THE CORROSION SOCIETY

SULFUR FAILURES in LOW H_2S SYSTEMS

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Elemental Sulphur Corrosion Seminar

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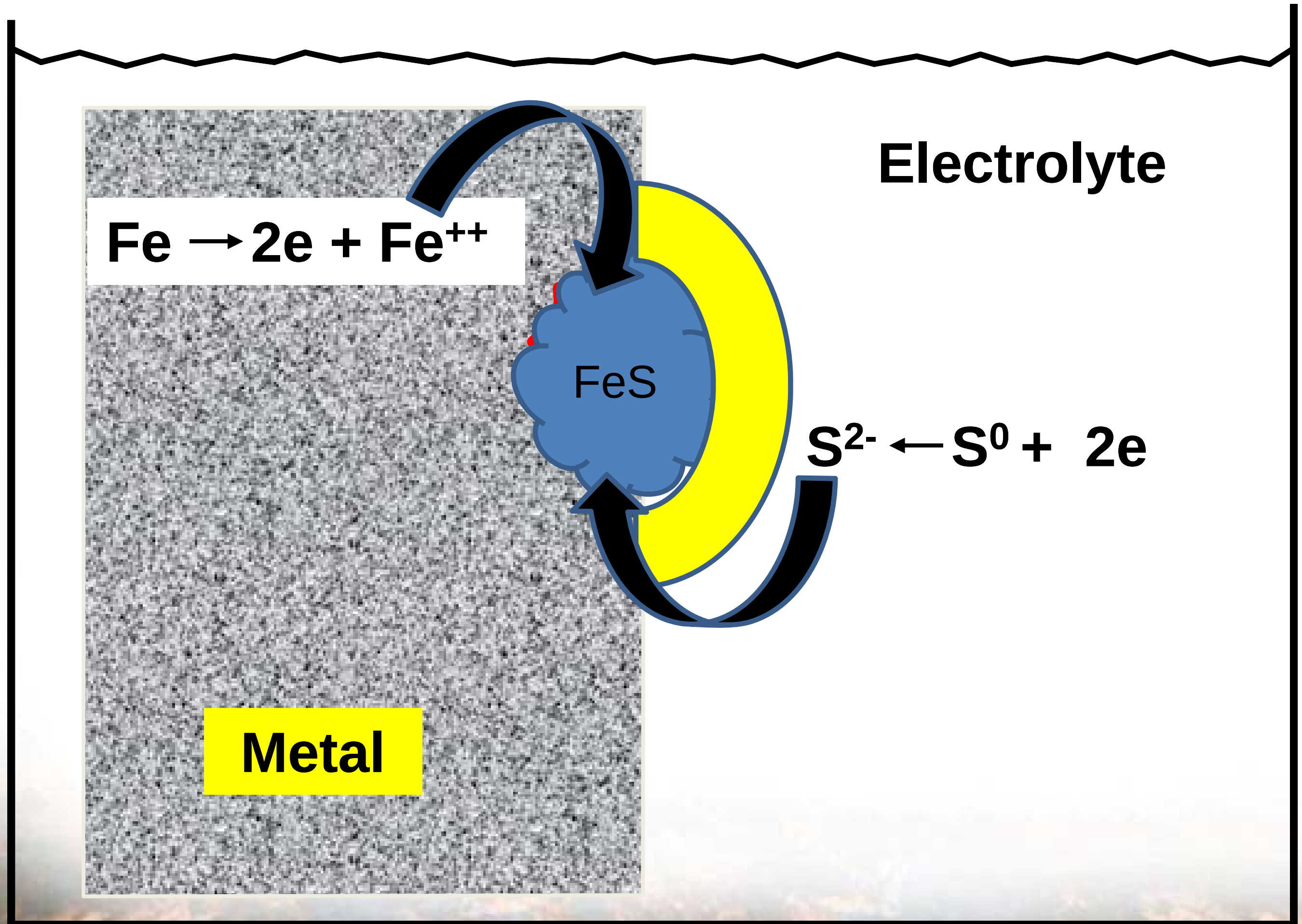
Sulfur Corrosion

- **Recognized mechanism in very sour production**
- **Usually found where H_2S > 10 -15%**
- **Systems generally hot, deep, no hydrocarbon production, produced brine**
- **Mitigated by preventing sulfur deposition and by corrosion inhibitor application**

Sulfur Corrosion

- **Sulfur requires contact with steel**
  - $Fe^{o} + S^{o} \rightarrow Fe^{++} + S^{=} \rightarrow FeS\downarrow$
- **Chloride required for severe corrosion**

The Corrosion Cell



Sulfur Corrosion

- Rates in excess of 20 mm/yr (800 mpy) possible
- Requires contact between metal and sulfur
- Iron sulfide may mediate corrosion activity

Corrosion Rate in D.W.

