http://upload.wikimedia.org/wikipedia/commons/9/99/MiRO1.jpg

MATERIALS OF CRUDE OIL REFINING: CORROSION PROBLEMS AND PREVENTION

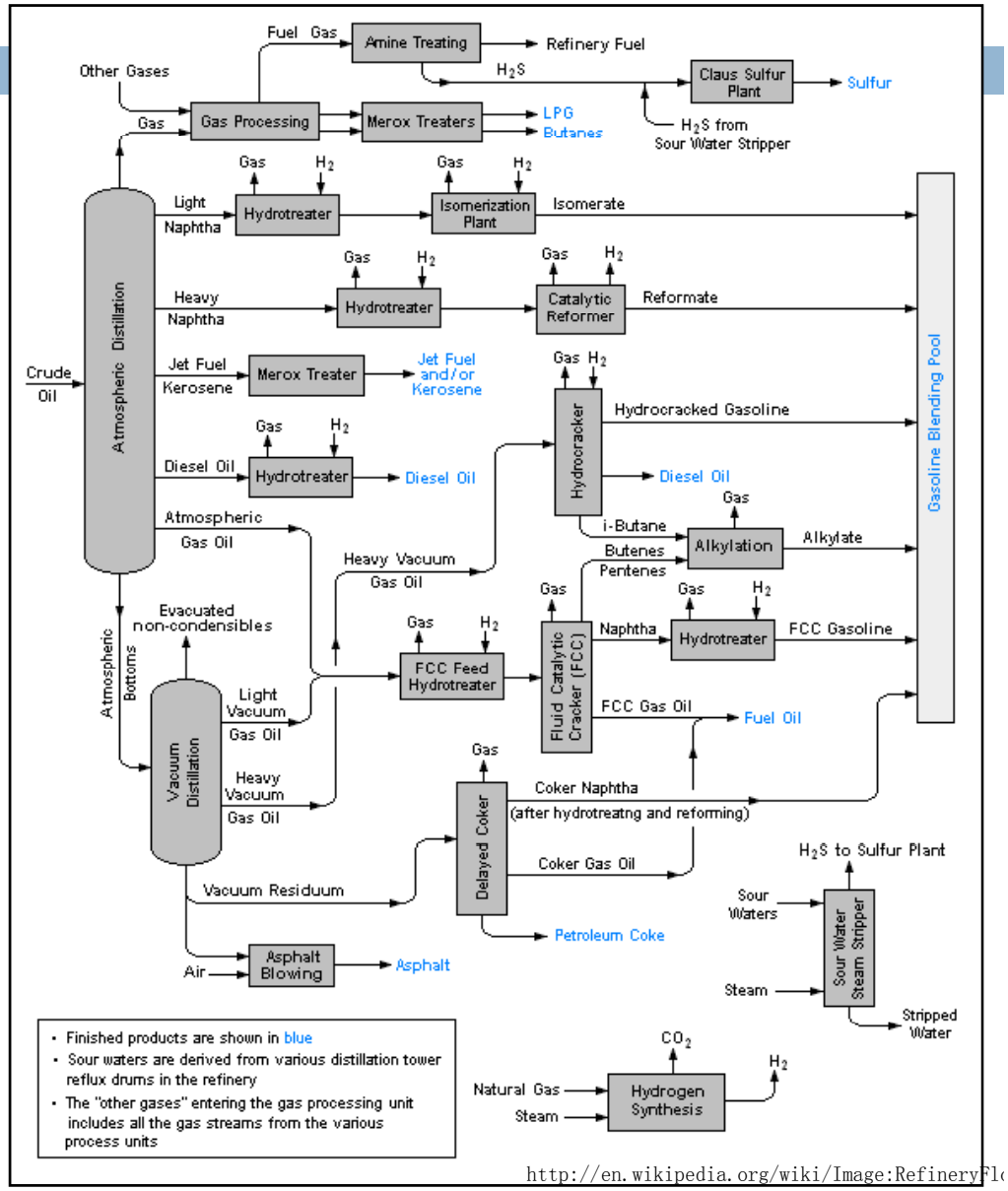
MSE 395 Final Presentation - Gareth Hughes

Overview

- Introduction to Refining and Corrosion
  - Brief look at types of corrosion
- Materials Used in Refineries
  - Ferrous Alloys
  - Other Alloys
- Corrosive Substances
  - Low Temperature
  - High Temperature
- Corrosion Protection Methods
- Conclusions

Crude Oil Refining

- Necessary to create useful hydrocarbon products
- Complicated system requiring many different pressure and temperature conditions
- Diverse environmental



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Corrosion in Refineries

- Controls operation of process line
  - Must be watched to prevent accidents
  - Causes reduction in heating and cooling efficiency
  - Requires periodic inspection and maintenance, which halts the entire production line
- Cost of corrosion: $3.7 billion annually
  - $1.4 billion equipment replacements
  - $1.8 billion maintenance expenses
  - $0.5 billion fouling removal

R.D. Kane, Corrosion in Petroleum Refining and Petrochemical Operations, *Corrosion: Environments and Industries*, Vol 13C, *ASM Handbook*, ASM International, 2006, p 967–1014

