Materials Selection Challenges in the Refining Industry

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Materials Selection for Process Plants

It's Complicated!

There Is No Recipe, But
There Are Lots Of Resources

Conventional Criteria for Materials Selection

- Key aspects of materials selection in process plants:
  - Strength & fracture toughness
  - Resistance to environment & temperature
  - Fabrication
  - Commercial Availability
  - Economy
  - Weight (e.g. offshore)
  - Product contamination (corrosion products)
- For process equipment it is often helpful to start with the question: “Why not carbon steel?” and proceed from there. If carbon steel is safe and effective, then it is usually economical too (>50% of the time)
- Consider potential damage mechanisms and engineer to manage them

API RP 571 Gives an Overview of 66 Damage Mechanisms Affecting Process Equipment

Each Mechanism is Summarized in a Few Pages:

- Description of Damage
- Affected Materials
- Critical Factors
- Affected Units or Equipment
- Appearance or Morphology of Damage
- Prevention/Mitigation
- Inspection and Monitoring
- Related Mechanisms
- References

> ➢ General information but no engineering guidance

Our discussion will focus on these Damage Mechanisms:

- Brittle Fracture
- Sulfidation
- Ammonium Bisulfide Corrosion
- High Temperature Hydrogen Attack

API RP 571 Includes Guidance on Which Damage Mechanisms are Potentially Applicable

- PFDs are provided for 16 different types of process plants
  - Crude Unit/Vacuum
  - Delayed Coker
  - Fluid Catalytic Cracking
  - FCC Light Ends Recovery
  - Catalytic Reforming (CCR and Fixed Bed)
  - Hydroprocessing
  - Sulfuric Acid Alkylation
  - HF Alkylation
  - Amine Treating
  - Sulfur Recovery
  - Sour Water Stripper
  - Isomerization
  - Hydrogen Reforming
  - Visbreaker
  - Caustic Treating

Key Materials Selection Considerations

1. Unexpected or Inconsistent Material Behavior is Not Acceptable
   - Example: Brittle Fracture
   - Example: Sulfidation Corrosion of low Si carbon steel

2. Degradation Can Be Manageable if it is Predictable
   - Example: Ammonium Bisulfide (NH_4HS) Corrosion

3. Inspection & Detectability Affects Necessary Design Margins
   - Example: High Temperature Hydrogen Attack

➢ Cannot tolerate susceptibility to damage that either is not detectable or may occur abruptly and cause failure between inspection & maintenance intervals

Brittle Fracture: Abrupt and Unforgiving

- Classic examples of brittle fracture include Boston molasses tank, WWII Liberty Ships, and many others
- Propensity for brittle fracture depends on stress, fracture toughness, and flaw size
- Older pressure vessels typically had good fracture toughness and flaw tolerance, but not always
- Occasional failures resulted
- ASME Code strengthened their requirements for fracture toughness for new vessels in 1986
- Industry has had to retroactively adjust, and now requires many older vessels to be warmed up prior to full pressurization

High Temperature Sulfidation Corrosion of Carbon Steel
>The Dilemma of Variable Si Content<

- Si level of ASTM A53 piping is not specified
- Si level of ASTM A106 piping – minimum of 0.1 wt%

Example: Corrosion of Carbon Steel Piping in FCC Fractionator Bottoms Piping at 150 psig and 650-700°F

- Results of one study show that carbon steels with <0.1 wt% Si content have significantly higher corrosion rates
  - >0.1 wt% Si content, the corrosion rate is less than 0.05 mm/year
  - <0.1 wt% Si content, the corrosion rate varies from 0.05 to 0.4 mm/year

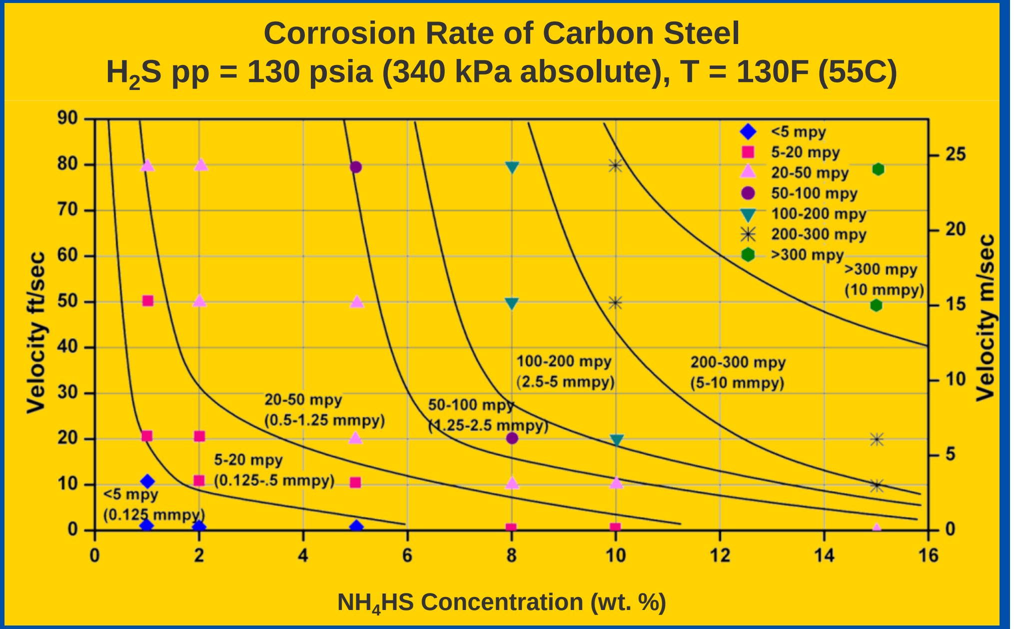
Result: Potential for Very Different Corrosion Rates in the Same Piping System!

