

Use of Duplex Stainless Steels in Hydroprocessing Reactor Effluent Air Coolers (REACs)

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Use of Duplex Stainless Steels in REAC Systems

1 Executive Summary

This technical report covers results of a survey of the petroleum refining industry concerning the use of duplex stainless steel (DSS) in hydroprocessing reactor effluent air cooler (REAC) systems. The API Committee on Refining Equipment Subcommittee on Corrosion and Materials (SCCM) commissioned this survey after several industry reports of weldment cracking failures with DSS REAC system components, including REAC header boxes, tube-to-tubesheet welds, and associated piping. REAC component weldment cracking has been addressed in SCCM documents, including API Recommended Practice 932-B and API Technical Report 938-C, in published conference papers, and in a report issued by the Materials Technology Institute (MTI).

Survey results and information from prior studies are used to summarize the weldment cracking issue and to prepare an approach for assessing the likelihood for in-service weldment cracking of DSS REAC system components.

Two types of weldment cracking are discussed:

- 1) in-service sulfide stress cracking (SSC) at weldments; and
- 2) hydrogen environment assisted cracking (HEAC) occurring during tightness testing in high-pressure hydrogen.

Most previously reported cases of REAC weldment cracking were from SSC due to elevated ferrite content in welds and heat affected zones (HAZ). An issue with DSS use in REAC environments has been that no effective nondestructive method for measuring ferrite at weld HAZ is available. Ferrite is controlled through control of welding parameters and welding procedure specification development. However, without a nondestructive test method for effectively measuring localized regions of high ferrite at weld HAZ, there is no assurance that high ferrite zones are not present.

This report provides a three-step process for assessing the likelihood of SSC in existing DSS REAC system components. It involves an evaluation of ferrite control during fabrication, a measure of environmental severity, and a consideration of in-service crack detection inspection results. It is suggested that this assessment process be used to prioritize metallurgy upgrades and in-service inspections.

For new hydroprocessing REAC system components, most refining operators are specifying Alloy 825 or Alloy 625 to avoid the risk of weldment cracking with DSS. Also, many refineries are upgrading existing DSS REAC components to Alloy 825 or 625 to avoid weldment cracking. Where DSS remains in service, the following may be evaluated:

- degree of confidence that highly effective crack-detection inspections can be completed and what inspection frequency is required to detect cracks prior to loss of containment;
- accessibility of weldments for inspection that is often limited; this influences the ability to perform highly effective crack-detection inspections;
- effect of surface temperature on inspection quality if crack-detection inspection is to be done while the unit is operating.

2 Scope

This report discusses the results of the API survey of the use of duplex stainless steels (DSS) in reactor effluent systems in petroleum refinery hydroprocessing units, including the reactor effluent air cooler (REAC) and inlet and outlet piping. Additional information from literature and from the authors' experience is included.

3 Terms, Definitions, and Acronyms

3.1 Terms and Definitions

3.1.1

ferrite control

Practices and procedures used during fabrication and welding to ensure that welds and heat affected zones in duplex stainless steel have the desired microstructure and are approximately balanced in ferrite and austenite.

3.1.2

hydrogen assisted cracking

A form of cracking due to hydrogen embrittlement.

3.1.3

hydrogen embrittlement

Loss of fracture toughness or ductility caused by the presence of atomic hydrogen within a metal or alloy.

3.1.4

hydrogen environment assisted cracking

A form of cracking that occurs by subcritical crack growth due to the combined effects of tensile stress and hydrogen embrittlement in a hydrogen gas environment.

3.1.5

hydrogen stress cracking

Cracking of a metal alloy under the combined action of tensile stress and the presence of hydrogen in the alloy.

3.1.6

internal hydrogen assisted cracking

A form of cracking that occurs by subcritical crack growth due to the combined effects of tensile stress and hydrogen embrittlement due to hydrogen precharged into the metal or alloy during manufacture, welding, or service exposure.

3.1.7

reactor effluent air cooler system

The reactor effluent air cooler system includes the equipment and piping subject to ammonium salting, NH_4HS corrosion, and associated fouling. This system usually begins at the last feed/effluent exchanger or first water injection point, and continues through the cold high-pressure separator (1, 2, and 3 separator designs) or cold high- and low-pressure separators (4 and 5 separator designs). The reactor effluent system specifically excludes the stripper, fractionator, and final separation sections. However, guidance in this document may be applicable to ammonium salt corrosion mitigation in those areas, as well.

3.1.8

sulfide stress cracking

A subset of IHAC, where alloys crack under the combined action of tensile stress and atomic hydrogen generated by corrosion in the presence of water and hydrogen sulfide.

