

The H₂S Limbo in Lean Amine – How Low Can You Go?

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ABSTRACT

A recent internal survey of Amine Best Practices Group (ABPG) member companies showed a variety of practices related to the limits set for H₂S content of lean amine systems. Industry wide, a substantial amount of conflicting vendor and consultant guidelines exist, which are all prophesied to be “safe” and correct. Some relax minimum H₂S concentration limits to zero on MDEA systems that are formulated with heat stable salt stripping promoter. Others state a limit on H₂S lean loading. This raises the questions such as “Do levels of H₂S really matter?” and “How low can we go?”. Some consultants have taken the stance that lean amine corrosion is totally controlled by heat stable salts in solution, and state emphatically that they do not see corrosion in systems without heat stable salts.

This paper reviews important chemistry and process considerations that influence corrosion in amine systems, how H₂S concentrations are influenced by the process and heat stable salt contaminants, and why there are so many varied guidelines in the industry. Corrosion control practices by ABPG member companies are provided with an objective towards establishing more consistent industry guidelines for safe H₂S lean amine concentrations in alkanolamines.

References

[Can You Over-Strip Amine Systems? \(Part 1\)](#), Amine Experts YouTube series as accessed online 4/28/2025.

“Is Amine System Corrosion Different from Sour Water System Corrosion?”, Hatcher, N.A. and Keller, A.E., 2008 Brimstone Sulfur Symposium, Vail, CO.

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“Measurement of iron and lead sulfide solubility below 100°C”, Diana Carolina Figueroa Murcia, Philip L. Fosbøl, Erling H. Stenby, Kaj Thomsen, Fluid Phase Equilibria 475 (2018) 118e126

"The Solubility of Iron Sulfides and their Role in Mass Transport in Girdler-Sulfide Heavy Water Plants", P.H. Tewari, G. Wallace, and A.B. Campbell, Atomic Energy of Canada Ltd., 1978. AECL-5960.

“KINETICS OF IRON CARBONATE AND IRON SULFIDE SCALE FORMATION IN CO₂/H₂S CORROSION”, Wei Sun thesis dissertation, Ohio University, 2006.

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“The solubility of FeS”, Rickard, D., Geochimica et Cosmochimica Acta 70 (2006) 5779–5789.



THE H₂S LIMBO IN LEAN AMINE – HOW LOW CAN YOU GO?

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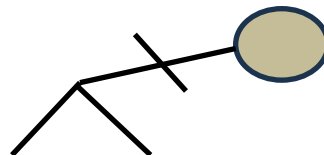
Nate Hatcher – on behalf of the industry Amine Best Practices Group (ABPG)

September 2025

CAN YOU OVERSTRIP AMINE?



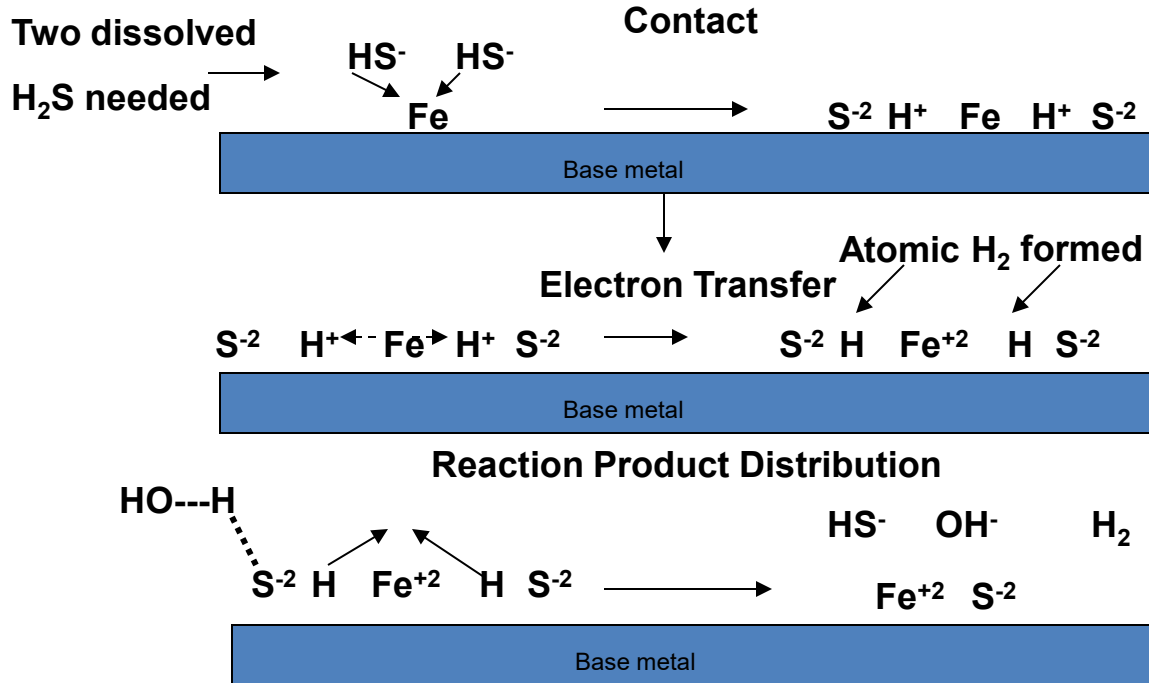
- According to a popular YouTube video series featuring a WWE-like masked character, the answer is NO
- The presenter points to heat stable salts being the real problem, and if they are properly managed then there is no issue for lean amine corrosion
- Internal surveys of Amine Best Practices Group SME's and amine vendors points to a huge subject for debate.
 - Why do we have velocity limits in H₂S bearing amine systems?
 - What are the right guidelines for heat stable salts?
 - Why do gas plant amines with low HSS and low, but non-zero H₂S sometimes have corrosion problems
- So how low can you go with the H₂S limbo?



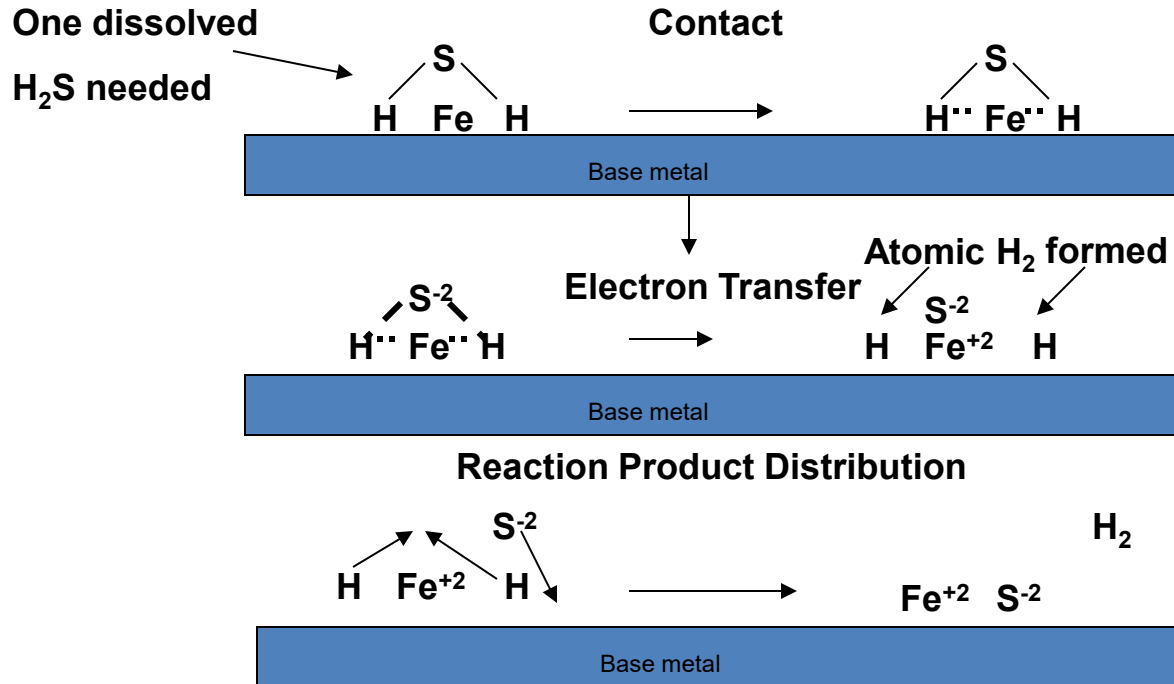
Hatcher & Keller, 2008 Brimstone Sulfur Symposium

