

Material, Fabrication, and Repair Considerations for Austenitic Alloys Subject to Embrittlement and Cracking in High Temperature 565 °C to 760 °C (1050 °F to 1400 °F) Refinery Services

API TECHNICAL REPORT 942-B
FIRST EDITION, MAY 2017

EFFECTIVE DATE: NOVEMBER 1, 2017



AMERICAN PETROLEUM INSTITUTE

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Introduction

The API Committee on Refinery Equipment, Subcommittee of Corrosion and Materials, identified a need to develop a technical report focusing on the materials, fabrication, and repair of austenitic stainless steels and nickel-iron-chromium alloys in high temperature 565 °C to 760 °C (1050 °F to 1400 °F) refinery services. Many of these alloys are subject to embrittlement and cracking after prolonged exposure to these temperatures. Susceptible equipment in the following processing units are addressed:

- fluid catalytic cracking units,
- hydrogen/syngas plants,
- catalytic reformers,
- cokers,
- hydroprocessing units.

This report summarizes industry experience and recommends methods to improve reliability and process safety, and increases industry awareness to high temperature embrittlement issues.

NOTE Embrittlement can be a serious personnel safety issue if plant personnel are not careful about hand-holds and foot-holds when inspecting embrittled piping and vessel components. There has been at least one case where an inspector was seriously injured when an embrittled support failed.

Material, Fabrication, and Repair Considerations for Austenitic Alloys Subject to Embrittlement and Cracking in High Temperature 565 °C to 760 °C (1050 °F to 1400 °F) Refinery Services

1 Technical Approach/Report Organization and Scope

As a basis of this report, technical literature, industry experience, and published case studies were reviewed. The review included materials of construction, damage mechanisms, and component-specific fabrication and repair issues.

The scope of this report includes the following wrought austenitic alloys: Alloys 800, 800H, 800HT®, and 300 series austenitic stainless steels, and corresponding welding consumables. Limits in chemical composition, microstructural requirements, and heat treating practices that mitigate susceptibility to embrittlement and cracking are identified. Potentially viable upgrades to commonly used alloys are identified where applicable.

The remainder of this report is organized as follows.

Section 3, Process Units, gives a brief process overview followed by an explanation of the various damage mechanisms found in that unit. Component specific considerations and examples of in-service damage are also included. Inspection recommendations and general repair method considerations are also included.

Section 4, Damage Mechanisms, contains detailed discussions of high-temperature damage mechanisms; including fundamental details of the solid state reactions, their rate of reaction, and recommended mitigation measures. Section 4 also incorporates fabrication and repair practices that can be used for cracked or embrittled equipment.

NOTE Excluded from the scope of this document are Hydrogen Reformer catalyst tubes, outlet pigtails and outlet headers. With the exception of catalyst tubes, these are covered in TR 942-A, *Materials, Fabrication, and Repair Considerations for Hydrogen Reformer Furnace Outlet Pigtails and Manifolds*. Also excluded are expansion bellows in elevated temperature service.

2 Acronyms and Abbreviations

For the purposes of this document, the following acronyms and abbreviations apply.

CCC	complete carbon monoxide combustion
CO	carbon monoxide
CRCR	continuously regenerated catalytic reformer
CVN	Charpy V-notch
FCCU	fluid catalytic cracking unit
FN	ferrite number
GTAW	gas tungsten arc welding
ID	inside diameter
MTR	material test report
NDE	non-destructive examination
NDT	non-destructive testing

PASCC	polythionic acid stress corrosion cracking
PCC	partial CO combustion
PFZ	precipitation free zone
PT	penetrant testing
PWHT	post weld heat treatment
SAGBO	stress assisted grain boundary oxidation
SRC	stress relaxation cracking
SS	stainless steel
T/C	thermocouple
TTT	time temperature transformation
UT	ultrasonic testing
UTSW	ultrasonic testing shear wave
WRC	Welding Research Council

3 Process Units

3.1 General

Table 1 summarizes common embrittlement mechanisms in each of the listed refinery process units. Implications for specific equipment are discussed in more detail in the section for each respective process unit. Information on damage mechanisms can be found in API 571 and in Section 4 of this document.

3.2 Fluid Catalytic Cracking Units (FCCUs)

3.2.1 Process Description

FCCUs are used to process heavy feedstocks, converting them to gasoline, diesel, and furnace oils. A simplified process flow diagram for the FCCU is shown in Figure 1 [1]. The catalytic reaction occurs mostly inside the riser prior to reaching the reactor at temperatures ranging from approximately 480 °C to 565 °C (900 °F to 1050 °F). In modern FCCUs, the “reactor” functions as a hydrocarbon/catalyst separator. During the process, the catalyst becomes deactivated as it becomes coated with carbon (coke). The catalyst is sent to the regenerator where it is exposed to air, promoting the burn off of coke at approximately 650 °C to 780 °C (1200 °F to 1475 °F).

Inside FCCU reactors and regenerators are cyclones which are used to separate the catalyst from the overhead vapor streams. Most regenerators have multiple sets of primary and secondary cyclones. Primary cyclones direct the vapor flow from inside the reactor or regenerator in a centrifugal pattern, forcing the heavier catalyst particles outward against the inside wall, and allowing the catalyst particles to then fall down into the catalyst bed. The lighter vapor stream exits out the top of the primary and into the secondary cyclone to remove residual catalyst from the vapor stream. Primary and secondary cyclones can be seen in Figure 2 [2].

Units that process heavier feeds are called resid fluid catalytic cracking units (resid FCCUs) and these feeds typically have higher sulfur contents. In addition, resid FCCU feeds typically develop higher carbon residues on the catalyst particles. Carbon residues, as indicated by the Conradson Carbon Residue test of Resid FCCU feeds, are significantly higher with up to 5 to 10 wt.%, compared to <1 wt.% for a typical FCCU feed. These heavier feeds also

Table 1—Process Units, Conditions, and Typical Austenitic Stainless Steel Damage Mechanisms*

Process Unit/ Affected Equipment	Operating Temperature Range	Sigma Phase Embrittlement	Stress Relaxation Cracking	Carburization	Creep
FCCU (regenerator)	650 °C to 800 °C 1200 °F to 1475 °F	Yes	Possible	Yes	Yes
H ₂ Plants (steam superheater tubes)	370 °C to 540 °C 700 °F to 1300 °F	Yes	Yes	Yes	Yes
Catalytic reformers (regeneration vessels)	515 °C to 565 °C 960 °F to 1050 °F	No	Possible	Yes	No
Coker (heater tubes)	574 °C to 760 °C 1065 °F to 1400 °F	Yes	Possible	Yes	Yes
Hydro processing plants recycle H ₂ heaters	545 °C to 675 °C 1010 °F to 1250 °F	Yes	Yes	Yes	Yes
*This table only lists mechanisms covered in this document.					

usually contain more metals, and require higher temperatures to crack. This can lead to increased carburization and sigma embrittlement of regenerator cyclones if higher burn temperatures are used.

There are two modes of regenerator operation: Complete Carbon-monoxide (CO) Combustion (CCC) or Partial CO Combustion (PCC). Both types of operation are subject to upsets (including “afterburns”) that can cause rapid localized temperature excursions.

Afterburn (CO combustion) in a regenerator can lead to localized high temperatures, up of 900 °C (1650 °F) or hotter, which can cause major damage to regenerator internals.

Causes of afterburn in a PCC Regenerator include the following.

