



**Sulfur Species Associated With Sour Gas:
Elemental Sulfur is Not Your Only Worry...**

Baker Hughes Inc.


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**NACE Northern Area
Mini-Symposium
Elemental Sulfur Corrosion and Its Mitigation**

**October 8, 2010
Calgary, AB**



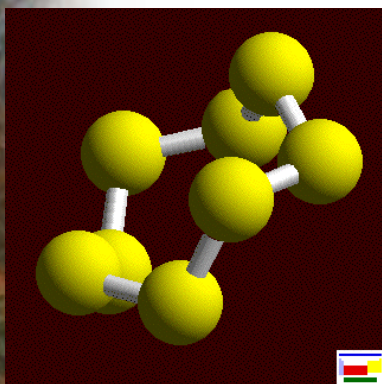
Outline

- Some Basic Sulfur Chemistry
 - Types of Sulfur Species
 - Formation of Elemental Sulfur
 - Transport Mechanisms
 - Analytical Methods
 - Corrosion Implications
 - Mitigation Options
 - Concluding Remarks
- 

Sulfur – Some Common Properties



- Stable solid at ambient conditions
- Melts at 113°C
- Sublimes readily
- Soluble in many organic solvents, particularly CS₂
- Broad range of oxidation states (-2 to +6)



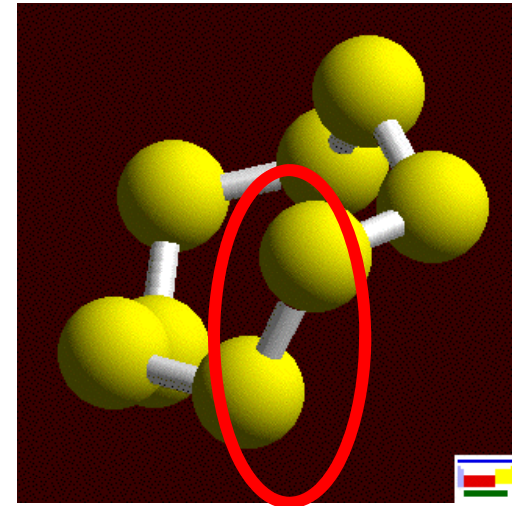
Sulfur Species Associated With Sour Produced Fluids

Total Sulfur

- H_2S (gas & liquid)
- Mercaptans $[\text{R-S-H}]$ (gas & liquid)
- Thioethers $[\text{R-S-R}']$ (gas & liquid)
- Disulfides $[\text{R-S-S-R}']$ (gas & liquid)
- Molecular Polysulfides $[\text{R-(S)}_x\text{-R}']$ (gas & liquid)
- Ionic Polysulfides $[\text{H-(S)}_x\text{]}^{-1}$ (aqueous)
- Sulfates (aqueous)
- Thiosulfates (aqueous)
- FeS (all phases)
- S_8 (all phases)

“Reactive” Sulfur

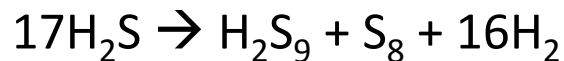
- Elemental sulfur $[\text{S}_8]$
- Di- and polysulfide linkages $[\text{R-S-S-R}']$



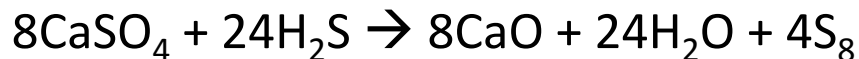
These species contain sulfur atoms bonded to other sulfur atoms

