Corrosion, Erosion, and Wetted Parts
A Heavy Metal Discussion
By Eric Lofland
Scope of This Presentation

• Explain some of the basic features of steels
• Define the principle problems in material selection
• Provide historical examples and mechanisms for these problems
• Define and summarize the basis of NACE MR0103 and MR0175 codes
• Offer some advice for how to tackle challenging applications
What Is A Metal, Really?
What Is A Metal, Really?

• Generally a crystalline solid at room temperature
• Exhibits metallic bonding
• High melting point
• Conduct electricity and heat
• Great material for a chemical process
Some Basic Crystalline Structures

- Structures form a lattice
- That lattice strongly influences the physical properties of a metal
- Can be viewed like a physical structure
Phase Diagram of Iron

Austenite solid solution of carbon in gamma iron

Austenite in liquid

Primary austenite begins to solidify

CM begins to solidify

Magnetic (1414°F) point $A_2$

$A_2$ $A_3$

Austenite to pearlite

Pearlite and ferrite

Pearlite and Cementite

Cementite, pearlite and transformed ledeburite

Magnetic change of $Fe_3C$

Hypo-eutectoid

Hyper-eutectoid

Steel

Cast Iron

$\gamma = $ Austenite

$\alpha = $ Ferrite

$\delta = $ Delta iron

CM = Cementite

2066°F

1333°F

1310°F

1130°F

910°F

723°F

760°F

L + $Fe_3C$

$Fe_3C$

210°F
Ferrite

- α-phase Iron
- Body-centered cubic structure
- Ferromagnetic
- Does not dissolve much carbon due to lack of space in the lattice
Austenite

- γ-phase Iron
- Face-centered cubic structure
- Not magnetic
- Dissolves more carbon due to more lattice space
Martensite

- Formed by rapid quenching of austenite
- Body-centered tetragonal structure
- Magnetic
- Needle-like microstructure
- Harder, but more brittle
Austenite vs. Martensite

Austenite

Martensite
What Is Steel?

- Alloy consisting primarily of iron
- Other metals added for various properties
- Carbon steel – primarily iron and carbon
- Stainless steel – chromium added for corrosion resistance, forms a passive layer of chromium oxide
- High strength, relatively low cost
A Basic Guide to Stainless Steel Alloys

- Carbon adds structural strength
- Chromium adds corrosion resistance
- Nickel stabilizes the austenite phase
- 200 and 300 series – Austenitic
- 400 series – Martensitic and Ferritic

<table>
<thead>
<tr>
<th>SAE designation</th>
<th>Type</th>
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<tbody>
<tr>
<td>1xxx</td>
<td>Carbon steels</td>
</tr>
<tr>
<td>2xxx</td>
<td>Nickel steels</td>
</tr>
<tr>
<td>3xxx</td>
<td>Nickel-chromium steels</td>
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<tr>
<td>4xxx</td>
<td>Molybdenum steels</td>
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<td>8xxx</td>
<td>Nickel-chromium-molybdenum steels</td>
</tr>
<tr>
<td>9xxx</td>
<td>Silicon-manganese steels</td>
</tr>
</tbody>
</table>

(Jeffus 635)
What Causes An Installation to Fail?
What Causes An Installation to Fail?

• Excess temperature or pressure
  • Physical property of selected material
  • Outside the scope of this presentation

• Erosion
  • Material is subject to excessive wear and tear

• Corrosion
  • Material is not chemically compatible service
Erosion

• The gradual destruction of a material due to physical stress

• Opposed to corrosion, which is caused by chemical stress

• Physical stresses include
  • Hydrodynamic stress
  • Solid particulates
  • Flashing and cavitation

• Solutions are based on physical properties of materials
Erosion by Particulate

• Caused by particle impacts with a surface

• Dependent on particle properties, velocity, angle, and frequency of impact

• Most predictive equations for damage are empirical

• Of particular concern for elements in the flow path and elbows in pipe

• Of particular interest for the oil and gas industry
Erosion by Particulate – The Mechanism

Brittle Mechanism
Erosion by Particulate – Kinetic Energy

• Damage caused by particles is directly related to kinetic energy

• Most empirical models incorporate mass and velocity as important factors

\[ E_K = \frac{1}{2} m v^2 \]

- \( E_K \) = Kinetic energy of impact
- \( m \) = Mass of particle
- \( v \) = Velocity of particle
Erosion by Particulate – Other Factors

- Frequency and duration of exposure
  - What is the solids content?
  - How often does exposure occur?

