

Hydrogen Induced Cracking of Low Strength Steels in Geothermal Fluids

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ABSTRACT

Typically, low strength steels and annealed stainless steels are specified for geothermal energy applications because of the risk of Sulfide induced Stress Corrosion Cracking (SSCC) and Hydrogen Induced Cracking (HIC) in the presence of H₂S containing fluids. Recent experience has demonstrated the risk of SSCC and HIC, sometimes known as Hydrogen Embrittlement (HE), of low strength steels subject to high residual stress derived from fabrication techniques. Unexpected cracking, discovered in two geothermal pressure vessels, was attributed to HE cracking in the welds. Fitness-for-purpose assessments completed on the two vessels found one suitable for operation, with a temporary repair, while a replacement vessel was being fabricated but the second required immediate removal from service for repair. The cause of cracking was attributed to use of submerged arc welding leading to high residual stress in the welds of the 32 mm thick vessel walls. The vessels were made in compliance with the ASME VIII Div 1 design code that allows vessels up to 32 mm wall thickness to be fabricated without Post Weld Heat Treatment. The vessels also met the requirements of NACE MR1075 for resistance to sulfide stress cracking, having hardness less than HRC 22. The experience gained suggests some general “rules of thumb” for avoidance of HE cracking in vessels used for geothermal service:

1. The number of weld passes must be as many as the wall thickness in millimeters ie for a 32 mm wall at least 32 passes should be applied.
2. All vessels should be stress relieved unless it can be proven that this is not necessary by the manufacturer for the welding procedure chosen.
3. Care should be taken to ensure any closing welds are correctly stress relieved.

1. INTRODUCTION

Historically, selection of materials for pressure vessels exposed to mixtures of geothermal steam and brine with high levels of hydrogen sulfide have been required to comply with NACE International standard NACE MR0175 (last published in 2003) in the same manner as for sour gas environments in the petrochemical industry. This standard has now been replaced by a joint NACE/ISO standard that is published in 3 parts, NACE MR0175/ISO 15156-1:2001(E), NACE MR0175/ISO 15156-2:2003(E) and NACE MR0175/ISO 15156-3:2003(E).

The new joint international standard builds on guidelines that were present in the previous NACE standard with enhancements from European standards with similar concerns, Milliams and Tuttle, 2003. A common premise for the NACE standard which was initially released in 1975 has been that carbon steels having hardness less than Rockwell C 22 (< 22 HRC) will in most cases have

immunity to Sulfide Stress Corrosion Cracking (SSCC) and Hydrogen Embrittlement (HE). A caveat that has also been present since before 1975 is the need for design stresses less than yield stress.

These guidelines were not simply “rules of thumb” but were based on laboratory measurement and documented experience in the oil and gas industry, Milliams and Tuttle, 2003. The applicability of these “rules of thumb” was demonstrated for geothermal applications for example by Marshall and Tombs, 1969. This demonstration was done for relatively low H₂S concentrations that would normally not be of major concern to oil and gas industry materials selection experts but in the absence of significant hydrocarbon it is believed that the standard should be strictly applied for any H₂S containing geothermal environments.

Two pressure vessels made using low carbon steel which met the requirements of the NACE MR0175 standard and had hardness less than 22 HRC (248 HV) were found to be cracked after 2 and 3 years of service in a geothermal steam/brine environment and a geothermal steam environment respectively. The cracks were associated with circumferential seam and stake welds in one vessel and with nozzle welds in the other.

In each case an assessment of the cracking propensity was carried out: cracking distribution, depth of cracking, and metallographic examination. Defect assessments defined fitness-for-purpose to allow continued operation while repairs and replacements were planned. A sample of cracked weld material was available from one of the vessels. This paper describes the root cause of the cracking including the cracking distributions, engineering critical defect assessments and material properties that led to the observed cracking and procedures specified to repair the vessels.

2. BRINE ACCUMULATOR AND STEAM PURIFIER VESSEL CRACKING

In December 2002 severe cracking was detected in a brine accumulator in a geothermal power station after 2 years of service, see Figure 1. In the following year, severe cracking was detected in a steam purifier of the same power station, see Figure 2. The station was commissioned in 2000. Both vessels were critical to the operation of the station.



Figure 1: View of Brine Accumulator Vessel.



Figure 2: View of Steam Purifier Vessel

2.1 Vessel Operations

The brine accumulator takes separated water from two vertical separator vessels at a separator station located in the steam field. Relatively short steam and brine pipelines take the fluids from the separator station to the power station. The steam passes through the steam purifier located outside the power house just before the steam turbine.

The temperature of the separated brine/steam in the brine accumulator is 212°C at saturation pressure, while the steam entering the purifier is at a temperature of 209°C and operating pressure of 19.5 barg.

The brine in the brine accumulator is a low chloride fluid, around 2,700 mg/kg, with a low tendency for silica scaling at the temperatures encountered in the brine accumulator. The brine is near neutral to slightly alkaline pH at temperature

The purifier is intended to remove dissolved and suspended solids from the steam by a small amount of condensation, encouraged by injection of cold condensate, the design consists of internal screens and drains to achieve the required purification. The steam/condensate had a partial pressure of H₂S of 0.25 kPa at a pH of 5.9 (neutral pH is 5.6).

The brine and steam are both expected to form iron sulfides and iron oxides on the surface of carbon steel components that block the corrosive environments from the metal surface. The brine is expected to precipitate thin silica scales over time.

The vessels experience a planned annual shutdown when the station undergoes preventative maintenance and occasional short duration planned and unplanned outages.

2.2 Vessel Design and Materials

The vessels were designed to ASME VIII Div 1.

Materials selection required compliance with NACE MR0175 for both of the vessels. A plain carbon steel to ASME SA 516 Grade 70 was used. Manway and relief nozzles of the purifier were to SA 106 Grade B.

NACE standard MR0175 specifies, that for carbon steels in the normalised and welded condition, that the steels should have a hardness lower than 22 HRC, (equivalent to 248 HV). The standard does not specifically require a Post Weld Heat Treatment (PWHT) for stress relief unless the steel used has been cold worked, reference is made to the requirements of ASME VIII Div 1 in this standard.

ASME VIII Div 1 pressure vessel code only requires vessels with wall thicknesses greater than 1 ¼ inch (32mm) to be stress relieved. Both vessels were designed with 32 mm wall thickness and were not stress relieved.