- Amine is NOT corrosive
- Dissolved H_2S and CO_2 oxidize carbon steel in presence of liquid water
- FeS (iron sulfide) and FeCO_3 (iron carbonate) are the oxidation products
- FeS formation acts to coat carbon steel and slow oxidation
- Physical and chemical means to remove protective FeS accelerates corrosion
- Corrosion of rich amines and sour water both were successfully fit simultaneously:
$$\text{Corrosion rate, mpy} = K_o e^{-(aV+b)/RT} [(a\text{H}_2\text{S})^n (a\text{HS}^-)^p + c]$$
- Equation does *not* hold for lean amines with heat stable salts or mixed CO_2 systems

H₂S OXIDATION OF CARBON STEEL IN AMINE SOLUTION - NORMAL LOADINGS



EFFECT OF HIGH RICH AMINE LOADINGS ON CORROSION MECHANISM



Effects of High Acid Gas Loading

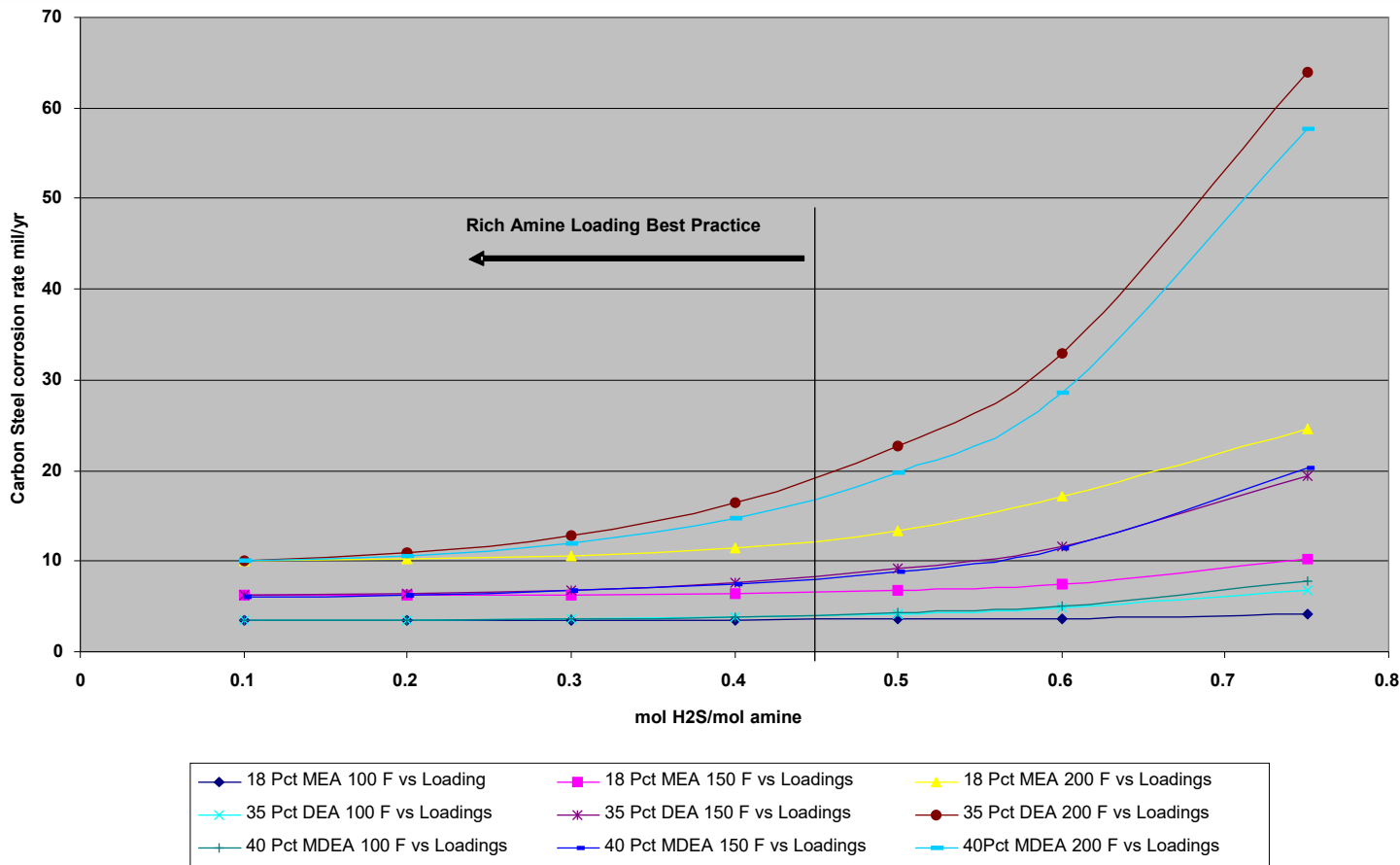


- Increase in total reactant concentration speeds oxidation kinetics
- Increase in higher “potency” reactant exacerbates above problem
- Higher hydrogen production rate - escaping hydrogen permeates from surface to solution - less uniform FeS on base metal surface

