UNIVERSITY OF CALGARY

High Temperature Sulfidation of Carbon Steel under Claus Waste Heat Boiler Conditions

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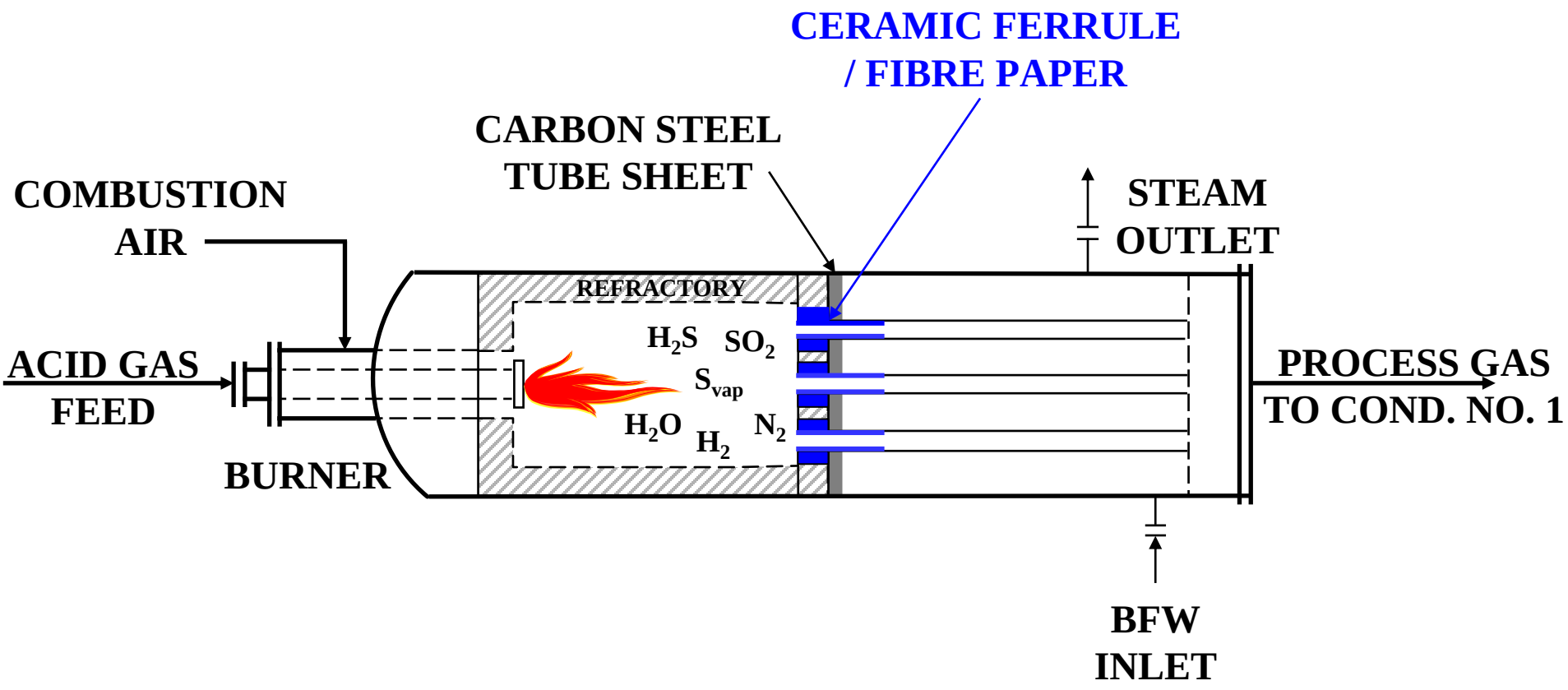
Overview of Claus Thermal Reactor and Waste Heat Boiler



- 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

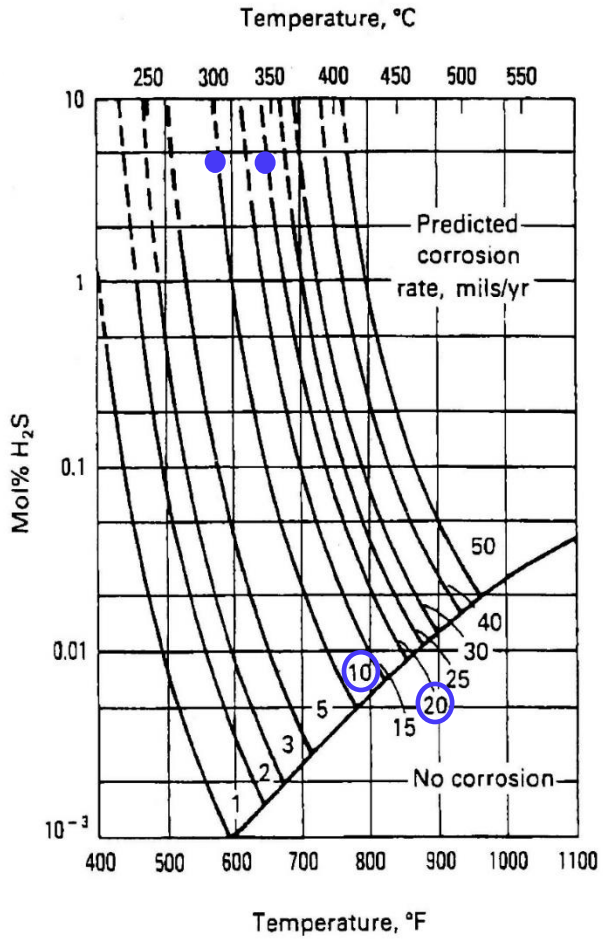
High Temperature Sulfidic Corrosion of Carbon Steel