ASME SA 516 Grade 70 has a specified minimum yield strength 262 MPa (typically 354-368 MPa) and a minimum tensile strength of 483 MPa (typically 522-537 MPa). The brine accumulator materials mill certificates indicated a Charpy Impact at -40°C of 105-146 J. The vessel details are given in Table 1. The purifier had an Type 304 stainless steel base.

3. BRINE ACCUMULATOR DAMAGE ASSESSMENT

3.1 Cracking

The brine accumulator is shown schematically in Figure 3. The shell was made from five strakes welded to domed ends. Each strake was made from rolled steel (MR0175 allows hot rolled carbon steels) with a longitudinal weld that was located about ¾ the way up the vessel, these were identified as S1 to S5 welds. The position of these was staggered from one strake to the next on opposite sides of the vessel. Six circumferential welds were present, C1 to C6.

Table 1 Pressure vessel design details.

	Brine accumulator	Steam purifier
Wall thickness (mm)	32	32
Diameter (mm)	2500	1981
Welding of longitudinal and circumferential seams	Submerged arc to SFA, 5.17, F7A2 –EM12K	Not Available
Weld preparation / procedure	Double V with initial welding on the inside, air arc gouge from outside and then external welding	Not available
Post weld heat treatment	None	None
Test pressure	39 barg	41.2 barg
Maximum design pressure	26 barg	26 barg
Normal working pressure	17 barg	23 barg
Operating temperature	193°C brine/203°C steam	222°C steam
Date of commissioning	February 2000	February 2000
Previous inspection	Minor cracks were found visually during a previous inspection. These disappeared during grinding	No cracking found previously
Fluid level in vessel	30% of volume	None

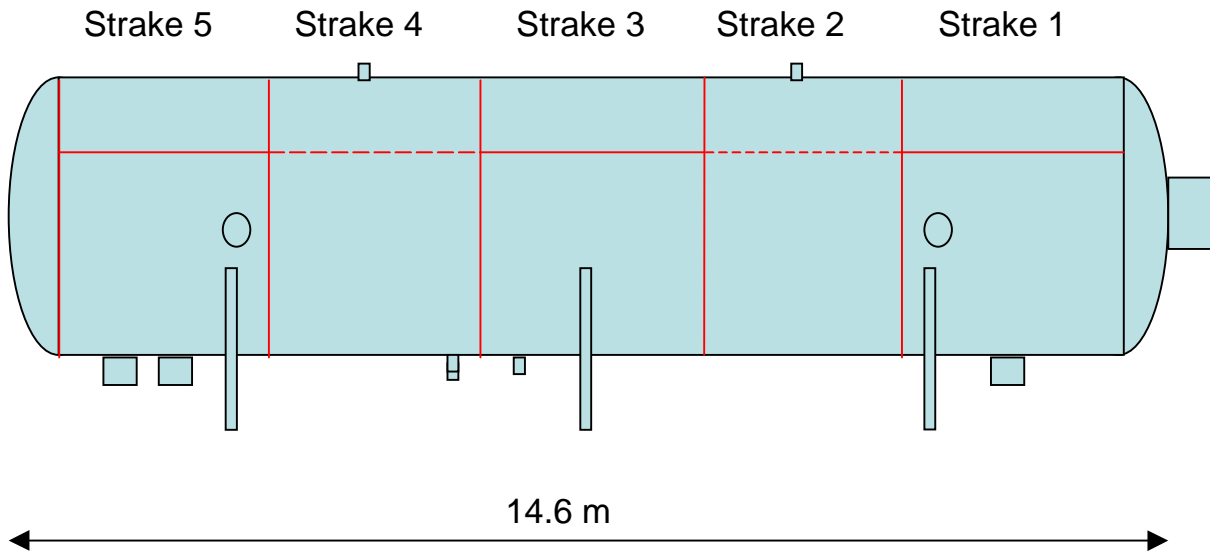


Figure 3: Illustration of brine accumulator weld layout.



Figure 4: The typical surface of the vessel with a fine crack seen in the formed corrosion products and appearance after removal of corrosion products.



Figure 5: Vertical cracking in a longitudinal seam weld as seen after removal of corrosion products.

During operation the water level was about $\frac{1}{2}$ way up the vessel and a distinct water line could be seen with the lower portion having evidence of a different scale compared to the top. The top portion of the vessel was covered with a layer of oxide/corrosion product, Figure 4, presumed to be a

mixture of mill scale, welding slag from the submerged arc welding process and corrosion product formed in service. Cracks were evident in these deposits over a number of welds.

Removal of the corrosion products and scales by grinding revealed a greater distribution of cracks, Figures 5 and 6. The majority of the cracks ran transverse to the welds and appeared to be either centered about the centerline of the weld or one of the heat affected zones.

A contracted NDT operator was engaged to find and measure all of the cracks in the vessel, Table 2. Inspections were carried out using black light magnetic particle inspection and Ultrasonics. Cracking was seen in all 5 of the horizontal longitudinal seam welds but only in a few of the circumferential welds. The distribution of the detected cracks were reported as follows, Table 2:

- The cracks appeared in discrete regions, they were not evenly spaced along the entire length of the welds and significant portions of the welds were crack free.
- The cracks ran either vertically or horizontally.
- All the cracks in the circumferential welds were close to the junction with the adjacent longitudinal weld.
- The cracks were relatively straight and were not heavily branched
- The cracks were open and easy to detect
- The deepest crack found was nearly through wall.

Table 2 shows:

- Number of cracks in vertical direction, perpendicular to seam welds and parallel to circumferential welds.
- Longest and deepest vertical cracks.
- Number of cracks in horizontal direction, parallel to seam welds and to perpendicular circumferential welds.
- Longest and deepest horizontal cracks.

No cracking was seen at the outside surface of the vessel in the areas where insulation was removed for inspection of external welds.



Figure 6: Horizontal crack transverse to circumferential weld C5 seen after removal of the corrosion products.

The welds had what appeared to be at least one large capping pass applied to both the inner and outer surfaces. These had not been ground and typically the caps were about 3 mm higher than the adjacent plate. No significant welding defects were detected. However, at least one weld repair was present. This repair had been applied at the time of manufacture.

A survey of surface hardness was completed, Table 3. The average hardness measurements taken were all below 250 HV (< HRC 22) and there was no indication that the vessel had not been made in accordance with the requirements of the NACE MR0175 or ASME VIII Div 1 standards.

A similar hardness survey was carried out in the adjacent steam separators, Table 4. Hardness values were up to 256 HV (< 23 HRC). However, no cracking was detected.