Ammonium Bisulfide Corrosion: Success Story!

- N and S in crude oil are converted to NH_3 and H_2S by hydroprocessing
- Solid NH_4SH salts are washed out by water injection, but the resulting solution is corrosive
- Salt concentration, H_2S partial pressure, velocity (shear stress), temperature, and other contaminants such as cyanides and chlorides are factors
- Corrosion can be highly localized and therefore difficult to find
- Corrosion can be aggressive; ½" (12.7mm) per year or more under severe conditions

Ammonium Bisulfide Corrosion

- Empirical observations and field data were helpful, but unexplained failures continued to occur
- Joint industry project conducted over 10 years to systematically study the phenomenon and develop correlations for the key factors
- A commercially available software package was developed which provides reasonable predictions of corrosion rates
- Now widely used by industry for aiding materials selection, establishing operating limits, and setting inspection requirements.



Source: NACE Paper #06576 Prediction and Assessment of Ammonium Bisulfide Corrosion Under Refinery Sour Water Service Conditions (used with permission)

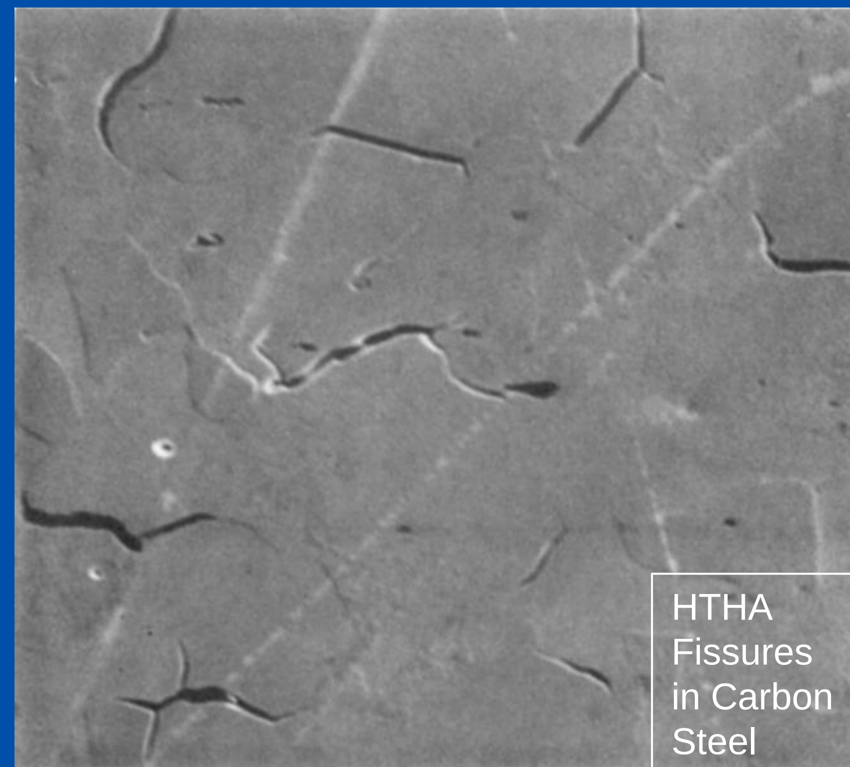
NET RESULT: Corrosion is now predictable and therefore manageable

High Temperature Hydrogen Attack (HTHA)

Basic Mechanism:

1) At T > 400°F (204°C) H_2 dissociates and diffuses into steel
2) Atomic H reacts with iron carbide to form CH_4 (methane)
3) Methane molecule is too large to diffuse through steel so it is trapped
4) Trapped methane causes fissures and cracks internal to the steel

HTHA is difficult to detect by inspection, and therefore best prevented by design and operation

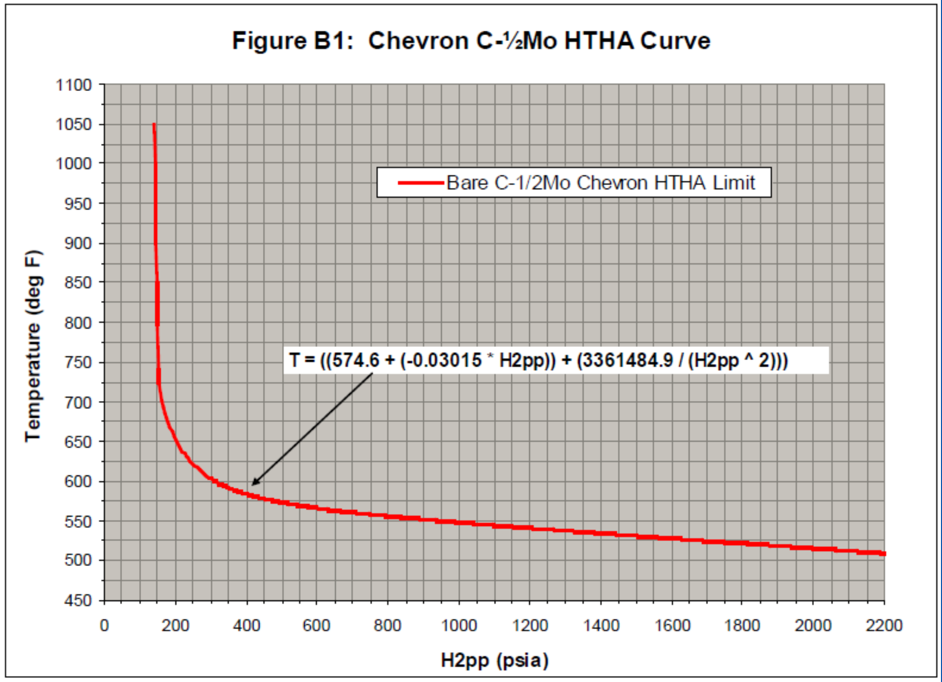


HTHA Fissures in Carbon Steel

Image from Chevron USA

API RP 941 Figure 1 Contains Limits for Ferritic Steels to Prevent High Temperature Hydrogen Attack

