SAND2016-2596 C

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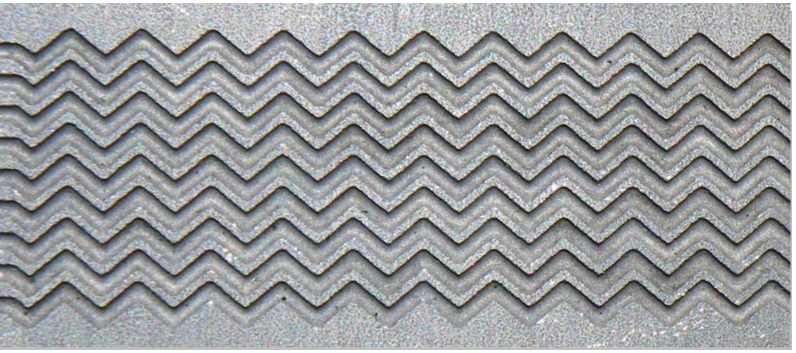

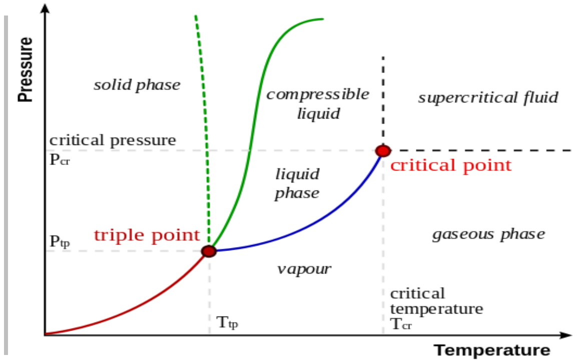

Short Duration Corrosion Performance of Carbon Steels in SCO_2 at 260°C

Matthew Walker, Alan Kruizenga, Elizabeth Withey, Darryn Fleming, Jim Pasch

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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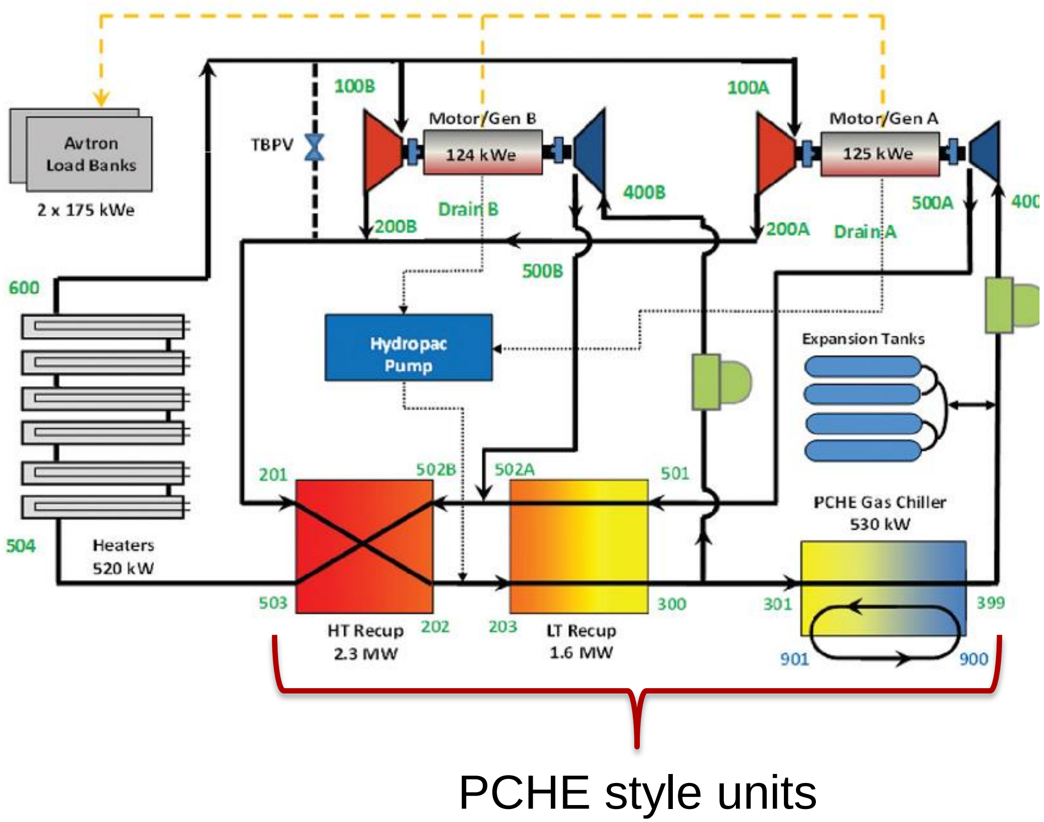
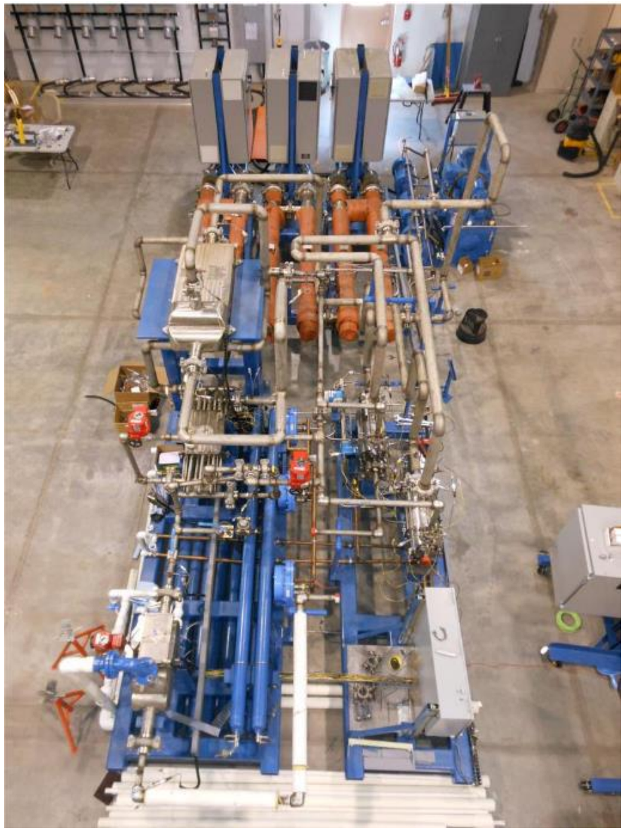
Leading the development of a game-changing technology

SCO_2 Recompression Brayton Cycle (RCBC)

- SCO_2 is a highly recuperative cycle: projected capital costs expect 40-60% of cycle cost due to heat exchangers
- Can cost savings be achieved in other areas of the system?





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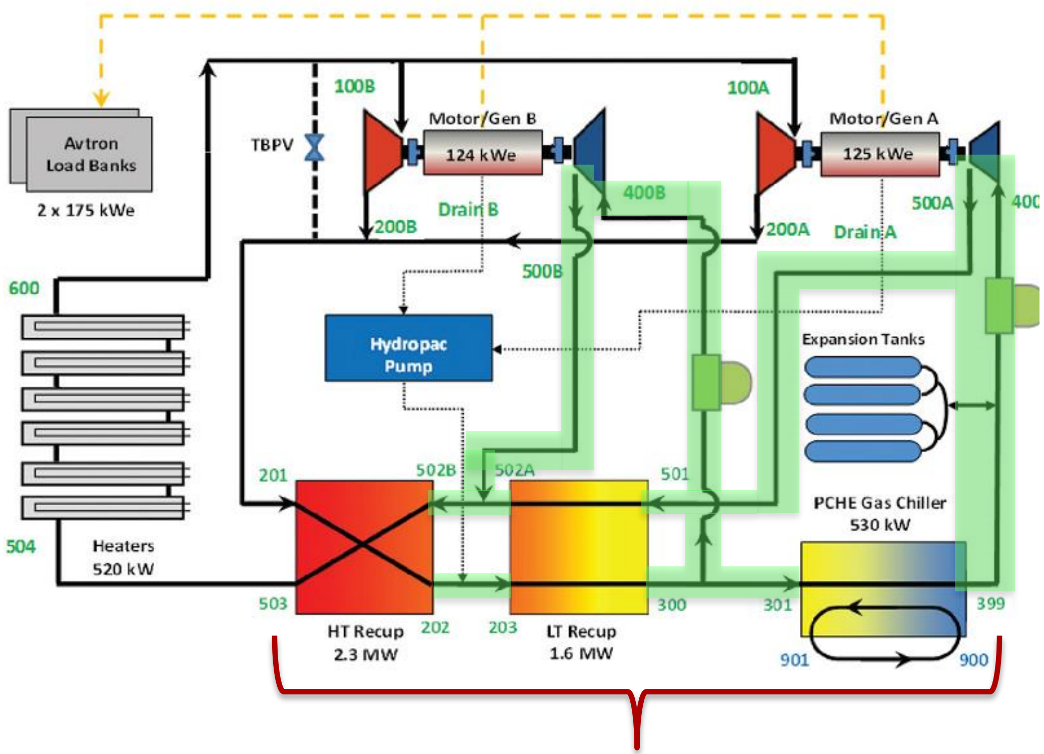


PCHE style units

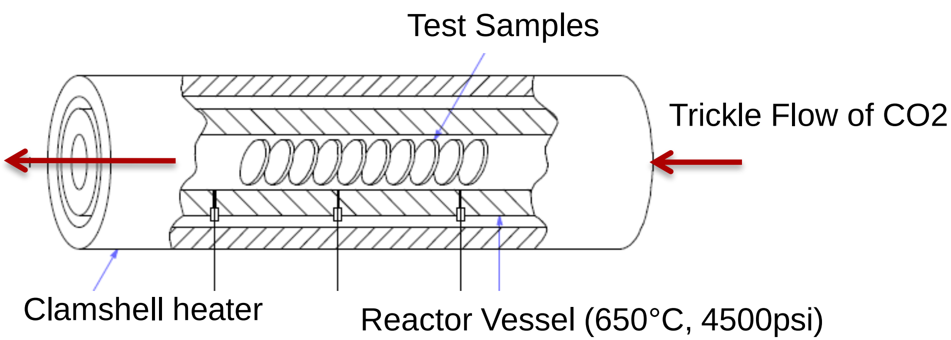
- **<u>System Piping</u>**
  - Significant portion at < 260^{o}C (573K)
- **<u>Pipe wall thickness similar for carbon steel as for 316 (~ 0.25 inches)[A]</u>**
- **<u>Carbon steel ~ 44% cheaper than 316</u>**

[A] For ID 2” Pipe @ P = 30 MPa and 600K using data from ASME B31.1 (2014

Expanding SCO_2 materials testing capabilities at Sandia

SCO_2 Materials Test Facility

- Test Volume size: 2”x 24” (cylinder)
- Up to 650°C, 3500psi
- CO_2 currently, also other fluids possible



Facility used to test materials performance over operational range of system requirements.

