MATERIAL SELECTION FOR REPAIR OF DAMAGED PROCESS PIPING IN HIGH-TEMPERATURE SULFIDATION SERVICE IN THE NO. 4 CRUDE UNIT

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MATERIAL SELECTION FOR REPAIR OF DAMAGED PROCESS PIPING IN HIGH-TEMPERATURE SULFIDATION SERVICE IN THE NO. 4 CRUDE UNIT[1]

Executive Summary

On August 6, 2012, a fire occurred in the No. 4 Crude Unit ("Crude Unit") at the Richmond Refinery, owned and operated by Chevron U.S.A. Inc. ("CUSA"). While the investigation into the cause of the fire is ongoing, preliminary information indicates that the fire occurred in the area of a leak in a 5-feet-long section of the 200-feet-long 4 side-cut carbon steel pipe in high-temperature service. It is believed that the leak resulted from accelerated sulfidation corrosion in the 5-feet-long section of pipe, which had low-silicon content (less than 0.10 wt% Si).

CUSA has submitted applications to the City of Richmond for permits pursuant to the California Fire Code ("CFC") to replace fire-damaged piping in high-temperature sulfidation ("HTS") service in the Crude Unit with 9 Chrome alloy pipe ("9Cr"). Because questions have been raised by certain members of the public about CUSA's selection of 9Cr, the City has temporarily delayed issuing permits for such work and Bill Lindsay, Richmond City Manager, has requested additional information concerning CUSA's selection of material.

As explained below, CUSA's selection of 9Cr pipe to replace fire-damaged pipe in HTS service satisfies all engineering and fire-safety standards, and other industry recommended practices, for the use in the Crude Unit. While certain members of the public and the Chemical Safety Board ("CSB") have suggested 300-series stainless steel ("300 SS") as an alternative material based on its increased resistance to sulifdation corrosion, the use of 300 SS would introduce a new damage mechanism not present with 9Cr that is more difficult to monitor and inspect than sulfidation corrosion.

Materials Selection Process

As the owner and operator of the Refinery, CUSA has the responsibility and technical expertise necessary for selecting materials for a particular service based on sound engineering and industry practices. In selecting materials, CUSA relies upon experienced materials engineers, who use their expert judgment to choose robust and predictable materials suitable for the planned service, taking into account the risks presented. Any material selection must be supported by a comprehensive monitoring and inspection program to ensure that the selected material is performing consistent with expectations.

[1] Prepared with the assistance of Barbara Smith, Senior Business Manager, Richmond Refinery, CUSA.

The material selection process is complex and based upon consideration of multiple factors, including operating conditions (particularly temperature), operating history, process chemistry, velocities and other flow conditions, local unit conditions, potential unusual operating conditions, and turnaround considerations. It is also important to consider the risk from all possible damage mechanisms, as well as the ability to monitor the equipment against those damage mechanisms. Otherwise, a decision could inadvertently shift the risk from one damage mechanism to another. Whenever possible, CUSA selects a material that best addresses these multiple considerations.

The City's Scope of Review

Once materials are selected for the repair work, CUSA applies for permits from the City, which reviews the permits for compliance with the California Building Standards Code, inclusive of the California Building Code ("CBC") and the CFC, as implemented by the City.[2] The installation of "process piping" such as the piping being replaced as part of the Crude Unit repair is regulated in two ways:

- Support structures for the piping systems require a building permit pursuant to the CBC;
- The materials for process piping and the design of the piping system are reviewed for compliance with the CFC.

Pursuant to the CFC, the City's permitting role is to confirm that the materials CUSA has selected to replace fire-damaged piping in HTS service in the Crude Unit comply with the engineering standards of the American Society of Mechanical Engineers ("ASME") Code for Process Piping ("ASME B.31.3") and the fire-safety standards of the National Fire Protection Association ("NFPA") Flammable and Combustible Liquids Code ("NFPA 30").[3]

Technical Analysis for Replacement of Fire-Damaged Pipe in HTS Service in the Crude Unit

Pursuant to ASME B31.3 and NFPA 30, carbon steel, 5 Chrome alloy ("5Cr"), 9Cr, and 300 SS are suitable for service in the Crude Unit. In addition to adhering to these engineering and fire-safety standards, it is important to consider a material's sulfidation resistance when selecting materials for HTS service. API 939-C identifies carbon steel with adequate silicon, 5Cr, 9Cr, and 300 SS as examples of materials suitable for HTS service, depending on various factors.[4] An additional consideration in selecting materials for HTS service is prior experience and information concerning a material's past performance in that service.[5]

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[2] See Richmond Municipal Code ("RMC") § 6.02 et seq.
[3] A further description of the manner in which engineering and fire-safety standards are promulgated and incorporated into the City's review is provided in Appendix I.
[4] See Appendix II.
[5] Id.

Taking into account the above-described factors, as well as the risks presented, the Refinery Materials Engineer exercised her expert judgment and selected 9Cr as the appropriate material for replacement of fire-damaged piping systems in HTS service in the Crude Unit. This decision was later confirmed by other experts who have since reviewed the decision.

As noted, 9Cr satisfies all regulatory engineering and fire-safety standards for containment and processing of crude oil. Further, as shown by the Modified McConomy Curves in the API 939-C ,the sulfidation corrosion rates of carbon steel with adequate silicon, 5Cr, 9Cr, and 300 SS demonstrate that each may be suitable for HTS service in the Crude Unit, in particular when one takes into account the Crude Unit's operational history.[6] Thus, based on all applicable technical standards and recommended practices, 9Cr is a suitable material for replacing the fire-damaged piping systems in HTS service in the Crude Unit, and provides significantly increased resistance to sulfidation corrosion when compared to the low-silicon carbon steel component involved in the August 6 incident.

CUSA understands that certain members of the public and the CSB have commented that 300 SS might be a better material for the repair work based on its higher sulfidation resistance as compared to 9Cr, in particular in light of the February 2012 loss of containment that occurred at the BP Cherry Point Refinery, where the pipe that failed was 9Cr and the damage mechanism was sulfidation corrosion.

While the BP Cherry Point incident may seem relevant to the selection of 9Cr for parts of the repair work, based on the publicly disclosed BP investigation of this incident, we do not believe the incident presents an analogous situation to the Richmond Crude Unit. The piping in that instance appears to have been a semi-stagnant "dead-leg" which, after 29 years in high-temperature service, allowed corrosives to build-up in a vapor space at the top of the piping, leading to the failure. We understand that the flowing lines in HTS service in the BP Cherry Point refinery had no problems, and that BP replaced the pipe in question with 9Cr. Thus, this incident does not support a conclusion that 9Cr is not suitable for HTS service, but rather supports industry efforts to eliminate "dead-leg" systems as much as possible and emphasizes the importance of existing industry standards requiring a specific "dead-leg" inspection program for "dead-legs" remaining in service.

Importantly, the selection of 300 SS would also introduce a new damage mechanism to the Crude Unit in the form of stress corrosion cracking ("SCC") from chlorides, and potentially from "polythionic" acids, that would not occur with 9Cr.

Whereas 9Cr is immune to SCC, chlorides in the presence of water may cause SCC of any 300 SS piping at temperatures above about 140ºF. Losses of containment due to chloride SCC are well-documented in the literature.[7] Further, CUSA has identified 10 instances of SCC in stainless steel pipes in high-

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[6] Id.

[7] ASM Metals Handbook, Volume 13C "Corrosion: Environments and Industries;" "Corrosion in Petroleum Refining and Petrochemical Operations," R.D. Kane editor

temperature service in crude units, mostly from chlorides.[8] The pipes that cracked in these instances were in similar or analogous service to the piping being replaced as part of the repair of the Crude Unit, which is subject to potential risks from chloride SCC because the crude oils processed contain chlorides, as does ambient moisture such as that from the drift from the adjacent No. 3 CAT Cooling Tower.

Another potential damage mechanism with 300 SS is “polythionic” SCC, which occurs when sulfur scales combine with oxygen and water to form sulfurous acids that can crack “sensitized” stainless steel. Although the potential for this damage mechanism can be mitigated by using the appropriate grade of stainless steel, it is still a relevant consideration.[9]

A final but vitally important consideration in selecting materials for a particular service is the ability to monitor the equipment against damage mechanisms. A key reason for the selection of 9Cr is its predictable corrosion rate, which makes monitoring of sulfidation corrosion more effective. On the other hand, SCC from chlorides or polythionic acids results in microscopic cracks that are difficult to detect prior to failure. Thus, the use of 9Cr presents less overall risk that 300 SS when it comes to detecting and predicting corrosion, and does not introduce a new damage mechanism to the Crude Unit.

CUSA’s selection of 9Cr adheres to the applicable engineering and fire-safety codes and is the best choice for purposes of fire and operational safety because it effectively reduces the risk from, and provides the ability to effectively monitor, sulfidation corrosion, while avoiding the risk of SCC altogether.

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[8] See Appendix III.

[9] The benefits of stainless steel do sometimes outweigh the potential for SCC, such as when a refinery processes “naphthenic acid” crudes. The Richmond Refinery does not process such naphthenic crudes, however, so this is not a consideration for the selection of materials for repair of the Crude Unit.

Appendices

Appendix I	Application of Technical Standards to No. 4 Crude Unit Repair Work Through California Building Standards Code
Appendix II	American Petroleum Institute Recommended Practice 939-C – Guidelines for Avoiding Sulfidation (Sulfidic) Corrision Failures in Oil Refineries
Appendix III	Incidents of Stress Corrosion Cracking in Stainless Steel Piping Circuits in High-Temperature Service in Crude Units

APPNDIX I: APPLICATION OF TECHNICAL STANDARDS TO NO. 4 CRUDE UNIT REPAIR THROUGH CALIFORNIA BUILDING STANDARDS CODE

The City of Richmond's Permitting Authority

- The City of Richmond's review of permit applications for the repair work being undertaken by Chevron to the No. 4 Crude Unit and related equipment (Crude Unit) is conducted pursuant to the California Building Standards Code (CBSC), Title 24 of the California Code of Regulations (CCR), which has been adopted and incorporated by the City in Chapter 6.02 of the Richmond Municipal Code (RMC).

    - State law (Cal. Health & Safety Code § 18930 et seq.) provides that the CBSC are the minimum standards applicable to all "occupancies," i.e., all buildings and structures, in the state.

    - The California Building Standards Commission adopts these technical codes based on input from expert agencies, and reviews and amends the codes on a regular cycle. Cal. Health & Safety Code § 18929.1; *see also* (http://www.bsc.ca.gov/codes/adoptcycle.aspx).

    - Local agencies such as Richmond may adopt local modifications to provide more restrictive standards provided the agency makes express findings that amendments are necessary because of local climatic, geological or topographical conditions. Amendments are not effective until copies of both the express findings and the amendments have been filed with the California Building Standards Commission. Cal. Health & Safety Code § 18941.5.

