



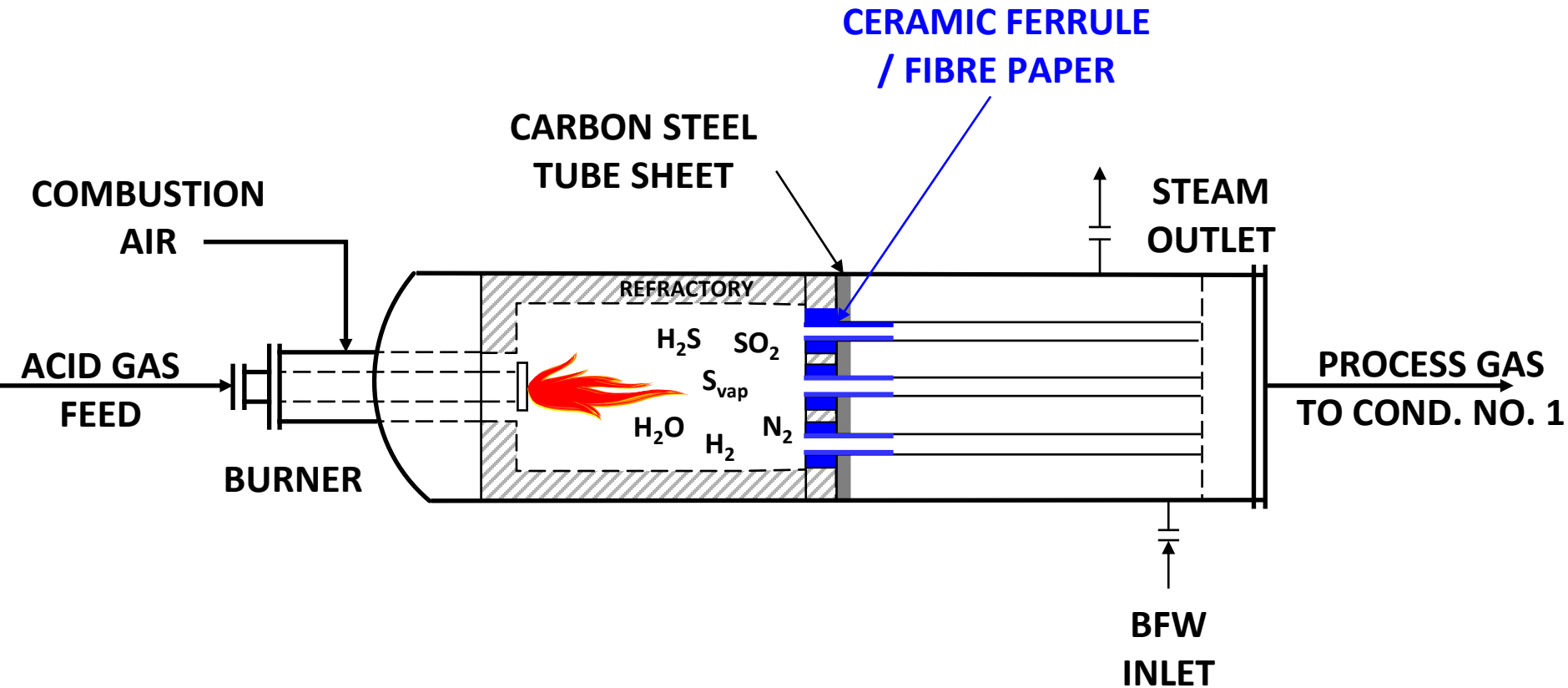
High Temperature Sulfidation in Claus versus Hydrotreating Environments

Christopher B. Lavery, Ruohong Sui, and Robert A. Marriott
Brimstone Sulfur Symposium, Vail, Colorado (Virtual)

September 14th-16th, 2021



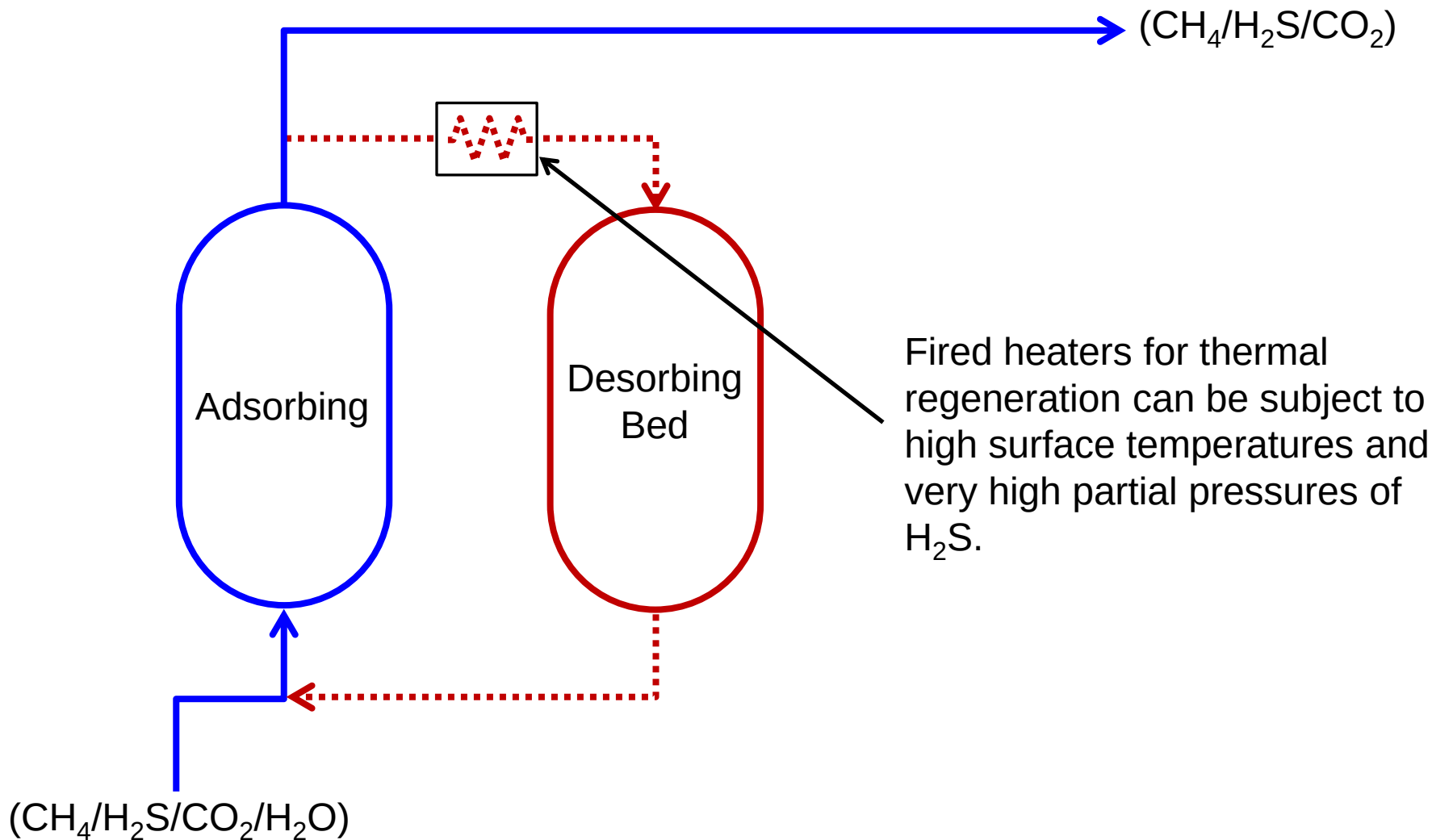
Overview of Claus Thermal Reactor and Waste Heat Boiler