Formation of Elemental Sulfur

- Condensation of H₂S at high P, T



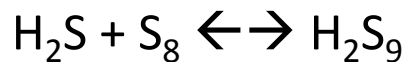
- Thermochemical reduction of sulfate



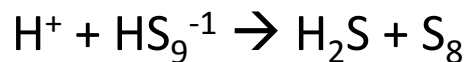
- Air oxidation of H₂S



- Dissociation of Sulfanes

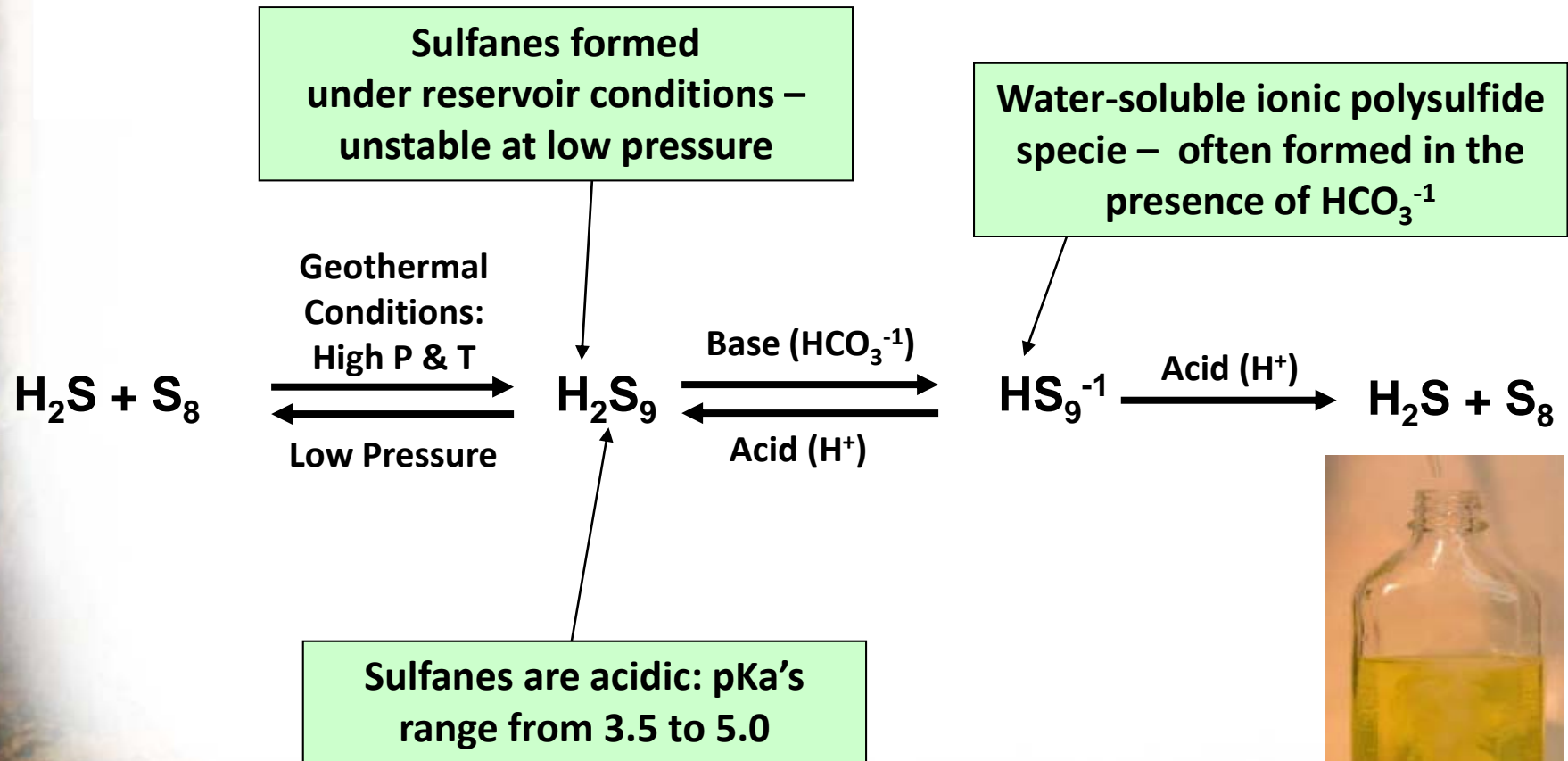


- Decomposition of ionic polysulfides

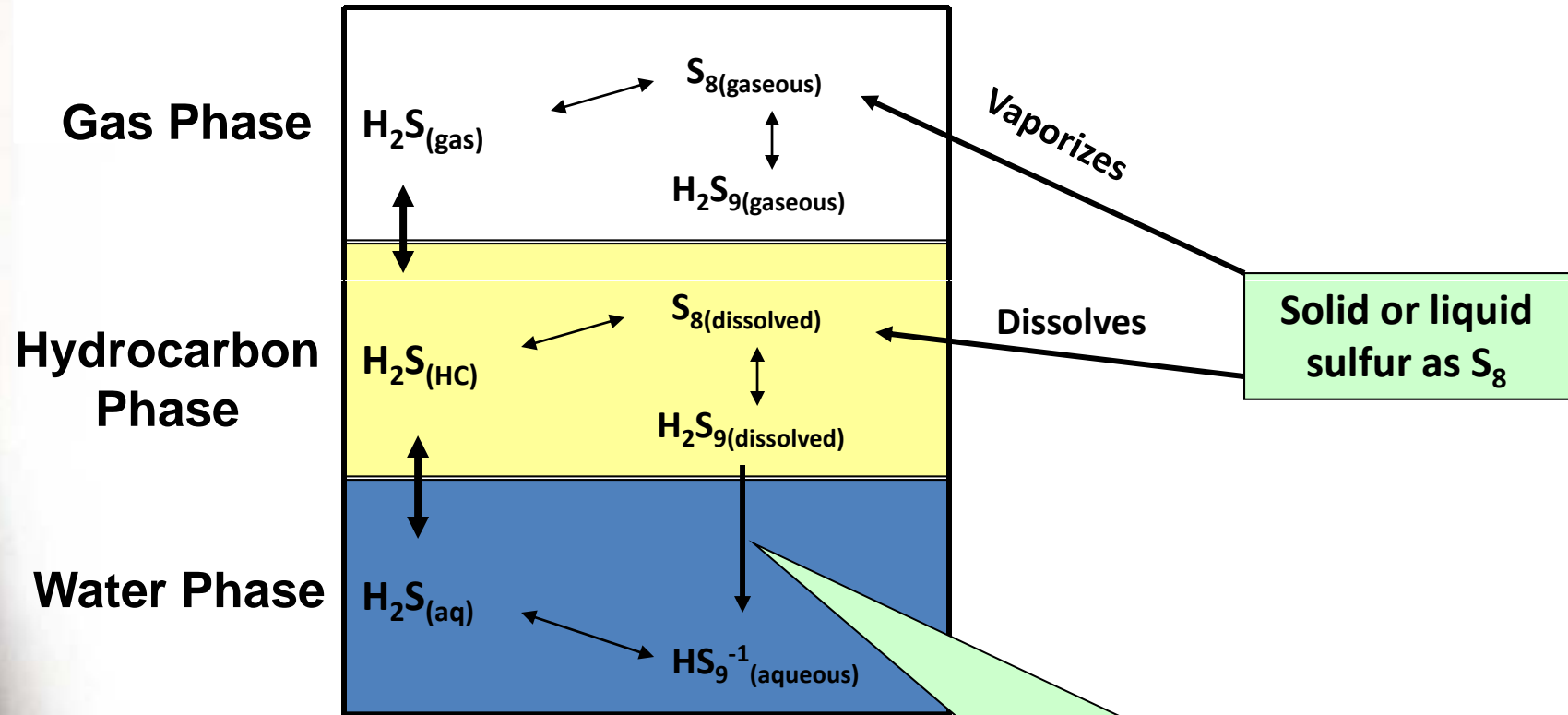


- Dissolution of sulfur in hydrocarbon liquids

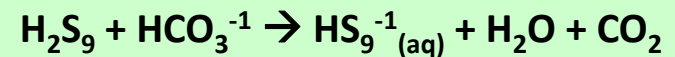
Sulfur Transport Mechanisms



Sulfur Species in Sour Systems – Transport Pathways



Acid-base Reaction with $HCO_3^{-1}(aq)$

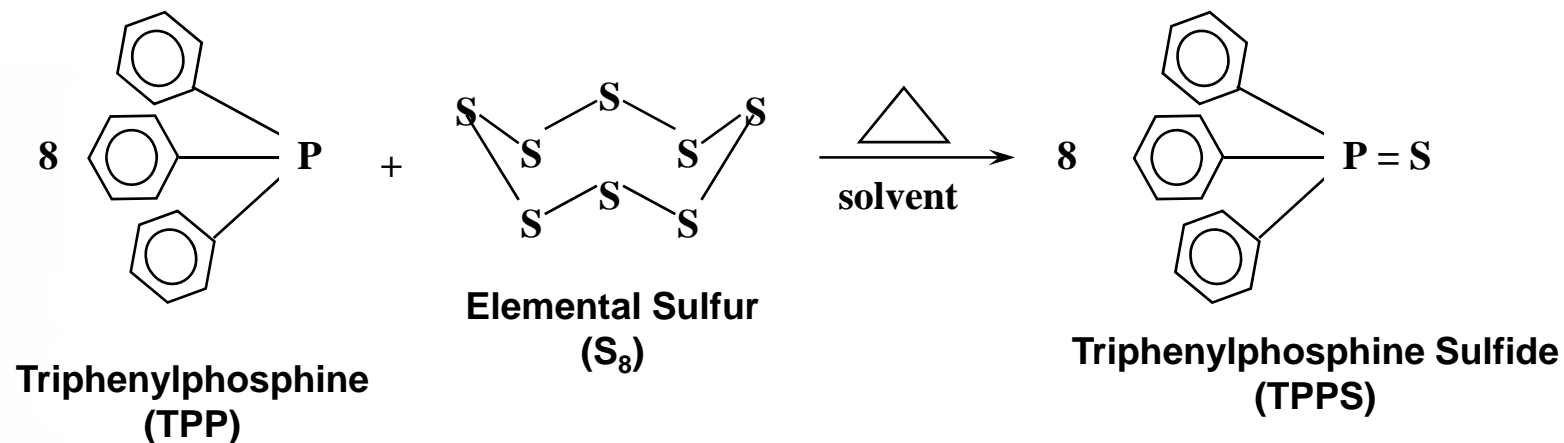




Identification of Sulfur Species

- Solid sulfur - simple chemical spot test (qualitative)
- Selective solubility (CS_2) followed by solvent evaporation
- GC/MS – organosulfur species
- HPLC – specific to elemental sulfur