- The CBSC includes multiple technical codes, divided into "Parts," including as applicable to the repair work:

    - The California Building Code (CBC), 24 CCR Part 2, which regulates demolition and repair of buildings and structures. 24 CCR § 1.1.3.

    - The California Fire Code (CFC), 24 CCR Part 9, which regulates structures, processes, premises and safeguards concerning, among other things, the "hazard of fire and explosion arising from the storage, handling or use of structures, materials or devices." CFC § 101.2.

    - The California Electrical Code (24 CCR Part 3) and the California Mechanical Code (24 CCR Part 4) are also applicable.

- The installation of "process piping," i.e., the piping in the Crude Unit through which flammable and combustible liquids flow, is regulated in two ways:

- Repairs of the support structures for the piping systems require a building permit pursuant to the CBC. A building permit must be obtained from the City's "Building Official" for all such work under the CBC. CBC § 3405.1.

- The selection of the materials for process piping and the design of the piping system require fire construction permits pursuant to CFC §§ 105.1 (General), 105.1.2.2 (Construction permit), 105.7 (Required construction permits), and 105.7.7 (Flammable and combustible liquids). The "fire code official," which in Richmond is the Fire Marshal, is responsible for reviewing and issuing fire construction permits. RMC § 8.16.030(c); CFC § 105.1.1.

Technical Standards of the CFC

- In reviewing and issuing fire construction permits, the Fire Marshal determines whether the proposed process piping systems comply with the general provisions of the CFC, as well as technical standards that are incorporated into the code as set forth in CFC Chapter 47 – Referenced Standards.

- The General Provisions applicable to storage, dispensing, use and handling of hazardous materials, including combustible liquids and flammable solids, liquids and gases, are set forth in CFC Chapter 27. Section 2703.2.2.2 of this chapter provides that supply piping for these materials "shall be in accordance with ASME B31.3."

    - American Society of Mechanical Engineers (ASME) standards are promulgated in accordance with American National Standards Institute (ANSI) protocols. This is a rigorous, public process which brings together technical expertise from all sectors (e.g., industry, government, NGO, education) to formulate technical standards for specific subject areas. (http://www.asme.org/kb/standards/about-codes---standards). The Committee for ASME B31.3 is a continuing one, and keeps all sections current with new developments in materials, construction, and industrial practice. New editions are published at intervals of two years. (The history of ASME B31, as well as process used by the B.31.3 Committee to develop and publish the standards, is discussed in further detail in the Forward and Introduction to ASME B.31.3.)

    - "ASME B31.3 - Process Piping" sets forth the engineering requirements deemed necessary for the safe design and construction of process piping typically found in petroleum refineries; chemical, pharmaceutical, textile, paper, semiconductor, and cryogenic plants; and related processing plants and terminals. ASME B31.3 sets forth, among other things:

        - References to acceptable material specifications and component standards, including dimensional requirements and pressure–temperature ratings

        - Requirements for design of components and assemblies, including piping supports

    - Requirements and data for evaluation and limitation of stresses, reactions, and movements associated with pressure, temperature changes, and other forces

    - Guidance and limitations on the selection and application of materials, components, and joining methods

    - Requirements for the fabrication, assembly, and erection of piping

    - Requirements for examination, inspection, and testing of piping

- In conjunction with CFC Chapter 27, CFC Chapter 34 – Flammable and Combustible Liquids, sets forth the requirements for prevention, control and mitigation of dangerous conditions related to storage, use, dispensing, mixing and handling of flammable and combustible liquids. Section 3403.6.2 - Design, fabrication and installation of piping systems and components, provides that "piping system components shall be designed and fabricated in accordance with the applicable standard listed in … Chapter 27 of NFPA 30.

    - The National Fire Protection Association (NFPA) is an international organization that develops scientifically-based consensus codes and standards, research, and education for fire and related safety issues. NFPA is an International Codes and Standards Organization (ISO), and all NFPA standards are developed in accordance with ISO protocols requiring a full, open, consensus-based process that brings together technical expertise from various fields to develop, revise and update standards on during a three to five years revision cycle. (http://www.nfpa.org/categoryList.asp?categoryID=124&URL=Codes%20&%20Standards&cookie%5Ftest=1).

    - "NFPA 30 – Flammable and Combustible Liquids Code" sets forth the fundamental safeguards for the storage, handling, and use of flammable and combustible liquids. Chapter 27 – Piping Systems, applies to the design, installation, testing, operation, and maintenance of piping systems for flammable and combustible liquids or vapors, and § 27.4.1 - Materials Specifications, provides that pipe and other materials used in piping systems "shall meet the material specifications and pressure and temperature limitations of ASME B31."

    - NFPA 30 also provides standards for the installation of piping systems (§ 27.6) and the testing of piping systems (§ 27.7).

- There are numerous other standards and codes incorporated into the CFC as set forth in CFC Chapter 47, including certain American Petroleum Institute (API) standards.

- API Recommended Practice 939-C – Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries, is not one of the standards incorporated into the CFC; nor is API Recommended Practice 580 – Risk-Based Inspections or API 581 Recommended Practice – Risk-Based Inspection and Damage Mechanisms. These recommended practices are applied voluntarily by the industry.

Scope of Fire Marshal Review and Approval of Permits

- When the Fire Marshal reviews and issues fire construction permits pursuant to the CFC, he is determining that the proposed process piping, including materials, complies with engineering (ASME B31.3) and fire-safety (NFPA 30) standards that have been promulgated and peer-reviewed by international standards organizations. CFC § 105.2.4.

- The Fire Marshal does not determine in the first instance whether a material proposed for use by an applicant, such as 9 Chrome alloy pipe, is adequate for the proposed service from an engineering or fire-safety perspective. Rather, the Fire Marshal confirms that a proposed material such as 9 Chrome has been recognized as suitable for the proposed service in the applicable technical standards. CFC § 105.3.

APPNDIX II: API RP 939-C (SUBMITTED IN HARD COPY ONLY)

APPNDIX III: INCIDENTS OF STRESS CORROSION CRACKING IN STAINLESS STEEL PIPING CIRCUITS IN HIGH-TEMPERATURE SERVICE IN CRUDE UNITS

SCC Incidents in 300 Series Stainless Steel Hot Piping Portions of Crude Units - Chevron				
18-8SS Issue Number	**Date**	**Author**	**Source**	**Summary**
Chevron 1	1970s	DL Cooke	Private communication between Dave Cooke and former Salt Lake inspector	Salt Lake: External cracking of stainless steel line attributed to water and chlorides used during firefighting operations.
Chevron 2	1971	WG Halsted	Chevron E-241.01	El Segundo: External cracking of 316SS piping at outlet of E-356 during startup, following shutdown, due to either chloride SCC or PTA SCC.
Chevron 3	1975	DE Ferrell	Chevron RT9915844	Hawaii: Internal PTA SCC of 304 Vacuum Column bottom line.
Chevron 4	1986	JW Coombs	Chevron 75.16.56	El Paso: Internal chloride SCC of No. 6 Crude Unit Atmospheric 304SS transfer line.
Chevron 5	2000 (reported in 2006 metallurgy review)	EH Niccolls	History brief summary captured in Chevron Pasc. Crude 1 Met Review (relevant excerpts)	Pascagoula: Internal cracking from chloride SCC to 317L SS piping at #6S/C.

*"Hot piping" refers to piping that operates above where liquid water or moisture would be expected during normal operation, nominally above ~400F

Footnote:

1) These do not include cases of SS instrument tubing cracking.

SCC Incidents in 300 Series Stainless Steel Hot Piping Portions of Crude Units - Industry				
18-8SS Issue Number	**Date**	**Author**	**Source**	**Summary**
Industry 1	1997	Tom Farraro (Citgo)	1997 NACE Refincor	Internal chloride SCC of 316SS transfer line at a low spot that was likely not drained.
Industry 2	1997	Ralph Blee (Exxon)	1997 NACE Refincor	Internal SCC of SS to Cr-Mo transfer line (either chloride or PTA SCC).
Industry 3	1998	Tom Farraro (Citgo)	1998 NACE Refincor	Internal chloride SCC after soda ash washing of SS in crude unit.
Industry 4	1998	CA Shargay (Fluor Daniel)	1998 NACE Refincor	External SCC in 316SS transfer line.
Industry 5	2004	Tom Farraro (Stress Eng)	2004 NACE Refincor	Internal chloride SCC of 304SS vacuum transfer line (SCC attributed to condensation at low points and concentration of salts during start up).

*"Hot piping" refers to piping that operates above where liquid water or moisture would be expected during normal operation, nominally above ~400F

Footnote:

1) The search for stress corrosion cracking in crude units also uncovered "dozens" of cases of chloride cracking in other units such as hydroprocessing. As we discussed during out meeting on November 26, 2012, the hot piping portion of crude units can experience during start-up and shut down conditions similar to hydroprocessing units.

Chevron 1

(Private communication between Dave Cooke and former Salt Lake inspector)

Chevron 2

MR. L. R. SHANK:

file

This work was requested by D. D. Price.

JG Kerr/RDSwitter

J. G. KERR
9-24-71

MATERIALS LABORATORY
RICHMOND

FAILURE OF STAINLESS STEEL PIPE, EL SEGUNDO NO. 2 CRUDE UNIT

FILE: E-241.01
SEPTEMBER 24, 1971
MDTR710012

At your request the Materials Laboratory conducted an investigation into the circumferential cracking of the stainless steel piping spool from the outlet of exchanger E-356 in the El Segundo No. 2 Crude Unit. The failure was discovered July 30 when the piping spool started leaking during the start-up after a shutdown. During the shutdown a vertical T-joint was welded into the two year old stainless steel piping spool. The field welds were stress relieved at about 1600F with an Ex-o-met stress relief kit while the piping spool was bolted up and highly restrained. The spool was found to be leaking at two circumferential cracks about 1/8 inch apart and about 1/2 inch long. The cracks were located on the opposite side of the pipe from the "T", and about 8-inches from one of the T-joint welds. At normal operating conditions the 6 1/2-inch OD stainless steel pipe contains gas oil at about 450F and about 225 psi.

A chemical analysis of the pipe indicates that it is made of Type 316L stainless steel. The results of the chemical analysis are given in Table 1. The pipe has a hardness of about Rockwell B 78. This indicates that the stainless steel pipe is annealed, and has a yield strength of about 30 ksi and a tensile strength of about 80 ksi.

A longitudinal cross section containing both circumferential cracks was cut from the pipe. Figure 1 shows photomicrographs taken at the ID and OD of a crack extending through the pipe wall. Apparently the cracking started at the OD since the crack is more open there. Also, several other cracks starting at the OD and not extending through the wall were found within a 1/4 inch of the crack shown in Figure 1. The tip of one of these cracks is shown in Figure 2. This crack appears to be intergranular and tightly closed.

