Review and Survey of Alkaline Carbonate Stress Corrosion Cracking in Refinery Sour Waters

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Foreword

This technical committee report describes the state of the art regarding alkaline carbonate stress corrosion cracking (ACSCC) experiences in certain sour waters found in petroleum refining plants. This report outlines where ACSCC has occurred in process equipment in petroleum refining service, the refining community’s current theory(ies) on the conditions and mitigation techniques that may have an impact on this type of damage, and analytical and inspection techniques that have been used to address the issue. The main focus of this report is on fluidized catalytic cracking units (FCCUs) and light ends recovery systems and associated sour water processing equipment where the majority of the damage has been reported. The technical committee has also chosen to include ACSCC in sour water stripper (SWS) units. This report is intended to provide the refining industry with a resource for current information that is available on ACSCC.

The main sections of this report include:

- What Is Alkaline Carbonate Stress Corrosion Cracking?
- Where Has ACSCC Occurred?
- What Conditions Are Observed When ACSCC Occurs?
- Literature-Proposed Regions for ACSCC Susceptibility
- Chemical Analysis in ACSCC Likelihood Assessment
- Inspection for ACSCC
- Mitigation of ACSCC

Supplemental information is provided in the following appendixes:

- Appendix A: Examples of ACSCC
- Appendix B: Graphs of TG 347 Survey Data
- Appendix C: Proposed Guidelines for ACSCC Susceptibility
- Appendix D: Examples of CO₂/Bicarbonate/Carbonate Equilibrium Curves

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ACSCC, or “carbonate cracking” as it is often referred to, manifests itself as surface-breaking cracks that typically develop at or near carbon steel welds under a combination of tensile stress and corrosion in an alkaline carbonate-containing environment.

The location of these cracks is usually in the base metal within 2 in (50 mm) of the weld. There have been individual reports of cracking occurring more than 3 in (80 mm) from the weld in the base metal of a highly cold-worked elbow and in a 10 x 6 in (250 x 150 mm) reducer that cracked in the middle of the reducer (see Appendix A, Example 4). There have been at least two reports of cracking in the weld metal itself.

When cross-sections of damaged areas were analyzed, the damage has consisted of intergranular oxide-filled cracks having an appearance similar to caustic stress corrosion cracking and amine stress corrosion cracking.

In the past, this type of damage has been found mainly in the pipeline industry on the outside surface of buried carbon steel pipelines in certain soil environments. Also, ACSCC has been found in carbon steel process vessels and piping that contain aqueous solutions with high concentrations of carbonate (e.g., potassium carbonate) that are used in the carbon dioxide \((\text{CO}_2)\) removal facilities associated with steam methane reformers, and in which CO2 and carbonate are the primary forms of corrosive compounds. Those environments are not addressed in this report. This report includes environments where sulfides (e.g., dissolved \(\text{H}_2\text{S}\)) are usually present.

From information available in literature, ACSCC appears to occur when certain parameters exceed a threshold value. These parameters include the carbonate ion (\(\text{CO}_3^{2-}\)) concentration and the pH of the aqueous solution. Also, ACSCC appears to occur when the corrosion (open-circuit) potential is in a certain range (active-passive transition). Other parameters may have an impact on the susceptibility to ACSCC. (See section titled “What Conditions Were Observed When ACSCC Occurred?” for additional information.)

Where Has ACSCC Occurred?

ACSCC of carbon steel exposed to refinery process streams has been reported since the early 1980s. Most of the reports have been associated with the FCCU main fractionator overhead systems and FCCU gas plants, but some reports have been associated with other refinery process services.

The reports of ACSCC damage have been sporadic, but the number of reported incidents has appeared to increase since 2000. This increase may be attributed to the fundamental operating change to the production of low-sulfur (S) products directly from the FCCU.

To further define this trend, TG 347 undertook an industry survey. Results of the survey are discussed in this report and summarized in graphs included in Appendix B. The responses received included 44 process units in 36 refineries. Survey responses were split into three process groups—FCCU, SWS, and cokers. The FCCU and SWS responses were split for further analysis into two populations: one with no ACSCC reported (85%) and the second with ACSCC reported either in piping or in vessels (15%). Unless otherwise stated, the statistics for the TG 347 survey presented in this report are based on individual cases (segments of the system operating under similar conditions) rather than units. Though requested based on some anecdotal reports of ACSCC in cokers, only one case of ACSCC in a delayed coker light ends unit was reported in the two survey responses involving cokers.

The cracking occurred in the piping between the second stage separator and downstream fractionator.

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(1) The carbonate ion discussed here is calculated from the composition of the solution and is not the total carbonate value typically reported by the laboratory.
Only 38% of ACSCC reported occurred in vessels including drums, exchangers, compressor knockout drums, and tanks. ACSCC was reported in only two vessels that had received a postweld heat treatment (PWHT). Mitigation steps (e.g., PWHT) that typically have been taken to reduce the potential for wet H₂S cracking in carbon steel vessels may have mitigated ACSCC also. This could not be confirmed by the TG 347 survey data because only 13% of the respondents provided any information on PWHT.

Most reported ACSCC damage occurred in piping components (62% of ACSCC reported). Many (60%, 9 of 15) of those reporting ACSCC in piping have not reported ACSCC in vessels. Piping typically has been deemed not as vulnerable to wet H₂S cracking damage and therefore did not often have PWHT as an additional mitigation measure in place. Of the 58% who provided information on PWHT in the TG 347 survey, no respondent indicated having performed PWHT on piping.

The vessels and piping in which ACSCC has occurred were in service for less than one year to well over 50 years. In at least one case, a section of piping in service for five to six months is known to have leaked as a result of through-wall ACSCC. See Appendix A, Examples 2 and 4, for details.

FCCU Main Fractionator Overhead and Gas Plant

The reported incidents of ACSCC include overhead lines, exchanger shells, sour water piping, reflux piping, and piping downstream from the coolers on the last stage of wet gas compression in the FCCU gas plant.¹,²,³,⁴,⁵

In most refineries where ACSCC has occurred, the ACSCC typically has not been found beyond the last stage of wet gas compression in the FCCU gas plant. One incident has been reported in the overhead system of a fractionator in a gas plant downstream from the FCCU wet gas compression section.

One failure of a sour water tank that only received sour water from an FCCU was confirmed to be ACSCC by metallographic analysis (see Appendix A, Example 1). The tank was repaired and coated, but did not receive PWHT.

A compilation of the areas in the FCCU where ACSCC has been reported during Technology Exchange Group (TEG) 205X/Group Committee T-8 corrosion information exchanges, and information reported to committee members through the TG 347 survey, is presented in Figure 1.
Figure 1

Simplified process flow diagram of a typical FCCU showing areas where ACSCC has been reported. (These data are not an example of a specific unit in which ACSCC was found but a compilation of data from various units.)

SWS Unit

Piping in a SWS unit was reported to have failed as a result of ACSCC. In this particular unit, the damage was found in the pumparound return line to the top section of the stripping tower. The ACSCC occurred near the weld in a 4 in (100 mm) section of piping (see Appendix A, Example 3). This unit is the most common type of SWS that uses one stripping tower to strip both the hydrogen sulfide (H\textsubscript{2}S) and ammonia (NH\textsubscript{3}) from the sour water.

During the STG 34 information exchange (TEG 205X) at Corrosion Technology Week 2007, an ACSCC failure of the U-bends in a carbon steel bundle in a SWS pumparound exchanger was reported. The U-bends of the ASME\textsuperscript{(2)} SA-179\textsuperscript{5} tubes had been induction heat-treated and still failed.

Others at the meeting reported success with a stress relief performed in a furnace to prevent stress corrosion cracking in similar services. The refiner chose to use a floating head bundle instead of the U-tube bundle to eliminate the cold-worked U-bends.