3.2 Acronyms

DHCT	delayed hydrogen cracking test
DSS	duplex stainless steel
GTAW	gas tungsten arc welding
HAC	hydrogen assisted cracking
HAZ	heat affected zone
HE	hydrogen embrittlement
HEAC	hydrogen environment assisted cracking
HSC	hydrogen stress cracking
HV	hardness Vickers
IHAC	internal hydrogen assisted cracking
MTR	material test report
NDE	nondestructive examination
PAUT	phased array ultrasonic testing
PCM	point counting method
ppmw	parts per million weight
PQR	procedure qualification record
PSA	pressure swing absorption
REAC	reactor effluent air cooler
SAW	submerged arc welding
SSC	sulfide stress cracking
SWUT	shear wave ultrasonic testing
TOFD	time of flight diffraction
UNS	unified numbering system
WFPT	wet fluorescent penetrant testing
WPS	welding procedure specification

4 Introduction

4.1 Survey Objectives

The API Committee on Refining Equipment Subcommittee on Corrosion and Materials (SCCM) commissioned a survey of petroleum refining operators who are using DSS in hydroprocessing REAC systems, including the REAC and inlet and outlet piping.

Survey objectives were to develop a database of both successful and unsuccessful use of DSS in REAC systems, and to identify operating conditions and fabrication variables that may indicate cracking susceptibility. The survey was designed based on recent experiences with in-service cracking of DSS REACs and piping due to SSC. After the survey form was issued, case histories of hydrogen embrittlement of DSS REACs during tightness testing in high-pressure hydrogen without prior exposure to sour service were identified. This mechanism is labeled HEAC and is discussed later in this report.

4.2 Background on the Use of DSS in Petroleum Refinery Hydroprocessing REACs

DSS has been used in petroleum refinery hydroprocessing unit REACs since 1985 ^[1], when the first use of 3RE60 DSS (UNS S31500) was reported in REACs. Singh et al. cited the successful use of 3RE60 DSS in REACs, which, at the time of publication, had been in service for about 11 years. In addition to the successful use of 3RE60, the authors noted two failures in REACs. One REAC made with plate similar in composition to the 3RE60 tubes failed during presulfiding on the initial unit startup. This failure was attributed to SSC (or hydrogen induced cracking) of high ferrite, coarse grained weld HAZs. Cracks were found in both tube-to-tubesheet welds and in header box weldments. The second failure involved a REAC that failed after four years of service. That REAC failed two weeks after its last startup. The failures occurred in the tubes at the HAZ of the tube-to-tubesheet welds and were attributed to SSC in the coarse-grained ferrite in the weld HAZ. This set of REACs was replaced with 2205 DSS (UNS S31803), and at the time of the publication (1994), the 2205 DSS REAC had been in service for approximately two years. The authors concluded that while there were some successful uses of 3RE60 DSS in REAC services, there were also unexpected and costly failures.

In 1997, Singh, Harvey, and Piehl ^[2] surveyed 46 operators of hydroprocessing units, focusing on general REAC corrosion. Material of construction was a variable considered in the survey. From the survey, eight DSS REACs were identified. One was the 3RE60 REAC reported in reference [1] that failed on startup, one was fabricated from 2304 DSS (UNS S32304) that was still satisfactory after seven years, and six units were fabricated from 2205 (UNS S31803), all without failures (except one unit that was destroyed by a fire unrelated to REAC weldment cracking).

2205 DSS was selected by some due to its resistance to ammonium bisulfide (NH₄HS) corrosion and its resistance to chloride stress corrosion cracking, and because it was an economical choice when compared to higher nickel alloy alternatives such as Alloy 825 or Alloy 625.

Reports of 2205 DSS REAC weldment cracking failures began around 2004 in industry forums. At the 2010 NACE Corrosion Technology Week, a state-of-the-art session on DSS REAC failures was held. At an API TR 938-C task group meeting in 2012, additional information on 2205 DSS REAC system failures was presented. The third edition of API TR 938-C ^[3], published in February 2015, added discussions about SSC failures in 2205 DSS REAC systems, and also added seven case histories of failure and 15 additional applications without cracking to industry experience summary tables (Table 11 in API TR 938-C, Third Edition).

In 2011, MTI initiated a project with the following objectives:

- 1) Review reported failures with refinery hydroprocessing REACs to understand and summarize their causes.

- 2) Develop best practice guidelines for design, welding, repair, and inspection of 2205 DSS equipment made from thick (>1-inch) plate.