Figure 3 shows an etched cross sections of one of the cracks not extending through the pipe wall. This photomicrograph clearly indicates that the cracking is intergranular. The photomicrograph in Figure 4 shows that carbides have precipitated at the grain boundaries, which suggests that the Type 316L stainless steel pipe has been sensitized.

Sensitization is the harmful precipitation of chromium carbides in a nearly continuous network around the metal grains of an austenitic stainless steel. The chromium content of these carbide particles is theorized to be so disproportionately high with respect to the metal itself, that a thin surrounding envelope is depleted of its chromium content. This reduces the thin envelope to non stainless steel behavior, and renders it susceptible to subsequent intergranular corrosion. The temperature range in which sensitization occurs is from about 800F to 1650F. Sensitization is a time-temperature effect which is most rapid from about 1250F to 1350F.

It does not appear likely that this failure was caused by stress relief cracking since Type 316L stainless steel is not generally believed to be susceptible to this kind of cracking. In general only the grades of stainless steel containing columbium are susceptible to stress relief cracking. Type 316L stainless steel would not be expected to lose much ductility during a stress relief heat treatment since no colubium is present to form columbium carbides and cause precipitation hardening. Therefore, Type 316L stainless steel should be able to plastically deform enough during a stress relief heat treatment to relieve the stresses needed to cause cracking. For these reasons it is not believed that this failure was caused by stress relief cracking even though the piping spool was bolted up and highly restrained during the stress relief heat treatment.

It is believed that the cracks are from intergranular stress corrosion cracking of the sensitized Type 316L stainless steel. Chlorides and polythionic acids are the most common corrosive agents found around the Refinery that cause stress corrosion cracking in Type 316L stainless steel. Chloride cracking generally starts as intergranular cracking and then develops as transgranular cracking. Polythionic acids only cause intergranular stress corrosion cracking. Therefore, it appears that the failure of the stainless steel pipe was caused by polythionic acids rather than chlorides, since only intergranular cracking was found.

"Polythionic acids" is used as a general term referring to sulfur acids, such as sulfurous acid. The intergranular failure of sensitized Type 316L stainless steel may occur in any plant where iron sulfide corrosion products are formed. During shutdowns the iron sulfide oxidizes on contact with air to form sulfur dioxide. In the presence of moisture, sulfurous acid is created. This process is described by the following two reactions:

(1) $4FeS + 7O_2 \longrightarrow 4SO_2 + 2Fe_2O_3$

(2) $SO_2 + H_2O \longrightarrow H_2SO_3$

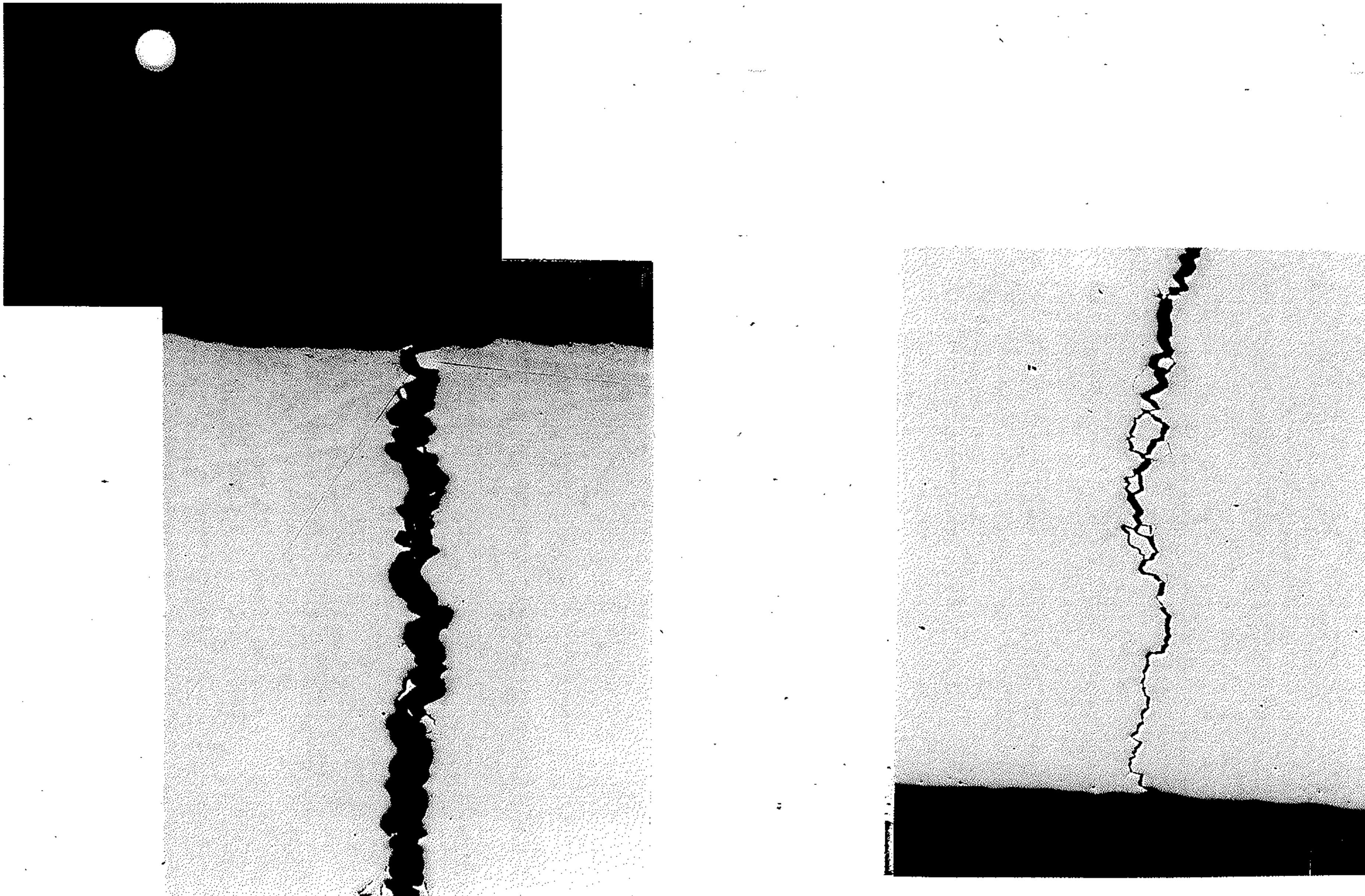
It is not clear how the outside of the stainless steel piping spool from the outlet of exchanger E-356 came in contact with polythionic acids. However, it appears that this did occur after the stress relief heat treatment during which the Type 316L stainless steel was sensitized. Even though the exposure of the outside of the pipe spool to polythionic acids is probably not common, precautions should be taken to prevent recurrence by keeping sulfur containing materials off the pipe. At the operating temperature of 450F it is possible but improbable that sulfur containing materials on the pipe could make iron sulfide. However at stress relief temperatures any sulfur containing material would corrode the stainless steel pipe leaving an iron sulfide residue that would produce polythionic acids after contact with air and water.

W. G. Halsted
W. G. HALSTED

WGH/jhh
Attach.
cc: B. P. Faas

Table 1.

Element	Percent
C	0.03
Cr	17.00
Cu	0.14
Mo	2.24
Mn	1.63
Ni	13.15
P	0.030
S	0.013
Si	0.65



Pipe OD   Pipe ID

FIGURE 1. Cross section of circumferential crack extending through pipe wall. unetched 50X.

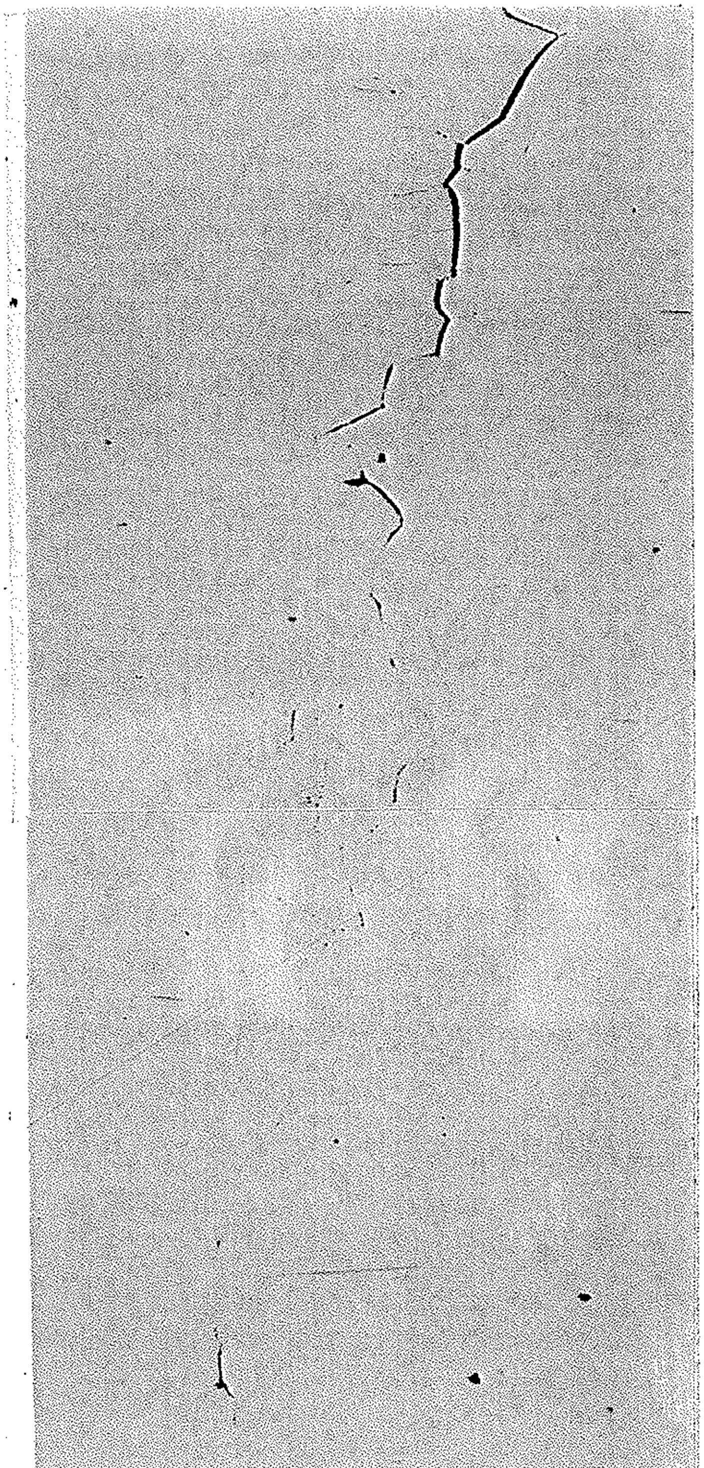


FIGURE 2. Cross section of crack tip not extending through pipe. unetched 250X.