Some SWS units use two separate stripping towers in series to strip the H\textsubscript{2}S and NH\textsubscript{3} from the sour water. In this particular type of SWS unit, most of the H\textsubscript{2}S and some of the NH\textsubscript{3} are stripped from the sour water in the first stripping tower. The partially stripped sour water from the bottom of the first tower is then sent to a second stripping tower, in which the majority of the NH\textsubscript{3} and remaining H\textsubscript{2}S are stripped from the sour water. Some believe that this type of SWS unit has a higher potential for ACSCC because of the higher NH\textsubscript{3} concentrations in the second stripping tower. However, no survey responses indicated ACSCC problems in this type of SWS unit.

\[\textsuperscript{(2)}\text{ASME International (ASME), Three Park Ave., New York, NY 10016-5990.}\]
What Conditions Are Observed When ACSCC Occurs?

This section discusses process parameters that could cause the environment in FCCUs and SWSs to move into or out of the region of ACSCC susceptibility. This information may be useful for identifying possible influences that an operator could use to trigger reassessment of the likelihood of ACSCC within a unit.

The chemistry of the resulting environment generated in each of the units in which ACSCC occurs is influenced by the feed, the operation of the various systems in the unit (especially fractionation), and water washing. Unfortunately, little data exist or were obtained in the survey to quantify these influences.

Presence of Water

In all areas in which ACSCC has been reported, there has been a separate liquid water phase present. This liquid water phase may be present during normal unit operations when water condenses as part of the process, water is injected for corrosion control or fouling prevention purposes, and/or water carries over from upstream vessels (e.g., main fractionator reflux drum).

TG 347 survey results show that more units with ACSCC use water wash (85% of the population reporting ACSCC) than those without ACSCC (46%). The range of wash water sources is broad in both cases, including water recycled from the FCCU, stripped sour water, and boiler feedwater. One respondent indicated that after ACSCC occurred, the volume of makeup water was being increased.

Other than three published papers, very little data concerning the composition of the water in which ACSCC occurs are available.\(^{(3,4,5)}\)

\[ \text{pH}^{(3)} \]

The pH of the water phase has a significant influence on the potential for ACSCC. One of the most significant influences on pH is the \( \text{NH}_3 \) content; therefore, the pH is typically in the basic range. The primary acidic components that could affect pH are \( \text{H}_2\text{S} \) and \( \text{CO}_2 \). These compounds may keep the water solutions in a lower-pH regime, depending on the relative \( \text{NH}_3 \) concentration. Literature reports indicate that ACSCC has occurred at a pH equal to or greater than 8.\(^{(3,4,5)}\)

\( \text{NH}_3, \text{H}_2\text{S}, \) and \( \text{CO}_2 \) gases in the process exist in equilibrium among the vapor, liquid hydrocarbon, and liquid water phases. The gases dissolved in the water exist in equilibrium with ions formed by hydrolysis of the gases.

The pH data reported in the TG 347 survey are summarized in Figure 2. The average pH\(^{(4)}\) in the cases in which ACSCC occurred (pH 9.2) is 0.5 pH unit higher than the average pH reported by the balance of the survey population (pH 8.7). Three cases in which ACSCC occurred, though, had reported pH values with significantly less scatter (9.0 to 9.9) compared to the reported pH values for those cases without ACSCC (5.5 to 11.0). Several FCCU cases reported no ACSCC despite pH in the range of 9.0 to 11.0.

These data confirm that pH alone cannot be used to determine the likelihood of ACSCC. The data do not indicate that ACSCC always occurs at a pH of 9 or greater. NOTE: It was not reported in the survey whether those units with no reported ACSCC had been inspected to confirm that there was no cracking.

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\(^{(3)}\) The method used to measure most of the reported pH values has not been identified in the literature or surveys.

\(^{(4)}\) Because the respondents did not uniformly provide “open cup” or “closed cup” pH information, the average pH values provided are a combination of both “open cup” and “closed cup” pH values. When available, “closed cup” pH values are used in place of “open cup” pH.
Carbonate Ion Concentration

Carbonate ion (CO$_3^{2-}$) concentration is not a value that is typically reported by the testing laboratory. Frequently used laboratory analyses for boiler feedwater P and M alkalinity measurements only provide a value for "total carbonate," which includes dissolved CO$_2$, bicarbonate ions (HCO$_3^{-}$), CO$_3^{2-}$, and any other alkaline species. See Figures D1 through D4 in Appendix D for how these various species interact in aqueous solutions. Published reports have not indicated a correlation between ACSCC and total carbonate. The published reports have correlated ACSCC with the equilibrium concentration of CO$_3^{2-}$ in the water.

Published reports indicate that concentrations of CO$_3^{2-}$ above 100 ppmw are sufficient to result in ACSCC depending on the pH of the system. The majority of respondents to the TG 347 survey reported only the total carbonate and not the CO$_3^{2-}$ concentration. Methods used to determine the total carbonate concentrations were typically not provided.

The average total carbonate concentration reported by TG 347 survey respondents for FCCUs in which ACSCC occurred is three times the value for FCCUs in which ACSCC did not occur (see Appendix B, Figure B1). The average CO$_3^{2-}$ concentration reported for FCCUs in which ACSCC occurred is approximately the same as the value for FCCUs in which ACSCC did not occur (see Appendix C, Figures C5 through C8). Because the survey respondents' methods to calculate the CO$_3^{2-}$ concentrations are unknown, the reported values may not accurately reflect the actual CO$_3^{2-}$ concentrations in the system. This, in combination with the overlapping range of data (2,500 to 1,000 ppmw CO$_3^{2-}$ for cases with ACSCC reported vs. 2,936 to 267 ppmw CO$_3^{2-}$ for cases with no ACSCC reported) and the small amount of information provided on CO$_3^{2-}$ concentration (only 12% of cases), did not allow TG 347 to draw any conclusions from the survey data.
Total Sulfide Concentration

H₂S impacts the pH of the solution, which has been reported to be one of the key parameters for ACSCC. Some literature indicates the need for a minimum of 50 ppm H₂S in the water for ACSCC to occur.⁶ In the TG 347 survey data, all the units meet this criterion. However, the TG 347 survey did not find any direct correlation between the total sulfide concentration in the water and the likelihood of ACSCC. The presence of sulfide is one of the significant distinguishing factors between the ACSCC mechanism and carbonate cracking described in other areas.

Presence of Polysulfide

Many of the reported cases of ACSCC have indicated that some form of polysulfide was being injected into the unit at the time the ACSCC was found.⁷ In most of the cases in which the type of polysulfide being injected was reported, it was ammonium polysulfide (APS). This is consistent with the knowledge that APS is the most common form of polysulfide used to control the impact of cyanides in FCCUs. There have been at least two reported cases in which polysulfide was not injected in the location where the ACSCC had occurred.¹³ There is no evidence to suggest polysulfide increases or decreases the potential for ACSCC.

Schutt⁷ reported that the “carbonate-dominated problem” (i.e., ACSCC) can be controlled by adding polysulfide to sour water dropout streams at dosages depending exclusively on temperature and pH. Schutt proposed that the tightly adherent sulfide surface film provides the protection for the steel. (See the subsection titled “Guidelines Proposed by Schutt” for more information.)

Some have theorized that a breakdown of the protective film initiated by the polysulfide may actually cause the formation of anodic and cathodic regions on the metal surface, which may increase the potential for ACSCC. The TG 347 survey does not provide significant insight on the theory.

TG 347 survey results indicate that the FCCU cases with ACSCC use polysulfide injection much more often than those units without ACSCC. It is not clear from the survey data whether the use of polysulfide preceded the ACSCC occurrence, or whether the polysulfide use was initiated after the ACSCC occurred. Most respondents did not indicate the type of polysulfide used; therefore, no determination could be made on the potential influence of polysulfide type.