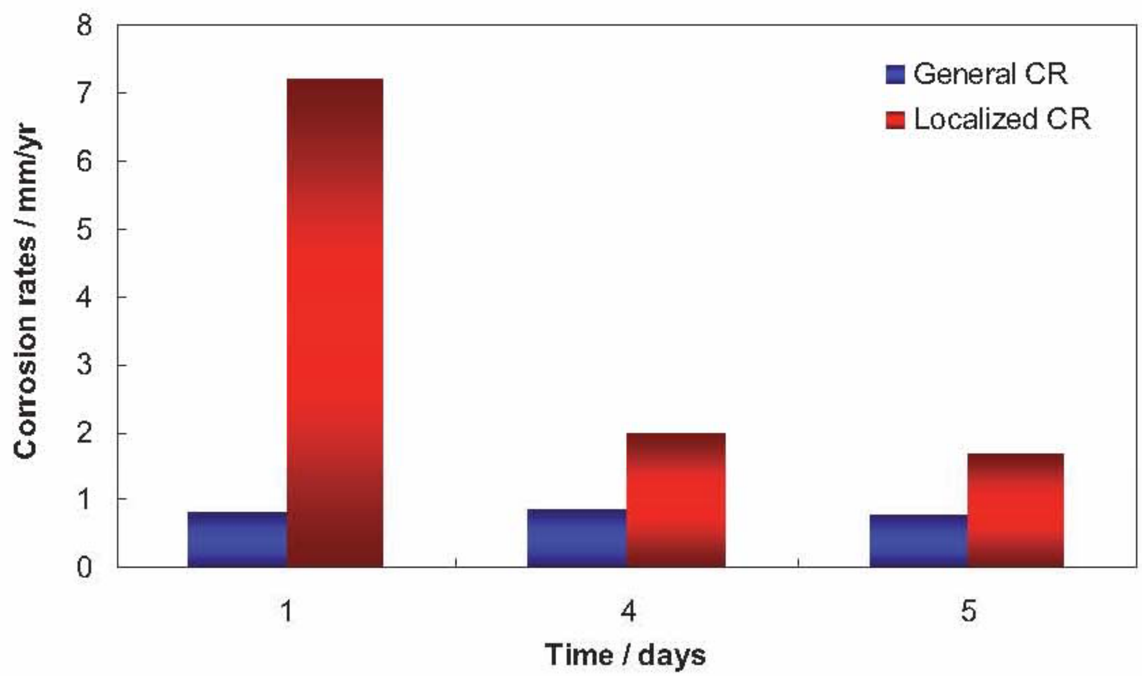
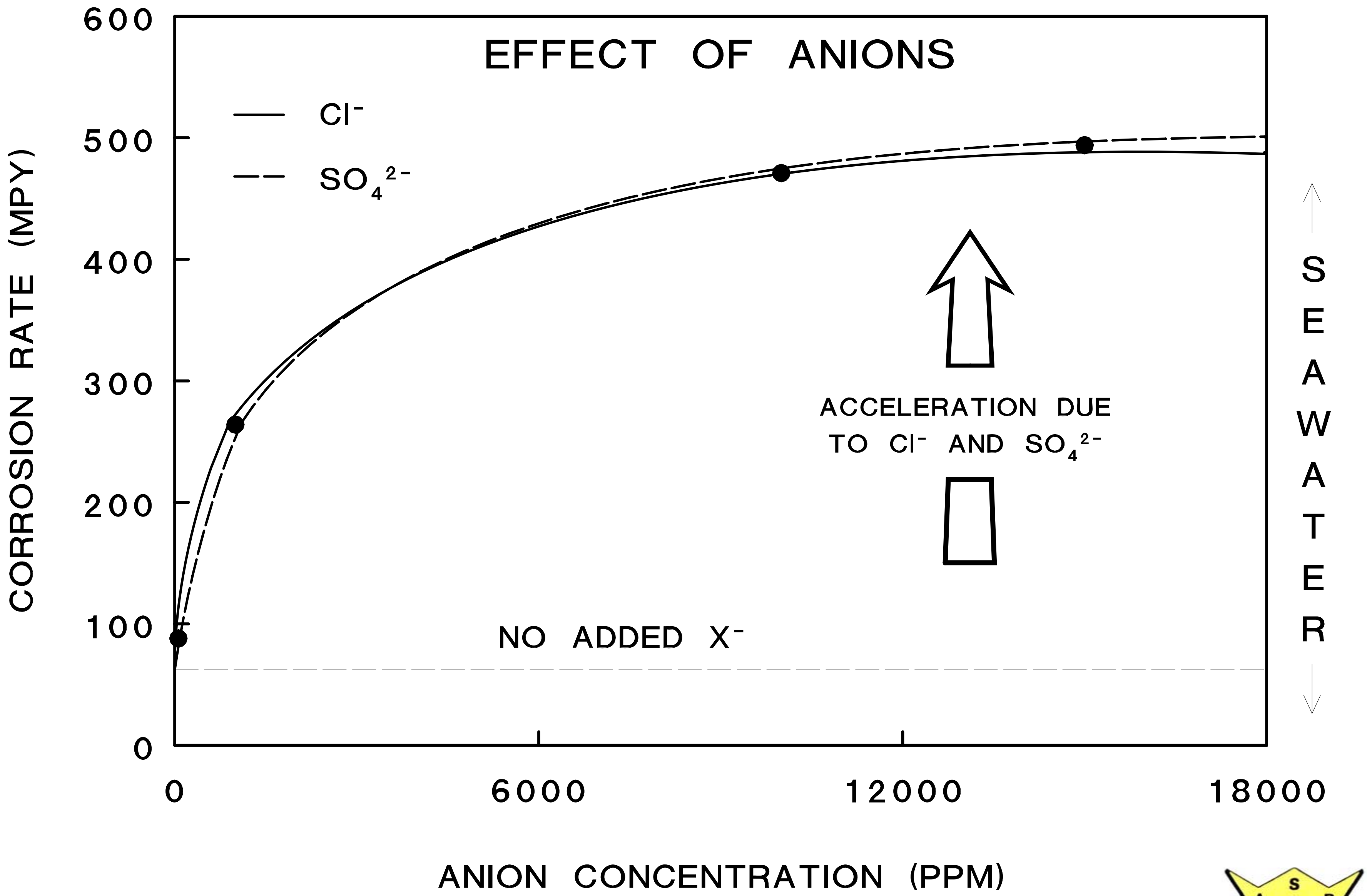


