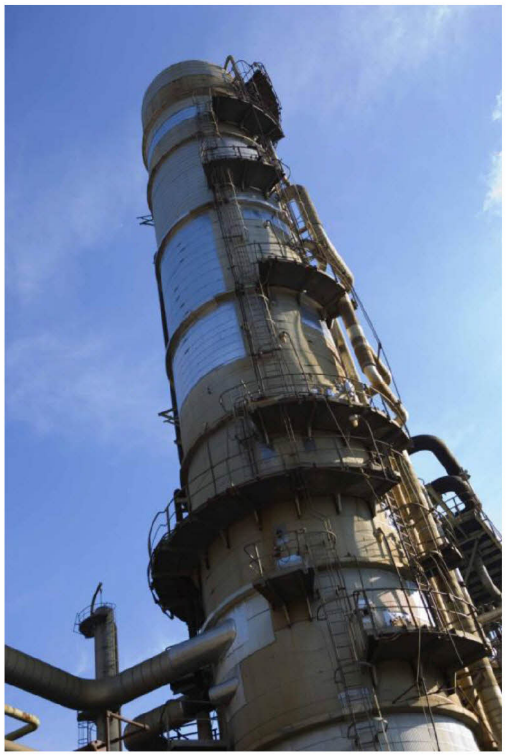
Homework Questions

Section 1: Materials Degradation in Crude Units



Senior Analyst and Inspector Training
Crude Units

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1.0 Introduction

1. What are typical outlet temperatures for the atmospheric and vacuum furnaces?

Atmospheric= 370°C (700°F)

Vacuum= 425°C (800°F)

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1.0 Introduction

2. Gas oils from the crude units typically go to other units for additional processing, such as an **FCC unit** or a **hydrocracker** .

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1.0 Introduction

3. Resid from the vacuum column may go to a **hydrotreater**, a **delayed coker**, or an **asphalt plant** for additional processing.

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1.0 Introduction

4. What organic acids are present to some degree in all crude oils?

Naphthenic acids

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1.0 Introduction

5. **Hydrolysis** is the process whereby salts in crude oils are converted to hydrochloric acid.

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1.0 Introduction

6. What's another name for high temperature H_2S attack?

Sulfidic corrosion or sulfidation

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1.0 Introduction

7. At approximately what temperature do sulfur compounds begin to decompose to form H_2S?

260°C (500°F)

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1.0 Introduction

8. In addition to health and safety concerns, mercury can cause what issue in the crude unit?

Liquid metal embrittlement (LME) – Susceptible materials include Monel, Copper Alloys (e.g., Admiralty Brass), Aluminum.

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1.1 Corrosion by Hydrochloric Acid

1. After desalting, crude normally contains about __0.5__ pounds of salt per thousand bbls of oil, or roughly, __2__ ppm.

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1.1 Corrosion by Hydrochloric Acid

2. What three types of problems could occur if we were to use 300 Series stainless steels in the portions of the crude unit that are exposed to aqueous chlorides?

Pitting, general corrosion, chloride stress corrosion cracking

300 series stainless steels have poor HCl resistance.

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1.1 Corrosion by Hydrochloric Acid

3. Which grade of titanium has the highest temperature resistance?

Grade 7, which is generally resistant to HCl up to 230°C (450°F).

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1.1 Corrosion by Hydrochloric Acid

4. HCl corrosion is controlled either by using **alloyed materials** or by **neutralization** .

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1.1 Corrosion by Hydrochloric Acid

5. What's the name of the salt that is formed when ammonia is used for neutralization?

Ammonium chloride (NH_4Cl)

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1.2 Corrosion by Ammonium Chloride

1. In the overhead, what do we want to condense first to avoid corrosion; ammonium chloride or water?

Water, because then the ammonium chloride dissolves in the water and salt does not form.