Cyanide

The first edition (December 2003) of API⁵ RP 571⁹ indicates, but without providing references, that cyanide in the sour water has been shown to increase ACSCC susceptibility, but the first edition (May 2000) of API Publication 581⁸ does not indicate any cyanide impact. This appears to be in conflict with the Schutt paper, ¹⁰ which indicates at cyanide levels > 140 ppm the amount of fissuring, hence ACSCC, is reduced. No change in fissuring rate is indicated at lower concentrations of cyanide according to Schutt. A connection between cyanide and wet H₂S cracking has been supported by numerous papers and reports, but a direct correlation to ACSCC at typical cyanide concentrations was not apparent from literature information.

TG 347 survey results indicate that FCCU cases with ACSCC averaged approximately the same cyanide level as those without ACSCC.

Corrosion (Open-Circuit) Potential

The corrosion (open-circuit) potential of the carbon steel exposed to the aqueous solution has been evaluated by Kmetz and Truax⁴ as a parameter that can be an indicator of ACSCC likelihood. The corrosion potential is a complex function of the water composition, material condition, temperature, etc., and is difficult to measure accurately in a field environment. Given the expected bounds of the other water chemistry parameters, when ACSCC occurs, the corrosion potential of carbon steel is likely to be in the region of the active-passive transition (~500 to ~600 mV vs. a saturated calomel electrode [SCE]). However, because of doubts about being able to measure the corrosion potential accurately in the field, and at the right time, it has not been measured routinely. Efforts are being pursued to make this a field-measurable value.

Information on corrosion (open-circuit) potential was not part of the TG 347 survey.

FCCU Influences

Feed Source

The FCCU feed composition has a significant influence on the potential for ACSCC because of the pH of the resulting sour water. One of the most significant influences on this pH is the NH₃ content of the resultant gas stream in the FCCU main fractionator overhead.

NH₃ is formed in the FCCU reactor when nitrogen (N) - containing feeds are processed and is generally considered to be directly proportional to the total feed N content. NH₃ may also be formed in the FCCU regenerator as a function of the N content of the coke on the spent catalyst. The NH₃ is believed to be combusted in a full-burn operation, but can be found in regeneration flue gas from partial-burn operations. Entrained gases from the

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⁵ American Petroleum Institute (API), 1220 L St. NW, Washington, DC 20005-4070.
regenerator can be brought back into the reactor depending on catalyst circulation rates and types. The NH$_3$ content in this entrained gas, though, may not be as significant as the NH$_3$ content resulting from the direct total feed N cracking reaction within the reactor.

TG 347 survey results indicate that the total N in the FCCU feed was almost three times higher in cases with ACSCC than in cases with no ACSCC (2,645 vs. 940 ppmw, respectively). NH$_3$ in the sour water averaged 200% greater in the cases with ACSCC than in cases with no ACSCC (4,801 vs. 2,510 ppmw, respectively).

The primary acidic components that could affect pH in FCCU sour waters are H$_2$S and CO$_2$. For a given CO$_2$ level, lower feed S levels caused by aggressive FCCU feed desulfurization reduce the amount of H$_2$S available in the condensing streams, allowing the pH to increase. The amount of H$_2$S is directly proportional to the total feed S content.

TG 347 survey results indicate that the FCCU feed S content in the cases with ACSCC is approximately 25% of that in the cases with no ACSCC (0.12 vs. 0.50 wt% S, respectively). When the cases are consolidated as units, the feed S of those units with ACSCC is approximately 13% of the feed S in those units with no ACSCC (0.09 vs. 0.68 wt% S, respectively) (see Appendix B, Figure B8).

When the information was provided in the survey responses, the units with ACSCC were processing a low-S feed. Typically, the low-S feed had been hydrotreated, but not always. Approximately 67% of all cases with no ACSCC had hydrotreated feed, while 92% of all cases with ACSCC had hydrotreated feed (see Appendix B, Figure B3). When the cases are consolidated as units, of those with information provided on hydrotreating, 100% of the units with ACSCC processed hydrotreated feed, while only 68% of those units without ACSCC processed hydrotreated feed (see Appendix B, Figure B4).

Calculating the average total N to S ratio in the FCCU feed on a weight basis shows the FCCU cases with ACSCC had a ratio of 269 while the ratio for cases with no ACSCC was about 42 (see Appendix B, Figure B2). When this ratio was plotted along with pH on a FCCU unit basis, a predictive scatter resulted from the plot (see Appendix B, Figure B9).

The survey results for NH$_3$ and H$_2$S concentrations are consistent with the expectation that increasing NH$_3$ and decreasing H$_2$S together increase the likelihood of ACSCC.

The magnitude of the influence of hydrogen chloride (HCl), which can enter the FCCU via external water wash sources or organic chlorides in the feed, is not completely clear. If HCl is present in significant concentrations, it can lower the pH. The average chloride concentration in the cases with ACSCC is 10% of the average chloride concentration in the cases with no ACSCC, with a very wide variation in levels (0.9 to 250 ppmw vs. 0.9 to 14,885 ppmw, respectively). In most FCCUs, this would be expected to be a minor factor.

**Fluid Solids Operating Parameters**

The operation of the fluid solids reactor and regenerator system has an impact on the amounts and type of oxidized carbon species (CO$_2$, carbon monoxide [CO]), in the resultant gas stream. The amounts of these gases help determine the amount of dissolved CO$_2$, bicarbonate, and carbonate in the condensed sour waters in the fractionation and light end streams.

The formation of the various oxidized carbon species is a result of the combustion by air (oxygen) of the coke carried into the FCCU regenerator. The majority of the gases obviously are released into the flue gas that is taken off the regenerator. Gases are entrained with the regenerated catalyst and transported back into the reactor where the entrained gases are then released into the reactor gases and flow into the fractionation section of the unit. The amount of entrained gases is affected by three variables.

- **Catalyst Circulation Rate:** Catalyst circulation rate has an impact on the total volume of entrained gases both in terms of absolute mass flow (the higher the mass flow, the more entrained volume of gas) and the time the gases have to be de-entrained in the regenerator (higher flow rates may mean less stripping of gas from the catalyst particles). Hence it is assumed that the higher the catalyst circulation rate, the higher the level of oxidized carbon gases that are entrained back into the reactor gas stream. At a first-cut level of analysis, the amount of H$_2$S, CO$_2$, NH$_3$, and oxygen would be expected to trend upward as circulation rate increases. However, there may be other subtle process differences that change this relationship quite drastically (e.g., catalyst pore size). The TG 347 survey results did not provide sufficient data to present any statistical results.

- **Type of Catalyst:** FCCU catalysts can be a wide variety of alumina-based solids with a pore structure to facilitate the catalyzed surface reaction of thermal hydrocarbon cracking. The type of catalyst therefore may have an impact on the volume of entrained oxidized carbon gases as the pore density may have an impact on the amount of entrained gas transported back to the reactor.

- **Mode of Regeneration Operation:** The mode of regeneration operation has a significant impact on the oxidized carbon species formed. Regenerators usually are operated in one of two modes—partial burn or full burn—that depend on the downstream processing of the flue gas. These operations affect the extent of oxidation of the carbon within the regenerator.
**Full Burn:** Full-burn operations inject sufficient air (oxygen) quantity into the regenerator to fully combust the coke and promote oxidation of the carbon to favor formation of CO₂ rather than CO. Downstream flue gas facilities are designed to recover only the heat energy directly from the flue gas.

**Partial Burn:** Partial-burn operations restrict the air (oxygen) quantity injected into the regenerator for combustion of the coke, thereby limiting oxidation of the carbon to favor formation of CO rather than CO₂. This allows for downstream heat recovery via the exothermic reaction of further combustion of CO into CO₂ in heat recovery units with combustion facilities such as furnaces or boilers. Hence the gases in the regenerator that are entrained back to the reactor are rich in CO.

