Geothermal Materials Selection – Old Lessons, New Directions

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Presentation Outline

- Geothermal Materials Selection
  - Rules of Thumb and Their Basis (H_2S Corrosion)
- New Rules for New Plant and Processes
  - Engineered Systems, i.e. pH Adjustment
- Anticipated Extremes for Future Development
  - CO_2 Rich, Acid Fluids
- Asset Integrity Management
  - Risk Based Assessment and Industry Groups.

Historical Rules of Thumb (H_2S, Chloride)

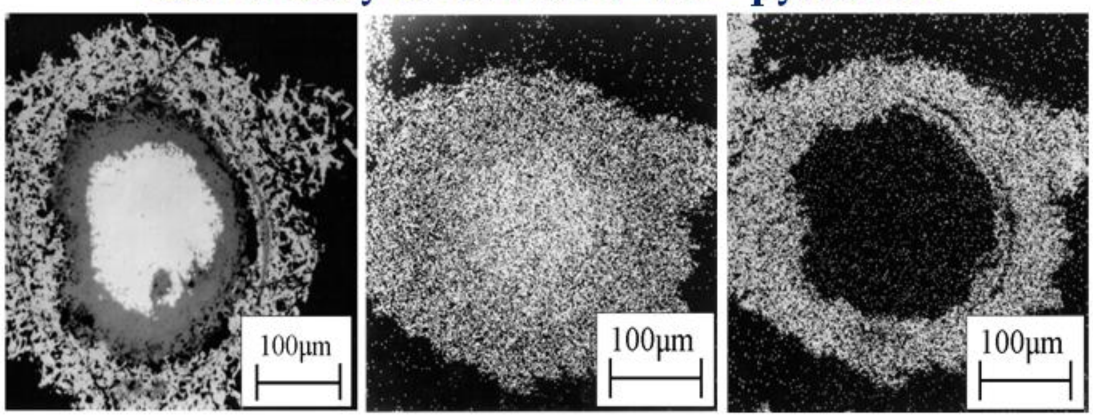
1. Carbon steel can be used in 2-phase fluid, steam and water because protective films are formed when oxygen is absent:
   – Oxygen must be avoided, design for scales and pitting.
2. Stainless steels are susceptible to pitting corrosion and Chloride Stress Corrosion Cracking (Chloride SCC) and Sulfide Stress Cracking (SSC):
   – Suitable corrosion resistant alloys must be selected.
3. Hydrogen readily diffuses into steels and high strength alloys suffer SSC or Hydrogen Induced Cracking (HIC/HE):
   – Low strength steels with low stress levels are preferred.

Oxygen Free Solutions with H_2S

Carbon steels form protective films in low chloride near neutral pH fluids

Kawerau Main Steam Pipeline
Form of Corrosion Products

Core of corroding Fe with layer of magnetite underlying an outer layer of iron sulfide - pyrrhotite