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1.2 Corrosion by Ammonium Chloride

2. True or False: The most important manifestation of ammonium chloride corrosion is attack under salt deposits.

True

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1.2 Corrosion by Ammonium Chloride

3. Rate the following metals from best to worst for their resistance to ammonium chloride corrosion:

Monel 304L SS Admiralty

Monel

Admiralty

304L SS

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1.2 Corrosion by Ammonium Chloride

4. Do we want the top of the atmospheric column to run wet or dry?

Dry

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1.2 Corrosion by Ammonium Chloride

5. True or False: Very little water is needed to cause severe chloride corrosion.

True

Lab tests have shown that only 0.3% water is needed for corrosion rates >1.3 mm/yr (50 mpy).

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1.3 Corrosion by Amine Hydrochlorides

1. In the atmospheric column, ammonium chloride corrosion can occur only at temperatures below about **105°C (220°F)**, whereas amine hydrochloride corrosion may be found up to temperatures of **150-175°C (300-350°F)**.

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1.3 Corrosion by Amine Hydrochlorides

2. True or False: We don't want amines to enter the atmospheric column.

True

They can lead to corrosion by amine hydrochloride.

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1.3 Corrosion by Amine Hydrochlorides

3. True or False: Upgrading to Monel will not prevent amine hydrochloride corrosion.

True

Amine hydrochlorides corrode Monel almost as quickly as they corrode carbon steel.

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1.4 High Temperature Hydrogen Sulfide Corrosion

1. H_2S corrosion can occur anywhere in the unit where H_2S is present and where the temperature exceeds the corrosion threshold of **260°C (500°F)** .

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1.4 High Temperature Hydrogen Sulfide Corrosion

2. True or False: All oil companies estimate H_2S corrosion rates the same way.

False

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1.4 High Temperature Hydrogen Sulfide Corrosion

3. True or False: 1¼ and 2¼ chrome steels are not significantly more resistant to hot H_2S corrosion than carbon steel.

True

5% Cr is typically needed to gain a significant advantage over carbon steel.

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1.4 High Temperature Hydrogen Sulfide Corrosion

4. True or False: 300 Series stainless steels are essentially immune to hot H_2S corrosion at temperatures we are likely to encounter in the crude unit.

True

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1.5 Corrosion by Naphthenic Acids

1. What crude unit sidecut is usually the most acidic (highest TAN)?

Vacuum Column Heavy Gas Oil (HGO)

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1.5 Corrosion by Naphthenic Acids

2. True or False: The addition of molybdenum to stainless steels increases resistance to naphthenic acid attack.

True

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1.5 Corrosion by Naphthenic Acids

3. True or False: Naphthenic acid corrosion can be very localized at locations with extremely high velocities.

True

Transfer lines and furnace outlet piping are particularly susceptible to nap acid corrosion.

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1.5 Corrosion by Naphthenic Acids

4. The threshold temperature for naphthenic acid corrosion is approximately **175°C (350°F)** .

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1.5 Corrosion by Naphthenic Acids

5. Rate the following alloys from best to worst in naphthenic acid corrosion resistance:

321 SS Carbon Steel 317L SS

"New" 316L SS "Old" 316L SS

Best:

317L SS

"Old" 316L SS

"New" 316L SS

321 SS

Carbon steel

Worst:

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1.6 Corrosion and SCC by Caustic (NaOH)

1. What's a good material to use when caustic temperatures exceed 200°F (95°C)?

Monel

The high nickel content provides protection.

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1.6 Corrosion and SCC by Caustic (NaOH)

2. What type of lines are at particular risk of caustic SSC?

Steam-traced lines, especially if they are not stress relieved.

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1.6 Corrosion and SCC by Caustic (NaOH)

3. True or False: 300 Series SS has somewhat better resistance to caustic cracking than carbon steel.

True

300 series SS has better cracking and general corrosion resistance in caustic.

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1.7 Wet H_2S Cracking

1. Name three methods for reducing the likelihood of wet H_2S cracking in the most severe environments.

Clad with stainless steel

Use Duplex SS

Apply coating

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1.7 Wet H_2S Cracking

2. When using properly qualified technicians and procedures, **eddy current testing** is the preferred method for detecting wet H_2S cracking.