TG 347 survey results indicate that the percentage of FCCU units that operate in the partial-burn mode is approximately the same in the cases with ACSCC as in those cases with no ACSCC (31 to 41%, respectively). Of those units in which ACSCC occurred, 31% operated in the partial-burn mode, and 69% operated in the full-burn mode. Five cases in one FCCU operated in both modes and have been included in the no ACSCC category, even though cracking was found in two of the cases, because metallography did not confirm ACSCC.

When the results are broken down by unit, TG 347 survey results indicate that the percentage of FCCUs that operate in the partial-burn mode is only 12% greater in the cases in which ACSCC was reported. Overall, 43% of those FCCUs with ACSCC operated in the full-burn mode, while 57% operated in the partial-burn mode.

Changes in the mode of regeneration operation can influence the chemistry of the condensed water in the fractionation and light ends sections of the FCCU. Partial pressures of the CO and CO₂ in the resulting fractionation gases can influence the CO₃²⁻ concentration in the condensed water, which can have an impact on the ACSCC susceptibility. Unfortunately, there were an insufficient number of TG 347 survey responses on the CO and CO₂ levels in the flue gas to report results.

Excess oxygen content in the flue gas of FCCUs with ACSCC was approximately the same as that reported for FCCUs with no ACSCC. Very low ppm levels of oxygen can make a difference in some refinery corrosion processes, but its influence on ACSCC is uncertain.

Oxidizing species might help stabilize the sulfide corrosion product film on the surface of the steel to help prevent ACSCC.

TG 347 survey results indicate that cases with ACSCC had approximately the same average regenerator temperature (normal flue gas outlet) as the cases with no ACSCC. Because of the limited number of responses, this may not be consistent with real-life operations.

**SWS Unit Influences**

The SWS overhead system(s) is influenced by the water sources to the SWS unit and the operation of the stripping tower(s).

**Feed Source**

Sour waters that are very high in NH₃ can increase the pH in the SWS overhead system and may potentially move the system conditions into the ACSCC region. The feed sources thought to have the most critical influence are the FCCU sour waters, delayed coker sour waters, and fluidized coker sour waters. If the SWS unit does not process sour waters from these sources, the presence of CO₂ is much less likely.

**Design Parameters**

The type of unit design most likely to contribute to ACSCC currently is not well understood. Some believe that SWS units with overhead condensers instead of a pumparound have a higher potential for operating at a pH and CO₃²⁻ concentration that can increase the likelihood for ACSCC.

If the SWS unit is designed with two stripping towers, one to remove H₂S and the other to remove NH₃, there is a high likelihood that the pH in the NH₃ stripper will be in the range for ACSCC. However, it is uncertain whether the CO₃²⁻ concentration would be sufficient to move into the ACSCC region. This largely depends on the operations of the H₂S stripper and how much CO₂ is removed there compared to how much CO₂ remains with the water and eventually volatilizes into the overhead of the NH₃ stripper.

**Operating Parameters**

The operation of the SWS unit can have a significant impact on the water composition in the SWS stripping tower and its overhead system. Operating parameters such as the reflux/pumparound rate and tower-top temperature can also influence the composition of both NH₃ strippers and combined NH₃/H₂S strippers in the overhead system.

**Literature-Proposed Regions for ACSCC Susceptibility**

Several attempts have been made with very limited data to try to establish regions of certain environmental parameters where ACSCC is likely to occur. The currently published guidelines are reviewed in this section. The published literature indicates that certain parameters must exceed a threshold value before ACSCC is likely to occur. This includes the pH and the CO₃²⁻ concentration of the aqueous solution. Also, ACSCC appears to occur when
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the corrosion potential is in a certain range (active-passive transition). There may be additional environmental parameters such as APS, cyanides, and sulfides that may influence the likelihood of ACSCC, but are not directly considered in any of these proposed guidelines.

Appendix C includes several figures that contain plots of the solution pH versus the CO$_3^{2-}$ concentration that are used to illustrate these proposed guidelines. Figures C1 through C4 in Appendix C show separate graphical representations of the guidelines for ACSCC proposed by Kmetz and Truax, Schutt, API 581, and API RP 571, respectively. The following subsections discuss each of these in more detail.

The four proposed guidelines in Figures C1 through C4 are shown along with individual ACSCC data points from the Kmetz and Truax paper. Figures C5 through C8 in Appendix C again show these four proposed guidelines along with the individual ACSCC data points from the TG 347 survey.

None of the proposed guidelines discussed here have been universally accepted and some are challenged in this technical committee report, but the information provides a basis for beginning the discussion on this subject.

Guidelines Proposed by Kmetz and Truax

Kmetz and Truax proposed the following general guidelines for predicting CO$_2$/H$_2$S/NH$_3$ environments prone to ACSCC:

- **Susceptible material (i.e., non-stress-relieved carbon steel)**
- **pH greater than 9.0 and CO$_3^{2-}$ concentration greater than 100 ppm**
- **pH between 8.0 and 9.0 with CO$_3^{2-}$ concentration greater than 400 ppm**
- **Electrochemical potential (i.e., corrosion potential) between –500 mV and –600 mV vs. SCE**

Other published papers on the subject provide very little data concerning the above-mentioned attributes of the water in which ACSCC occurs. Therefore, correlation with the guidelines proposed by Kmetz and Truax could not be verified.

Guidelines Proposed by Schutt

Based on polarization behavior of carbon steel test specimens, Schutt developed the following guidelines for the region where ACSCC was likely to occur:

- **Solution pH > 9**
- **Total sulfur < 0.5% and CO$_3^{2-}$ greater than 800 ppmw**
- **Total sulfur > 0.5% and CO$_3^{2-}$ greater than 1,200 ppmw**

Based on the laboratory slow strain rate results, Schutt reported that ACSCC is controlled by adding polysulfide to sour water dropout streams at dosages depending exclusively on temperature and pH. Schutt offered the following guidance for polysulfide inhibition of ACSCC:

- **Maintain 25 ppm active sulfide (cyanide titratable) when pH > 8 and temperature ≤ 150 °F (66 °C).**
- **Between 150 °F (66 °C) and 230 °F (110 °C), 25 to 250 ppm active sulfide (cyanide titratable) is required when the pH is > 8.**
- **Maintain 250 ppm active sulfide (cyanide titratable) when pH > 8 and temperature ≤ 230 °F (110 °C).**
- **Do not use polysulfide at temperatures greater than 230 °F (110 °C) because polysulfide starts decomposing at approximately 250 °F (121 °C).**

No field applications of this approach have been reported, presumably because the approach is not based on field experience and potential concern with over injection of polysulfide. Maintaining the targeted active sulfide (cyanide titratable) levels in a dynamic system like an operating unit is considered to be extremely difficult.

Guidelines Proposed in API 581

API 581 defines the following environmental factors for increased susceptibility to ACSCC:

- **> 50 ppm H$_2$S in the liquid water phase and pH of 7.6 or greater**
- **Non-stress-relieved carbon steel**
- **Medium-Risk**
  - 7.6 ≤ pH < 8.4 and CO$_3^{2-}$ > 1,000 ppm; or
  - 8.4 ≤ pH < 9.0 and 500 ppm ≤ CO$_3^{2-}$ ≤ 1,000 ppm; or
  - pH ≥ 9.0 and 100 ppm ≤ CO$_3^{2-}$ ≤ 500 ppm

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No specific relationship between polysulfide and temperature was presented in the Schutt paper to allow for determination of how the active sulfide (cyanide titratable) targets would need to be adjusted.