Determining suitability of mild steel for the Brayton cycle

Materials and Test Exposure

Per the Power Piping code (ASTM 31.1):

- X65Q
- A53, A106, and API-5L
- Seamless Low-Carbon Alloy
- Limited to 427°C (code indication carbide phase may be converted to graphite)

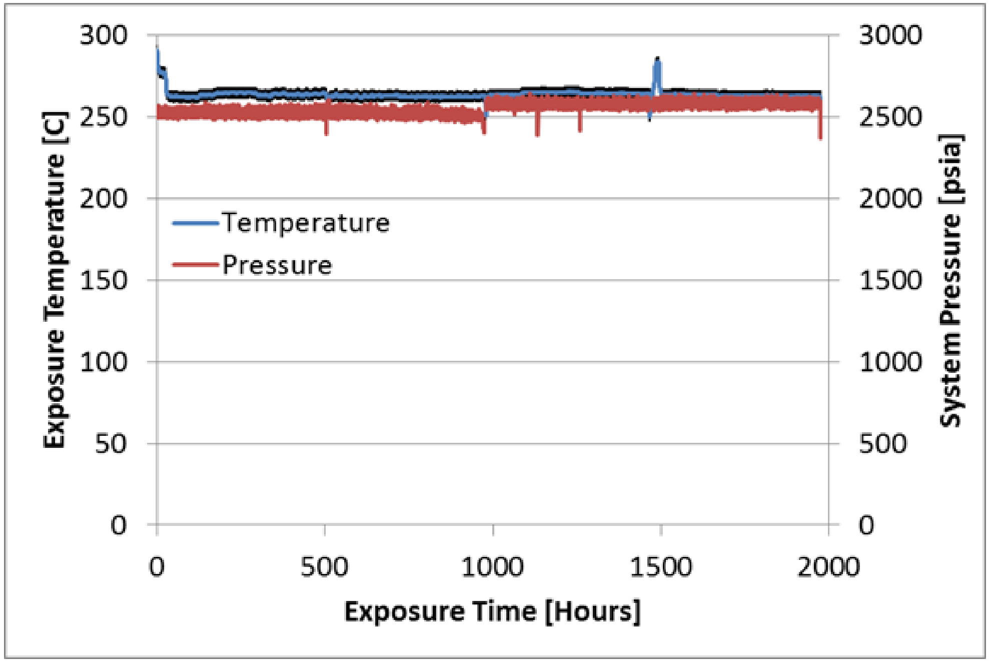
Fe	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	Al	V	B	Ti	Nb
Bal	0.15	0.97	0.012	0.003	0.18	0.09	0.05	0.07	0.11	0.31	0.034	0.0003	0.003	0.002

Samples were removed at:

- 506 hours
- 995 hours
- 1481 hours
- 1984 hours

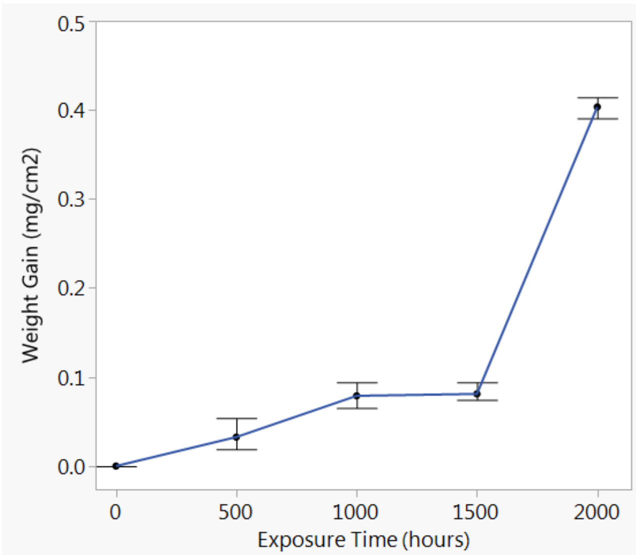
Exposure was 263±3°C
2550±35 psia

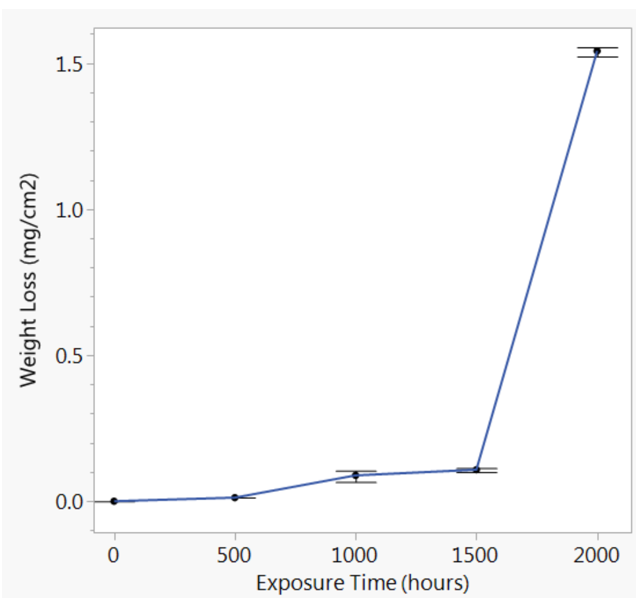
Industrial Grade CO_2 (99.5% Purity)

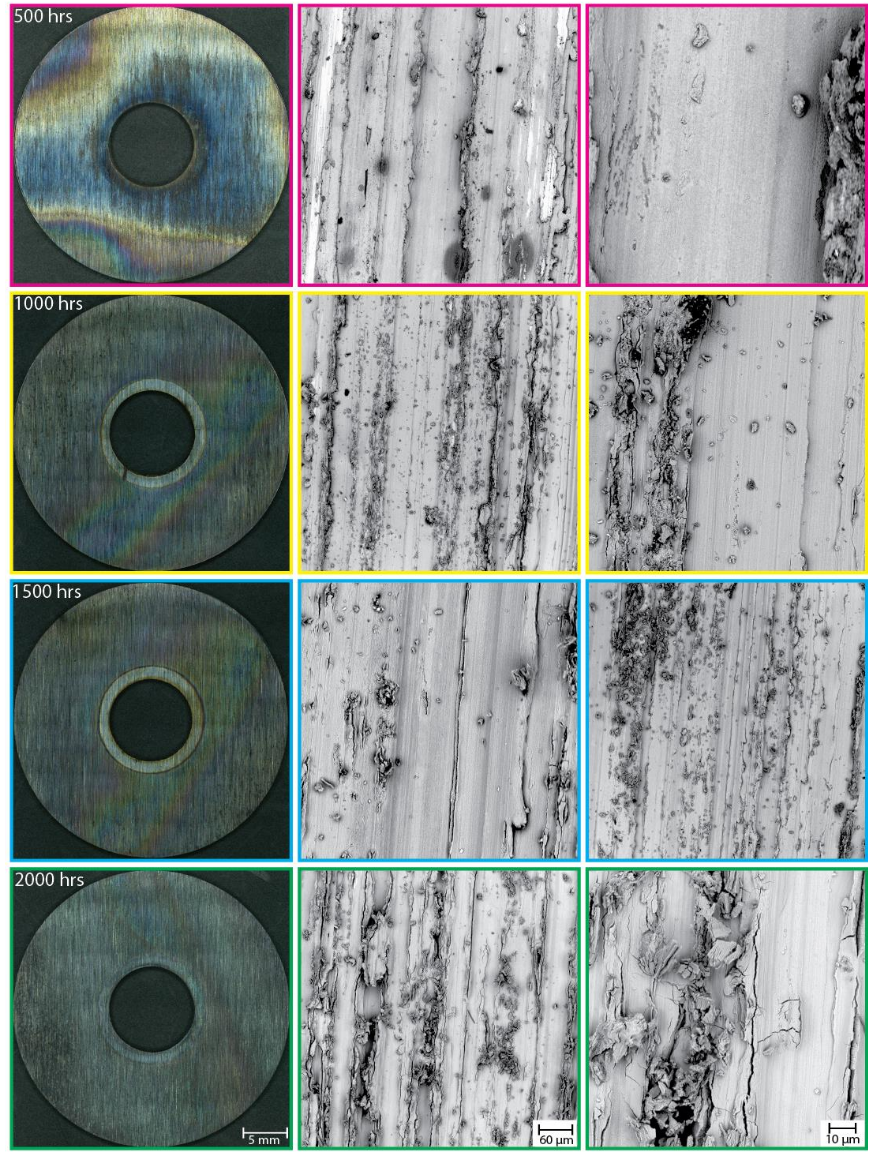


Consistent trend among the measurement approaches

Sample Corrosion Versus SCO_2 Exposure Time







Corrosion products are non-uniform and multilayered

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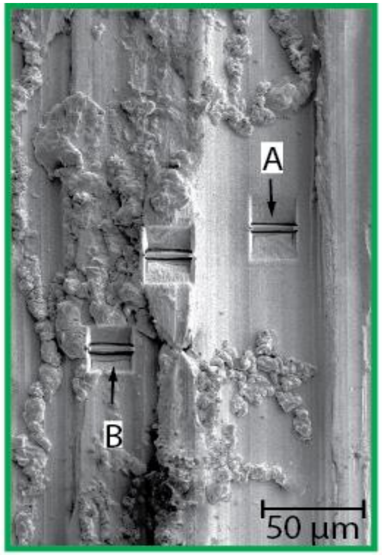
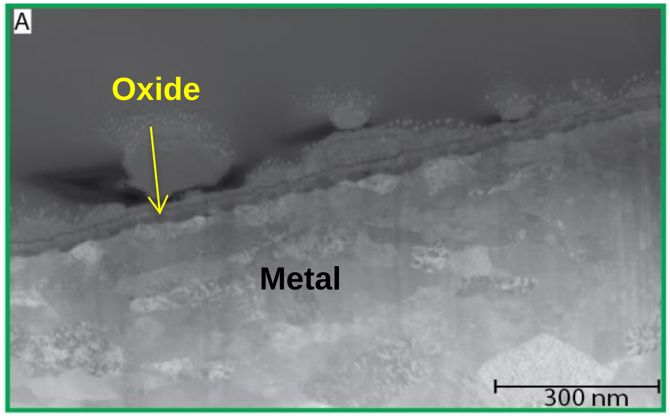
Oxidation Layer Morphology versus SCO_2 Exposure Time