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1.7 Wet H_2S Cracking

3. True or False: Water must be present for wet H_2S cracking to occur.

True, aqueous corrosion generates atomic hydrogen which drives the cracking mechanism.

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1.8 Sulfide Stress Cracking

1. Sulfide stress cracking (SSC) occurs only on high strength, high hardness steels. Cracking does not occur on materials lower in yield strength than **90 ksi (620 MPa)** or softer than Rockwell C **22**.

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1.8 Sulfide Stress Cracking

2. To minimize the possibility of SSC, limit the hardness of carbon steel welds to **200 Brinell** .

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1.8 Sulfide Stress Cracking

3. **Austenitic** materials are resistant to SSC under any conditions we are likely to encounter.

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1.9 Chloride Stress Corrosion Cracking

1. Limit hydrotest water to __50__ ppm chloride.

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1.9 Chloride Stress Corrosion Cracking

2. Where in crude units should we avoid the use of 300 Series stainless steels?

Atmospheric/vacuum column overhead systems (wet chlorides are likely).

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1.9 Chloride Stress Corrosion Cracking

3. Hot insulated stainless steel piping can chloride crack from the OD. Name 3 ways we can we prevent this from happening?

Keep the weather jacketing tight

Coat the OD (organic or TSA)

Wrap with aluminum foil

Stress relieve welds

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1.10 Polythionic Acid Stress Corrosion Cracking

1. For stainless to polythionic crack it must be exposed to sulfur-containing acids, it must be stressed, and it must be **sensitized**.

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1.10 Polythionic Acid Stress Corrosion Cracking

2. Where in crude units are we most likely to see polythionic acid SCC?

Furnace tubes and transfer lines

Although historically, PTA SCC in crude units has been rare.

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1.10 Polythionic Acid Stress Corrosion Cracking

3. Rank the following austenitic stainless steels in order of their resistance to polythionic acid SCC, from least resistant to most resistant:

321 304 316L 347

Least Resistant

↓

304

316L

321

347

Most Resistant

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1.10 Polythionic Acid Stress Corrosion Cracking

4. List some shutdown precautions to prevent polythionic cracking of sensitized stainless steels.

Keep equipment warm

Nitrogen blanket (prevent O_2 entry)

Keep the plant dry

(Possibly) soda ash wash

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1.11 Creep

1. True or False: Small increases in tube metal temperature can dramatically shorten creep life.

True, for every 28°C (50°F) increase in metal temperature remaining life is reduced by a factor of approximately 3.

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1.11 Creep

2. What's the danger in relying on thermocouples alone to assess proper furnace operation and the potential for creep damage of furnace tubes?

They may give low readings or not be located at the hottest location.

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1.11 Creep

3. As a rule of thumb, when a tube OD increases more than __2-3__ %, you should either replace the tube or carefully analyze its remaining life.

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1.11 Creep

4. What current methodology can be used to estimate the remaining creep life of furnace tubes?

Omega Analysis (also called Omega calculations)

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1.12 Corrosion at Injection Points

1. True or False: API 570 requires that special attention be given to injection points.

True

Inspection is required at least every 3 years.

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1.12 Corrosion at Injection Points

2. Name at least three injection point / quill design problems that should be avoided.

Use of a blunt end injection nozzle

Injection near a bend

Not injecting enough water

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1.13 Corrosion at Specification Breaks

1. Valves at spec breaks should conform to the piping standard for the **higher alloy** or **higher corrosion allowance** pipe class.

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1.13 Corrosion at Specification Breaks

2. True or False: Heat exchanger bypass lines are usually a good place to look for spec break-associated corrosion problems.

True

Example: A large fire in the Richmond Isomax unit was caused by an incorrect temperature prediction in a heat exchanger bypass line.