- **McConomy Curves**
  - 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

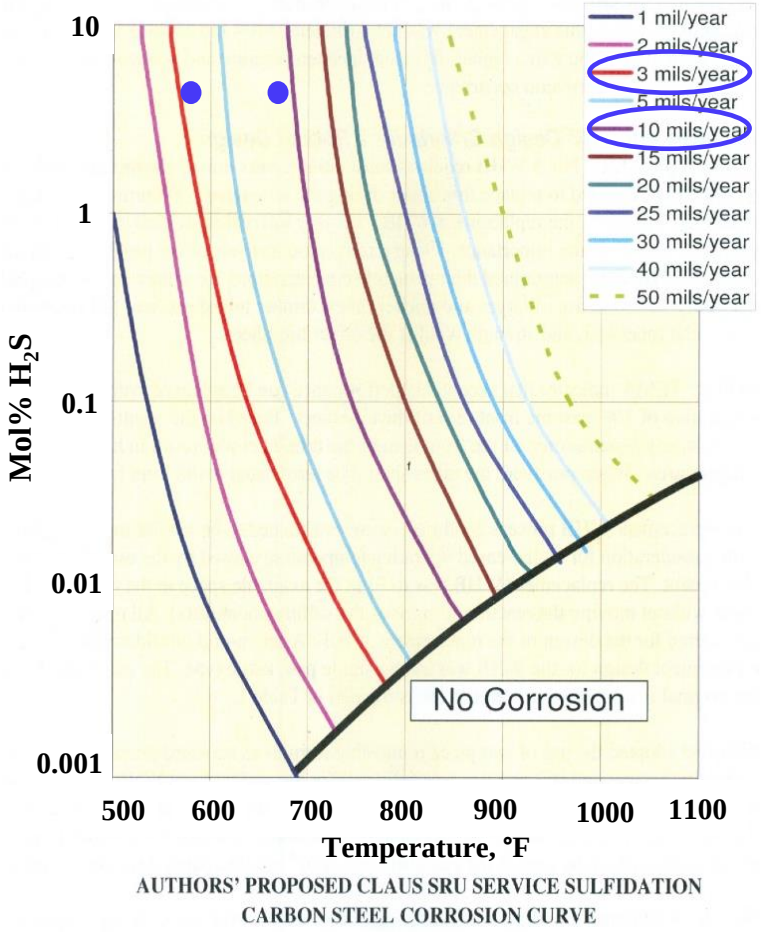
- **Couper-Gorman Curves**
  - Based on survey conducted by NACE Technical Committee T-8 on Refining Industry Corrosion (published 1971)
  - High temperature sulfidic corrosion in the presence of H_2
  - Naphtha and gas / oil curves
  - Used as design basis for Claus WHB tube / tube sheet corrosion

- **Claus-modified Couper-Gorman Curves**
  - Curves shifted to predict lower corrosion rates in Claus SRU service
  - Based on operational experience

Couper-Gorman (Naphtha) and Claus Modified Couper-Gorman Curves



Curves Shifted (100°F)

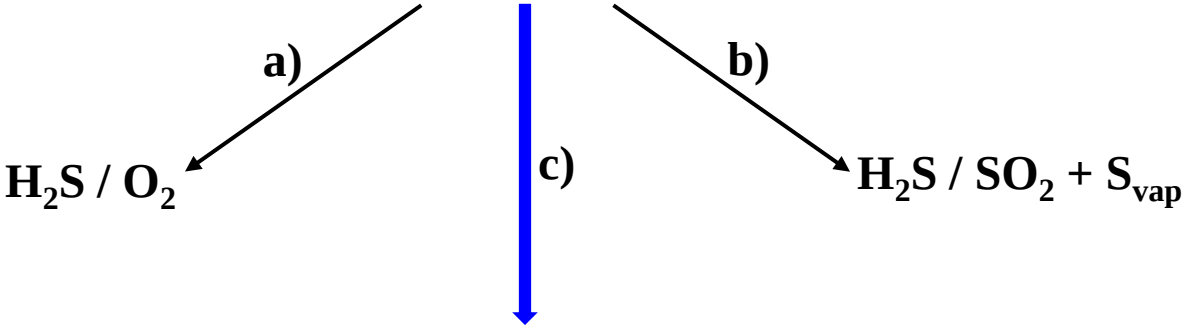


NACE Technical Committee T-8 on Refining Industry Corrosion

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

Laboratory Feed Setup

Possible Approaches



Use feed corresponding to post-H_2S combustion / pre-Claus reaction and rely on Claus reaction to form elemental sulfur:

$$3\ H_2S + 1.5\ O_2 + 5.64\ N_2 \longrightarrow 2\ H_2S + SO_2 + H_2O + 5.64\ N_2$$

~ 20% 10% 10% 60%

N_2 + H_2

55% 5%

- **Need to add H_2 to simulate WHB conditions in the lab experiments**

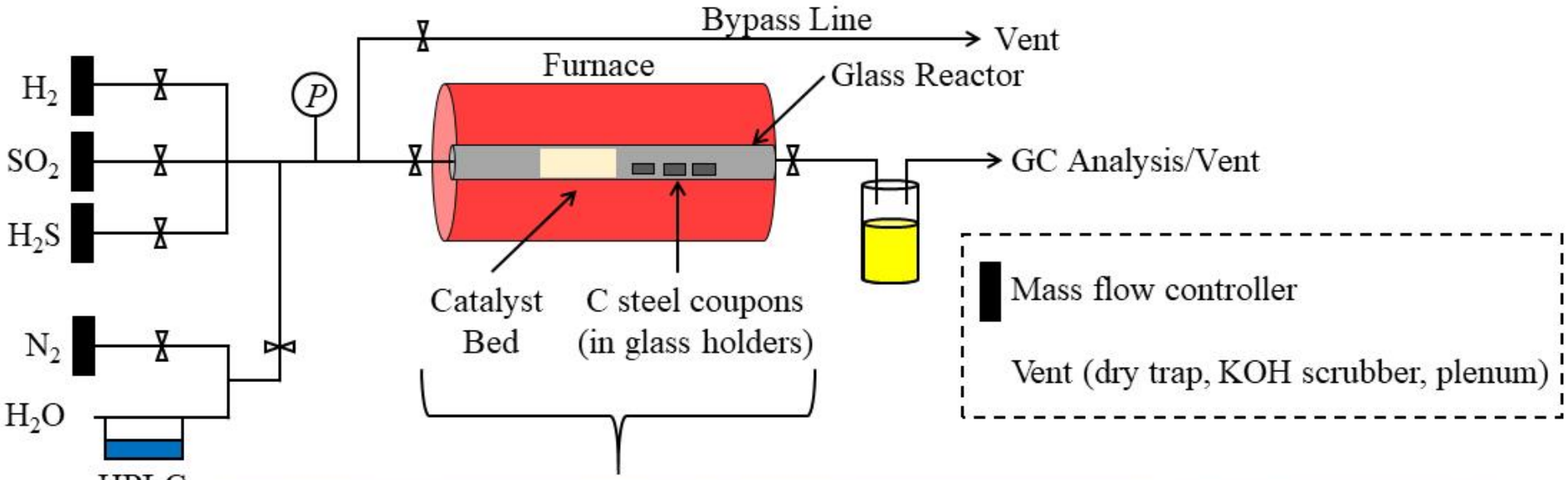
Experimental Conditions

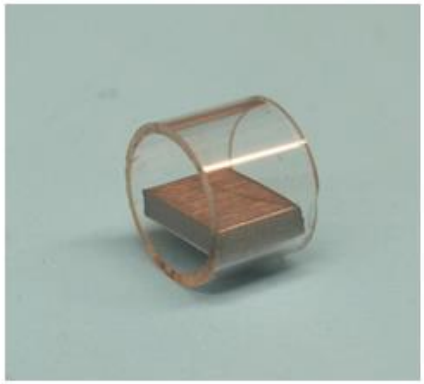
Temp. °C	H_2S / SO_2 mol%	S_2-S_8 mol%	N_2 mol%	H_2 mol%	H_2O mol%
300	2 / 1	3.9	58.5	5	29.6
325	2.8 / 1.4	3.8	58.2	5	28.8
350	3.6 / 1.8	3.8	57.9	5	27.9
375	4.4 / 2.2	3.8	57.6	5	27.0
400	5.2 / 2.5	3.8	57.5	5	26.0