- Lack of promoter activity that causes oxygen slip to the dilute phase. (Promoters are catalyst additives that enhance control of CO, SO_x, and NO_x.)
- Excessive air/coke ratio (too close to the stoichiometric ratio). Regenerators are intended to operate either with clearly less than stoichiometric air (PCC) or with excess air (greater than 1:1) where there is CCC operation.

Afterburns tend to be more of a problem with CCC operation. Reasons for afterburn in a CCC regenerator include: slow CO combustion in the dense bed, due to lack of promotion activity and localized deficit in the air supply to the bed, either from asymmetric design or air grid damage.

3.2.2 FCCU Damage Mechanisms

3.2.2.1 General

The rate of damage mechanism development depends on a complex set of factors that include: exposure time, temperature, thermal cycles, process upsets, the number of start-ups and shut-downs, peak temperatures, mode of operation (e.g. partial or full combustion), and operating upsets (such as afterburns). In particular, process upsets and rapid start-ups and shut-downs all generate abnormal stresses that can both initiate and propagate cracking.

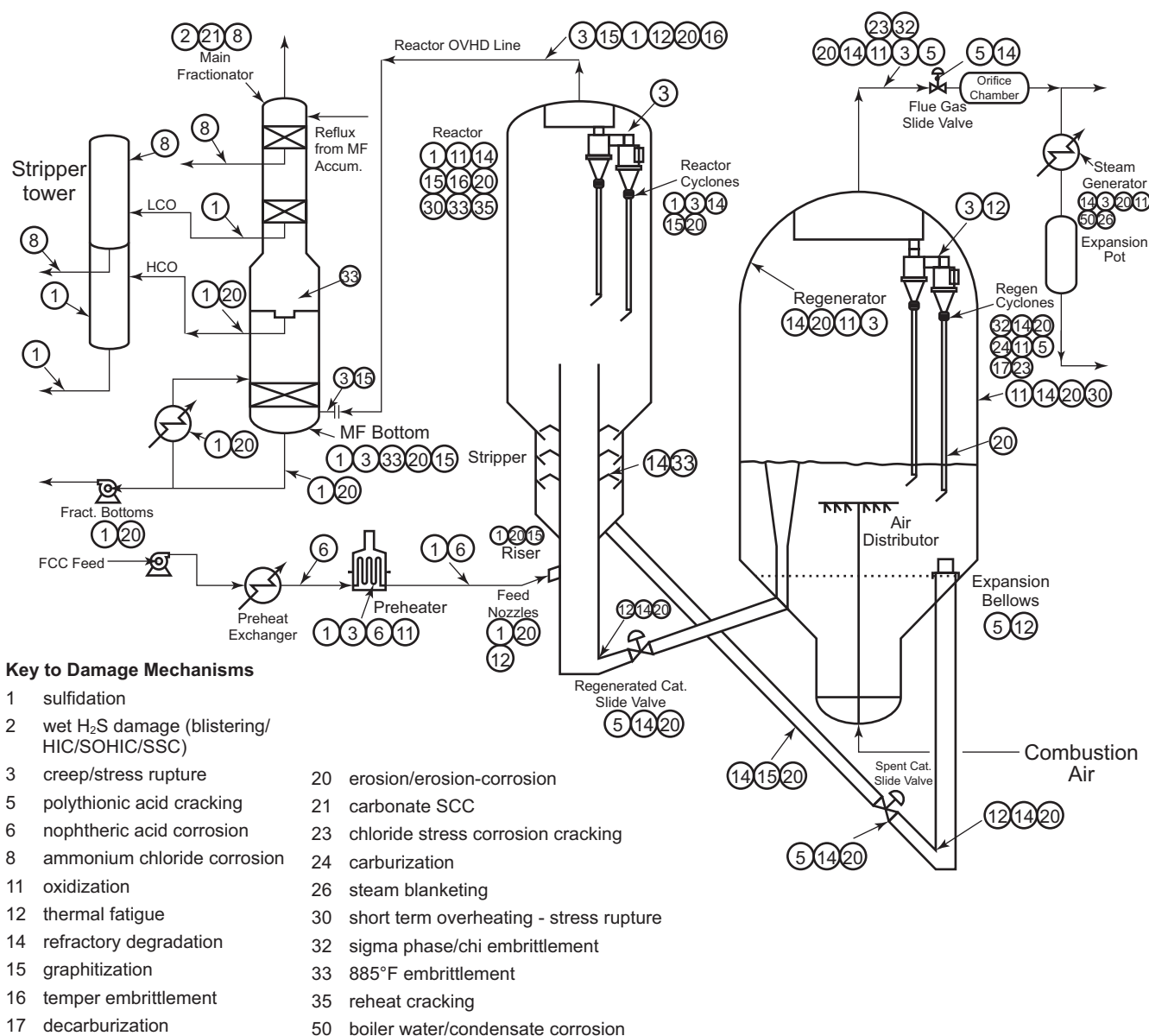


Figure 1—FCCU Simplified Process Flow Diagram

3.2.2.2 Sigma Phase Embrittlement

Sigma phase embrittlement is a common high temperature problem for austenitic alloys used in FCCU regenerators. Over time, high-temperature service promotes the formation of this hard, brittle, nonmagnetic phase. Sigma phase is an intermetallic compound of iron and chromium (FeCr) and is discussed further in 4.2. Sigma forms most readily from the ferrite phase in stainless steel welds in one year of service or less. However, sigma can also form from austenite given enough time at elevated temperatures.



Figure 2—Replacement of Primary (Outer Ring) and Secondary (Inner Ring) Cyclones

Weld solidification relies on ferrite contents of 3 % to 10 % to increase hot ductility and minimize the potential for solidification cracking. Therefore, in general, when exposed to typical regenerator operating temperatures, the weld metal exhibits higher percentage of sigma phase than the corresponding base metal, and will have more tendency to embrittle sooner.

3.2.2.3 Carburization

Typical operating conditions in FCCU regenerators cause low rates of carburization of the stainless steel cyclones and other internal components. Resid FCCUs regenerator internals, with their corresponding higher temperatures, have an increased susceptibility to carburization, as well as faster sigma formation. One resid FCCU using Type 304H stainless steel at 730 °C to 760 °C (1350 °F to 1400 °F) reported a cyclone life of only 5 to 6 years due to the development of deep carburized layers [3].

Afterburn in regenerators not only raises combustion temperatures, but because it involves the combustion of CO, can cause severely carburizing atmospheres.

FCCU internal components can also suffer sensitization [4]. Sensitization can be aggravated by excess dissolved carbon due to carburization and can make the material susceptible to polythionic acid stress corrosion cracking (PASCC). A polythionic acid can be formed when sulfide scales formed at high temperatures on the surface of a stainless steel are cooled and exposed to moisture. The polythionic acid can cause intergranular SCC on sensitized stainless steel which is referred to as "PASCC". This mechanism is covered more fully in NACE SP0170-2012 [78]. Some refiners reduce the potential for PASCC by minimizing moisture when the vessel is opened during shutdowns, while others use a neutralizing soda ash washing.

3.2.2.4 Creep

Long-term creep cracking can occur in the regenerator internal support structures. The shortening of creep life can be impacted by sigma formation, particularly in the welds.

Short-term creep/stress rupture is usually caused by afterburning episodes that result in local hot spots. Localized heating promotes high thermal stresses and weakens the material, increasing the potential for cracking. During afterburning, stresses can be high due to non-uniform temperature gradients inside the regenerator, resulting in distortion of cyclones, cyclone support structure, and regenerator plenums, and particularly at gas outlets.

