# Corrosion, Erosion, and Wetted Parts

A Heavy Metal Discussion

By Eric Lofland

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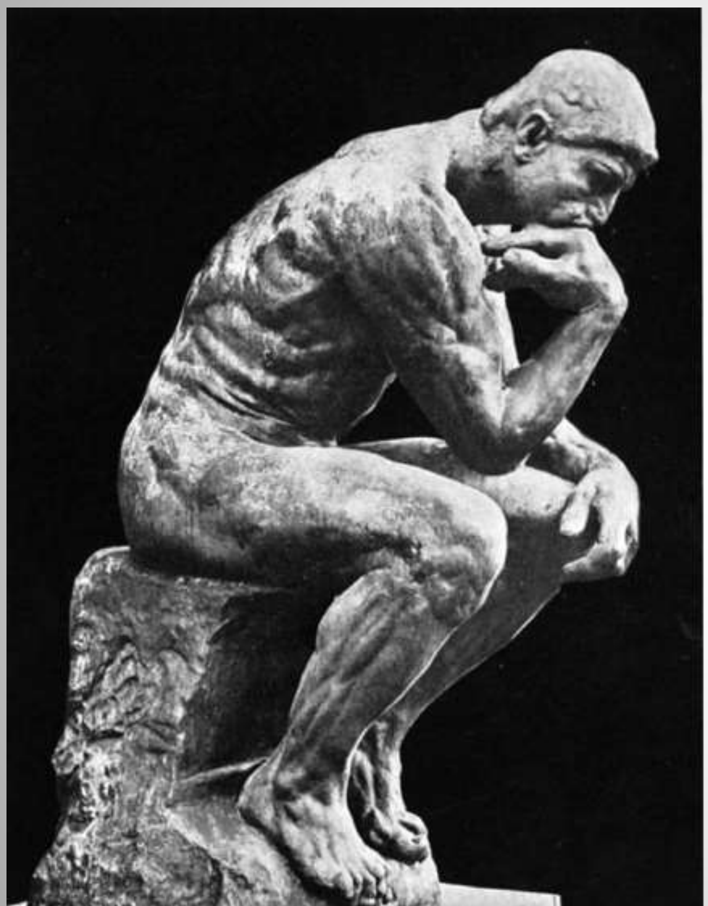
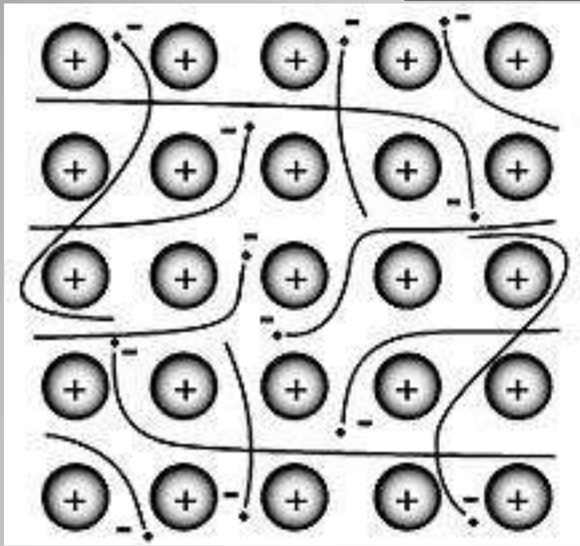
# Scope of This Presentation

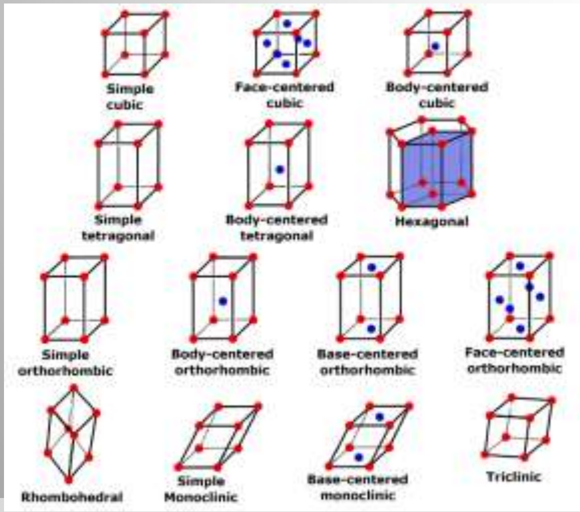
- Explain some of the basic features of steels
- Define the principle problems in material selection
- Provide historical examples and mechanisms for these problems
- Define and summarize the basis of NACE MR0103 and MR0175 codes
- Offer some advice for how to tackle challenging applications