- **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/cm^3), *A* (cm^2), *t* (h)**

$$Corrosion\ Rate\ (mpy) = (3.45\times10^6\times W)/(D\times A\times t)$$

Simplified Schematic of Experimental Setup





High Temperature Sulfidic Corrosion

$$Fe^0 \longrightarrow Fe^{2+} + 2e^-$$

$$H_2S \longrightarrow S^{2-} + 2H^+$$

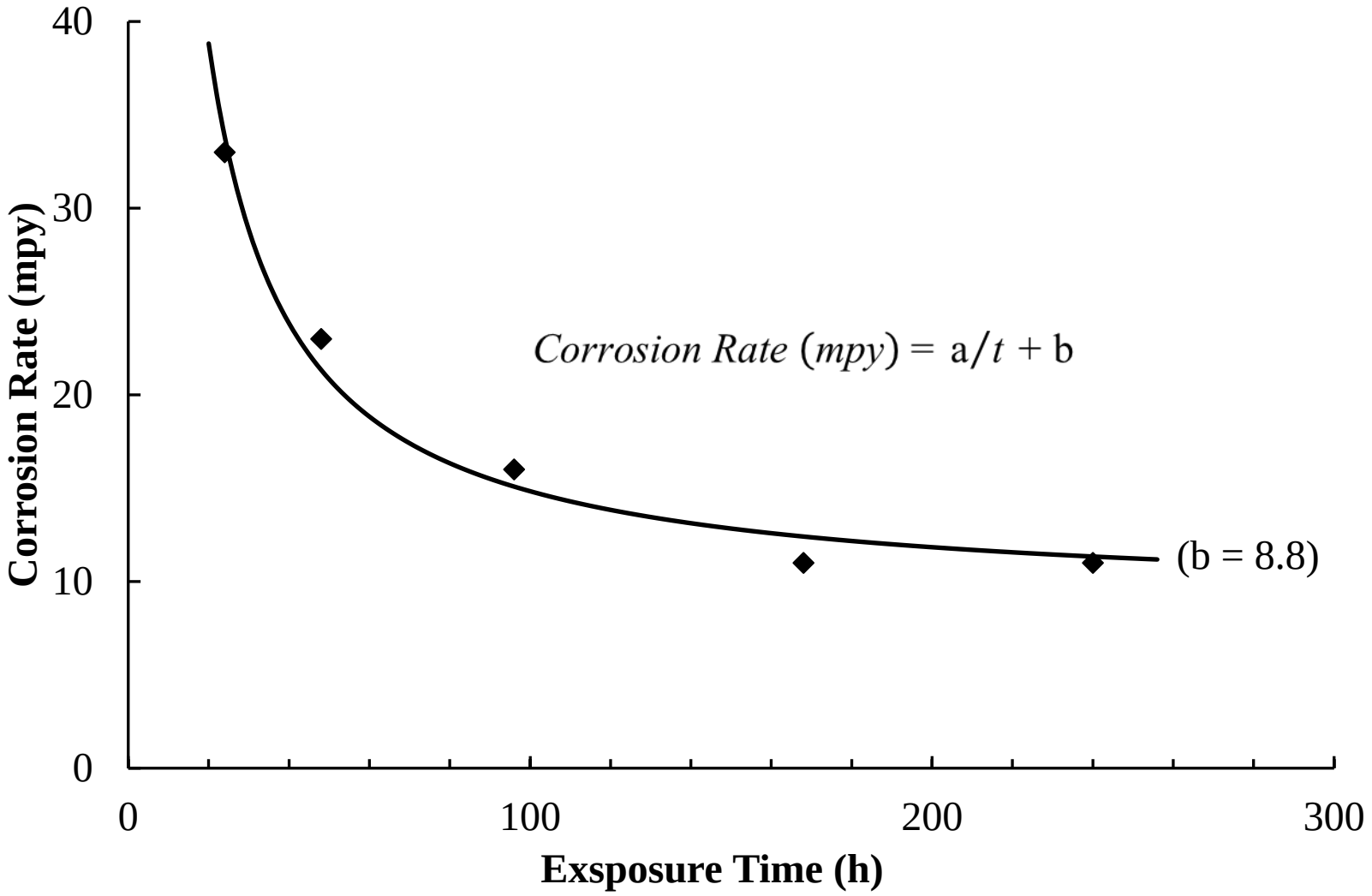
$$2H^+ + 2e^- \longrightarrow 2H_2$$

$$Fe^0 + H_2S \longrightarrow FeS + H_2$$

- **Nature and Stoichiometry of FeS**
  - Temperature, H_2S concentration, presence of other sulfur species, turbulence / erosion issues
  - Type of steel, heat treatment, Cr content, Si content, Mo content