- Triphenylphosphine (TPP/GC) – elemental sulfur and polysulfides

Quantitative Determination of Elemental Sulfur With TPP



1. Reaction rapid and quantitative - TPPS volatile but thermally stable
2. Analysis by GC-PFPD (phosphorus mode) - very sensitive
3. No interference due to hydrocarbons or organosulfur compounds

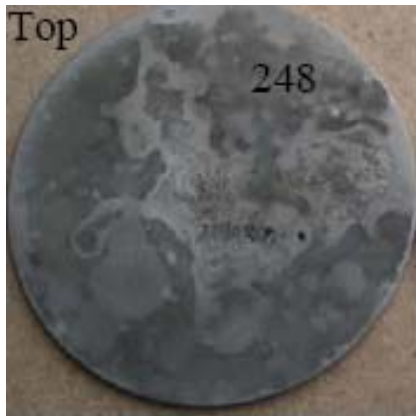
P. D. Clark and K. L. Lesage, *J. Chromatography Sci.* 27, 259-261 (1989).

Corrosion Implications

- When you see this, it's time to start worrying...



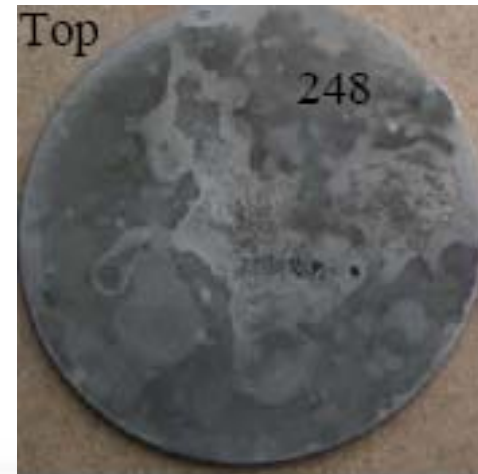
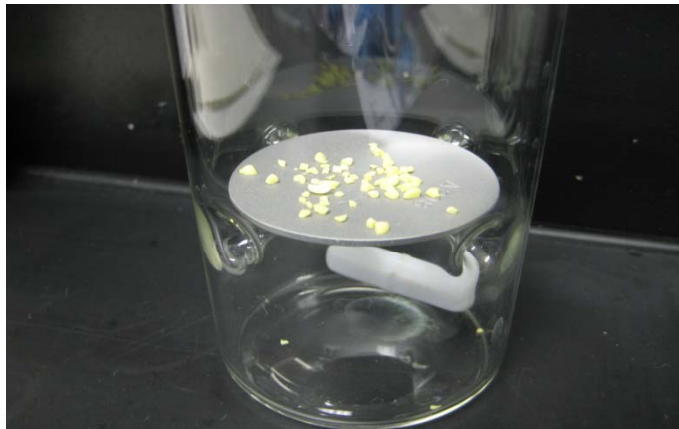
Corrosion Implications



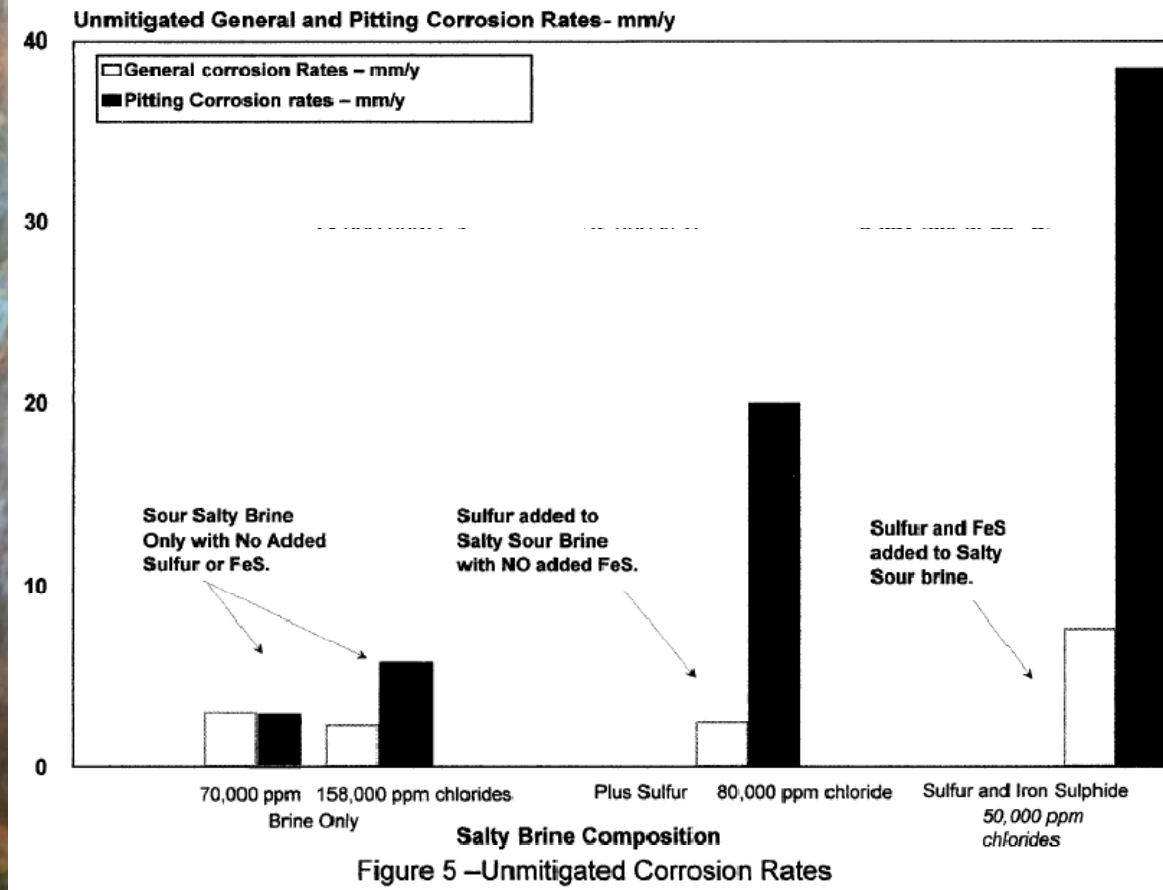
- Elemental sulfur is a powerful oxidant
- Wet elemental sulfur extremely aggressive toward carbon steel
- Corrosivity increases with presence of chlorides