API 581 states, "A heat treatment of about 1,150°F (621°C) for one hour per inch of thickness (one-hour minimum) is considered an effective stress relief heat treatment to prevent carbonate cracking of carbon steel." This is different from some of the other reported information.
• High-Risk
  o \( 8.4 \leq pH < 9.0 \) and \( \text{CO}_3^{2-} > 1,000 \text{ ppm} \); or
  o \( pH \geq 9.0 \) and \( \text{CO}_3^{2-} \geq 400 \text{ ppm} \)

Guidelines Proposed in API RP 571
API RP 571 defines the following environmental factors for increased susceptibility to ACSCC:
• \( > 50 \text{ ppm H}_2\text{S} \) in the liquid water phase and \( pH \) of 7.6 or greater
• Non-stress-relieved carbon steel
• \( pH > 9.0 \) and \( \text{CO}_3^{2-} > 100 \text{ ppm} \); or
• \( 8.0 < pH < 9.0 \) and \( \text{CO}_3^{2-} > 400 \text{ ppm} \)

API RP 571 also indicates that cyanide in the sour water has been shown to increase ACSCC susceptibility, but API 581 does not. API RP 571 is in direct conflict with the Schutt paper, which indicates that the amount of fissuring is reduced at higher cyanide levels (> 140 ppm). No change in fissuring rate is indicated at lower concentrations. A connection between cyanide and wet \( \text{H}_2\text{S} \) cracking has been supported by numerous papers and reports, but a direct correlation to ACSCC is not apparent from published literature.

The \( pH \) and sometimes the \( \text{CO}_3^{2-} \) concentration have been used to prioritize areas for inspection in refinery equipment. ACSCC risk assessment using API 581 and the damage mechanism description in API RP 571 takes into account whether the total sulfide is \( > 50 \text{ ppmw} \); however, accurate measurement of sulfide levels is usually considered less critical than accurate measurement of the \( pH \) and \( \text{CO}_3^{2-} \) concentration for risk-based inspection (RBI). A more precise value of total sulfide is sometimes desired for other risk assessment purposes (e.g., wet \( \text{H}_2\text{S} \) cracking).

The \( \text{NH}_3 \), cyanide, and polysulfide concentrations can also influence the likelihood of ACSCC. However, these species often are not included in routine monitoring and so may not be available for a determination of ACSCC likelihood. There are insufficient quantitative data on the effects of cyanide and polysulfide on ACSCC in the field to make their measurement deterministic for this purpose.

Chemical Analysis in ACSCC Likelihood Assessment

Sampling Considerations
The FCCU or SWS process water samples to be analyzed are inherently unstable upon removal from the process environment. This instability results from both physical (e.g., vapor/liquid equilibria) and chemical (e.g., oxidation) processes. For this reason, careful consideration and planning are typically given to how samples are collected, transported, and analyzed. Subject matter experts in the field of process chemistry typically provide appropriate guidance.

The specific practices that are used to collect and preserve representative samples for analysis depend on the process conditions (temperature, pressure, phases present, etc.) at the sample point and the analyses to be performed. Methods to minimize sample degradation and/or contamination usually include:
• using flow loops to collect samples;
• inerting sample containers prior to sample collection;
• minimizing headspace in the sample containers;
• using sampling cylinders to exclude oxygen during sampling and transportation;
• using floating piston sampling cylinders to minimize pressure changes during sampling and subsampling (oxygen is also excluded);
• using chemicals to preserve or stabilize samples in the field;
• on-site testing to minimize the time for degradation;
• some combination of these methods.

pH Measurement
pH is typically measured using a laboratory \( pH \) meter and glass electrode. ASTM\(^{(8)} \) D 1293\(^{11} \) provides details on the standardization and use of a \( pH \) electrode and meter system. The stability and robustness of the reference electrode in potentially highly sour solutions are typically considered in the selection of electrodes.

Measurement techniques are classified as “open cup” or “closed cup.” In the “open cup” method, the sample is transferred from the sample container to a beaker or other container that is open to the atmosphere for \( pH \) measurement.

\(^{(8)}\) ASTM International (ASTM), 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.
NACE International

In the "closed cup" method, the sample is transferred under system pressure into a flow-through cell that is sealed and pressurized (i.e., not open to the atmosphere) and contains the electrodes. This arrangement is more effective for minimizing off-gassing and consequent pH changes. pH changes of up to 0.5 to 1.0 pH unit have been reported when these precautions have not been used. Ionic modeling is often used to help assess the sensitivity of measurement to "open cup" and "closed cup" techniques. Because the pH value has been directly correlated to the likelihood of ACSCC in the literature and usually is also used to estimate the CO$_3^{2-}$ concentration, accurate pH data are very important.

**Total Carbonate Measurement**

Direct analyses for CO$_3^{2-}$ concentration are difficult in refinery process sour waters, so various total carbonate methods are used. Because of the presence of interfering species, simple alkalinity titrations are not applicable to the measurement of total carbonate in refinery process sour waters. In practice, means to separate the carbonate from interferences or more selective analytical methods are used.

Ion chromatography with aqueous caustic eluent is frequently used to measure total carbonate. ASTM D 4327 describes the principles of this type of analysis, but does not specifically address analysis for carbonate species. It often serves as a starting point to develop a specific method.

Other methods that have been used include coulometry. In this method the carbonate and bicarbonate ions are converted to CO$_2$ and stripped from the sample. The stripped gas is treated to remove H$_2$S before analysis for total carbonate in the coulometric cell. A similar apparatus in which the coulometric cell is replaced by a gas detection tube to quantify the liberated CO$_2$ is often used to measure total carbonate.

A CO$_2$-specific electrode has been used to measure the total carbonate concentration in sour waters. An advantage of this method is that it can be applied readily in the field with a standard pH meter and the CO$_2$-specific electrode. The CO$_2$-specific electrode is based on a gas-permeable membrane that allows dissolved CO$_2$ to diffuse from the sample (adjusted to known acidic pH) into a measurement chamber containing sensing and reference electrodes. Over its dynamic range, the electrode provides a response that is linear to the logarithm of the CO$_2$ concentration. In refinery sour waters, dissolved H$_2$S (and possibly other dissolved gases) sometimes diffuse through the membrane and interfere with the measurement of CO$_2$. There are various ways of treating the sample to prevent interference. Any method is typically developed with an analytical chemist who considers the particular ion-specific electrode being used. Once a sample is acidified, errors can accumulate rapidly with any delay before the measurements are taken.

**Carbonate Ion Estimation**

Kmetz and Truax used a special chemical equilibrium model to solve the simultaneous, aqueous equilibria for aqueous NH$_3$, H$_2$S, and CO$_2$. The total NH$_3$, total sulfide, and total carbonate concentrations were measured and used to calculate the concentrations of all aqueous molecular and ionic species, including the CO$_3^{2-}$ concentration. An additional benefit to this approach is that the solution pH is also calculated. The calculated and measured pH values are typically compared for validation of the analytical data. In addition to proprietary models that some companies have developed, several ionic modeling software programs to do this type of analysis are commercially available.

A less-accurate approach is to use only the equilibria for aqueous CO$_2$, HCO$_3^-$, and CO$_3^{2-}$ to estimate the fraction of total carbonate that exists as CO$_3^{2-}$. Several curves to span the range of process temperatures encountered are usually developed. This approach ignores the effect of ionic strength on the equilibria and does not allow for validation of the analytical data. For the large ranges of CO$_3^{2-}$ concentration (< 100, 100 to 500, 500 to 1,000, and > 1,000 ppm) used to classify environments for ACSCC likelihood assessment, the approach is considered by many to be of suitable accuracy. See Appendix D, Figures D1 through D4 for examples of these curves that illustrate the potential impact of temperature and other ionic species on the equilibrium concentrations.

**Total Sulfide Measurement**

Several methods to measure the total sulfide concentration in sour water are available. The most commonly used are those based on wet chemical titrations such as potentiometric titration using silver nitrate and colorimetric titration using iodine. Similar to the method described for total carbonate concentration, the dissolved sulfides are often converted to H$_2$S and stripped from the sample for quantification using gas detection tubes or other methods.