- Ceramic ferrule / fibre paper thermal protection system for the critical tube-to-tube sheet area
- Current guide for $T_{\max}$ design based on published correlations for high temperature sulfidic corrosion



Molecular Sieve Regeneration





High Temperature Sulfidic Corrosion of Carbon Steel

- **McConomy Curves (1963)**
 - Based on survey conducted by API Sub-committee on Corrosion (published 1963)
 - For high temperature sulfidic corrosion in H_2 -free environment
 - Curves decreased by a factor of 2.5 in mid-1980's
 - Perhaps most useful for metallurgy selection
- **Couper-Gorman Curves (1971)**
 - Based on survey conducted by NACE Technical Committee T-8 on Refining Industry Corrosion (published 1971)
 - High temperature sulfidic corrosion in the presence of H_2
 - Naphtha and gas / oil curves
 - Used as design basis for Claus WHB tube / tube sheet corrosion
- **Claus-modified Couper-Gorman Curves (McGuffie, Porter, Martens and Demskie (2011))**
 - Curves shifted to predict lower corrosion rates in Claus SRU service
 - Based on operational experience
- **Current ASRL Research Project**
 - Measurements under Claus conditions and high- H_2S conditions



Experimental Conditions

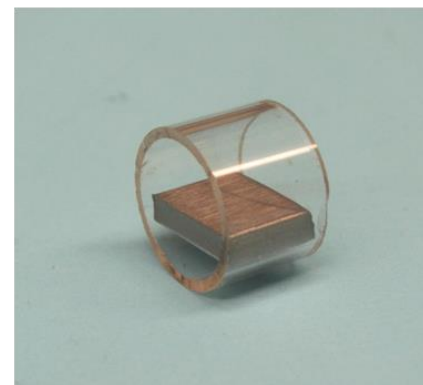
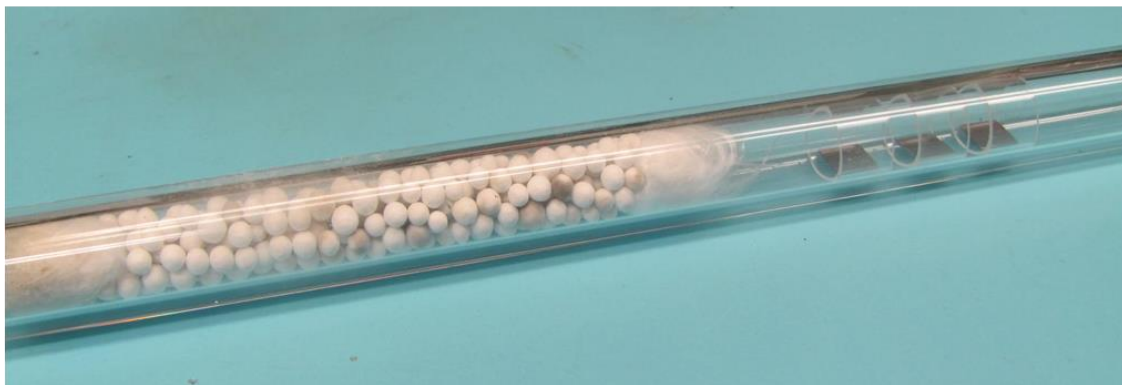
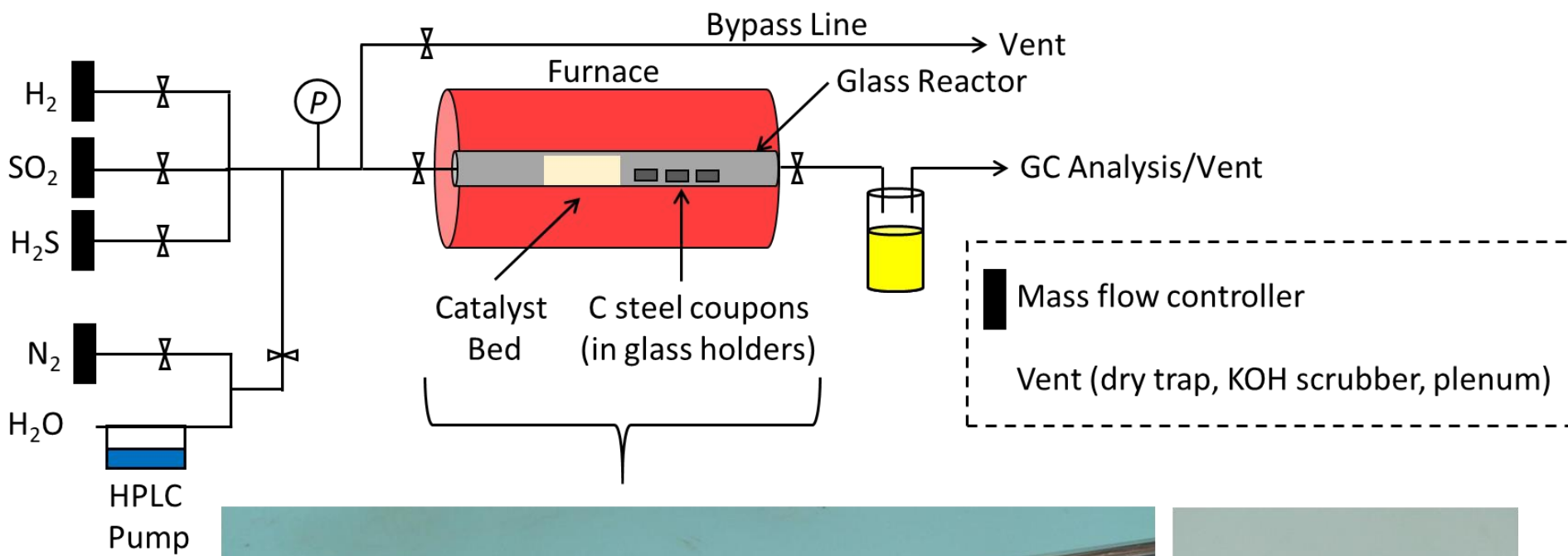
$T / ^\circ\text{C}$	$\text{H}_2\text{S} / \text{mol\%}$	$\text{SO}_2 / \text{mol\%}$	$\text{S}_2\text{-S}_8 / \text{mol\%}$	$\text{N}_2 / \text{mol\%}$	$\text{H}_2 / \text{mol\%}$	$\text{H}_2\text{O} / \text{mol\%}$
300	2.0	1.0	3.9	58.5	5.0	29.6
325	2.8	1.4	3.8	58.2	5.0	28.8
350	3.6	1.8	3.8	57.9	5.0	27.9
375	4.4	2.2	3.8	57.6	5.0	27.0
400	5.2	2.5	3.8	57.5	5.0	26.0