Laboratory Evaluation

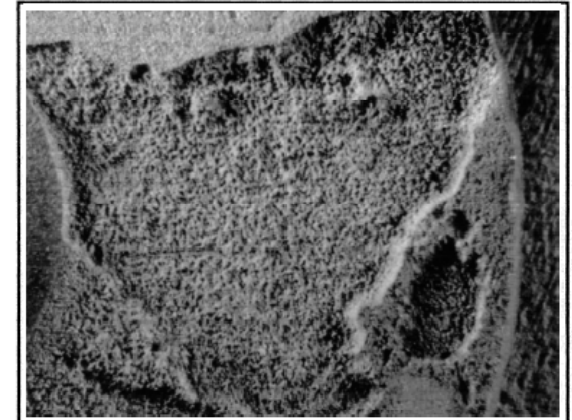
- Many companies have developed test procedures that incorporate elemental sulfur in direct contact with the metal
- Coupons are often pre-corroded to simulate pipeline conditions with the presence of an FeS film



FeS Deposits Also Increase the Likelihood of Pitting Corrosion



155 psi H₂S + 15 psi CO₂ ; 50,000Cl⁻ ; 100hrs. 50°C



BLANK
1BKR-1
add 1g Sulfur and 1g FeS on day one
8x
Corr. 7.6 mm/yr Pit. 39 mm/yr

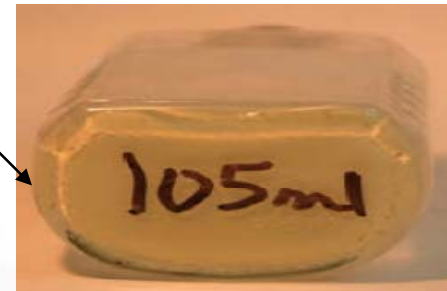
Source: NACE paper 03174 – CORROSION 2003

Corrosion Implications – Ionic Polysulfides

Acidification of Polysulfide Solution



Acid (H^+)