3.2 Metallurgy of Welds and Cracking

Figure 7 illustrates the in-situ metallography of the brine accumulator vessel walls in the area of cracking. Figure 8 shows a cross section of a weld area that was provided later. The parent plate shell material had a fine grained ferritic/pearlitic structure with a typical grain size of 0.01 mm. The welds had a coarse grained structure typical of a low carbon steel weld and the HAZ had a very coarse grain size up to 0.1 mm, with a coarse Widmanstatten structure.

The grains present in the capping welds were aligned perpendicular to the surface with a band of ferrite along the interdendritic grain boundaries. The weld had a typical distribution of inclusions seen as round black particles, these being variously rich in Mn/S, Fe/O and Al/O. The weld structure was typical of being produced by submerged arc welding with a high energy input. The cracking seen at the surface was relatively straight, at time branched and the cracks were open, Figures 4, 5, 6 and 7. The wide cracks were filled with corrosion product indicating the cracking had been present for some time.

The section of brine accumulator shell material provided later had a horizontal seam weld with a typical crack extending into the parent material. A cross section of this horizontal weld, Figure 8, also shows the results of a Vickers Hardness survey and macro etching. The hardness values were all less than 248 HV (< HRC 22). A total of 10 passes were used for the weld, 6 on the outside and 4 on the inside.

Two parts of a large weld crack were cut from the provided sample. One was sectioned through a crack, the second was broken open to reveal the fracture surface. The crack was open and filled with corrosion products, Figure 9. Three major cracks initiated and one propagated to within 5 mm of the outside wall. The crack directions, on the macro scale were all perpendicularly to the surface and were all relatively straight. The majority of the cracking was transgranular. However, on a microscopic scale side branches going backwards and at 90 degrees to the main cracks were in evidence.

The weld was etched using Nital to reveal the microstructure in the cracked areas, Figure 11. The cracks in the capping pass on the inside of the vessel followed distinct ferrite areas in the capping weld that were present along the interdendritic grain boundaries and these were subsequently corroded. This suggests that the cracks initiated intergranularly. The cracks that appear to be going in the reverse direction were also corroded out areas of ferrite. The crack tip area of the shorter cracks were in a weld tempered zone containing finely dispersed iron carbide in ferrite. The long crack ended in the capping weld of the outside of the vessel.

Table 2: Summary of cracking seen in the brine accumulator vessel welds.

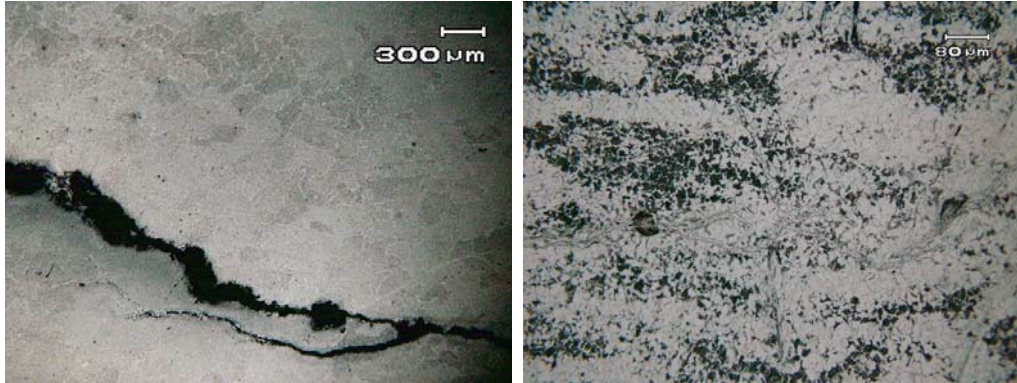
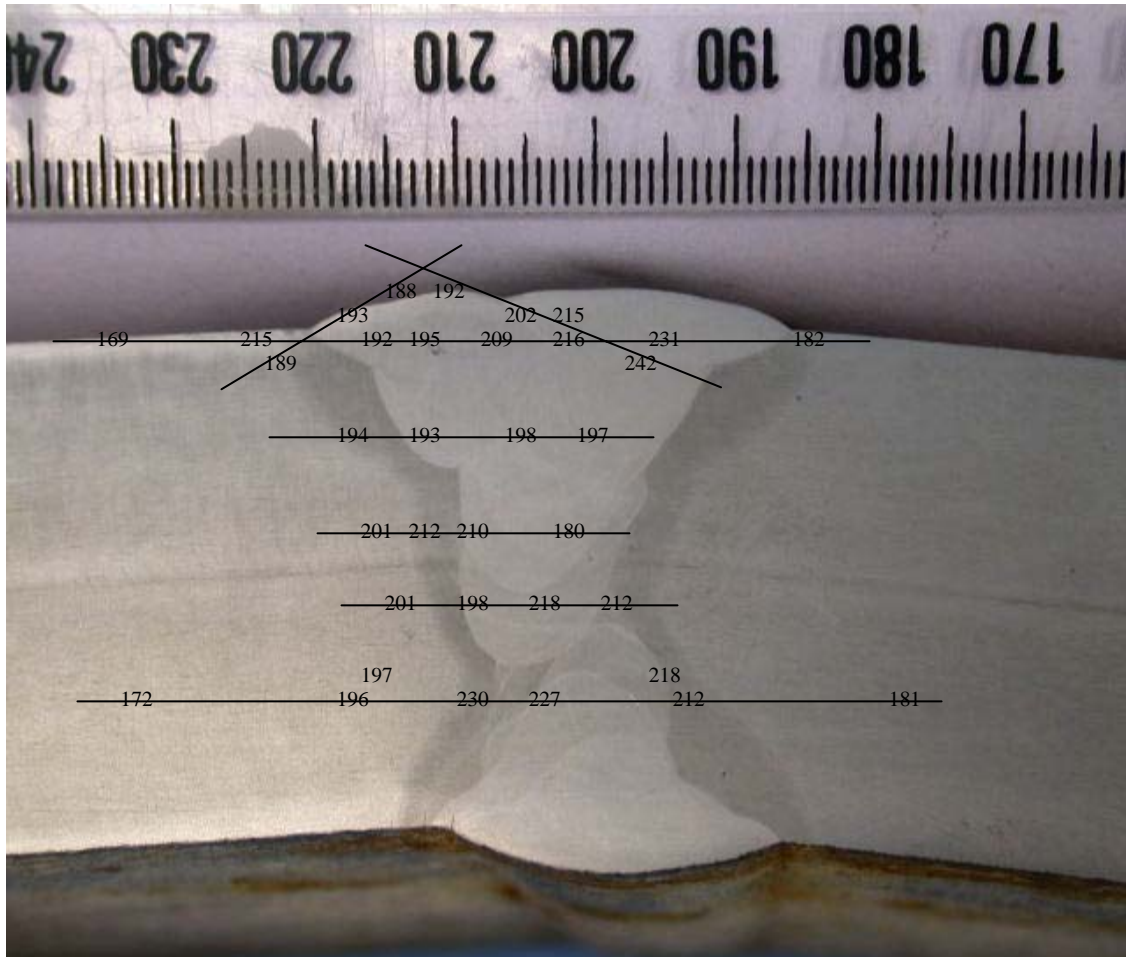
Stroke/Circumferential Welds	S1	S2	S3	S4	S5		C1	C2	C3	C4	C5	C6
Number of vertical cracks	26	7	5	24	33		0	2	0	0	0	0
Longest vertical crack (mm)	80	80	80	100	60			140				
Deepest vertical crack	20	22	30	27	20			11				
Number of longitudinal cracks	2	0		0	0		0	4	0	3	6	0
Percentage of weld crack free (%)	40	80	70	50	50		100	90	90	90	90	100
Longest longitudinal crack (mm)	100							20		85	80	
Deepest longitudinal crack (mm)	7							10		25	25	

