Setting the Standard for Automation™

Corrosion of Metals & NACE

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Standards
Certification
Education & Training
Publishing
Conferences & Exhibits

Agenda

Part 1

- Definitions
- Rusts formation

Part 2

- Stress Corrosion Cracking
- Sulfide Stress Corrosion Cracking

Part 3

- NACE Background

Part 4

- NACE Material recommendations

Part 1:

Definitions,
Materials,
Rust Formation

Definition of Corrosion

Corrosion:

A process that converts metal to a more stable form. It gradually destroys materials by chemical reaction with their environment.

Oxidation:

Is the process of taking electrons from a compound, such as a metal

Types of Metals

- Ferrous Alloys
  - Carbon
  - Low Alloy
    - Ex. Cr-Moly Steels
  - High Alloy Steels
    - Ex. SS steels
- Common Non-Ferrous Alloys
  - Nickel based alloy
    - e.g. Inconel, Monel, Hastelloy
  - Aluminum based alloy
  - Titanium based alloy
  - Cobalt based alloy

A little background on Metal & Water & Air

- Metal contains free electrons e^- and irons Fe^+
  (e^- is what makes the metal shiny)
- Water contains hydrogen and hydroxide ions, H^+, OH^-
- Salt water or seawater contains dissolved ions, Na^+ and Cl^-
- Air contains N, O_2, Ar, and H_2O

What happens with Air, Water, and Metal (Iron)?

- Oxygen takes electrons from the iron (reducing agent) or "Oxidation of Iron":

  $O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$

  $Fe \rightarrow Fe^{2+} + 2e^-$

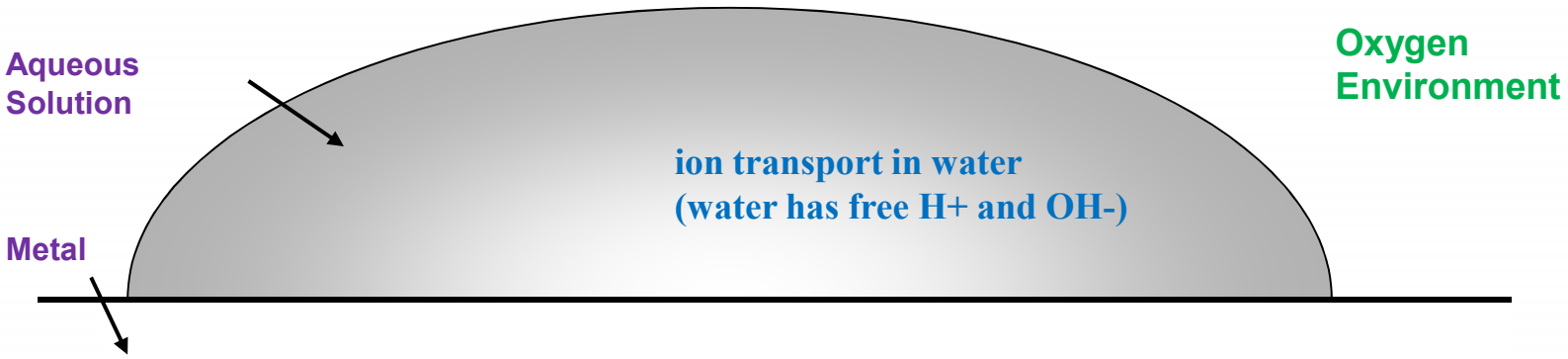
- Rust Formation (iron oxide, iron hydroxide)

  $Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$

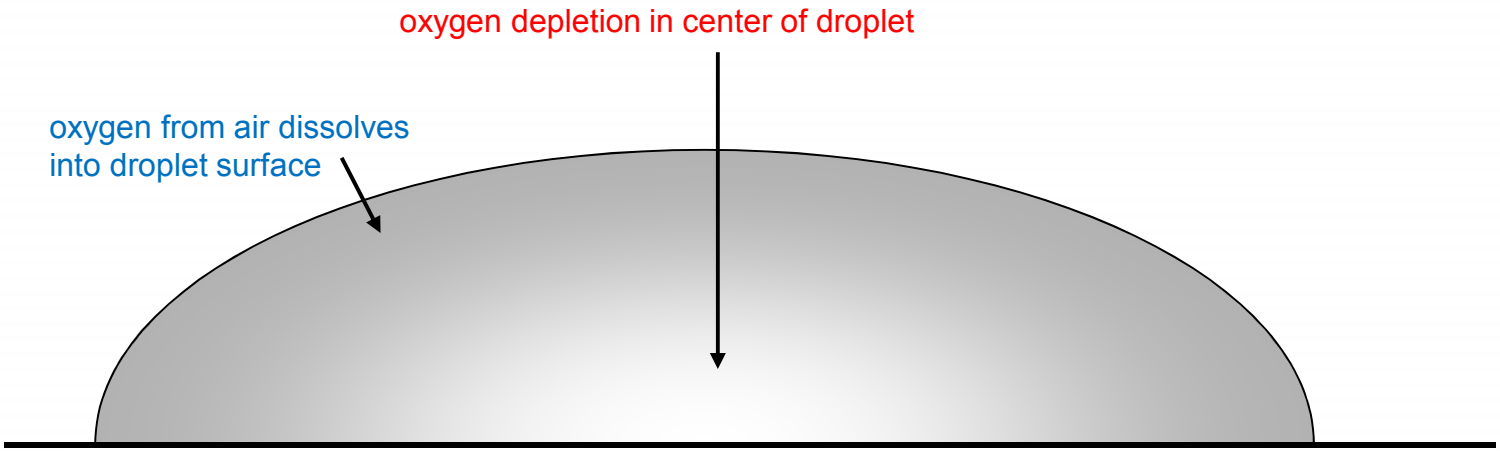
  (Equilibria can also be written in the dehydrated form)