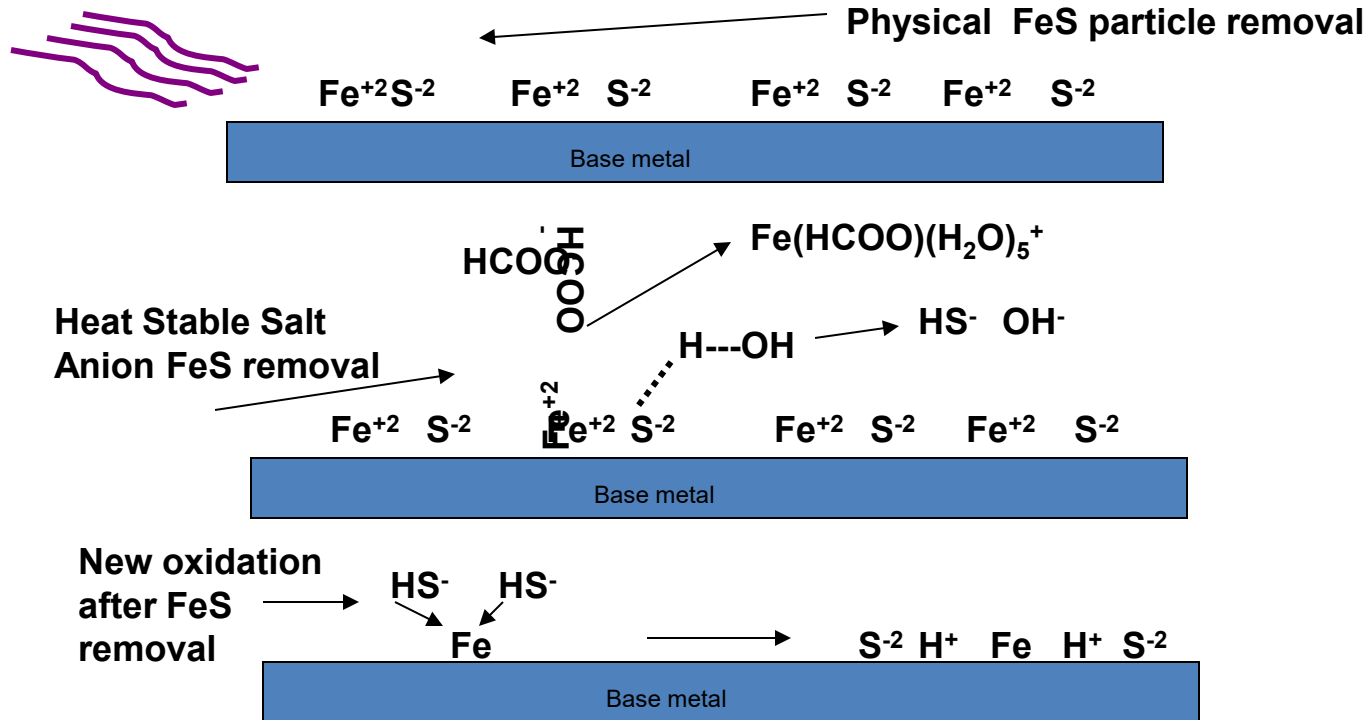
H ₂ S Loading mol/mol MDEA	% H ₂ S as HS ⁻	% H ₂ S as H ₂ S(aq)
0.25	98.8	1.09
0.45	97.5	2.45
0.65	95.1	4.86

* 40%wt MDEA using typical refinery HSS and sodium content in computations

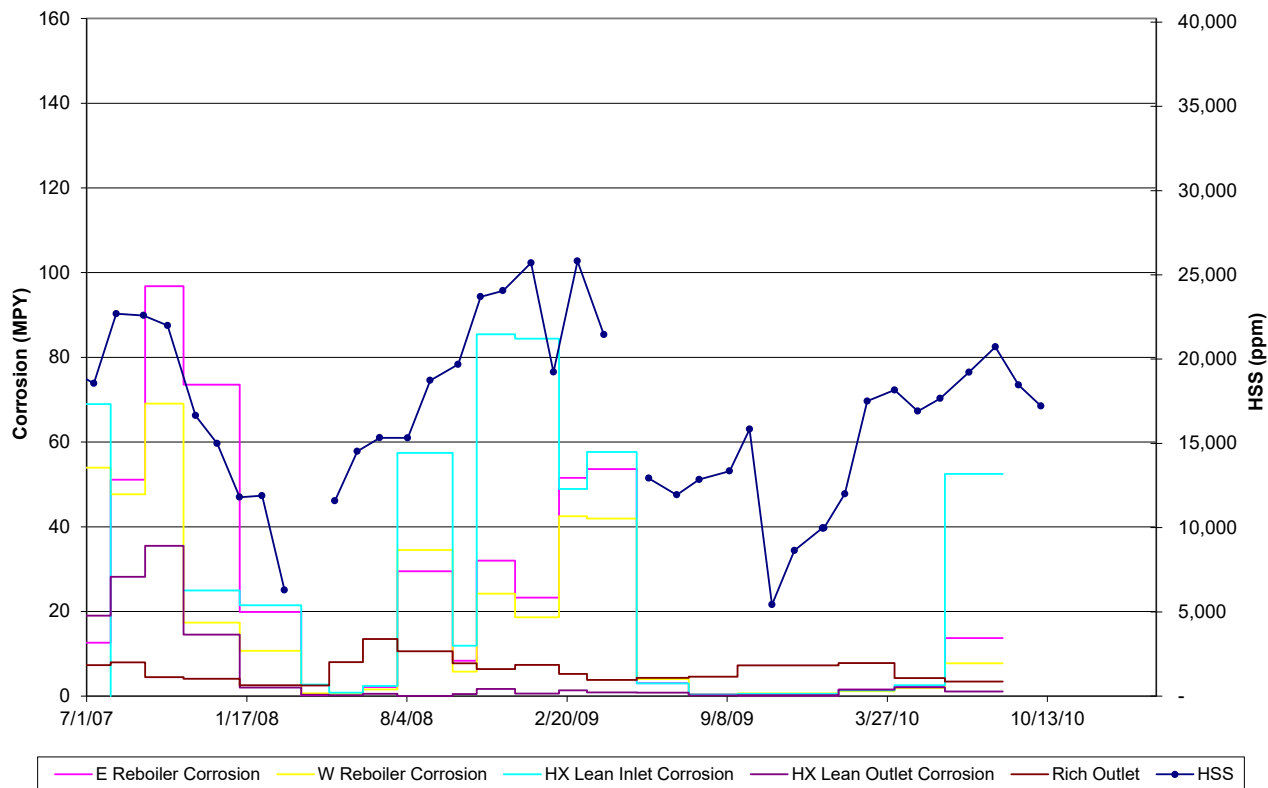
CORROSION RATE PREDICTIONS IN RICH AMINE



CORROSION IS NOT JUST H₂S OXIDATION OF CARBON STEEL



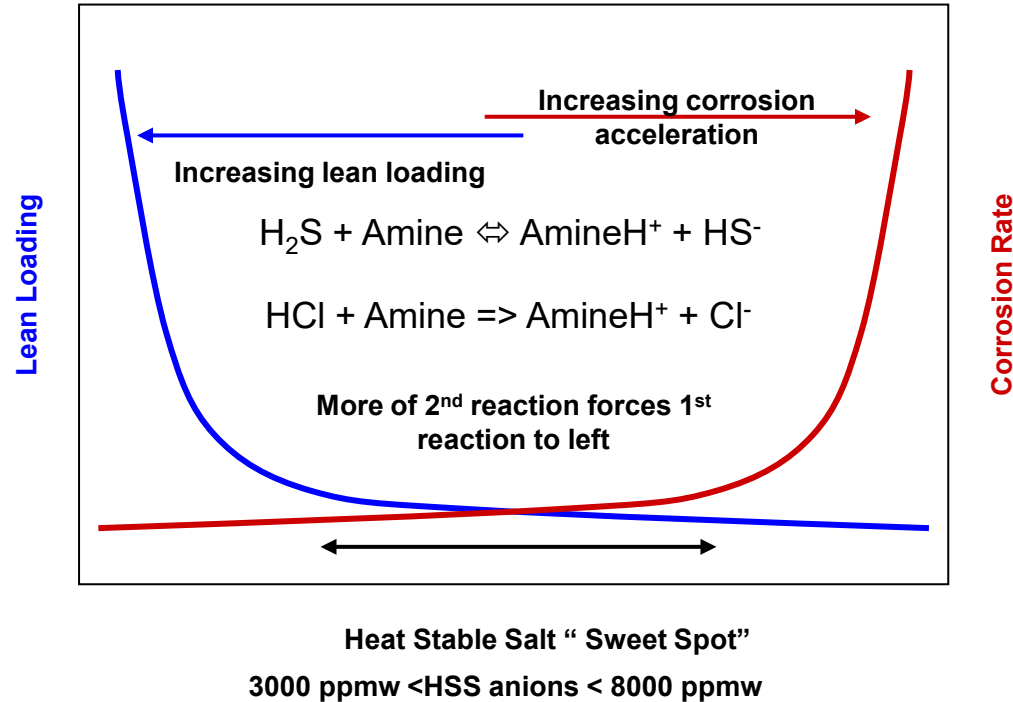
DEA CORROSION COUPON DATA vs. HSS ANIONS



IS MINIMUM H₂S LEAN LOADING IMPORTANT?