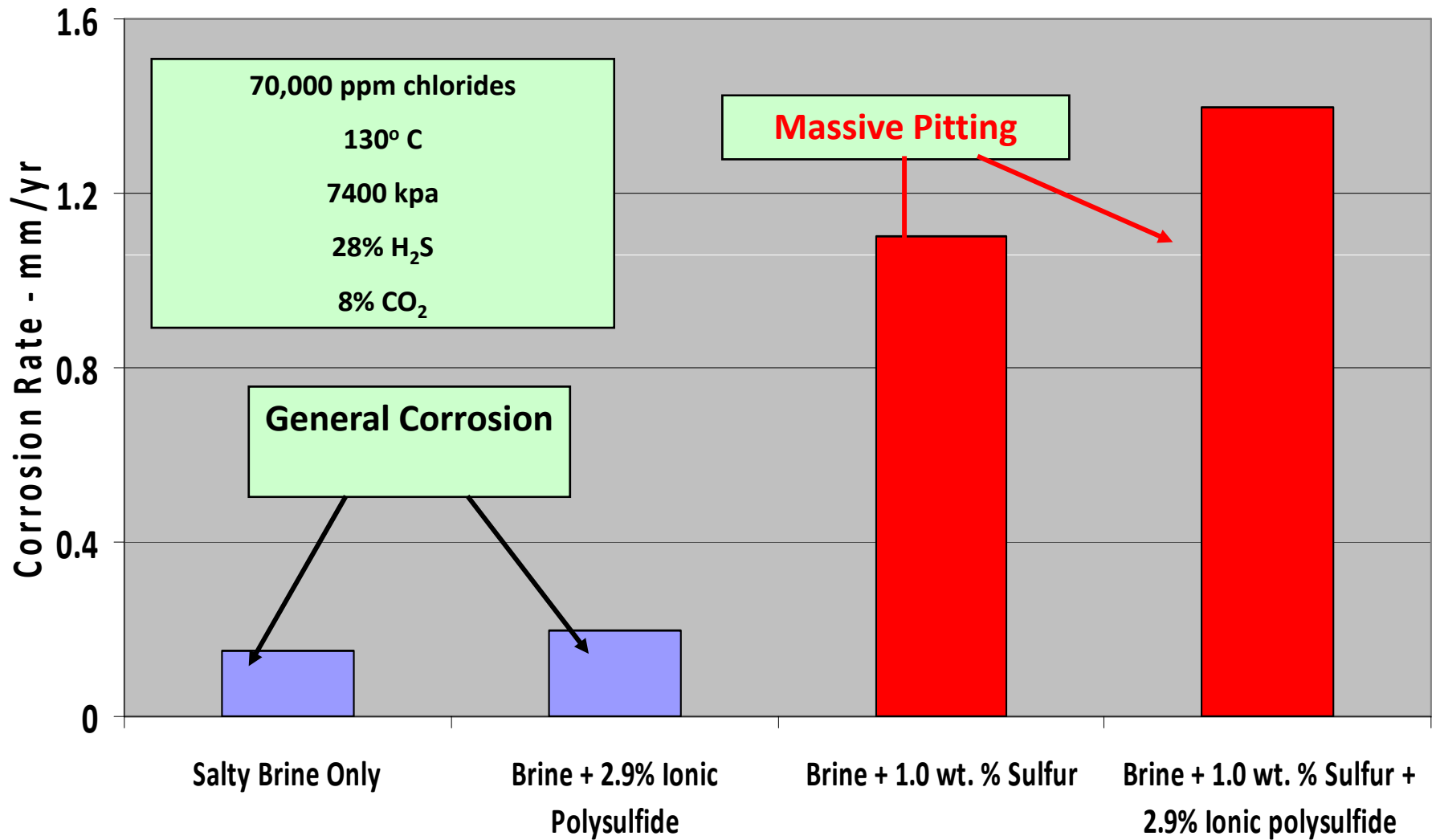


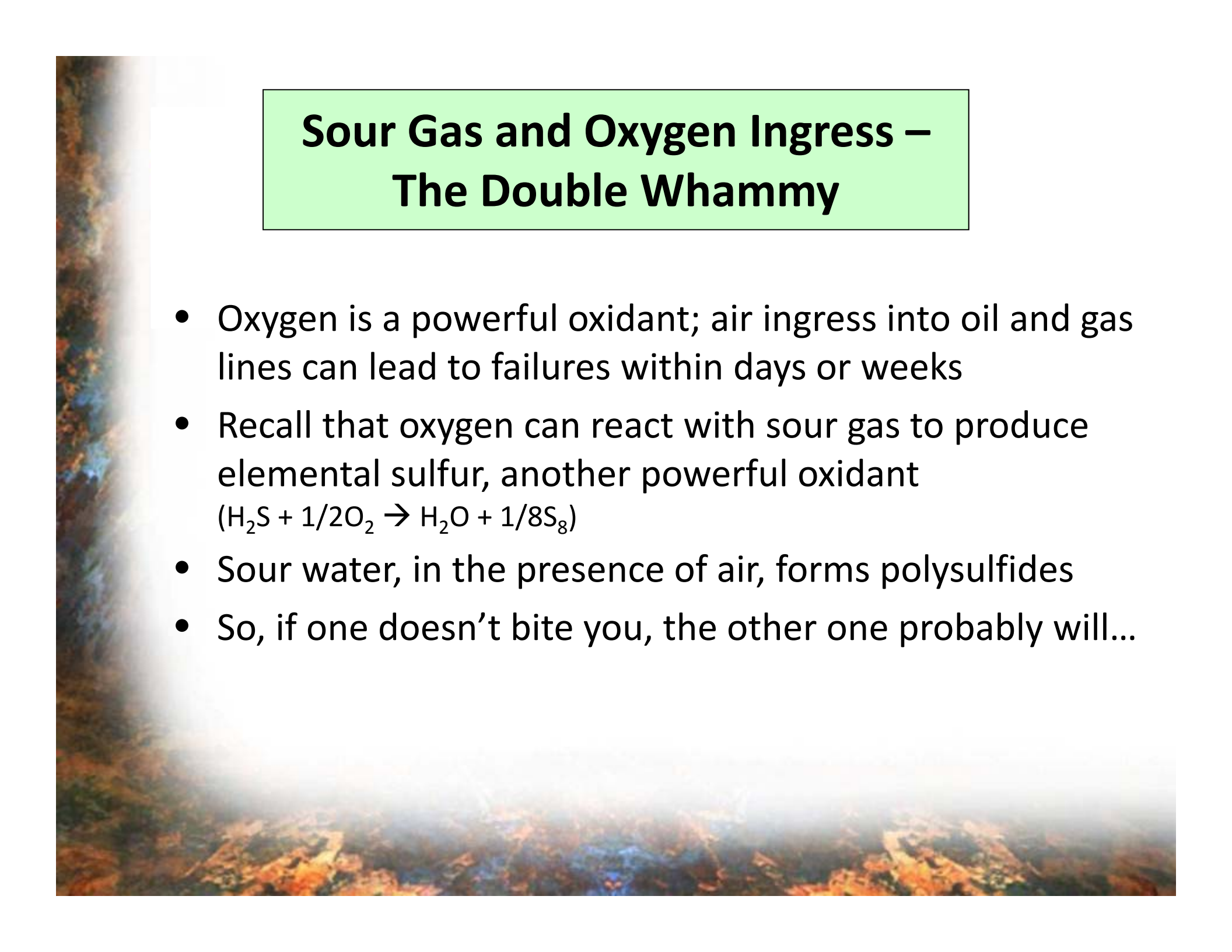
Corrosion Implications – Ionic Polysulfides

Corrosion Coupon in Polysulfide Solution




Corrosion Rates: Impact of Sulfur & Polysulfides





Sour Gas and Oxygen Ingress – The Double Whammy

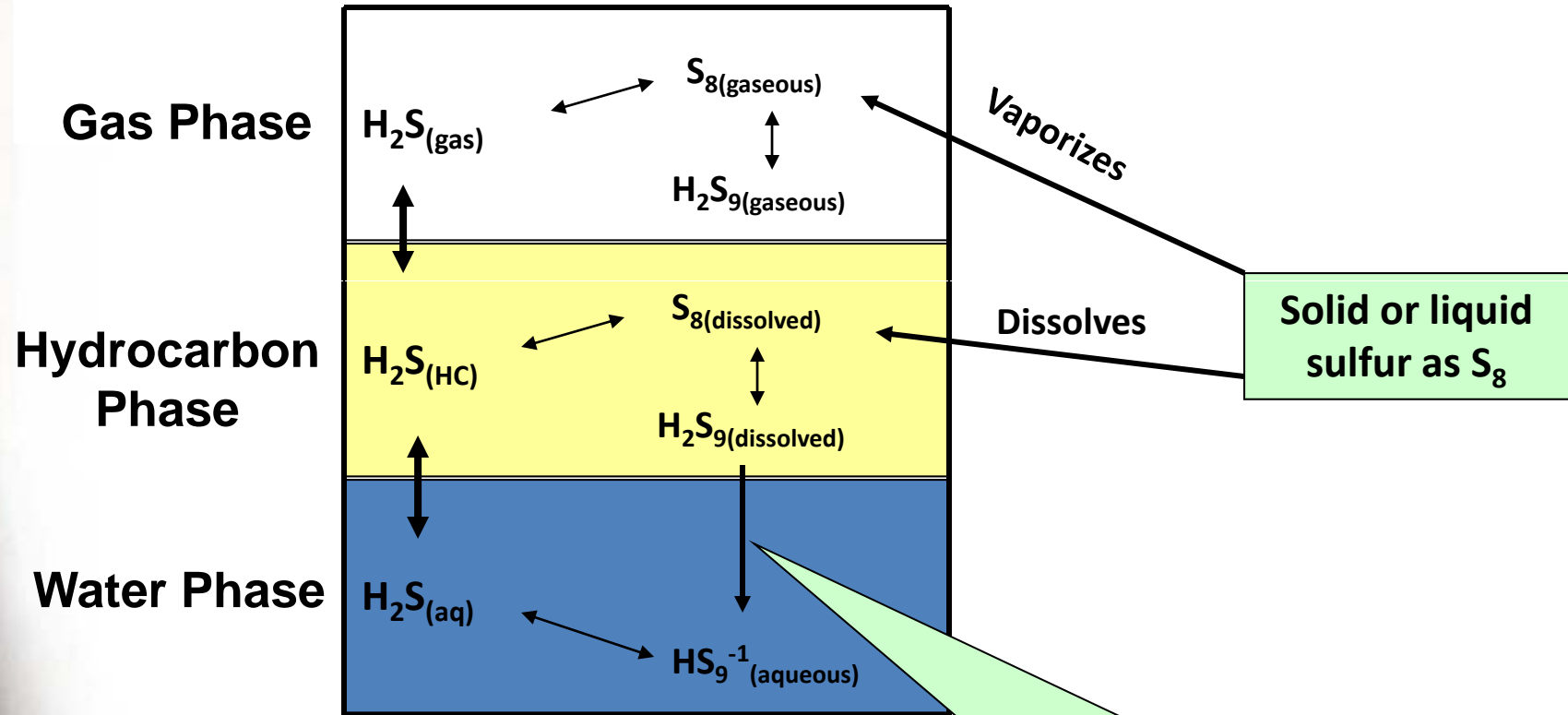
- Oxygen is a powerful oxidant; air ingress into oil and gas lines can lead to failures within days or weeks
- Recall that oxygen can react with sour gas to produce elemental sulfur, another powerful oxidant
($\text{H}_2\text{S} + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O} + 1/8\text{S}_8$)
- Sour water, in the presence of air, forms polysulfides
- So, if one doesn't bite you, the other one probably will...