- API RP 941 Figure 1 shows six curves for six different alloys, indicating regions of hydrogen attack susceptibility based on empirical data
  - Hydrogen partial pressure vs. temperature
  - An example of this relationship is shown below for C-½Mo



The Naphtha Hydrotreater (NHT) Process

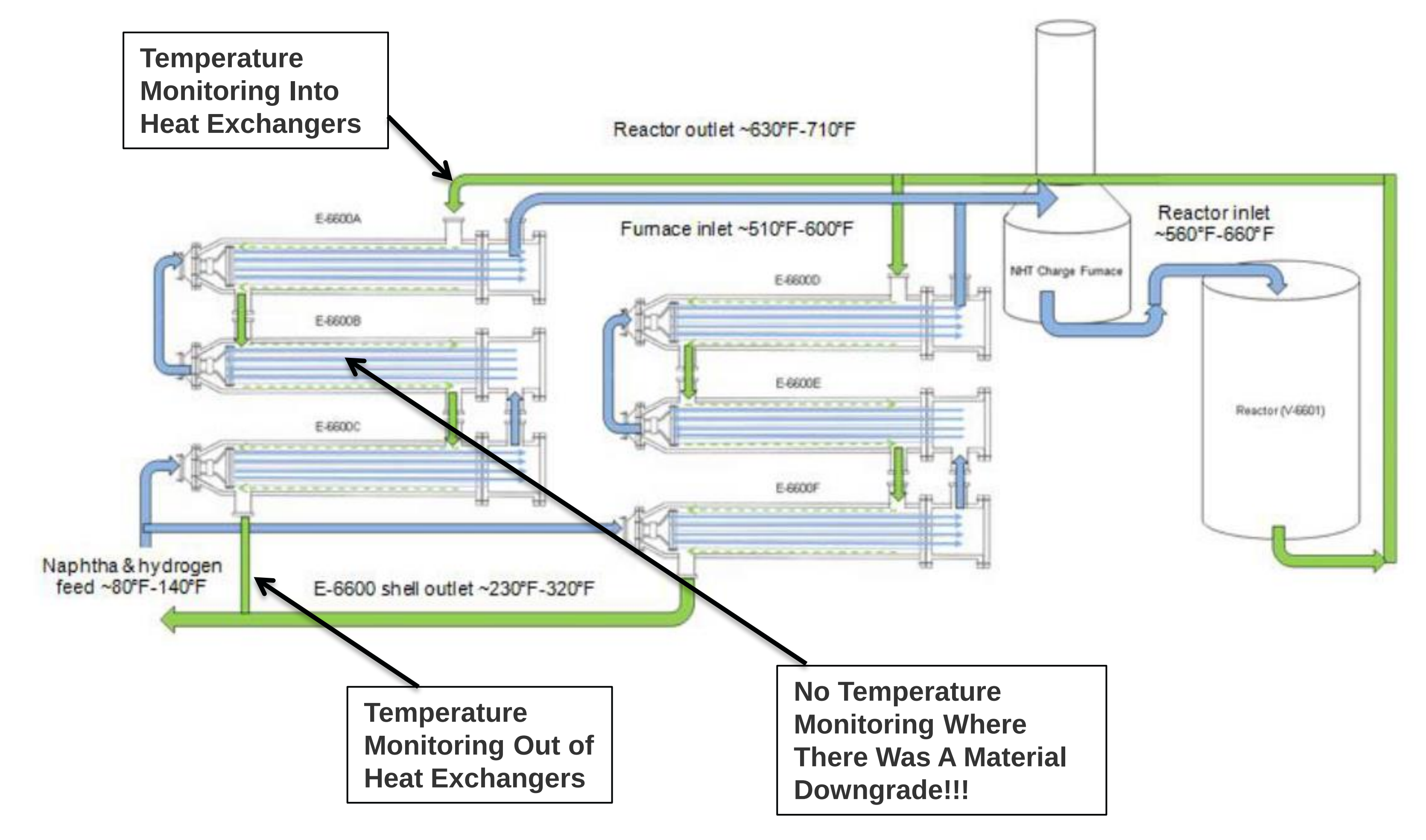
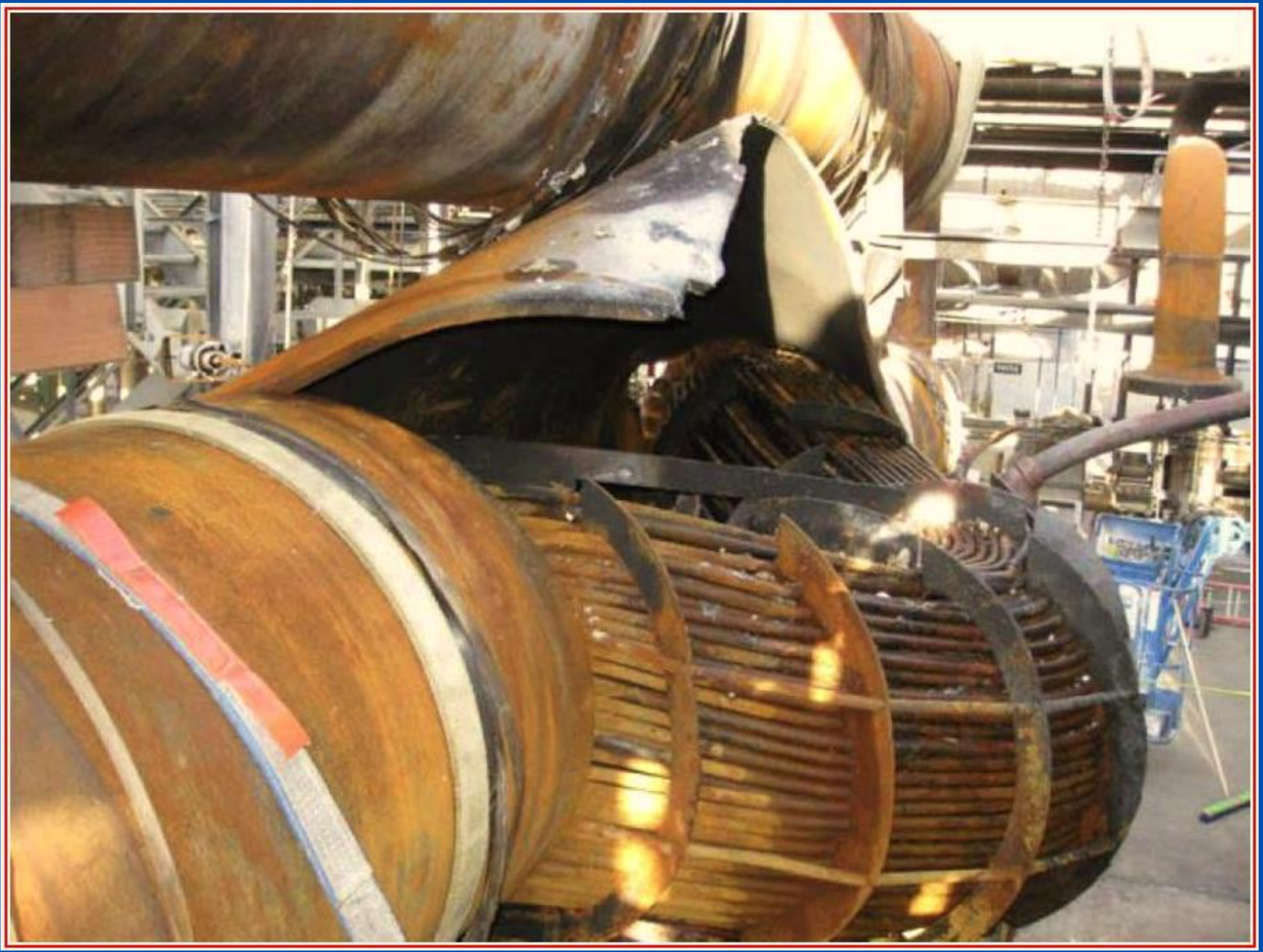