Detection of creep cracks is usually performed by visual inspection or by liquid penetrant testing. To determine the extent of creep damaged material, field metallography and replication techniques can be used prior to deciding the amount of material to repair or replace.

3.2.2.5 Stress Relaxation Cracking

Stress relaxation cracking (SRC) is usually associated with fabrication heat treatments or short-term thermal in-service failures due to low creep ductility, but has not been widely reported in FCCUs. For Type 347 stainless steel and Alloy 800 series components with wall thicknesses greater than 12 mm (1/2 in.) or for fillet weld joints, fabrication, and in particular repair welding procedures, should consider measures such as stress relief to avoid or minimize this damage mechanism. Experience has shown that SRC is unlikely with 304H stainless steel. Refer to Table 3 and Table 4 for susceptibility to SRC for different materials.

3.2.3 Component Specific Considerations

3.2.3.1 Regenerator Cyclones

Regenerator cyclones are commonly fabricated from Type 304H stainless steel; however, other 300 series stainless steels have been used. Primary embrittlement is due to sigma phase formation, although carburization can also occur.

In-service cyclone cracking failures have not been reported, however, there have been cases of cyclones dropping while the regenerator was being shut down. Failures during shut down are often due to the fact that sigma phase is reasonably tough at high temperature, but typically loses toughness when cooled below about 260 °C (500 °F) (more details are given in Section 4).

Based on comments captured in the minutes of meetings of NACE Committee TEG 205X (formerly T-8) on Refining Industry Corrosion, regenerator cyclones are seldom replaced due to sigma phase content alone, but occasionally are replaced when they become too brittle to repair efficiently. It is more common to see cyclones replaced in order to increase capacity or improve efficiency. Decisions to repair or replace them should be judged case-by-case. If repairs are very difficult during a given shutdown, it may be more cost effective to build new cyclones to be installed during the subsequent shutdown.

Measures to predict cyclone repairability can include weldability testing, Charpy V-notch (CVN) toughness testing, or bend testing. Some predictive methods include removal and testing of coupons from aged components such as from the barrel of a cyclone.

Mechanical testing of cyclones replaced due to poor repairability often show low toughness, typically with CVN test values of less than 20 J (15 ft-lb) at ambient test temperature.

Bend tests on butt welds can also be used to gauge repairability. Test welds can be deposited using a small coupon removed from a cyclone. The ability to perform repair welding would be suspect if the test welds fail to pass a 90-degree bend test at ambient temperature [or with a 150 °C (300 °F) preheat temperature if desired].

Another weldability test is a simple gas tungsten arc welding (GTAW) autogenous weld (no filler metal) on an actual cyclone, which can be done without removing a coupon. If penetrant testing shows crack indications, there is a high potential for cracking during weld repairs.

If carburization is suspected, the carburized layer needs to be removed by grinding or by other methods prior to welding. Carburized stainless steel can be magnetic; therefore, a simple magnet test can be used to detect carburization. More details can be found in Section 4.

Inspection of cyclones typically includes visual examination looking for distortion, cracking and loss of protective refractory. Penetrant Testing (PT) and Ultrasonic Testing Shear Wave (UTSW) of support clips and other high stress locations are also typically performed.

3.2.3.2 Regenerator Refractory Anchors and Hexagonal Mesh

Many regenerator components have erosion resistant refractory which is typically held in place using hexagonal mesh or shaped wire anchors made of austenitic grades of stainless steels such as Types 304 or 304H. Examples of hexagonal mesh are shown in Figure 3, Figure 4, and Figure 5 [5].

Hexagonal mesh is typically made from thin materials that can be deformed and shaped to fit the curvature of regenerator cyclones. There are other designs, such as "Flexmetals," that use a secured rod to provide a pivot point that allows freeform rolling to very small diameters, down to 150 mm (6 in.).

Sigma phase formation (sigmatization) of hexagonal mesh is expected for all regenerating operating conditions. In addition, hexagonal mesh can be prone to embrittlement and corrosion from carburization, oxidation, and sulfidation near the base metal.

For steels and other iron-based alloys, oxide scales formed from high temperature exposure are dense and black. High-temperature oxidation resistance of alloys is improved primarily by increasing chromium content, and secondarily, by increasing silicon. For most hexagonal mesh applications, the minimum alloy for oxidation resistance is an austenitic stainless steel with 18 % Cr.

As metals are heated in an air or steam environment, the rate of oxide scale formation increases logarithmically, until spalling occurs. When the temperature threshold for spalling is reached, metal loss rates can increase rapidly. For austenitic stainless steels containing 18 % to 20 % chromium, the spalling threshold temperature is about 900 °C (1650 °F). Higher chromium stainless steels, such as Types 310 or 330, have higher spalling threshold temperatures,



Figure 3—Example of New Hexagonal Mesh Welded Inside a Regenerator Cyclone



Figure 4—Large Areas of Internal Hexagonal Mesh and Refractory that Failed in a Brittle Manner

on the order of 1095 °C (2000 °F). Spalling damage, if it occurs, indicates that operating temperature excursions have occurred that exceeded 900 °C (1650 °F).



Figure 5—Example of External Refractory that Failed After a Short Time in Service

There have been a significant number of recent (2008 through 2011) Type 304/304L and Type 321 stainless steel hexagonal mesh failures that have caused loss of internal refractory resulting in plugged cyclones. This has forced shut downs of the units and caused significant reliability issues.

Factors contributing to premature hexagonal mesh failures are still under investigation at this time, although based on available information, some certain commonalities have been observed.

- When it occurs, the damage mechanisms generally cause refractory systems to fail in approximately 4 to 6 years, though there has been a case where failure occurred after only two years [4].
- Since embrittlement and corrosion occurs behind the refractory, damage is often not obvious from visual inspection.
- Cases have been reported in both complete and partial combustion units.

In the example shown in Figure 5, the regenerator cyclones were made of Type 304H stainless steel, and the hexagonal mesh and anchors were replaced with Type 321 stainless steel (previously Type 304 stainless steel). The refractory was in good condition, with the hexagonal mesh to cyclone welds being intact. Failures were within the Type 304 stainless steel hexagonal mesh, which was found to be very brittle and easily broken by hand pressure. Metallurgical examination revealed extensive carburization through the full thickness of the hexagonal mesh, including hexagonal mesh surfaces covered by the refractory. There was minimal wall loss at the exposed ends of the anchor system.

Iron sulfide and iron oxide scales were observed on the hexagonal mesh surface. Since sulfides can cause the chromium oxide layer to become porous, the presence of sulfides in the scale may be significant. Sulfidation and oxidation were most prevalent where the metal was carburized. Replacement hexagonal mesh was made of

Type 310 stainless steel. Although Types 304 and 321 stainless steel are reported to resist SO₂ to 800 °C (1470 °F), Type 310 stainless steel is resistant up to 1050 °C (1922 °F). However, Type 310 stainless steel is more prone to sigma phase formation than Types 304, 321, or 330 stainless steel. Since the hexagonal mesh flexes during start-ups and shut-downs, there is a concern that hexagonal mesh could fail due to embrittlement due to the high volume of sigma phase in the Type 310 stainless steel. Due to its overall good track record and performance or cost concerns with alternatives, Type 304H remains the industry workhorse for regenerator internals.