- Corrosion is accelerated at low pH (more acidic) and presence of other ions

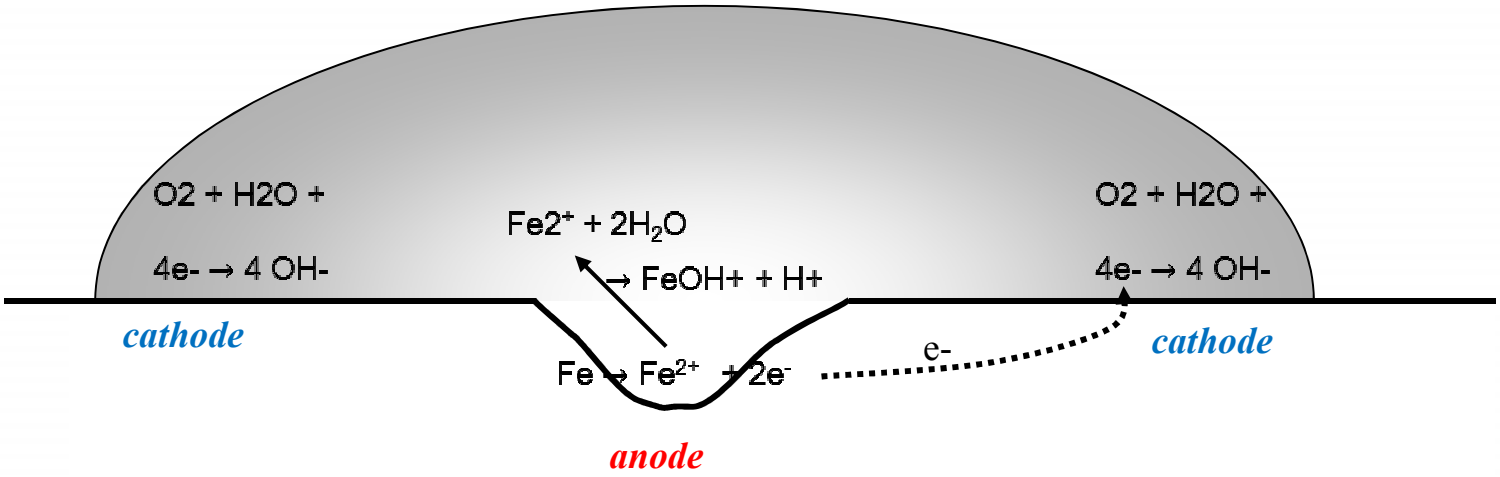
The Chemistry of Air, Water, and Iron (Aqueous Corrosion)