FIGURE 16 – Comparison of general and localized corrosion rates at 25°C.

Wet Sulfur Corrosion Rate versus Sulfate and Chloride Ion Concentration



Sulfur Deposition

Sulfur can be generated in three ways

- deposition from high H_2S gas streams where pressure and/or temperature drops
- deposition from polysulfide solutions
- From reactions with oxygen.

Sulfur Deposition by Oxygen

- from the reaction of H_2S with oxygen.

  $$\mathbf{2\,H_2S + O_2 \rightarrow 2\,H_2O + 1/4S_8}$$

- Equilibrium constant is large ($Log_{10}K_0 = 68.41$)
- Gibbs Free Energy = -387.98 kJ/mol
- Reaction favored, rapid and complete
- Also in deposits by reaction between oxygen and mackinawite

  $$\mathbf{Fe_9S_8 + 6O_2 \rightarrow 3Fe_3O_4 + S_8.}$$

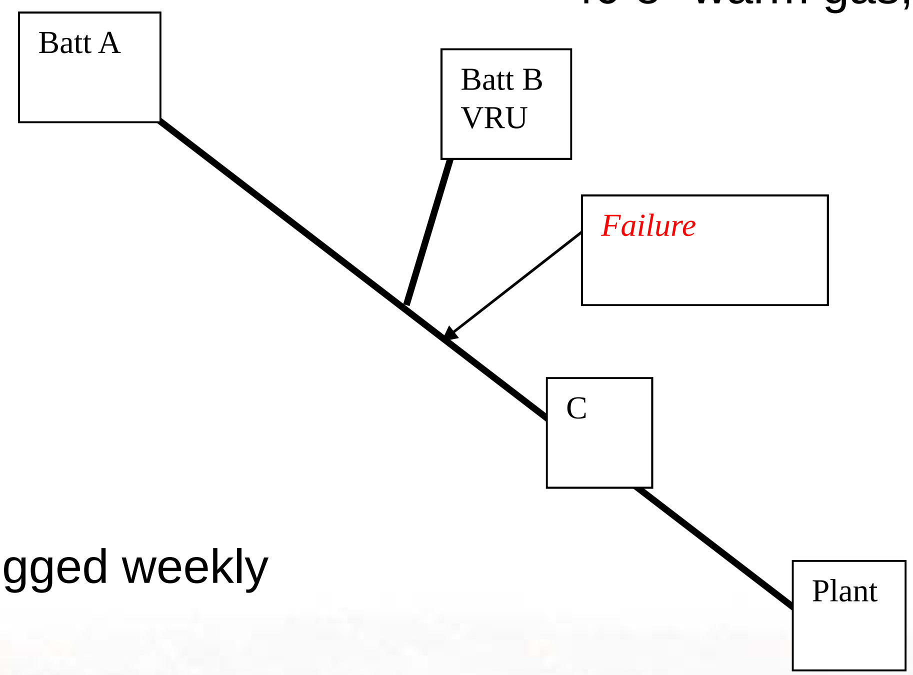
CASE 1 – VRU Gas

- Gas Line from oil battery – cold slightly sour (0.008% H_2S)
- Input from second battery, includes VRU gas – warm
- Failure downstream of tie- in
- ILI shows no corrosion upstream of tie in on either line
- Line in laminar flow

Case 1 Map

20 e^3 dry cold gas, slightly sour

40 e^3 warm gas, sweet



Note: Line pigged weekly

CASE 1 – VRU Gas

Pressure kPa	4600	**% CO_2**	0.94
Temperature deg C.	25	**% H_2S**	0.008
Gas e3m3/day	60	**Sp. G.**	0.6
Hydrocarbon m3/day	0.10	**Sp. G.**	0.7
Water m3/day	0.001	**Sp. G.**	1.0005
Date Built	2000		
Line Length	7.91	km	

Failure before cleaning

XRD of Wall scale

Compound	Chemical Formula	Abundance
Quartz	SiO_2	65-75%
Sulphur	S_8	**8-12%**
Mackinawite	FeS	5-10%
Kaolinite	$Al_2SiO_5(OH)_4$	5-10%
Illite	$KAl_2Si_3AlO_{10}(OH)_2$	1-5%
Lepidocrocite	$FeO(OH)$	1-5%

Failure Pit Clean

Mechanism

- Warm gas contains oxygen, but no condensation occurs
- Warm wet gas encounters dry sour gas and condenses
- Sulfur deposits by reaction with O_2
- Source of chloride?

CASE 2 – Solution Gas

- Oil battery supplied solution gas to plant.
- As system aged, slight H_2S content appears
- As gas volume decreased, dehydration system shut in
- Methanol used for hydrate control
- New gas wells tied in further downstream to supply gas to plant

