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STRESS CORROSION CRACKING: CASE STUDIES IN REFINERY EQUIPMENT

Graham R. Lobley [1]

1:Metallurgical Engineering Specialist, Consulting Services Department, Saudi Arabian Oil Company

E-mail: lobleygr@aramco.com.sa

ABSTRACT

Two examples of stress corrosion cracking (SCC) in refinery equipment are presented to highlight the lessons learned to prevent recurrence of such failures. In each failure analysis case study, the cracking is characterized using various metallurgical laboratory techniques, including metallography and fractography, in order to identify the mode of failure. Examples of polythionic acid SCC (PASCC) in a sensitized austenitic stainless steel and caustic SCC in carbon steel equipment are presented. PASCC of 304 stainless steel charge heater tubes occurred in a naphtha hydrotreater during shutdown, after about 18 years in service. Caustic SCC of carbon steel piping in an LPG Merox gas sweetening plant occurred in non-stress-relieved downstream piping, due to caustic carryover from the Merox unit. Cracking characteristics are discussed and options to avoid recurrence are presented.

Keywords: *Failure analysis, polythionic acid, caustic, metallography, fractography.*

الملخص

نقدم فيما يلي مثالين للصدع في المصافي بسبب الإجهاد والتآكل لتوضيح الدروس المستفادة لمنع تكرار حدوث مثل هذه الأعطال. ويتم تمييز الصدع في كل دراسة تحليلية لهذه الأعطال باستخدام أساليب مخبرية مختلفة لدراسة المعادن، بما في ذلك علم التركيب المعدني وعلم دراسة التصدع لتحديد نوع العطل. كما تقدم أمثلة للصدع بسبب الإجهاد والتآكل التي حدثت نتيجة للحامض متعدد الكبريت في الفولاذ الحساس الذي لا يصدأ والمادة الكاوية القلوية في معدات الفولاذ الكربوني. وحدث صدع بسبب الإجهاد والتآكل نتيجة للحامض متعدد الكبريت في الفولاذ الذي لا يصدأ من نوع ٣٠٤ في أنابيب معمل إزالة الكبريت بالهيدروجين والوسيط الكيميائي للنفتا خلال إيقاف المعمل بعد تشغيله لحوالي ١٨ سنة. وحدث صدع بسبب المادة الكاوية القلوية في أنابيب الفولاذ الكربوني في معمل (ميروكس) لتحلية غاز البترول السائل نتيجة لنقل المادة الكاوية القلوية من معمل ميروكس دون أن يتم معالجة منطقة الأنابيب حرارياً لإزالة الإجهاد وستناقش خصائص الصدع والخيارات لتجنب حدوثه.

1. INTRODUCTION

Stress corrosion cracking (SCC) is an environmental cracking process caused by the combined effects of tensile stress and a specific environment on a susceptible material. Catastrophic SCC failures have occurred in some applications, but more often in the petroleum industry, a small leak is encountered. Examples of well-known environment - metal pairs which pose particular risks of SCC include chloride - austenitic stainless steels, caustic – carbon steels and ammonia - copper alloys. Most of the specific environments for particular alloys have been known for several decades, but occasionally new environments capable of causing SCC are discovered.Despite the sustained efforts of corrosion engineers, SCC failures continue to occur in many industrial applications, particularly within the petrochemical and process industries. The process industry sector in particular includes numerous potentially aggressive chemical environments, so that SCC is often a principal mode of failure of plant equipment, perhaps accounting for around 25% of major failures in the oil industry. In some cases, plant personnel are unaware of the measures that must be implemented to avoid SCC in service. This article reviews two case studies and highlights the lessons learned to prevent recurrence of SCC.

2. POLYTHIONIC ACID STRESS CORROSION CRACKING

2.1. Introduction

The 304 stainless steel charge heater coil of a naphtha hydrotreater unit (NHT) was found to be extensively cracked following unit shutdown, when soda ash washing was applied. The NHT is fired on fuel oil/gas. The coil carries sour naphtha (350 ppmw S) feed and hydrogen is added to the feed at a process temperature of 330 °C (see simplified process flow diagram, Fig. 1). The unit had been in service for about 18 years and had been successfully shut down and restarted several times previously in its lifetime.