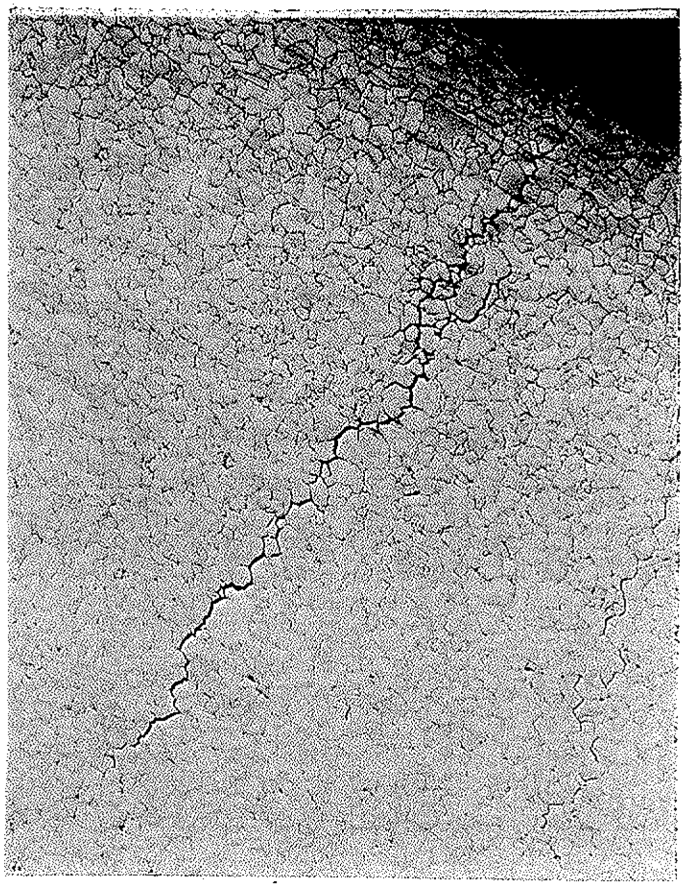


FIGURE 3. Cross section of crack not extending through pipe.

etched 42.5X.

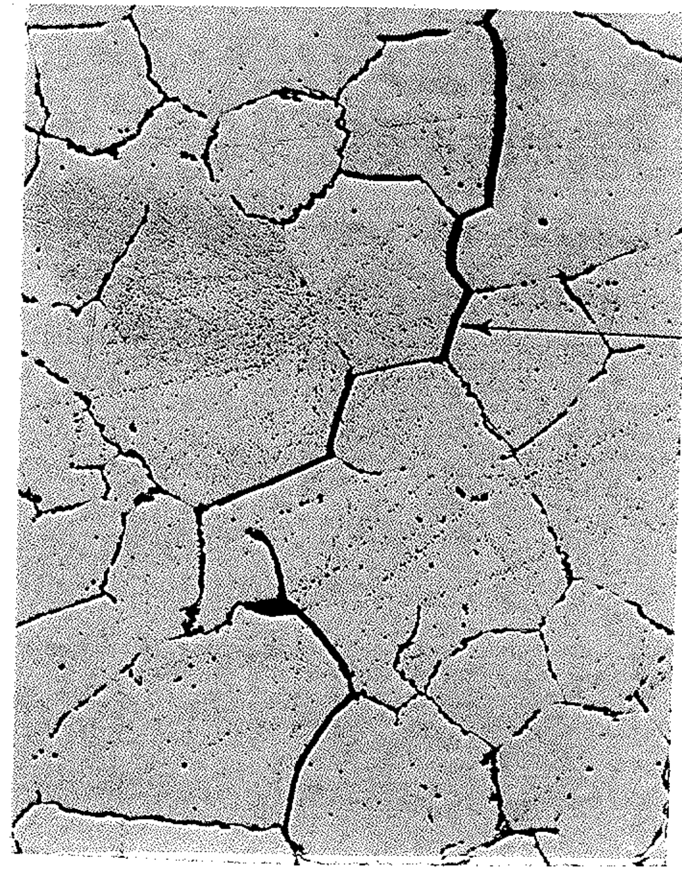


FIGURE 4. Cross section of crack tip showing carbide precipitates at grain boundaries.

etched 500X.

File

MEMORANDUM GO-144

TO: MR. L. R. Shanks El Segundo Engineering October 4 1971

FI MR. W. G. Halsted Materials Laboratory Richmond

SUBJECT: Failure Of Stainless Steel Piping, El Segundo No. 2 Crude Unit OUR FILE: E-241.01

YOUR FILE:

After mailing the September 24 report titled "Failure Of Stainless Steel Pipe, El Segundo No. 2 Crude Unit", file E-241.01, R. L. Piehl from the Materials Laboratory supplied me with additional information concerning the intergranular stress corrosion cracking of sensitized Type 316L stainless steel. Apparently it is possible for chlorides to produce only intergranular cracking, with no transgranular cracking, in heavily sensitized austenitic stainless steel. Therefore polythionic acids or chlorides could have caused the intergranular cracking in the stainless steel piping spool from the outlet of exchanger E-356.

It is more likely that the outside of the pipe came in contact with chlorides than polythionic acids. Therefore it is more probable that the failure was caused by chloride stress corrosion cracking. It is recommended that precautions should be taken to prevent recurrence by keeping chlorides and sulfur containing materials off the pipe.

Chevron 3

File

MEMORANDUM

RT0112843

(A) RT99158444

Engineering Department
Materials Laboratory
Richmond, California

November 26, 1975

FAILED TYPE 304 VACUUM BOTTOMS LINE,
HAWAIIAN REFINERY
Materials Lab File: P-100.43

MR. R. L. BREDEHOFT:
Hawaii

The attached Materials Laboratory report concludes that a sensitized Type 304 line in vacuum bottoms service at 680F failed by sulfur acid cracking from the ID. Sensitization may have occurred during fabrication but more probably was the result of service. Cracking by this mechanism would have occurred during shutdowns when moisture contacted internal sulfide scale. Because of the fire hazard presented by the possible formation of additional cracks, we recommend that all Type 304 parts of the pipe spool be replaced. The use of a stabilized stainless steel, like Type 321 or Type 347, in stress relieved replacement piping, should prevent both cracking and corrosion. Carbon steel or chrome-moly steels will prevent cracking, but can corrode rapidly at 680F in the presence of H_2S, the corrosion rate depending on the quantity of H_2S present. Careful study of projected corrosion rates based on service experience with related equipment should be made before any of the chrome-moly steels are used.

J G Kerr/jhh
J. G. KERR

DEF/jhh

cc: E. H. Edwards - S.F.
R. D. Switters - S. F.
B. P. Faas - El Segundo
C. M. Anglin - Hawaii
F. A. McMillin - CRC
D. F. Boaz - Inspection
W. B. Floyd - El Segundo
R. C. Dover - Pascagoula

Hawaiian

FAILED TYPE 304 VACUUM BOTTOM LINE, HAWAIIAN REFINERY

FILE: P-100.43
NOVEMBER 25, 1975

BACKGROUND

In mid-September the 6-inch diameter portion of the vacuum bottoms line in Hawaii's Crude Unit developed cracks adjacent to a weld joining the line to a reducing elbow. The bottoms line was reportedly fabricated of Type 304L was 304 stainless steel. The cracks, which were in the 12 o'clock position on the line were weld repaired with E-308 manual weldmetal and the line was placed back in service. After only one day of operation, a second crack appeared at about the 4 o'clock position in the same general area. The line had been in vacuum bottoms service at 680F and 350 psig for 15 years without incident. Because the line is insulated, metal wall temperature was probably very close to the 680F stock temperature. No records were available to indicate whether the pipe had been stress relieved.

Thirty inches of the line, including the cracked segment, were replaced with Type 321. Welds were made with E-347 manual weldmetal and were stress relieved at 1600F for one hour. A brace was installed near the failed area to reduce the loads applied by a nearby valve manifold. The cracked area was flame-cut from the 30" pipe section removed; both pieces were sent to the Materials Laboratory for an investigation of the failure mechanism.

INVESTIGATION

After cleaning with a solvent to remove tar, the ID of the cracked piece from the line appeared as shown in Figure 1. Several cracks are visible. Similar examination of the OD found only one short crack that could be observed visually but that was not picked up by dye penetrant inspection, even after the piece was warmed to 125F. The cracks are either very tight or are plugged with scale and vacuum resid. All cracks are away from weld zones.

The results of a chemical analysis of a sample of the pipe material, listed in Table 1, showed the pipe to be Type 304 and not Type 304L.

Metallographic examination of a cracked portion of the pipe wall found that cracks were entirely intergranular and originated at the line ID, as shown in Figure 2. No cracks were observed in weldmetal or in weld heat affected zones. Huey tests of two pipe samples, one near the cracks and the other 30" away from the weld, found that the entire section of pipe was severely sensitized. Corrosion rates measured in the Huey tests, listed in Table 2 were virtually identical for both samples. Figures 3 and 4 suggest that weld heat affected zones are not as severely sensitized as pipe material.

DISCUSSION

Failure most probably occurred by a sulfur acid or polythionic acid cracking mechanism in the sensitized Type 304 pipe. These acids can form when iron sulfide scales come in contact with water. Since the inside of the line is well above the dew point of water, even at the 350 psig operating temperature, cracking most probably occurred during shutdowns. Similar cracks may have formed elsewhere in the piping. Even if it were possible to find and repair all cracks in the approximately 100 feet of Type 304 pipe remaining, additional cracking is a distinct possibility.

Records do not indicate whether the pipe spool was stress relieved. If it had been, local stress relief of welds would have been the most probable method because of the size and configuration of the spool. Local stress relief of welds would not have caused sensitization of the portion of pipe from which Sample B (see Table 2) was drawn. Therefore, service exposure seems to be the most probable cause of sensitization, although a furnace stress relief could have produced the same effect. The bottoms temperature of 680F is somewhat below the 700F temperature that Socal considers to be the lower limit for sensitization of Type 304 stainless steel. However, we have settled on this lower limit from tests using exposure times shorter than the 100,000 hours of service accumulated by the vacuum bottoms line.

no 700 includes 75° safety margin

680 is too low to sensitize in ? yrs

High Hardness suggests sensit. from stress relief.

(non SR'd 304L should be ok.)

Because additional cracking may occur in sensitized areas, and because the entire line, not just weld areas, may be sensitized, the Type 304 pipe spool should be replaced. Leaks that may form will probably be small, but the risk of spontaneous combustion of oil saturated insulation presents a substantial fire hazard. Type 304L sections may not need replacement, but no nondestructive means presently exists to distinguish either Type 304 from Type 304L or sensitized areas from unsensitized areas.

Factors to be considered in the selection of materials for replacement piping are presented in Table 3. Sensitized austenitic stainless can fail as described above, and so Type 304 should not be used. Although Type 304L would probably not have failed as above, Type 321 or Type 347 is prefered for improved resistance to sensitization during service. All austenitic stainless steels may be susceptible to chloride cracking from the OD under insulation, either from salts leached from the insulation or from salts carried in the atmosphere in Hawaii's oceanside environment. We, therefore, recommend stress relief.