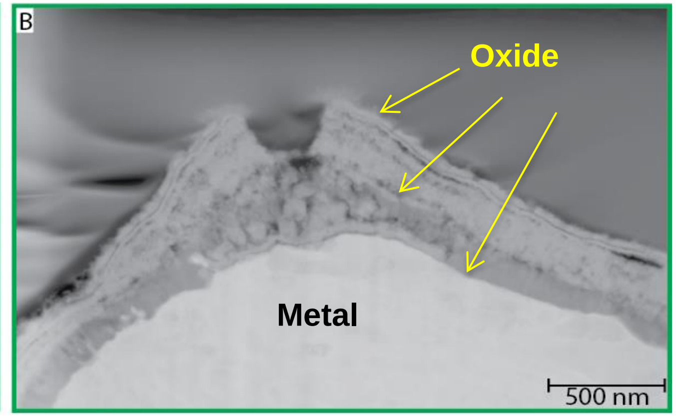


500 hrs

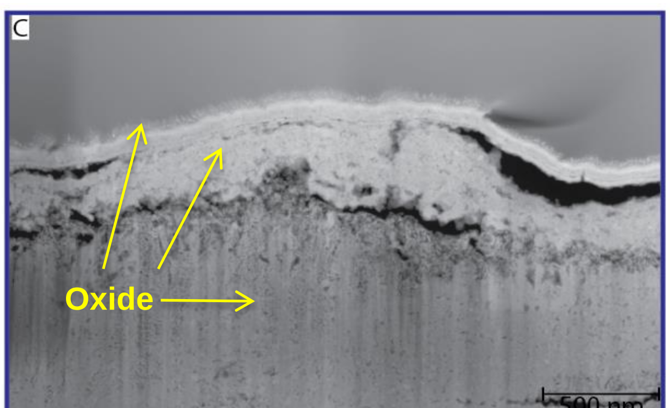
Low Area

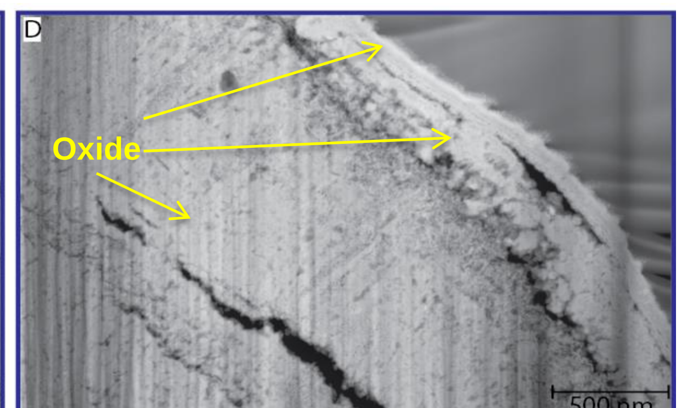


Raised Area



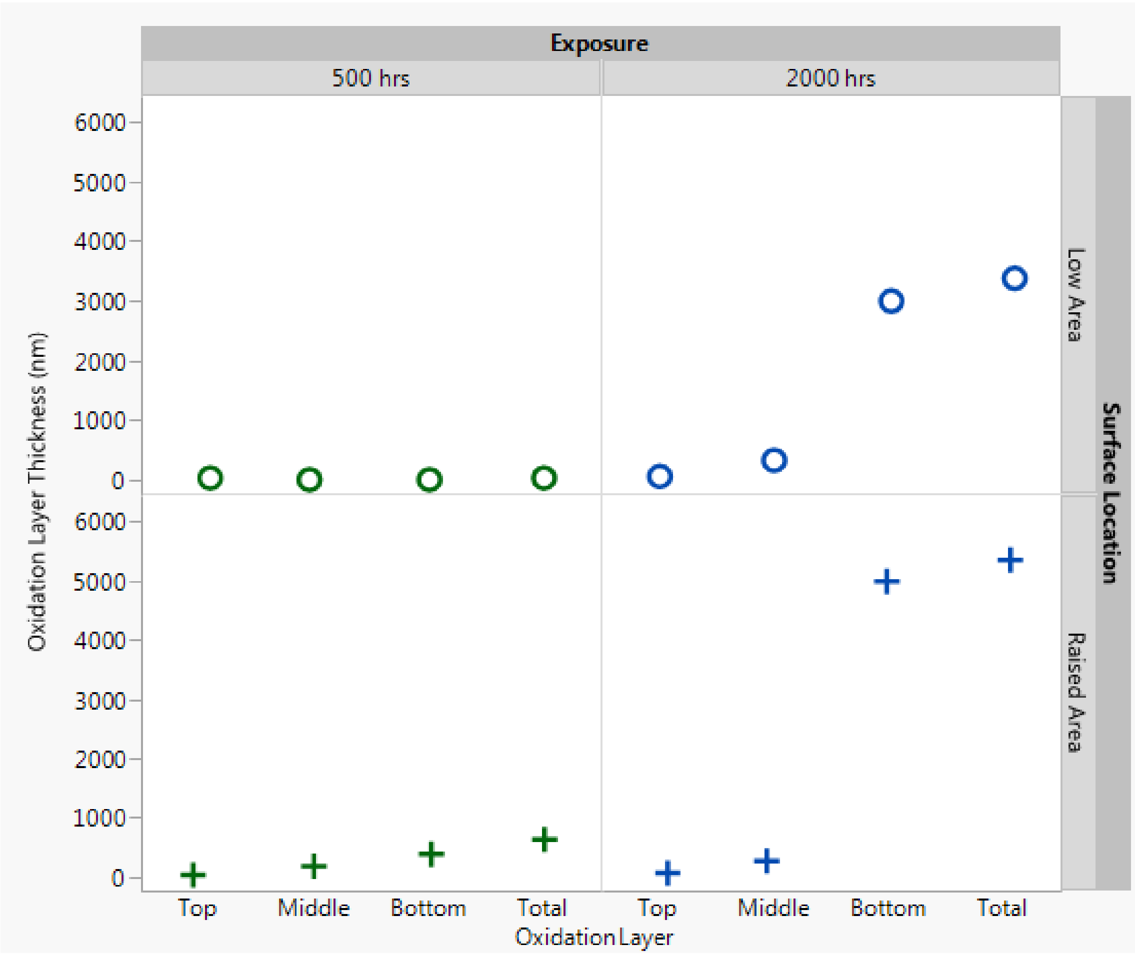
2000 hrs



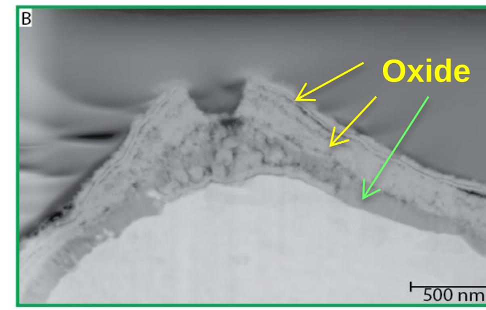


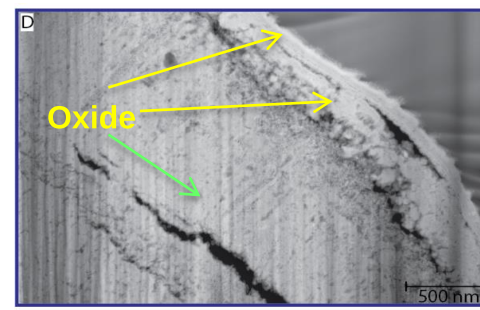
Internal Oxide Layer Growth --> Increased Corrosion Rate

Oxidation Layer Thickness versus SCO_2 Exposure Time



Raised Area

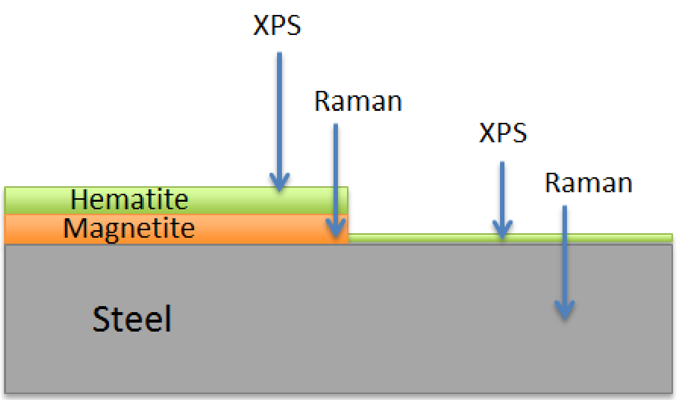


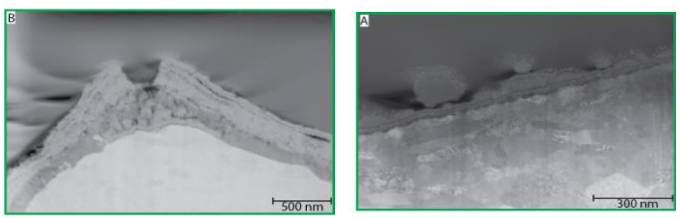


Characterization of surfaces reveals separate oxide phases

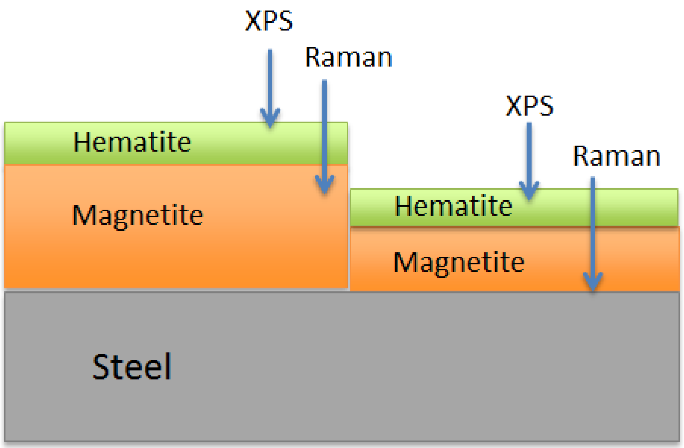
Summary of XPS and Raman Surface Analyses