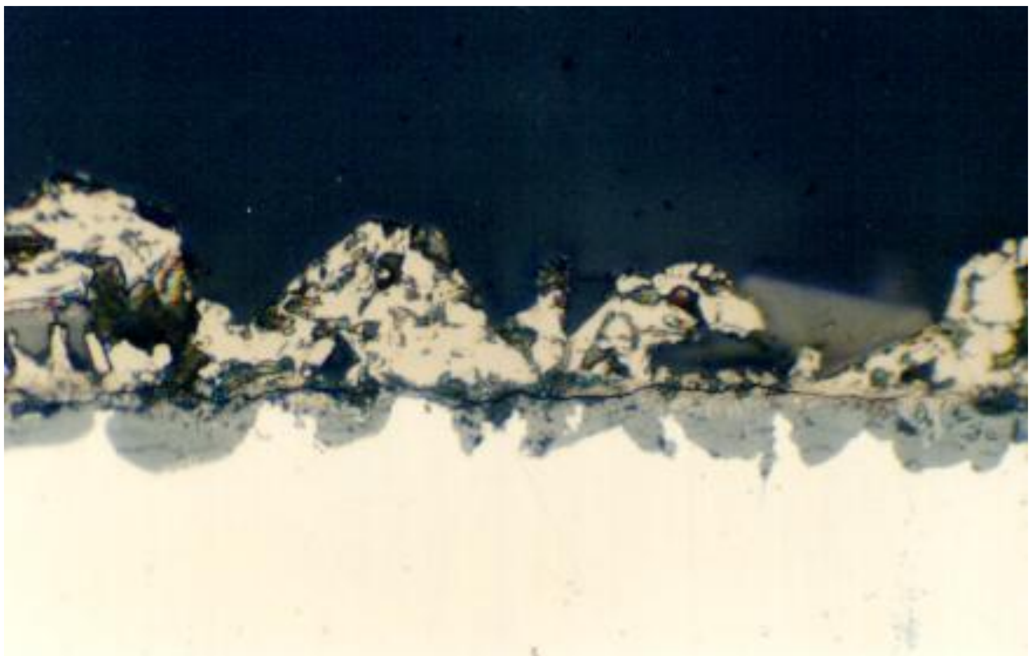
Optical Image　　Fe map　　S map

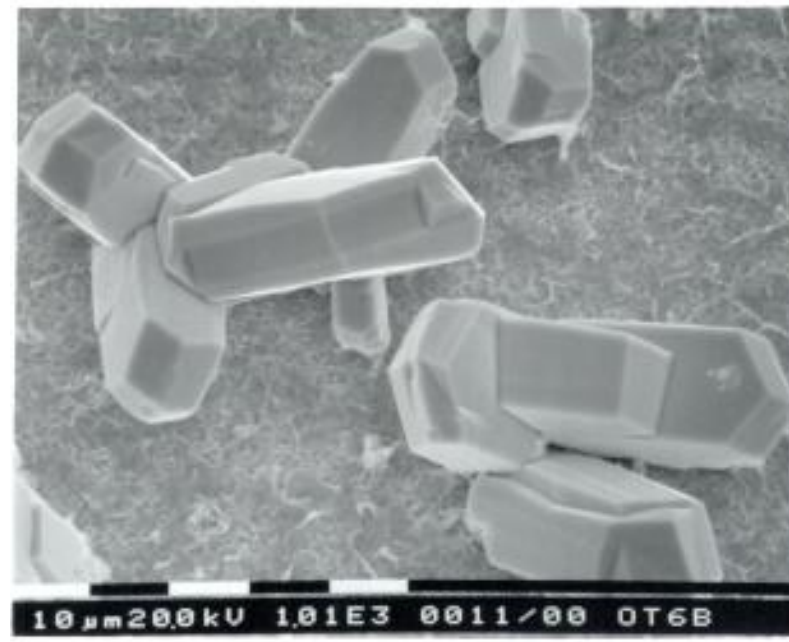
Lichti, 2006

Oxygen Free Solutions with H_2S

Carbon steels form protective films in low chloride near neutral pH fluids

T = 160 C, pH = 6, H_2S = 10-4 mol/kg, SiO_2 = 4 mg/kg





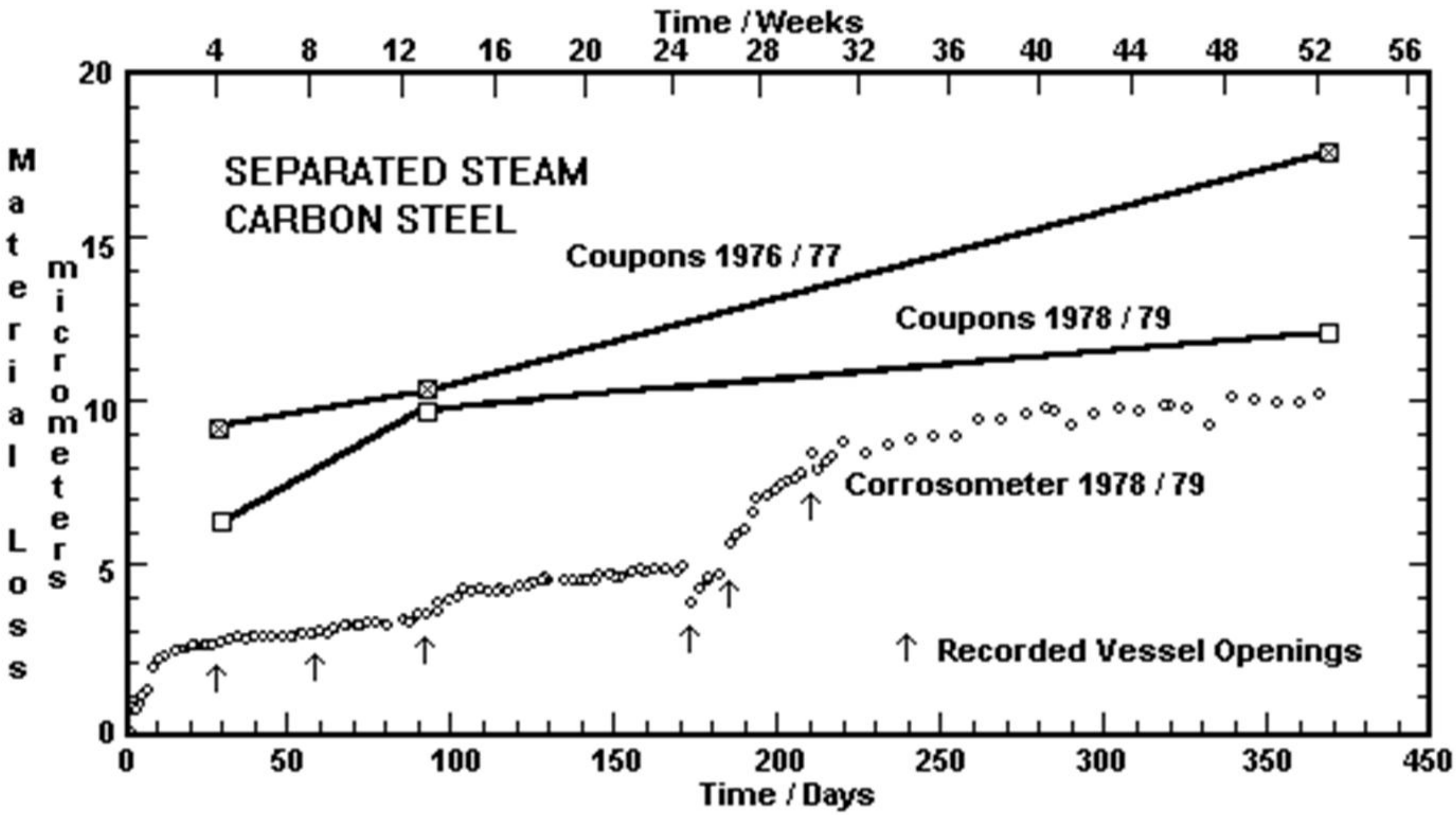
572 hours **244 hours**

Carbon steel corrosion and corrosion products

Inman, 1994

Oxygen Effect at Shutdown

Carbon steels form protective films in low chloride near neutral pH fluids

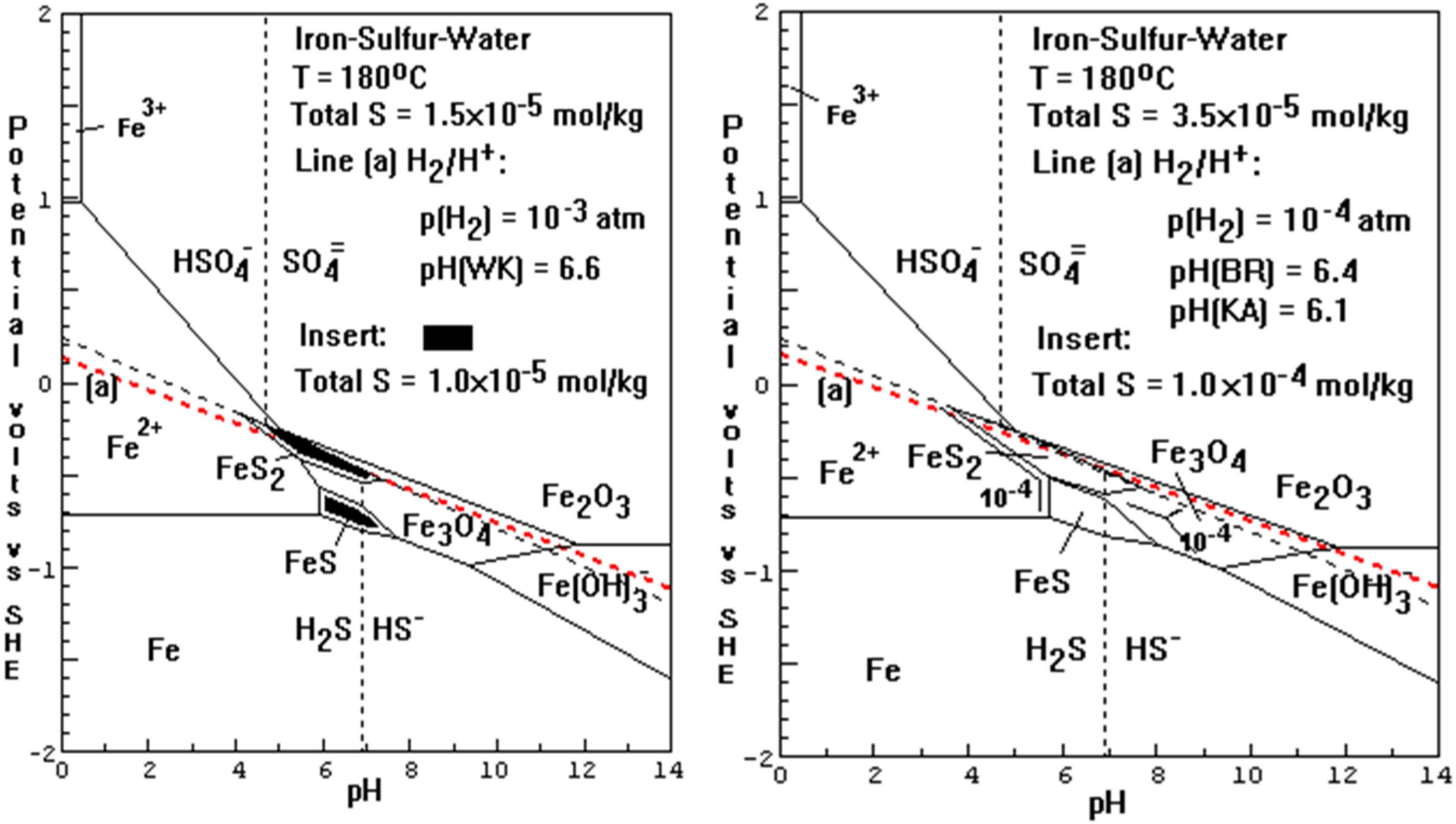


Lichti, 2006

Broadlands-Ohaaki Separated Steam (Well BR22)

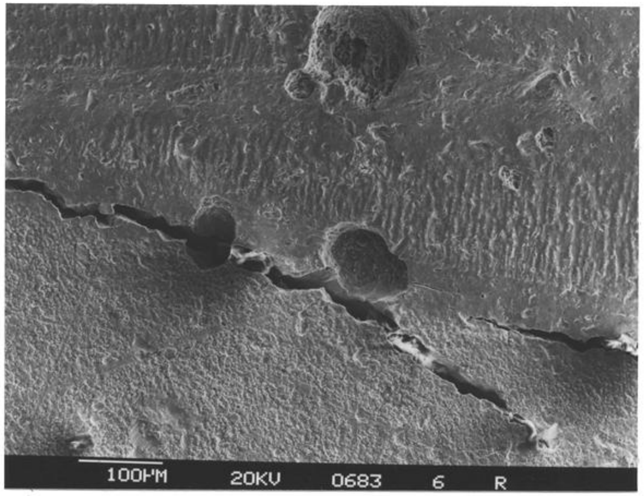
Oxygen Contamination Effects

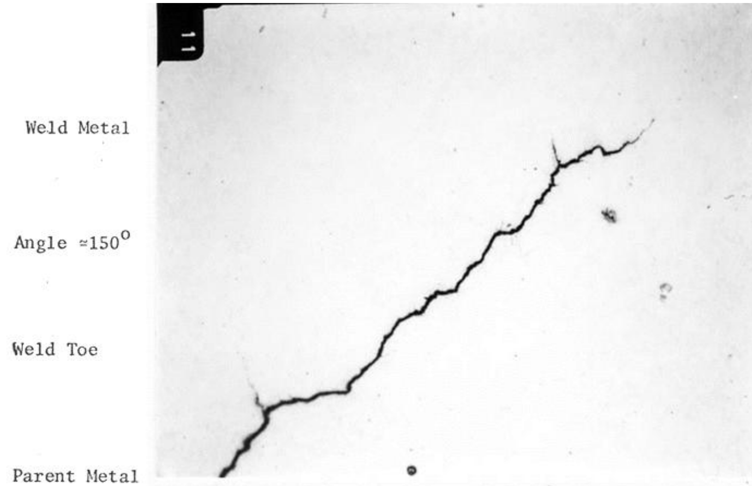
Carbon steels form protective films in low chloride near neutral pH fluids