# 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

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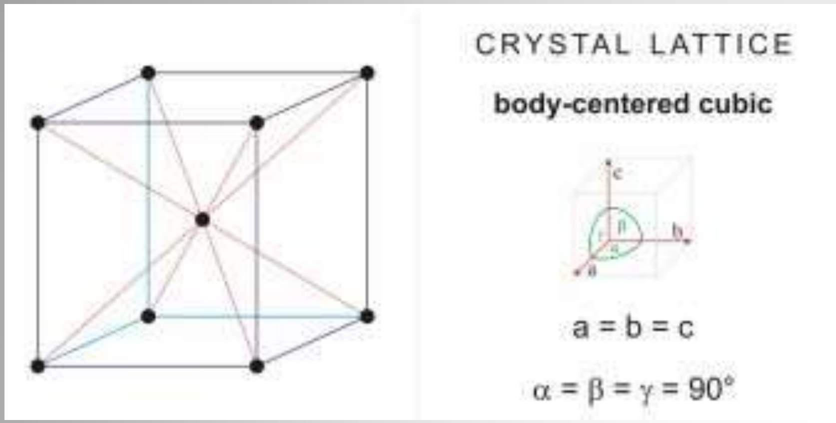
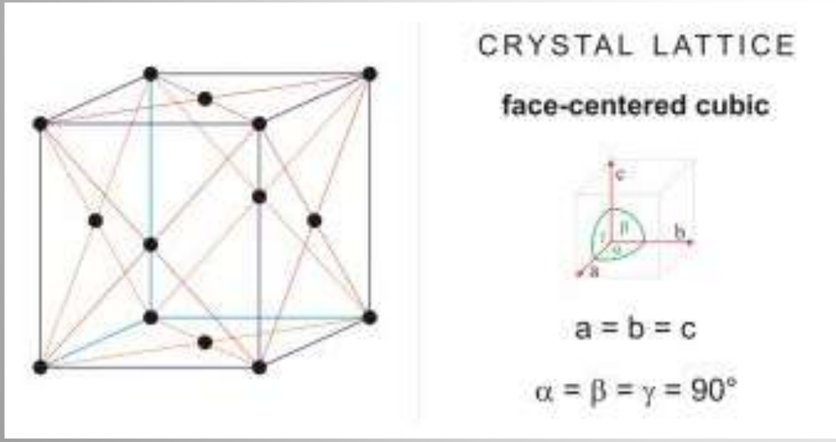
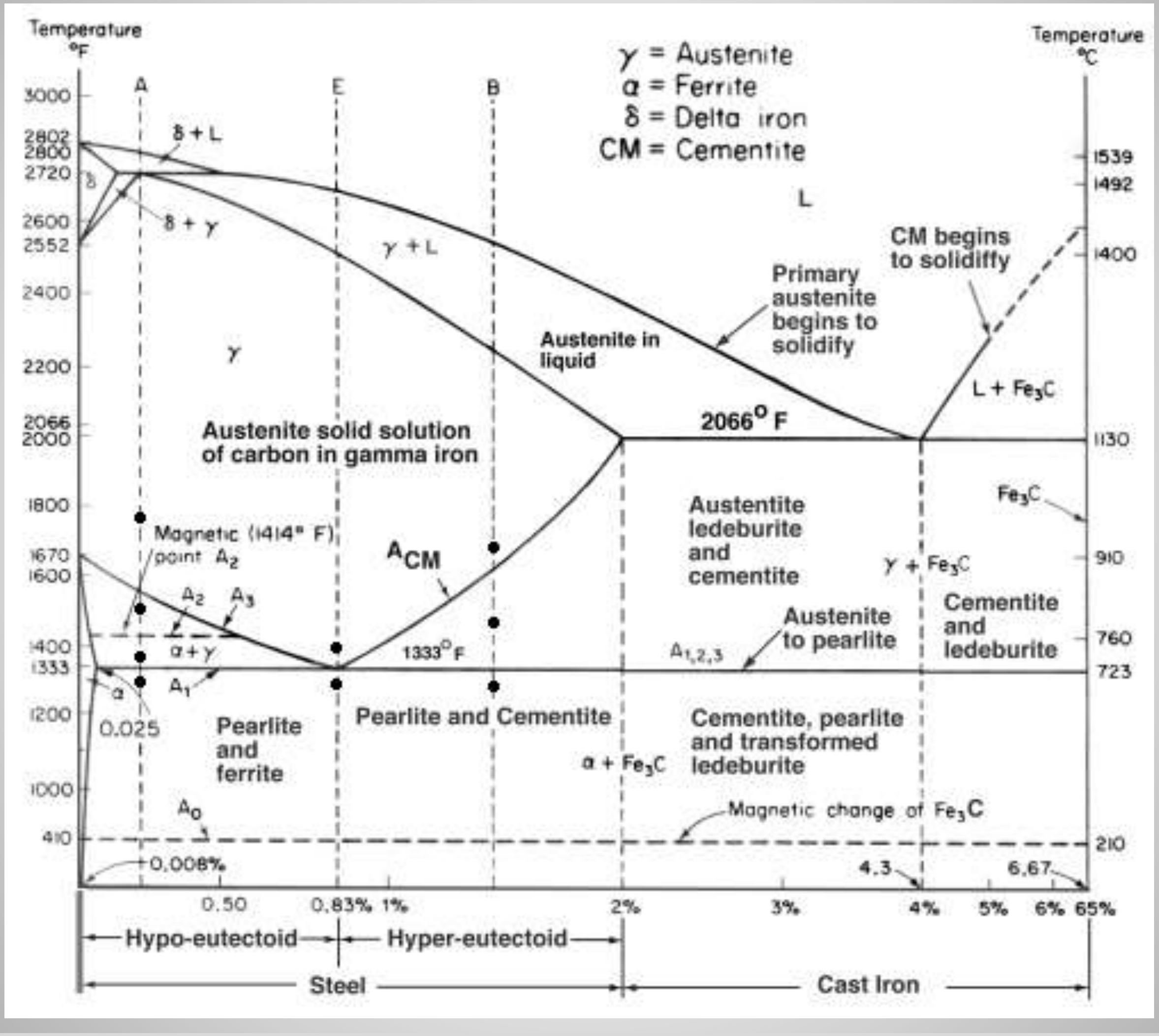
# Some Basic Crystalline Structures