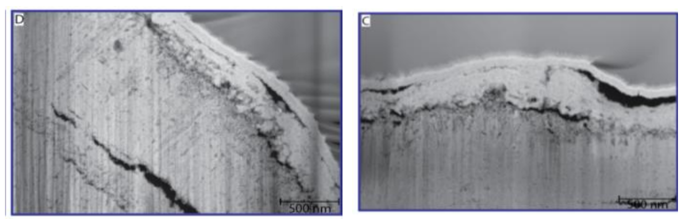
500 h sample





2000 h sample





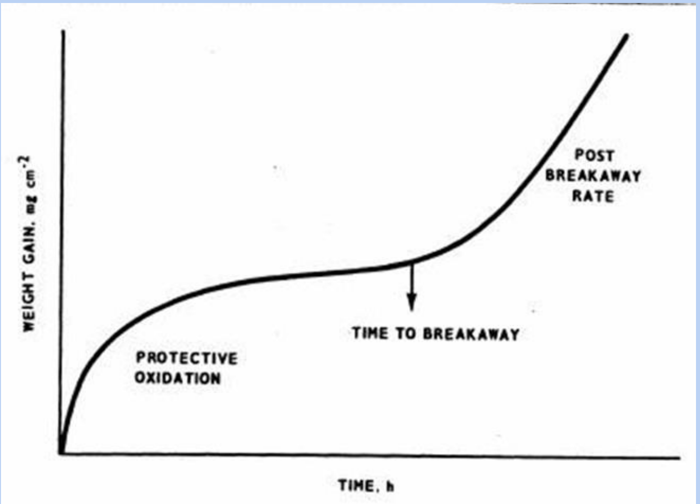
Probing Depths

XPS	2-3 nm
Raman	>1 μm
XRD	>1 μm

- Surface layer is Hematite (Fe_2O_3) --- XPS reveals only Fe^{3+} at the surfaces
- Raman and XRD indicate the presence of both Hematite (Fe_2O_3) and Magnetite (Fe_3O_4)
- Combination of these analyses reveals a bi-layer structure with corrosion being dominated by Magnetite growth over time

Results consistent with mild steel corrosion in CO_2

Behavior of Mild Steel during CO_2 Exposure

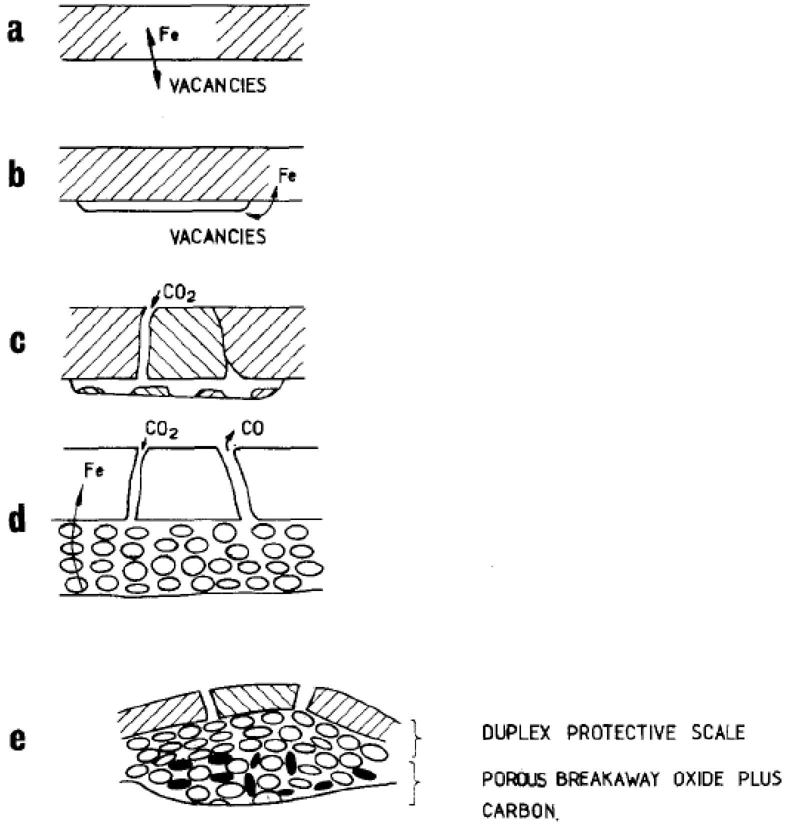


J. Ferguson, B.N.E.S. International Conference on Corrosion of Steels in CO_2, September 1974.

$$3Fe + 4CO_2 = Fe_3O_4 + 4CO$$

$$2Fe + 3CO_2 = Fe_2O_3 + 3CO$$

$$2CO = CO_2 + C$$

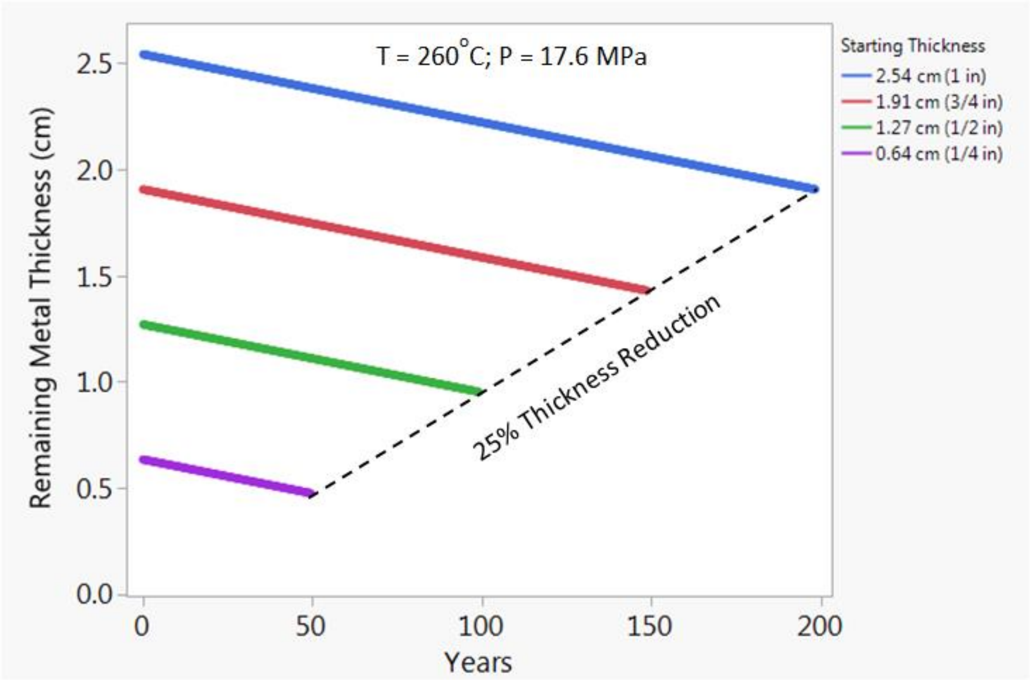


G. Gibbs, Oxidation of Metals, Vol. 7, No. 3, 1973

Low corrosion rate merits consideration in SCO_2 systems

Summary of Results

- Weight loss data used to determine:
  - Time to breakaway ~ 1500 hrs
  - Post-Breakaway Corrosion Rate: 0.032 mm/year (1.25 mils/year)
- Applicability of mild steel for components in SCO_2 Brayton cycles
  - Low corrosion rate projects long lifetime for parts
  - Susceptibility of scale to spalling is a concern as it grows thicker; this could lead to component erosion ---- Need to look at longer term exposure



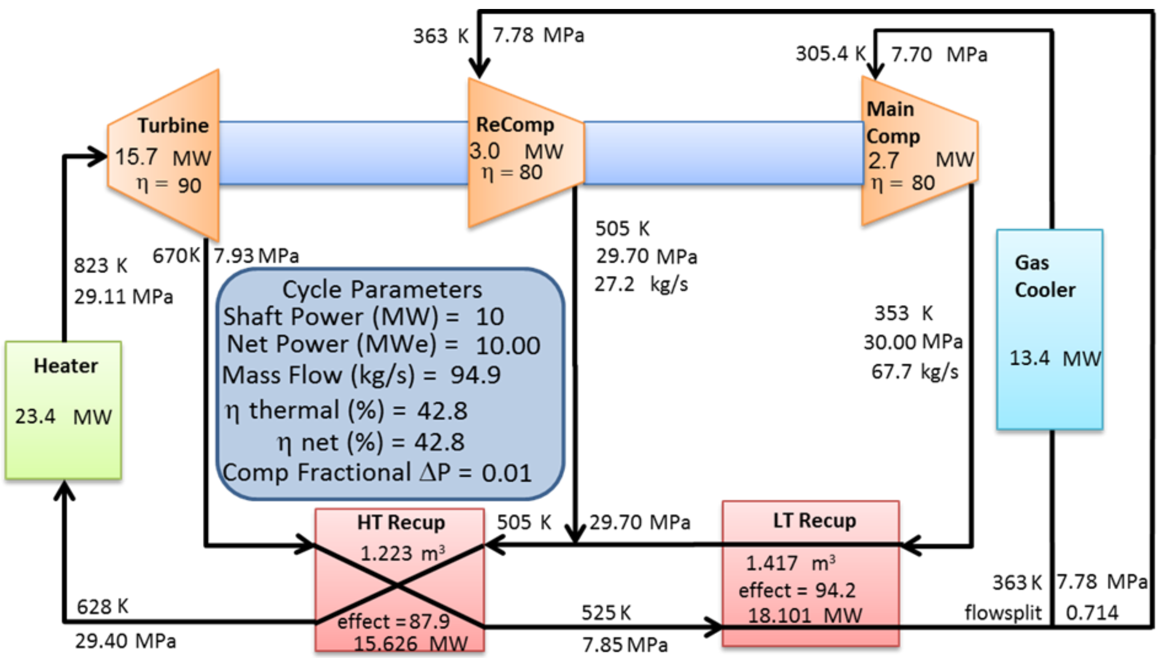
Identifying Material Options for a 10 MW RCBC Systems