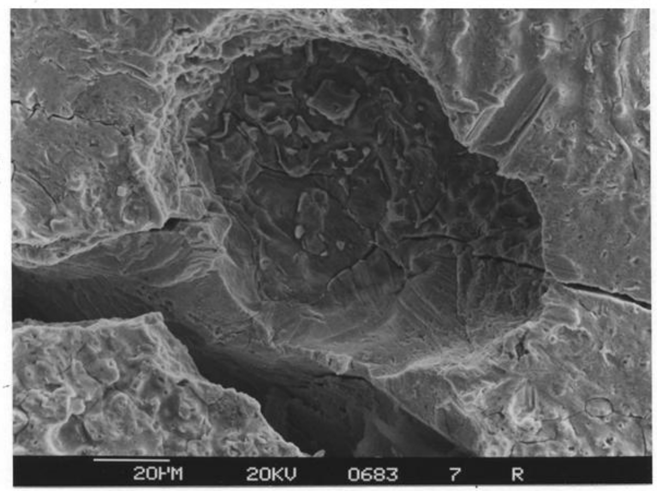


Lichti, unpublished results

NZ Geothermal Steam Comparison - Potential-pH Stability Diagrams





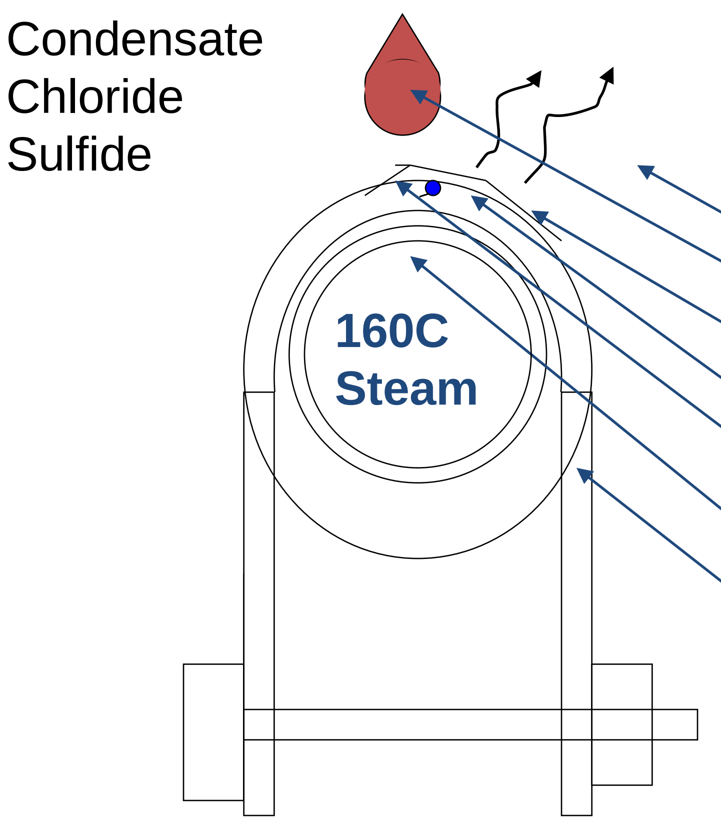


Damage Mechanisms for CRAs (in this case):

- Localised Corrosion (at weld toe)
- Weld Attack (variable metallurgy)
- Fatigue and Corrosion Fatigue (propagation)
- Chloride Stress Corrosion Cracking or Sulfide Stress Cracking (side branching)
- Crevice Corrosion
- Acid Attack
- Sticksion and Galling

Lichti, 2006

Heated U-Bend with Steam Condensate



Susceptible to pitting corrosion and chloride and sulfide SCC

REQUIRED SCC CONDITIONS

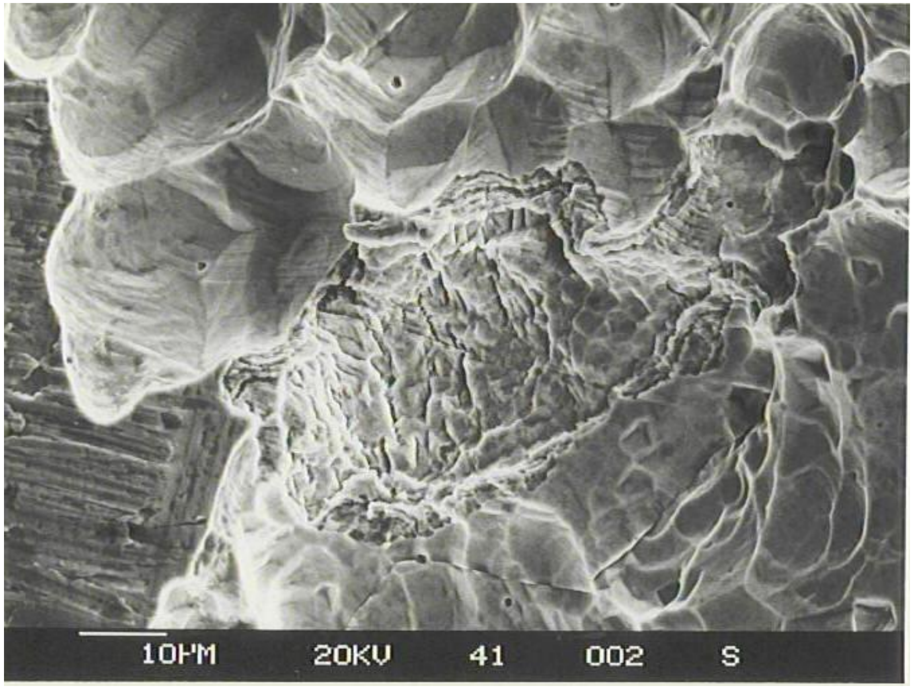
+ Aeration (oxygen)
+ Corrosive Species
+ Evaporative Concentration
+ Moisture (wetness)
+ Tensile Stress (Residual)
+ T > 60 C
+ Material Susceptibility

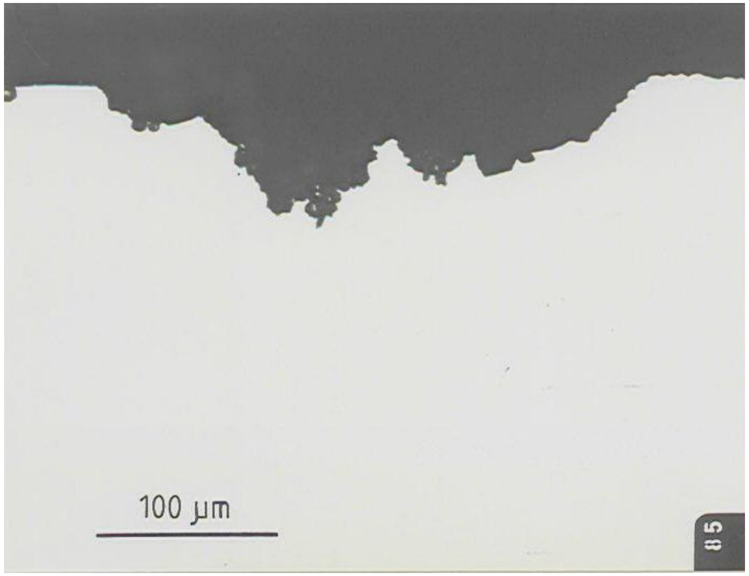
Lichti et al 1995

Selection of Corrosion Resistant Alloys

Cl SCC REQUIRED CONDITIONS

+ Aeration (oxygen)
+ Corrosive Species
+ Evapourative Concentration
+ Moisture or wetness
+ Tensile Stress (residual)
+ T > 60ºC
+ Material Susceptibility