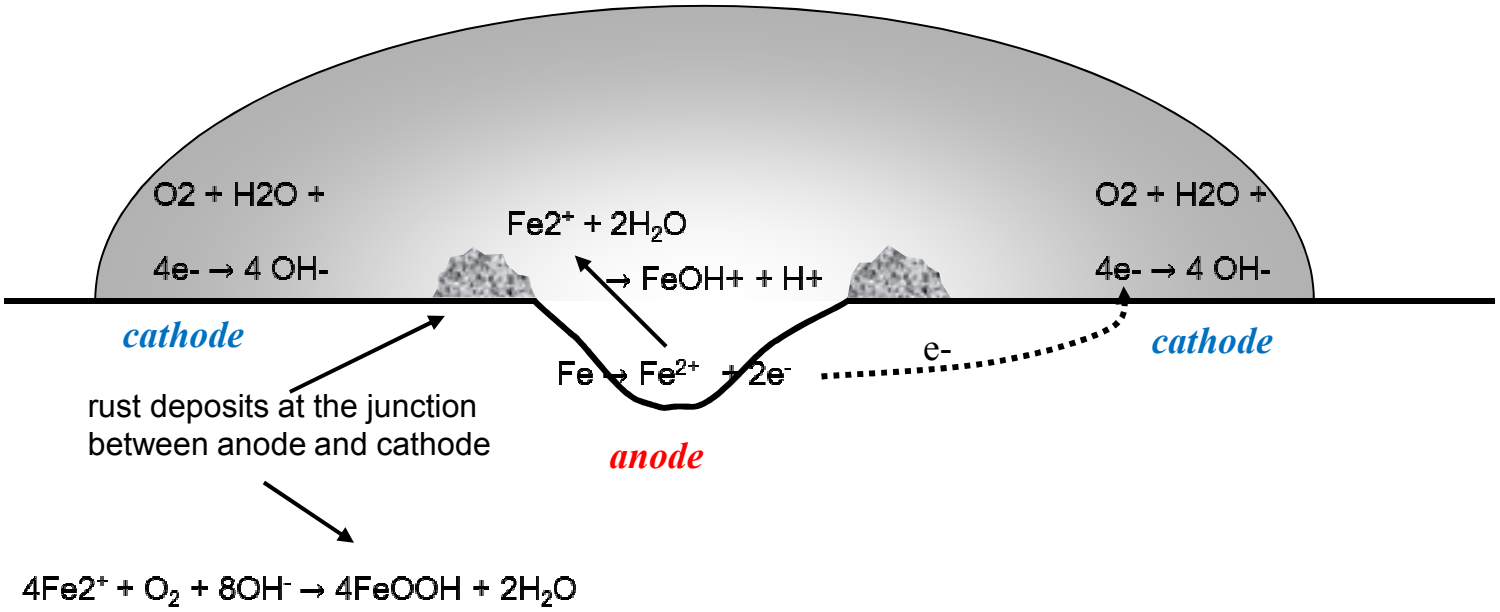
Rust Formation



Rust Formation

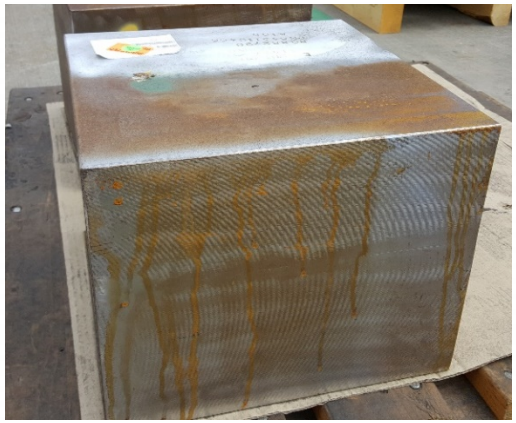


Rust Formation



Corrosion of common materials

- **Carbon and Alloy Steels**
  - Rusts form on the surface of the metal
  - Corrosion continues down into the metal



- **Aluminum**
  - A thin invisible oxide skin forms immediately (Aluminum Oxide or Sapphire)
  - This microscopic layer prevents further oxidation

Part 2

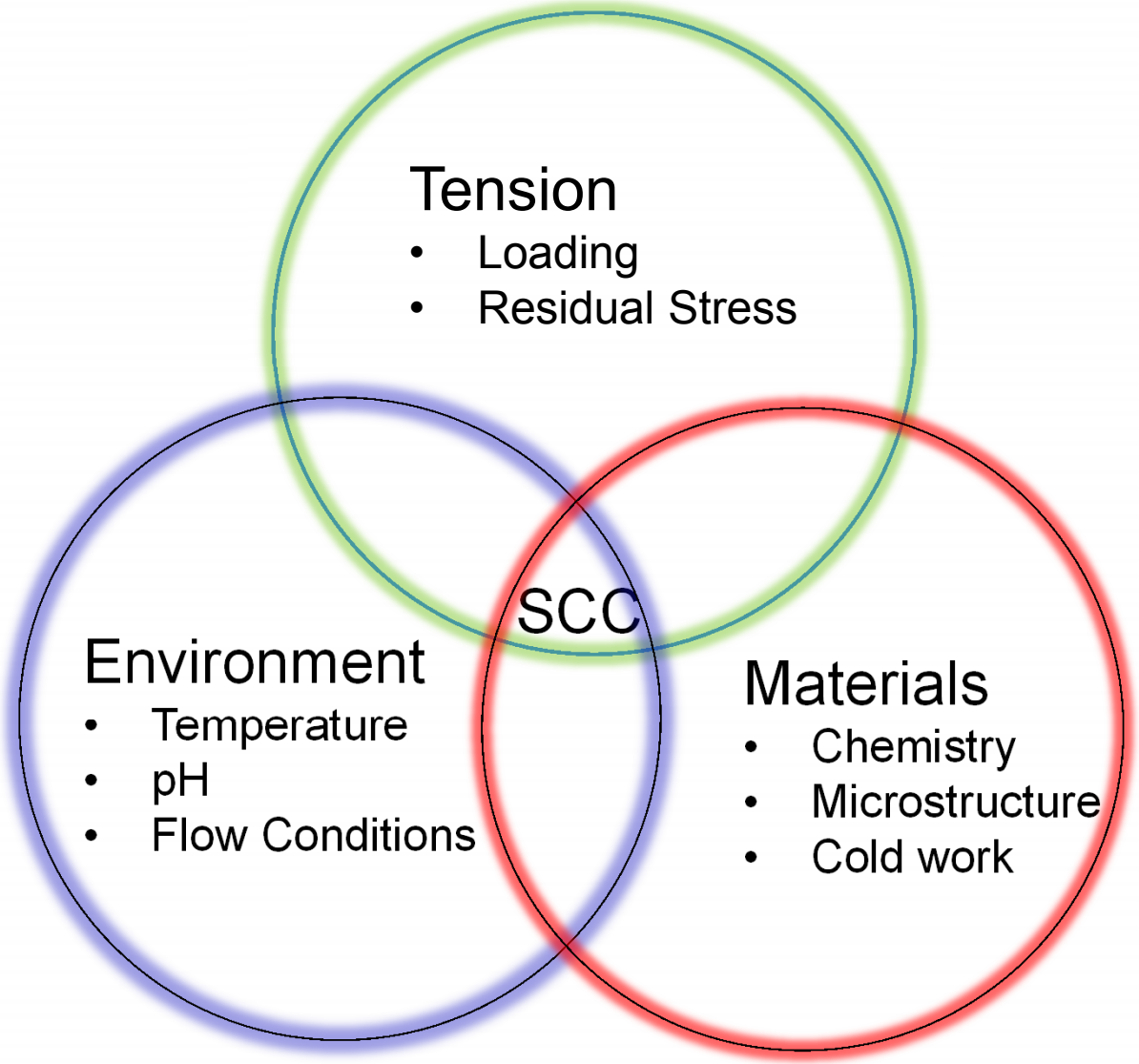
Stress Corrosion Cracking (SCC) & Sulfide Stress Corrosion Cracking (SSCC)

