and stress fall within a coincident range.

CO/CO₂ SCC in low alloy steel occurs in a narrow band of local conditions at temperatures between 60°C (140°F) and 175°C (347°F) [5]. The stress is provided as a result of vessel residual welding stresses. It is also known that the susceptibility to cracking is significantly increased in the presence of oxygen, but the presence of oxygen is unlikely in the case of an ATR.

Incidences of CO/CO₂ SCC in industry are not widespread largely due to the unique nature of the chemical environment required for cracking. The refining industry rarely experiences these conditions so few cases of CO/CO₂ SCC have been reported [6]. On the other hand, CO/CO₂ corrosion and SCC are on going risks in methanol and ammonia industries where there are high levels of wet CO/CO₂. A failure in a methanol loop was reported at ENIP, Algeria in 2007 [7]. In this particular case evidence of stress corrosion cracking was seen at the bottom of pits in the parent material. The failure occurred below the dew point, approximately 130°C (270°F). This temperature is similar to that of the shell in the ATR at bottom closing circumferential.

CO₂ corrosion is often experienced in conjunction with CO/CO₂ SCC and was observed on the samples taken from the inside of the ATR. CO₂ dissolves in water to form carbonic acid, which reacts with carbon steel and low alloy steel.

The rate of corrosion is strongly dependent on temperature, CO₂ partial pressure, pH and flow rate in the liquid/gas. At temperatures above 80°C (176°F) there is a propensity to form a protective iron carbonate film, which limits the subsequent corrosion rate. In addition, where flow rates are low, the protective corrosion products are not removed and hence corrosion rates are also lower.

CO/CO₂ SCC is likely to occur when there is a high stress and conditions are close to the active/passive boundary. In CO₂ dominated systems the active/passive boundary is dependent on a variety of parameters (pH, CO₂ partial pressure, temperature and the presence of other chemical species such as organic acids). Under critical conditions of inhibition/active corrosion, microscopic electrochemical cells are created, and in the areas where corrosion occurs hydrogen is generated and some of the hydrogen absorbs into the steel.

When the amount of absorbed hydrogen in steel is above a critical level, HE cracking can occur if the hardness is excessive and the temperature is suitable. HE is not likely to occur above 82°C (180°F) and does not occur above 149°C (300°F) [8]. Due to the conditions in SCC it is probable the hydrogen can only be concentrated above critical limits in microscopic areas (i.e. on thousands of a millimeter scale). As a result the rate of cracking is related to the rate of hydrogen generation, which is then associated with the rate of the corrosion in the crack. The depth of corrosion seen was not large and the period of 6 years for the cracking to occur is considered conceivable.

The possibility of molecular H₂ in the process stream contribution to cracking via HE was also considered. For molecular H₂ to contribute to the
cracking, the H₂ has to dissociate to H⁺ and be present in the steel at concentrations greater than 3 ppm. At the reported H₂ partial pressure and operational temperature, dissociation will be very low and the equilibrium partial pressure will not result in concentrations approaching 3 ppm. Hence, HE from H₂ in the process stream is unlikely.

The cracking can be termed as being CO-CO₂-H stress corrosion cracking.

The highest risk of cracking occurs when the following conditions are all present:

- High hardness i.e. >>250 HV (hardness up to 380 HV was found in the HAZ of the cracked closing weld in the ATR).
- High stresses (the high hardness of 380 HV indicates the PWHT was not successful).
- Condensed water and high partial pressures of CO and CO₂ (indicated by the observed corrosion mechanisms).
- Temperature of about 60 to 100°C (140 to 210°F) (the weld is water cooled with the water inlet close to the weld).

Conditions for CO-CO₂-H cracking at the bottom closing circumferential weld were optimal. In addition, the condition at the cracked thermowell nozzles and the pressure tapping were also optimal as they are all water cooled and the local PWHT was not effective in reducing the hardness and local high levels of residual stress.

It is assumed that the metallurgical condition of the top closing weld is identical to the bottom closing weld. At the top weld location the water in the jacket is hotter, likely near boiling, and the heat transfer rate through the refractory is likely higher due to the higher process gas temperature than at the bottom. As a result the inner wall temperature in the top weld is above the critical region for cracking. Conversely, at the bottom the water is near 60°C (140°F) and the heat transfer rate through the refractory is lower due to a lower process gas temperature. However, there is a very low possibility of cracking in this weld during a shutdown if the conditions are suitable.

It is probable that the other seam welds in the vessel did not crack as they had all been fully furnace PWHTed. This conclusion is supported by phased array UT and hardness results on random welds which did not reveal any abnormal condition.