- 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

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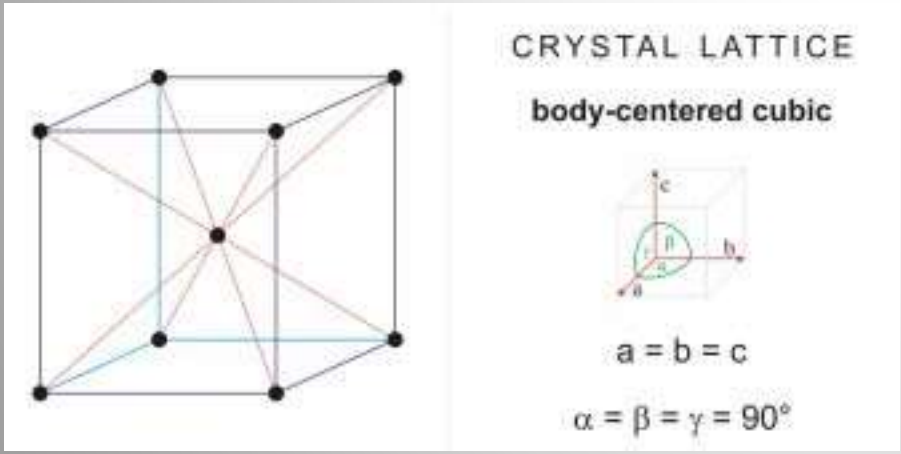
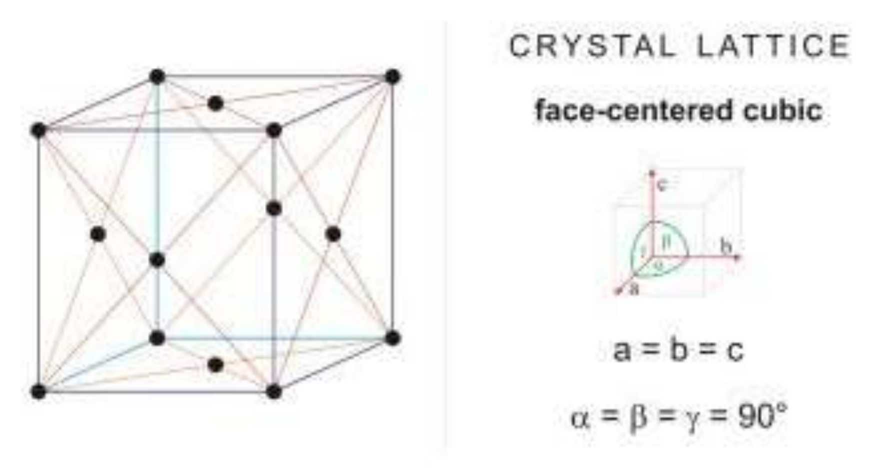
# Ferrite



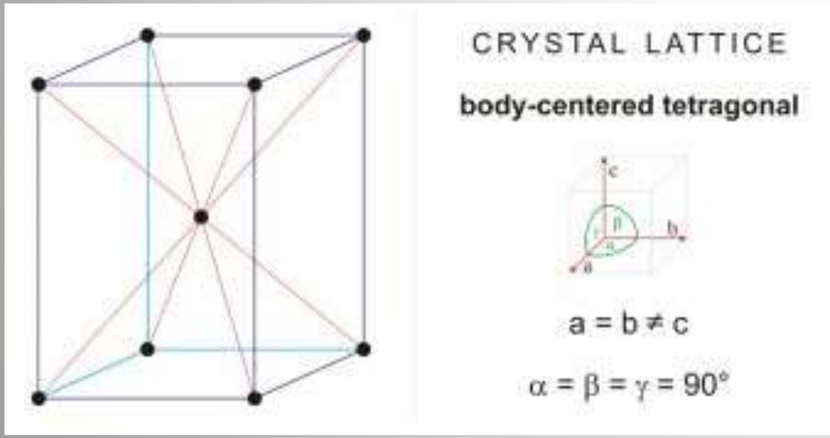

- α-phase Iron
- Body-centered cubic structure
- Ferromagnetic
- Does not dissolve much carbon due to lack of space in the lattice

# Austenite



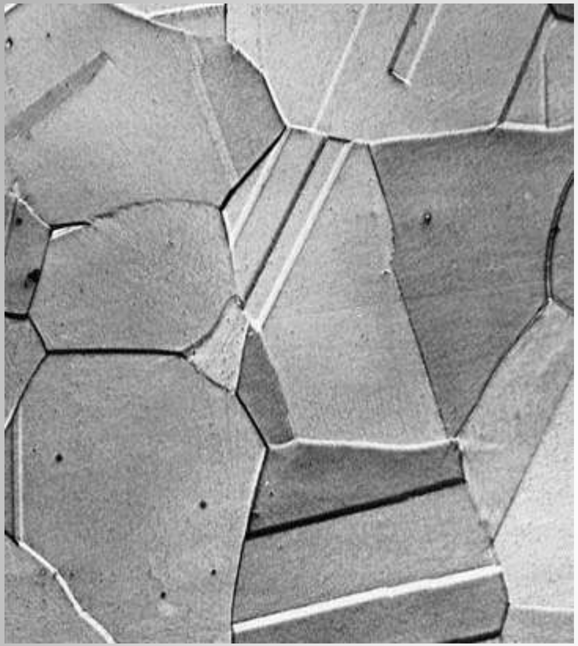

- γ-phase Iron
- Face-centered cubic structure
- Not magnetic
- Dissolves more carbon due to more lattice space