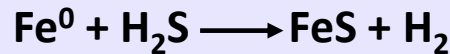
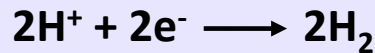
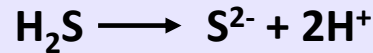
- Equilibrium furnace calculation gives *ca.* 5% H_2 (100% H_2S / air)
- Carbon steel coupons; experimental temperatures of 300, 325, 350, 375, and 400°C
- Calculated liquid sulfur dew-point: 280°C
- Weight loss corrosion rates; W (g), D (g/cm³), A (cm²), t (h)

$$\text{Corrosion Rate (mpy)} = (3.45 \times 10^6 \times W) / (D \times A \times t)$$



Simplified Schematic of Experimental Setup

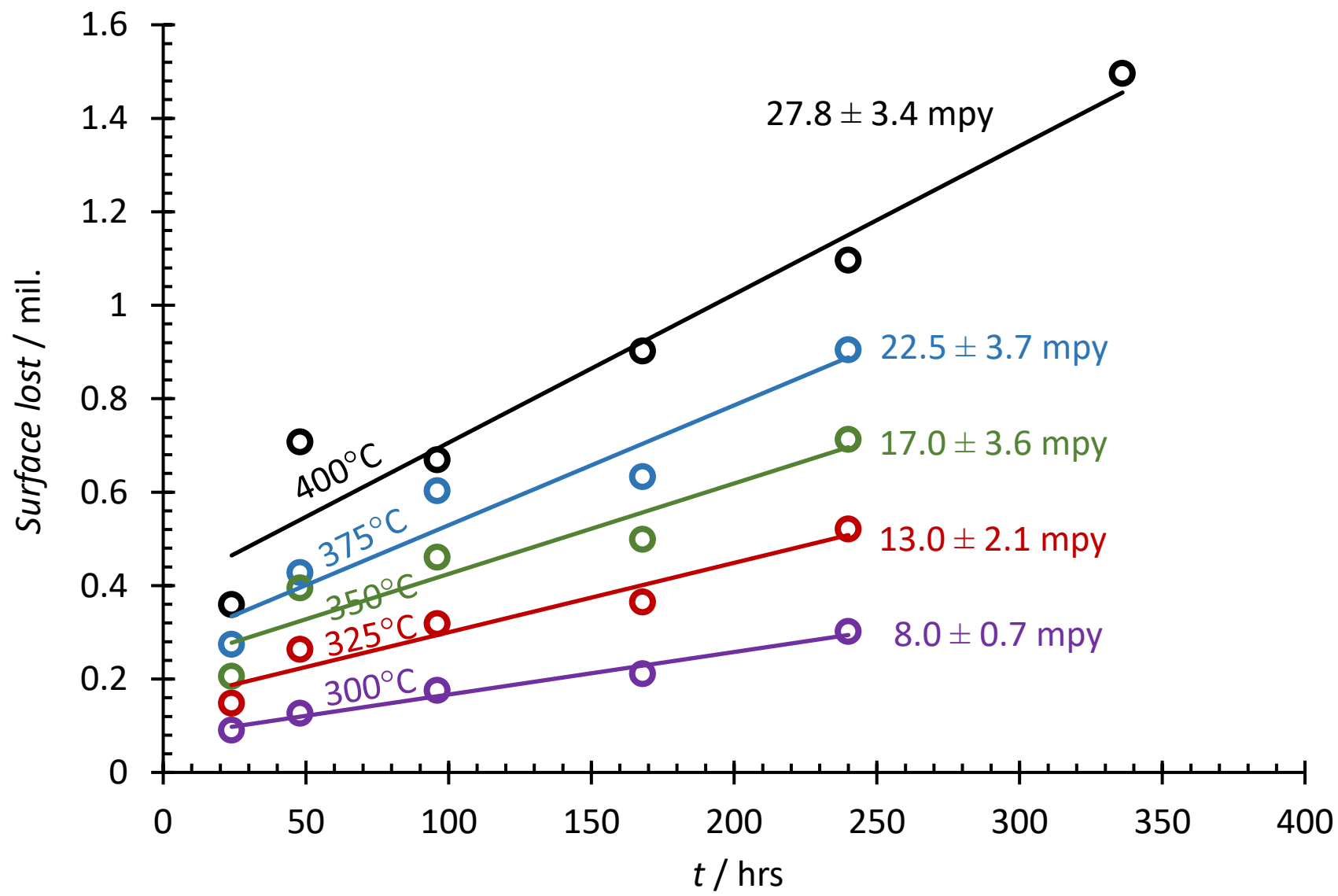




- **Factors that Impact the Nature and Stoichiometry of FeS**
 - Temperature, H_2S concentration, presence of other sulfur species
 - Type of steel, heat treatment, Cr content, Si content, Mo content
- **Fe_xS_y Semi-Protective Layer**
 - Limits the rate of diffusion of corrosive species
 - Ongoing sulfidation is limited by sulfur diffusion through the FeS film which is increasing in thickness (rate order related to film stoichiometry)
 - Initial period of rapid corrosion followed by a more gradual decrease and eventual stabilization in rate (parabolic rate)