Sandia National Laboratories

10 MW System Component Materials Selection for TIT's 550^{o}C and 700^{o}C

- Defining exposure conditions and performance requirements
- Identification of alloys and their characteristics that satisfy the performance requirements for each component

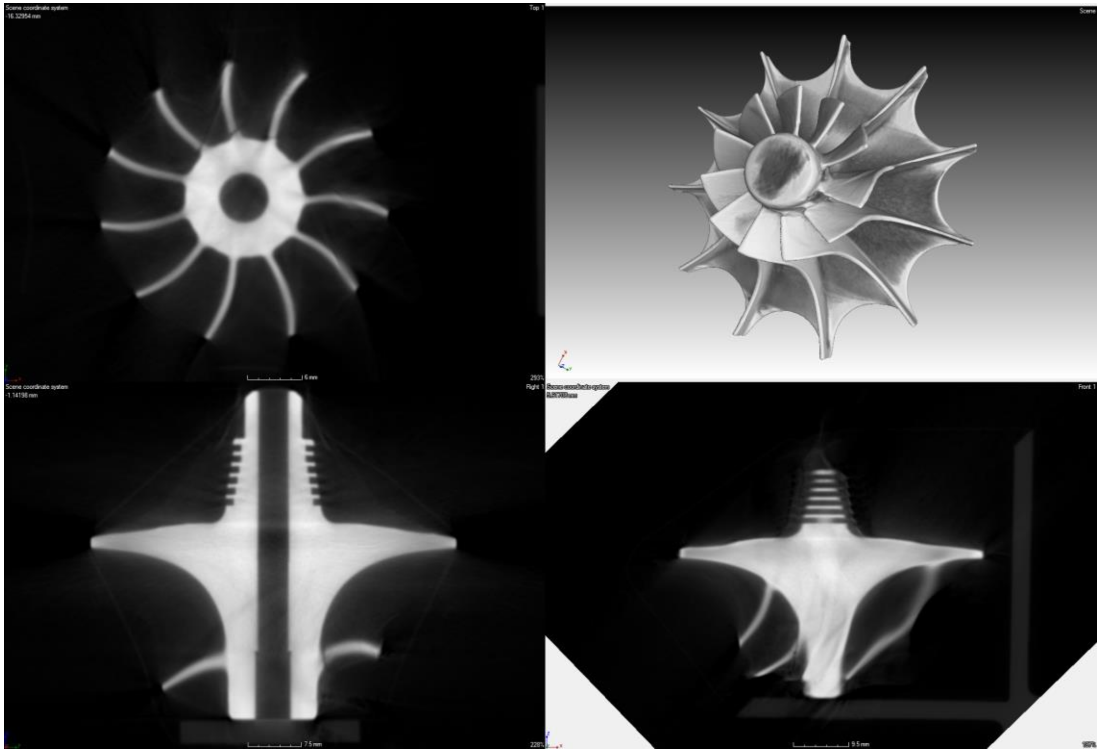
TIT = 550^{o}C, Wet Cooling



Understanding and Resolving Turbine Degradation

Turbine Degradation Root Cause Analysis (RCA)

- RCA conducted in February 2016 provided many possible causes of turbine degradation
- Next phase is to prove/disprove prioritized list of causes



Computed Tomography (CT) being used to identify turbine degradation

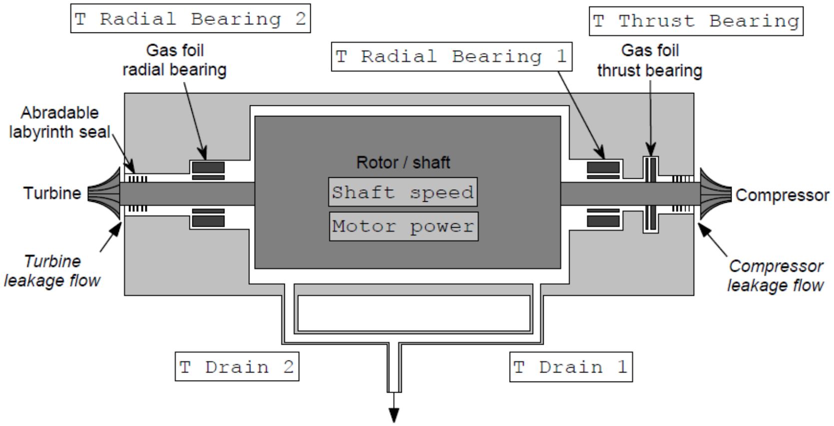
Identifying Bearing Foil Material Behavior in CO_2

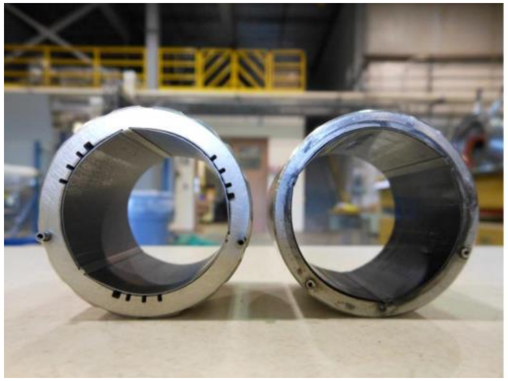
Bearing Foil Experimental Plans

Source	Temperature, °C	Pressure, psi	Duration, hrs
Mohawk Innovative Technologies	315, 550	300	500, 1000, 1500, 2000
Xdot Engineering and Analysis			
Baseline			

Measurements (Pre + Post Exposure):

- Microstructure of base metal plus coating
- Coating adhesion strength
- Coating surface roughness
- Coating coefficient of friction





Identifying Gas Chemistry Influence on Alloy Corrosion

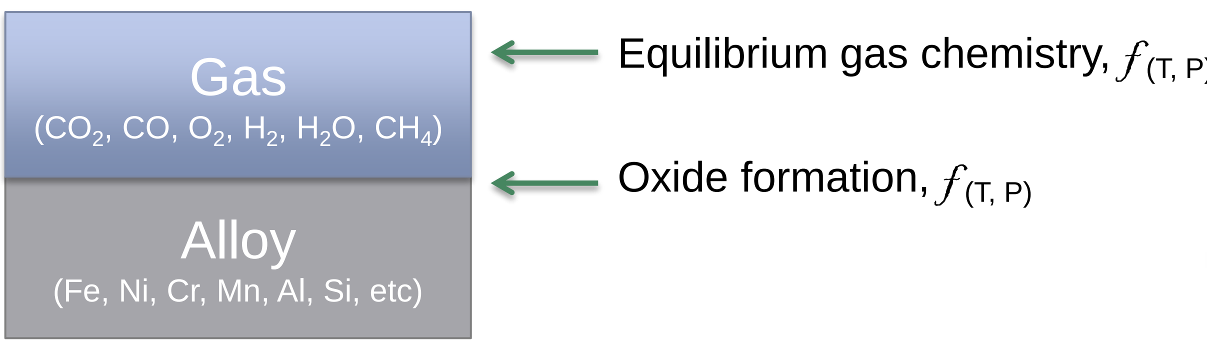
Multiple Approaches to Gas Chemistry Understanding

- **Corrosion experiments**
  - Alloys: 625, 316, HR120, Grade 91, T22
  - T = 550ºC
  - Pressure = 1 atm
  - Duration = 500, 1000, 1500, 2000 hours

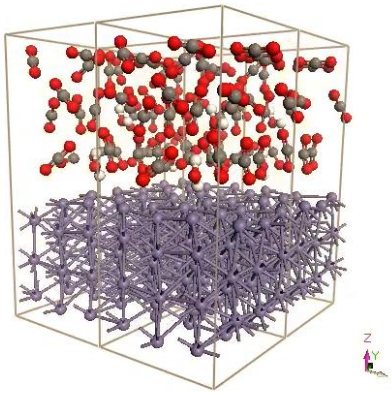
CO_2	CO	O_2	H_2O	H_2	CH_4
Research Grade 99.999%	< 2ppm	< 2ppm	< 1ppm	< 2ppm	< 4ppm
Industrial Grade 99.5% *	A	B	C	D	E
99.5%	0.5%				
99.5%		0.5%			
99.5%			0.5%		
99.5%				0.5%	
99.5%					0.5%

* Need to measure gas for specific impurity concentrations

- **Thermochemical modelling of gas chemistry - alloy interactions using FactSage**



- **Molecular dynamics simulations of interfacial processes**
  - Simulations up to 850 K are underway to understand the interaction of CO_2 with Fe and Ni surfaces
  - Impurity gases / alloy constituents will be included later



Questions?