Figure taken from Tesoro Anacortes NHT Investigation Report, July 21, 2011. Copyright 2011 Tesoro Refining & Marketing Company LLC. All rights reserved. Used by permission from Tesoro.

Tesoro Anacortes 2010 Heat Exchanger Shell Failure Due to High Temperature Hydrogen Attack



This Incident Resulted in Several Fatalities

Source: Chemical Safety Board News Release - April 1, 2011
http://www.csb.gov/assets/1/16/Tesoro_Anniversary_-_Safety_Message_-_Final.pdf

In Addition to API RP 571 The Industry Has Many Stand-Alone Documents on Specific Damage Mechanisms

- API RP 941 – High Temperature Hydrogen Attack
- API RP 945 – Amine Stress Corrosion Cracking
- API RP 939C – Prevention of Sulfidation Corrosion Failures
- API 939D & 939E – Ethanol Stress Corrosion Cracking
- API RP 530 – Heater Tube Thickness Calculation (Creep)

- NACE MR0103 – Materials Resistant to Sulfide Stress Cracking
- NACE RP0169 – Control of External Corrosion of Underground Piping
- NACE SP0472 – Prevention of Environmental Cracking of CS Welds
- NACE SP0403 – Avoiding Caustic SCC of CS Equipment
- NACE RP0170 – Protection of Austenitic SS for Polythionic SCC
- NACE RP0198 – Control of Corrosion Under Insulation and Fireproofing
- NACE SP0590 – Prevention of Deaerator Cracking (corrosion fatigue)
- NACE technical publications: materials for sulfuric acid, hydrofluoric acid, carbonate SCC

The Importance of Context for Materials Selection

- Materials selection is one aspect of a system that also includes design, fabrication, operation, inspection, and maintenance.

- Some Key Elements for Process Plant Equipment:
  - Equipment design
  - Anticipated operating conditions
  - Design life
  - Access for inspection & maintenance
  - Relative importance of long term reliability depends on:
    - Spared equipment vs. non-spared
    - Pressure boundary vs. internal components (consequences)

- Difficult to anticipate what conditions will be in the coming years
  - Defining Integrity Operating Windows (limits) and using the Management of Change process are necessary