- Subject to heated debate in the industry
- Varying guidelines from vendors, consultants and operating experiences in the industry
- Confusion results from lean loading being affected by heat stable salts in refining systems
- Corrosion in mixed H₂S and CO₂ systems involves competition of 3 species for surface iron and the solubility of iron in solution



ABPG OPERATING COMPANY GUIDELINES



Anonymous Company	Amine Type	Refinery Lean H2S Lower Limit		Refinery TGU Lean H2S Lower Limit		Refinery Lean HSS Limits		TGU Lean HSS Limits		Degradation Product Limit	Chloride Limit	Additional Information
		mol/mol	ppmw H2S	mol/mol	ppmw H2S	HSAS wt% as amine	ppmw total anions	HSAS wt% as amine	ppmw total anions		ppmw	
Company A	Midstream	-	-	-	-		<8000	-	<8000	<250 ppmw bicene <1.5 wt% THEED (DEA)	<100	Do not target a certain amount of H2S in the stripper bottoms (most plants don't have much H2S).
	Refining	>0.002	>~200-300	-	-		<8000	<2 wt%	<8000	-	Only if H2S-free	Some systems such as MDEA blended with H3PO4 carry no lower limit for loading after metallurgy upgrades.
Company B	MDEA	>0.002	-	-	-	<2 wt%		<1 wt%		<4 wt% THEED	<500	If running below 0.002 m/m with good filtration and no signs of corrosion, does not force to higher lean loading limit. Working to no only report m/m loading but wt ppm H2S in lean amine as well.
Company C	MEA	>0.01	-	-	-	<1 wt%					<500 ppm	Have not seen corrosion attributed to lean loading being too low without HSAS exceeding upper limit.
	DGA	>0.01	-	-	-	<3 wt%					<500 ppm	
	DEA	>0.001	-	-	-	<3 wt%					<500 ppm	
	MDEA	>0.001	-	-	-	<3 wt%		<1 wt%			<500 ppm	
	Flexsorb™	#N/A	-	No limit	-			<10 wt%			<500 ppm	
Company D	MDEA	none	-	-	-	<3 wt%		-		-	-	Target <0.01 m/m loading with no hard lower limit.
Company E	DEA	>0.005	-	-	-	-		-		-	-	Have not seen a corrosion incident directly related to lean loading but acknowledge it may be a contributing factor.
	DGA	>0.005	-	-	-	-		-		-	-	
	MDEA	>0.005	-	>0.001	-	-		-		-	-	
Company F	MEA	>0.1	-	-	-	<2.5 wt%	Varies by anion	-	Varies by anion		<500	
	DGA	>0.05	-	-	-	<2.5 wt%		-				
	DEA	>0.02	-	-	-	<2.5 wt%		-				
	DIPA	>0.02	-	-	-	<2.5 wt%		-				
	MDEA	>0.001	-	>0.0005	-	<2.5 wt%		<1.5 wt%		<3000 ppmw bicene		
Company G	MDEA	-	-	-	-	<2 wt%		<1 wt%		-	-	JIP showed corrosion peaked at ~10 wt ppm H2S and began to decrease again at >100-130 wt ppm.
Company H Downstream	MEA	-	-			<2 wt%	Varies by anion *				<1000	CO2 system, so no H2S limit
	DEA	0.0025	<50 or >250			<3 wt%	Varies by anion *				<1000	*Formate+ acetate < 6000 ppm
	MDEA	-	<50 or >250		<50 or >250	<3 wt%	Varies by anion *	<2.5 wt%	Varies by anion *	MMEA+DEA < 1.5 wt% (TGU only)	<1000	Do allow systems that struggle to maintain 250 ppm H2S in lean amine to strip harder and ALWAYS remain below 50 ppm
Company H Upstream	DEA	0.0025	<50 or >250			<3 wt%	Varies by anion *			soft limit of ~6 wt% THEED	<1000	Some units struggle to keep above lower H2S limit when HSS are high. See evidence of Fe in amine climb. Haven't seen evidence of THEED impacting corrosion rate (even up to 7 wt%).
	aMDEA	-	-			<3 wt%	Varies by anion *				<1000	Little to no H2S in most of these units
	Flexsorb				-			< 3 wt%	Varies by anion *		<1000	Deliberately lowered HSS limit after through wall regenerator corrosion
	DGA	-	-			<3 wt%	Varies by anion *				<1000	Little to no H2S in these units

VENDOR H₂S & HSS GUIDELINES



Anonymous Company	Amine Type	Refinery Lean H ₂ S Lower Limit		Refinery TGU Lean H ₂ S Lower Limit		Refinery Lean HSS Limits		TGU Lean HSS Limits		Degradation Product Limit	Chloride Limit	Additional Information
		mol/mol	ppmw H ₂ S	mol/mol	ppmw H ₂ S	HSAS wt% as amine	ppmw total anions	HSAS wt% as amine	ppmw total anions		ppmw	
Vendor A	MEA	0.002	200			8% of amine bound or 1.44%wt	14400				1000	
	DEA	0.0015	150			8% of amine bound or 2.4%wt	24000			3.5% of amine or 1.05%wt amine Bicene: 1% of amine or 0.3%wt amine	1000	
	DGA	0.0015	150			8% of amine bound or 4.8%wt	48000				1000	
	DIPA	0.0015	150	0.0001	10	8% of amine bound or 2.4%wt	24000	5% of amine bound or 2.5%wt	25000		1000	
	MDEA	0.0001	10	0.0001	10	8% of amine bound or 4%wt	40000	5% of amine bound or 2.5%wt	20000	5% of amine or 2.5%wt amine Bicene: 1% of amine	1000	
Vendor B	MDEA	None	None	None	None	<2.5 wt%	Varies by anion	<1 wt%	Varies by anion	<2000 ppmw bicene for main, <1000 ppmw bicene for TGU	<500 ppm	For refineries who do not practice neutralization.
Vendor C	MEA	0.1-0.15	-			<2 wt%						
	DGA	0.05-0.07	-			<2 wt%						
	DEA	0.02-0.025	-			<2 wt%						
	DIPA	0.02-0.025	-			<2 wt%						
	MDEA	0.005-0.01	-	0.002-0.005	-	<2 wt%		<2 wt%		soft limit of <1 wt% bicene	<100 ppm	Vendor C views lean H ₂ S loading as a grey area. Would encourage customer to meet spec over corrosion as a priority

PART II – IRON & IRON SULFIDE SOLUBILITY



- Sweet vs. Sour chemistry noted in the gas field – Smith & Pacheco, 2002
- Iron sulfide solubility in water ~10 ppmw at 25°C (77 °F)
 - Total iron measurements > 10 ppmw imply big time issues
 - Informal vendor guidelines for <7 ppmw iron in solution