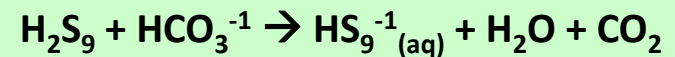
Common Sources of Oxygen Ingress

- Casing vents
- Stuffing box
- Pig senders/receivers
- Dump valve packing
- Water storage tanks – not blanketed
- Vapor recovery units (VRU's)
- Trucked in fluids
- Methanol
- Compressors

Sulfur Species in Sour Systems – Transport Pathways



Acid-base Reaction with $HCO_3^{-1}(aq)$



Sulfur Dissolved in Hydrocarbon Liquids (Field Condensate)

Dissolved Sulfur Concentration (analyzed by ASRL)	Comments
135 mg/L	Collected in sample bottle
25 mg/L	Collected in sample bottle
215 mg/L	Collected in pressure cylinder
17 mg/L	Bottle broke in transit
26 mg/L	Condensate was charcoal filtered and analyzed in Baker Hughes' Sugar Land Laboratory using a procedure analogous to ASRL's
1,210 mg/L	Collected in sample bottle

Laboratory Test Conditions – Sulfur in Hydrocarbon Liquids

Parameter	HSAT/Laminar Flow Tests
Temperature	75°C
P_{H_2S}	200 psi
P_{CO_2}	150 psi
Water/Oil	80/20
Coupon Metallurgy	X52

Laminar Flow Test

- Replicates low flow conditions
- Stirring at 100 rpm
- Oil and water phases do not mix
- Interfacial effects can be studied



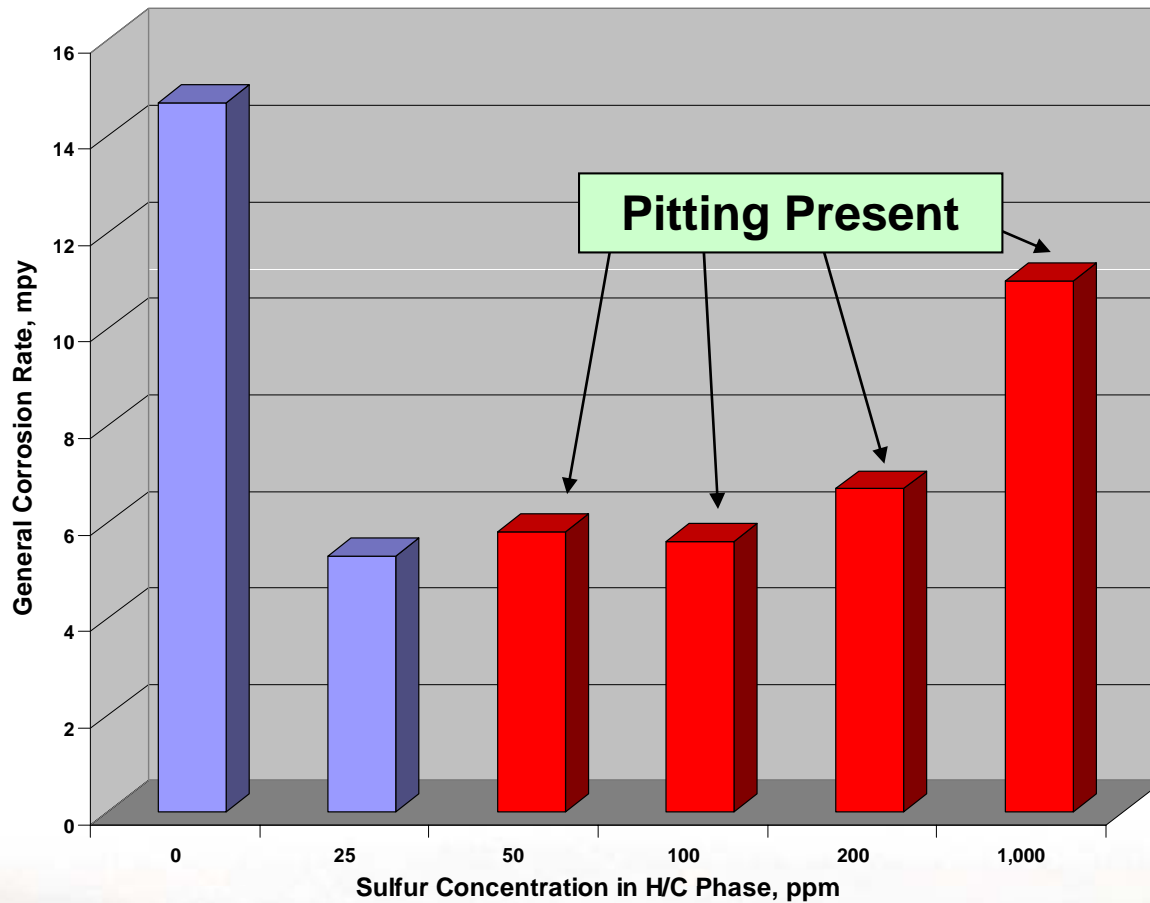
Note the yellow color from the dissolved S_8