2.2. Examination

Tube sections from the heater coil were received for laboratory evaluation. These sections showed several transverse cracks, some with significant crack opening (Fig. 2). Beneath a rust flash, the internal coil surfaces were coated with a fairly thick, powdery black deposit, which was sampled for chemical analysis. Microsections taken across the cracks confirmed that the cracking had started from the internal, process side of the tube (Fig. 3). Metallography showed that cracking was intergranular with some branching (Figs. 4a, 4b). An intergranular failure was also confirmed by fractography of an opened crack (Fig. 4c). Electrolytic etching of a microsection in oxalic acid (ASTM A262 Practice A) revealed wide, ditched grain boundaries, indicative of sensitization (Fig. 4d). X-ray diffraction (XRD) revealed that the black deposit inside the tubes was 80% iron sulfide (FeS), balance iron oxide hydroxide FeOOH. The tube material met the compositional requirements of the specified ASTM A271 TP304. The alloy analysis was 18.5%Cr, 9.95%Ni, 1.55%Mn, 0.64%Si, 0.07%C.

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2.3. Discussion

Sensitization is a degraded condition in austenitic stainless steels which is caused by chromium depletion immediately adjacent to the grain boundaries. In the normally used solution annealed condition, chromium is uniformly distributed within the austenite microstructure. However, if the alloy is heated in the approximate sensitization range 370 – 815 °C (700 – 1500 °F) [NACE, 1997],], chromium carbide precipitation occurs at the grain boundaries. A narrow region adjacent to the chromium-rich intergranular precipitates is depleted in chromium, with dramatically lowers the corrosion resistance. Sensitization can occur either during weld fabrication or in subsequent service operation.

In the early 1960s [Samans, 1964], stressed and sensitized 304 stainless steels were first reported to suffer intergranular stress corrosion cracking in a solution of polythionic acids ($H_2S_XO_6$), which may form in petroleum refinery units during shutdown. Only reaction of sulfide, moisture and oxygen is necessary. In the presence of sulfide corrosion products, such conditions are met during shutdown, when moisture originates from general humidity, washing or steam out and oxygen as air enters the unit upon opening to atmosphere. Subsequently, this particular form of intergranular SCC was called polythionic acid stress corrosion cracking (PASCC). However, Piehl considered that the corrosive species actually responsible for the intergranular SCC was probably sulfurous rather than polythionic acids [Piehl 1964], which also forms readily during refinery shutdown conditions. Both authors agreed that service temperatures below 800 °F (427 °C) would not result in the required sensitization of austenitic stainless steels. More recent work [Moller 1984] has suggested that of the polythionic acids, only tetrathionic acid ($H_2S_40_6$) causes SCC in sensitized 304 stainless steel. Cracking has also been reported in refinery equipment with lower operating temperatures. Moller [Moller 1984] cites a case of PASCC of an AISI 304 flange from a hydrodesulfurizer. The plant had operated for 138,000 hours (15.75 years) and the flange experienced temperatures up to 384 °C (720 °F). The 304 flange eventually became sensitized after prolonged exposure at relatively low temperatures.

Unless suitable precautions are taken, in accordance with NACE RP0170 [NACE, 1997], austenitic stainless steels which have been exposed to sulfur-bearing refinery process streams within the sensitization range may become susceptible to intergranular stress corrosion cracking. NACE RP0170 practice recommends soda ash neutralization washing and nitrogen purging procedures (note this NACE procedure is currently under revision). Investigation revealed that the soda ash neutralization procedures were not properly documented and followed and that the protective alkali film was wrongly water washed at the end. An important question is what is the lowest service temperature below which sensitization does not occur. In our case, the process stream temperature is 330 °C, which initially appeared too low to cause sensitization. However, the internal metal skin temperature is actually higher (approximately 405 °C) due to conduction, since this is a fired heater.

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2.4. Conclusion and Recommendations

1. PASCC failure occurred in a sensitized 304 stainless steel, after 18 years' service.
2. NACE RP0170 shutdown procedures should be carefully followed for austenitic stainless steel equipment.
3. Upgrade the coil to AISI 347 stainless steel, which is significantly more resistant to sensitization. This alloy should be given a stabilization heat treatment.

3. CAUSTIC CRACKING OF CARBON STEEL PIPING

3.1. Introduction

In an LPG Merox system, an ASTM A105 8-inch carbon steel elbow of developed a small leak. Merox is a gas sweetening process, which removes mercaptans by an oxidation process and is performed in a caustic solution.

The carbon steel piping (ASTM A53 grade B) and equipment of the system (heat exchangers and splitter) were not originally stress relieved. The failure location was apparently from the weld, close to the 6 o'clock position, near a drain point. While preparing the original elbow for re-welding, plant inspectors noticed that there were transverse cracks within the heat affected zone of the weld. It was therefore decided to replace both elbows and locally stress relieve. As the carbon steel line was not stress relieved and an incident of caustic carryover had occurred a short time before the failure, inspection personnel began to suspect that caustic stress cracking might be the cause of the elbow failure. The equipment had been in service since 1972, but it was suspected that occasional caustic carryover incidents may have started following upgrade of another refinery unit in 1995. The stream temperature downstream of the C3/C4 splitter (Fig. 5) is 93 °C and approximately 15 wt% caustic is used in the Merox unit.