Rules of Thumb For Fixed Equipment in Refineries

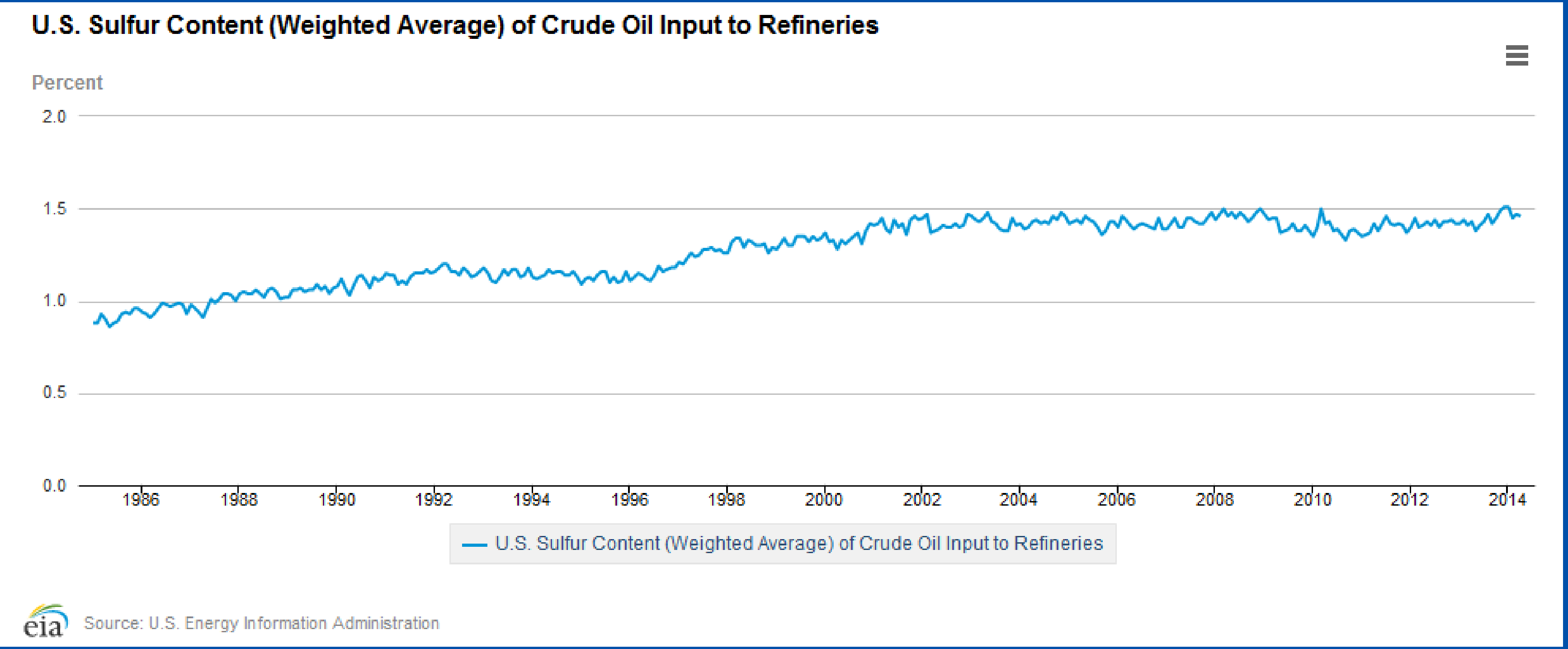
(Applies to piping, pressure vessels, heat exchangers, fired heaters, etc.)

- Design Life
  - Intended design life is usually 5-20 years for components that are not on the pressure boundary and are replaceable or spared
  - Design life is usually 10-40 years minimum for equipment on the pressure boundary; due to conservative design & operation it typically lasts much longer
- End of Life Condition
  - Replacement or end-of-life is usually condition-based rather than time-based. Strategy for most equipment is to monitor or periodically check its condition and replace as needed, rather than replacing on a predetermined schedule. Run to failure only if consequences are limited.
- Access for Inspection & Maintenance
  - Most inspection and maintenance activities should be required no more often than every 5 years and preferably 10 years; more often is burdensome (there are some exceptions)
  - Inspection is required at ½-life or more frequent per piping & vessel code
  - Major maintenance is normally scheduled at 5 year (or longer) intervals
  - Batch processes or stand-alone processes may be more accessible for maintenance and inspection

Suitability of Materials for Service Can Be An Ongoing Challenge

- Materials Selection is Adequate at the Time of Design, but…..
  - Changing feedstocks (increasing S, acid content, gravity of crude oils)
  - Changing product specifications (e.g. S reductions, vapor pressure limits)
  - Increasing plant throughput
  - Changing market demands (shifting product slate)
  - Changing process operating conditions
  - Aging equipment
- Q: Is the existing material adequate for proposed new conditions???
  - Important to establish Integrity Operating Windows (limits)
  - Important to use the Management of Change process

Evolving Characteristics of Refinery Feed Stocks



http://www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=pet&s=mcrs1us2&f=m