The MTI project report ^[4] summarized eight failure case histories, of which seven were the same cracking cases included in the API TR 938-C, Third Edition. The MTI project also summarized available failure analysis information for the eight cases, and supported the observation that failures were caused by SSC due to high ferrite in welds and HAZ. Case histories reviewed included cracking of REAC header box weldments, tube-to-tubesheet welds, and piping circumferential weldments. Guidance on fabrication requirements and on in-service inspection was included.

API RP 932-B ^[5], Third Edition, published in June 2019, included a summary of the understanding of weldment cracking issues in 2205 DSS in REAC systems. It also included a plot of the cold separator sour water NH₄HS concentration and REAC operating pressure for 10 failures (some duplication with MTI). Refer to Figure 13 of API RP 932-B, Third Edition. API RP 932-B indicated that there is a higher incidence of weldment cracking with NH₄HS concentrations higher than 4 wt. % and with operating pressure higher than 1000 psig. Issues with welding thick components and high ferrite in weldments were also indicated to be important variables. Weld cracking was attributed to hydrogen embrittlement.

The MTI study ^[4], API RP 932-B ^[5] and API TR 938-C ^[3] attribute DSS REAC weldment cracking to be due to hydrogen embrittlement, hydrogen stress cracking (HSC), or SSC. The MTI study identified cracking of all header box pressure boundary and internal fillet welds, and included the following:

- cracking of header box corner weldments such as top and bottom plate to tubesheet or plug plate weldments;
- cracking of tube-to-tubesheet welds;
- cracking of repair welds;
- cracking of internal header box fillet welds;
- cracking of piping butt weldments.

From the review of case history failure analysis reports, the MTI study concluded that SSC due to high ferrite, and sometimes high hardness associated with tube and header box weldments, was the cause of failure. Often, high ferrite has been in a narrow zone of the HAZ adjacent to the weld fusion line. High hardness (greater than HV₁₀ 310) has not always been observed, whereas high ferrite has always been identified in cracked weldments.

High hardness did not seem to be as important as high ferrite content, with cases of cracking occurring below the generally accepted HV₁₀ 310 hardness limit. The petroleum refining industry uses NACE MR0103 ^[6] guidelines for prevention of SSC as it contains requirements for DSS base metals and weldments. For 2205 DSS, ferrite is limited to 35 % to 65 % and hardness is limited to HV₁₀ 310 average/320 maximum in weldments. Many petroleum refining companies further limit maximum ferrite in weldments to <60% for severe SSC services, such as REAC systems.

ASME PVP2016-63927 ^[7] reported on a study undertaken to evaluate the effect of ferrite level on the internal hydrogen assisted cracking (IHAC) of a series of autogenous 2205 DSS GTAW welds with ferrite ranging from about 60 % to about 90 %. Results showed a strong correlation of the quantity of weld metal ferrite with time to failure in the delayed hydrogen cracking test (DHCT). Welds with nominally 65 % ferrite failed in 203 hours, whereas welds with 91 % ferrite failed in 8 hours. The DHCT tests seemed to closely reproduce failures that have occurred in service, and were consistent with guidelines to limit ferrite to 60 % maximum at weldments.

NACE paper 2019-13263 ^[8] shows an example of SSC of a DSS REAC header box at a narrow high ferrite region along a weld HAZ, and summarizes some of the issues with DSS in REAC systems:

- 1) There is no effective commercial nondestructive method to evaluate weld HAZ for quantity of ferrite. Ferrite control is done through welding procedure qualification (PQR) testing. PQR samples for all welding procedure specifications (WPS) are tested with a point counting method (PCM) or image analysis (IA) method to measure ferrite in base metals, weld deposits, and HAZ. Nondestructive methods, such as magnetic measurements, are unable to capture narrow high ferrite regions deep beneath the surface of thick plate weldments due to limitations in interaction volume and geometry.
- 2) Narrow zones of high ferrite adjacent to the fusion line of welds are difficult to characterize. Weld and HAZ microstructures are heterogeneous. PCM type measurements can average out or miss localized high ferrite regions, particularly in the HAZ. Average ferrite criteria may not be as meaningful as maximum ferrite at local areas. Also, the reliability and accuracy of quantification methods may need to be considered.
- 3) Magnification used during measurements of ferrite influences measured ferrite levels. With low magnification, features cannot be identified and result in measurement error. Ferrite measurements may increase with higher magnification, so too high of a magnification may overestimate ferrite content.

MTI's *Guidelines for Measuring the Amount of Ferrite in Duplex Stainless Steels* ^[9] includes a discussion of the difficulties in measuring the ferrite of welds and weld HAZ, and suggests that an alternate to a numerical ferrite acceptance criterion should be developed.