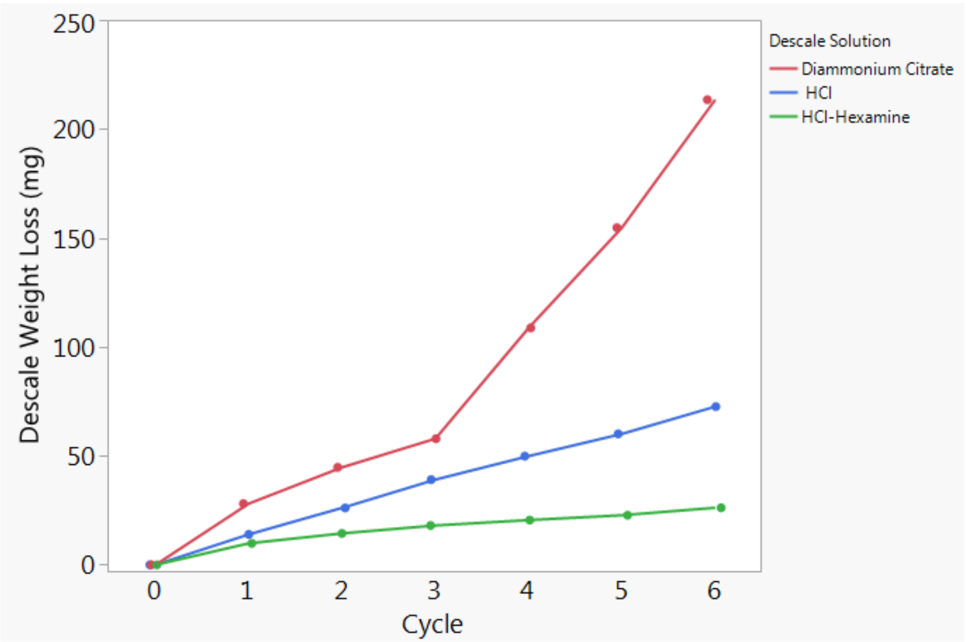
Backup Slides

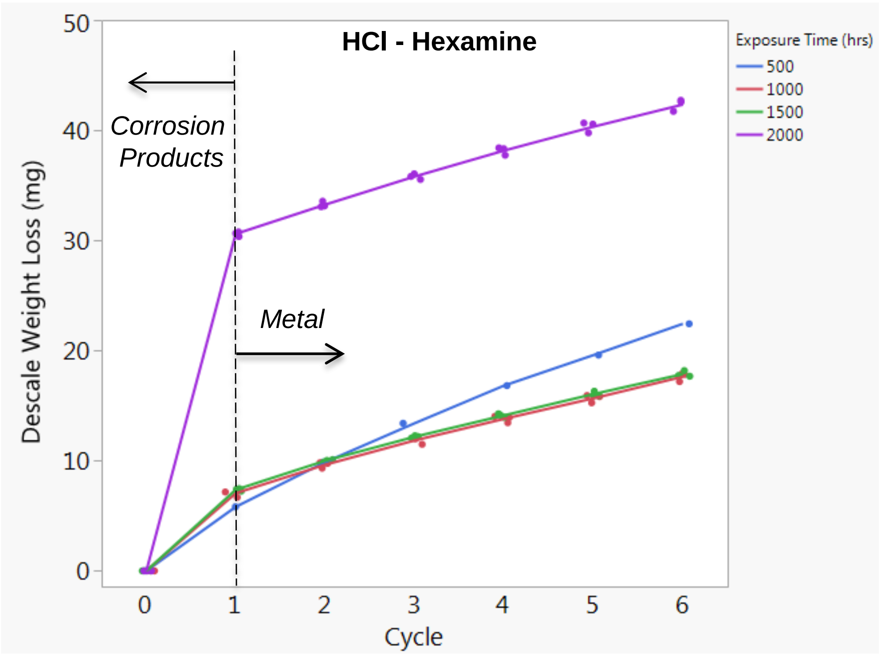
Two approaches for determining extent of corrosion

Corrosion Measurements

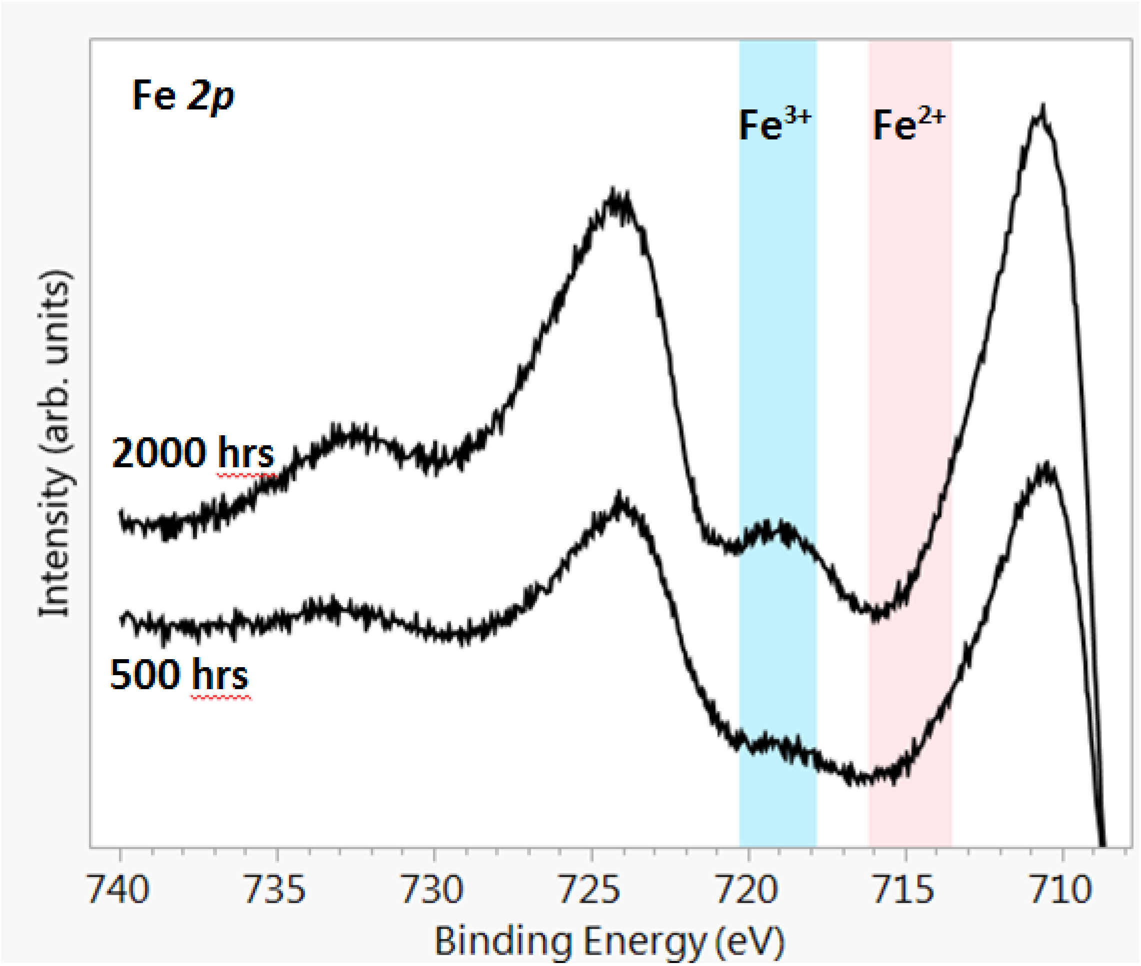
- Post-exposure sample weight gain measurements
- Measuring corrosion products through descale chemical treatment
  - Three descale solutions evaluated (ASTM G1-03)

Solution	Solution Temp (°C)	Cycles	Cycle Duration (min)
6M HCl (21 wt %)	20-25	6	10
6M HCl (21 wt %) + Hexamethylene tetramine (0.3 wt %)	20-25	6	10
Diammonium Citrate (20 wt %)	75-90	6	10



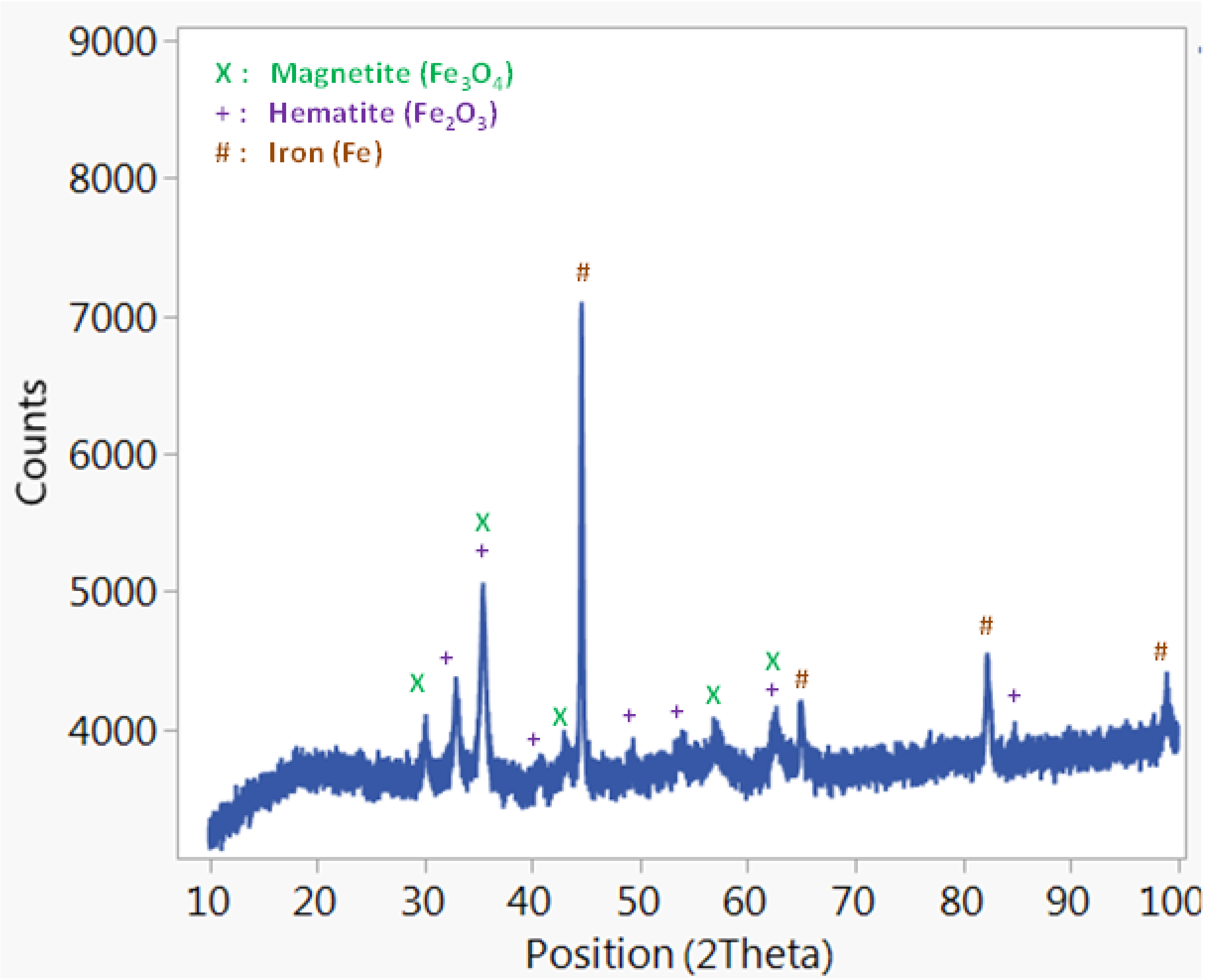


XPS



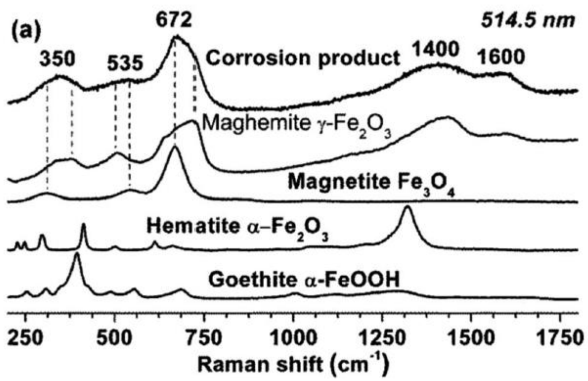
Fe 2p
Fe3+
Fe2+
2000 hrs
500 hrs
Intensity (arb. units)
740
735
730
725
720
715
710
Binding Energy (eV)