**Closing Welds with local PWHT**

The ATR was made in three major pieces that were each furnace PWHT. These were joined with closing welds that were locally PWHTed, as shown in Figure 7. Closing welds with local PWHT have been a major issue in the reliability of thick walled pressure equipment operating in hydrogen and ammonia environments. Cracking at closing welds has resulted in serious cracks in at least two superheaters, three ammonia converters and three waste heat boilers [9][10][11][12][13][14][15]. At the time the cracks in the ATR were observed, a repair was being carried out on cracked closing welds in the ammonia converter of a neighboring ammonia plant. The cracks in the ATR is possibly one of the first major “failures” due to cracking at locally PWHTed closing welds to be seen in a methanol plant.

![Figure 7 - The original local heat treatment carried out on closing weld of the ATR (ASME VIII Div 1)](image)

The local PWHT of the closing welds was for 4 hours at 690°C ± 20°C (1274°F ± 68°F). Five bolt type thermocouples were used on the OD. The
PWHT records showed that these all read the same until the end of the soak. However, 40 minutes after the soak, they varied by 40°C (104°F).

When a local PWHT of a weld is carried out ASME Section VIII Div 1 requires the volume of the weld +50 mm (2 in) either side it to be at the required soak temperature. The code also requires the portion of the vessel outside the soak band to be protected so that the temperature gradient is not harmful.

The heating carried out for this ATR was modeled assuming the heating band was 0.75 m (30 in) wide (estimated from Figure 7). Figure 8 shows that the temperature at the ID edge of the weld could reach above 670°C (1238°F) if the OD was at 690°C (1274°F). This difference is just within the tolerance specified for the temperature range. In addition, if the heating band had been shorter, the heating could not physically have been done to the code as the temperature of the ID would not be within the 690°C ± 20°C (1274°F ± 68°F). It is also important to note that due to the heat flux the heating elements would have to be considerably hotter than 690°C (1274°F). Thermocouple reading the metal temperature would have to be isolated from the heating pads to read the correct result.

Modeling of the thermally induced stresses due to the thermal gradients showed that the vessel wall would be at yield during the heat treatment and as result very high residual stresses could be produced and the thermally induced stresses could be harmful. This is not in accordance with the code requirement.

Hardness measurements on the OD of the weld/HAZ were in excess of the specified 233HB (250HV). Weld procedure qualification tests showed that a PWHT at 690°C (1274°F) would drop the hardness in the weld HAZ to less than 250HV. Therefore it was concluded that the temperature did not reach 690°C (1274°F) in the metal as indicated in the records. This is primarily due to the fact that measurement thermocouples were also used to control the temperature. In addition, there was likely to be a high difference in the average metal temperature during the PWHT as shown by the variation in the temperature after the soak was completed.

![Figure 8 – Model of thermal profile in region of local PWHT assuming the surface temperature was constant at 690°C (1274°F)](image)

Heat treatment of thick-walled vessels is strongly recommended to be done in accordance with BS5500 [16] or WRC Bulletin 452 [17] rather than ASME VIII Div 1. These require a significantly wider heating band of width 5√Re (where R is radius and e is wall thickness) and insulation band of a width of 10√Re. In addition, the temperature at the edge of the outer insulation has to be greater than half the target heat treatment temperature. This would require the heat treatment approach to have looked like Figure 9.

The thermowell and pressure tapping nozzles were locally PWHTed after they were attached to the vessel. This PWHT was probably very inadequate as the welds were close to the thick wall of the vessel and it is highly unlikely that a small heating element could heat the weld to the required temperature with the huge heat sink of the vessel wall. If these had been heat treated to the requirements of BS 5500 the entire circumference of the vessel would be required to be heated as shown in Figure 9.
How Close was the Vessel to Catastrophic Failure?

An engineering critical assessment was carried out in accordance with BS7910/API 579 [18, 19] on defects in cracked closing weld. This showed, for a crack 360° around the ID that the maximum allowable defect size at the working pressure of 36barg (520psi) (stress 63MPa (9.13 Ksi)) in weld material was as follows:

- 18.5 mm (0.728 in) deep if no PWHT had been carried out and the residual stress was at yield.
- 49 mm (1.9 in) deep if the PWHT was successfully completed.

The minimum actual crack depth was 17 mm (0.669 in) and the average actual depth was about 40 mm (1.575 in).

The maximum allowable through thickness defects at the working pressure was calculated to be 521 mm (20.5 in). The actual length of the leak at the outer surface was 686 mm (27 in)!

This assessment shows that the crack size present was well in excess of the code allowable defects size. This assessment does not however, predict the failure size but does indicate that the vessel had a high risk of catastrophically failing and there was no confidence that a leak before break would have occurred. If a break had occurred the consequences would have been enormous as the pressure forces were about 30 times higher than the weight of the vessel.

Root Cause

The cracks in the closing weld and the thermowell nozzles occurred by CO-CO₂-H stress corrosion cracking. The following are the key factors of the cause of the cracking:

- Inadequate PWHT of the closing weld leaving excessively high hardness in the weld HAZ and high residual stress.
- The design of the vessel to operate with the wall temperature in the critical range of 60 to 100°C (140 to 212°F) where condensation, CO/CO₂ corrosion and CO-CO₂-H SCC can occur.