4.3 Summary

Many DSS REACs have remained in service successfully, with some in service for more than 30 years. However, several incidences of cracking failures of both REACs and associated piping have occurred in industry. Some failures have resulted in major plant damage and long outage time. Weld cracking is most likely due to locally high ferrite at welds and HAZ that leads to SSC in the REAC system sour water. Some refiners have been replacing DSS REACs with Alloy 825 to avoid in-service cracking risk. Others have made risk assessments and continue to operate with DSS REACs, often with periodic in-service crack detection inspection.

5 Survey Results and Discussion

5.1 Survey

Table 1 shows the survey form that was issued in a spreadsheet to the distribution lists of the API Subcommittee on Corrosion and Materials and Subcommittee on Inspection and Mechanical Integrity (SCIMI) in November 2018. As indicated in the transmittal, survey responders have been kept anonymous. Data that could be used to identify companies or individuals responding is either not included in this report or is otherwise masked to protect the responder's identity.

Responders were asked to complete a column for each response and to add columns as needed, i.e., Equipment 1, 2, 3, etc. Some responders included multiple equipment in the same column, such as the REAC and inlet and outlet piping. Others added a column for each equipment item, e.g., a column for the REAC, another column for the inlet piping, etc. Each column of response is a "survey record."

Questions were selected to obtain input on the following categories:

- 1) fabrication and design variables;
- 2) operating and process variables;

3) in service inspection practices and findings.

In this section, results from the survey are discussed according to these categories.

Table 1—API DSS Survey Form

Question Number	Question	Equipment 1
1	Name of refinery (will be kept confidential)	
2	Unit (naphtha hydrotreater, hydrocracker, etc.)	
3	Equipment number (tag) (will be kept confidential)	
4	Header box material specification i.e. UNS/ASME/DIN, EN, ISO specification (only DSS are covered in this survey)	
5	Did your purchase specification go beyond the standard's requirements? If yes, how?	
6	Tube material specification, i.e., UNS/ASME/DIN, EN, ISO specification (only DSS are covered in this survey)	
7	Did your purchase specification go beyond the standard's requirements? If yes, how?	
8	Service (naphtha, kerosene, diesel, gas oil, etc.)	
9	Inlet piping material specification, i.e., UNS/ASME/DIN, EN, ISO specification (only DSS are covered in this survey)	
10	Outlet piping material specification, i.e., UNS/ASME/DIN, EN, ISO specification (only DSS are covered in this survey)	
11	Please submit a simplified PFD showing the REAC system configuration. Alternatively, describe the process flow and where the REAC is positioned in the flow (vapor, liquid, total effluent, etc.)	
12	Operating pressure (psig, barg, MPa, etc.)	
13	Design pressure (psig, barg, MPa, etc.)	
14	Inlet temperature (°F or °C)	
15	Outlet temperature (°F or °C)	
16	Does the REAC receive continuous water wash? (Y/N)	
17	Does the REAC receive intermittent water wash? (Y/N)	
18	Does the water wash comply with API RP 932-B, 2 nd edition? (Y/N)	
19	If the water wash is not in compliance with API 932-B, 2 nd edition, what is not in compliance?	

Question Number	Question	Equipment 1
20	Does the reactor go through in situ catalyst pre-sulfiding operation? (Y/N)	
21	Typical pH in product separator	
22	Do you have evidence of REAC salt plugging problems (Y/N)	
23	Separator sour water wt.% NH_4HS (typical and maximum)	
24	N in feed (ppmw)	
25	H_2S partial pressure	
26	Hydrogen partial pressure	
27	Sour water chloride concentration (ppmw)	
28	Years in service	
29	For header box, what are tubesheet, plug sheet, and top/bottom plate thickness?	
30	Were corner joints (top/bottom plate to plug or tube sheet) welded only from outside?	
31	What welding processes were used for corner joint?	
32	Were tube-to-tubesheet welds single or multiple pass?	
33	Did tube-to-tubesheet welds have filler metal added or were they autogenous?	
34	Describe WPS/PQR ferrite testing requirements (sampling of base metal, HAZ and weld deposit, magnification for evaluation, acceptance criteria)	
35	Describe other WPS/PQR requirements (impact test, corrosion test, hardness with acceptance criteria)	
36	Ferrite checks on outside of weldments during production welding? (Y/N) How?	
37	Ferrite checks on inside of weldments during production welding? (Y/N) How?	
38	Were any ferrite results out of compliance with requirements?	
39	Hardness checks on outside of weldments during production welding? (Y/N) How?	
40	Hardness checks on inside of weldments during production welding? (Y/N) How?	
41	Were any hardness readings out of compliance?	
42	Did header boxes have internal fillet welds?	