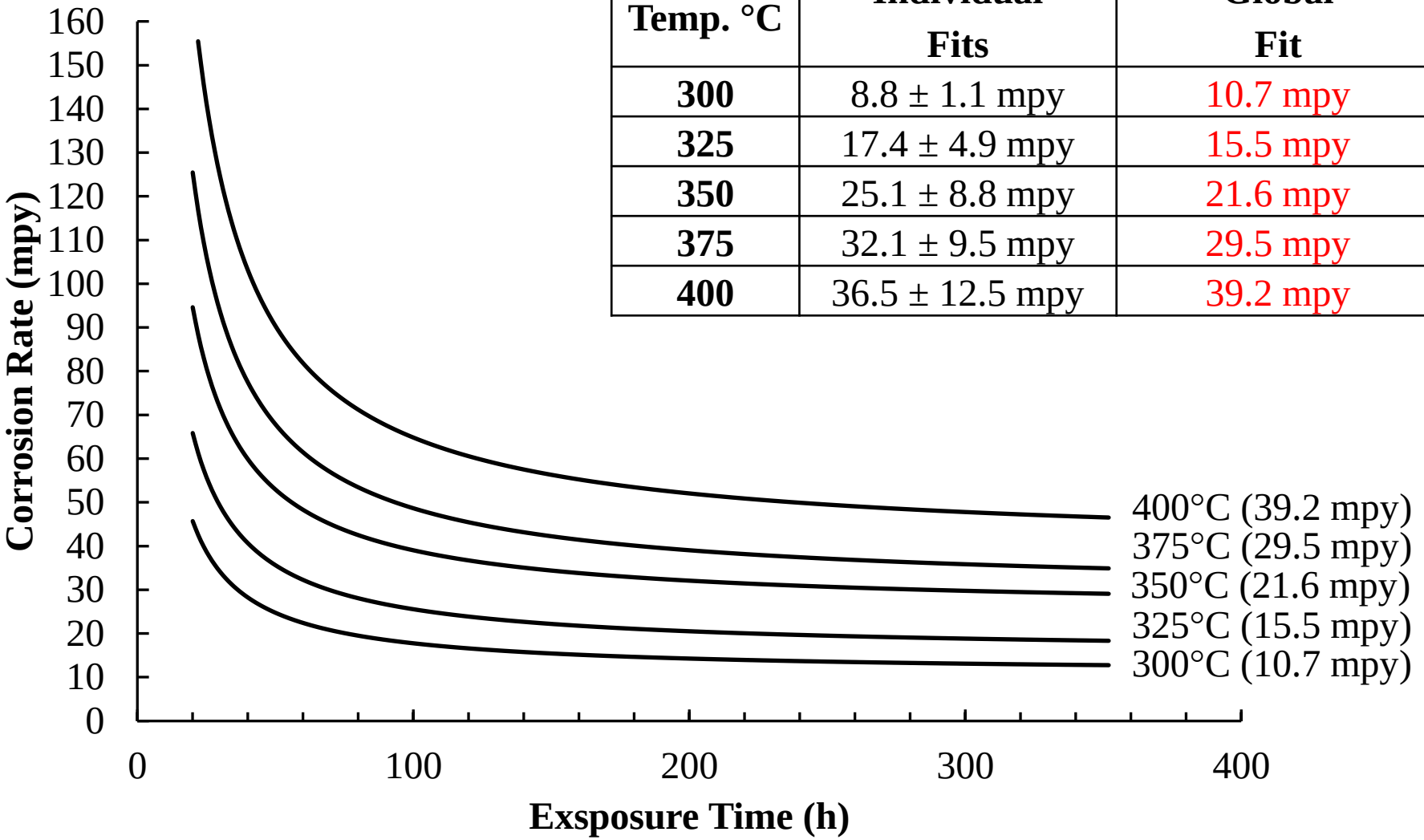
- **Fe_xS_y Semi-Protective Layer**
  - Limits the rate of diffusion of corrosive species
  - Ongoing sulfidation is limited by sulfur diffusion through the FeS film which is increasing in thickness
  - Initial period of rapid corrosion followed by a more gradual decrease and eventual stabilization in rate

Corrosion Profile at 300°C



Corrosion Profiles using Global Expression; H_2S (2-5 mol%)

Temp. °C	Individual Fits	Global Fit
300	8.8 ± 1.1 mpy	10.7 mpy
325	17.4 ± 4.9 mpy	15.5 mpy
350	25.1 ± 8.8 mpy	21.6 mpy
375	32.1 ± 9.5 mpy	29.5 mpy
400	36.5 ± 12.5 mpy	39.2 mpy