- Angle of impact
  - Brittle objects struck directly will sustain more damage

- Relative Hardness
  - The higher the hardness of the particle as compared to the target, the greater the damage
Erosion by Particulate – What Does It All Mean?

• Many proposed equations predicting erosion rate from the previous factors

• For choosing a material, exact rate of loss is difficult to predict and less useful than a qualitative assessment

• Consider the following order of importance when assessing risk:

  Velocity > Relative Hardness >> Particle Size = Solids % > Angle of Impact
Most Important: Velocity

- Paramount importance
- Most equations raise velocity to an exponent
- Liquid streams have lower velocities, usually lower risk

Velocity > Relative Hardness >> Particle Size = Solids % > Angle of Impact
Very Important: Hardness

• Is the particulate hard enough to cause damage?

• Globules in hydrocarbon streams are usually not considered.

• Sand on the other hand…

Velocity > Relative Hardness >> Particle Size = Solids % > Angle of Impact
Less Important: Size, Solids %, and Angle

- Particle Size
  - Larger particles have low velocity

- Solids %
  - More useful for trying to estimate “when” than “if”

- Angle of Impact
  - Occasionally useful to assess where the particle is going

Velocity > Relative Hardness >> Particle Size = Solids % > Angle of Impact
Erosion by Flashing and Cavitation

- Flashing and Cavitation occur when a liquid changes phase due to pressure drop.
- Both phenomena greatly increase the physical stress on wetted parts.
- Liquids near boiling point or at areas of heavy pressure drop are at the greatest risk.
Erosion by Flashing and Cavitation

- Volume of a vapor at STP is about 3 orders of magnitude greater than liquid.

- An in-depth explanation of these phenomena is outside the scope of this presentation.
Signs You Are Facing Erosion

- High velocity stream with solid particulate
- Hard solid particulates in stream
- Liquid stream near boiling point
- Liquids stream with high pressure drop
Industry Solutions to Erosion

• Step 1: Can the source of wear be mitigated or removed completely?

• Step 2: Consider a hardened alloy to extend life of wetted parts.

• Step 3: Verify selected material against existing similar installations if possible.

• Step 4: Verify that the selected material is chemically compatible with the process fluid.
What Alloys to Use in Erosive Services

- Martensitic steels (400 Series) may be acceptable for less rigorous installations.

- Precipitation-hardened steels such as 17-4PH are also acceptable for slightly more rigorous installations.

- For highly rigorous applications, consider hardfacing an element with Stellite 6 or other chromium-cobalt alloys.

- In extreme cases, an entire element can be made out of Stellite 6.
Corrosion

- The gradual destruction of a material due to chemical attack
- Opposed to erosion, which is caused by physical stress
- Chemical attacks can occur on multiple vectors
- Solutions are based on chemical properties of materials on a case-by-case basis
Corrosion – The Math

• Corrosion is a chemical reaction

• Common chemical reaction model

For chemical A in reaction $A + B \rightarrow C + D$, 

$$-r_A = Ae \frac{-E_a}{RT} C_A C_B$$
Corrosion – The Math
For chemical A in reaction \( A + B \rightarrow C + D \),

\[
-r_A = Ae^{-\frac{E_a}{RT}} C_A C_B
\]

\(-r_A\) = Rate of disappearance of A (Corrosion)

\(A\) = Prefactor (Constant)

\(E_a\) = Activation Energy (Constant)

\(R\) = Universal gas constant

\(T\) = Temperature

\(C_A\) = Concentration of A

\(C_B\) = Concentration of B
Common Vectors for Corrosion

• Acid/Base Reactions
• Hydrogen Embrittlement
• Sulfide Stress Cracking
• Stress Corrosion Cracking
Problem #1 Acids and Bases

- Acids and bases attack metals via different mechanisms to form ionized salts.
- Strongly influenced by temperature and concentration of acid/base.
- Charts are available for chemical compatibility of common alloys with various chemicals.
Possible Metallurgy Solutions

• For low concentrations of corrosives, austenitic (300 Series) stainless steels can work (Iron-Chromium-Nickel).

• For higher concentrations, more exotic compounds are required.
  • Hastelloy C (Nickel-Molybdenum-Chromium)
  • Monel (Copper-Nickel)
Problem #2 Hydrogen Embrittlement

- Hydrogen atoms diffuse into the surface of a metal

- Hydrogen atoms recombine to form $\text{H}_2$ bubbles in the metallic matrix

- Bubbles in the metallic matrix greatly embrittle the metal, which leads to failure under normal operating conditions
Assessing Risk and Determining the Solution

• Any metal exposed to hydrogen, particularly at elevated temperatures, is susceptible

• Harder metals are more susceptible to embrittlement

• Common solutions include prevention and heat treatment to remove hydrogen
Problem #3 Sulfide Stress Cracking

- $\text{H}_2\text{S}$ causes embrittlement and cracking of metals
- Causes sudden catastrophic failure
- Particularly important in oil/refining applications, due to the high quantities of $\text{H}_2\text{S}$
- Complex mechanism extensively studied by NACE
What is NACE?