Table 3: Results of internal surface hardness survey of the brine accumulator

	Minimum HV (HRC)	Average HV (HRC)	Maximum HV (HRC)
Plate material	169 (<6)	182 (6)	193 (9)
Longitudinal weld	201 (11)	224 (17)	268 (25)
Longitudinal HAZ	197 (10)	207 (13)	234 (19)
Circumferential weld	200 (11)	220 (16)	238 (20)
Circumferential HAZ	207 (13)	217 (15)	227 (17)

Table 4: Results of internal surface hardness survey of one of the steam separators.

	Average HV (HRC)	Maximum HV (HRC)	Minimum HV (HRC)
Plate material	191 (9)	203 (12)	174 (<6)
Longitudinal weld	195 (10)	216 (15)	181 (6)
Circumferential weld	215 (15)	230 (18)	206 (13)
Circumferential HAZ	256 (23)	271 (26)	242 (20)

**Figure 7: In situ metallography around accumulator cracking in the weld (on left) and the parent material (on right).****Figure 8: Cross section of typical horizontal seam weld in brine accumulator. Vickers Hardness (BS427: Part 1:1961) results, HV10.**

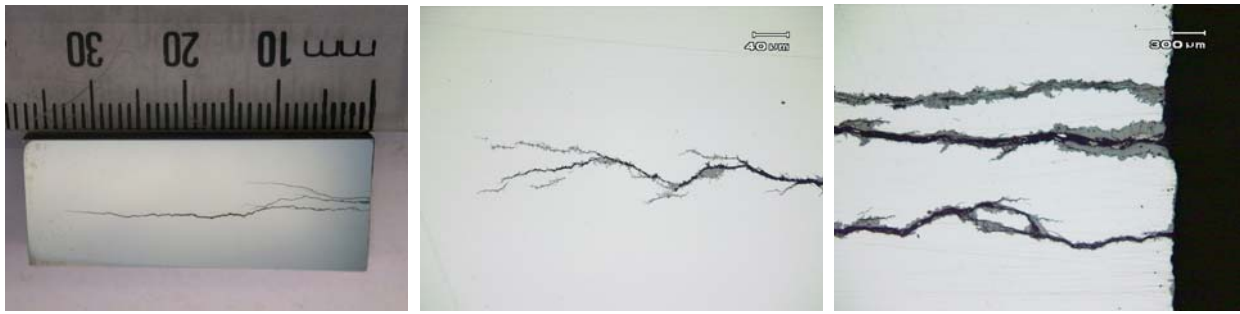


Figure 9: Open crack in longitudinal seam weld filled with corrosion products.

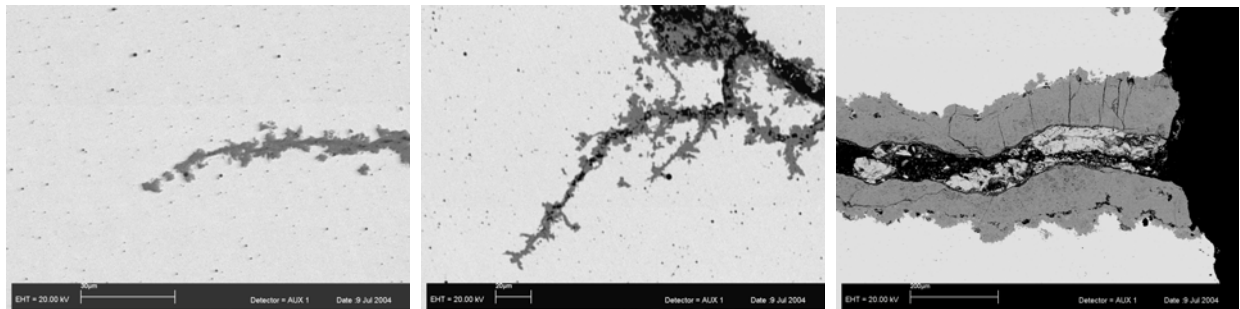


Figure 10: SEM views of the crack tip, side branches and crack initiation sites.

The crack opening and crack tip areas were examined in detail using a Scanning Electron Microscope (SEM) with Energy Dispersive X-ray (EDX) analysis facility. The results are summarized in Figure 10. There were no remnants of the crack that had not been subsequently corroded. Corrosion products and scales seen in the cracks were as follows:

- Crack tip areas: Fe/O with occasional islands of Fe/O/S

- Crack mouth area: S/Fe in central area, Fe/S crystals within the S/Fe areas, a layer rich in Si/O, Fe/O next to the metal surface.

These analysis are consistent with products seen in similar environments, namely magnetite (Fe_3O_4) in the crack tip and next to the metal surface at the crack mouth, a layer of silica (in this instance separating the magnetite from the iron sulfides and iron sulfides that were mainly pyrite (FeS_2) with some pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$).