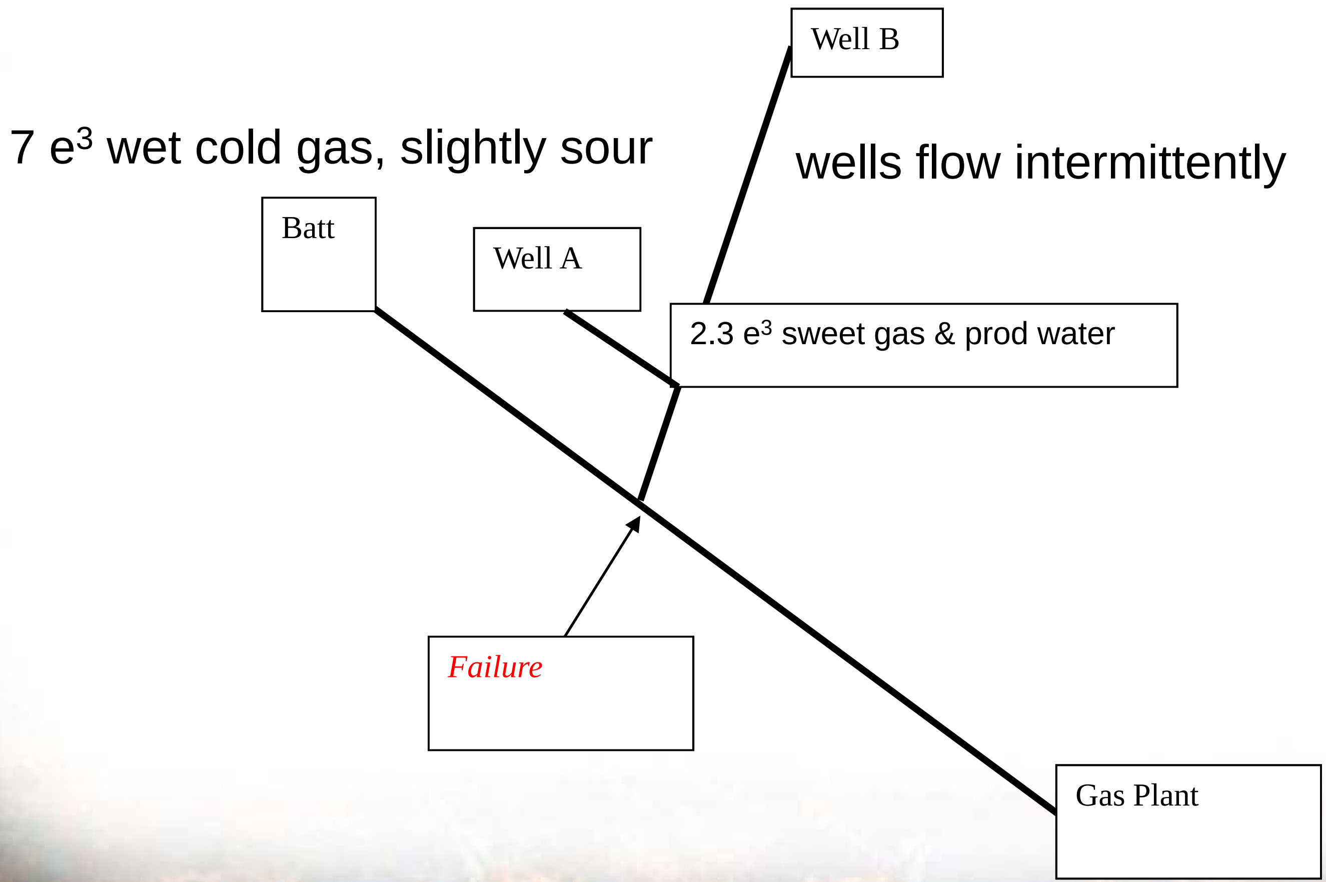
CASE 2 – Solution Gas

- Line failure occurred downstream of sweet wells tie-in
- Yellow deposit in flowline upstream of tie-in
- ILI showed no damage upstream of tie-in
- Severe pitting damage downstream of tie-in

CASE 2 - Solution Gas

Pressure kPa	200	**% CO2**	1.12
Hydrocarbon m3/day	0.30	**H2S**	Tr
Water m3/day	0.2		
Date Built	1991		
Line Length	8.8	km	
Line Size	114.3	mm	
Wall	3.2	mm	
ID	107.9	mm	
CALCULATED VALUES			
Line Volume	90.30	m3	
Superficial Gas Velocity	5.85	m/s	
Superficial Liquid Velocity	0.0006	m/s	
Uphill Flow Regime (Taitel)	Slug		
Downhill/Horizontal Flow	Wave		

Case 2 Map



Well B
7 e3 wet cold gas, slightly sour
wells flow intermittently
Batt
Well A
2.3 e3 sweet gas & prod water
Failure
Gas Plant

Failure Orientation

Failure before cleaning

XRD of Wall scale

Compound	Chemical Formula	Abundance
Siderite	$FeCO_3$	35-45%
Quartz	SiO_2	25-35%
Sulphur	S_8	20-30%
Magnetite	Fe_3O_4	5-10%

Failed Segment

Failure Pit

Mechanism

- Warm gas from the treaters condenses in the line along with methanol.
- H_2S present in the gas phase would dissolve in the water methanol