Ion chromatography is also frequently used for total sulfide measurement. Sulfide ion-specific electrodes are very sensitive to the presence of sulfide ions. A corresponding pH measurement is typically made to convert the sulfide ion concentration to total sulfide concentration.

**Ammonia Measurement**

Total NH$_3$ in refinery process waters is usually measured using ion chromatography, flow injection analysis, or an ion-specific electrode.

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(iii) Details on the modeling program used to do this analysis are not available.
Inspection for ACSCC

Historically, ACSCC has been found initially as the result of an online leak. For those TG 347 survey respondents who reported ACSCC in piping, approximately 50% indicated leakage associated with the ACSCC. Several survey respondents reported that, after initial cracking was found and temporary repairs were complete, follow-up inspection revealed additional areas of cracking that had not resulted in process leaks. Some chose to clamp areas of significant damage and use external inspection techniques to monitor the areas with minor or no crack indications until a plan could be developed to address the damage. The monitoring revealed some interesting behavior. The cracks did not grow in a continuous manner. Some cracks remained inactive for long periods of time and then grew. Other areas without indications were later found to have significant cracking, in some cases sufficient to require the installation of additional clamps.

Mitigation of ACSCC is typically accomplished through one of the following strategies:

Stress Relief

When TG 347 survey respondents provided information about mitigation or repair methods, the use of a PWHT was typical. This is normally accomplished by PWHT of welds to a temperature of 1,150 °F (621 °C), in accordance with WRC(11) 452.13 Attachment welds that are directly exposed to the process environment and those attached externally, whose heat-affected zone may see process exposure, are typically addressed as part of the stress-relieving process.

Care is typically taken to ensure that adequate PWHT is provided to remove residual stress created by welding. In some cases, increased PWHT temperature, a more gradual cooldown, and restrictions on the temperature gradient from the PWHT area were used.

Although few reports of additional ACSCC have been received on vessels and piping that had been repaired and received a PWHT, little follow-up information is available on the water composition to confirm continued operation at process conditions in which ACSCC occurred in the past. One such experience was discussed during Group Committee T-8 corrosion information exchanges and documented in REFIN’COR Paragraph 90F9.2.5 The discussion appeared to attribute the ACSCC susceptibility to improper PWHT. There have been some reports in which, in addition to potential residual stresses, applied stress may have contributed to susceptibility of some components outside the weld area. Based on the discussion concerning the testing that was done, the speakers indicated that, in some circumstances, the use of a piping code PWHT does not always achieve a sufficiently high temperature at the inside diameter (ID) surface of the pipe to be effective and/or the temperature gradient may be too steep between the area receiving PWHT and the adjoining base metal. Others have expressed similar views (refer to WRC 452 and AWS(12) D10.10(14).

The ACSCC failure of carbon steel (ASME SA-179) U-bend tubes noted earlier and additional information shared at Corrosion Technology Week 2007 indicate that the use of induction heating instead of heat treating in a furnace

Mitigation of ACSCC

(10) Some refiners have used temperatures as high as 1,200 °F (650 °C) for stress relief to ensure a complete stress relief for piping components.

(11) Welding Research Council (WRC), PO Box 201547, Shaker Heights, OH 44120.

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may not provide a sufficient amount of time at temperature to confidently reduce the potential for ACSCC.

There is no theoretical reason to assume ACSCC can only occur at welds. Residual welding stresses are sufficiently high to cause cracking. Improper heat treatment of welds can push the residual stress field farther from the weld, or fail to properly relieve shrinkage stresses. Further discussion can be found in AWS D10.10.

**Coatings**

Coatings are commonly used as barrier systems to isolate carbon steel from external alkaline environments such as soil. Nonmetallic coatings have been used with success as barrier systems in petroleum refining environments. When coatings are chosen for internal applications, the maximum exposure temperature of the component, including the potential for steam exposure, are typically assessed.

The TG 347 survey indicated the application of a coating to a tank bottom for mitigation of ACSCC only.

**Resistant Alloys**

Alloy plate or carbon steel clad with an alloy resistant to ACSCC has also been used. The cost of alloy or cladding has been justified for systems in which high-pressure steam-outs are common or corrosion of carbon steel is an additional concern. Materials such as austenitic stainless steels (e.g., UNS S31603 [type 316L]) or nickel alloys (e.g., UNS N06625 [alloy 625]) are often selected for their resistance to ACSCC and their corrosion resistance.

**Water Washing**

Susceptible systems known to operate below the threshold temperature for water condensation and having the potential for ACSCC are typically thoroughly water washed to ensure complete removal of the carbonate-rich environment prior to any exposure to steam. Chemical cleaning has been considered when the ability to remove all carbonate from the entire system, including low points and dead legs, was uncertain.

On-stream water washing is sometimes useful in controlling the process environment. It is typically initiated to control fouling or sour water corrosion. However, trends toward reducing sour water volume are consistent with increasing likelihood for ACSCC. Good water/oil/vapor separation also helps control the scope of equipment exposed to an environment likely to cause ACSCC.

One respondent to the TG 347 survey indicated that they had increased the makeup water rate after finding crack indications in the hope of diluting the potential “bad actors.”

**Inhibitors**

Some inhibitors may have a beneficial effect in the prevention of ACSCC. Metavanadate inhibitors have been used to prevent ACSCC within the CO2 removal section of hydrogen manufacturing units, but not in FCCUs.

The use of corrosion inhibitors, typically organic film-forming inhibitors, to assist in corrosion control is common in the refining industry and has seen significant use in FCCU systems. In addition to corrosion control, corrosion inhibitors are sometimes applied with the goal of reducing the occurrence of wet H2S cracking. One paper on the subject indicated the use of inhibitors in an attempt to minimize the impact of ACSCC.

TG 347 survey results indicate that both oil-soluble and water-soluble corrosion inhibitors are used at approximately the same frequency (8 to 9% of FCCU cases for each type of inhibitor). In FCCU cases with ACSCC that use a corrosion inhibitor, all use an oil-soluble corrosion inhibitor. Water-soluble corrosion inhibitors were only used in units with no ACSCC.

TG 347 survey results indicate also that the percentage of units that use a corrosion inhibitor is approximately the same for the units with ACSCC as for those units with no ACSCC (26% and 30%, respectively). The results also indicate that the cases with ACSCC were three times more likely to have polysulfide and/or an oil-soluble corrosion inhibitor present than those with no ACSCC. Only 41% of all FCCU cases in the survey reported the use of polysulfide and/or an oil-soluble corrosion inhibitor.

**References**

2. REFIN*COR (latest revision) (Houston, TX: NACE International).

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(14) One respondent indicated that addition of an inhibitor was begun after ACSCC had occurred.
Appendix A
Examples of ACSCC

This appendix is intended to provide supplementary information only, although it may contain mandatory or recommending language in specifications or procedures that are included as examples of those that have been used successfully. Nothing in this appendix shall be construed as a requirement or recommendation with regard to any future application of this technology.

Example 1:
A sour water tank containing sour water from an FCCU leaked in 2003. The leaks were found on the bottom of the tank and were caused by both pitting and ACSCC. Figure A1 contains a photo of the as-received coupon removed from the tank bottom and Figures A2 and A3 contain photomicrographs of the ACSCC. Unfortunately, little additional information was available.


Figure A1

Photo of as-received Coupon #2 removed from the tank bottom.

Figure A2

Photomicrograph of ACSCC in Coupon #2. (2% nital etch—magnification not given)
Photomicrograph of crack tip in Figure A2. (2% nital etch—magnification not given)

Example 2:

A refiner processing hydrotreated feed experienced extensive damage to carbon steel vessels and piping throughout the FCCU caused by ACSCC. Table A1 summarizes information provided in the TG 347 survey, including the process service involved, age of the component, operating temperature and pressure, the extent of damage, and comments about how the ACSCC was found and action taken.