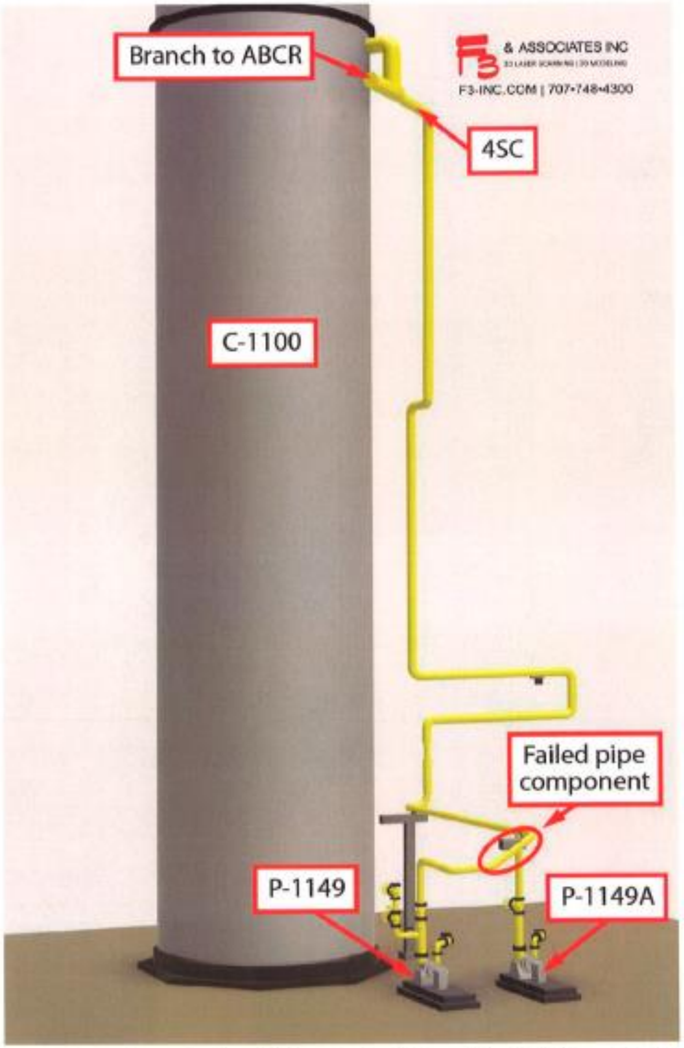
Other trends include increasing crude oil acidity, increasing heavy oil, high salt content, and other challenges

Opportunities

- Collaboration of Academia, Government Laboratories, and Industry
  - Example: Corrosion Under Insulation inspection work, and atomistic corrosion modeling with Los Alamos
- Tremendous opportunities within the Energy Sector
  - For both “Traditional” and Alternative Energy spaces

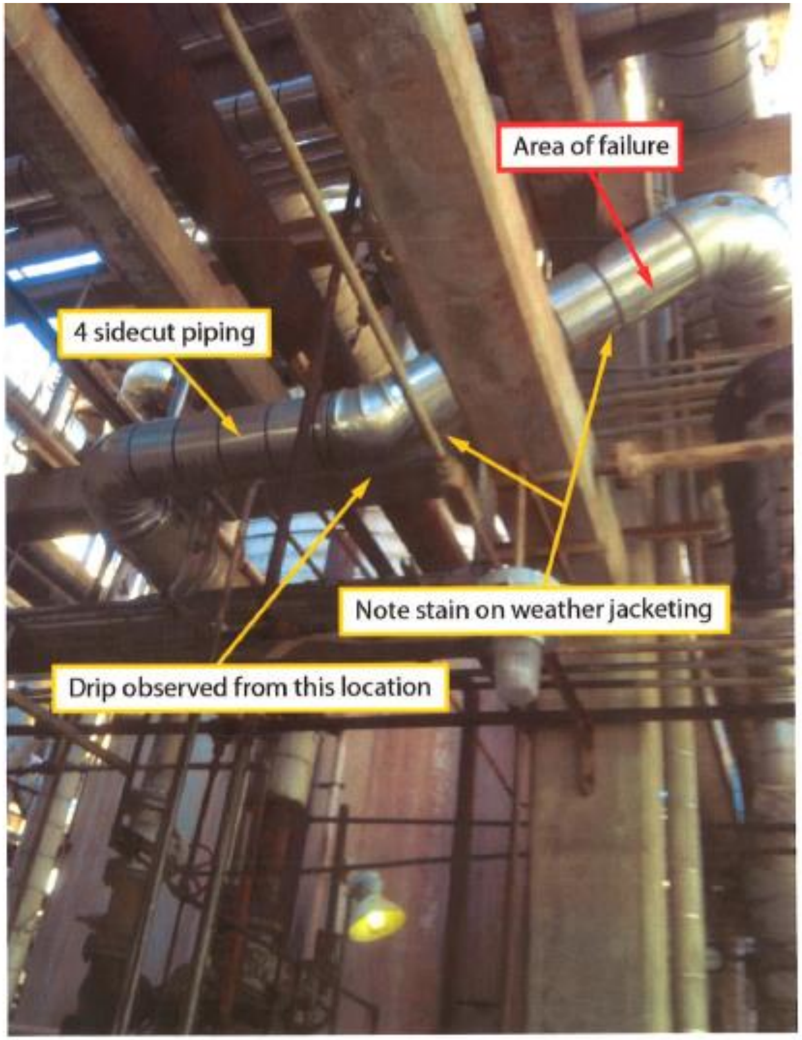
Appendix:
Chevron Investigation Report for the August 6, 2012 Fire

Source: Richmond Refinery 4 Crude Unit Incident, August 6, 2012
(Report prepared by the CUSA Richmond Investigation Team, April 12, 2013)