# Martensite

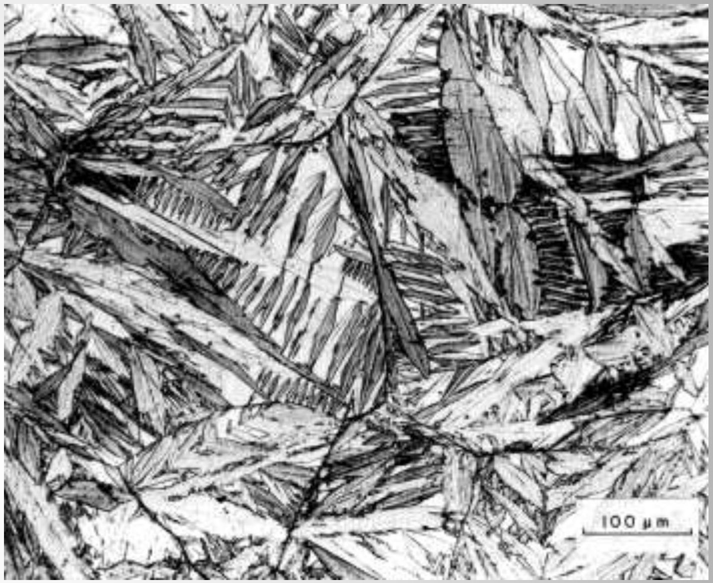



- Formed by rapid quenching of austenite
- Body-centered tetragonal strucure
- Magnetic
- Needle-like microstructure
- Harder, but more brittle

# Austenite vs. Martensite



Austenite




Martensite

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# 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

| SAE designation | Type |
|---|---|
| 1xxx | Carbon steels |
| 2xxx | Nickel steels |
| 3xxx | Nickel-chromium steels |
| 4xxx | Molybdenum steels |
| 5xxx | Chromium steels |
| 6xxx | Chromium-vanadium steels |
| 7xxx | Tungsten steels |
| 8xxx | Nickel-chromium-molybdenum steels |
| 9xxx | Silicon-manganese steels |

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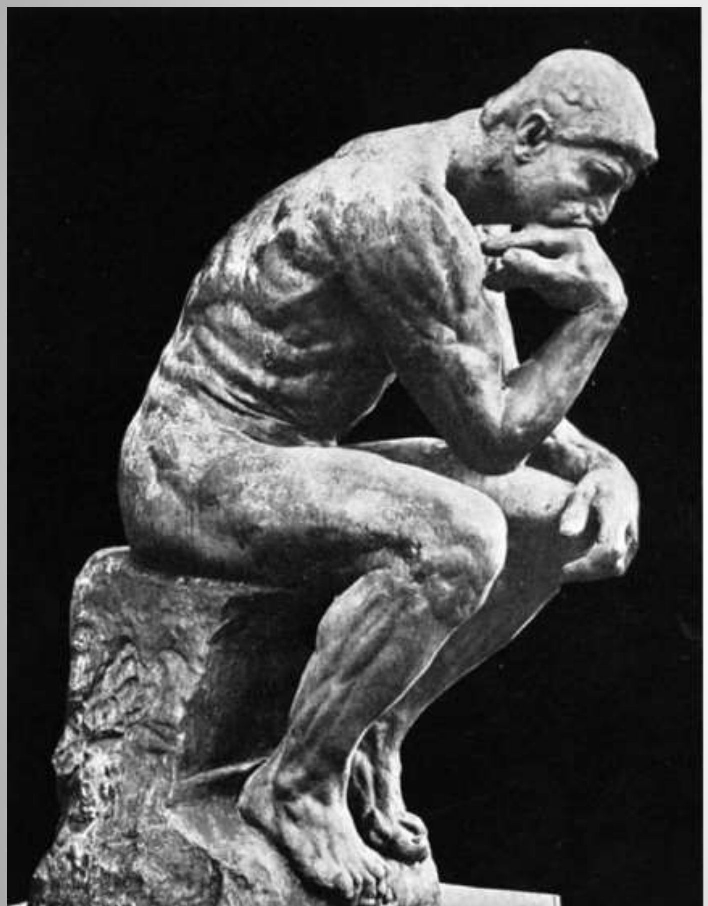
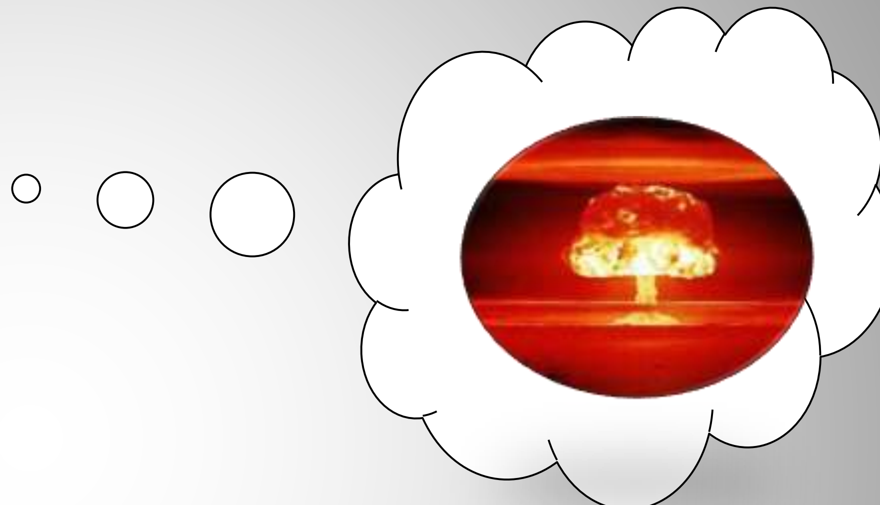
# What Causes An Installation to Fail?