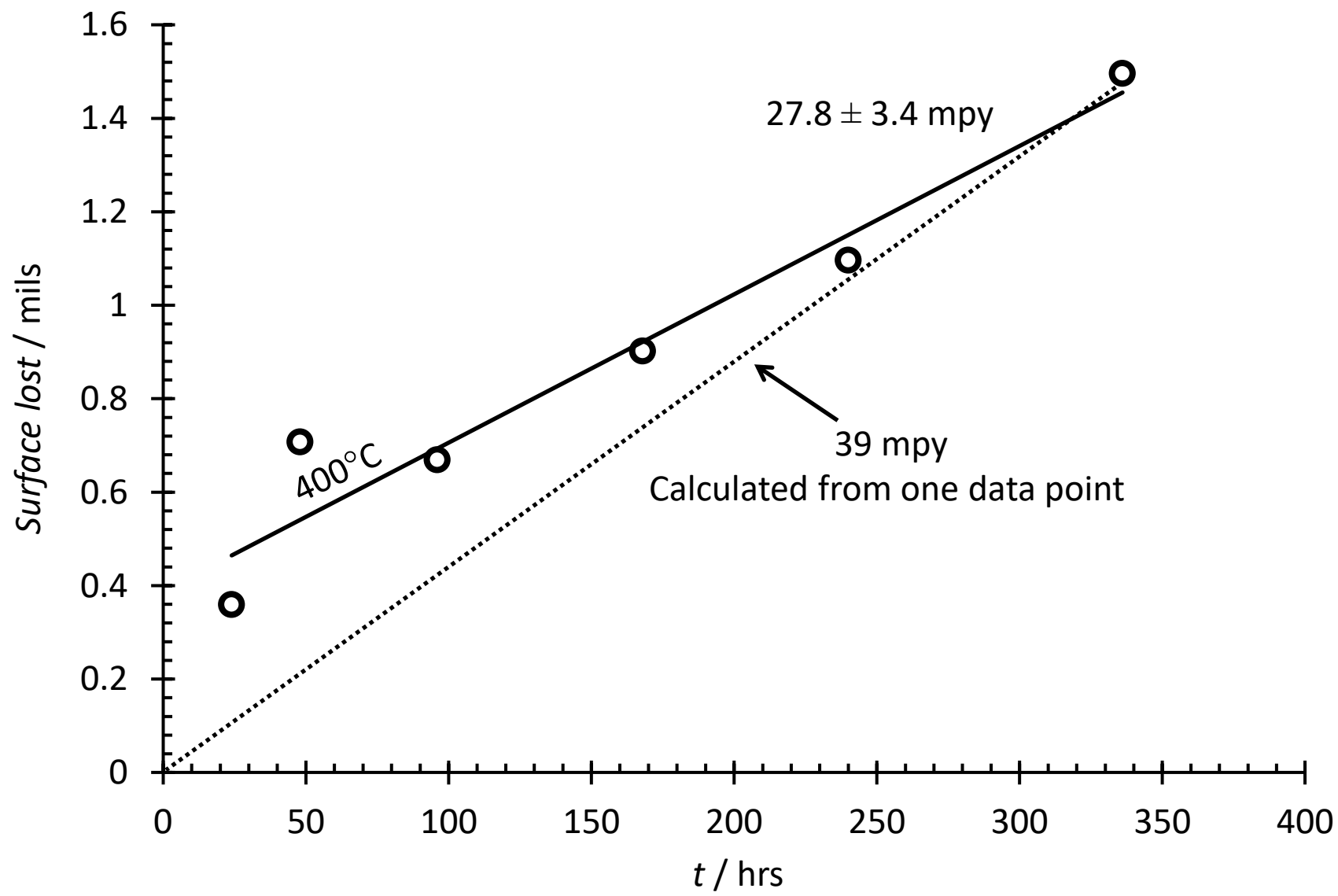


Corrected Corrosion Rates





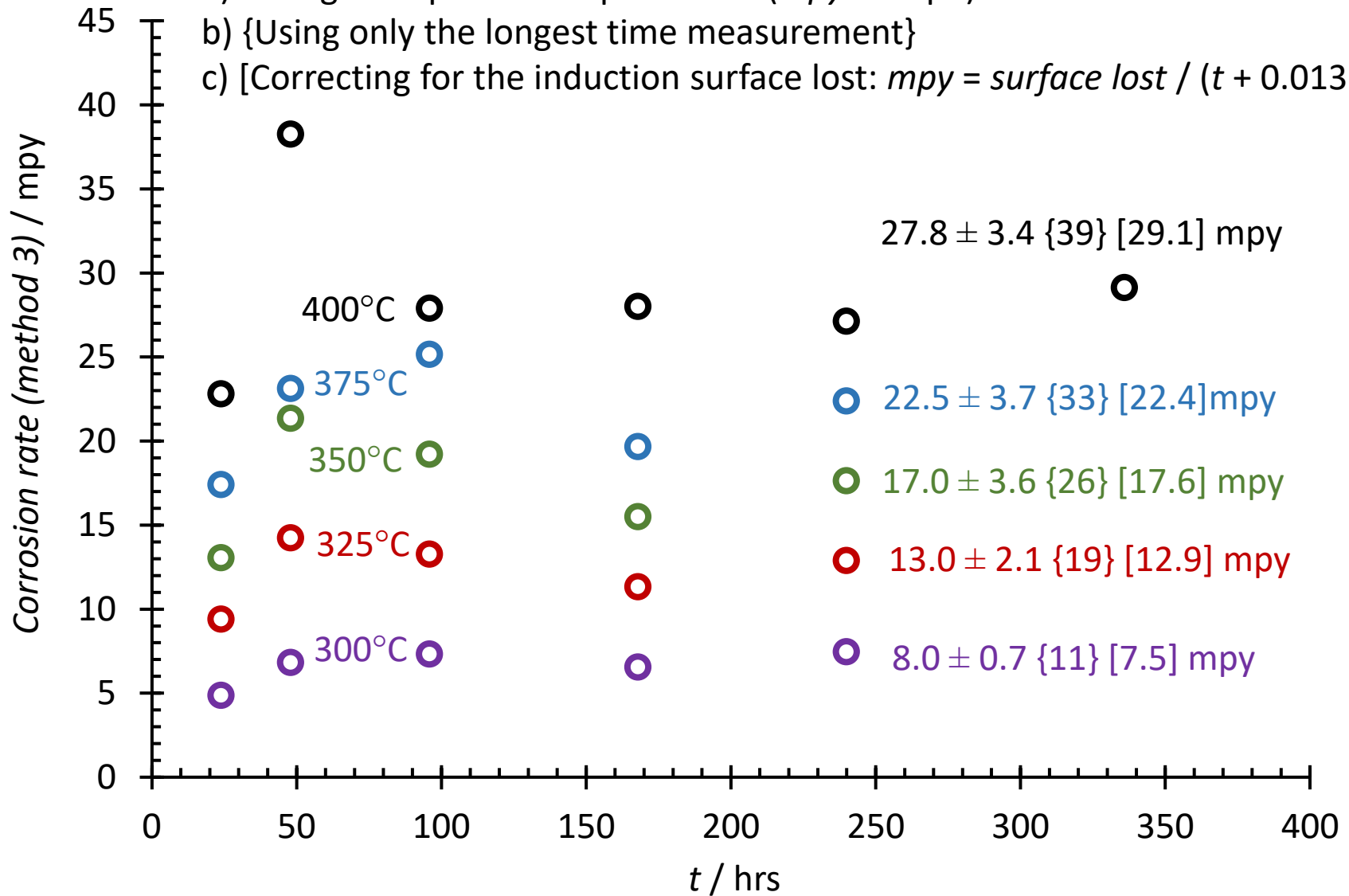
Corrected Modelling Results





Can we Obtain Rates from One Measurement?

- a) Fitting multiple time experiments (*mpy* = slope)
- b) {Using only the longest time measurement}
- c) [Correcting for the induction surface lost: $mpy = \text{surface lost} / (t + 0.013 \text{ years})$]





Comparison to Existing Correlations at Corresponding T and H_2S Concentration

$T / ^\circ\text{C}$	$x / \text{mol}\%$						<i>Corrosion Rate / mpy</i>		
	H_2S	SO_2	$\text{S}_2\text{-S}_8$	N_2	H_2	H_2O	This work	Couper-Gorman ^a	Martens et al.
300	2.0	1.0	3.9	58.5	5.0	29.6	7.5	7	3
325	2.8	1.4	3.8	58.2	5.0	28.8	12.9	15	5
350	3.6	1.8	3.8	57.9	5.0	27.9	17.6	20	8
375	4.4	2.2	3.8	57.6	5.0	27.0	22.4	30	13
400	5.2	2.5	3.8	57.5	5.0	26.0	29.1	45	20

^aNaphtha desulfurizers, whereas the Gas / Oil desulfurizers curves indicate even larger rates

Outstanding questions.....

What are the corrosive sulfur species in a Claus thermal reactor?

What role does H_2 play?

What happens to agreement with Couper-Gorman curves in an O_2 enrichment environment?



Which Species are Important for our Claus Conditions?

<i>T</i> / °C	<i>x</i> / mol%						<i>Corrosion Rate</i> / mpy		