Alloy 2RK65
63 weeks at 100ºC
Drip solution of :

- **geothermal steam condensate**
- **30 mg/kg chloride added**

Cl SCC Cracks May Propagate by Corrosion Fatigue

Lichti et al 1995

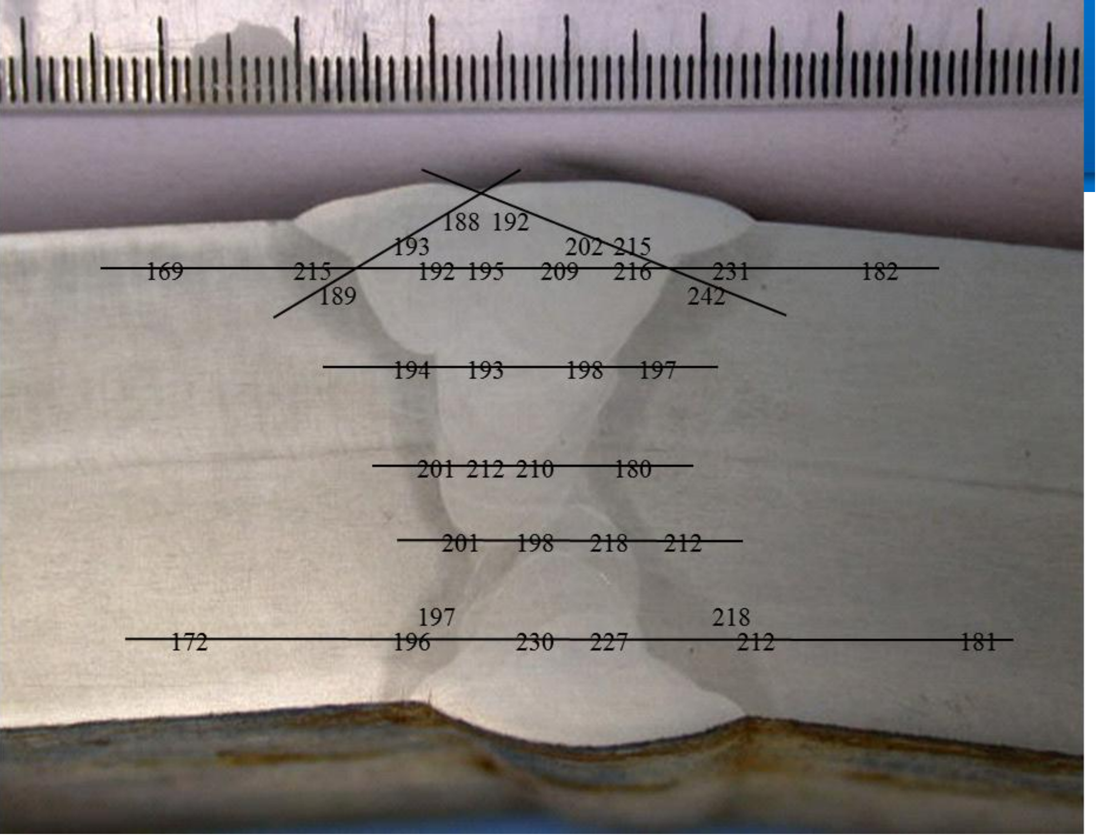
Low Strength Steels Resist Sulfide SCC

Hydrogen readily diffuses into steels and high strength alloys suffer Sulfide Stress Cracking (SSC) or Hydrogen Induced Cracking (HIC/HE)

ANSI/NACE MR0175/ISO 15156-1:2009(E), -2, -3

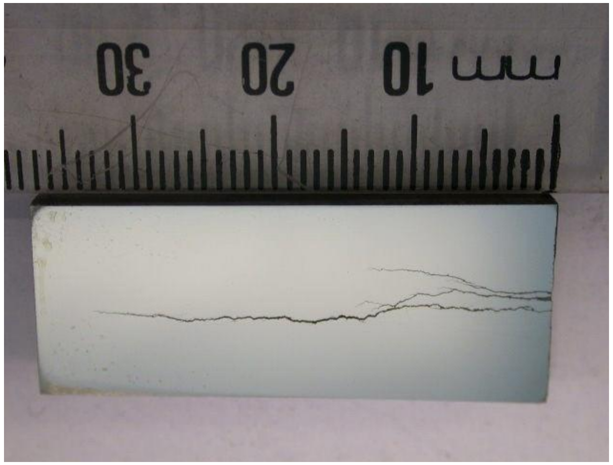
Standard Material Requirement for Sulfide Stress Corrosion Cracking Resistant Metallic Materials for Oilfield Equipment

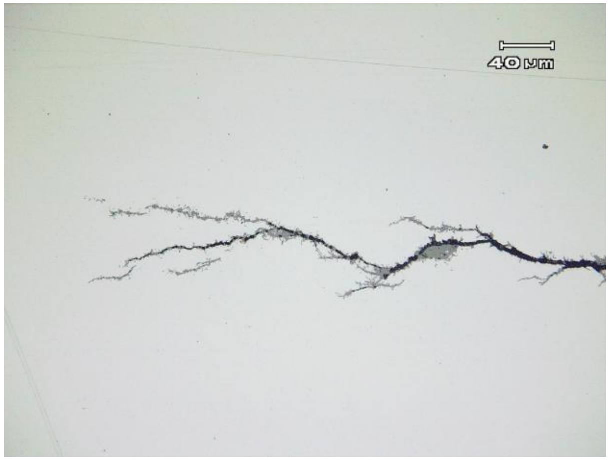
- Sour Water and Sour Gas Systems Definitions.
  - Geothermal Systems Always Considered as “sour.”
- Hardness and Cold Work Limits for Accepted Alloys.
  - Use as low a Strength as can be tolerated by the Design.
- Heat Treatment Processes Specified.
- Materials for Specific Facilities Identified.



Fabricated Vessel

- **Meets hardness criteria of NACE Standard**
- Thickness at limit for heat treatment (ASME).
- Welded with limited number of passes – high heat input.
- High Residual Stress.
- HE or SSC?

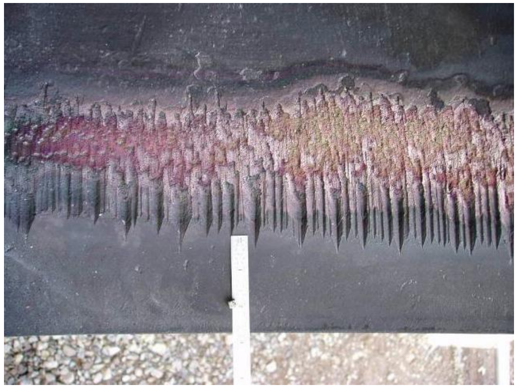




pH Adjust and Heavy Metal Scaling

- Elemental Arsenic and Antimony observed with some pH adjusted Brines.
  - Galvanic and erosion corrosion sometimes observed
  - Reasons for heavy metal scaling not known
- GNS Science Sponsored Laboratory Studies
  - Effect of temperature
  - Effect of pH
  - Effect of aeration / oxidising potential
  - Effect of heavy metal (arsenic vs antimony) and Area Ratios