- Sulfur deposited by reaction of H_2S with O_2 in methanol
- Particulate sulfur would be deposited in the pipeline and carried downstream by the flow.

Mechanism

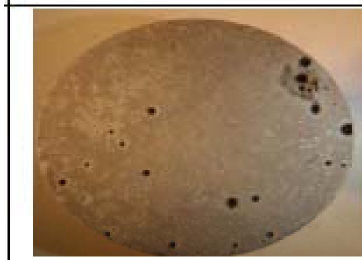
- Condensed water contains no chloride, hence no corrosion
- Produced brine from sweet gas wells enters system at tie-in
- Flow insufficient to move water
- Stagnant brine + sulfur = corrosion

Corrosion Prevention

- Avoid oxygen ingress
  - Check VRU seal quality
  - Wellhead gas compressors
  - Leaking valves
- Methanol Use
- Apply corrosion inhibitors

Autoclave Testing

Cleaned Specimens

Surface Photograph	Close-up Photograph
	
Overall light etch	
	
Overall surface etch with pitting	
	
Overall light etch with a few pit initiation sites	
	
Overall light etch with a few pit initiation sites	

Weight Loss Results

Chemical	Weight Loss (mg)	Corrosion Rate (mpy)	Pit Depth (mils)	Pitting Rate (mpy)
A	5.80	1.37	N/A	N/A
B	76.6	18.1	30.0	1436
C	43.2	10.2	N/A	N/A
D	48.5	11.4	N/A	N/A

Final Thoughts

- Understand system and hazards
- Potential sources of Oxygen
  - VRU
  - Methanol
- Consider batch inhibition