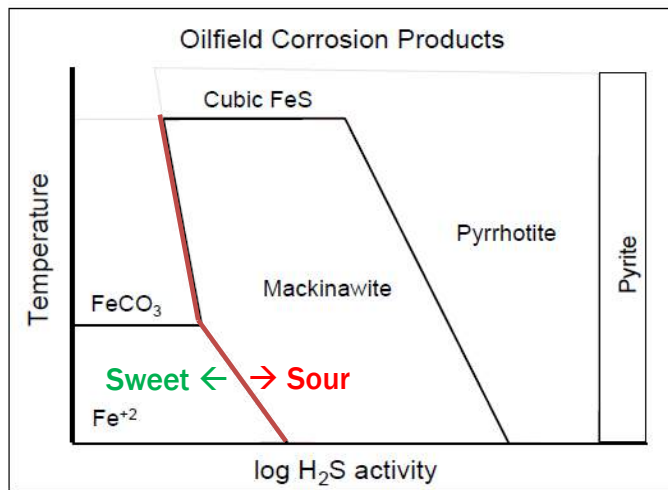


FIGURE 1
Corrosion Product Relationships

Types of Iron Sulfides– Spooner 2006

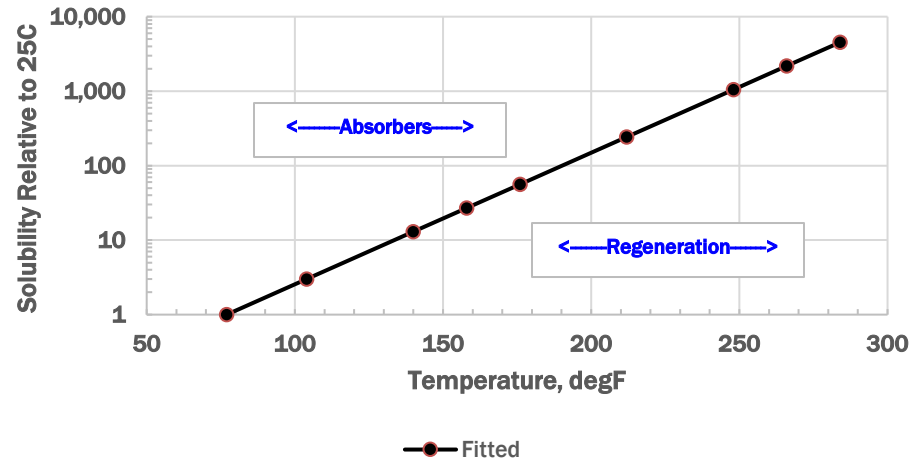
- Mackinawite, FeS_{1-x}
- Pyrrhotite, FeS_{1+x}
- Pyrite, FeS₂
- Greigite, Fe₃S₄ – rxn product of Mackinawite, not common
- Troilite, FeS – stoichiometric iron sulfide, rare except in meteorites

IRON SULFIDE SOLUBILITY



- Figueroa, 2018 measured solubility of powdered iron sulfide in water vs T
- Huge solubility change in typical amine loop
 - Note log scale
 - Small reductions in T lead to large changes in solubility
 - Particles known to stabilize foam
 - One reason amine units anecdotally do not like change
- Not filtering solids will result in some re-dissolution in the regenerator
- Large solubility reduction across lean side of lean/rich exchanger
- Particles abrade surface and generate more particles

Iron Sulfide Solubility in Water Relative to 25C

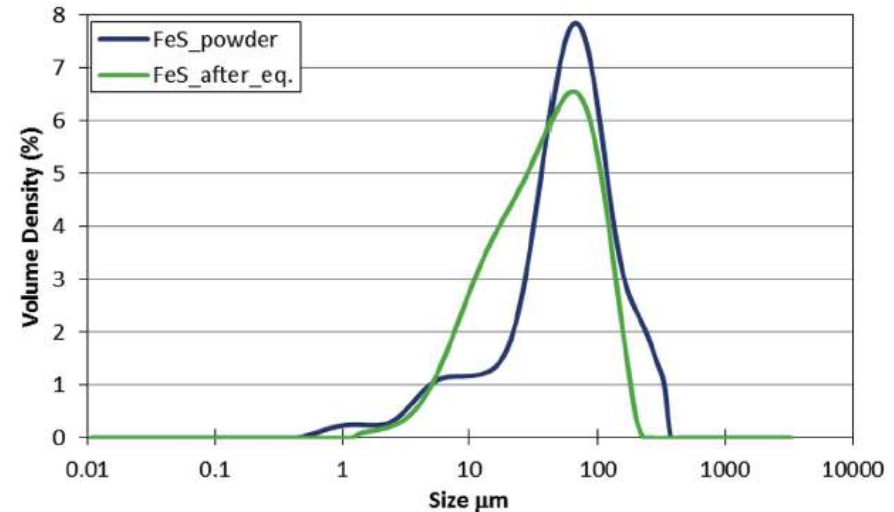


IRON SULFIDE PARTICLE SIZE DISTRIBUTION



- Implications for filtering
- 10 μ absolute would leave 20% of particles in solution
- Larger systems are usually slipstream
- Really need 5 μ absolute for *this* system to remove most of the particles
- Reason why most media-type filters work best after some cake has built up on surface

D.C. Figueroa Murcia et al. / Fluid Phase Equilibria 475 (2018) 118–126



IRON SULFIDE SOLUBILITY – TEWARI, 1978



Tewari, P. H., Wallace, G., Campbell, A. B., & Atomic Energy of Canada Ltd., Pinawa, Manitoba. Whiteshell Nuclear Research Establishment. (1978). The solubility of iron sulfides and their role in mass transport in Girdler-Sulfide heavy water plants.

		Relative Dissolution Rate@ pH=3.5 and 25°C	Relative Solubility @25°C & 1.8MPa H ₂ S	Equilibration Time
	Rate of Dissolution into Acid			
Mackinawite	1st order in H ⁺	1.00E+05	6000	Hours
Troilite	1st order in H ⁺	1.00E+04	80	Hours
Pyrrhotite	Independent of pH between 0.9-4.0	10-50	10-40	Days
Pyrite	Independent of pH between 0.9-4.0	1	1	Years

Pyrrhotite exists as hexagonal and monoclinic.

Preconditioning surfaces that would otherwise be mackinawite by converting to pyrrhotite and pyrite.

Solubilities of iron sulfides decrease with increasing pH (basicity). Note that cooling increases pH. → Another reason why amine units don't like change.

IRON SULFIDE SOLUBILITY – TEWARI, 1978



Tewari, P. H., Wallace, G., Campbell, A. B., & Atomic Energy of Canada Ltd., Pinawa, Manitoba. Whiteshell Nuclear Research Establishment. (1978). The solubility of iron sulfides and their role in mass transport in Girdler-Sulfide heavy water plants.

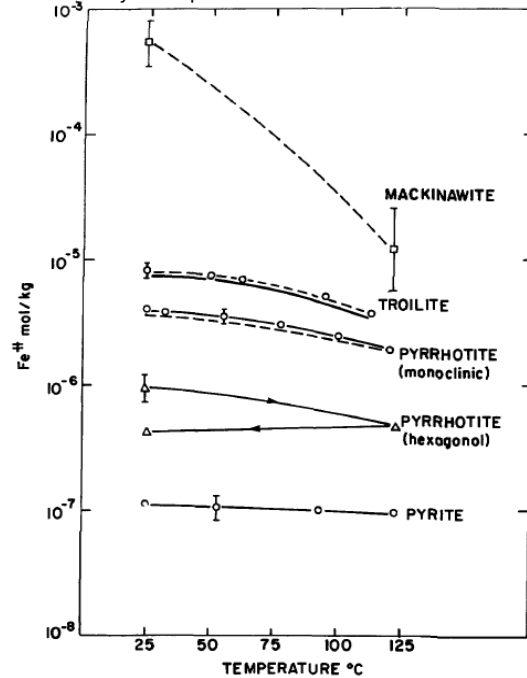


FIGURE 2 Solubility of iron sulfides at 1.8 MPa H_2S pressure. The adjacent curves for troilite and pyrrhotite represent 0.1 MPa (top) and 1.8 MPa (bottom) H_2S pressure. The arrows on pyrrhotite (hexagonal) curves show direction of temperature change.