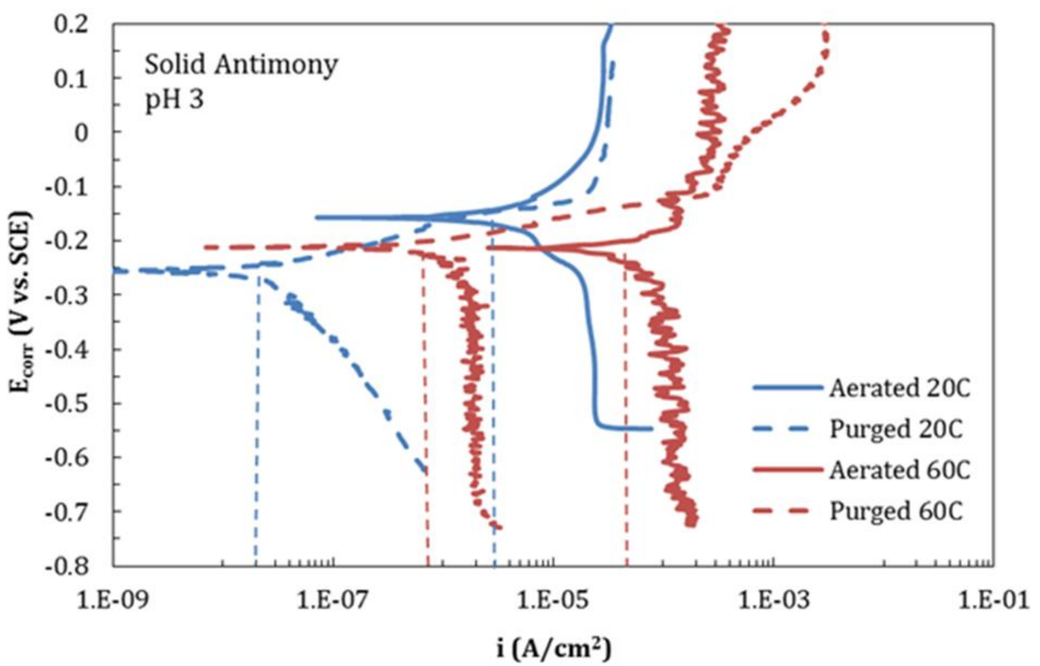
Erosion Corrosion associated with heavy metal deposition



Amend and Yee, 2013

pH Adjust and Heavy Metal Scaling

- GNS Science Sponsored R&D on Galvanic Corrosion
  - Effect of temperature
  - Effect of pH
  - Effect of aeration / oxidising potential
  - Effect of heavy metal (arsenic vs antimony) and Area Ratios



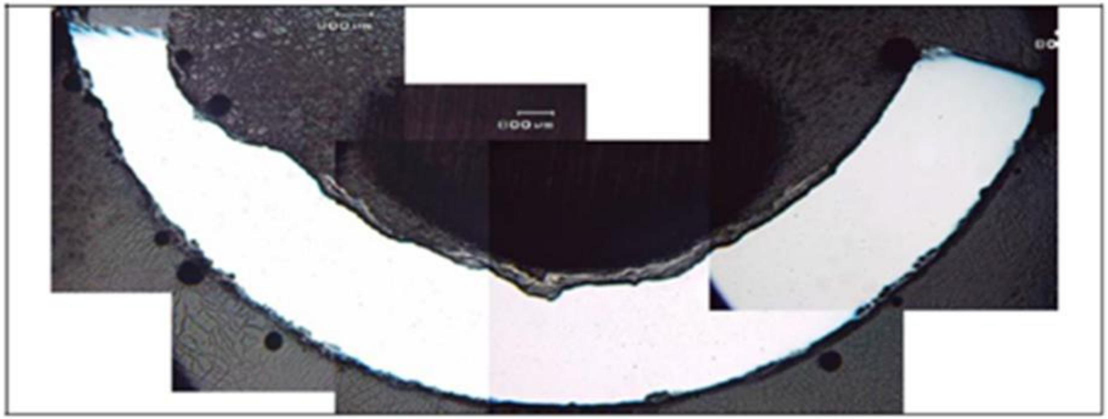
Equal Areas:
CS Corrosion Rates:
0.40 mm/year
0.04 mm/year
1.7 mm/year
0.2 mm/year

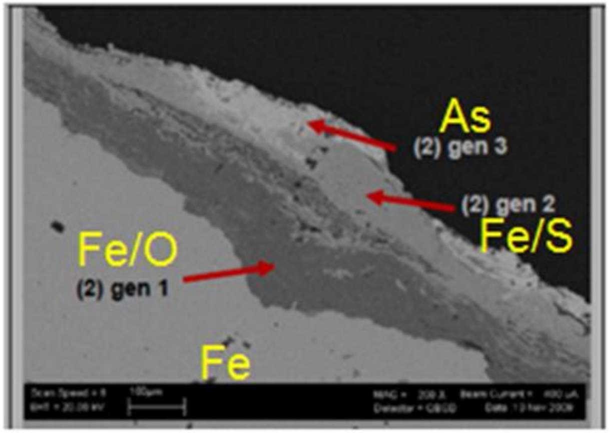
Lichti, et al, 2015

Process Induced Acidity

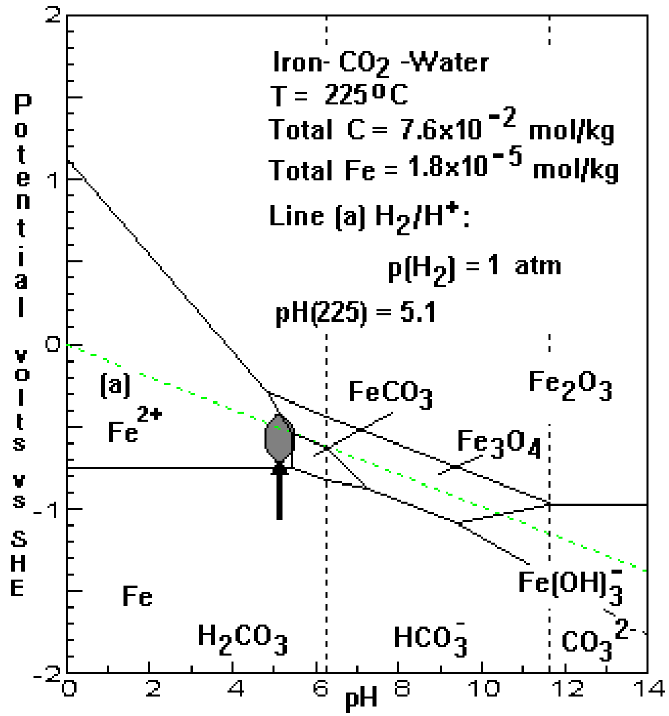
- Chemistry changes in heat exchanger leading to elemental arsenic precipitation
  - Oxidation of steel and reduction of heavy metal
  - Galvanic corrosion contribution to the failure

Oxidation of Iron	$Fe \rightarrow Fe^{2+} + 2e^-$
Reduction of Arsenic	$AsO^+ + 2H^+ + 3e^- \rightarrow As_{(s)} + H_2O$