Another example involved refractory failure due to carburization of Type 321 stainless steel hexagonal mesh. In this case, examination of failed hexagonal mesh indicated that extensive carburization had occurred through the total thickness of the thin material. The carburization was homogenous, with carbide precipitation throughout the material. A denser layer of carburization was also visible on the outer extremities of the hexagonal mesh sample.

3.2.3.3 Internal Support Rods and Bars

Depending on the design, cyclones can be suspended from the dome of the regenerator by bars and rods or by the cyclone outlet tubes and hanger straps. Support components are usually made of Type 304H stainless steel. Creep failures have been reported in these components [6].

Creep voids were found at the failed end of the cyclone support rods and are shown in the referenced paper. Various stages of creep damage can be seen, including isolated voids, elongated voids, linked voids and macro cracking. Therefore, it is likely that this bar failed due to long-term creep damage.

There have been a number of support failures where it was suspected that afterburning events produced local hot spots and corresponding high thermal stresses resulting in support rod failures due to short-term stress rupture.

PT inspection of these components can be used to detect advanced stages of creep damage. Depending on the configuration, straight beam ultrasonic testing techniques of rod type supports can be used to detect advanced stages of concealed damage.

Sigma phase embrittlement of the support bars is also a concern. There have been cases where failure occurred during a shut-down as a result of transient thermal stresses on embrittled support structures.^{ibid.}

3.2.3.4 Regenerator Plenum

The plenum acts as a header that channels flue gas from the cyclone gas outlet tubes to the overhead outlet nozzle.

Failures have been reported in plenums as a result of short-term stress rupture or long-term creep. The high temperatures and localized stresses needed to cause short-term stress rupture damage are often attributed to afterburning episodes. Long-term creep is more likely an issue at known high stress locations such as gas outlet tube-to-plenum welds. These can be inspected by PT if accessible or ultrasonic testing (UT) shear wave from the outside of the plenum to gas tube connection.

Some regenerator plenums have internal water sprays to reduce overhead flue gas temperatures due to downstream equipment temperature limitations. Several cases of thermal fatigue cracking were reported where injected water impinged on the plenum wall. Often, the refractory has spalled and thermal fatigue damage can appear as a fine network of cracks on the plenum floors or walls, distorted floors, and cracked fillet welds at gas outlet tube reinforcement pads.

With transgranular thermal fatigue cracking due to water injection, multiple cracks will be visible and indicate variations in stress orientation. Variations in crack width indicate that the cracking occurred over a period of time, not as a one-time event. Tight cracks will appear to be newer and indicate that the cracking is still active.

Thermal fatigue cracks can also occur when thermal growth of the plenum that combines with a stress concentration at a fillet weld that attaches the plenum skirt to the head. Cracks can form at the toe and root of the fillet weld [7].

These cracks can grow during startups and shutdowns, particularly during abrupt temperature fluctuations. Newer designs use a reinforced stub with a full penetration fillet weld [8].

Repairs of these components are often made using 16Cr-8Ni-2Mo ("16-8-2") stainless steel weld metal. This is a variant of 308 series stainless filler metal, with lower chromium to produce less ferrite to reduce sigma phase. The addition of 2 % Mo improves creep strength in this ductile filler metal. More details on this filler metal are in Section 4 repair sections.

3.2.3.5 Flue Gas Overhead Duct Piping

Flue gas outlet piping from the regenerator is generally made from Type 304H stainless steel for hot wall designs. While sulfidation, oxidation, and carburization are generally not problems in overhead ducts, thermal stresses and low ductility due to sigma phase embrittlement of welds and base metal has resulted in online leaks.

Some sections are refractory lined to reduce skin temperature, thereby reducing thermal growth and the accompanying mechanical problems. When refractory is used, the refractory lining is terminated far enough upstream of any power recovery system (expander) to prevent spalled refractory from entering into the rotating equipment.

Piping and equipment designers should consider applied and induced loads from low-cycle thermal expansion during shut-down and start-up conditions. Significant damage can occur during rapid shutdowns due to upset conditions such as a loss of power.

Large diameter piping often utilizes mitered joints for elbows. These welds are subject to high stresses since thermal expansion and contraction is significant at the welds which are located at stress concentration points. As such, many users perform dye penetrant inspection of these joints during turnarounds.

Piping flexibility analysis of flue gas piping should include spring hanger and pipe support audits. These audits should include visual inspections of all piping supports to ensure that both spring cans are properly operating in both the hot and cold conditions and that piping shoes did not fall off of pedestals, restricting thermal movement, causing corresponding high localized stresses. Low-cycle thermal fatigue and creep/stress rupture can occur as a result.

Repair of equipment in FCCU regenerator overhead piping is complicated by its large diameter which is often inherently stiff and inflexible piping. The high ductility and strength of the 16-8-2 or similar filler metal, along with its resistance to sigma phase embrittlement, improves the reliability of repairs (see Section 4).

3.2.3.6 Metallurgical Embrittlement Considerations

Sigma phase embrittlement of high-ferrite weld deposits result in low ductility when cooled below about 260 °C (500 °F) and also in an inability to tolerate large thermal transients during process upsets. For this reason, cracks or leaks are often found during shut-downs or on-line following a rapid uncontrolled temperature swing.

Figure 6 [9] shows an example of a large diameter Type 304H stainless steel flue gas mitered elbow joint that was replaced after 11 years of service due to severe distortion and cracking. It operated at an average temperature of 715 °C (1320 °F) and suffered chronic cracking at the welds on the intrados that seemed to occur each time the unit was shut down and the piping was cooled to ambient temperature. The cracking was attributed to sigma phase embrittlement and required lengthy repairs involving crack removal and re-welding. On occasions, the old weld had to be removed as a window which encompassed both sides of the weld and replaced with inserts and a new weld. In another refinery with similar problems, the mitered elbows were replaced by formed elbows.

In a case [10] of creep cracking shown in Figure 7, Figure 8, and Figure 9, a crack 2.4 m (8 ft) long developed in a longitudinal weld seam in a 180 cm (72 in.) diameter Type 304H stainless steel duct that was flux-cored arc welding (FCAW) with Type 308H stainless steel consumable.



Figure 6—An Example of a Mitered Joint After Removal From Service

Interdendritic creep cracking was found in the large welds at the outside diameter (OD) of the piping. The pipe longitudinal seam welds appeared to have been welded with a two pass submerged arc weld procedure. Test of material removed from the weld showed high levels of sigma phase and that the weld had half the remaining creep life of the base metal.



Figure 7—Creep Failure on a FCCU Regenerator Overhead Line

In a fourth reported case, inspection noted a 1 m (3 ft) crack in a circumferential duct weld. Cracking was attributed to the presence of bismuth in the FCAW welding consumable. Bismuth limits of 0.002 wt% (as given in API 582) should be observed when service temperatures are above 538 °C (1000 °F).