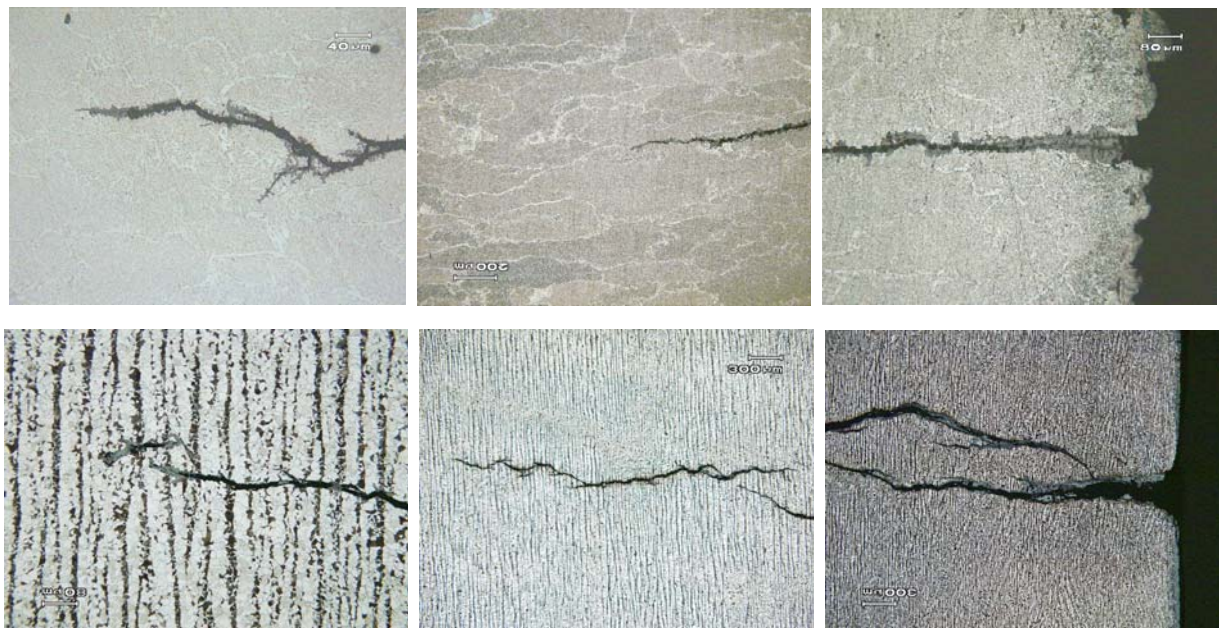


Figure 11: Microstructure in areas of cracking; Top in weld metal, Bottom in parent metal.

3.3 Fitness for purpose assessment of brine accumulator

The vessel defects were of concern because of their size and the number of cracks prevented consideration of vessel repair. However, it was desired to operate the vessel for a period of time while a replacement vessel was being fabricated.

A fitness-for-purpose assessment was carried out using BS7910 Level 1 (and using mill certificate tensile and impact property data) with a view to defining the risk of vessel bursting during operation. The transverse cracks in the longitudinal welds, at a maximum of 160 mm long and 27 mm deep were shown to be acceptable. In addition it was shown that the cracks would leak before burst. These cracks had initiated in the weld and had only propagated a short distance into the parent material suggesting that the cracking was associated with residual stress. The hardness of the parent material was much less than 22 HRC indicated a strength less than 690 MPa. As a result, once the cracks enter the parent material crack propagation will decrease especially as the residual stress will diminish.

However, the defects running perpendicular to the applied hoop stresses in the vessel needed to be separately assessed as these cracks remained in the HAZ and weld material where a residual stress equivalent to the yield stress of the plate was assumed, 350 MPa. This stress was significantly greater than the applied pressure stresses of 100 MPa. The deepest longitudinal cracking in the HAZ of the longitudinal weld was for 2 cracks in series, a 100 mm crack plus a gap of 70 mm plus a 70 mm crack with these being 7 to 8 mm deep, giving an interacting defect 240 mm long and 8 mm deep. This defect was shown to be unacceptable for service with the assumed high residual stress which is required for a Level 1 assessment.

These cracks were repaired by preheating to 200°C for 1 hour to remove hydrogen, then repair welded using a temper bead weld process and then subjected to crack testing after 48 hours. Minor surface cracking was found and shown to be fit-for-purpose. After a hydro test at a pressure of 39 barg the vessel was approved for operation by an independent inspection authority.

The defects were, however, considered unacceptable for long term operation as a result of the risk that the cracks could continue to grow to unacceptable levels. The vessel replacement plans continued.

3.4 Operation of the brine accumulator after the assessment and replacement vessel fabrication changes

Following the defect assessment and the repair of the large defect it was recommended that the vessel could be returned to service. This was approved by the statutory authority and the power station was returned to service without significant downtime. However, a condition of continued operation was that the vessel should be inspected on a monthly basis to ensure cracks were not growing. The replacement vessel was made of ASTM A516 Grade 70, using conventional welding methods as outlined in ASME IX for V and Double V preparation multi pass-welds. Although the vessel wall was only 32 mm a full PWHT followed by hydro test was completed. The specification for the new vessel was therefore modified from that of the original vessel in that:

1. A number of weld passes were required to ensure that a fine grained weld structure was obtained with some degree of tempering of prior weld passes.
2. Post weld heat treatment was required.
3. A maximum hardness of 250 HV (< 22 HRC) was specified.

The original repaired brine accumulator vessel was safely operated for the time required to fabricate the replacement vessel.

4. STEAM PURIFIER DAMAGE ASSESSMENT

4.1 Cracking

The steam purifier is shown schematically in Figure 12. The base of the vessel was made of stainless steel while the upper shell was made from 32 mm carbon steel as noted in Table 1. The inlet and exit nozzles were reinforced while the manway and relief nozzles were not. All of the welds had more than one finishing pass on the inner surface.