Table A1
Summary of ACSCC in One FCCU Reported in TG 347 Survey

<table>
<thead>
<tr>
<th>Component/Process Service</th>
<th>Age, y</th>
<th>Operating Temperature, °F (°C)</th>
<th>Operating Pressure, psia (kPa)</th>
<th>Extent of Damage</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deethanizer overhead 6 in (150 mm) piping to sponge absorber</td>
<td>18</td>
<td>130 (54)</td>
<td>200 (1,380)</td>
<td>Cracked</td>
<td>ACSCC found by SWUT; piping replaced.</td>
</tr>
<tr>
<td>Deethanizer overhead 8 in (200 mm) piping to sponge absorber</td>
<td>18</td>
<td>130 (54)</td>
<td>200 (1,380)</td>
<td>Leaked</td>
<td>ACSCC confirmed metallographically by corporate laboratory; piping replaced.</td>
</tr>
<tr>
<td>Fractionator reflux accumulator naphtha piping</td>
<td>2</td>
<td>101 (38)</td>
<td>160 (1,100)</td>
<td>Leaked</td>
<td>ACSCC confirmed metallographically by local laboratory, reviewed by corporate laboratory; piping replaced.</td>
</tr>
<tr>
<td>Intermediate pressure separator drum light naphtha piping</td>
<td>~10</td>
<td>96 (36)</td>
<td>280 (1,930)</td>
<td>Leaked</td>
<td>ACSCC confirmed metallographically by corporate laboratory; piping replaced.</td>
</tr>
<tr>
<td>Intermediate pressure separator drum light naphtha piping</td>
<td>0.5</td>
<td>96 (36)</td>
<td>280 (1,930)</td>
<td>Cracked</td>
<td>ACSCC confirmed metallographically by local laboratory, reviewed by corporate laboratory; piping replaced.</td>
</tr>
<tr>
<td>Intermediate pressure separator overhead piping to top of deethanizer</td>
<td>16</td>
<td>95 (35)</td>
<td>280 (1,930)</td>
<td>Leaked</td>
<td>ACSCC confirmed metallographically by corporate laboratory; piping replaced.</td>
</tr>
<tr>
<td>Intermediate pressure separator</td>
<td>16</td>
<td>96 (36)</td>
<td>280 (1,930)</td>
<td>Cracked</td>
<td>ACSCC found by visual inspection and WFM; vessel replaced.</td>
</tr>
<tr>
<td>Fractionator reflux accumulator</td>
<td>54</td>
<td>101 (38)</td>
<td>160 (1,100)</td>
<td>Suspected</td>
<td>Not inspected because ACSCC confirmed in connected piping; vessel replaced.</td>
</tr>
</tbody>
</table>
### Table A1 (Continued)

<table>
<thead>
<tr>
<th>Component/Process Service</th>
<th>Age, y</th>
<th>Operating Temperature, °F (°C)</th>
<th>Operating Pressure, psia (kPa)</th>
<th>Extent of Damage</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-pressure stage condenser floating head covers on the shell side</td>
<td>54</td>
<td>95 (35)</td>
<td>200 (1,380)</td>
<td>Cracked</td>
<td>ACSCC found by visual inspection and WFMT; exchanger floating head covers replaced.</td>
</tr>
<tr>
<td>Fractionator overhead naphtha/LCGO exchanger (shell side). This exchanger changed service in 1999. Therefore, it had only been in service subject to ACSCC for 4 years.</td>
<td>59 (4)</td>
<td>~180 (82)</td>
<td>80 (550)</td>
<td>Cracked</td>
<td>ACSCC found by visual inspection and WFMT; WFMT just prior to service change in 1999 revealed no cracking indications; shell not replaced.</td>
</tr>
</tbody>
</table>

### Example 3:

This ACSCC failure occurred in a SWS unit that treats a total refinery sour water stream, one-third of which originated in the FCCU. No ACSCC has been reported in the associated FCCU. The failure occurred in a 4 in (100 mm) diameter ASTM A 234\textsuperscript{13} elbow in the cooled reflux return piping that was in service for 23 years before leaking. Operating conditions were 100 psig (70 kPa) and 130 °F (54 °C) nominally. The reflux stream was drawn off the stripping tower seven trays below the top and pumped through a cooler before returning through the piping containing this elbow to the top tray of the tower. Although this reflux stream is not normally sampled for sour water quality conditions, it is estimated that this sour water contains 1.2 wt% NH\textsubscript{3} and 3,200 ppmw H\textsubscript{2}S, with a pH of approximately 10.

Figure A4 contains photographs of the as-received coupon taken from the failed elbow. Figure A5 (scanning electron microscopy [SEM] photomicrograph) and Figures A6 and A7 (photomicrographs) illustrate the characteristics of the ACSCC.
Figure A4

Photograph illustrating the as-received coupon containing a portion of the failed elbow welded to adjacent pipe.
Figure A5

SEM photomicrograph illustrating the intergranular cracks on the inside surface of the elbow. Note the corrosion products visible inside the crack.

Figure A6

Photomicrograph illustrating the cracks visible on the inside surface. Note the branching propagation (unetched—magnification 500X).
Example 4

This example discusses ACSCC that occurred in piping in a FCCU processing hydrotreated feed. The piping had been installed over a period of 52 years, with the age of the piping components ranging from 52 years to 6 months prior to the detection of ACSCC. Because of timing, components with the through-wall cracks and significant cracks were clamped, while those components with minor or no cracking were monitored. The ACSCC occurred intermittently with no cracking activity for a period that was followed by a period of significant cracking activity, which included newly found cracking in components with no crack indications previously.

Components in the same piping systems that were not replaced and were not given a PWHT experienced additional ACSCC following installation of the replacement components (main fractionator overhead dead leg and main fractionator overhead drum level gauge). The new stress-relieved (1,200 °F [650 °C] for 2 h) pipe spools did not show any new crack indications after two years of operation.

Figure A8 shows the locations within the FCCU where ACSCC was found. Figures A9 through A13 illustrate the ACSCC found in several different piping components.
Locations in FCCU where ACSCC was found.
Photographs of as-received 4 in (100 mm) diameter ASTM A 53 Grade B pipe from the reflux line on the main fractionator (top left); cracks on inner surface after abrasive blasting and application of dye penetrant (bottom right); and closeup of crack (bottom center). Installed in 1952 (52 years of service).
Photomicrograph of cracks associated with the weld and an arc strike for crack seen in Figure A9(a). (nital etch—pipe wall thickness approximately 0.237 in [6.02 mm])

Figure A10

Photograph of as-received 4 in (100 mm) diameter ASTM A 53 Grade B pipe from the reflux line on the main fractionator (top left); cracks on inner surface after abrasive blasting and application of dye penetrant (bottom right). Installed in 1952 (52 years of service).
Photomicrograph of crack seen in Figure A10(a). (nital etch)
Photographs of as-received 18 in (460 mm) diameter API 5L Grade B pipe with two 1 in (25 mm) diameter gasoline wash injection nozzles from the inlet to the second-stage compressor (top left); cracks on inner surface of 1 in (25 mm) injection nozzles after abrasive blasting and application of dye penetrant (bottom left and right). Installed in 1982 (21 years of service).
Photomicrographs of crack in 1 in (25 mm) injection nozzle (as polished) from Figure A11(a) (top); closeup of the crack (bottom right). (nital etch—pipe wall thickness approximately 0.218 in [5.54 mm])
Photomicrographs of small crack seen in Figure A11(b) bottom right as polished (top) and after nital etch (bottom).
Photographs of as-received 3 x 4 in (76 x 100 mm) diameter tee upstream from the interstage hydrocarbon pump (top left); cracks on inner surface after abrasive blasting and application of dye penetrant on the 4 in (100 mm) diameter section indicated by the white arrows on as-received photo (bottom right). Installed in 2002 (6 months of service).
(b)

Photomicrograph of one of the cracks seen in Figure A12(a). (nital etch—pipe wall thickness approximately 0.237 in (6.02 mm)
Crack after abrasive blasting and application of dye penetrant. This is the reduced area of ASTM A 106 Grade B 10 x 6 in (250 x 150 mm) carbon steel reducer in the piping system from the surge drum to the gas plant. Originally installed in 1983 (20 years of service).
Photomicrograph of crack seen in Figure A13(a). (nital etch—pipe wall thickness approximately 0.280 in [7.11 mm])
Appendix B
Graphs of TG 347 Survey Data

This appendix is intended to provide supplementary information only, although it may contain mandatory or recommending language in specifications or procedures that are included as examples of those that have been used successfully. Nothing in this appendix shall be construed as a requirement or recommendation with regard to any future application of this technology.