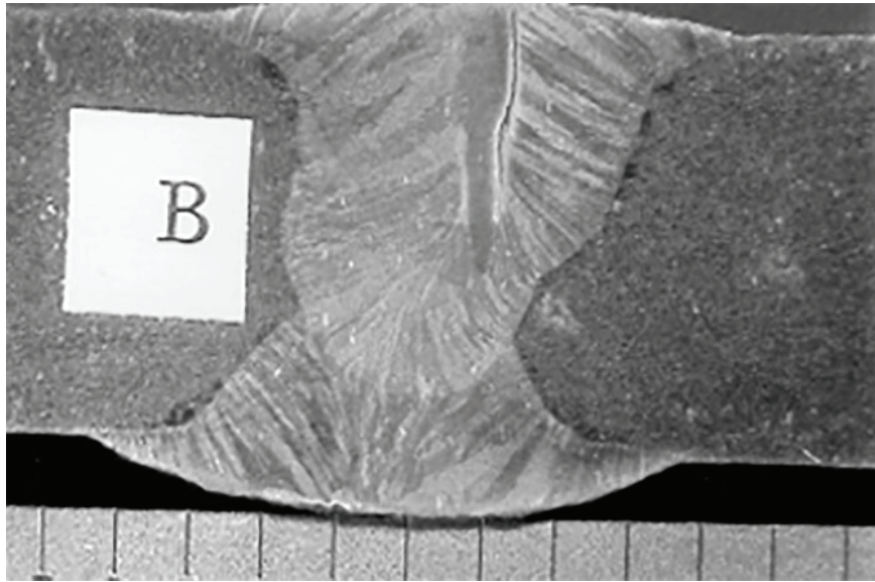


Figure 8—A Two Pass SAW Weld Was Found with Creep Cracking in the Outside Weld Bead

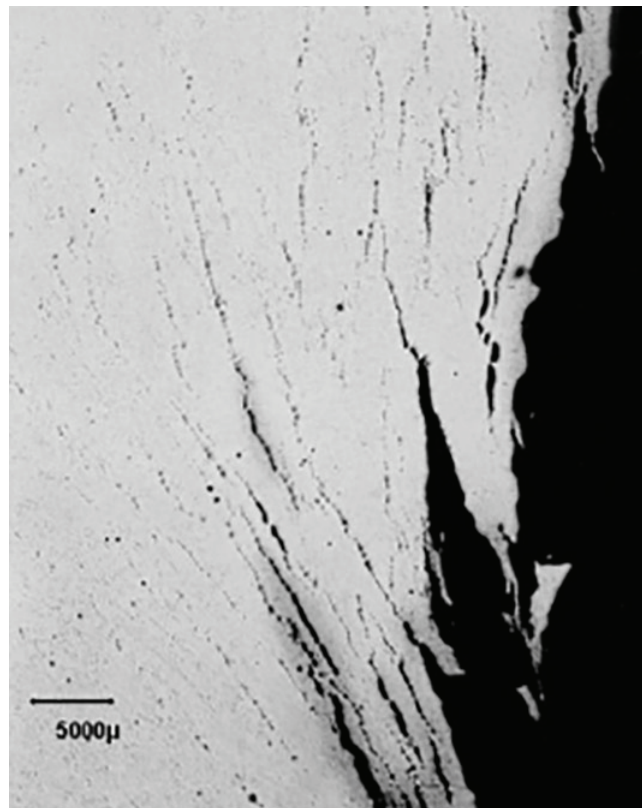


Figure 9—Interdendritic Creep Voids and Cracking in a Weld Cross Section

Another case involved a hot wall piping design that was 25 years old with operating temperatures at about 640 °C (1184 °F). Approximately 10 years prior, portions were replaced using Type 321H stainless steel welded with Type 347 stainless steel filler metal without post weld heat treatment (PWHT). After a failure, samples of weld metal were cut out for laboratory analysis. The Type 347 stainless steel weldments were found to be extremely brittle and the delta ferrite had transformed to sigma. Weld samples exhibited very low ductility when bent. Metallographically,

3.3 Hydrogen/Syngas Plants

3.3.1 Process Description

3.3.1.1 General

Key to Damage Mechanisms

- 3 creep/stress rupture
- 10 high temperature hydrogen attack
- 11 oxidation
- 14 thermal fatigue
- 16 refractory degradation
- 21 carbonate stress corrosion cracking
- 22 amine cracking
- 23 chloride stress corrosion cracking
- 25 steam blanketing
- 27 thermal shock
- 30 short term overheating - stress rupture
- 32 sigma phase/chi embrittlement
- 35 reheat cracking
- 39 dissimilar metal weld (DMW) cracking
- 42 CO₂ corrosion
- 45 amine corrosion
- 50 boiler water/condensate corrosion
- 59 metal dusting

Hydrogen Reforming Process Flow:

The diagram illustrates the Hydrogen Reforming process, starting with Methane Feed and Steam entering the Steam/Methane Reformer. The reformer effluent passes through a Waste Heat Exchanger, then a High-Temperature Shift Converter, and finally a Low-Temperature Shift Converter. The gas then goes through a Methanator Preheater and a Bypass before entering the Methanator. The Methanator effluent passes through a CO₂ Stripper, a CO₂ Absorber, and a CO₂ K.O. Pot. The final product is H₂. Various damage mechanisms are indicated by numbered circles throughout the process.

Figure 10—Hydrogen Reforming Process Flow Diagram

Reformer product gases leave the furnace at temperatures ranging from 790 °C to 860 °C (1450 °F to 1580 °F). Reformer effluent is typically cooled in waste heat recovery boilers that operate at conditions which can promote embrittlement and cracking. Waste heat boilers equipped with a bypass tend to suffer sigma phase embrittlement and metal dusting of their austenitic stainless steel liners and bypass valve components. An alternate design employs a secondary reformer in place of a waste heat boiler. In this design, the hot syngas from the primary reformer outlet is used to heat incoming feed and generate additional syngas. The secondary reformer vessel, internals, and associated piping are typically fabricated from austenitic stainless steels and are exposed to temperatures covered by this document. These components can be susceptible to stress relaxation cracking, sigma phase embrittlement and metal dusting, which is a significant concern; however, metal dusting is outside the scope of this document.

3.3.1.2 Preheater Feed Coil Inlet Header and Coil in the Reforming Furnace

In unit designs which have a preconverter, such as shown in Figure 11 [11], there is typically a feed/steam preheat coil in the convection section of the reforming heater which has inlet and outlet temperatures of approximately 510 °C (950 °F) and 640 °C (1184 °F). A typical design temperature for this coil is 825 °C (1517 °F). The materials for the tubes and headers are typically grades of stainless steel such as Type 321 stainless steel and Alloy 800H/800HT®. The inlet piping and vessel are Cr-Mo steels, but the outlet piping can be either Cr-Mo steels or austenitic stainless steels.