Piping class called for SR of shop ass'd spools so SR is likely.

Carbon steel or chrome-moly steel piping would eliminate all risk of failure by cracking, if properly fabricated. However, at 680F, these materials can corrode in the presence of H_2S. Corrosion rates will be dependent upon H_2S concentrations and on alloy composition. The corrosion rates of carbon steel or Cr-Mo equipment operating at similar metal temperatures (not stock temperatures) in resid service should be examined carefully before any of these materials are used. Increased chromium concentration improves resistance to H_2S.

CONCLUSIONS AND RECOMMENDATIONS

1. The Type 304 vacuum bottoms line was severely sensitized and probably failed by sulfur acid cracking. Sensitization may have occurred during service.
2. Because the rest of the line presents a fire hazard from possible formation of additional cracks, we recommend replacement of the entire pipe spool. Type 304L sections may not be sensitized and would, therefore, not require replacement. Simple tests on small samples (as small as a sliver 1/4" wide x 1/2" long) sent to the Materials Laboratory could determine whether the material is sensitized. The 4-inch piping should be tested in this way before replacement.
3. For replacement piping, we recommend the use of stress relieved Type 321 or Type 347. Carbon steel, a Cr-Mo steel (up to 9 Cr-1/2 Mo) or Type 410 stainless steel may be used if operators can establish that H_2S concentrations and, therefore, corrosion rates will stay at satisfactory low levels.

D.E. Ferrell

DEF/jhh

D. E. FERRELL

Table 1

Chemical Analysis

	Btms Line	304	304L
C	0.056	0.08 max.	0.0035 max.
Cr	19.00	18-20	18-20
Ni	10.60	8-11	8-13
Mo	0.18		
Mn	1.74	2.0	2.0
Si	0.50	0.75	0.75
P	0.025	0.04	0.04
S	0.007	0.03	0.03
Cu	0.17		

Table 2

Huey Tests on Two Samples from Pipe Wall
(per ASTM A262, section "C")

	1st 48 hours	2nd 48 hours
Sample A	1150 mpy	2150 mpy
Sample B	1065 mpy	2120 mpy

Sample A - Close to weld, but away from HAZ

Sample B - At opposite end of 30" pipe sample from Sample A

Table 3

Choice of Replacement Materials
Possible Failure Mechanisms

	Stress Relieved	Not Stress Relieved
304	a, b	b, c
304L	b	c
321	–	c
347	–	c
C.S.	d	d
5 Cr	d	e

a – Will sensitize during stress relief. Can fail by sulfur acid cracking from ID during shutdowns when liquid water is present.

b – May sensitize during service. Can fail by sulfur acid cracking.

c – May fail by chloride cracking under insulation during shutdowns, when liquid water is present and metal temperature is $>$150F.

d – May fail by H_2S corrosion during service.

e – May fail by sulfide cracking from ID if BHN $>$ 215 during shutdowns when liquid water is present.

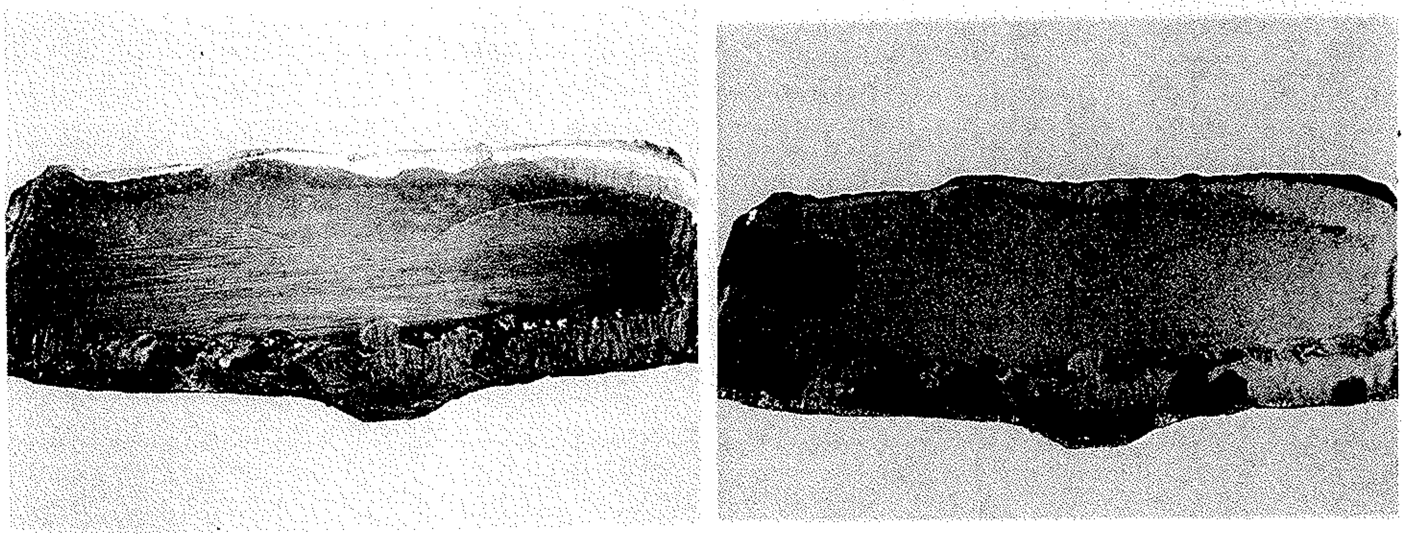


FIGURE 1. Photographs of ID of vacuum bottoms line showing cracks on cleaned metal surface (left) and penetrant inspected surface (right). Weld in line is at bottom of picture. Dye check did not reveal all cracks, indicating that cracks are tight and/or filled with vacuum resid.

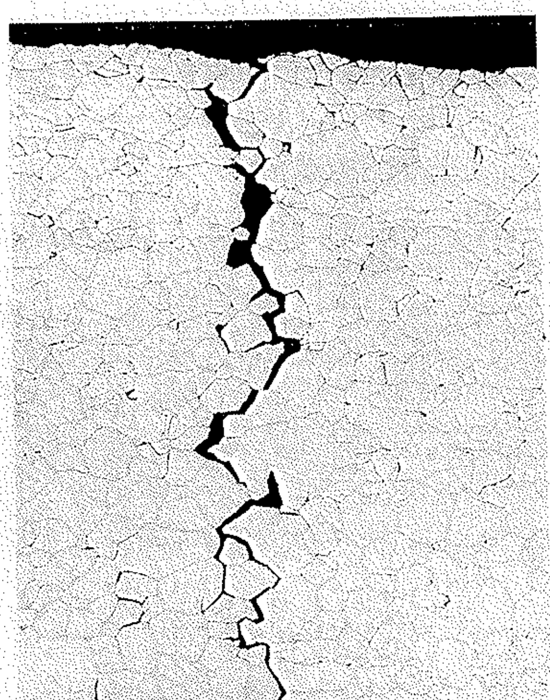


FIGURE 2. Light etch of cracked pipe cross section shows that crack is entirely intergranular and that material is probably severely sensitized.

100X
10% oxalic acid etch
15 sec.

FIGURE 3.

HAZ of pipe weld is partially ditched after A262 etch for 30 sec.

500X
ASTM 262 oxalic acid etch, 30 sec.

FIGURE 4. Pipe material away from heat effects of welding is severely ditched after identical etching treatment as Figure 3. Huey tests show this part of pipe is severely sensitized.

500X
ASTM A262 oxalic acid etch, 30 sec.

Chevron 4

75·16·56 El Paso

MEMORANDUM GO-144

L. Wilson — El Paso — 7/2 1986

J.W. Coombs — MAT LAB – Rich

SUBJECT: No 6 CDU – Atm Transfer Line — OUR FILE: P-100. ~~XX~~ 176

El Paso Refinery — YOUR FILE:

Quick notes with photos — confirming subject cracking failures at 2 locations are both from chloride stress corrosion cracking

First failure (15" spool between Flanges) is shown as-rec'd in FIG 1. We made 2 metallographic sections (micros) at locations #1 & 2. Fig 2 shows the repair weld attempt with a single wide crack. Fig 3 shows this crack at 50x, with the branching side cracks typical for Cl⁻ SCC'g.

Fig 4 is a MACRO photo of Sample #2, showing several wide cracks – also the location of a tight crack – again shown at higher power in FIG 5. It is a typical Cl⁻ stress corrosion crack.

Fig 6 is a typical section taken from the second failure (delivered by Steve Cash) from the other side of the 150 lb flange. That long section was riddled with ID cracks, most all in the lower half of the pipe – indicating perhaps a water level. Cracks were mostly

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MEMORANDUM GO-144

LW

FROM: JWZ

7/2 1981

Pg 2

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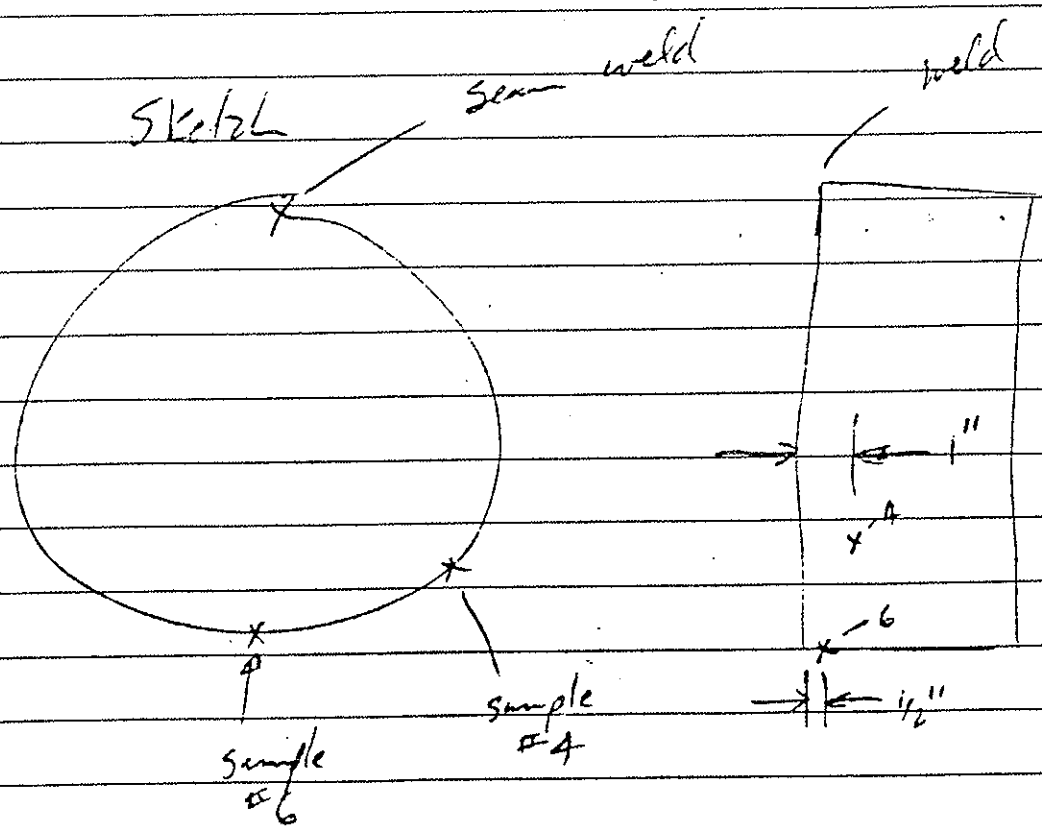
within 1-2" of the weld.