	H ₂ S	SO ₂	S ₂ -S ₈	N ₂	H ₂	H ₂ O	This work	Couper-Gorman ^a	Martens et al.
300	2.0	1.0	3.9	58.5	5.0	29.6	7.5	7	3
325	2.8	1.4	3.8	58.2	5.0	28.8	12.9	15	5
350	3.6	1.8	3.8	57.9	5.0	27.9	17.6	20	8
375	4.4	2.2	3.8	57.6	5.0	27.0	22.4	30	13
400	5.2	2.5	3.8	57.5	5.0	26.0	29.1	45	20
350^c	3.6	1.8	3.8	62.9	---	27.9	19.0	20	8
400^c	5.2	2.5	3.8	62.5	---	26.0	26.4	45	20
350^c	3.6	---	---	86.4	---	10.0	7.5	20	8
350^c	---	1.8	---	88.2	---	10.0	5.4	0	0
350^c	---	---	3.8	96.2	---	---	5.4	0	0

H₂ doesn't make a significant difference at these conditions.

H₂S, SO₂ and sulfur species contribute to corrosion loss under Claus conditions.

^csingle experiment at 240+ hours and corrected for the induction surface lost: *surface lost* / (t + 0.13 years)¹²



A Semi-empirical Corrosion Rate Equation

$$rate(\text{mpy}) = kp_{H_2S}^n = Ae^{-B/T} p_i^n$$

- H_2S , SO_2 and sulfur species contribute to corrosion loss under Claus conditions, which is much more complicated than we previously thought.

$$p_i \neq p_{H_2S}$$

$$p_S = p_{H_2S} + p_{SO_2} + \sum_{x=2}^8 p_{S_x}$$

$$rate(\text{mpy}) = Ae^{-B/T} p_S^n$$

$$\ln(rate) = \ln A - \frac{B}{T} + n \ln p_S$$

- We need a variance of partial pressures (which can include oxygen enrichment and/or the molecular sieve cases)



Oxygen Enrichment and Pure H₂S?