Laminar Flow Test



Enables testing of a related series where only one variable is changed

Laminar Flow Tests – Blank Corrosion Rates

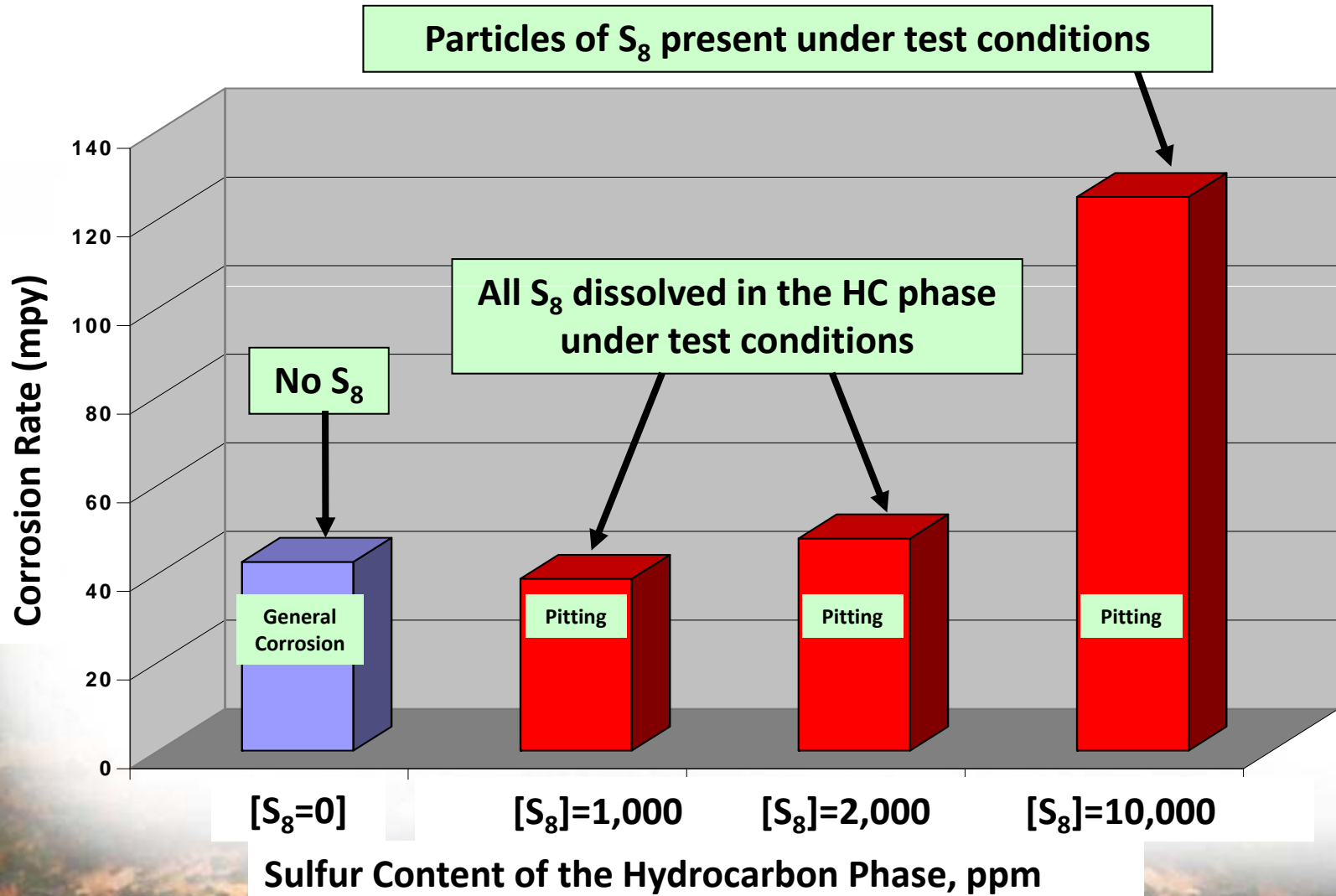


High Speed Autoclave Tests (Rotating Cage)

- High Pressure
- High Temperature
- Replicates shear stress conditions in the pipeline or well