Sample # 4 was at 4 o'clock – the crack was about 1" from the weld – at the leak site.

Attached is the NACE RP-01-70 standard that calls for low Cl^- water (50 ppm max), 7% soda ash (to neutralize polythionic acids) + .5% $NaNO_3$ (to inhibit Cl^- SCC'g during heat up or steam out when H_2O evaporates).

Sketch



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19

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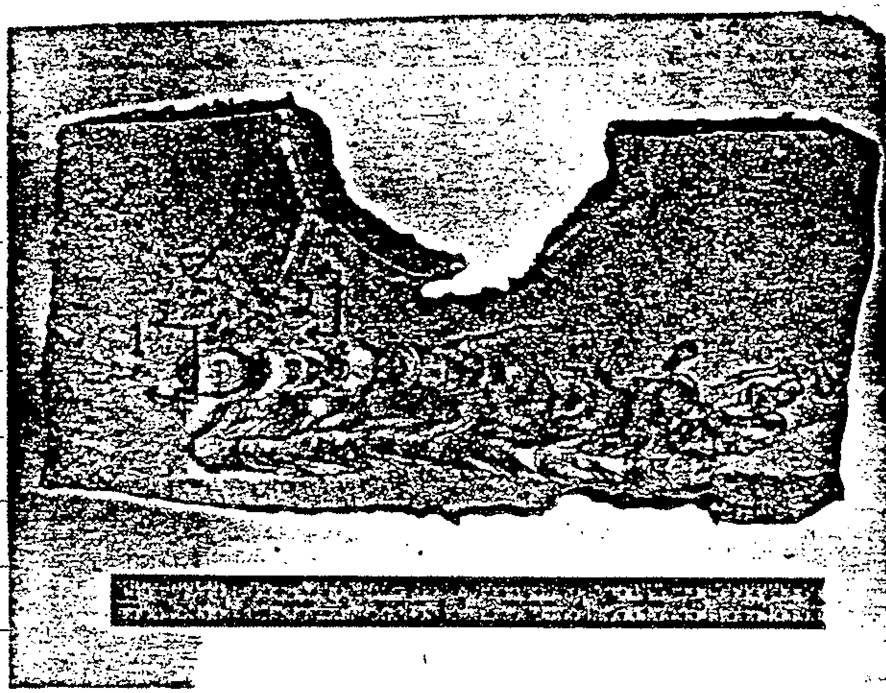
FIG 1



Repair weld attempt

Photo of Section From O D

Micros taken at #1 & #2 locations

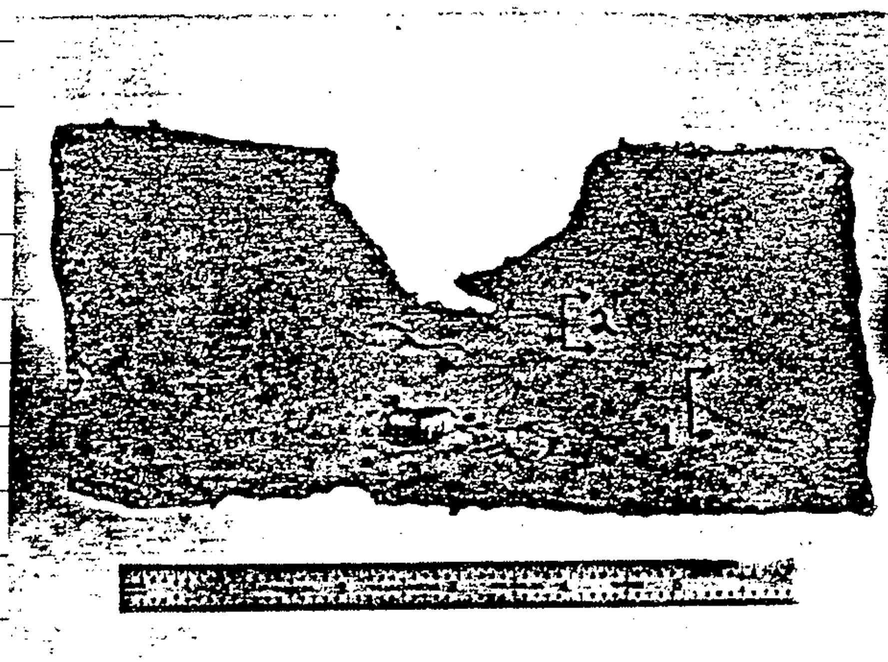


Photo of Section from I D

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GO-144 (8-7C)

Flange Weld

Repair overlay weld attempt

Sample # 1

wide. crack

MAG 12X

Note lack of cracks in Flange Weld HAZ

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FIG 3

OD

ID

No. 1 Sample MAG 50 X

Wide crack at leak location - plus branchy transgranular Cl SCC's along edge. They show growth from ID to OD.

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GO-144 (9-70)

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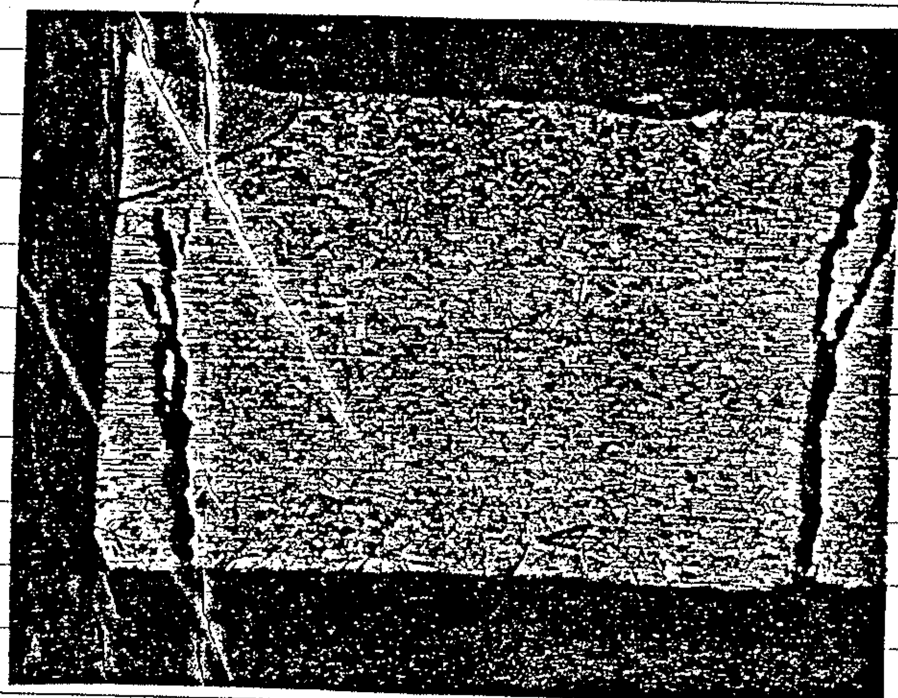
FIG 4

Repair weld



OD

ID

Sample #2

tight Cl SCC
shown in other
photo at 150 X

Older wider cracks were opened by high stresses from nozzle weld & repair weld attempts

MEMORANDUM GO-144

FIG 5

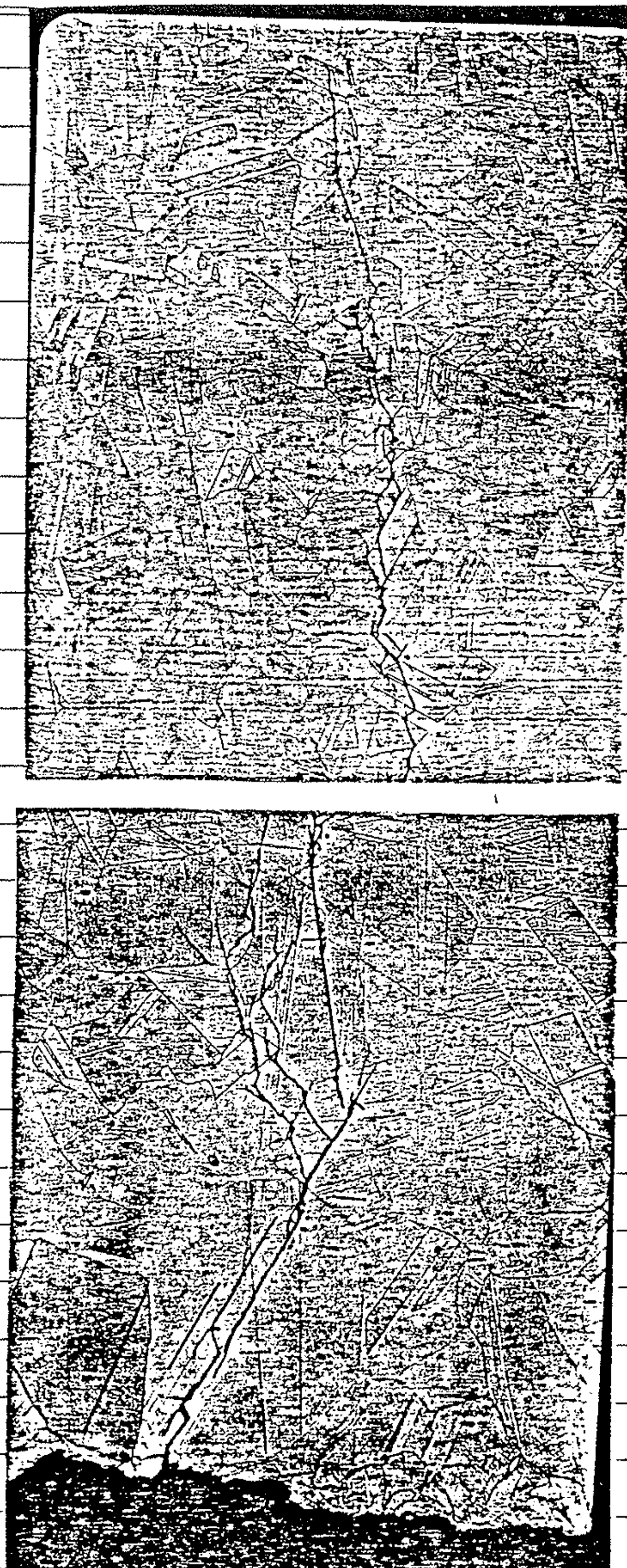
19

UBJECT:

OUR FILE:

YOUR FILE:

to OD



Sample # 2

Typical branchy transgranular crack from pipe ID.