3.2. Examination

Fig. 6 shows the portion of the elbow received for investigation. In the weld preparation area, networks of transverse cracks were clearly visible under low power examination (Fig. 6, bottom). Microsections were taken transversely across the cracks. Branched intergranular cracks were noted (Fig. 7), which were filled with dark grey corrosion products. The elbow was a low carbon steel composition (0.11%C, 0.47%Mn, 0.22% Si, 0.034%P, 0.021%S). Energy Dispersive Spectroscopy microanalysis of the opened surfaces of one crack revealed mainly iron and oxygen, with significant levels of sodium also present. This confirmed that the cracks were filled mainly with iron oxides and the detection of sodium is consistent with caustic carryover into the piping downstream of the Merox unit. These findings confirm that caustic stress corrosion cracking was responsible for the elbow failure.

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3.3. Discussion

Caustic stress corrosion cracking of steels is one of the oldest known forms of SCC, dating back to the days of the early steam locomotives, when it was responsible for countless explosions of riveted boilers [Trethewey et al., 1985]. Incidents of caustic cracking of low alloy steels in nuclear and fossil-fueled power plants from 1969 onwards focused interest in this form of SCC within the power industry [Lyle, 1983]. Within the process industries, caustic SCC has caused numerous failures in welded steel piping and pressure vessels exposed to caustic solutions at high temperatures. During the early 1990s, several incidents of caustic stress corrosion cracking of carbon steel were encountered within company gas plants and refineries [McIntyre 1994]. The NACE caustic soda service graph [NACE, 1985] indicates a “safe” region where stress relief of carbon steels is not specified below certain operating temperatures and caustic concentrations, but in some cases cracking was encountered at nominal process temperatures within the safe region [McIntyre, 1994].

Several specialists have reviewed possible explanations for the intergranular crack path typical of caustic cracking in ferritic steels. Microsegregation of certain elements may be responsible for creating grain boundary heterogeneity, and in this case intergranular corrosion is expected in the absence of any stress [Parkins, 1994]. This is the case for caustic and mild steels and it has been suggested that phosphorus is the segregating element [Parkins, 1994, Jones et al., 1995]. In SCC in high pH caustic solutions, iron dissolves as oxyanions ($HFeO_2^-$) and magnetite (Fe_3O_4) is precipitated within the crack [Scully, 1966] This can be understood by referring to the potential-pH stability diagram (Pourbaix diagram) for iron. Electrochemistry plays an important role in cracking, as caustic SCC has been found to occur over a fairly narrow range of electrode potential corresponding to a transition zone between a passive magnetite film and the oxyanion [Parkins, 1994, Jones et al. 1992]. If the protective film is ruptured, localized dissolution and SCC may occur.

Following the recent field experience within the company [McIntyre, 1994], engineering standards have been tightened to require postweld heat treatment to stress relieve piping and equipment in all caustic service, including conditions where caustic carryover may occur. All new carbon and low alloy steel equipment is now therefore stress-relieved for this service, but automatic retrospective action for all existing piping and equipment was not taken, except in selected cases. In considering inspection for SCC, wet fluorescent magnetic particle testing (WFMPT) was recommended as the most sensitive and preferred method [McIntyre, 1994]. WFMPT requires access to the process side surfaces. As cracking is invariably near welds, external inspection methods such as ultrasonic or radiography testing are more difficult to interpret, since defect indications can include real SCC cracks as well as lack of weld fusion.

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3.4. Conclusion and Recommendations

1. Caustic stress corrosion cracking was confirmed within the heat affected zone of the carbon steel elbow.
2. Internally inspect both the splitter and reboiler by WFMPT at the next shutdown.
3. Plan to replace the present piping with stress-relieved piping during the next shutdown.

4. SUMMARY

SCC of the types discussed can be prevented by optimal material specification and by carefully following established mitigation procedures. Contractor's on-site work, e.g. soda ash washing treatments, should also be actively monitored to ensure compliance with approved practices.