# 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

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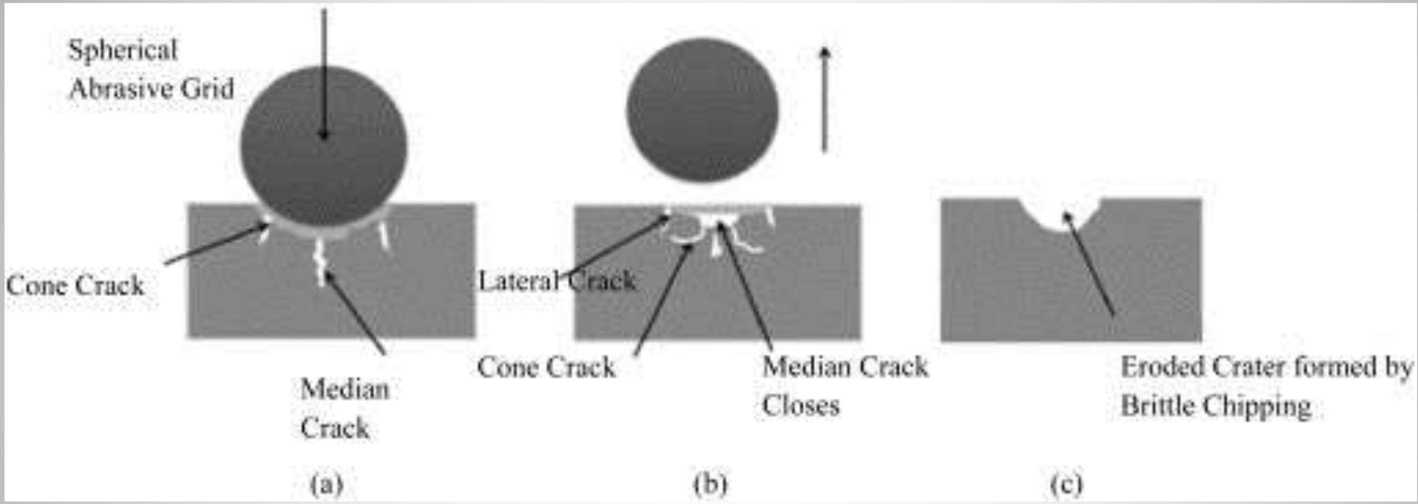
# Erosion by Particulate

- 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

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# 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

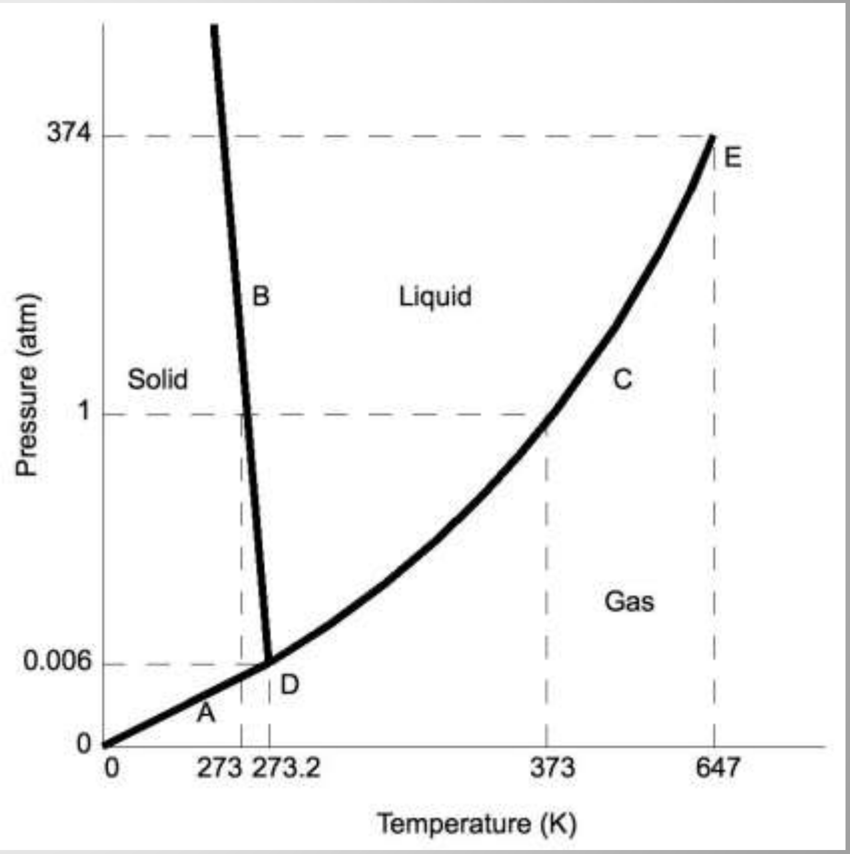
# Less Important: Size, Solids %, and Angle

- 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

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# 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


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# 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 $A + B \rightarrow C + D$,

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

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# Corrosion – The Math

# 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

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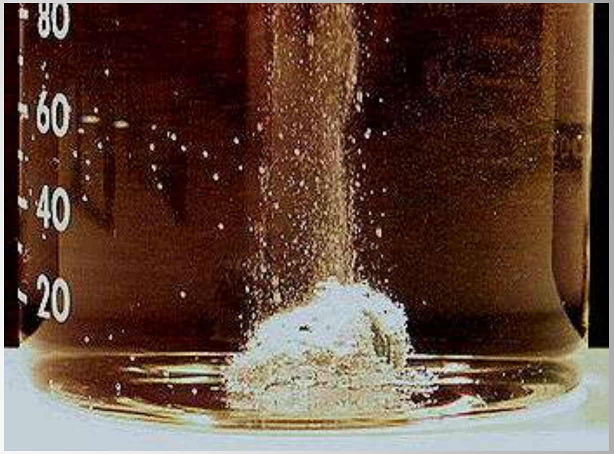
# Common Vectors for Corrosion