Stress Corrosion Cracking (SCC)

- Failure of ductile metals subjected to stress, especially at high temperature
  - Stress concentration
  - Residual stress from fabrication

- SCC can appear bright and shiny, while being filled with microscopic cracks

Stress Corrosion Cracking



Stress Corrosion Cracking

- SCC Induced from combined influence of tensile stress and corrosion environment

SCC in heat exchanger tube

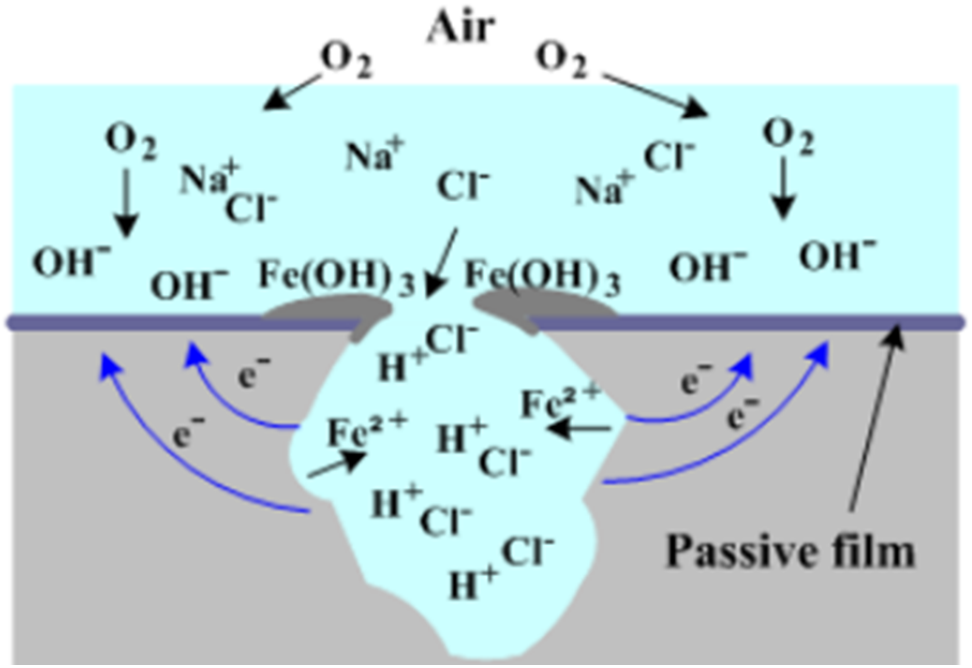
- An example is Chloride stress corrosion in austenitic stainless steel at high temperature.


316 corrosion cracking

Chloride Stress Corrosion

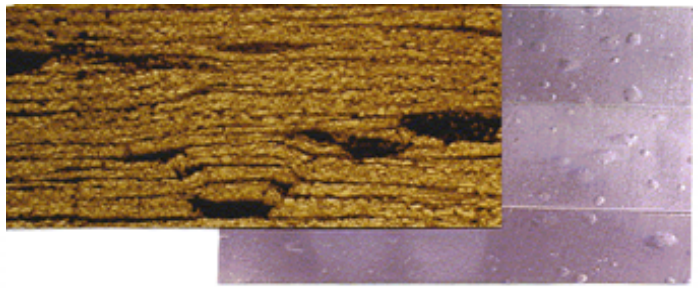
- Chlorides aggravates the conditions for pitting corrosion of most metals (including stainless steels, aluminum) by enhancing the formation and growth of the pits

- Seawater has 2% Chloride



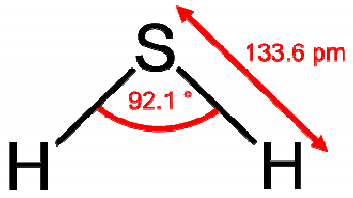
Sulfide Stress Corrosion Cracking

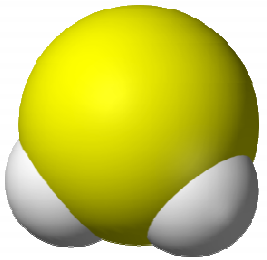
Metals exposed to Hydrogen Sulfide, H_2S, can suffer sudden brittle failure due to **Sulfide stress corrosion cracking (SSCC)**



H_2S or Hydrogen Sulfide

- A colorless gas with the characteristic foul odor of rotten eggs
- Poisonous
- Flammable
- Generated from the bacterial breakdown of organic matter in the absence of oxygen
- A common by-product of produced hydrocarbons such as crude or natural gas