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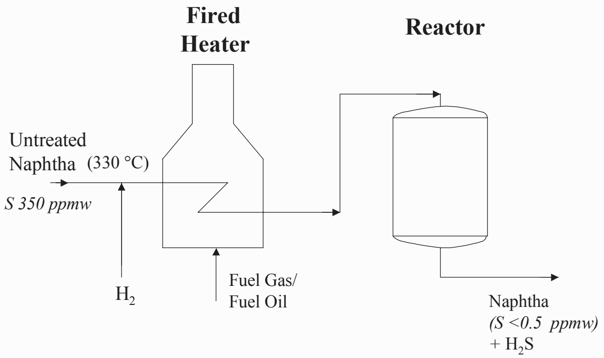


Fig. 1: simplified flow diagram of Naphtha Hydrotreater unit

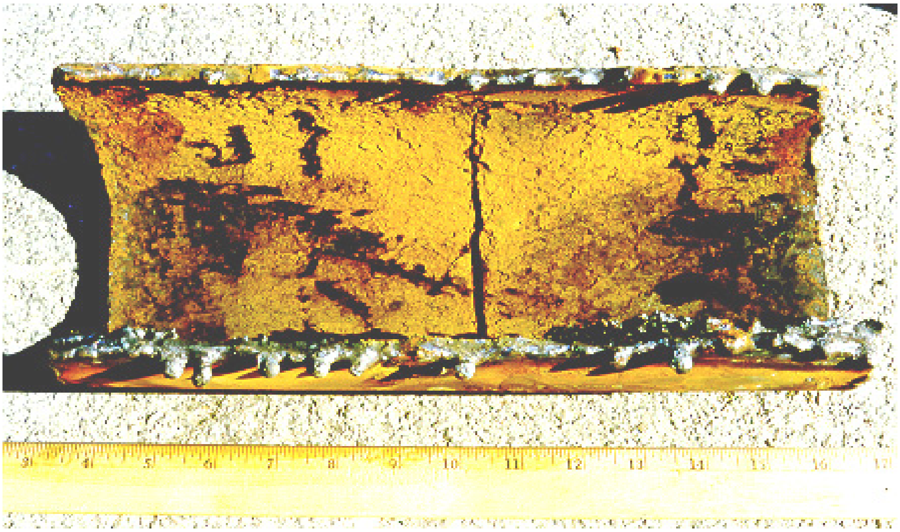


Fig. 2: transverse cracks in heater coil

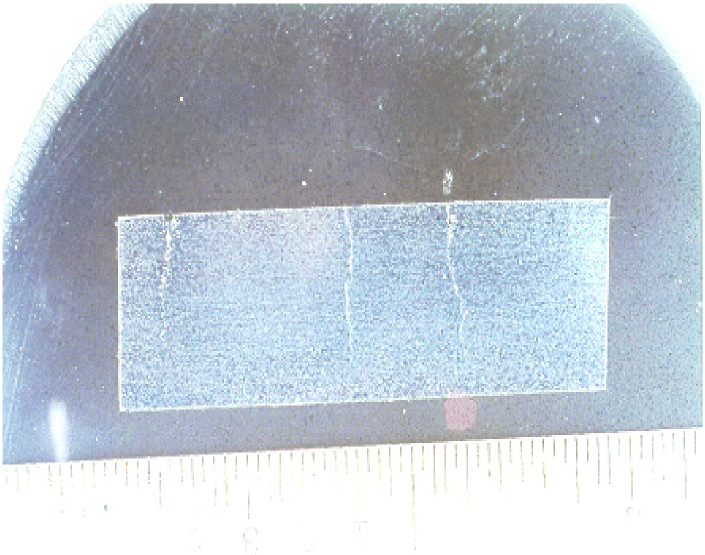
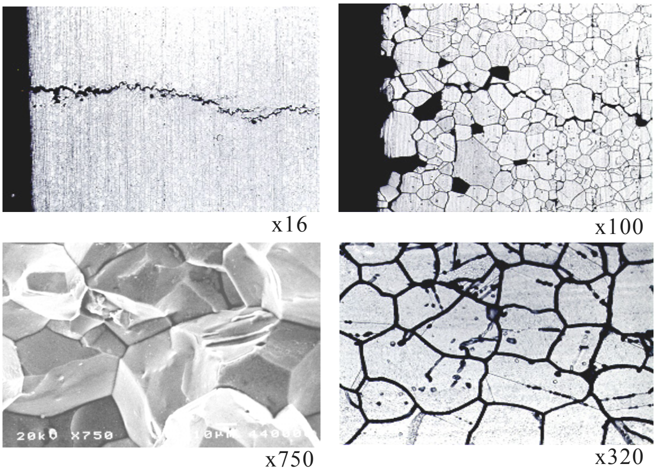