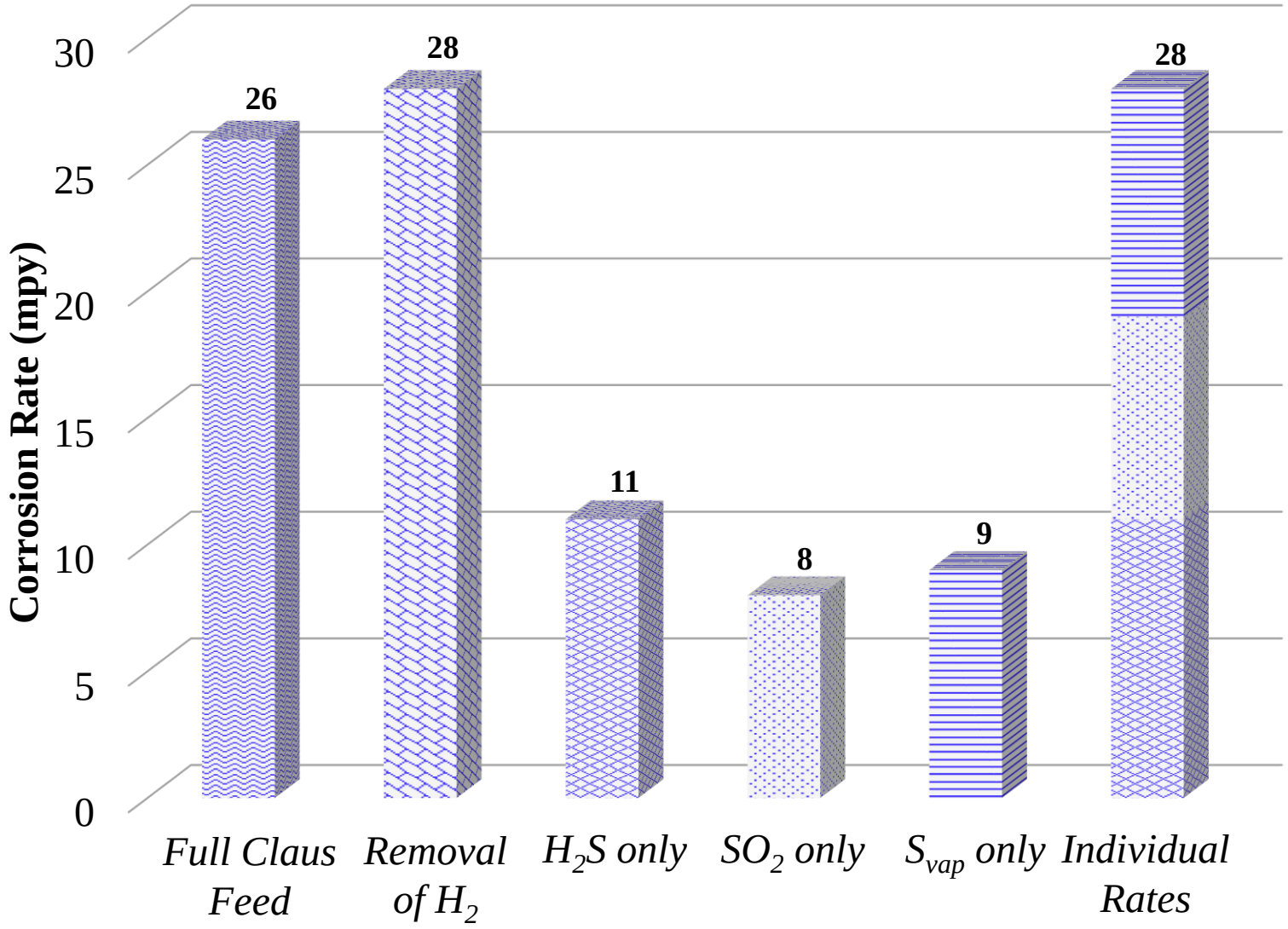


Comparison to Existing Correlations at Corresponding *T* and H_2S Concentration

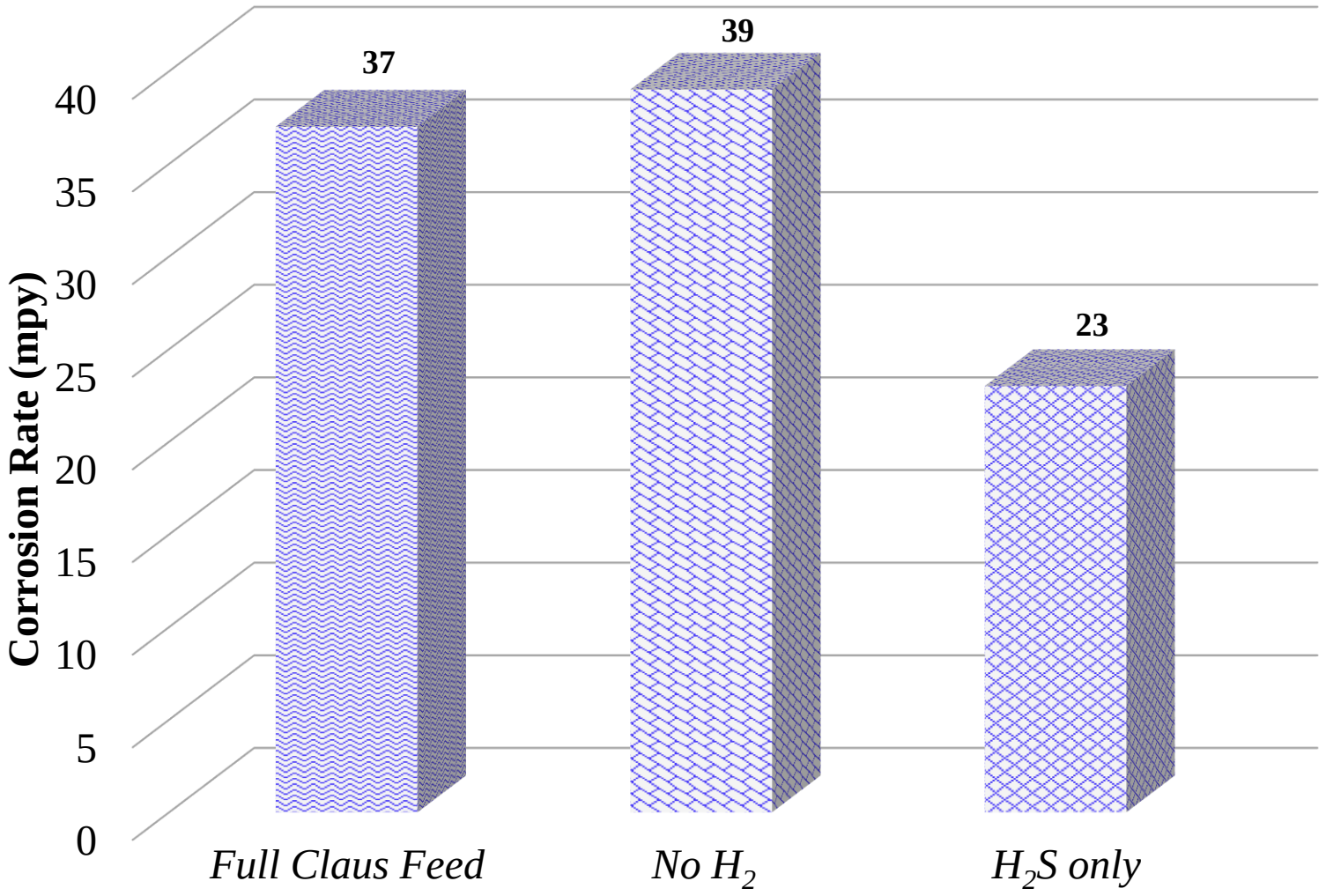
Temp. °C	Corr. Rate (mpy) This work	Corr. Rate (mpy) Couper-Gorman[a]	Corr. Rate (mpy) Couper-Gorman[b]	Corr. Rate (mpy) Martens et. al.
300	11	*ca.* 7	*ca.* 15	*ca.* 3
325	16	*ca.* 15	*ca.* 20	*ca.* 5
350	22	*ca.* 20	*ca.* 40	*ca.* 8
375	30	*ca.* 30	*ca.* 60	*ca.* 13
400	39	*ca.* 45	*ca.* 80	*ca.* 20