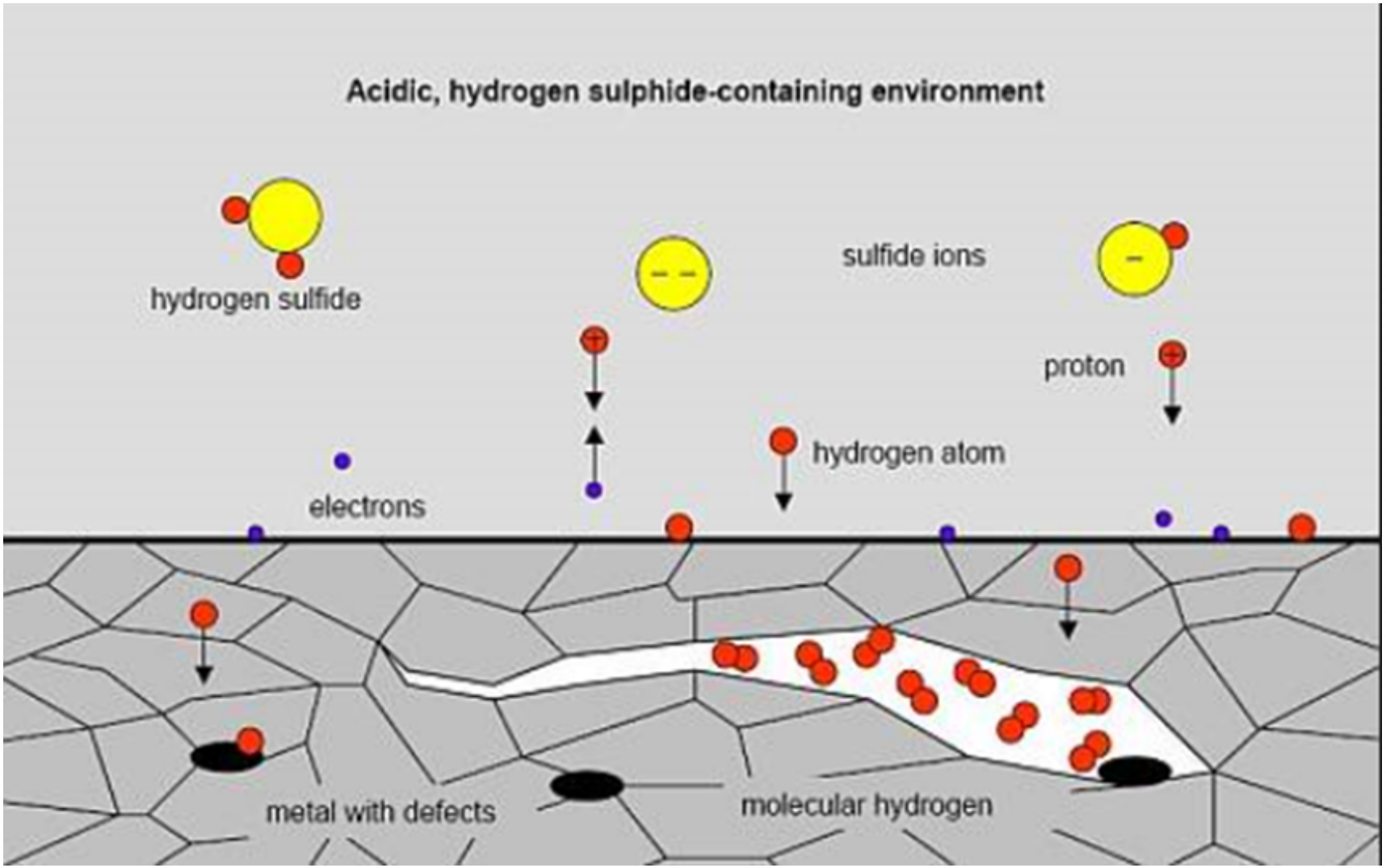




Sour Gas and Crude

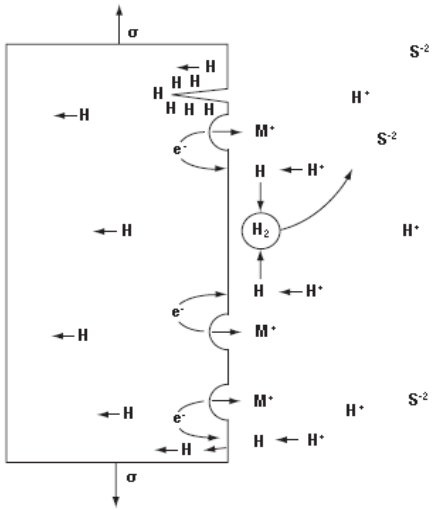
- Gases that include more then 4PPM or 5.7mg per meter cubed of H_2S are referred to as Sour Gas
- Crude that contains a minimum of 0.5% by weight of sulfur and contains small amounts of H_2S & CO_2 are referred to as Sour Crude