The root cause is related to the design specification of the vessel and the QA/QC in the fabrication stage. The failure was not caused by any operational issues.

Could this Incident have been Prevented?

As indicated above, the issues with closing welds in ammonia plant have been well known for some time, yet designers and fabricators continue to make vessels to ASME Section VIII Div 1 rather than other codes such as BS5500. The decision is primarily due to construction cost. Even so, the issue has not been previously identified in methanol plants.

When a risk based assessment (RBA) is carried out on a methanol plant, CO₂ corrosion is identified as a major risk in the process equipment and there is also a risk of CO/CO₂ SCC [21]. However, on the previous RBA carried out, that plant did not have an ATR and as a result, this was type of vessel in this application had not been previously assessed.
An RBA had not been carried out on the Atlas plant at the time of the incident and secondary reformers are not renowned for cracking at closing welds. However, a previous RBA of ammonia plant had identified cracking at closing welds as a risk in a secondary converter. Even if RBA had been carried out on the vessel it is probable that any inspection carried out would have been at top closing weld due to ease of access as it would have been assumed that the operating conditions would have been similar to those in the bottom closing weld. Phased Array or TOFD of top closing weld would have been recommended and no cracking would have been found as the weld was not cracked. The only way to adequately monitor the condition of the bottom closing weld would be to cut windows in the water jacket and carry out Phased Array or TOFD.

The failure has indicated the short fall in the specification of new equipment. The Atlas plant was purchased by its current owners during plant construction after the vessels were ordered and as a result had no input into the original vessel specification. It has emphasized the need to the following:

1. Ensure the appropriate codes and specifications are used in the design and fabrication of equipment. In future the option of using closing welds with local a PWHT on thick wall walled vessels will be critically reviewed by Methanex.
2. The need to carry out RBA of the plant to identify the major risks and to focus inspection accordingly. For key items this should be done as part of the design so that the vessels can be designed so that they can be suitably fabricated and be inspected without having to carry out major modification to the equipment.
3. The need to review and audit manufacturer’s procedures. For example, carrying out a local PWHT on a thick walled vessel with 5 thermocouples is severely lacking (typically >25 thermocouples should be required).

The previous failures of the thermowells and pressure taps should have provided an indicator that there was a possibility that other failures could occur. If a root cause analysis had been carried out and a RBA of the associated equipment had been performed, the presence of the closing welds in the vessel that received a local PWHT should have been identified and should have been inspected. This emphasizes the benefits of carrying out detailed analysis of any failure and carrying out RBA.

Conclusions

1. The ATR was close to catastrophically failing in May 2010. The cracks present in the bottom closing weld were around the complete circumference of the vessel and through-wall for over 680 mm (27 in). Assessment using the BS7910 code indicated that the defect was greater in size than the allowable to prevent catastrophic failure.
2. The cracking occurred as a result of CO-CO₂-H stress corrosion cracking. In the region at and ahead of a crack tip, the crack propagation is predominantly hydrogen embrittlement. The CO/CO₂ corrosion in the cracks is the source of hydrogen. This type of cracking occurs when high stresses, high hardness, temperature of 60 to 100°C (140 to 212°F) and condensed CO/CO₂ are present. The cracked weld was operating in the optimum conditions for this corrosion mechanism.
3. The top closing weld was not cracked probably due to a higher operating temperature than the bottom closing weld.
4. The failure occurred at a closing weld that had been given a local PWHT designed to ASME Section VIII Div 1.
5. Numerous other failures have occurred in ammonia industry at closing welds NH₃/H₂ environment. Typically the issues occur within the first 4-8 years of operation. This failure occurred in 6 years.
6. ASME Section VIII Div 1 requirements for the local PWHT are not ideal and can result in a lack of attaining the specified temperature and can introduce large residual harmful stresses. It is strongly recommended that more
stringent codes such as BS5500 or WRC bulletin 452 should be specified for heat treatment of any thick walled vessel.

7. The cracked closing weld was not locally PWHTed to the manufacturers specified 690°C (1274°F) in accordance with ASME VIII Div 1. This conclusion is shown by the following:
   a. Hardness values in excess of 300HV indicating that some parts of the weld were never heated to the required temperature.
   b. Finite element modeling indicated the inside of the weld would be 20°C (68°F) colder than the outside of the vessel resulting in high thermal stresses in excess of the material’s yield strength.
   c. The small number of thermocouples used showed a variation of 40°C (104°F) once the heating was stopped indicating that there was likely to be a high difference in the average metal temperature during the PWHT.

8. The vessel was not heat treated to the design requirements as hardness levels well in excess of the specified 233HB were present

9. The vessel was designed so that the shell temperature was below the dew point. An acid resistant coating was designed to be applied to prevent corrosion. There was no evidence of this coating being applied.

Addendum

Remedial works were performed and the ATR was restored and put into service six weeks after the major leak occurred.

References

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