[a]Naphtha desulfurizers, [b]Gas / Oil desulfurizers

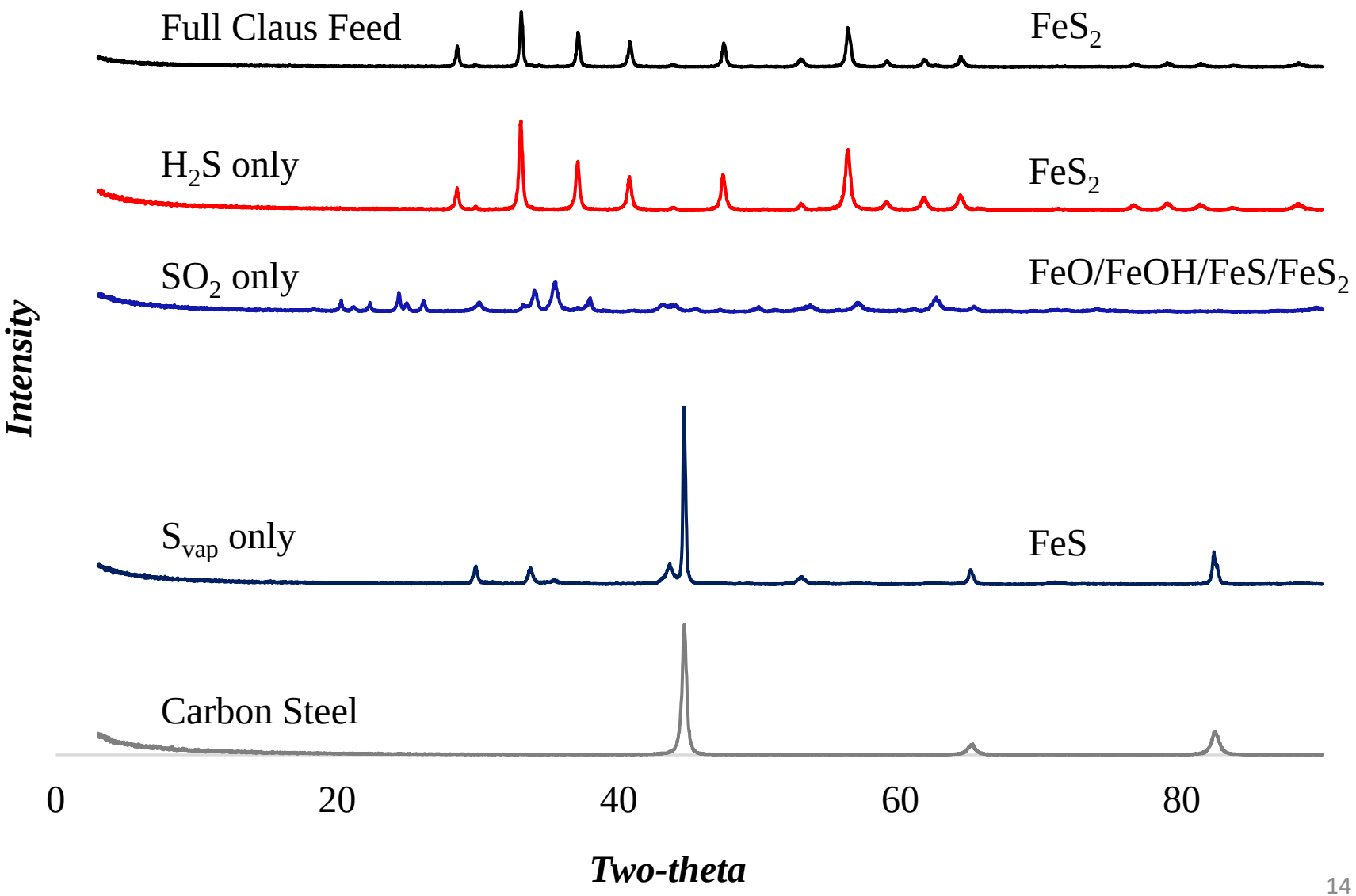
Stabilized Corrosion Rates Measured at 350°C



Stabilized Corrosion Rates Measured at 400°C

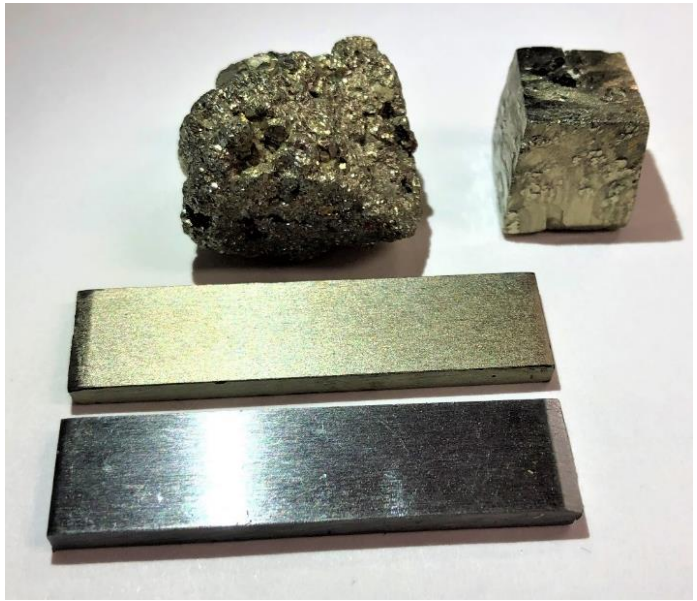


XRD Analysis of Various Corrosion Scales



Conclusions and Future Work

- **Global Expression**
  - Most accurate for conditions (H_2S 2-5 mol%) similar to those employed in this study
- **Results match best with naphtha Couper-Gorman curves**
  - Most likely just serendipitous
  - Presence/absence of 5 mol% H_2 did not influence corrosion rates significantly
- **Corrosion Scale Formed (FeS_2)**
  - H_2S, SO_2, and S_{vap} all contribute to overall corrosion rate
  - H_2S plays key role in formation of pyrite (FeS_2)
- **Recommend Lowest Temperature Practically Possible**
  - In agreement with recent recommendation of ≤315°C
- **Need to Investigate other Scenarios**
  - More varied H_2S concentrations (O_2 enrichment)
  - Impact of NH_3
  - Other alloys



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