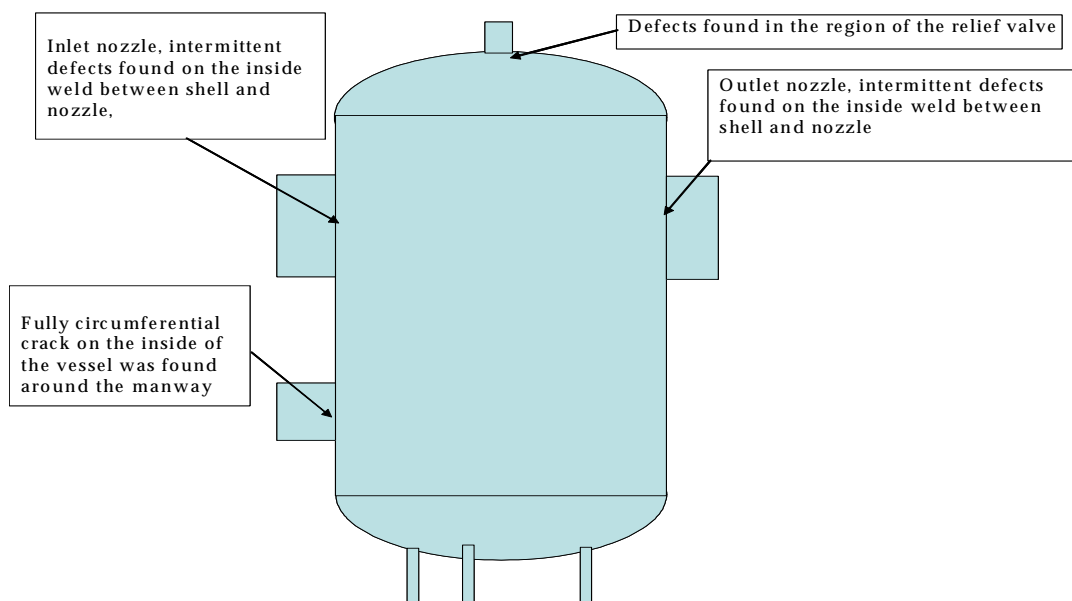


Figure 12: Illustration of cracking distribution of steam purifier welds.

Cracking was observed on the inside surfaces in the nozzle to shell welds. The small diameter relief nozzle had shallow radial cracks. The inlet and outlet nozzles had short cracks along the circumference of the welds, as illustrated in Figure 13, while the manway had a longer circumferential crack that went right around the nozzle. A contracted NDT

operator characterized the length and depth of the cracks as noted in Table 5.

A survey of the inner surface hardness was completed on three nozzles, Table 6. Hardness values were up to Vickers 248 (< HRC 22).

Table 5: Distribution of cracks found in the steam purifier.

	Number of cracks	Longest (mm)	Deepest (mm)	Location/ Orientation	Distribution
Inlet nozzle / shell weld	Numerous (160 to 420 mm)	420	22	HAZ and in weld / Parallel to weld	Even around circumference
Outlet nozzle / shell weld	Numerous (35 to 280 mm)	280	15	Lack of fusion	Around one quadrant
Manway / shell weld	1	Continuous	22	HAZ in plate at toe of weld / lack of fusion	Continuous around circumference
Relief valve	6	61	19	Radial ie transverse to weld	Star pattern around nozzle

Table 6: Hardness survey average value results for three nozzle welds in the steam purifier.

	Relief valve		Manway		Outlet nozzle	
	HB (Brinell)	HV (HRC)	HB	HV (HRC)	HB	HV (HRC)
Parent (main shell)	149	144 (<1)	217	219 (15.4)	243	248 (22)
Weld	153	148 (<1)	165	161 (<1)	147	141 (<1)
Adjacent to weld	126	118 (<1)	142	136 (<1)	236	240 (20)

The cracking on the relief nozzle was similar to that seen in the brine accumulator being perpendicular to the weld. The cracking in the manway and the inlet nozzle was in the toe of the weld on the plate side, while the cracking in the outlet nozzle was in the toe of the weld on the nozzle side, see Figure 13. The longest flaw found on the inlet nozzle was 420 mm long and 22 mm deep.

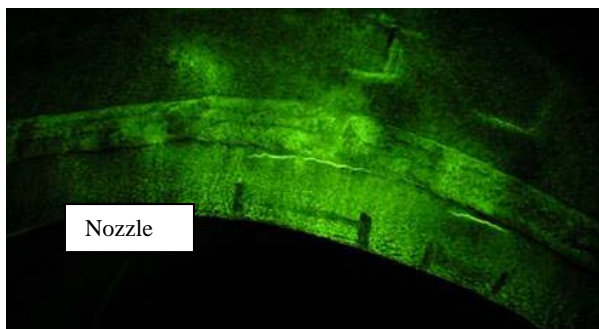


Figure 13: Illustration of cracking at the top of the outlet nozzle at the toe of the weld on the nozzle side at the 12 O'clock position.

4.2 Metallurgy of welds and cracking

In-situ metallography and replication techniques were used to determine the structure of the welds and HAZ areas in the cracked regions. Figure 14 shows cracking in the outlet nozzle that has similar characteristics to the cracking seen in the brine accumulator with the major difference being that the cracking appeared to have initiated in the coarse grained HAZ where the structure is more prone to hydrogen embrittlement, however this could not be confirmed as no laboratory samples were available.

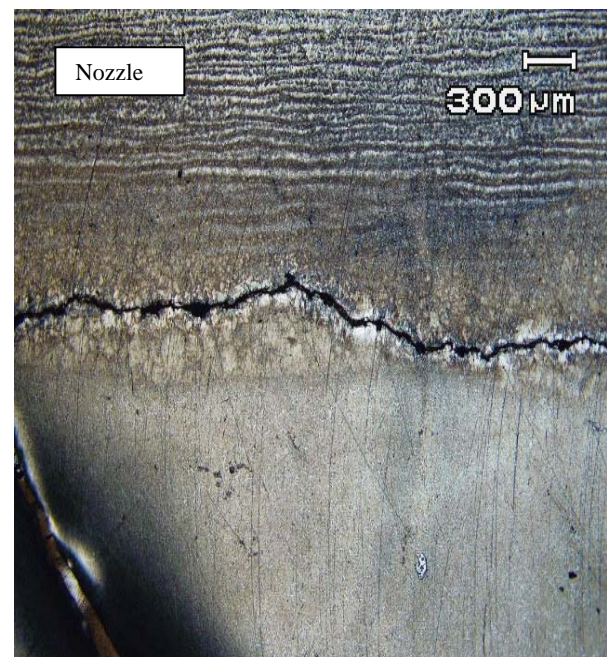


Figure 14: Microstructure in the area of typical cracking next to the outlet nozzle at the 3 O'clock position.

4.3 Fitness-for-purpose assessment of steam purifier

The 22 mm deep flaws in the manway and inlet nozzles were selected for fitness-for-purpose assessment.

The fitness-for-purpose assessment was carried out in accordance with BS7910:1999, Level 2. This method assesses flaws against both brittle fracture and plastic

collapse. To carry out the assessments Crackwise version 3.151 was used, this software follows the procedures specified in BS7910:1999. This assessment concluded that the longest flaw found in the inlet nozzle was unacceptable, Figure 15. The maximum allowable flaw depth for a 420 mm long crack was shown to be 18 mm. Although this defect was at the unacceptable limit a more refined assessments may have indicated acceptability for continued operation but the fully circumferential defect in the manway was of a similar depth and much longer and was also unacceptable, so the vessel was removed from service for repair.