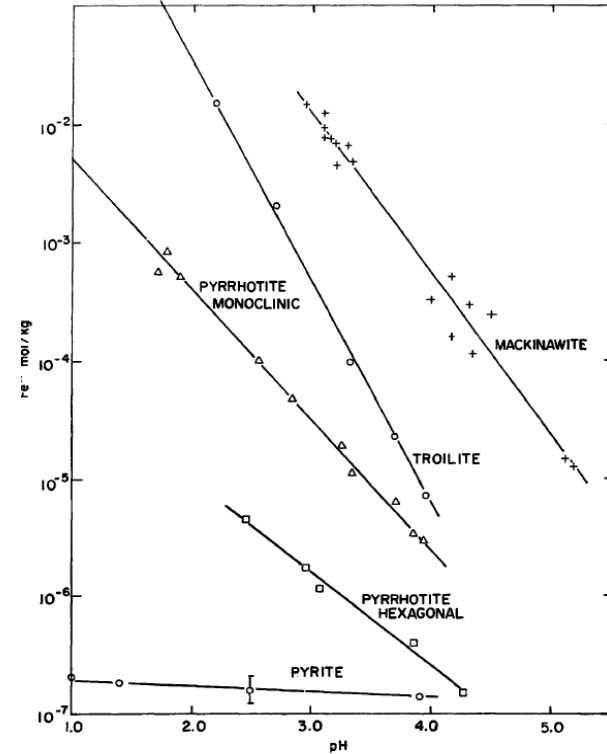
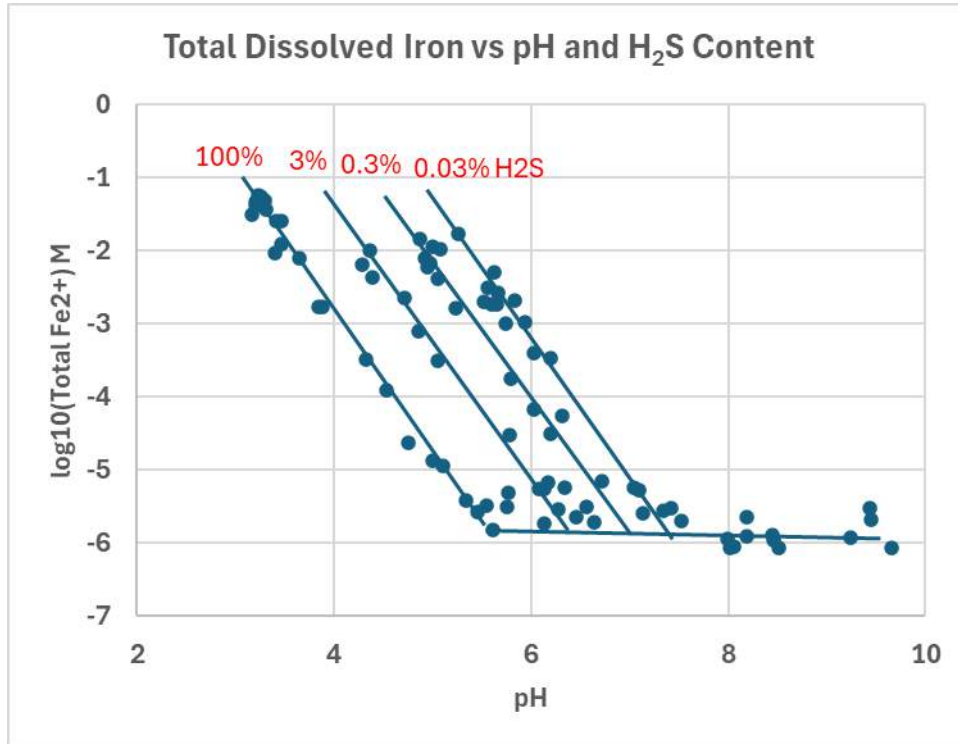


FIGURE 3 Dependence of dissolved Fe^{++} on pH at 25°C and 0.1 MPa H_2S pressure.

pH Dependency of FeS Solubility



- Alkaline solutions show a flat solubility limit for dissolved iron.
- pH doesn't matter if there is high H₂S

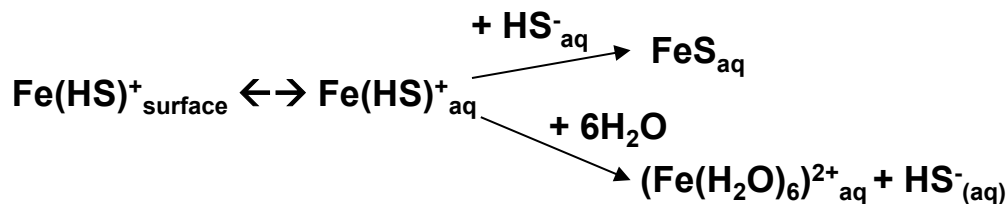
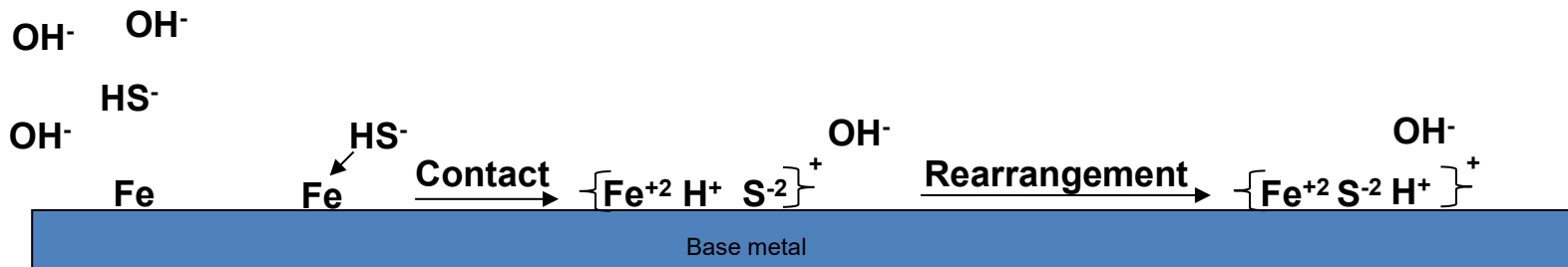
Rickard, D. The solubility of FeS. *Geochimica et Cosmochimica Acta* 70 (2006) 5779-5789.

Mackinawite is the dominant form of iron sulfide at low H_2S concentration and temperature. Observations under scanning electron microscope led to the following mechanism.

- H_2S diffuses to the steel surface
- H_2S then reacts with steel to initially form mackinawite surface scale
- Mackinawite scale dissolves into HS^- and $\text{Fe}(\text{HS})^+$
- $\text{Fe}(\text{HS})^+$ diffuses away from surface allowing more H_2S to react with exposed iron
- Continued production and removal of thin mackinawite “tarnish”

→ Mackinawite scales are not stable because they are in continual flux.