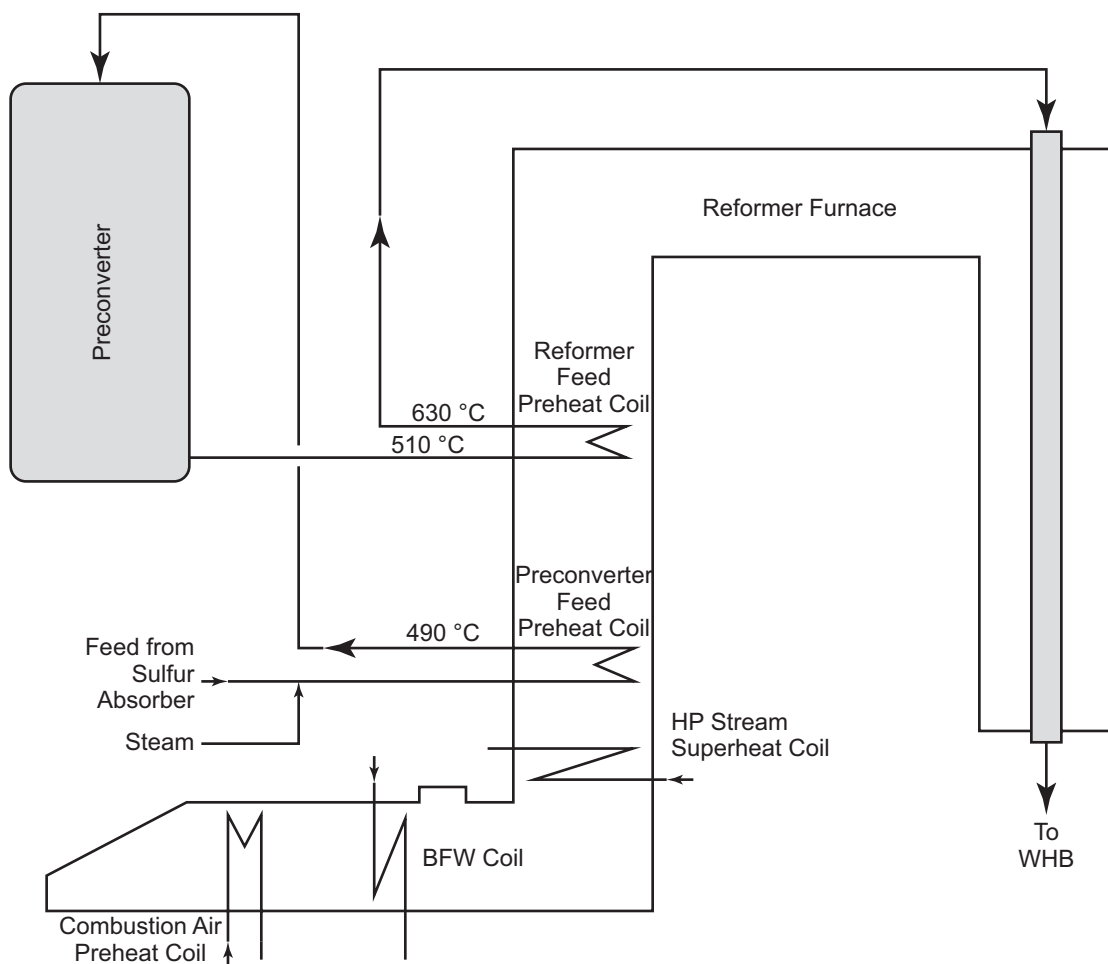


Figure 11—Reformer Feed Preheat Coil Arrangement in Units with a Preconverter

Stress relaxation cracking has occurred at stainless steel tube and outlet header welds on the Reformer Feed Preheat Coil. In one unit, leaks were detected after seven and nine years of service. The coil was then replaced with the same materials, but with the addition of PWHT to relieve residual stresses. The replacement coil has operated successfully up to the time of the report, but had only been in service for a few years.

Stress relaxation cracking failures have been reported in the inlet header piping. There are no reported failures attributed to sigma phase, perhaps due to operating temperatures being at the very low end of sigma phase precipitation temperature range. SRC failures have also been associated with heavy (thick) pads fillet welded to the OD of the inlet headers.

Reformers that have Preconverters utilize higher reformer inlet temperatures between 566 °C to 630 °C (1050 °F to 1166 °F) and the inlet piping to the reformer section are normally fabricated with Type 304H or Type 347H stainless steel.

3.3.1.3 Superheater Tubes

Wrought 300 series stainless steels and Alloys S800H and 800HT® are commonly used for the hottest convection section tubes and headers. Stress relaxation cracking, a mechanism associated with fabrication stresses and heat treatments, and short term stress rupture in-service failures have been reported in these alloys.

Steam superheater coil failures from various refinery processes have been included in this section (hydrogen reformers and hydrotreaters). One reported failure [12] occurred in Alloy 800H tubes in the convection section of a reformer heater operating at approximately 675 °C (1250 °F). Tube metal temperatures were monitored using skin thermocouples (T/Cs) that were protected by T/C shields. T/C shields, shown in Figure 12 *ibid.*, are used to reduce temperature measurement errors due to radiation from burner flames and other furnace components. While the original shields did not crack, thermocouple replacements required new shields that cracked at the attachment welds when placed back into service.

Failures were attributed to stress relaxation cracking. Cracks, shown in Figure 13 *ibid.*, were slightly branched intergranular cracks and had a Ni-rich filament which is typical of this damage mechanism. The original welds made without PWHT did not crack; however, the post-fabrication welds that were made on aged material without PWHT cracked. It was concluded that the aged material suffered a loss of creep ductility and cracked due to high residual stresses from welds which relaxed during high-temperature service. Cracks were removed by grinding. The affected tubes were then solution heat treated at 1150 °C to 1177 °C (2100 °F to 2150 °F) for one hour to restore ductility. Welds were deposited, and afterward were stress relieved at 900 ±14 °C (1650 ±25 °F) for 1½ hours. In this way, the residual stresses were relaxed before aging could occur (with the subsequent loss of creep ductility).

In another steam-methane reformer convection section feed preheat coil, stress relaxation cracking and sigma phase embrittlement were observed in pipe welds and in forged fitting-to-outlet header welds operating between 517 °C (963 °F) and 630 °C (1166 °F). Damage was observed after about nine years of service. The tubes were Alloy 800H and the header was Type 321 stainless steel.

In another case, circumferential cracking was observed after three months of service in Alloy 800HT® steam superheater coil welds in a hydrocracker heater. Subsequent investigation revealed intergranular fissuring and oxidation with intergranular and transgranular penetration on both the tube ID and OD. The average operating temperature was 616 °C (1140 °F), with occasional excursions to 766 °C (1412 °F).

Details for avoiding SRC and repair procedures are given in Section 4. Typically, repairs include the use of a solution annealing procedure to improve ductility while welding followed by a stress relief procedure to reduce the potential for future cracking.

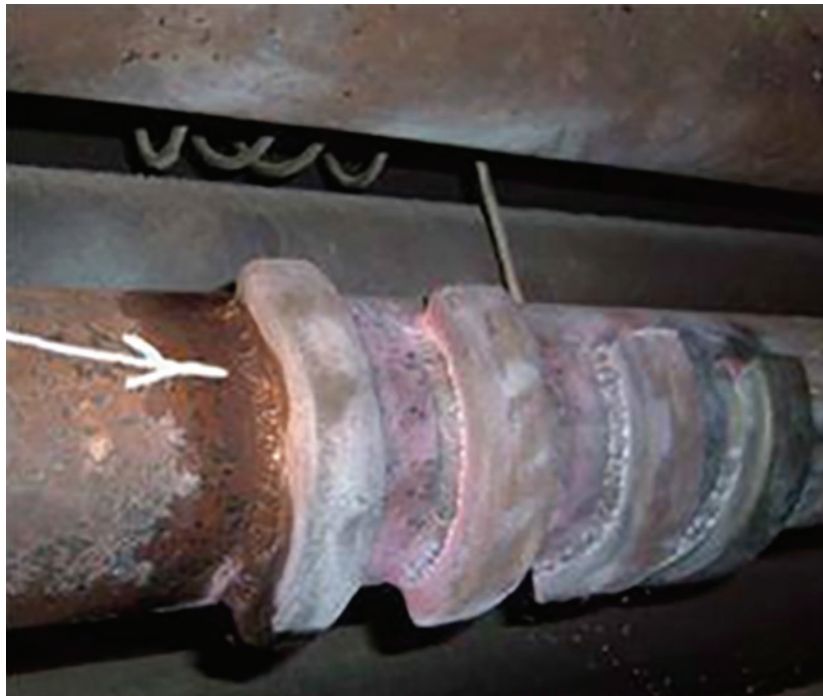


Figure 12—Multiple T/C Shields Welded to an Alloy 800H Superheater Tube



Figure 13—Cross Section of a Crack at the Toe of One of the TC Shields Showing Intergranular SRC

3.3.2 Reformer Effluent Heat Exchanger

Figure 14 [13] shows the inlet channel of a reformer effluent heat exchanger with syngas on the tube side and superheated steam [2.7 MPa (400 psig)] on the shell side that cracked during service. The inlet channel and tubesheet that were fabricated from Alloy 625 while the tubes were 2¹/₄Cr-1Mo with Alloy 601 ferrules installed at the inlet. The tubes were strength welded to the tubesheet with Inconel 52 filler metal, AWS A5.14, and ERNiCrFe-7. The shell was fabricated from A516-70 carbon steel in 1999.