Prior to repair additional NDT was completed in the region of the reinforcement pads on the inlet and outlet nozzles. The NDT identified significant regions of lack of fusion, clusters of small inclusions and small areas of porosity in the roots of welds of the external reinforcement pads. Where practical these were designated for removal but some were embedded at depths where removal by grinding was not possible. These impossible to remove defects were assessed and were considered acceptable under operating conditions as they fell below the assessment line of Figure 15.

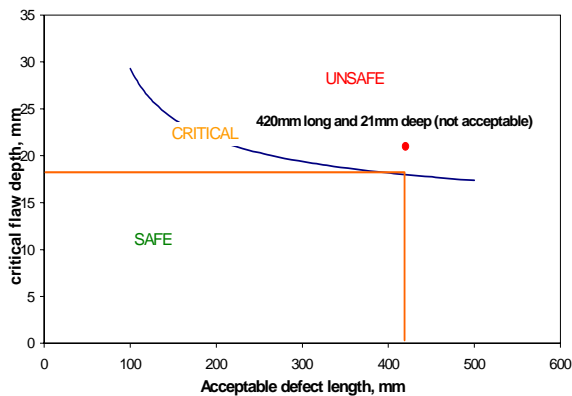


Figure 15: Maximum acceptable flaw length as a function of flaw depth for inlet/outlet nozzles.

4.4 Repair and Hydro Test

On completion of the repair a conservative PWHT was designed to give suitable stress relief of the welded areas without undue sensitization of the Type 304 stainless steel lower portion of the vessel and other weld attached internal fittings.

It was also required to perform a hydro test, however, concern was expressed for the risk of failure from the embedded flaws under ambient temperature and high pressure conditions.

An additional fitness-for-purpose assessment was completed on the embedded flaws in the reinforcement pads. The nominal hoop stress, as a result of a 40.2 barg pressure hydro test (1.75 x operating pressure as recommended by ASME VIII Div 1), was calculated to be 127.5 N/mm². In accordance to the defect assessment this pressure would cause the 49 mm high flaw that was present to fail, Figure 16. The assessment shows that a maximum nominal stress of 100 N/mm² could be tolerated under hydro test conditions, this correspond to a pressure of 35 barg. This pressure was used for the hydro test, being 1.5 x the operating pressure to ensure vessel integrity without risk of ligament failure in the reinforcement pads.

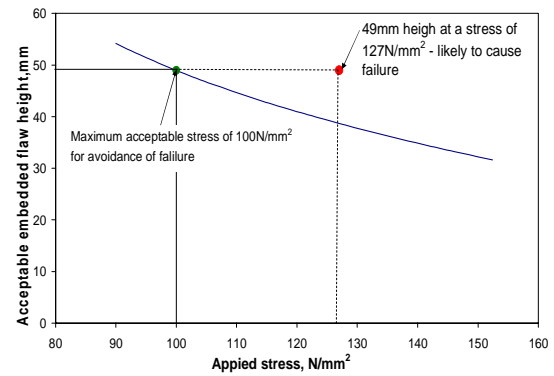


Figure 16: Applied stress as a function of acceptable flaw height for embedded flaws.

5. CAUSE OF CRACKING

The results suggest that the transverse cracking, in the brine accumulator, initiated and propagated along interdendritic boundaries delineated by ferrite in the capping weld. The cracks were typical of Hydrogen Embrittlement (HE) or Hydrogen Assisted Stress Corrosion Cracking (HSCC). HSCC is a special case of HE sometimes known as Hydrogen Assisted Cracking (HAC) or more commonly Sulfide Stress Corrosion Cracking (SSCC). The cracks may have initiated from corrosion pitting on the capping weld and the coarse grained aligned dendritic grains produced by the submerged arc welds appear to be particularly susceptible to corrosion and cracking. The sub-surface corrosion along the ferrite boundaries also indicates that these areas were prone to corrosion. Once the cracking initiated and a significant stress concentration effect was present the cracking was typical of transgranular HE.

The degree of corrosion present suggests that the cracks had been present for some time in service. It is not known if the cracking and corrosion occurred due to HE at a lower temperature with subsequent high temperature corrosion or due to corrosion and HE at the service temperature. In either case, the straight nature of the cracking and the presence of multiple parallel cracks indicates that they were primarily propagating in the presence of a high residual stress.

During welding high residual stresses are produced that are predominantly parallel with the axis of the weld in unrestrained positions. These are often at the yield stress of the material. The stress distribution across a weld depends on the sizes of the weld beads and the order of welding. Where numerous small weld beads are used each weld bead tempers prior passes and the average stresses are reduced especially in the middle of double V type welds. However, where large weld beads are applied, as in this case, the converse occurs and high residual stresses are expected across the entire width of the vessel.

It is known that hydrogen cracking can occur through wall in welds. However, it is more likely that as cracks are formed that there is a balance between an increasing stress intensity due to the crack length and a reduction in the residual stress due to the presence of the crack and crack opening. As the cracks deepen, the later will become dominant and it is therefore not surprising to see cracks 90% through the wall thickness which must have effectively stopped propagating. However, for this size of crack only minor stress increase will cause final failure of the crack ligament.

In summary the cause of the cracking was believed to be due to HE or HSCC in hydrogen charged weld metal in an H₂S

containing environment. The welding process contributed significantly to the cracking as the high energy submerged arc welds gave a coarse grained microstructure that was more susceptible to cracking than the fine grained microstructure expected of multi-pass welds. This process also leads to high levels of residual tensile stress across the majority of the weld. These remained because the vessel was not given a PWHT.

Hydrogen readily diffuses into carbon steel vessel and pipeline walls exposed to geothermal fluids, McAdam et al, 1981. Surface hydrogen concentrations are dependant on the corrosion rate, but virtually all of the hydrogen generated diffuses into the steel because of the presence of hydrogen sulfide that acts as a "poison" that promotes uptake of hydrogen. At high temperatures this hydrogen diffuses through the steel and exits on the outside surface. Exposed surfaces can passivate by formation of corrosion products or scales that block the corroding metal from the environment and over time the volume of hydrogen produced and the volume of hydrogen in the steel is decreased. The diffusion of hydrogen out of the metal is temperature dependant and if for example silica scaling occurs at temperatures over 100°C and there is rapid blocking of the surface from the corrosive solution then the amount of hydrogen generated is likely to be small and what is present will diffuse away over a matter of hours.