Figure B1

Average of total carbonate in sour water reported for each FCCU case. (The X-axis identifies the unique number for a particular FCCU case after sorting for ACSCC and pH.)
Figure B2

The two high points with no ACSCC are parts of units downstream of areas where cracking was found.

Total nitrogen-to-sulfur ratio in feed versus average pH (both open cup and closed cup) for each FCCU case. (The X-axis identifies the unique number for a particular FCCU case after sorting for ACSCC and pH.)
Figure B3

Average ammonia-to-sulfide ratio in sour water versus average pH (both open cup and closed cup) for each FCCU case.

○ ACS CC  ● No ACS CC
Figure B4

Average of percent hydrotreated feed for each FCCU. (The X-axis identifies the unique unit number for a particular FCCU after sorting for ACSCC and total nitrogen-to-sulfur ratio.)
Figure B5

Average total nitrogen in feed for each FCCU. (The X-axis identifies the unique unit number for a particular FCCU after sorting for ACSCC and total nitrogen-to-sulfur ratio.)
Figure B6

Average basic nitrogen in feed for each FCCU. (The X-axis identifies the unique unit number for a particular FCCU after sorting for AC SCC and total nitrogen-to-sulfur ratio.)

FCCU Unit

Basic Nitrogen in Feed (ppmw)

AC SCC  No AC SCC
Figure B7

Average nitrogen (basic and total) in feed for each FCCU. (The X-axis identifies the unique unit number for a particular FCCU after sorting for ACSCC and total nitrogen-to-sulfur ratio.)
Figure B8

Average sulfur in feed for each FCCU. (The X-axis identifies the unique unit number for a particular FCCU after sorting for ACSCC and total nitrogen-to-sulfur ratio.)
Total nitrogen-to-sulfur ratio in feed for each FCCU. (The X-axis identifies the unique unit number for a particular FCCU after sorting for ACSCC and total nitrogen-to-sulfur ratio.)
This appendix is intended to provide supplementary information only, although it may contain mandatory or recommending language in specifications or procedures that are included as examples of those that have been used successfully. Nothing in this appendix shall be construed as a requirement or recommendation with regard to any future application of this technology.

Kmetz and Truax guidelines that have been proposed to define the region where ACSCC is likely to occur along with the pH and carbonate ion concentration data from CORROSION/90 paper no. 206.
Schutt guidelines that have been proposed to define the region where ACSCC is likely to occur along with the pH and carbonate ion concentration data from CORROSION/90 paper no. 206.4,7
API 581 guidelines that have been proposed to define the region where ACSCC is likely to occur along with the pH and carbonate ion concentration data from CORROSION/90 paper no. 206.4,8

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API RP 571 guidelines that have been proposed to define the region where ACSCC is likely to occur along with the pH and carbonate ion concentration data from CORROSION '90 paper no. 206.

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**Figure C4**

Carbonate ion (CO$_3^{2-}$) concentration, ppmw vs. pH

- Double diamond: ACSCC Likely
- Diamond: ACSCC Unlikely
- Square: No ACSCC Reported
- Triangle: Unknown
ACSCC data received in the TG 347 survey along with the proposed Kmetz and Truax guidelines for ACSCC susceptibility that have been used to define the region where ACSCC is likely to occur.¹⁴ (CAUTIONARY NOTE: Because the analysis method(s) used to determine the carbonate ion concentration is not known, the plotted data points may be in error.)
ACSCC data received in the TG 347 survey along with the proposed Schutt guidelines for ACSCC susceptibility that have been used to define the region where ACSCC is likely to occur. ¹,² (CAUTIONARY NOTE: Because the analysis method(s) used to determine the carbonate ion concentration is not known, the plotted data points may be in error.)
ACSCC data received in the TG 347 survey along with the proposed API 581 guidelines for ACSCC susceptibility that have been used to define the region where ACSCC is likely to occur.\(^1,8\) (CAUTIONARY NOTE: Because the analysis method(s) used to determine the carbonate ion concentration is not known, the plotted data points may be in error.)
ACSCC data received in the TG 347 survey along with the proposed API RP 571 guidelines for ACSCC susceptibility that have been used to define the region where ACSCC is likely to occur.\(^1\) (CAUTIONARY NOTE: Because the analysis method(s) used to determine the carbonate ion concentration is not known, the plotted data points may be in error.)
Appendix D
Examples of CO₂/Bicarbonate/Carbonate Equilibrium Curves

This appendix is intended to provide supplementary information only, although it may contain mandatory or recommending language in specifications or procedures that are included as examples of those that have been used successfully. Nothing in this appendix shall be construed as a requirement or recommendation with regard to any future application of this technology.

Figure D1
pH vs. Fraction of Total Carbonate
(Carbon Dioxide Only, 77 °F [25 °C], 14.7 psia [101.3 kPa])

pH vs. fraction of total carbonate at 77 °F (25 °C) determined by simulation at the same total carbonate level as Figure D2. (HCl and NaOH were used as the titrants to adjust the pH.) Comparing Figure D1 to Figure D2 indicates the significant change in the equilibrium as the temperature of the system or sample changes. The arrows indicate what percentage of the total carbonate would be carbonate ion (CO₃⁻²) at a pH slightly over 10. (CAUTIONARY NOTE: This is not valid at any other environmental conditions.)
pH vs. fraction of total carbonate at 200 °F (93 °C) determined by simulation at the same total carbonate level as Figure D1. (HCl and NaOH were used as the titrants to adjust the pH.) Comparing Figure D2 to Figure D1 indicates the significant change in the equilibrium as the temperature of the system or sample changes. The arrows indicate what percentage of the total carbonate would be carbonate ion (CO$_3^{2-}$) at a pH slightly over 10. (CAUTIONARY NOTE: This is not valid at any other environmental conditions.)
pH vs. fraction of total carbonate at 77 °F (25 °C) determined by simulation at the same total carbonate level as Figure D1 but with equal amounts of ammonia and carbon dioxide added to the solution. (HCl and NaOH were used as the titrants to adjust the pH.) Comparing Figure D3 to Figure D1 indicates the impact that adding ammonia may have on the system equilibrium. The arrows indicate what percentage of the total carbonate would be carbonate ion (CO$_3^{2-}$) at a pH slightly over 10. (CAUTIONARY NOTE: This is not valid at any other environmental conditions.)
pH vs. fraction of total carbonate at 77 °F (25 °C) determined by simulation at the same total carbonate level but with equal amounts of hydrogen sulfide and carbon dioxide added to the solution. (HCl and NaOH were used as the titrants to adjust the pH.) Comparing Figure D4 to Figure D1 indicates the impact that adding hydrogen sulfide may have on the system equilibrium. The arrows indicate what percentage of the total carbonate would be carbonate ion ($CO_3^{2-}$) at a pH slightly over 10. (CAUTIONARY NOTE: This is not valid at any other environmental conditions.)