Very classic

Chloride stress corrosion crack

Material = 304 S/S
Not sensitized

MAG 50X

ID

FIG 6

19

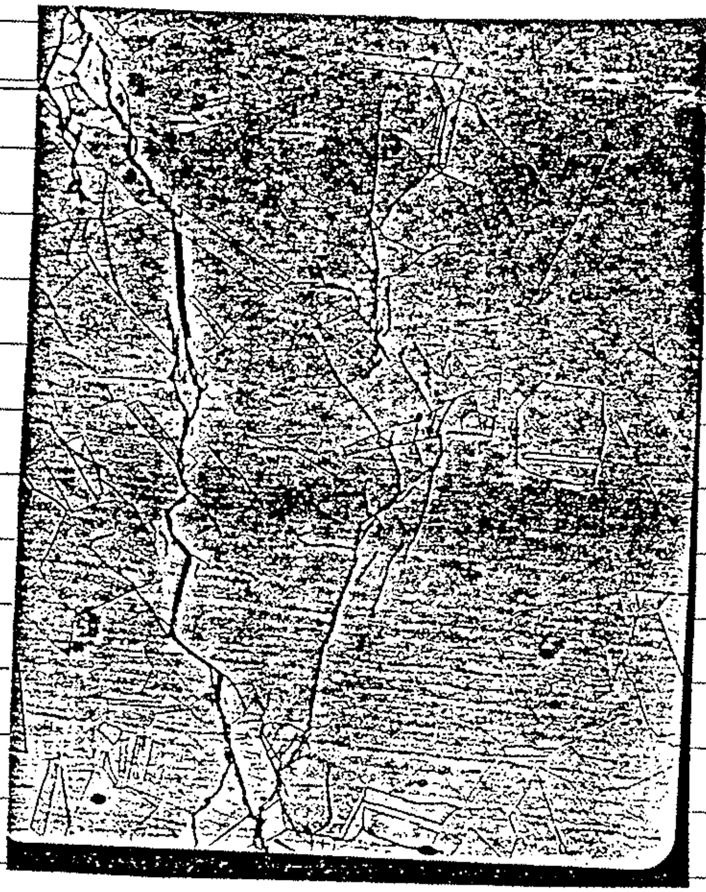
SUBJECT:

OUR FILE:

YOUR FILE:

to OD

Crack tip



May 100X

Again, typical transgranular Cl⁻ SCC from the ID.

Sample # 4
May 50X

Chevron 5

Chevron

Corrosion Mitigation Plan

Crude 1
Pascagoula Refinery

Chevron Products Company

March 2006 (Updated May 2007)

Ned Niccolls – Author, Energy Technology Company

Waldo Jurisson and Morris Bryant, Inspection– Contributor

Alice Burch and Angie Clark, Process – Contributor

Andrew O'Connor, Metallurgy – Contributor

Code 31.1 piping advises against using carbon steel above 775F to avoid graphitization of carbon steel, and only gives allowable stresses to 800F for carbon steel. The ASME/ANSI Process Piping Code 31.3 advises against using carbon steel above 800F to avoid graphitization of carbon steel, although it provides allowable stresses for much higher temperatures. Currently Crude Unit 1 limits the carbon steel piping to 825F which is safe for a number of years because at 825F the rate and amount of graphitization will be slight. However, even allowing this higher 825F limits plant operation.

The alloy piping should be used until the temperature drops to below 800F. Note the corporate piping manual currently advises limiting carbon steel to 750F to assure no graphitization, but we will revise the manual to match the Code wording. [Update 5/07: Rechecking the temperature found the carbon steel to be actually operating at only 680°F – no action required.]

8. C-1102 Vacuum Column Type 317 Stainless Steel Packing and #6 s/c Stainless Piping

Recommendation: Upgrade the C-1102 top bed packing to Inconel or ceramic, whichever is most economic. See also related recommendations below for on-line monitoring and shutdown inspection work.

Background

We are challenged by having very little knowledge as to the actual process or corrosion conditions of this corrosion loop. The type 317 stainless steel packing shows signs of corroding, and the #6 s/c piping system contains chlorides which could lead to pitting and stress corrosion cracking of the 317L stainless steel.

In 1998 the top packing in C-1102 was heavily fouled and the 317 stainless packing had holed through in some center portions of the bed. We believe this was due to corrosion at chloride deposits. Naphthenic acid corrosion is possible, but less likely with the 317 stainless metallurgy. The crude unit is now again seeing signs of packing in various components of the 6th sidecut. An informal examination of packing samples in 2004 indicated chloride corrosion. In 2000 an 8" discharge line from P-1116 cracked underneath scale deposits from what was believed to be chloride cracking.

Reviewing the UT and RT data of the #6 s/c indicates we could be seeing moderately high corrosion rates of the stainless piping. We believe that is an artifact of the relatively new piping and the difficulty of monitoring thin stainless piping. While we cannot yet prove that the general corrosion rate of the stainless is low, we expect that it is low and the real threat is from pitting or cracking at locations where deposits and water can collect.

Fortunately the 2003 inspection of the bare C-1102 column shell at the top packed bed location showed only mild pitting of the carbon steel. The exchangers in the 6th sidecut circuit also have shown little damage, due to 2205 Duplex stainless installed in 1998 in E-1103 and E-1146A. The carbon steel E-1146B bundle showed moderate ID and OD pitting and was retubed in kind in 2003. The 40-year-old E-1128 carbon steel fin fan exchangers showed fouling but very little

Recommendation 2: Conduct annual AUT (or scanning UT if AUT is impractical) inspection of the bottom head and nozzles of C-1105 (discuss).

2. **Loop # 12 (System 12, 6 s/c piping)**

   Recommendation 1: Conduct AUT, and possibly some RT, upstream and downstream of P-1116A (also simply do an external visual walk-through). Do the first AUT in the first quarter of 2006, conduct follow-up AUTs on about one year intervals as long as the chloride issue remains.

   Recommendation 2: Take a sample from as close to the column as practical, to measure chloride and water content. Take the first sample in the first quarter of 2006, plan follow-up samples once per quarter as long as the chloride issue remains.

   Recommendation 3: Recheck the carbon steel piping portion that appears to be showing activity. Specifically note the carbon steel piping leading to the E-1128's, and the E-1128 fouling.

   Background

   Until proven otherwise, we need to assume the stainless sidecut piping is corroding like the stainless column packing. Unfortunately, this corrosion is likely to be highly localized and could even cause chloride stress corrosion cracking (there was one case of P-1116A discharge piping that was suspected of chloride cracking in 2000). This system has had significant and possibly sporadic corrosion since at least the 1990s, but it appears to have worsened in recent years. It is very difficult to confidently determine corrosion rates from the existing UT data, due to relatively recent upgrade to stainless for much of the system, and substantial scatter in the data.

3. **Possible Mismatch of Some Piping Metallurgy Entering the C-1101, C-1102, C-1103 columns (See 2.1, items 1-5)**

   Recommendation: If we determine there is a mismatch of piping metallurgy entering the C-1101, C-1102, and C-1103 columns, then a TML at each mismatch should be established within the next few months to monitor that location until the piping or nozzle can be upgraded at the 2008 shutdown. See the detailed notes in Section 3.0 for specific locations which may have mismatches.

4. **Loop #3 (System 3, Top of Atmospheric Column and Overhead Piping)**

   Recommendation 1: Conduct bi-annual AUT of the carbon steel sections of overhead piping, with order of priority being the piping into the E-1101s, and the piping in and out of the E-1120 fin-fans.

   Recommendation 2: RT additional low points/drains in the overhead piping systems, especially in area of dwg 003-11 (note point 30).

   Background

   Note that the atmospheric overhead compressor section appears to have areas of localized corrosion.

Equipment	Material	Description and Historical Data	Max Temp	TAN	Sulfur (wt%)	Corrosion Rate		Remaining Life Range
						Hist.	Calc.	
(Channel: cw)								
E-1124 A/B Tubes	Tubes: Admiralty SB-111-445 T/S: NRB SB-171-464	02 – installed; 04 – A&B: very light uniform corr.	200	NA	4 H2S	?	< 3	> 10

3.12 Corrosion Loop #12 (System #12): Vacuum column 6th side cut, and 7/8 sidecuts

This corrosion loop consists of the #6 sidecut piping and associated equipment from the C-1102 vacuum column, through E-1103 and E-1146A/B. From E-1146A/B the # 6 sidecut goes both back to the C-1102 column via the E-1128 air cooler, and to the Isomax 2 plant via the E-1140 air cooler.

This system also includes the C-1102 vacuum column #8 sidecut from C-1102 through E-1141A to E-1112. From E-1112 the #8 sidecut goes both to the Isomax 1 plant (and to Isomax feed storage), and back to C-1102.

Carbon steel has shown surprisingly high corrosion rates since at least the 1990s, and some historical notes link the higher rates with processing naphthenic acid crudes. We now believe water and chlorides are important factors. Upgrading much of this system to 317L SS in recent years will greatly reduce the general corrosion, but the stainless is susceptible to pitting under deposits, or possibly even chloride stress corrosion cracking. The 317SS packing in the C-1102 column has seen significant chloride corrosion. There is still some CS in the lower temperature piping that is showing some activity and needs rechecking.

This loop also contains #7/#8 sidecut piping and associated equipment. **Note that some of the lower temperature piping is still carbon steel and seeing moderate activity. The hotter portion of this piping is in the range where relatively small increases in temperature (20-30F) and TAN levels could substantially increase carbon steel corrosion in this part of the circuit. Discuss if we should put in a probe here, or other monitoring.**

Make sure the emergency wash oil line near the outlet of P-1119 going from C-1102 to C-1103 is the right metallurgy and is covered somewhere.

Industry 1 & 2

97C5.1-01: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Mike Beaton (Petro-Canada) - asked for experience with PASCC of stainless steels used in crude and vacuum units used for protection against naphthenic acid corrosion. After discussion this was further clarified as "L" grade (low-carbon) and regular-grade materials. A show of hands indicated no problems with "L" grade material.

97C5.1-02: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Tom Farraro (Citgo) - reported a cracking problem in a solid type 316 SS transfer line that was probably caused by chloride SCC after it was soda ash washed one time. The cracking occurred at a low spot between two pipe supports that didn't get drained. This incident was about 10 years ago and since that time soda ash washing has not been used, and no further incidents of cracking have occurred. I1

97C5.1-03: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Ralph Blee (Exxon) - commented that during a PMI inspection two short lengths of stainless steel were found at the inlet to a crude column and a vacuum column, welded to Cr-Mo transfer lines. These lines had been in service approximately 30 years and both were cracked in the weld HAZ area. The piping had never been soda ash washed; however, it was not determined whether the cracking was due to chlorides or PASCC. I2

97C5.1-04: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Kevin Ganschow (Chevron) - described some experiences in crude units many years ago with naphthenic-acid-type corrosion on the undersides of trays and in the vapor space of columns. He asked whether anybody tried or had any experience using corrosion probes in the vapor space of a column to take corrosion rate measurements in that area.