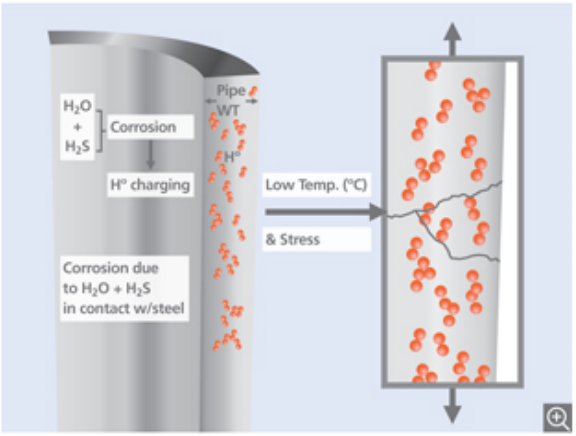
Sulfide Stress Corrosion Cracking



Sulfide Stress Corrosion Cracking

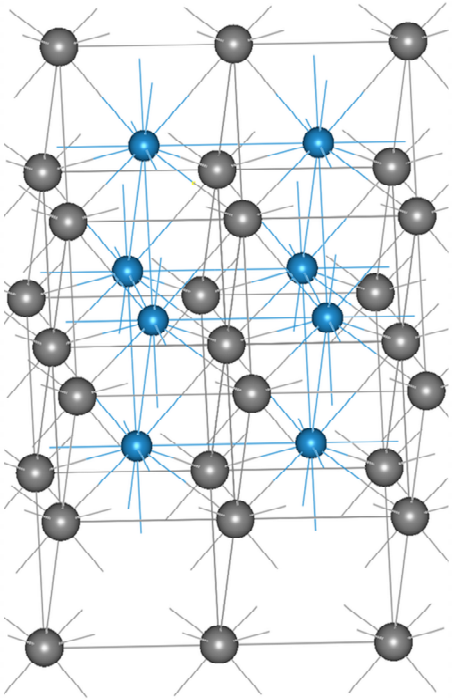
- SSCC is a form of hydrogen embrittlement
- Hydrogen ions pickup electrons from the base metal producing hydrogen molecules
- Some hydrogen molecules will diffuse in the base material and embrittle the crystalline structure





SSCC is a form of Hydrogen Embrittlement

- Hydrogen embrittlement is also called Hydrogen Induced Cracking (HIC)
- Atomic hydrogen is small enough to diffuse through metals
- The crystal lattice structure of the metal can become saturated with Hydrogen
- Mechanical properties of the metal are diminished
- Metal becomes more prone to cracking



Sulfide Stress Corrosion Cracking

- SSCC is most severe at ambient temperature in the range of 20F to 120F.
- Above 120F SSCC occurs at a slow rate
- Below 20F (-7C) hydrogen diffusion is slow

Surface Cracks High Stress

Pitting

Sulfide Stress Corrosion Cracking

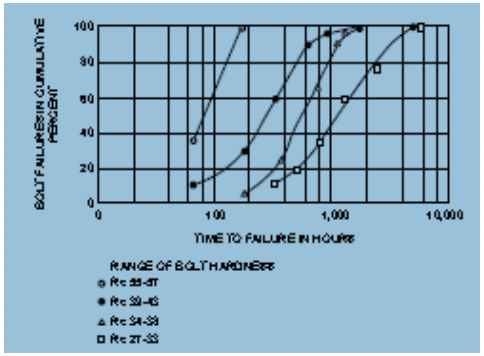
Factors Contributing to SSCC

- Chemical composition, strength, heat treatment and microstructure of the material
- Hardness increase the susceptibility to SSCC
- Acidity (pH) of the process environment
- H2S concentration or “Partial Pressure”
- Process temperature and time

Sulfide Stress Corrosion Cracking

Most Influential Variable to SSCC - **Material**

- SSCC is directly related to material strength and hardness level
- Example: when carbon steel is heat treated to higher hardness levels, the time to failure decreases
- Years of field experience have shown that good SSCC resistance is obtained below 22 HRC for carbon and low alloy steels



Part 3

NACE

What is NACE?

NACE = National Association of Corrosion Engineers

During the 1950's, a valve on a Christmas tree failed due to Sulfide Stress Cracking (SSCC). H_2S was released into the environment, killing four oilfield workers and five residents in a nearby house.

In response to this, the Texas Railroad Commission requested that NACE create a standard to prevent sulfide stress cracking in Christmas tree equipment.

MR0175

- MR = Material Requirement
- 0175 = First MR issued in 1975

NACE Specifications

- A wide variety of NACE specifications exist.
- For Sour (H_2S) services

  NACE MR0103-2010, Refinery Environments

  NACE MR0175/ISO15156-1, -2, -3, 2009, Oil and Gas Production

  Equipment covered, general principles

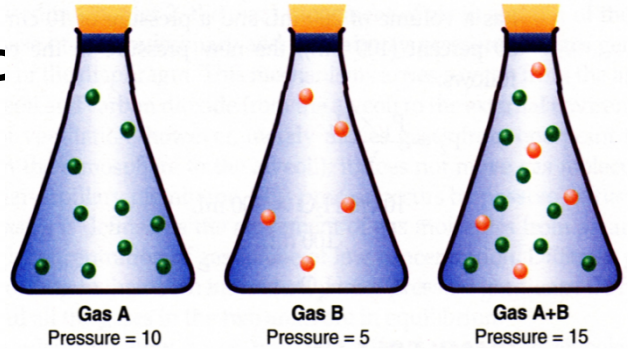
  Carbon/low alloy steels, cast irons

  Cracking resistant CRA (corrosion resistant alloys)

Partial Pressure

Partial pressure: The pressure of a mixture of gases is equal to the sum of the pressures of all of the constituent gases alone.