<i>T</i> / °C	<i>x</i> / mol%						<i>Corrosion Rate</i> / mpy		
	H ₂ S	SO ₂	S ₂ -S ₈	N ₂	H ₂	H ₂ O	This work	Couper-Gorman	Martens et al.
300	2.0	1.0	3.9	58.5	5.0	29.6	7.5	7	3
325	2.8	1.4	3.8	58.2	5.0	28.8	12.9	15	5
350	3.6	1.8	3.8	57.9	5.0	27.9	17.6	20	8
375	4.4	2.2	3.8	57.6	5.0	27.0	22.4	30	13
400	5.2	2.5	3.8	57.5	5.0	26.0	29.1	45	20
350^c	3.6	1.8	3.8	62.9	---	27.9	19.0	20	8
400^c	5.2	2.5	3.8	62.5	---	26.0	26.4	45	20
350^c	3.6	---	---	86.4	---	10.0	7.5	20	8
350^c	---	1.8	---	88.2	---	10.0	5.4	0	0
350^c	---	---	3.8	96.2	---	---	5.4	0	0
290^c	4.0	2.0	9.9	9.2	---	75.0	16.3	5	2
300^c	4.4	2.2	9.8	9.2	---	74.4	19.0	7	3
350^c	7.4	3.7	9.4	9.1	---	70.4	29.8	20	8
400^c	11.2	5.6	9.0	8.7	---	65.5	50.9	45	20
350^c	100 (100 psig)						21.5	20	8

For H₂S > 1 mol%, both Couper-Gorman and Martens et al show negligible concentration dependence.



A Semi-empirical Corrosion Rate Equation

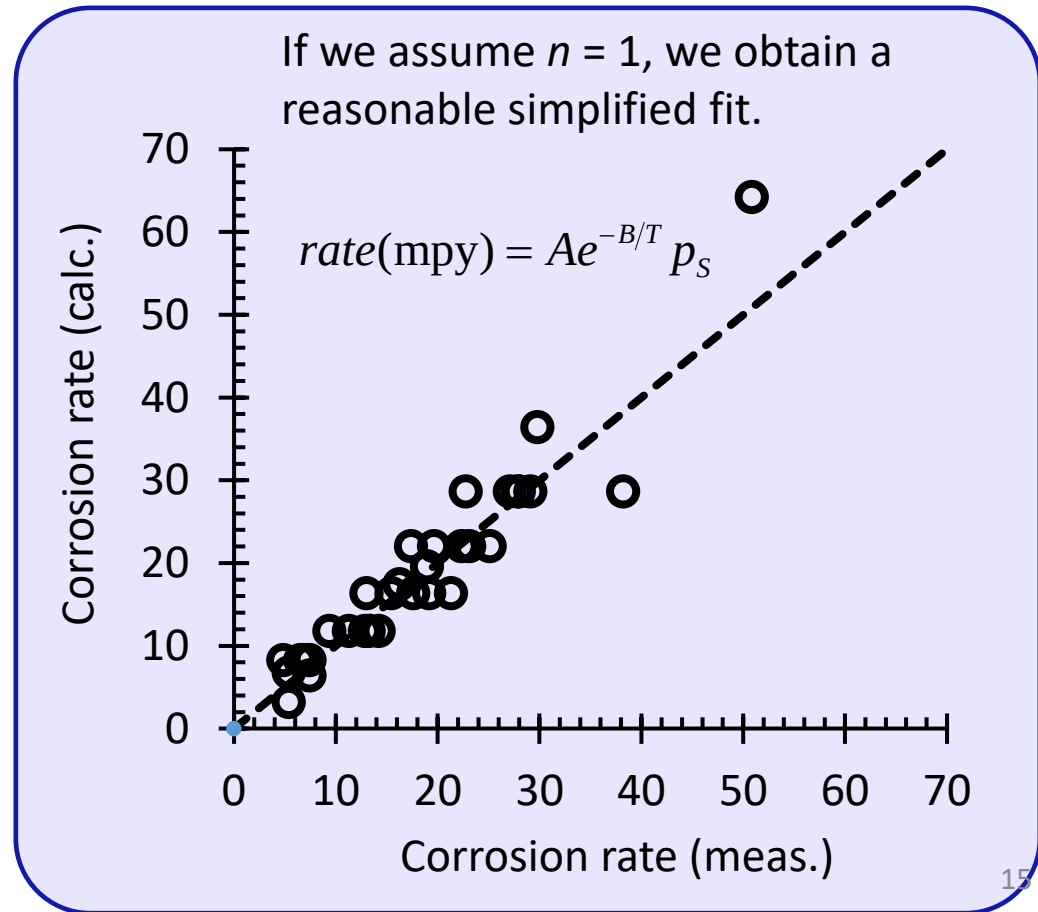
$$rate(\text{mpy}) = Ae^{-B/T} p_S^n$$

Fitting to our new data (without the high-pressure H_2S) shows $n = 0.82 \pm 0.6$; $R^2 = 0.957$

Why doesn't the high pressure H_2S fit this model?

Is there a water vapour dependence?