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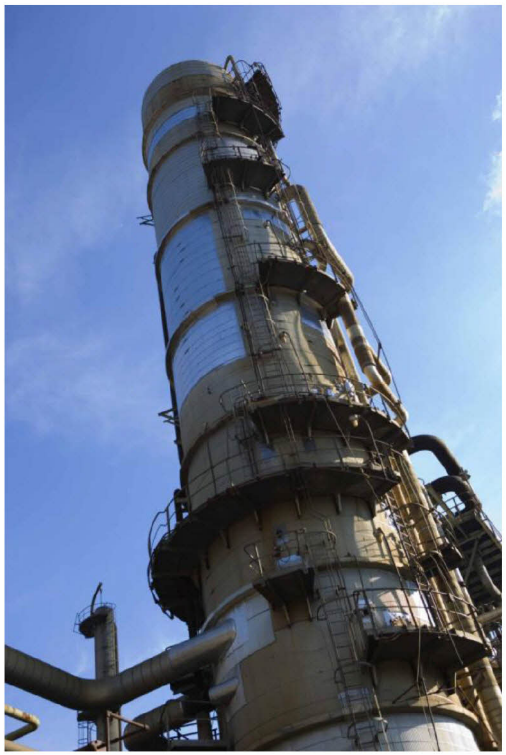
Homework Questions

Section 2: Component Review



Sr. Analyst and Inspector Training
Crude Units

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2.1 Desalters

1. What's the minimum pH we should have in a desalter?

5.5

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2.1 Desalters

2. What's the minimum water injection rate into the cold crude upstream of the desalter?

   2% liquid volume of the crude.

   What's the purpose of this water injection?

   To help prevent under deposit corrosion and improve crude dehydration.

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2.1 Desalters

3. The exchangers upstream of the desalter should have a maximum tube skin temperature of **350°F (175°C)** .

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2.2 Caustic Injection Systems

1. What's the potential danger of injecting caustic upstream of the crude preheat exchangers?

Stress corrosion cracking can occur in the crude pre-heat exchangers, especially if caustic settles out in the stagnant areas.

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2.2 Caustic Injection Systems

2. **Monel** is the preferred material to use for the caustic injection quill.

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2.3 Atmospheric Furnace / Vacuum Furnace

1. You find heavy and flaky oxide scale on a 5 Cr-1/2 Mo furnace tube. What type of damage is likely?

Oxidation (note the scale can be 4-5 times thicker than the metal consumed).

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2.3 Atmospheric Furnace / Vacuum Furnace

2. Why wouldn't we use 12 Cr steels for furnace tubes?

They become brittle at operating temperatures.

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2.3 Atmospheric Furnace / Vacuum Furnace

3. Hot H_2S corrosion of furnace tubes is usually uniform. List some situations which might lead to localized corrosion.

Local differences in temperature

Vapor vs. liquid services

Presence of hangers

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2.3 Atmospheric Furnace / Vacuum Furnace

4. Why might we use 300 Series stainless steels for furnace tubes?

   High creep and rupture strength.

   What type of 300 Series would we prefer for new construction?

   347 SS for resistance to high temperature H_2S corrosion and sensitization.

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2.4 Atmospheric Transfer Line / Vacuum Transfer Line

1. What 300 Series SS is preferred for transfer lines in units running non-naphthenic crudes?

   321 SS (minimize PTA SCC)

   What SS should we use for high naphthenic crudes?

   317L or high-Mo 316L

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2.4 Atmospheric Transfer Line / Vacuum Transfer Line

2. What's the best material for thermowells for units running highly naphthenic crudes?

Inconel 625 (Mo=9%)

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2.4 Atmospheric Transfer Line / Vacuum Transfer Line

3. True or False: Localized corrosion is common in outlet headers and transfer lines of units running naphthenic crudes.

True

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2.5 Atmospheric Column

1. What's the preferred alloy for column cladding and why?

410S, it is immune to H_2S corrosion and the "S" (low carbon) grade has better properties in the HAZ of welds.

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2.5 Atmospheric Column

2. For the top of the column to run dry, the overhead vapor line temperature (upstream of water injection) must be **25°F (15°C) above the salt or water dew point** . .