- 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

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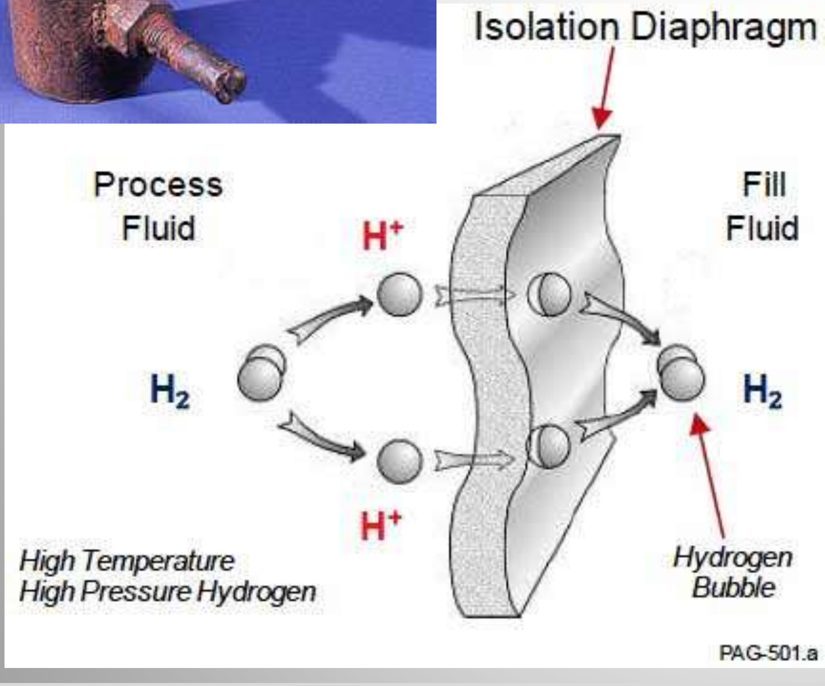
# Possible Metallurgy Solutions

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

- For higher concentrations, more exotic compounds are required.
  - Super-Austenites (Iron-Extra Chromium-Extra Nickel-Molybdenum-Nitrogen)
  - 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 $H_2$ bubbles in the metallic matrix
- Bubbles in the metallic matrix greatly embrittle the metal, which leads to failure under normal operating conditions

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# 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

- $H_2S$ causes embrittlement and cracking of metals
- Causes sudden catastrophic failure
- Particularly important in oil/refining applications, due to the high quantities of $H_2S$
- Complex mechanism extensively studied by NACE

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# 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

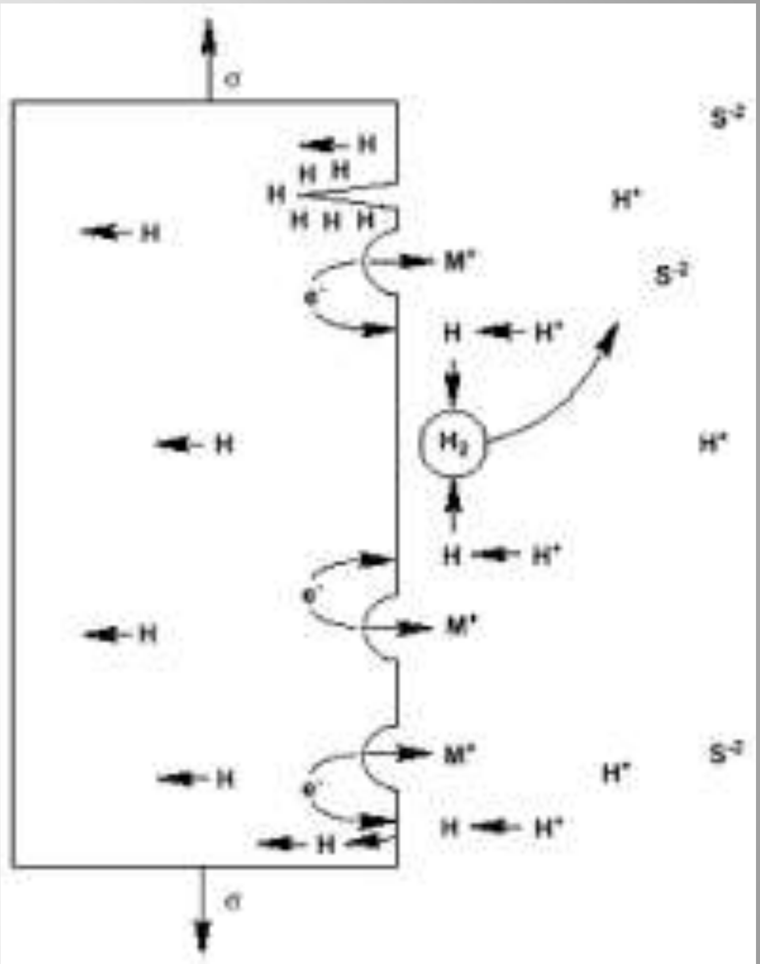
- NACE MR0103 was created for downstream (refining) environments.
  - Generally less rigorous

# 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 $H_2S$ 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



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# Sulfide Stress Cracking - The Mechanism