Literature demonstrates that the rate order is related to the sulfidic species (film)

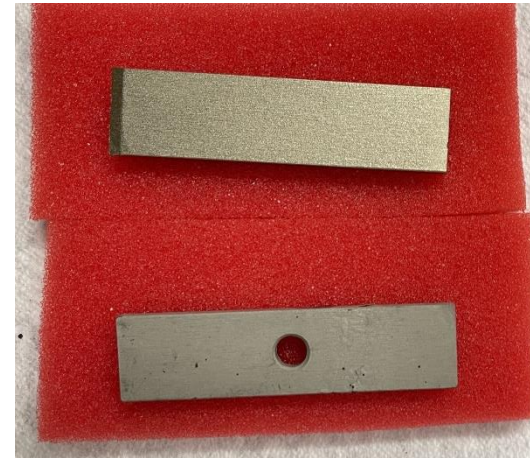
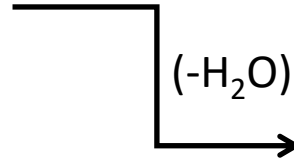
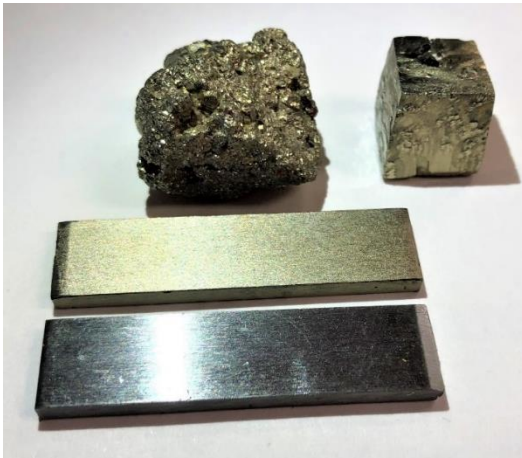




What scale is formed?

- When wet H_2S is present, we always observe a shell of pyrite (FeS_2)
- Removal of H_2O results in shell of pyrrhotite (FeS_x ; $x = 1-1.6$)

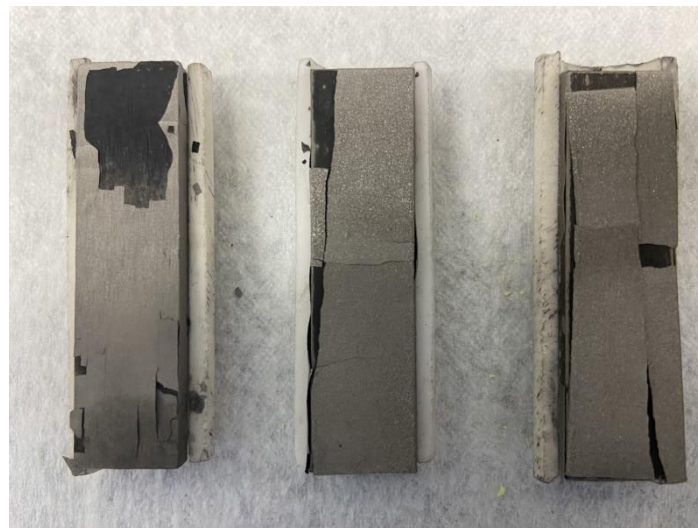
3% H_2S /
10% H_2O



7.5 mpy

4.7 mpy

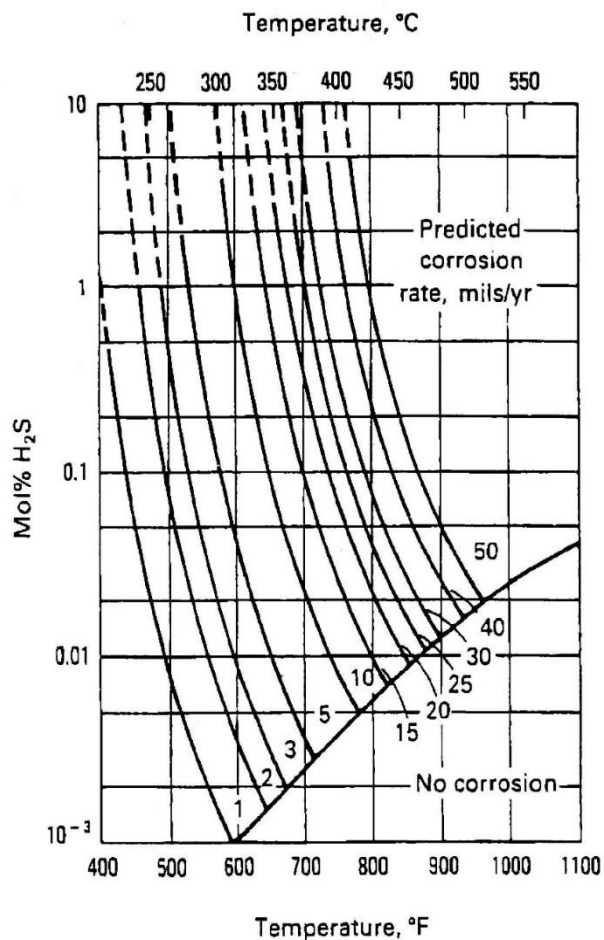
- At higher H_2S pressures (100% H_2S / 100 psig) also generates pyrrhotite