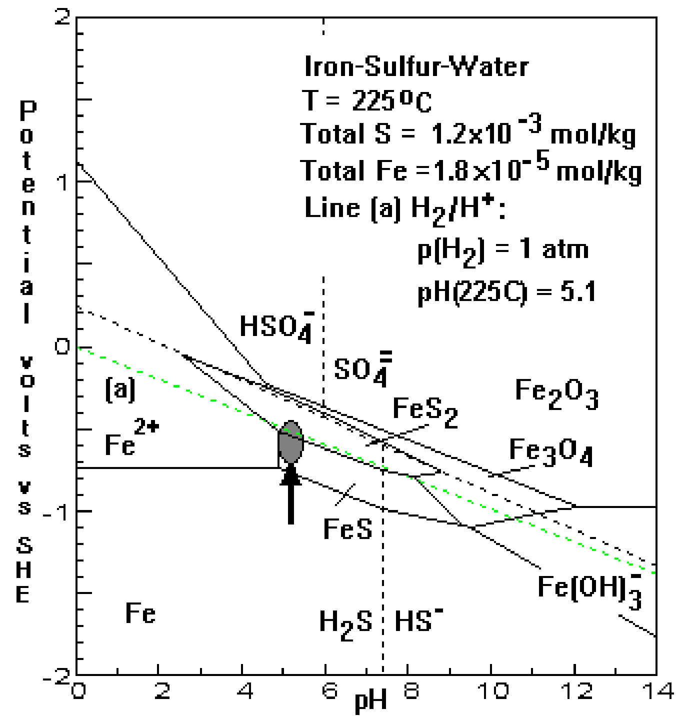




CO_2 Corrosion - Corrosion Product Stability



Model Chemistry with pCO2 = 6.9 bara



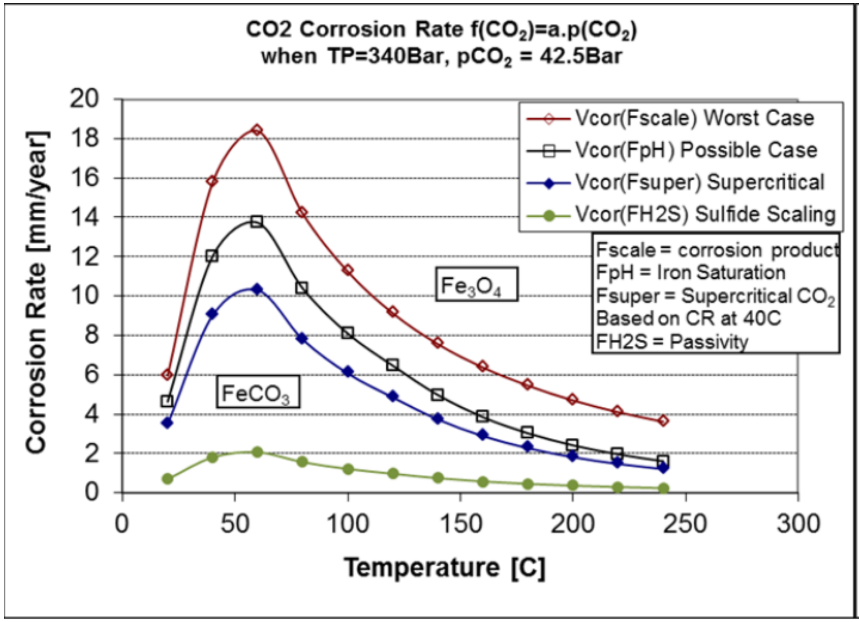
Model Chemistry with pH2S = 0.02 bara

Lichti, unpublished results

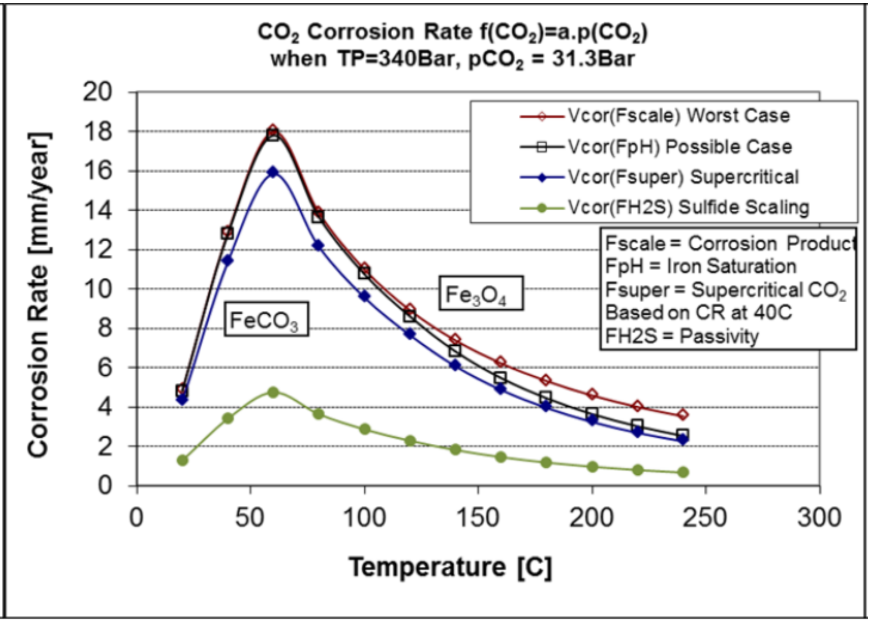
Engineered Systems CO_2 Corrosion

Factors leading to risk of CO_2 Corrosion:

- Partial pressure of CO_2 – lower pH gives higher risk
- Temperature – lower temperatures give higher risk
- Flow Velocity – lower soluble iron in solution gives higher risk
- Inhibitors – H_2S at a low level reduces the risk of CO_2 Corrosion



T > 120ºC



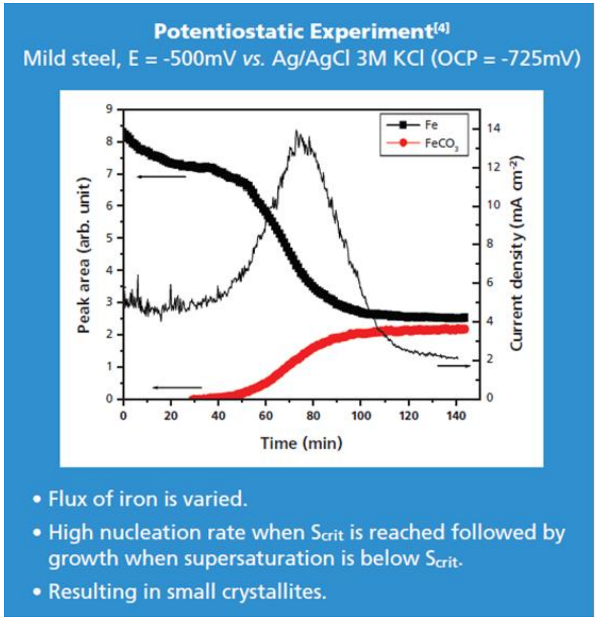
T < 120ºC

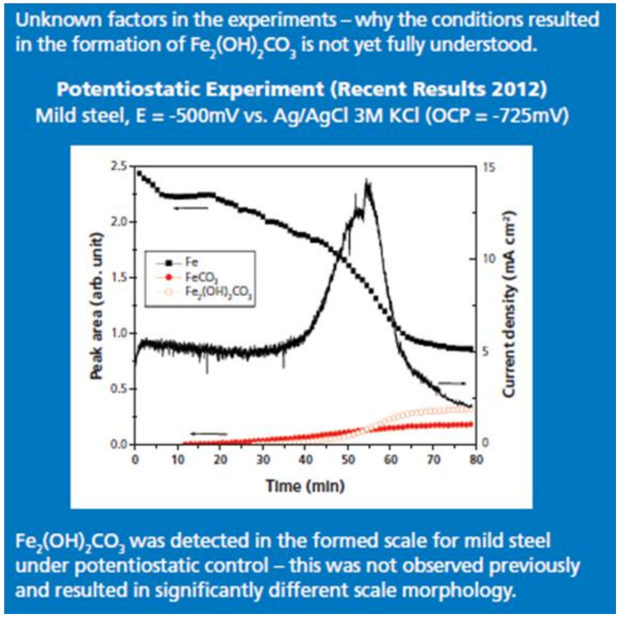
Humphreys et al, 2015

Oil and Gas R&D on CO_2 Corrosion

In-situ synchrotron X-ray diffraction (XRD) on Properties of Protective Films

- Study of Controlling Parameters for CO2 Corrosion
  - Effect of Alloying, Inhibitors, Flow Velocity, H2S Concentration
- Extension of New Zealand MBIE project - Qatar University, Callaghan Innovation, Quest Integrity, GNS Science, University of Auckland, plus industry interested parties