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2.5 Atmospheric Column

3. If we find corrosion of 12 Cr trays and cladding, what's the likely cause?

Ammonium chloride corrosion (top trays)

or

Naphthenic Acid (flash zone)

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2.5 Atmospheric Column

4. True or False: Chevron strongly opposes adding neutralizing amines to the column.

True

Amines + HCl → amine hydrochloride salts

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2.6 Corrosion of the Atmospheric Column Overhead System

1. With good desalting and caustic injection the chloride content of the overhead water should be no more than **20** ppm?

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2.6 Corrosion of the Atmospheric Column Overhead System

2. Our BP for overhead corrosion control advocates that the pH of the overhead accumulator water be maintained between **7.0** and **7.5**.

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2.6 Corrosion of the Atmospheric Column Overhead System

3. True or False: Chevron's BP advocates not using filming amines.

True

Chevron recommends against the use of neutralizing amines in crude units, aqueous ammonia is preferred.

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2.6 Corrosion of the Atmospheric Column Overhead System

4. True or False: Vertical overhead-feed exchangers are preferred to horizontal ones.

True

Since 1975, the overhead-feed exchangers in new Chevron crude units have been vertical, with the overhead on the tubeside. Vertical exchangers allow for more uniform flow throughout the exchanger and equal distribution of wash water.

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2.6 Corrosion of the Atmospheric Column Overhead System

5. The water injection rate into the overhead should be **30** % greater than that needed to saturate the overhead vapors.

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2.6 Corrosion of the Atmospheric Column Overhead System

6. List some of the benefits of overhead water injection:

Prevents ammonium chloride deposits.

Lowers chloride concentrations.

Stabilizes the pH.

Minimizes pH variations from initial to final drops of condensate.

With vertical heat exchangers, when water is injected into the overhead vapor line all tube surfaces are washed by the water.

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2.6 Corrosion of the Atmospheric Column Overhead System

7. Some of the basic process changes that all crude unit personnel should be aware of include:

Crude slates, particularly in terms of higher S content (H_2S), N (ammonia), nap acids, mercury.

Temperatures, either increasing or decreasing.

Imported streams bypassing the desalters.

Introduction or reduction of corrosion inhibitors or dispersants.

Wash water injection rates.

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2.7 Sidecut Systems

1. Name the three possible corrosives present in atmospheric sidecut systems:

H_2S

Chlorides

Naphthenic acids

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2.7 Sidecut Systems

2. True or False: 1st sidecut piping can be subject to severe corrosion if high levels of chlorides are present.

True

Recall the Pascagoula 1st sidecut example.

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2.8 Vacuum Column

1. What “spec break” in the column needs special inspection attention?

The point where the cladding ends.

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2.8 Vacuum Column

2. Naphthenic acid corrosion in the column is usually fairly uniform but can be localized in some instances. Where should you look for localized naphthenic acid corrosion?

Downcomer areas, undersides of trays, structured packing.

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2.8 Vacuum Column

3. Corrosion of the vacuum column packing can lead to what potential problems?

Collapse of the packed bed.

Catalyst fouling from metals in the RDS feed.

Packing remnants in the vacuum side-cut pump strainers.

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2.9 Vacuum Overhead System

1. An increase in corrosion probe activity in the overhead may be the result of **air (oxygen)** leakage into the vacuum system.

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2.9 Vacuum Overhead System

2. Why is HCl corrosion historically much less severe in the vacuum overhead versus the atmospheric overhead system?

The high dilution of the chlorides (HCl) from the condensed steam from the ejectors.

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2.10 Atmospheric and Vacuum Bottoms, Piping, and Exchangers

1. True or False: Hot H_2S corrosion rates in the bottoms system can change dramatically with nominal temperature increases.

True

See Figure 2.10A

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2.10 Atmospheric and Vacuum Bottoms, Piping, and Exchangers

2. What spec breaks need careful inspection attention in the bottoms system?

The transition between Cr alloys and CS.

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