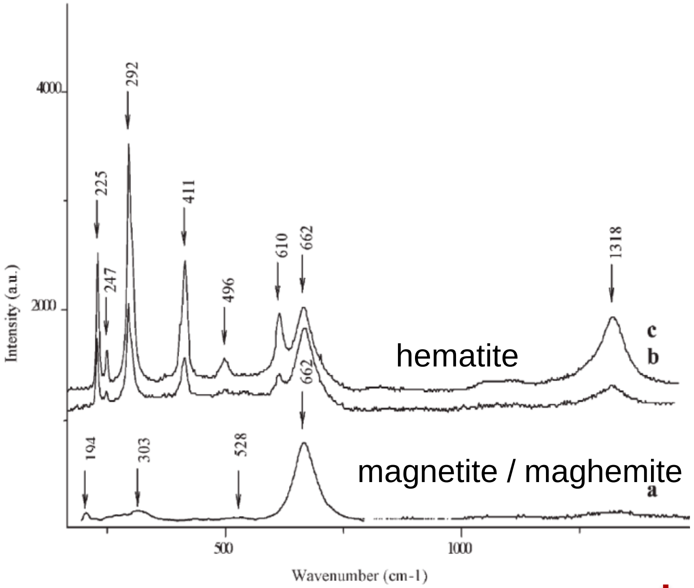
XRD

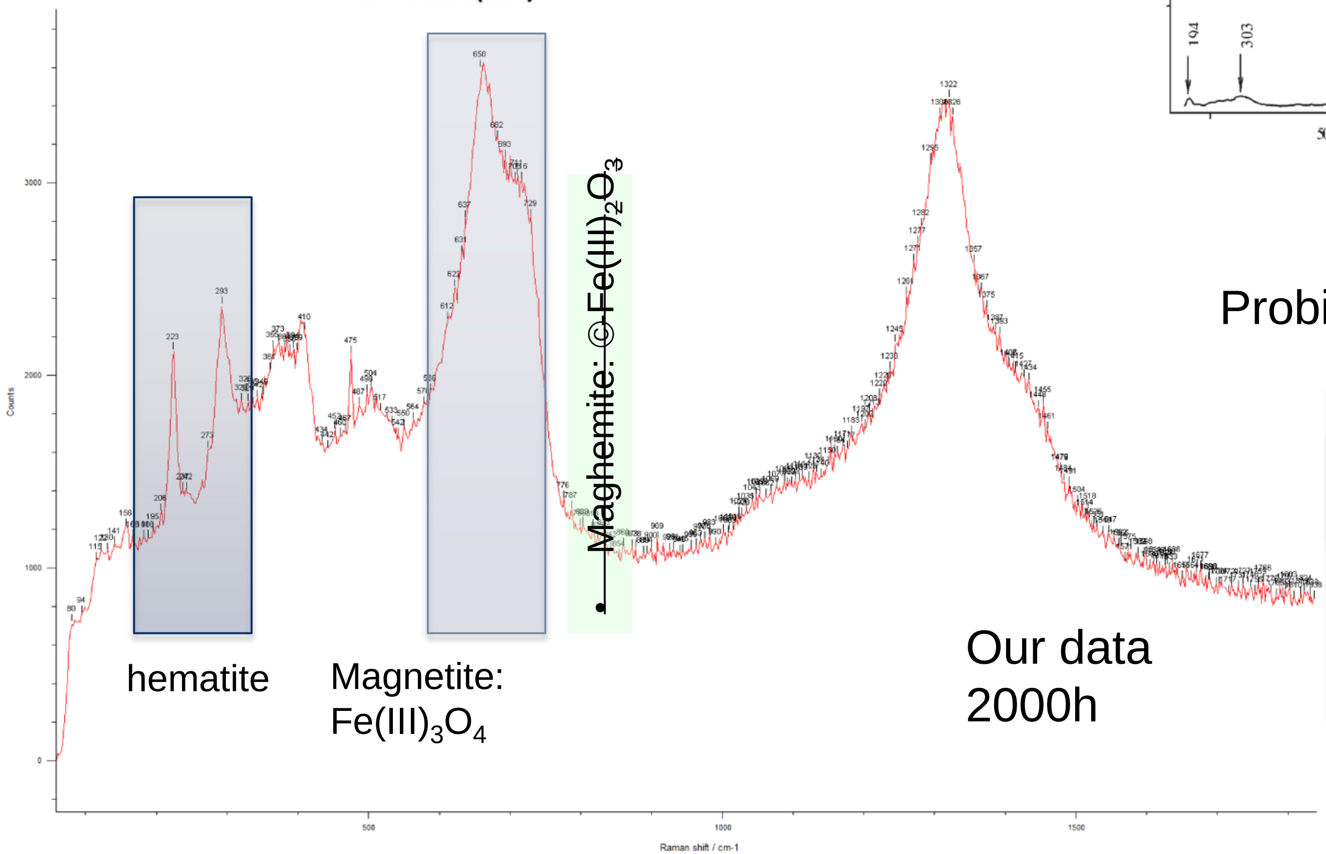


X : Magnetite (Fe_3O_4)
+ : Hematite (Fe_2O_3)
# : Iron (Fe)
9000
8000
7000
6000
5000
4000
Counts
10
20
30
40
50
60
70
80
90
100
Position (2Theta)