Dalton's Law: $P_{TOTAL} = P_1 + P_2 + P$



Ideal gas law can be used to calculate either pressure or moles

$P_{(pressure)}V_{(volume)} = n_{(number\ of\ moles)}R_{(ideal\ gas\ constant)}T_{(temperature)}$

Partial pressure = total pressure x mole fraction

NACE MR103 versus MR0175

NACE MR0103 (Materials Resistant to SSC in Corrosive Refining Environments)

- Published in 2003
- Downstream (refining and gas processing)
- Similar but less strict than MR0175
  - Chloride SCC not a common concern in refinery unlike MR0175
  - No limits to H2S partial pressures, temp limits, and pH restrictions
  - Welding without PWHT is allowed for some materials
  - Allows more grade of stainless steels including the “H” grades
  - Allows more grades of Nickel alloys

NACE MR0103 vs MR0175

ISO 15156/NACE MR0175 (SSC Resistant Metallic Materials for Oilfield Equipment)

- Upstream (Oil & Gas Production)
- Temperature limitation to avoid SCC in steels especially stainless steels
- Chemistry limitations such as nickel content in alloy steel <1%
- PWHT after welding is required to reduce hardness

ISO 15156/MR 0175 General Principles

- Only concerned with cracking of metallic materials
- Environmental / Service conditions must be evaluated, defined and documented before selecting materials
- The end equipment user shall decide if MR0175 applies in their service conditions

ISO 15156/MR 0175 Application

Standard defines materials for a variety of different equipment & processes

- Drilling, well construction and well servicing equipment
- Gas lift equipment, wellheads, flowlines, and Christmas trees
- Sour Water handling equipment
- Natural gas treatment plants
- Transportation pipelines for liquids, gases, and multi-phase fluids.

ISO 15156/MR 0175 Application

Sour Gas Services

- Pressure must be above .4 MPa (65 psia)
- The partial pressure of H_2S is greater than .0003 Mpa (.05 psia)
- Rules equate to approximately 50 ppm H_2S

Sour Oil/Water Services

- The maximum oil/gas ratio is 900:1 NM3/M3 (5,000 SCF/barrel)
- The gas phase contains a maximum 15% H_2S
- The partial pressure of H_2S in the gas is .07 MPa (10 psia)
- If operation pressure is greater than 1.8 Mpa (265 psia), use sour gas rules

ISO 15156/MR 0175 Exclusions

- NACE MR 0175 only applies to **METALLIC** components used in oil and gas production in H_2S-containing environments.
- NACE MR 0175 does not apply to non-metallic materials e.g. WC
- NACE MR 0175 does not apply to coating materials.
  - ✓ Properties of base material must comply with NACE not that of the coating.
  - ✓ Effect of coatings on cracking resistance should be considered.

Part 4

Material Selection

Common ways to minimize corrosion

- Coat the surface to minimize chemical reactions
  - Plating
  - Coating such as Teflon
  - Paint
- Use a more corrosion resistant metal
- Overlay with corrosion resistant material
- Control the environment

Materials Heat Treatment

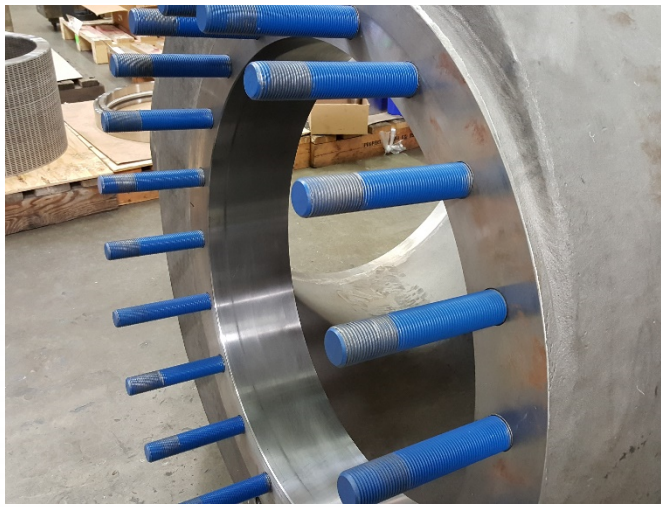
HT	Definition
Anneal	Usually refers heating a cold-worked metal to soften it by allowing it to recrystallize.
Austenitic or Normalize	Heating a ferrous alloy above its upper critical temperature – to the austenite phase on the phase diagram.
Cold-work	Plastic deformation of metal usually at room temperature to increase hardness.
Hot-working	Any metal-forming operation that is performed above a metal's recrystallization temperature.
Precipitation/age hardened	Hardening and strengthening of a metal alloy by extremely small and uniformly dispersed particles that precipitate from a supersaturated solid solution.
Solid solution	Single crystalline phase containing two or more elements
Solution-annealing	Heating a material to, and holding it at temperature for long enough to dissolve any carbides followed by rapid cooling to ensure carbides cannot re-precipitate and reduce corrosion resistance.
Stress relieved	Heating a metal to a suitable temperature and holding for long enough to reduce residual stresses, and then cooling slowly enough to minimize the development of new residual stresses
Tempered	Heating steel to a temperature below the lower critical temperature, to decrease hardness and increase toughness of hardened steel

Carbon Steels Compliant with NACE

Material	NACE Part 2. Para #	Heat Treatment	HRC max	Other
A105 (K03504)	A.2.1.3a	Acceptable when used in one of the following heat-treatment conditions: a) hot-rolled (carbon steels only); b) annealed; c) normalized; d) normalized and tempered; e) normalized, austenitized, quenched, and tempered.	187 HBW	
A234-WPB (K03006)	A.2.1.3b & A.1.6		197 HBW	Pipe fittings made from ASTM A234-WPB or WPC shall be thermally stress-relieved following any cold deformation that results in a permanent outer fibre deformation greater than 5 %. Thermal stress relief shall be performed in accordance with an appropriate code or standard. The minimum stress-relief temperature shall be 595 °C (1100 °F). The final maximum hardness shall be 197 HBW.
A234-WPC (K03501)	A.2.1.3b & A.1.6		197 HBW	
A106 A (K2501)	A.2.1.2		22 HRC	Carbon and low-alloy steels shall be thermally stress-relieved following any cold deforming by rolling, cold forging or other manufacturing process that results in a permanent outer fibre deformation greater than 5 %. Thermal stress relief shall be performed in accordance with an appropriate code or standard. The minimum stress-relief temperature shall be 595 °C (1 100 °F). The final maximum hardness shall be 22 HRC.
A106 C (K03501)				
A216- WCB (J03002)				
A216- WCC (J02503)				
A350-LF2 (K03011)				
A352 LCB (J03003)				
A352 LCC (J02505)				