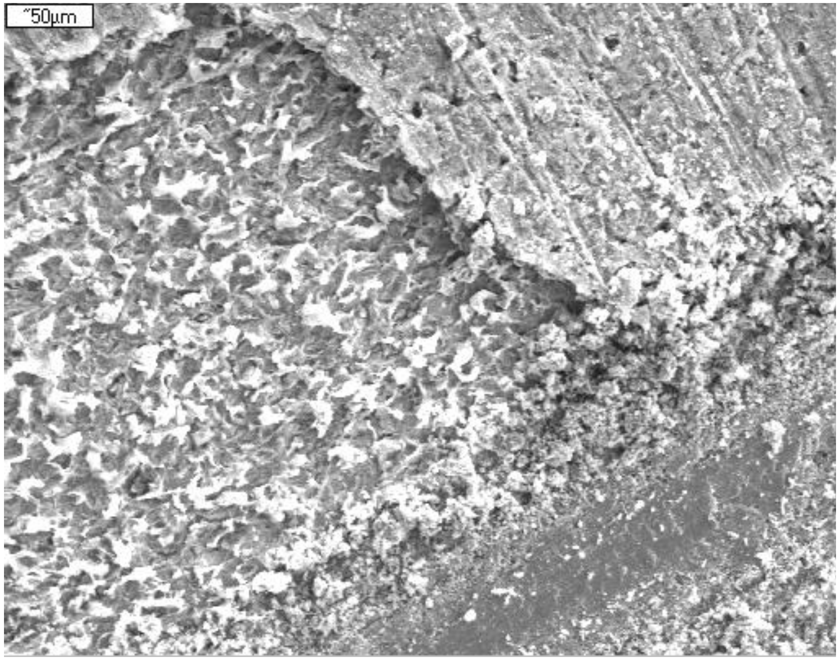


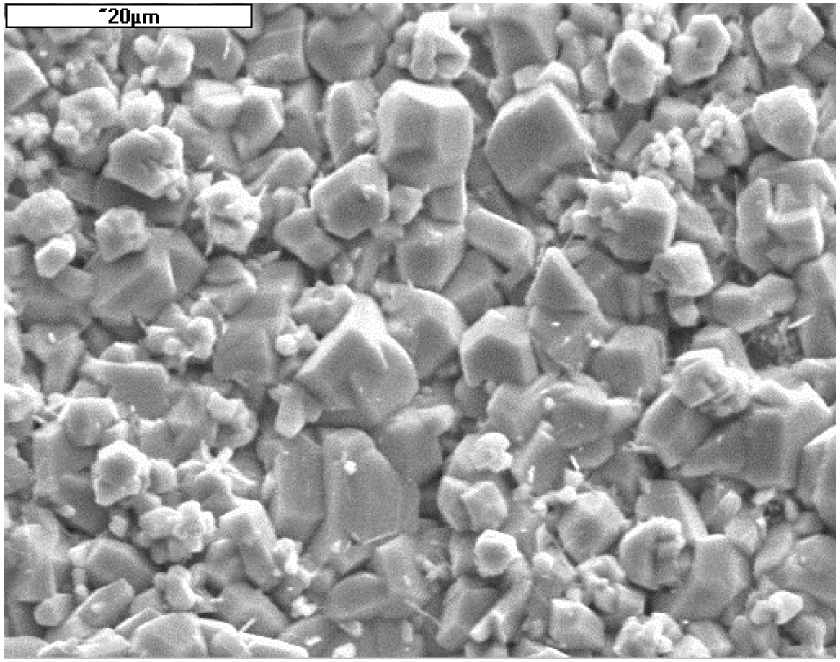


Ko et al, 2012

pH Adjust and Acid Well Environments

Acidic Environments have different film properties



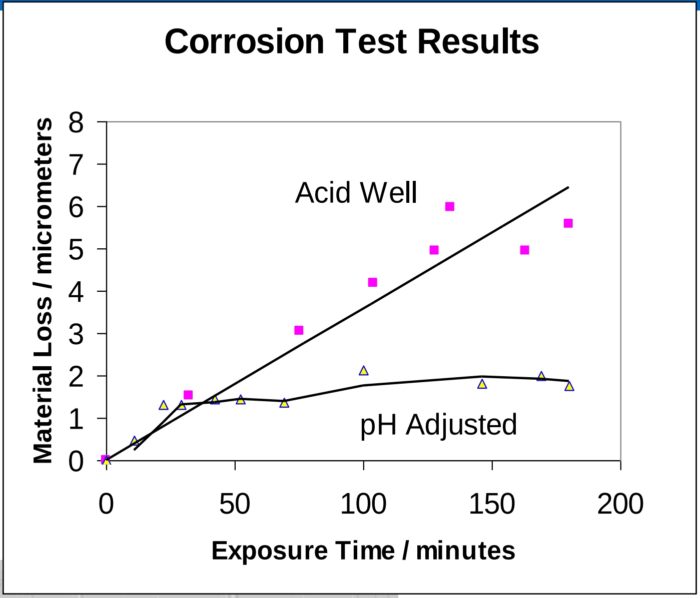


S4, pH 3, 150^{o}C, $SO_4^{=}$ + HS^{-}, 24 h
Major Fe(1+x)S Mackinawite
Minor: FeS Troilite

S4, pH 5, 150^{o}C, $SO_4^{=}$ + HS^{-}, 12 h
Major: FeS Troilite
Minor: Fe(1+x)S Mackinawite

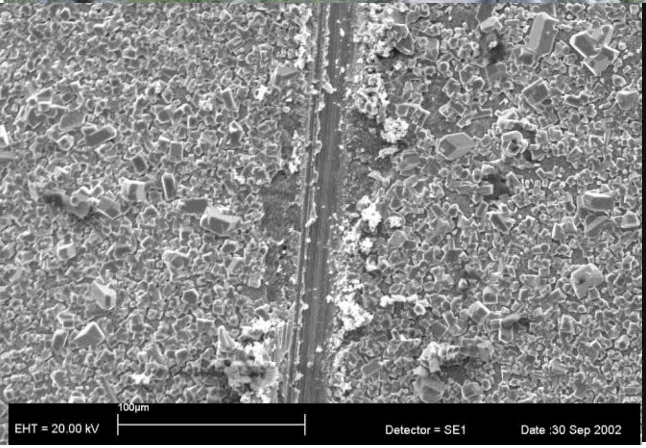
Lichti, Engelberg and Young, 1999

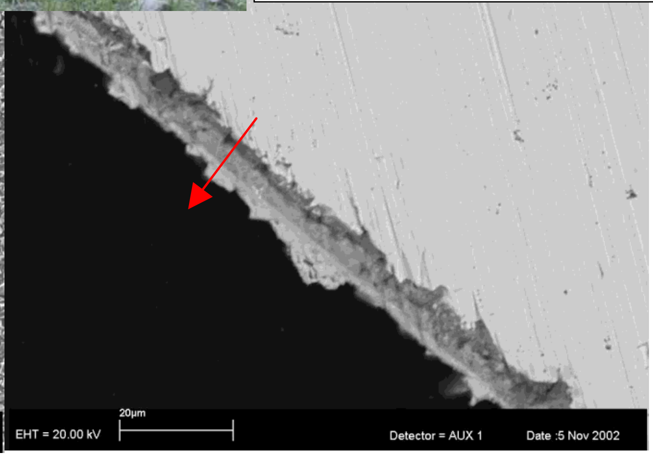
Field and Laboratory pH Adjustment

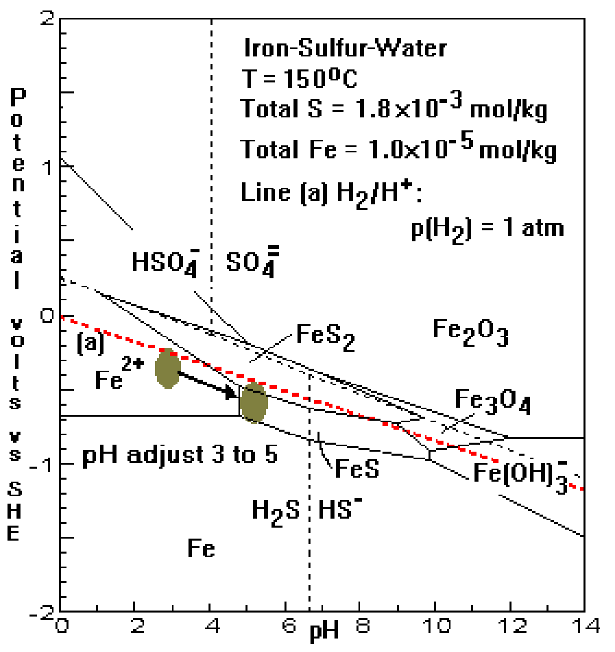


Villa et al, 2001

Lichti, Klumpers and Sanada, 2003







	Bottom	Middle	Top
	wt%	wt%	wt%
Fe_3O_4	93	79	3
FeS	7	21	97

Risk Based Assessment - Concepts

- Risk Based Assessment / Aging Power Plants
  - Likelihood of Failure: Damage Mechanisms, Location of Damage, Rate of Damage Accumulation
  - Consequences of Failure: Health and Safety, Environmental, Cost of Repair and Unplanned Outage
- Risk = Likelihood * Consequences
- Risk Based Inspection: Maintenance Planning, Focused Turnaround Efforts, To Industry Codes, No Unplanned Outage – Living Documentation for Lessons Learned
- Integrity Operating Windows – Management of Change, Validity Range for Risk Assessment