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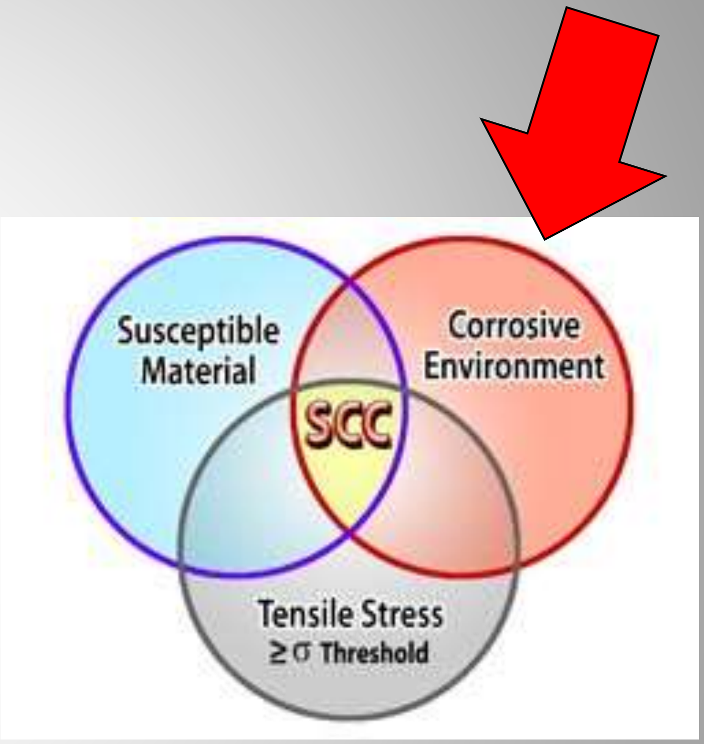
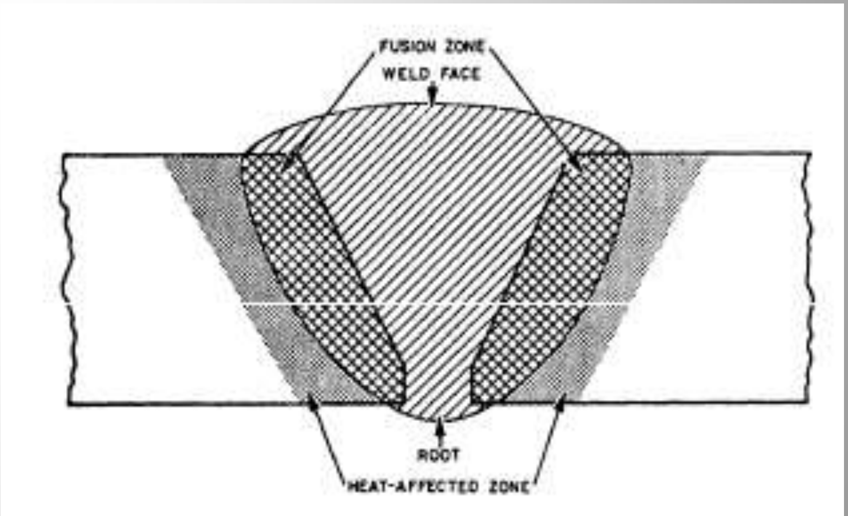
# The Environment – What Factors into SSC?

- Concentration of $H_2S$ 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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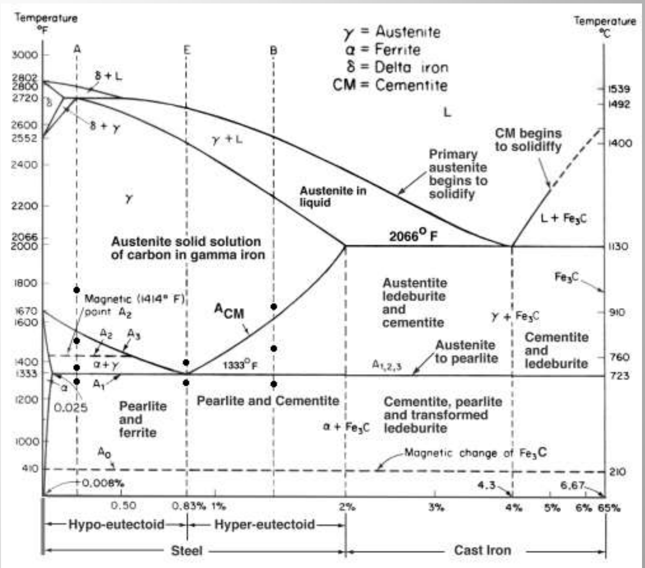
# How Hard Could It Be?

- 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

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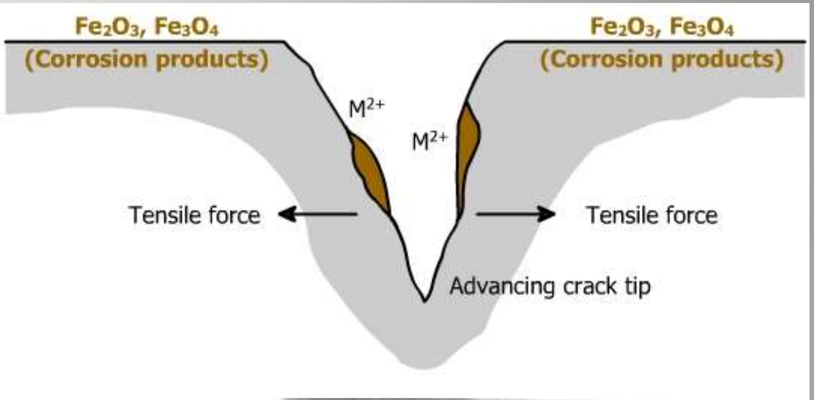
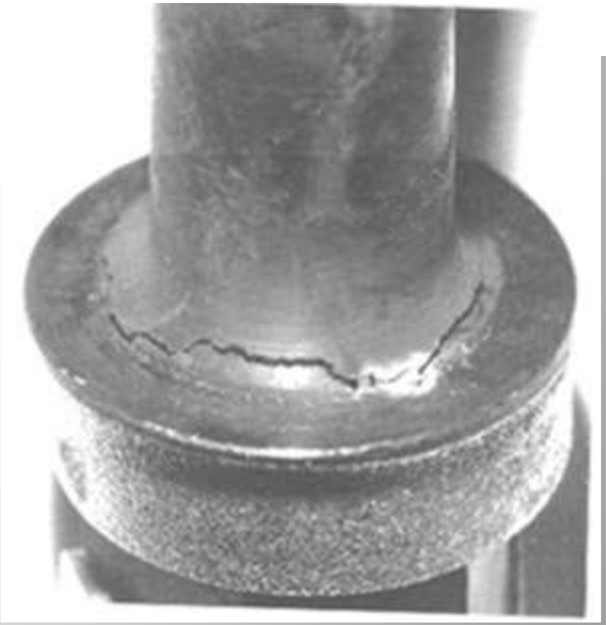
# Historical Example – Season Cracking