97C5.1-05: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Dannie Clarida (Conoco) - commented he has no experience with corrosion monitoring devices installed in a vacuum tower, but there has been experience with a vacuum tower clad with 410S in an area where naphthenic acids caused corrosion in both liquid space and vapor space, in the packed section as well as some trayed areas. This is not exactly an answer to the question, but certainly corrosion in the vapor space areas was observed.

97C5.1-06: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Keith Lewis (Shell International) - asked Kevin whether he was going to try to force condensation on the corrosion probe because naphthenic acid corrosion does not occur in the vapor phase itself.

97C5.1-07: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Kevin Ganschow (Chevron) - responded that he was thinking about the possibility of an air-cooled type of probe so that the end of the probe is cooled such that it causes some type of condensation to occur on the probe.

97C5.1-08: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Bill Fahey (Petrolite) - commented that some years ago he saw a probe consisting of a hollowed-out cylindrical coupon through which wash oil, or if it was an overhead, water, was injected to cool the probe down. He tried it but had problems with packing, so it didn't really work well, but the idea was to put a coolant through and then let the coolant enter into the process.

Industry 3

corrosion cracking. More specifically, he asked whether soda ash wash is being used in these types of units. A quick survey was made of the audience: approximately 20 indicated taking no precautions at all; approximately 4 indicated that some precautions are taken if the material is believed to be sensitized; no one indicated that they always take precautions.

98C5.1-07: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Andy Gysbers (Imperial Oil) - commented that equipment in crude distillation units is likely to be coated with a thick resid material, which in turn poses less risk of a polythionic acid stress corrosion cracking problem. If this material is removed, there could be a problem.

98C5.1-08: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Keith Lewis (Shell International) - commented on one case in which soda ash washing was used in a crude unit stainless steel furnace in conjunction with mechanical pigging to remove coke deposits. In this case the soda ash solution was used as the pigging fluid to protect the base material after the coke was removed.

98C5.1-09: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Kirk Baker (Chevron) - described a similar situation to the one mentioned by Keith. His case was a resid stripper furnace with type 317L SS roof tubes and the skin temperature was 538°C (1,000°F). These tubes were mechanically cleaned by pigging and left open for inspection for an extended period of time. For this reason a soda ash wash was applied.

98C5.1-10: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Jorge Hau (PDVSA) - asked whether anybody had experienced polythionic stress corrosion cracking in a vacuum tower. There were no responses.

98C5.1-11: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Tom Farraro (Citgo Petroleum) - commented that they do apply the soda ash wash to the stainless steel piping in their vacuum units because of some past problems due to polythionic acid stress corrosion cracking. However, he added that in one case they did experience chloride stress corrosion cracking after using the soda ash, due to leaving soda ash solution in low spots.

I3

98C5.1-12: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Jorge Hau (PDVSA) - asked why people are using "L" grade materials for nonwelded components such as structured packing. There were no responses.

98C5.1-13: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Keith Lewis (Shell International) - referred to some early laboratory work published by Joerg Gutzeit that showed that austenitic stainless steels in the sensitized condition are more susceptible to naphthenic acid corrosion at high TAN numbers. His question was whether anyone had seen examples from plant conditions in which accelerated naphthenic acid attack has occurred in materials known to be sensitized. His particular interest is a hydrocracker feed furnace that could have sensitized type 321H SS tubes and be exposed to feed with a TAN 1 to 2.

Industry 4

I4

98C5.1-14: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Cathy Shargay (Fluor Daniel) - responded by saying that she knew of one case in a vacuum unit in which a type 316 SS transfer line was sensitized and did suffer from stress corrosion cracking externally, but there was no internal accelerated attack due to naphthenic acid.

98C5.1-15: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Brian Hopkinson (PDVSA) - added that he had never used "L" grade SS materials in his plants and he had never experienced accelerated localized naphthenic acid attack due to sensitized material.

98C5.1-16: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Tom Farraro (Citgo) - also commented that in several of their units they have a mixture of "L" and regular grade SS materials and they have never seen accelerated localized corrosion due to naphthenic acid attack of sensitized material.

98C5.1-17: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Elizabeth Babaian-Kibala (Nalco Exxon Chemicals) - asked what experiences people are having with high-temperature corrosion probes for naphthenic acid and corrosive crude services.

98C5.1-18: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Deyauan Fan (Shell Oil) - responded by saying that he has experienced both coking and sulfidation problems with high-temperature E/R probes in these services.

98C5.1-19: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Felix Perdieus (Exxon) - responded that they have had good experience with eight corrosion probes installed in hot oil services in their distillation unit. The probes give a reasonable estimate of corrosion rates. A couple of the probes have had to be replaced because they've reached their end of life. The safety people in the refinery are becoming more convinced that this type of probe can be handled safely.

98C5.1-20: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Walt Jenkins (Techsoft) - commented that his previous employer had 10 to 15 probes installed in high-temperature service. These probes did give reliable results. He added that it is necessary to have special tools to pull these probes out of service. Probes were preferred to coupons because they had to be removed much less frequently. When asked about using different types of access fittings for removing and reinstalling probes, Walt commented that in most services they used a standard valve packing arrangement; however, in high-temperature high-pressure services they might consider using the more expensive custom-designed special access fittings.

98C5.1-21: CRUDE AND VACUUM UNIT (NAPHTHENIC ACID CORROSION):
Mike Nugent (Tosco) - added that that in the CORROSION/98 paper no. 577, "Experience with Naphthenic Acid Corrosion in Low Tan Crudes," he describes very good experience with 9 probes operating at about 260°C (500°F) for a period of six years. They now have 11 probes installed in this service. The readings from the probes correlate very well with the results from corrosion coupons and with their inspection experience.

Industry 5

2004C5.2-04: CRUDE DISTILLATION/VACUUM UNITS:
Rob Smith (Marathon Asland) commented that they alloyed up areas to resist naphthenic acid corrosion, but were concerned about CL-SCC. He commented that previous REFIN·COR minutes did not contain a great deal of information relating to this particular concern. He wondered if that was because people had not experienced these failures, or if everybody understood that they were chloride stress corrosion cracking and did not report them. He suspected that this may be the situation. He was looking for any experiences people actually had, whether they were related to shutdowns and/or to desalter upsets. If so, were there any special measures to prevent such failures by alloying further up or special washing or neutralization?

2004C5.2-05: CRUDE DISTILLATION/VACUUM UNITS:
Tom Farraro (Stress Engineering) commented that they did have one vacuum unit that had a solid 304-SS transfer line. The furnace outlet operated at about 399°C (750°F). It operated for about 20 years when they were not running any naphthenic acid crude. When they started running some naphthenic acid crudes the line failed. However, it did not fail from naphthenic acid or sulfidation corrosion, but rather CL-SCC. Some condensation occurred during an outage which accumulated in the low points in the line. The acidic salts then concentrated during startup and caused stress corrosion cracking. It was subsequently replaced with a SS clad line.

For a number of years, they also experienced numerous failures on solid SS piping in hydrotreaters and hydrocrackers, as well as, crude units. In almost every case, the cause of the failure was not during normal operations. It was always due to some type of upset or something that was done improperly during a shutdown or a start up. In one case, a desalter upset resulted in extensive chloride stress cracking in the crude preheat train. The train was operating in the 288 to 315°C (550 to 600°F) temperature range and normally there should not have been any water present, therefore, chloride stress cracking should not have occurred. They managed to upset the desalter with sufficient severity that a slug of water went through the system. As a result, they had dozens of cracks. He recommended, whenever possible, not to use solid austenitic stainless steel in a refining environment, but to use clad instead. If solid alloys have to be used, use alloys other than 300-SS. One problem on clad lines is that it may not be possible to use clad on small-bore connections. In such cases, he recommended to upgrade the small connections to Alloy-625 or Alloy-C, which are resistant to chloride cracking. He could not recall a single solid stainless steel piping system in their refineries that did not have a failure due to chloride stress cracking at one time or another. Every single solid SS piping that he had in every unit, regardless of the service, ended up with at least one failure due to chloride stress cracking. For some reason it was unforeseen or unexpected.

2004C5.2-06: CRUDE DISTILLATION/VACUUM UNITS:
Cathy Shargay (Fluor Daniel) commented that they always prefer clad construction. However, solid construction may be more economical at times.

2004C5.2-07: CRUDE DISTILLATION/VACUUM UNITS:
Joerg Gutzeit (Consultant) also pointed out the there also exists an external CL-SCC risk for solid SS construction.

2004C5.2-08: CRUDE DISTILLATION/VACUUM UNITS:
Bill Neill (Corrosion & Materials Technology Inc.) commented that he was working with a refinery on their first titanium bundle. This refinery's experience was very favorable with rolling the tube ends into the tube sheet. However, this particular client had already gotten a bid to weld the tube ends. He asked if people have an approach as far as number of grooves and the number of weld passes when they weld titanium tubes into the tube sheet.

2004C5.2-09: CRUDE DISTILLATION/VACUUM UNITS:
Andy Gysbers (Imperial Oil) commented that it was their practice to sea weld all titanium tubes. Their experience had been not to rely on mechanical rolls. He had seen bundles which passed the shop hydrotest, shipped from shops, and arrive in the field with enough relaxation to leak on the in-service hydrotest. Their practice was to then seal-weld all titanium tube bundles (in addition to mechanical roll). They will accept autogenous seal welding.

2004C5.2-10: CRUDE DISTILLATION/VACUUM UNITS:
Dick Horvath (Shell Global Solutions) asked if the seal weld is done before or after the mechanical rolling.

2004C5.2-11: CRUDE DISTILLATION/VACUUM UNITS:
Andy Gysbers (Imperial Oil) commented that they seated the tubes, did the seal welding, and then fully rolled the tube. Otherwise, there is a concern of creating a sealed gap causing pinhole leaks through the weld.

2004C5.2-12: CRUDE DISTILLATION/VACUUM UNITS:
Deyuan Fan (Shell Global Solutions) commented that Jim McMaster published a paper about the various tube-to-tube sheet joint designs for titanium heat exchangers and the pros and cons of seal welding and mechanical rolling. The reference is below.

Jim McMaster, "Titanium for Mechanical Equipment in Industrial Corrosion Service," page 34, "Industrial Applications of Titanium and Zirconium" Symposium of ASTM Committee B-10 on Reactive and Refractory Metals and Alloys, New Orleans, LA, Oct 1979.

2004C5.2-13: CRUDE DISTILLATION/VACUUM UNITS:
Dana Williams (Marathon Ashland) asked a question related to crude