H₂S OXIDATION OF CARBON STEEL IN AMINE SOLUTION- LOW LOADINGS IN ALKALINE SOLUTIONS

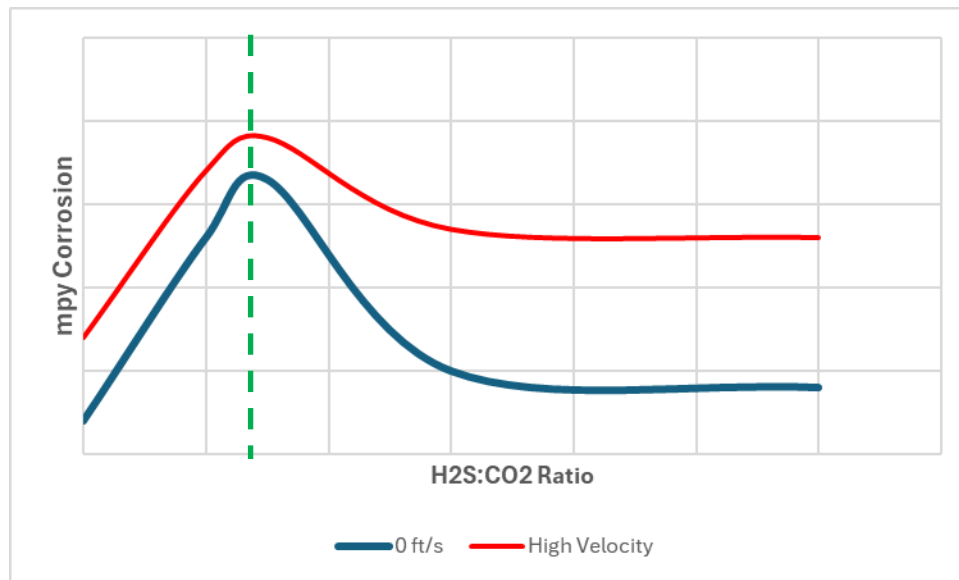


- **Lean amine JIP led by Honeywell circa 2011**
 - Several ABPG member companies participated
 - **18%wt MEA, 45%wt DGA, 30%wt DEA, 45%wt MDEA studied varying:**
 - Temperature: 180-265 °F
 - Velocity (sheer stress)
 - H₂S:CO₂ ratio in lean amine 0:1 to 6:1
 - Heat stable salts 1-3 %wt in solution with 9:1 formate:thiocyanate ratio
 - Carbon steel, 304 SS, Alloy 2205, Alloy 825
 - Peak corrosion rate vs. H₂S content varies with the amine
- **ABPG field data**
 - DEA Gas Plant with minimal HSS
 - MEA Plant with Chromium as a corrosion indicator
 - MDEA TGU with varying HSS levels & H₂S/CO₂ ratio

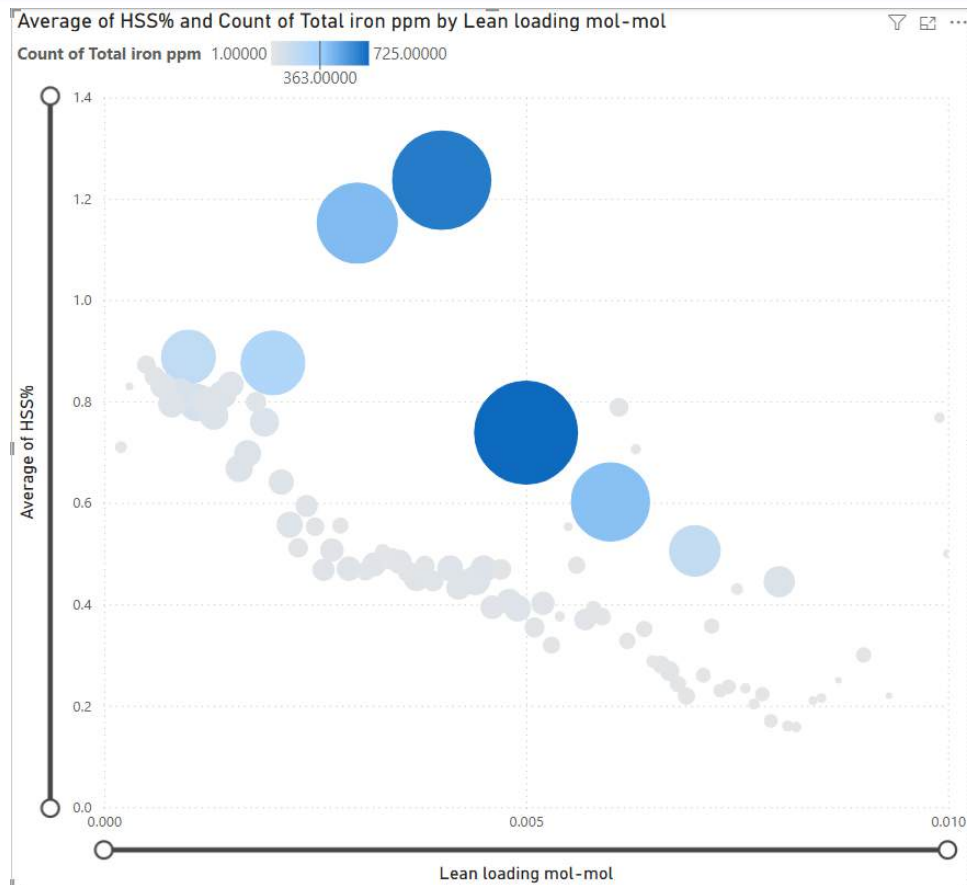
Lean Amine JIP Peak Corrosion Rates vs. H₂S



Amine	H ₂ S ppmw	Peak H ₂ S mol/mol
MEA	~500	0.005
DGA	~440	0.003
DEA	~150	0.0015
MDEA	~65	0.0005