- 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



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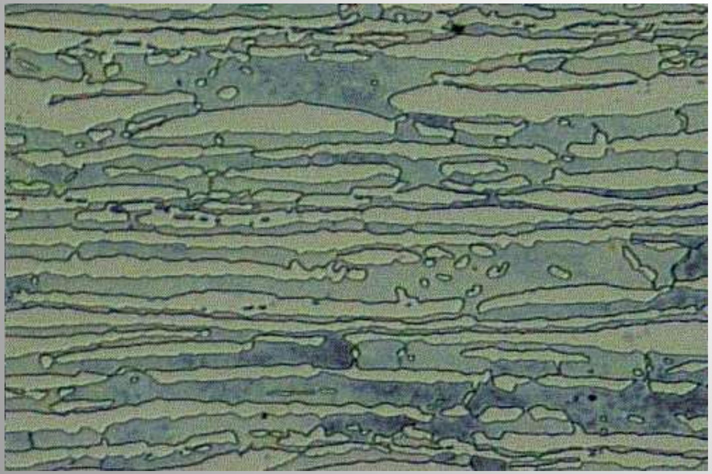
# Possible Metallurgy Solutions



- 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

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# The Moral of The Story

- 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.

# Work Cited

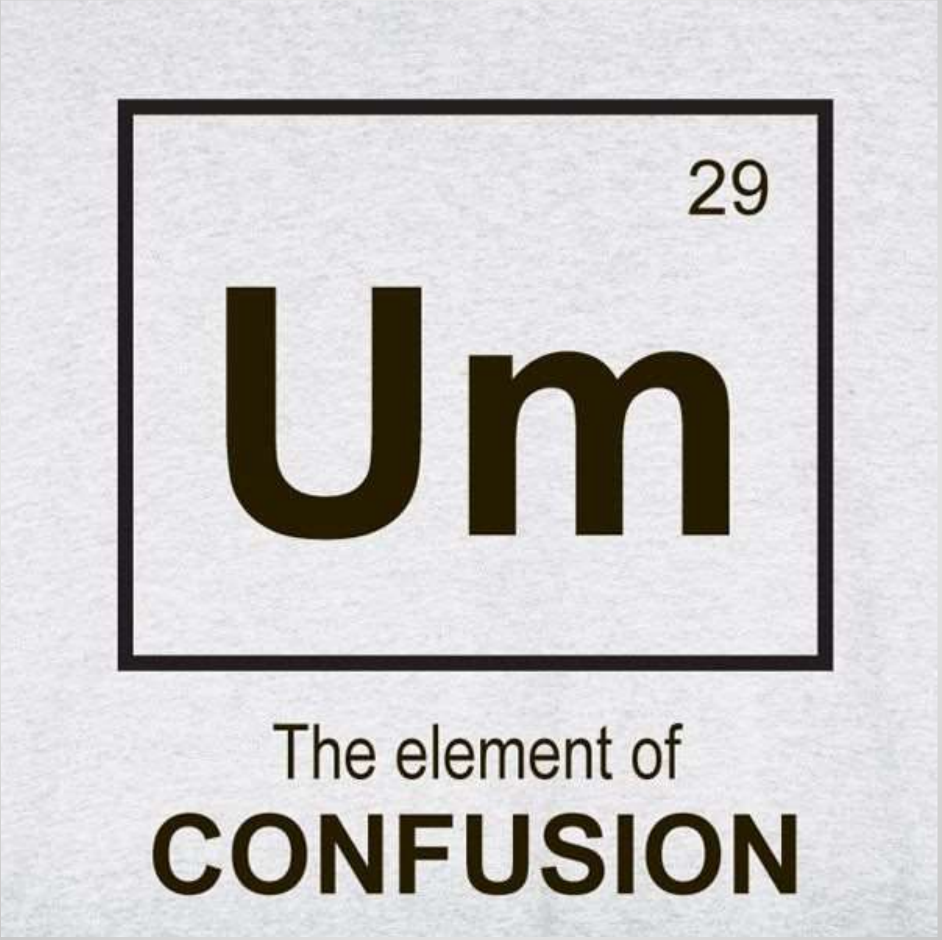

- A comprehensive review of solid particle erosion modeling for oil and gas wells and pipelines applications, Parsi et al, Journal of Natural Gas Science and Engineering, Volume 21, Pg 850-873.

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

- NACE MR0103-2012, Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments, NACE International, 2012.

- NACE MR0175-2015, Petroleum and natural gas industries—Materials for use in H2S-containing environments in oil and gas production, NACE International, 2015.

# Questions?

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