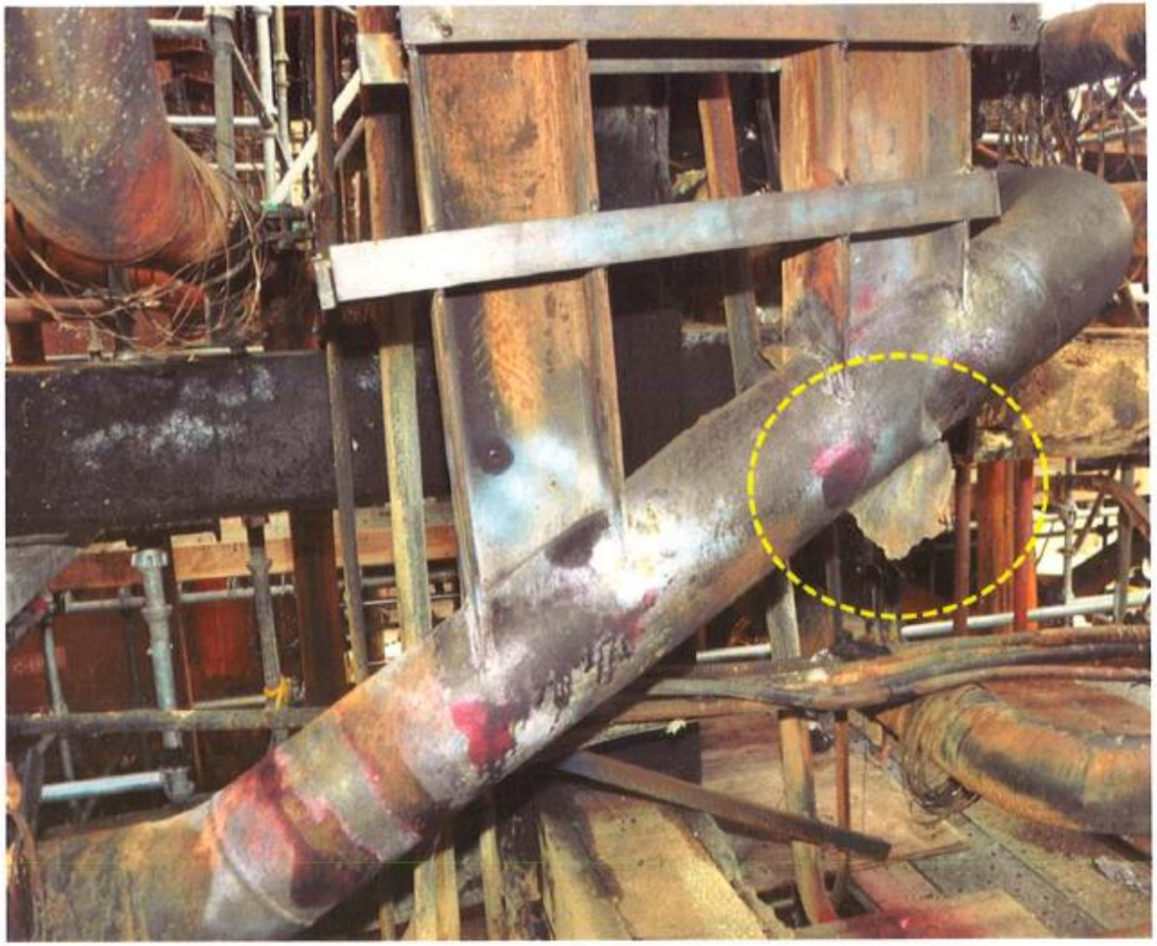
Three-dimensional model showing the 4SC and the ABCR drawn via a 20-inch nozzle from the C-1100. Note: the ABCR piping is not shown beyond the initial branch.

Source: Richmond Refinery 4 Crude Unit Incident, August 6, 2012
(Report prepared by the CUSA Richmond Investigation Team, April 12, 2013)



Photograph taken by STL2 during the initial response to the leak, but before the pipe rupture. The area where the rupture subsequently occurred (indicated by a red arrow) is approximately 16 feet from the ground.

Source: Richmond Refinery 4 Crude Unit Incident, August 6, 2012
(Report prepared by the CUSA Richmond Investigation Team, April 12, 2013)



Photograph of the ruptured pipe component during inspection prior to removal. Area of the rupture is circled in yellow.

Source: Richmond Refinery 4 Crude Unit Incident, August 6, 2012
(Report prepared by the CUSA Richmond Investigation Team, April 12, 2013)