Lichti, et al, 2012

Typical Damage Mechanisms

Lichti et al, 2005

Ramos et al, 2003

- Erosion at Elbows
- Passive Film Formation
- Localised Pitting Corrosion

Lichti et al, 2003

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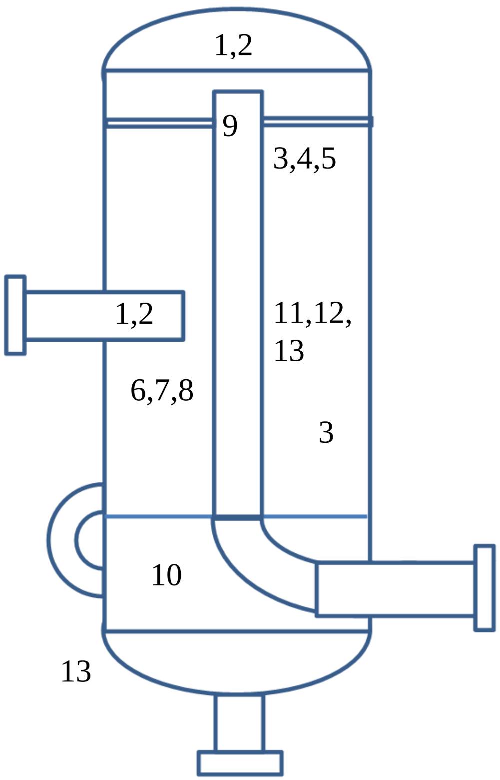
Damage Mechanisms to Look For



Damage Mechanisms

1. Erosion Corrosion
2. Solids Erosion
3. SSC and HE
4. Fatigue
5. Corrosion Fatigue
6. Surface Corrosion (Uniform)
7. Localized Corrosion (On-Line)
8. Localized Corrosion (Standby)
9. Silica Scaling (Flashing)
10. Monomeric Silica Scaling (Surface Deposition)
11. Heavy Metal Deposition
12. Galvanic Corrosion
13. External CUI

Inspection Techniques

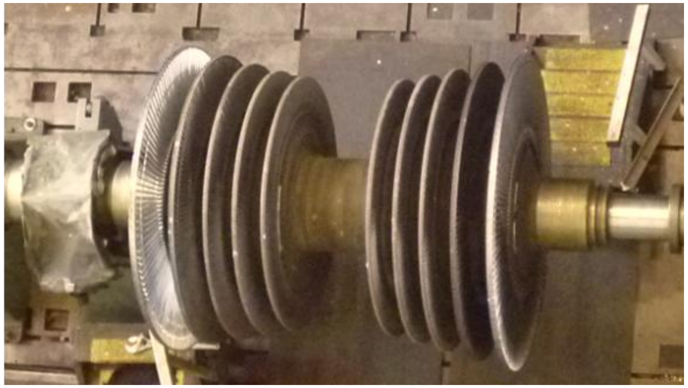
A. Internal Visual (Mechanical Measurements)
B. UT Wall Thickness
C. MPI
D. Portable Hardness
E. Portable XRF (Corrosion Product / Scale Collection and Analysis)
F. Dye Penetrant

Following the format in API 571

Lichti et al, 2013

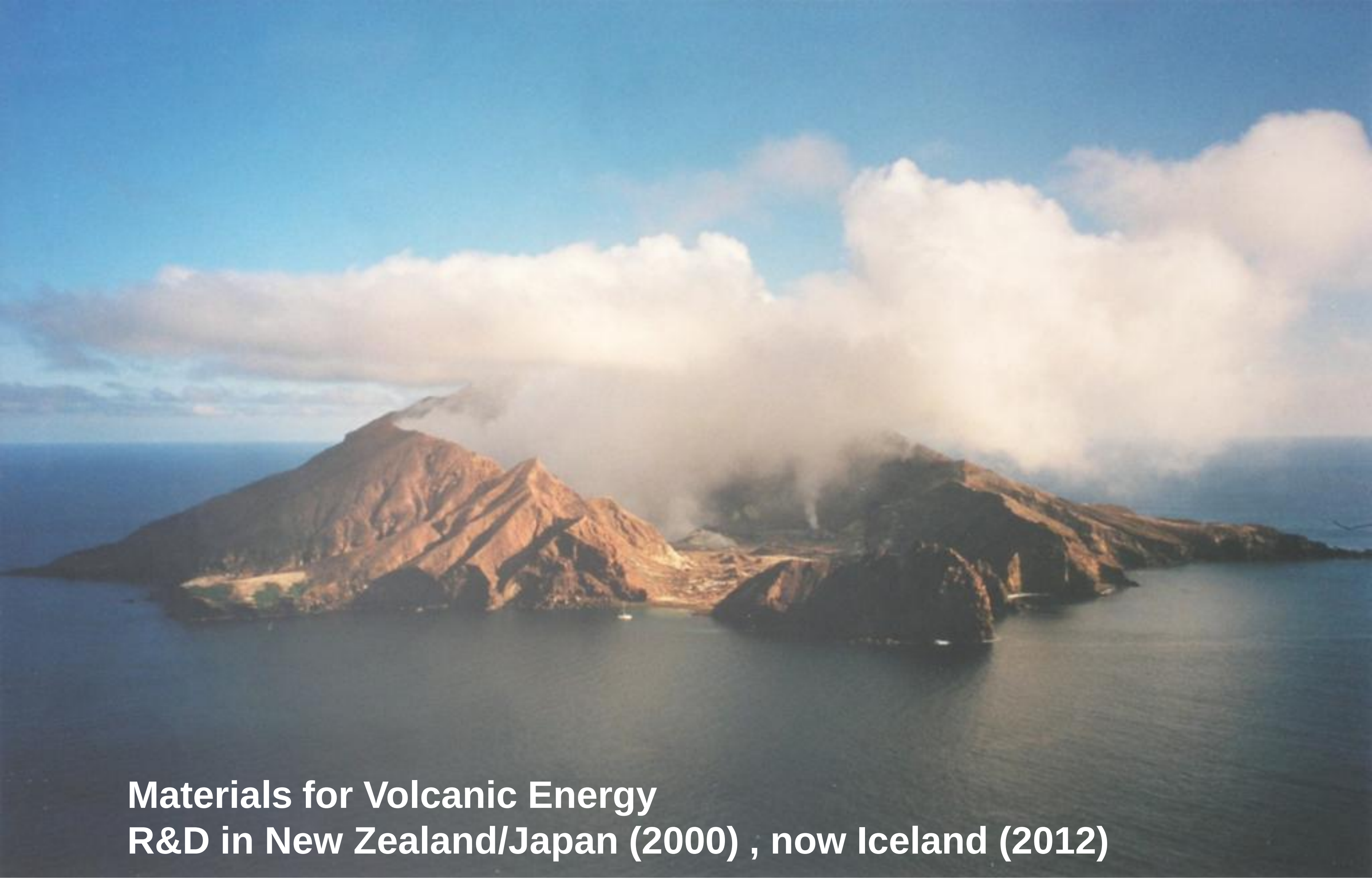
Geothermal Steam Turbine Users Group

- To understand damage mechanisms and expected lifetimes of geothermal steam turbines and associated components
- To participate in joint research projects
- To share experiences and exchange information
- To share information on design upgrades
- To research, develop and optimise inspection and refurbishment / replacement strategies



In Summary – Many Rules … But

1. Oxygen corrosion can be controlled
2. Corrosion Resistant Alloys can be selected
3. ANSI/NACE MR0175/ISO 15156-2&3:2009(E) must be applied
4. Process and materials changes should be approached with caution:
   - New material-environment combinations present new problems
   - Start with the basics and test to verify assertions
5. Learning from Experience and Sharing
   - Anticipation of Issues and Industry Groups



White Island, New Zealand: ?,000 MWe for ?? Years

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