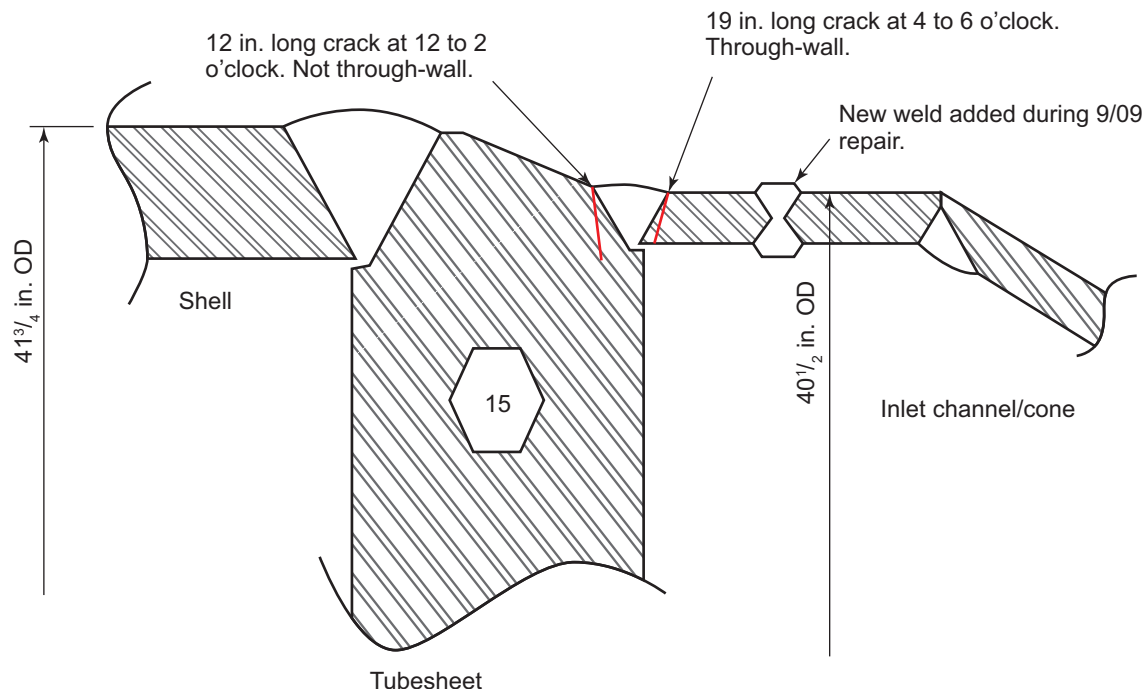


Figure 14—Tubesheet-to-Inlet Channel Cone that Cracked in Service

After 10 years of operation, the channel was cut off to repair ferrules at which time it was also discovered the tubes had suffered metal dusting. A new weld was added to re-install the channel and the exchanger was placed back in service. Approximately two months later, the inlet channel leaked, causing a fire.

The leak was from a 48 cm (19 in.) long crack on the stub side of the new channel-to-tubesheet weld. A second 30 cm (12 in.) long crack was found on the tubesheet side of this weld. Figure 15.^{ibid.} shows one of the cracks, all of which originated from the OD. Hardness values of the Alloy 625 were found to range from 42 to 45 HRC. Cracking was intergranular and displayed creep voids ahead of the crack. The failure was attributed to SRC.

The existing channel and stub were removed and the existing tubesheet was heated to 482 °C (900 °F) for 7 hours to bake out any residual hydrogen. Alloy 625 full penetration tubes to tubesheet strength welds were made. A new annealed Alloy 625 channel was installed, and the unit was brought online.

To reduce the hot inlet channel outer diameter skin temperature by approximately 110 °C (200 °F), a band of insulation on the inlet channel was removed and a steam ring was added at the tubesheet.

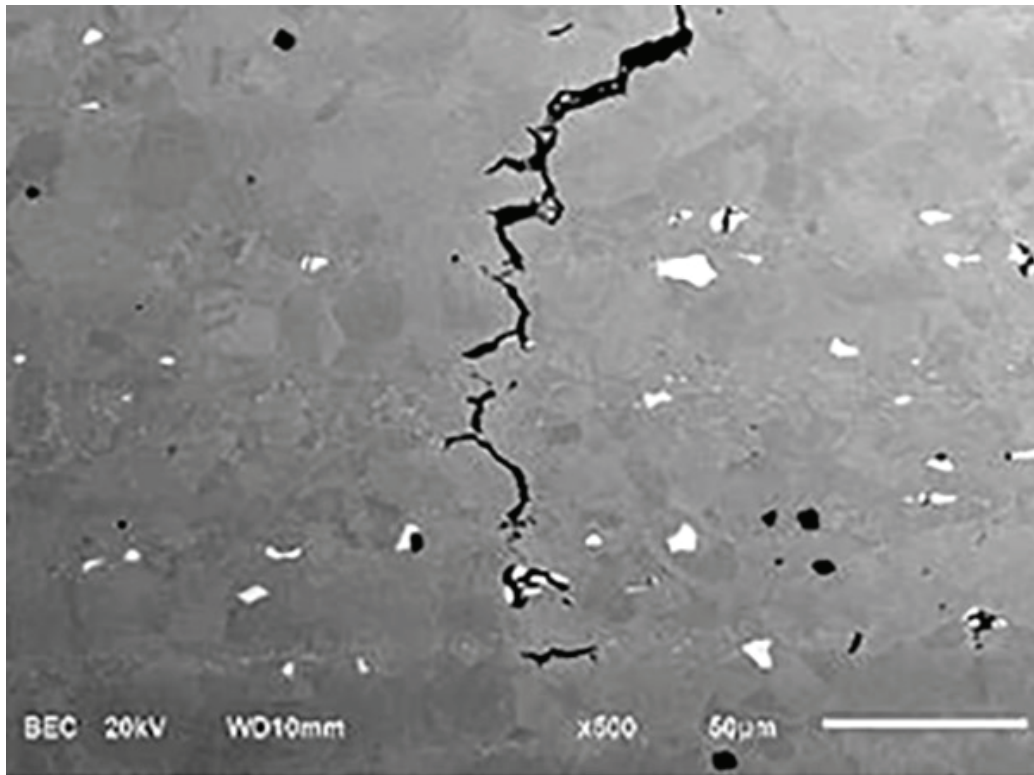


Figure 15—Cracking From the OD Was Intergranular and Was Attributed to SRC

3.4 Catalytic Reformers

3.4.1 Process Description

Catalytic reformers convert low octane refinery feeds into a high-octane product called “reformate”. A simplified process flow diagram of a catalytic reformer is shown in Figure 16 [1]. Reformate is added to gasoline stocks to increase the octane number.