Materials Used - Conditions Found

- Materials must exhibit a number of properties
  - Resist high temperatures and pressures
  - Resist hydrocarbon impurities
  - Resist air and water intrusion cycles
  - Display warning of corrosion (no spontaneous failure)
  - Must maintain strength in fire and sudden temperature changes to stop spreading of fire if accidents occur
- Limits materials to metals
  - Plastics too low temperature
  - Ceramics not strong enough and brittle

B.B. Morton, Metallurgical Methods for Combating Corrosion and Abrasion in the Petroleum throughout Industry, *J. Inst. Petrol.*, Vol 34 (No. 289), 1948, p 1-68

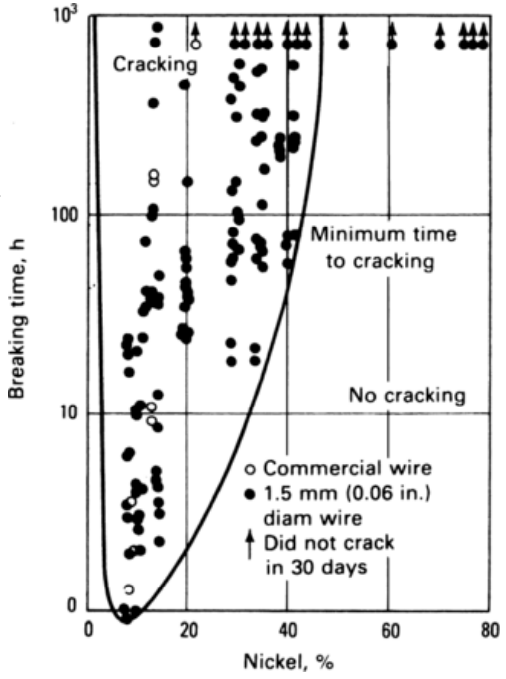
Materials Used - Ferrous Alloys

- Most common type of material used
- Standard carbon steel used to 80% of components and almost all structural applications
  - Limited corrosion resistance, mainly storage applications
- Low-alloy C-Cr-Mo steel used for applications of higher temperatures, hydrogen, and sulfide exposure
  - Used for some elevated temperature applications
- Stainless steels used exclusively for high temperature sulfidic and naphthenic acid conditions
  - Considerably more expensive and slightly reduced strength

A.J. Freedman, G.F. Tisinai and E.S. Troscinski, Selection of Alloys for Refinery Processing Equipment, *Corrosion*, Vol 16 (No. 1), 1960, p 19t-25t

Materials Used – Other Alloys

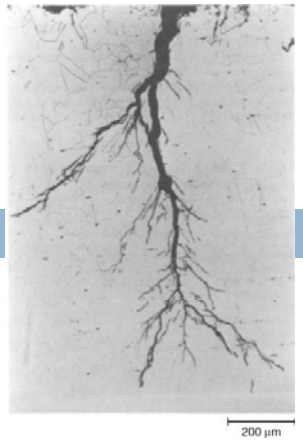
- Used for specific applications where cheaper ferrous alloys would fail
- Copper
  - Used for heat exchangers
  - Increased temperature conduction, but corrosion problems with contaminated water
- Nickel
  - Used for very high temperature corrosion resistance
  - Often alloyed with other metals to improve chloride resistance
- Titanium
  - Used for low temperature, but very corrosive sulfidic and chloridic environments
  - Coolers and condensers using seawater



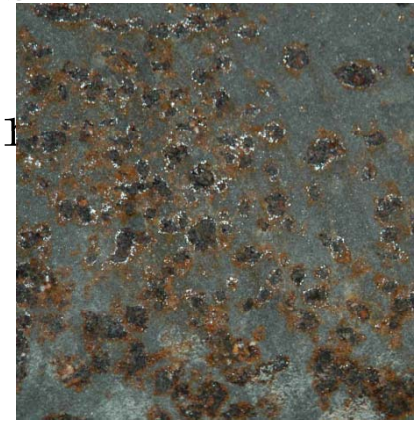
Effect of nickel alloying on 17%–24%Cr stainless steel on resistance to stress corrosion cracking in boiling 42% magnesium chloride solution

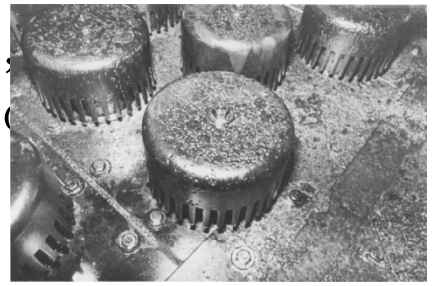
A. J. Freedman, G. F. Tisinai, and E. S. Troscinski, Selection of Alloys for Refinery Processing Equipment, *Corrosion*, Vol 16 (No.