The propensity for HE to occur depends on the strength of the steel, the levels of stress, stress concentrations, the microstructure, composition and hydrogen concentration in the steel, Lopez et al, 1999.

HE is observed in carbon and low alloy steels that have high strength when moderate applied stress are applied. As a result of this a common industry standard is to limit the hardness of these types of steel to 250 HV as in NACE MR0175 and in the new joint standard MR0175/ISO 15156-2:2003(E). However, this is NOT an absolute limit and the recent joint standard reiterates that the responsibility for approval of stress levels, heat treatments and hardness should be with the end user. Testing carried out in geothermal environments by Marshall and Tombs, 1969, showed that a range of steels suffered from stress cracking in geothermal condensate when they were loaded to high stress intensities. Even H40 casing steel with tensile strength of 400 MPa (hardness approximately 120 HV) was shown to crack under these conditions, however the applied stresses required for cracking were above the yield stress. Residual stress is known to be sufficient to cause cracking in susceptible microstructures, Warren, 1987.

Stress concentration has a significant effect on HE. One of the major causes of cracking in the steam purifier was the presence of welding defects which were only identified during repair of the vessel. In the brine accumulator the cracks do go a short distance into the parent metal, again driven by the existing crack in the weld material.

The microstructure has a significant effect. Coarse grained steels are more prone to HE than fine grained steels and tempered martensitic steels with a fine uniform microstructure are less susceptible than pearlitic steels. Continuous bands of ferrite on grain boundaries in welds are more susceptible to cracking as has been shown in this case.

Minor variations on the composition of low alloy steels have little effect on the susceptibility to cracking (Ni content is specifically restricted).

The concentration of hydrogen in the steel, both in service and at shutdown also has a major effect on the susceptibility to cracking. Hydrogen charging in geothermal environments is initially high when corrosion first occurs but reduces as protective corrosion products form and the corrosion rate reduces, McAdam et al, 1981. The period of crack propagation is open to debate. Hydrogen cracking would normally be expected to be minimal at operating temperature, rather the hydrogen charged material would tend to crack primarily at periods of shutdown when the vessel walls were below 100°C, Warren, 1987. However, the corrosion in the cracks occurs at the operating temperature and it could be argued that the cracks grow when an excessively high level of hydrogen is formed at the crack tip.

The characteristics of the cracking in the two vessels indicated that the same issues were present in both. They were both made in accordance with ASME VIII Div 1 and both had average hardness values below the levels set by MR0175/ISO 15156-2:2003(E). However, they were both made using high energy submerged arc welding. This process has become more common over recent years and allows deep welds to be produced faster than previously, thus reducing manufacturing costs. The large weld beads produced have a coarse grain structure in the weld and HAZ. In addition, the coarse weld beads do not give significant temper of previous weld passes and as such the residual stresses are potentially at yield throughout the weld.

The cracking observed here suggests that if cracking is to be prevented in conditions where high levels of hydrogen can be present in the steel that additional specifications over those required by ASME VIII Div 1 and MR0175/ISO 15156-2:2003(E) should be used. For example, to minimize the risk of cracking it is recommended that more and smaller weld passes should be applied and post weld heat treatment should be used for vessels approaching the specified maximum thickness unless proven otherwise. Methods for proving fabrication variations are outlined in MR0175/ISO 15156-2:2003(E), however, these are difficult to design and prove effective. Our recommendation would be to do PWHT.

6. SUBSEQUENT INSPECTIONS

The replacement brine accumulator vessel was inspected after one year of service. No cracking was apparent. Minimal deposition of silica was noted and only a very thin layer of corrosion products had formed. A small number of shallow pits were found with hollow caps of brown scale and these were attributed to shutdown corrosion. The pit caps were removed to allow repassivation on startup.

The repaired steam purifier has been in service for one year and no problems have been reported.

7. CONCLUSIONS

Numerous transverse weld cracks and a limited number of longitudinal welds were present in longitudinal seam welds in the brine accumulator vessel after 5 years of service. In addition small cracks were seen in the circumferential weld areas next to the seam welds.

A number of longitudinal cracks were present in the HAZ of the nozzle welds in the steam purifier.

Hardness surveys indicated the vessels complied with the requirements of NACE MR0175. The susceptibility of a steel to Sulfide SCC and HE is dependent on tensile strength, applied stress, microstructure, composition and the

environment. The hardness limitation of HRC 22 (250 HV) is normally suitable to help prevent cracking. However, it is known that steels with hardness significantly lower than this can experience Sulfide SCC and HE if they have susceptible microstructures and the applied stress is very high ie at or above yield. This was believed to be the case in both vessels where the cracking observed was typical of Sulfide SCC and HE and was primarily in the weld material and HAZ but at times propagated into the surface regions of the parent material.

ASME VIII Div 1 specifically allows vessels < 32mm wall not to be stress relieved. Vessels complying with this standard and MR0175, have for many years given trouble free service in vessels containing geothermal environments. However, both vessels considered here had significant cracking present that was not fit for long term service.

The large submerged arc weld passes used produced a coarse grained microstructure in the weld and a coarse grained HAZ. This type of welding has become commonplace for fabrication of ASME VIII Div 1 vessels. However, the process results in high residual stress and an unacceptable microstructure for resistance to Sulfide SCC and HE in geothermal environments.

The replacement brine accumulator vessel, fabricated using conventional multi-pass welding with a PWHT was found to be crack free after one year of operation.

The repaired purifier vessel has been in service for one year with no known problems.

Cause of Cracking

The main cause of failure was the use of submerged arc welding with only 10 weld passes and a lack of PWHT on the 32 mm wall thickness welded vessels operated in an H₂S environment. The cracking in both vessels was attributed to SSCC and HE. The welds were particularly prone to this as they had a coarse structure, a coarse HAZ and high residual stress throughout.

Avoidance In Future

ASME VIII Div 1 allows vessels of < 32 mm wall thickness not to be heat treated. The requirement is noted in NACE documents to be marginal and suggests if a PWHT is to be avoided then testing of heavy walled fabricated components is required to agreed conditions. However these are difficult to do and can be costly. Alternatively all vessels approaching this thickness should be given a PWHT.

In our opinion, avoidance of HE cracking in vessels used for geothermal service requires an additional set of "rules of thumb":

1. The number of weld passes must be as many as the wall thickness in millimeters i.e. for a 32 mm wall at least 32 passes should be applied.
2. All vessels should be stress relieved unless it can be proven that this is not necessary by the manufacturer for the welding procedure chosen.
3. In addition, care should be taken to ensure any closing welds are correctly stress relieved.

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