Currently, catalytic reformer units are classified into two generic types; fixed bed (cyclic and semi-regenerative) and moving bed which are referred to as “continuously regenerated catalytic reformers” (CRCRs), and one is shown in Figure 17 [14].

Fixed bed units generally operate below 524 °C (975 °F). Metallurgy of the reactors in this style unit is generally either low-alloy Cr-Mo steels or carbon steel lined with insulating refractory. Heater tubes are typically 2¹/₄Cr-1Mo steel or 9Cr-1Mo steel. Fixed bed units are not included in this report since they generally do not utilize austenitic stainless steels or alloys.

CRCRs utilize stacked Cr-Mo reactors that operate at 516 °C to 565 °C (960 °F to 1050 °F). Catalyst flows downward from the top reactor to the bottom reactor. CRCRs have two high-temperature sections, the reactor section which includes reactors and heaters, and the regenerator section where catalyst is cycled through a series of vessels to remove coke and prepare it for reuse.

3.4.2 Reactor Section

In a CRCR unit, the process stream is heated before entering each reactor in fired heaters that usually use Cr-Mo alloys, but sometimes use Type 321H or Type 347H stainless steel or Alloy 800H type materials. Problems have been

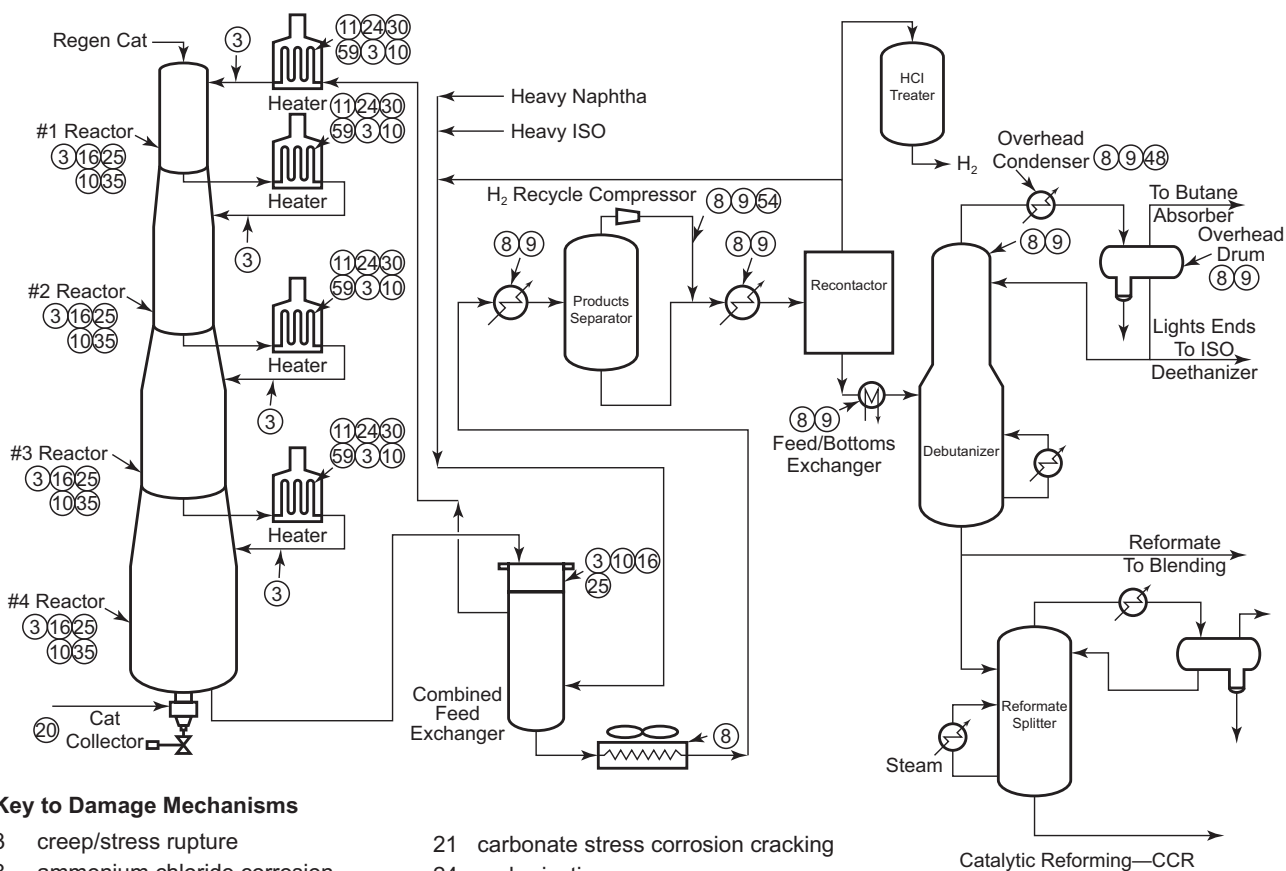


Figure 16—Catalytic Reformer Simplified Process Flow Diagram

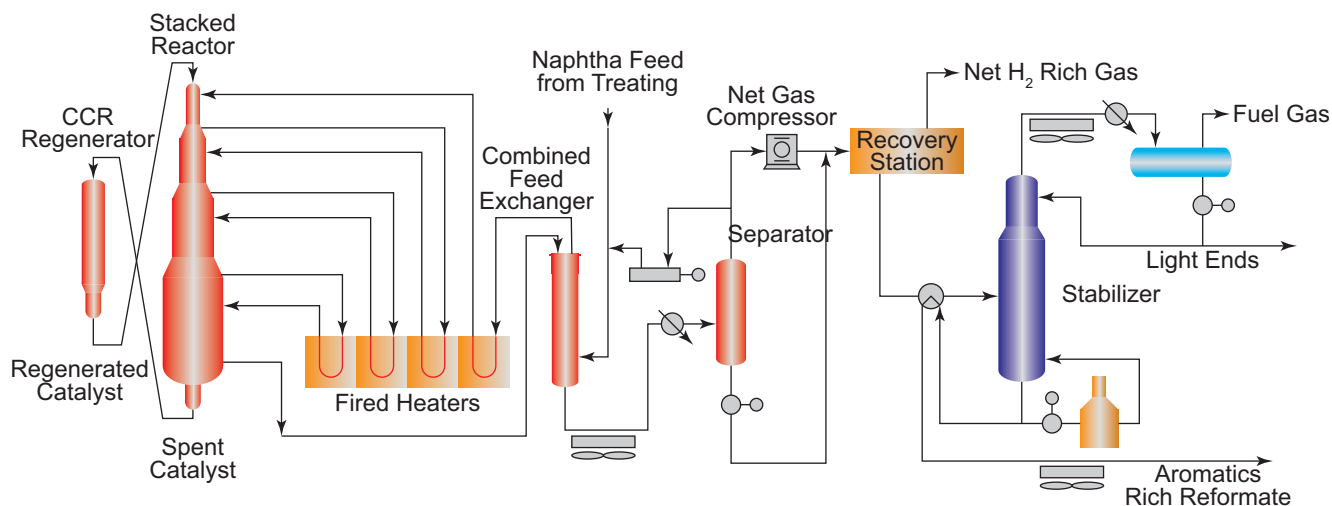


Figure 17—Continuous Regenerating Catalytic Reformer