Bolting Materials Compliant with NACE

UNS	NACE Part 2. Table #	HRC max	Heat Treatment
A193-B7M (G41400)	A.4	22	Acceptable when used in one of the following heat-treatment conditions: a) hot-rolled (carbon steels only); b) annealed; c) normalized; d) normalized and tempered; e) normalized, austenitized, quenched, and tempered;
A320-L7M (G41400)			



For bolting materials other than low alloy steels reference NACE MR 0175 Part 3/ISO 15156-3 Table A.1.

CRA's Compliant with NACE

UNS	NACE App	NACE Part 3. Table #	Cl Conc. Max. mg/l	pH	PP H2S kPa (psi)	Temp max. oC (oF)	S-resist	HRC max	Condition
S41000 (410SS)	ANY	A.18	See remarks	≥3.5	10 (1.5)	See remarks	NDS [a]	22	1) austenitized and quenched or air-cooled, 2) tempered, then cooled to ambient temp& 3) tempered, then cooled to ambient temp.
	Valve & choke components	A.23	See remarks	≥3.5	See remarks		NDS [a]	22	
S17400 (17-4PH Cond H1150M/ H1150D)	Non-pressure containing components[1]	A.28	See remarks[b]				NDS [a]	33	Either double age hardened or double age-hardened process.
	Valve & choke components[1]	A.27	See remarks	≥4.5	3.4 (0.5)	See remarks	NDS [a]	33	
	Misc equipment[1]	A.28	Environmental limits for this alloy for these applications have not been established.				NDS [a]	33	
S30400 (F_{PREN} 18-20),	Seal rings & gaskets[4]	A.5	See remarks				NDS [a]		

CRA's Compliant with NACE

UNS	NACE App	NACE Part 3. Table #	Cl conc. Max. mg/l	pH	PP H2S kPa (psi)	Temp max. oC (oF)	S-resist	HRC max	Condition
S31600 (S316SS) (F_{PREN} 22-28)	ANY[1,5]	A.2	5000	W 5.0	10.2 (1.5)	93 (200)	No	22	Solution-annealed and quenched or annealed and thermally stabilised heat-treatment condition.
			See remarks		100 (15)	60 (140)	No	22	
			50	See remarks			No	22	
	Seal rings & gaskets[4]	A.5	See remarks				NDS[a]		
	Instrument tubing[3]	A.4	See remarks[b]				NDS[a]		
S31803 (F_{PREN} 31-38)	ANY[6]	A.24	50	See remarks[b]			NDS[a]		Solution-annealed & liquid-quenched.
S20910 (Nitronic 50) (F_{PREN} 29-38)	ANY[2]	A.2	See remarks		100(15)	66(150)	No		Annealed or hot-rolled (hot/cold-worked) cond.
	Valve stems, pins & shafts	A.3	See remarks				NDS[a]	35	If in cold-worked condition must be solution annealed
S31254 (254 SMO) (F_{PREN} 42-45)	ANY	A.8	See remarks		100(15)	60(140)	No		Solution-annealed
		A.8	50	See remarks[b]			No		
		A.8	5000	See remarks	100(15)	171(340)	No		
		A.8	5000	See remarks	700(100)	121 (250)	No		
		A.8	5000	See remarks	310(45)	149(300)	No		

Non-Ferrous Materials Compliant with NACE

UNS	NACE App	NACE Part 3. Table #	Cl conc. Max. mg/l	pH	PP H2S kPa (psi)	Temp max. oC (oF)	S-resist	HRC max	Condition
Inconel 625 (N06625) Type A	ANY	A.12/ A.13	See remarks				Yes		Solution-annealed or annealed condition
Inconel 625 (N06625) Type C	ANY	A.12/ A.14	See remarks		200 (30)	232 (450)	No	40	Be in the annealed and cold-worked condition and meet all of the following: 1. Max 40 HRC 2. Max yield strength achieved by cold-work is1034 MPa (150 ksi)
			See remarks		700 (100)	215 (425)	No	40	
			See remarks		1000 (150)	204 (400)	No	40	
			See remarks		1400 (200)	177 (350)	No	40	
			See remarks			132 (270)	Yes	40	
Inconel 718 (N07718) wrought	ANY	A.32	See remarks		200 (30)	232 (450)	No	Any one of the following conditions: 1) solution-annealed to max 35 HRC; 2) hot-worked to a max of 35 HRC; 3) hot-worked & aged to max 35 HRC; 4) solution-annealed & aged to max 40 HRC (CCI usually uses 718 in this form).	
			See remarks		1400 (200)	204 (400)	No		
			See remarks		2300 (330)	199 (390)	No		
			See remarks		2500 (360)	191 (375)	No		
			See remarks		2700 (400)	149 (300)	No		
			See remarks			135 (275)	Yes		
Elgiloy (R30003)	Springs	A.39	See remarks[b]				NDS[a]	60	Cold-worked and age hardened condition

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