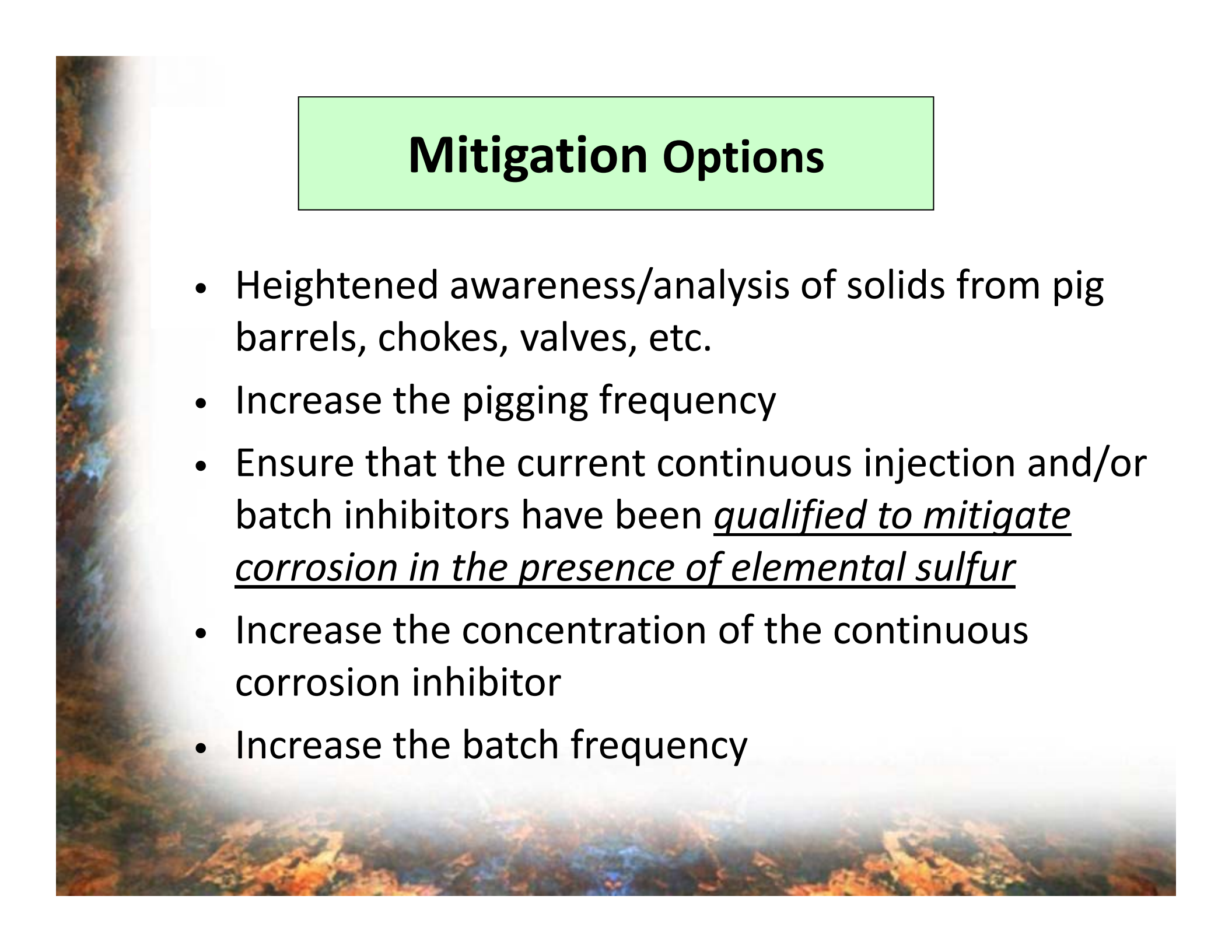


HSAT Test Results: S₈ Dissolved in the Hydrocarbon Phase



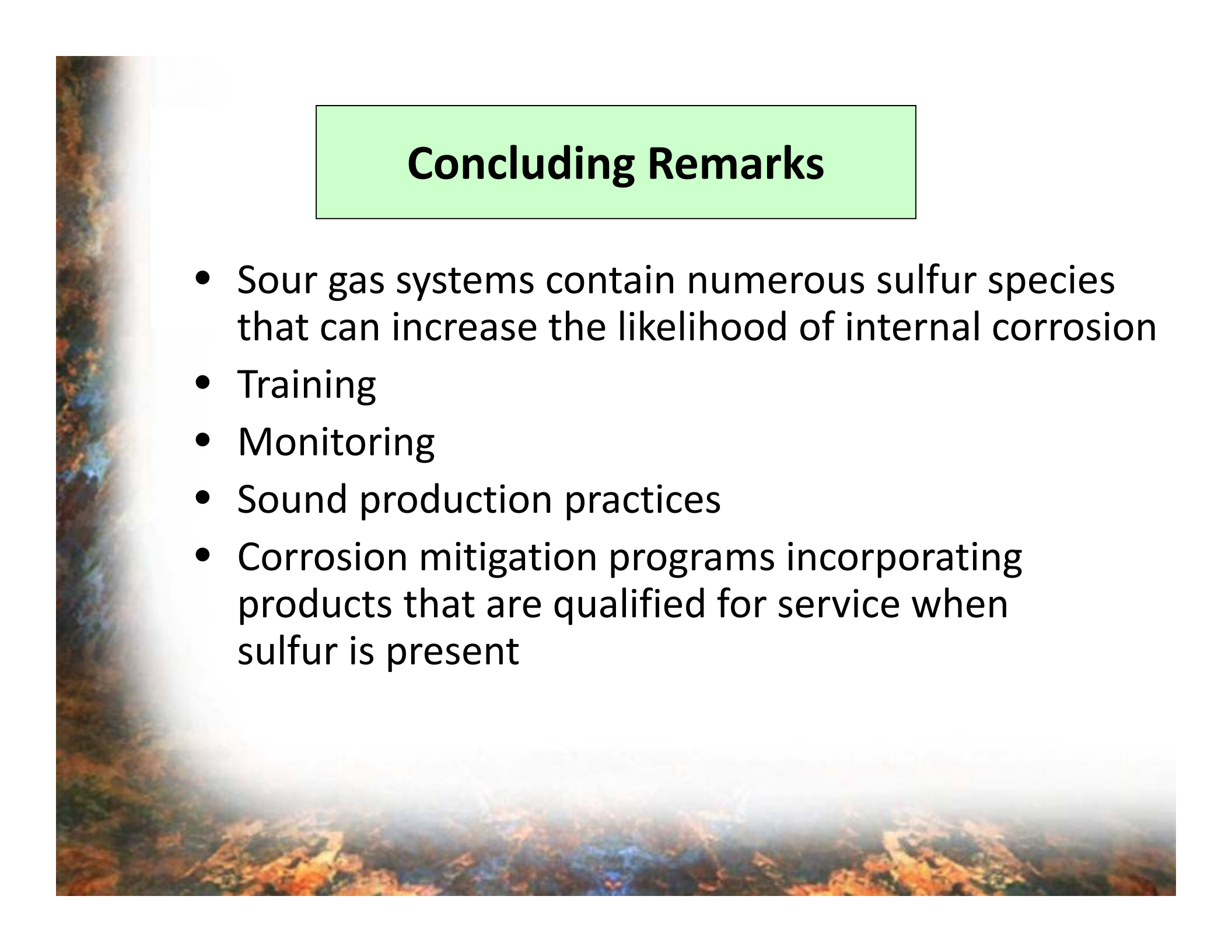
**With So Many Sulfur Species and Pathways
That Increase the Likelihood of a Pipeline Failure,
What Can I Do?**






Mitigation Options

- Heightened awareness/analysis of solids from pig barrels, chokes, valves, etc.
- Increase the pigging frequency
- Ensure that the current continuous injection and/or batch inhibitors have been qualified to mitigate corrosion in the presence of elemental sulfur
- Increase the concentration of the continuous corrosion inhibitor
- Increase the batch frequency



Concluding Remarks

- Sour gas systems contain numerous sulfur species that can increase the likelihood of internal corrosion
- Training
- Monitoring
- Sound production practices
- Corrosion mitigation programs incorporating products that are qualified for service when sulfur is present



Thank-you for Your Attention!

- Added thanks to:
 - NACE - Calgary Section for the opportunity to present this information
 - Dr. Leslie May and Dr. John Lerbscher for technical discussions and input
 - Wellington Wamburi, Sherman Kung and Chris Dilley for performing the laboratory experiments