• NACE International was established in 1943

• Formerly known as the National Association of Corrosion Engineers

• Professional organization that publishes test methods, standard practices, and standards for material selection

• Review and revise the perennial standards to prevent Sulfide Stress Cracking, NACE MR0103 and MR0175
NACE MR0103 vs. NACE MR0175

- NACE MR0175 was created for upstream (oil and gas production) environments
  - Generally more rigorous than downstream
  - Higher chloride ion concentration
  - Lower pH

- NACE MR0103 was created for downstream (refining) environments.
  - Generally less rigorous
NACE: Important Notes

- Read NACE Safely!
- Neither standard makes an effort to rank materials based on SSC resistance.
- NACE does not suggest materials to use.
- Both standards are living documents and can be added to.
Sulfide Stress Cracking - The Mechanism

• Metals react with $\text{H}_2\text{S}$ in process fluid to release atomic hydrogen

• Atomic hydrogen accumulates in the metal matrix

• Reaction is cathodic (electrons are donated to metals)

• Tensile stresses in the metal form cracks
Sulfide Stress Cracking - The Mechanism

- Susceptible Material
- Corrosive Environment
- Tensile Stress ≥ σ Threshold

Ambitech
The Environment – What Factors into SSC?

- Concentration of H$_2$S in aqueous or gaseous phase
- Temperature
  - Substances are “charged” with hydrogen at high temperatures
  - Failure occurs most frequently at ambient temperatures
- pH and Chloride Ion Concentration
  - Extreme pH in either direction
  - Chloride ions accelerate SSC
Residual Stress and PWHT

- Welds are a focal point of SSC
- When a material is welded, the area is heated unevenly
- Variable tensile forces develop due to temperature differences
- Post Weld Heat Treatment relieves the stress
- NACE provides hardness limits for alloys
- Hardness is ameliorated by temperature change
- NACE provides acceptable procedures
- These often include moving between metallic phases
How Does This Affect My Installation?

- Austenitic steels tend to have less stringent hardness requirements
- Welds are of particular concern – PWHT often required
The NACE Takeaway

- NACE is not so much a metal selection guide as it is a set of practices.
- A good place to start is to use existing installations to choose an alloy.
- Use NACE to identify vulnerabilities and as a guide to make the alloy work, making changes as required.
- Vendors of instruments often have NACE certificates for instruments.
Problem #4 Stress Corrosion Cracking

• Family of reactions that proceeds via a different mechanism from Sulfide Stress Cracking

• Does NOT affect the finish of the metal

• Can occur at low reactant concentrations

• Commonly seen in chloride solutions with austenitic steels and ammonia solutions with copper alloys
Historical Example – Season Cracking

• British forces in India were forced to spend a lot of time inactive during monsoon season.

• Ammunitions were stored in barns.

• It was found that brass cartridges would spontaneously crack.

• It was discovered in 1921 that this was caused by ammonia from horse urine in the barns.
Stress Corrosion Cracking – The Mechanism

• Annodic reactions occur in irregularities of metal surface

• Metal is oxidized to a positive ion, which is dissolved in water

• Reaction site forms ions that attract ionic reactants

• Attracted ions concentrate at the reaction site and make things worse
Possible Metallurgy Solutions

- Use a metal that is chemically compatible

- For season cracking, use a non-copper alloy if possible or the anneal the metal

- For chlorides, consider a duplex steel (part austenite, part ferrite)

- In extreme cases, exotic alloys such as Hastelloy or titanium alloys can be used
• Consider all possible scenarios when choosing materials for your process.

• Try eliminating or mitigating an erosive service first. If this fails, harden the materials.

• Choose materials that are chemically compatible with your process under ALL possible conditions.

• Develop a communicative relationship with your process engineer.
• A comprehensive review of solid particle erosion modeling for oil and gas wells and pipelines applications, Parsi et al, Journal of Natural Gas Science and Engineering, Volume 21, Pg 850-873.

• Chloride stress corrosion cracking in austenitic stainless steel, Parrot and Pitts, Harpur Hill, 2011.


Questions?

The element of
CONFUSION