Corrosion Problems



- Split into two categories
  - Low temperature (below 260°C)
    - Corrosion mostly by pitting and stress corrosion cracking
    - Always in the form of aqueous or other liquid solutions
  - High temperature (above 205°C)
    - Corrosion mostly by uniform thinning, local attack, and erosion-corrosion
    - Generally in the absence of water, taking the form of liquid or gaseous hydrocarbons

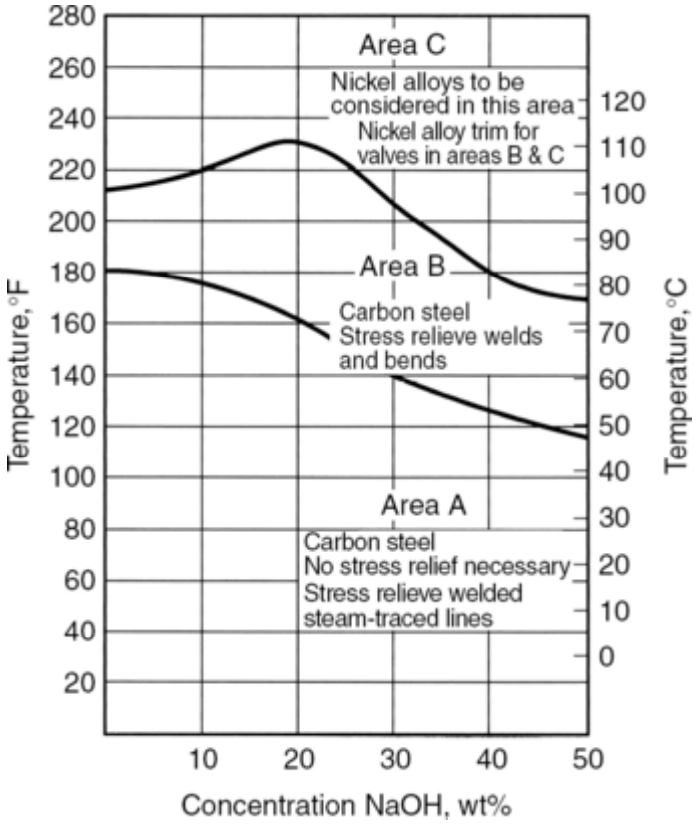




R. Baboian, *Corrosion Engineer's Handbook*, 3rd ed., NACE International, 2002, p 192

Low Temperature Corrosives

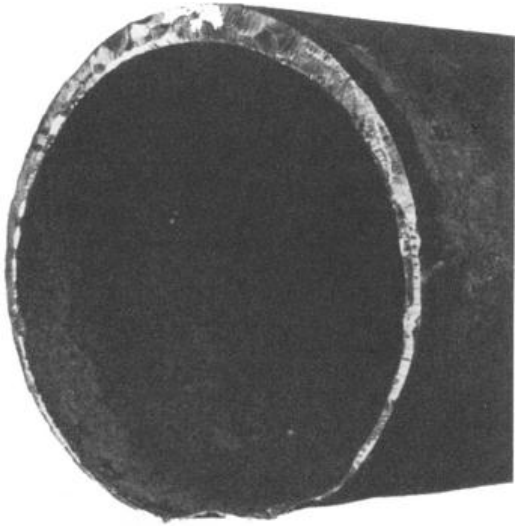
- Most widespread form of corrosion, but less severe
- Caused by two sources:
  - Contaminants in crude oil process stream
    - Air and water
    - Hydrogen sulfide
    - Sour water – combination of water with ammonia, hydrogen cyanide, and organic sulfides
  - Chemicals introduced, such as solvents, neutralizers, and catalysts
    - Caustic soda most prevalent



C.G. Munger, Deep Pitting Corrosion in Sour Crude Oil Tankers, *Mater. Perform.*, Vol 15 (No. 3), 1976, p 17 – 23

High Temperature Corrosives

- Most dangerous form of corrosion
  - High temperatures and high pressures can cause ignition
- Primarily caused by sulfur compounds in the crude oil in concentrations of 0.1% to 5.0%
- Corrosion occurs when sulfides react with metal to form metal sulfides and H_2S
- Metal corrodes faster on the heated side of furnace tubes
  - Dependent on the metal surface temperature, rather than the stream temperature



M.L. Medvedeva, Specifics of High-Temperature Corrosion Processes During Oil Recovery, *Chemical and Petroleum Engineering*, Vol 36 (Nos. 11-12), 2000, p 749-754

Corrosion Control Methods

- Monitoring
  - Off-line methods - checks during maintenance
    - Tell when equipment must be replaced
  - On-line methods - report corrosion as it happens
    - Allows control of corrosion by actively changing process variables
- Careful material selection
  - Model the system before construction and determine corrosive areas
- Physical material barriers
  - Application of corrosion resistant coatings or cladding
    - Layers of stainless steel
    - Walls of acid resistant concrete

R.D. Kane, D.C. Eden, and D.A. Eden, Innovative Solutions Integrate Corrosion Monitoring with Process Control, *Mater. Perform.*, Feb 2005, p 36 - 41

Conclusions

- Important area of research for efficient production of fossil fuels
- Much is known about corrosion, but methods for control are still basic
- Refinery process complicated, so many forms of corrosion must be prevented concurrently
- In a world of limited petroleum resources, efficient production is extremely important