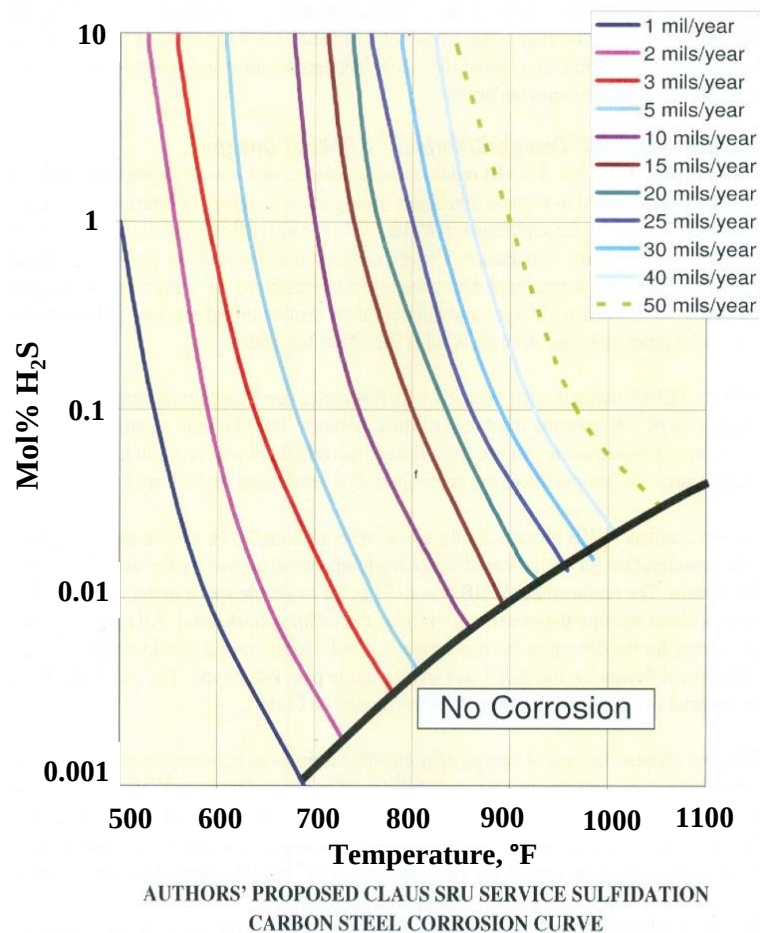
21.5 mpy



The Current High-temperature Sulfidation Charts



*Curves
Shifted
(100°F)*



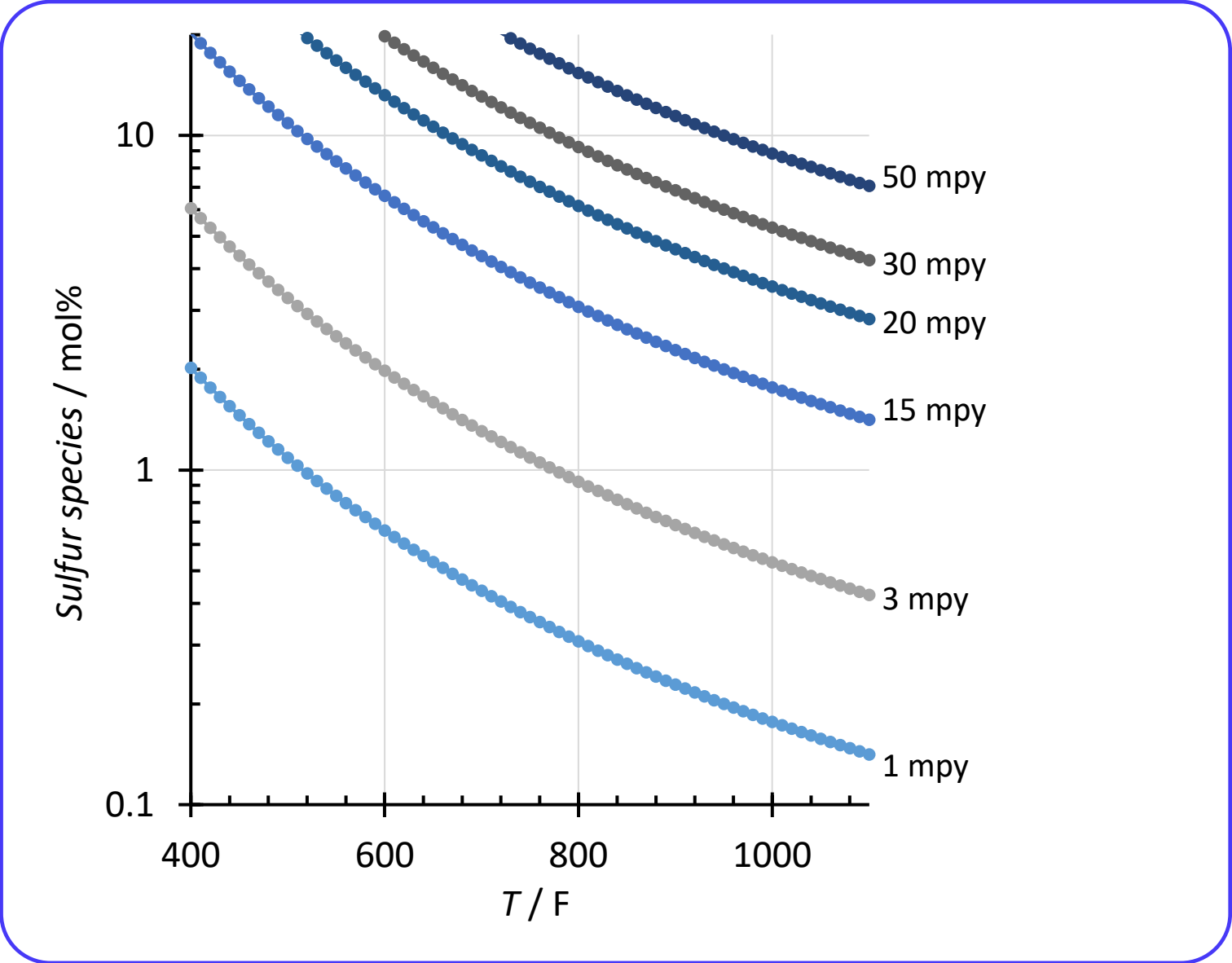
NACE Technical Committee T-8 on Refining Industry Corrosion

S. McGuffie, M. Porter, D. Martens and M. Demskie, ASME PVP2011 Conference

ASSET software also does not calibrate with full Claus speciation.



Preliminary Modelling based on Experimental Data at Claus Conditions Only





Conclusions or more questions?

- Parabolic measured rates have been corrected for “onset” versus “steady-state” corrosions with H_2S and other Claus species, *i.e.*, care must be taken to avoid errors associated with the initial rate method
- For regular Claus conditions (without oxygen enrichment or CO_2) our low-temperature experiments agree with the Couper-Gorman curves for naphtha desulfurization
- Additional experiments show that
 - SO_2 and sulfur species contribute to the measured corrosion rate
 - H_2 does not influence the rate (0-5 mol%)
- Oxygen enrichment studies show a more significant concentration dependence when compared to Couper-Gorman or the Marten et al. curves (likely also a significant H_2O dependence)
- Multiple corrosion scales have been observed, which influence the mechanism and rate order
- H_2S , H_2O and CO_2 will be investigated further to better understand the kinetics
- Effect of silica leaching
- 310SS and HR-160 will be investigated next at Claus conditions



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