Raman







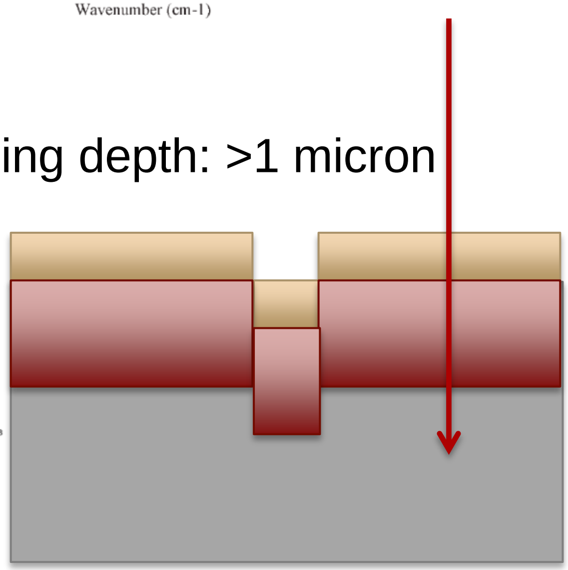
Maghemite: γ-Fe(III)$_2$O$_3$

hematite

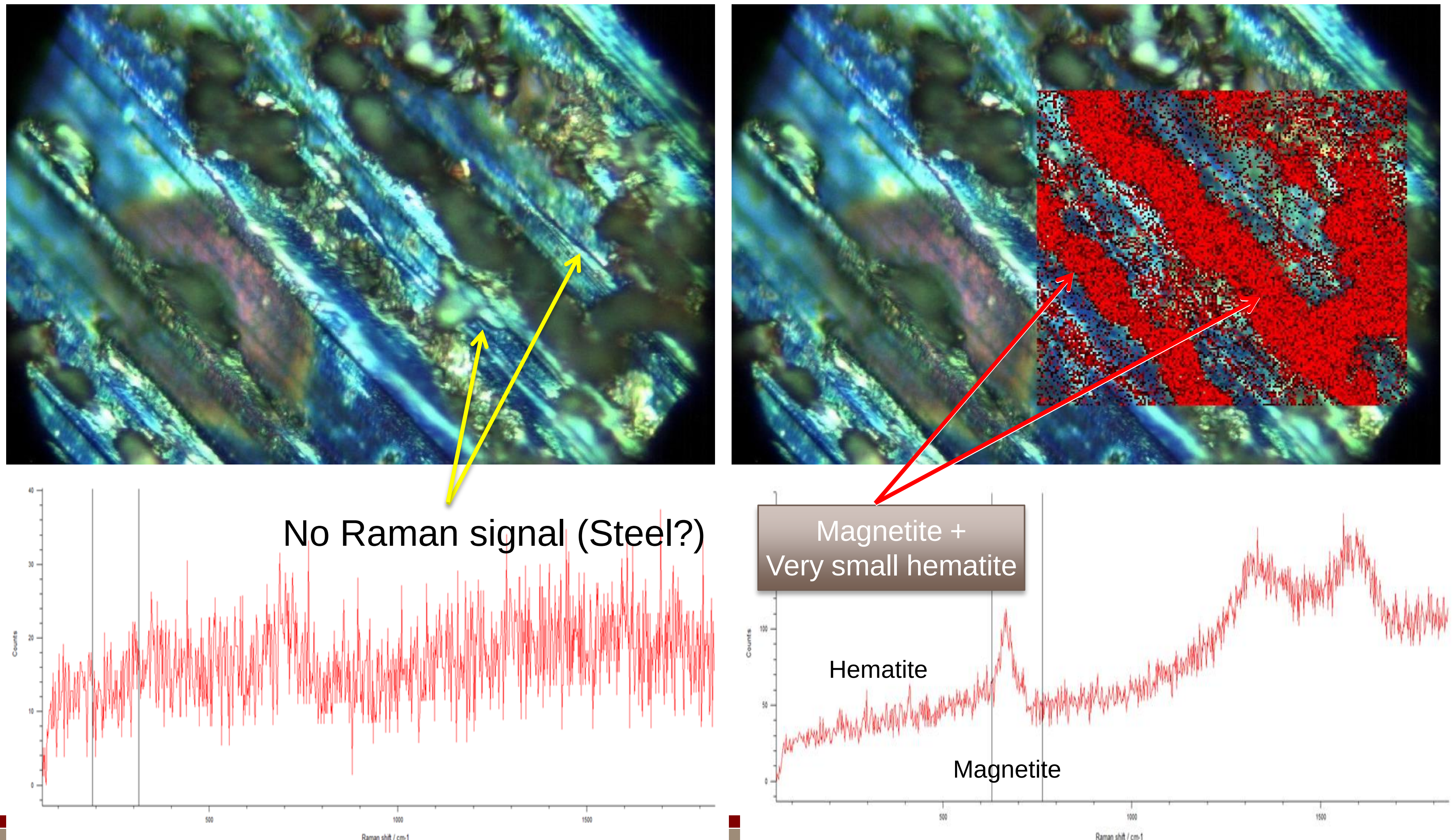
Magnetite: Fe(III)$_3$O$_4$

Our data 2000h

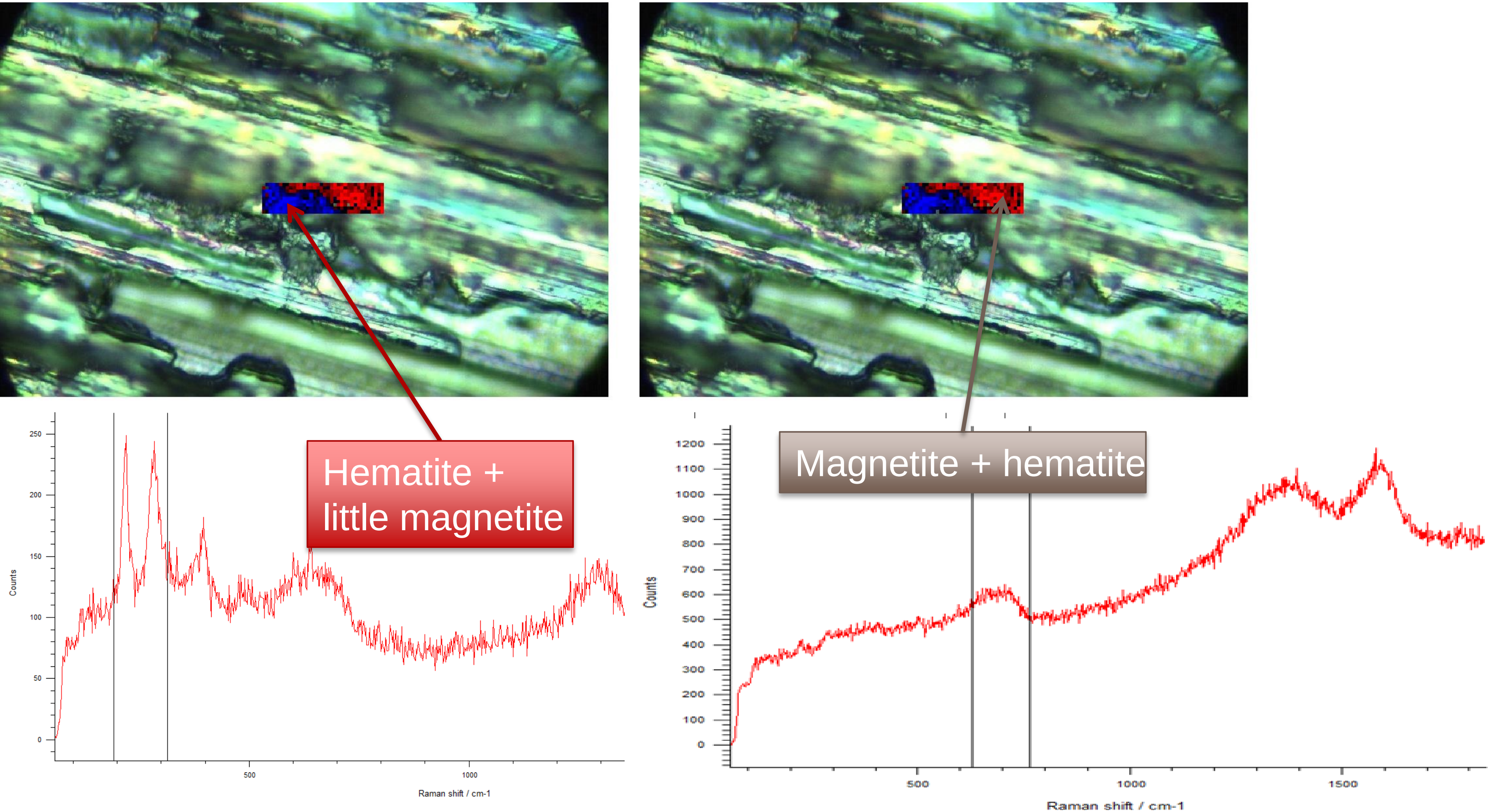
Probing depth: >1 micron



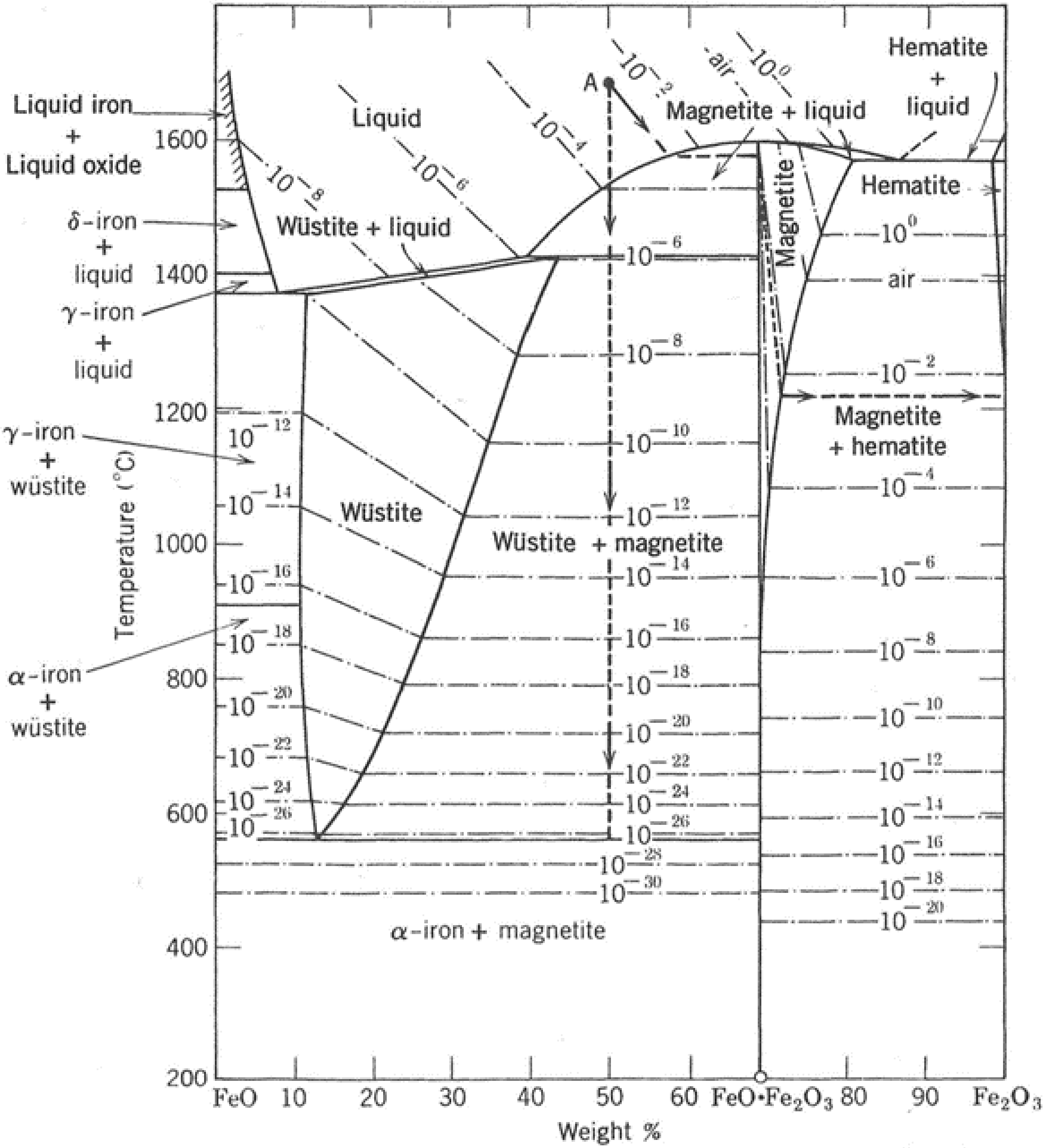
500 h Raman


No Raman signal (Steel?)
Magnetite +
Very small hematite
Hematite
Magnetite
Raman shift / cm-1
Raman shift / cm-1

Raman, 2000h sample



Both phases exist in the 2000 samples



Liquid iron
+
Liquid oxide
δ-iron
+
liquid
γ-iron
+
liquid
γ-iron
+
wüstite
α-iron
+
wüstite
Temperature (°C)
1600
1400
1200
1000
800
600
400
200
Liquid
Wüstite + liquid
Wüstite
Wüstite + magnetite
α-iron + magnetite
Magnetite + liquid
Hematite
+
liquid
Hematite
Magnetite
Magnetite
+ hematite
air
A
FeO
10
20
30
40
50
60
FeO•Fe2O3
80
90
Fe2O3
Weight %