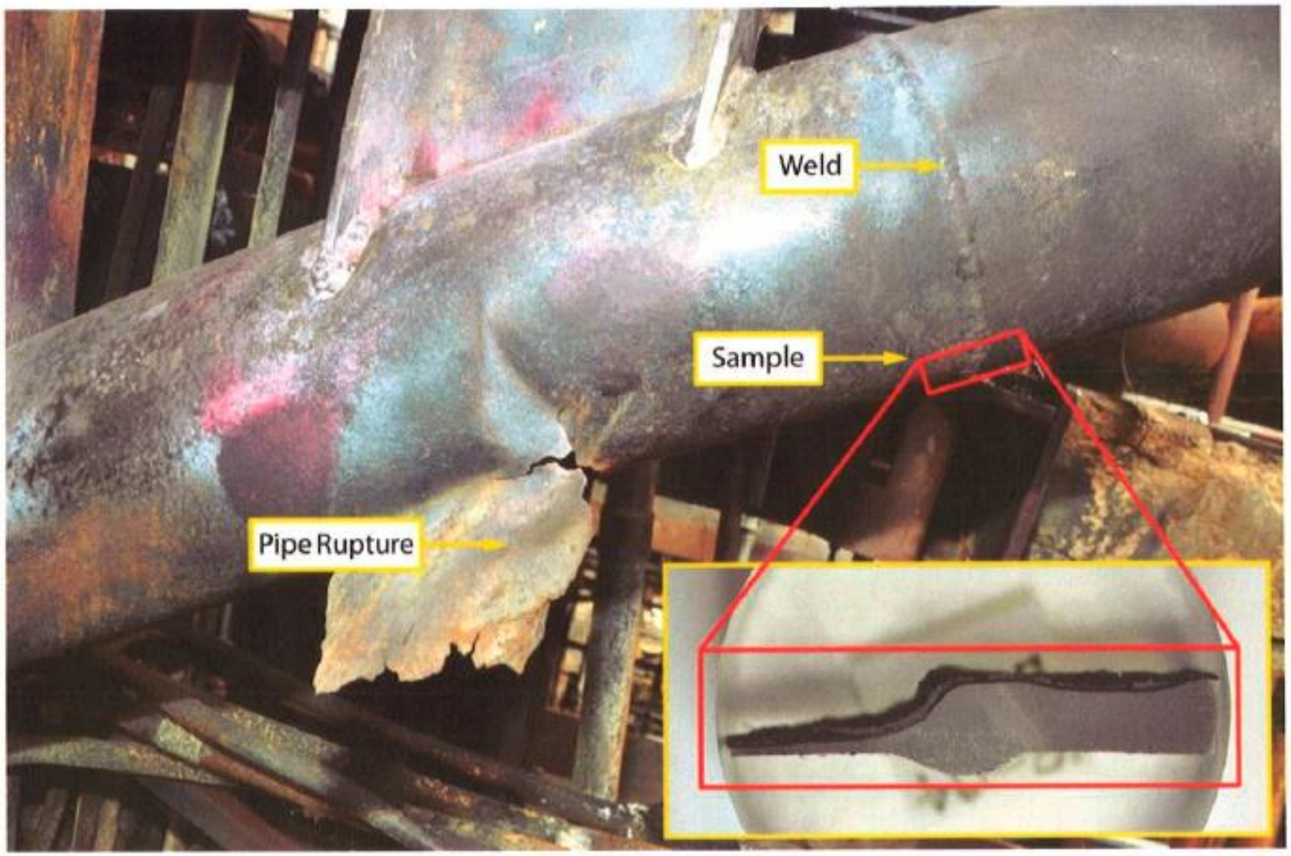


Image showing the location where the sectioned sample was removed from the ruptured pipe component.

Source: Richmond Refinery 4 Crude Unit Incident, August 6, 2012
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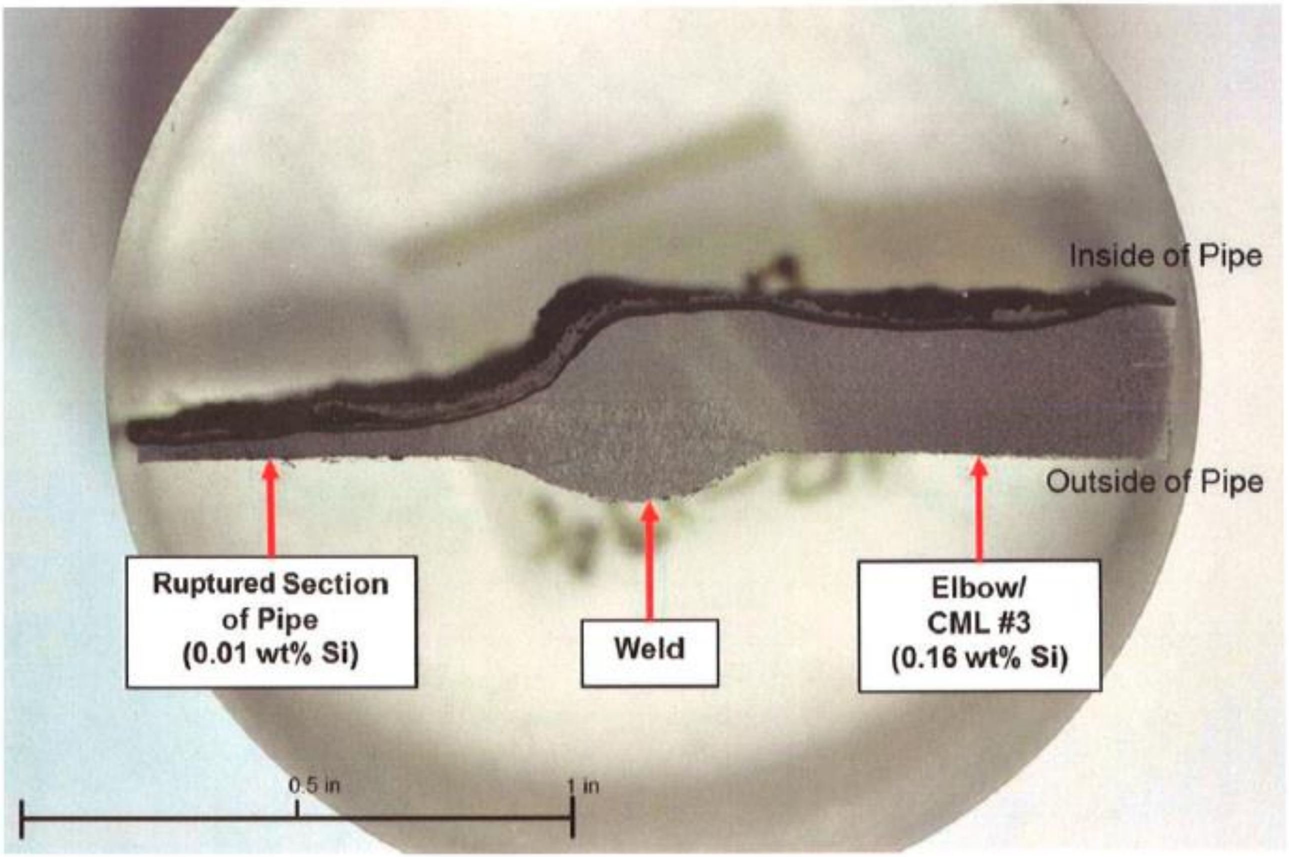

Cross section through the weld of the subject pipe showing thicknesses of the ruptured section (left) and the adjacent elbow, where CML #3 is located.