Fig. 3: cracking from ID surface (top)



x16 x100

x750 x320

Fig. 4

(a) intergranular cracking (b) intergranular cracking

(c) intergranular cracking (d) sensitized material

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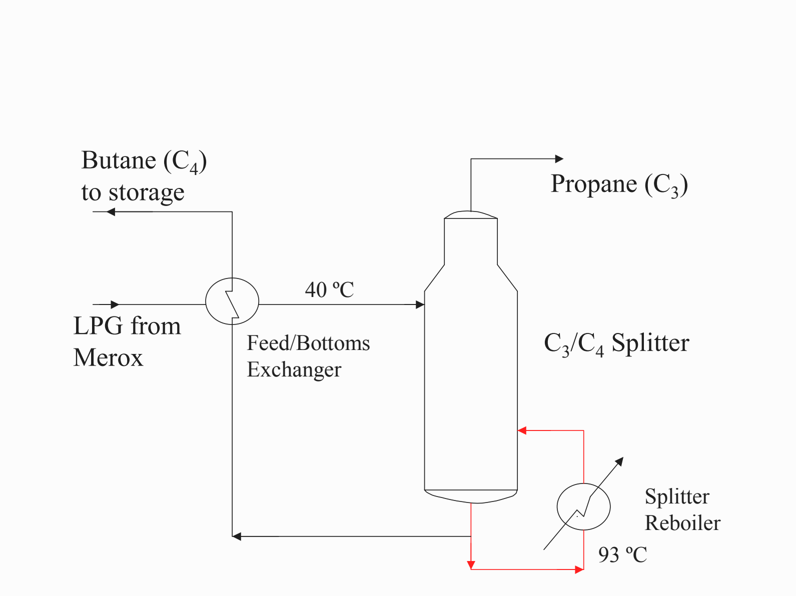

Fig. 5: simplified flow diagram of LPG Splitter

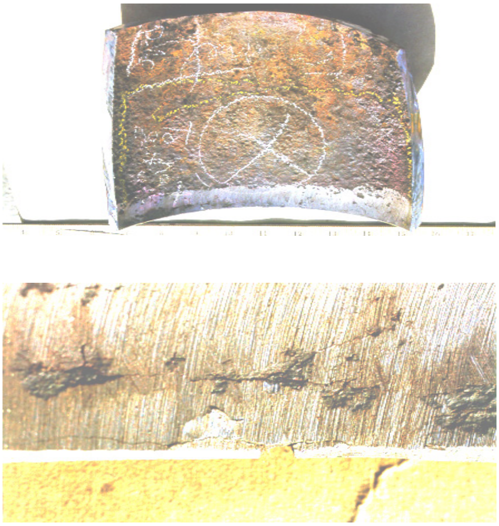

Fig. 6: elbow section

Top: as received

Bottom: view of cracking

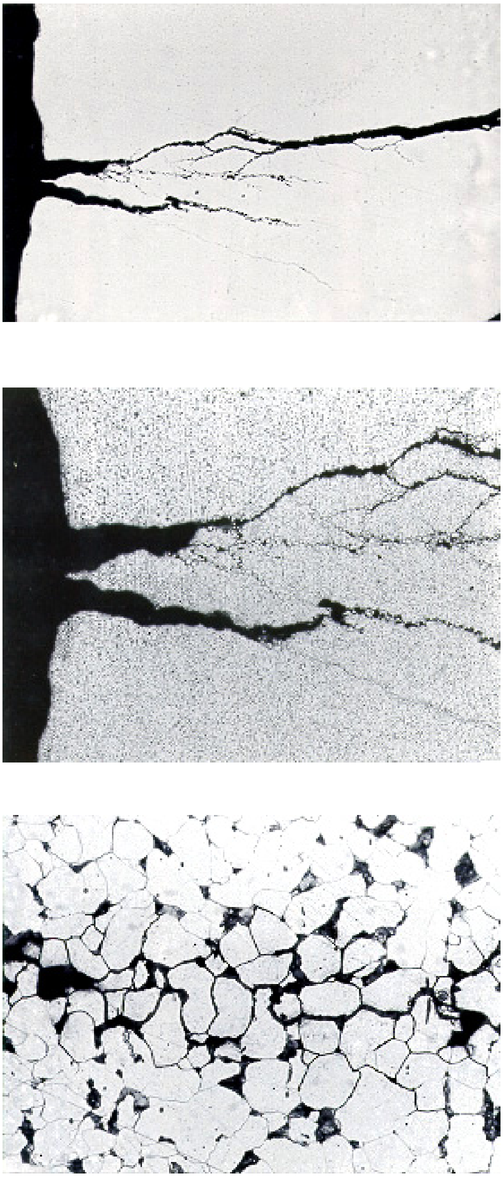

Fig. 7: microsections
top unetched x16
centre etched x32
bottom x400

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