ABPG Case Study 1: DEA Gas Plant w/ Minimal HSS

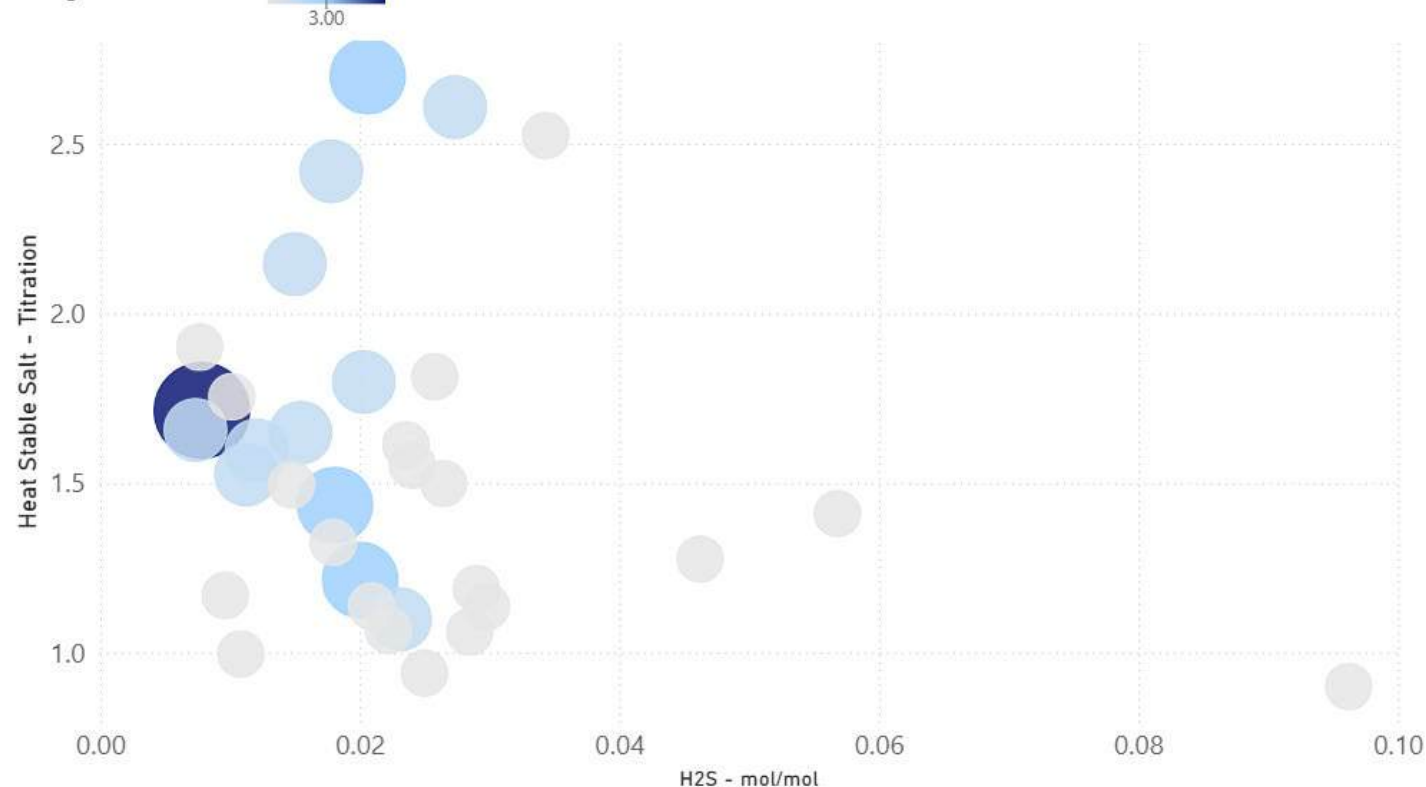


ABPG Case Study 2: MEA Plant



Average of Chromium by H₂S - mol/mol and Heat Stable Salt - Titration

Average of Chromium 1.00 3.00 5.00

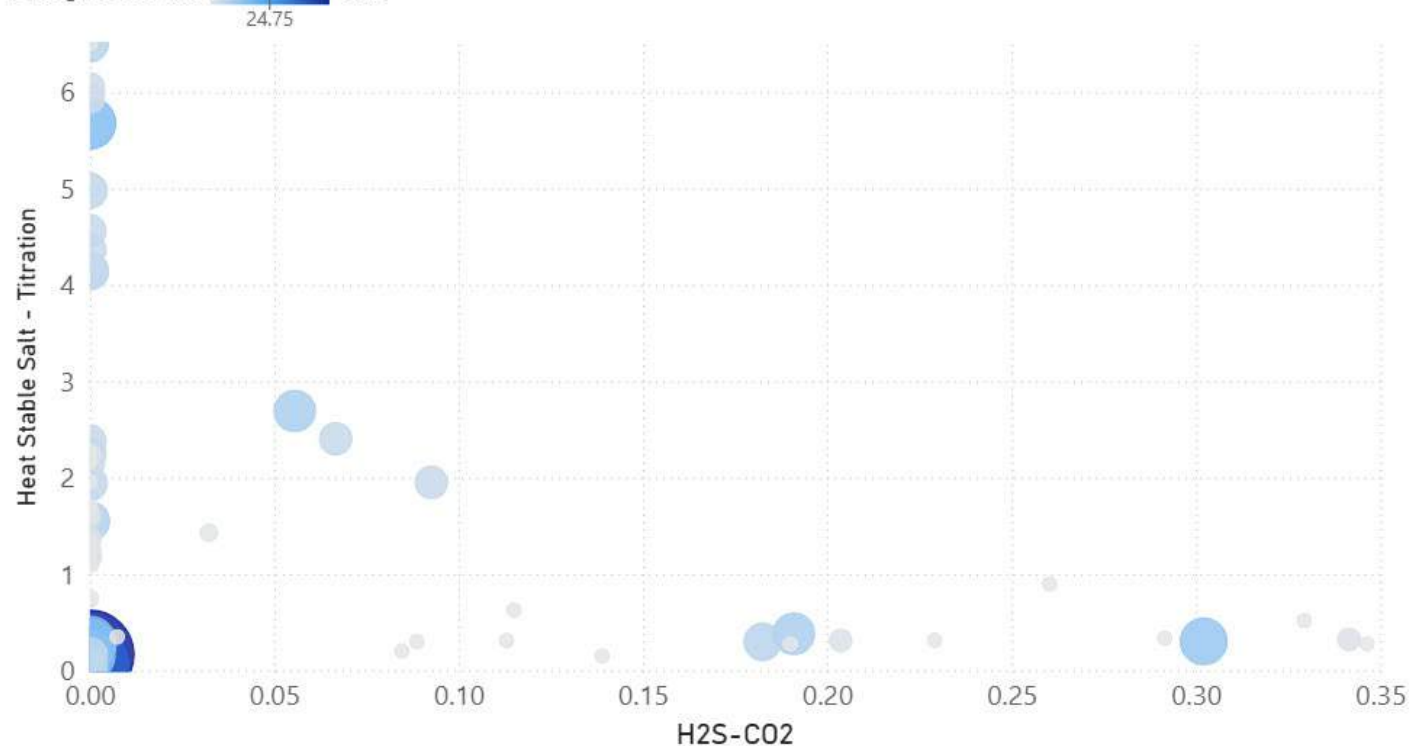


ABPG Case Study 3: MDEA TGU – H₂S/CO₂ Ratio



Average of Iron by H₂S-CO₂ and Heat Stable Salt - Titration

Average of Iron 0.50 24.75 49.00



PART IV RELIABLE OPERATING LIMITS



- Lean amine JIP suggests lower limits at 2-3x H₂S concentration of peak corrosion
 - MEA and DGA: 1000-1500 ppmw H₂S
 - DEA: 400-500 ppmw H₂S
 - MDEA: 200-300 ppmw H₂S
- Reality is usually that some H₂S originally present will react in the sample bottle
 - $\text{H}_2\text{S} + \text{Fe}^{2+} \rightarrow \text{FeS} + \text{H}_2$
 - $5/2 \text{O}_2 + 2\text{H}_2\text{S} + 2\text{Am} \rightarrow 2\text{AmH}^+ + \text{S}_2\text{O}_3^{2-} + 2\text{H}_2\text{O}$
- Enforcing a minimum lean H₂S loading is impractical unless amine samples are collected in a bottle pickled with argon or N₂ and titrations conducted in a glove box
- Setting a floor and roof on regenerator stripping steam through simulation with the current HSS levels may be more practical in many cases or metal-up the regenerator + hot and intermediate lean amine circuits
- When HSS levels cannot be controlled and equipment design permits, stripping H₂S and CO₂ to zero may be a better outcome than trying to maintain some residual loading

- Corrosion in amines is both a system-wide problem and a localized problem
 - Iron dissolved in the regenerator can precipitate in the colder lean amine causing erosion corrosion
 - When exposed to H_2S in the absorber, dissolved iron precipitates as iron sulfide in bulk en masse in the rich amine
 - Iron sulfide that is not filtered is either removed by settling out in equipment or will be redissolved in the regenerator and loop back around
 - High-capacity structured packing systems need full flow lean and rich filtration if HSS are not controlled
- JIP + ABPG data support peak corrosion exists at low, but non-zero H_2S concentration
 - Amine type dependent, likely related to passivation film stability
 - Without HSS in refineries, it is thermodynamically hard to strip H_2S to these levels
 - Gas plants with CO_2 may be susceptible without HSS
 - When HSS are high enough, low H_2S loadings are almost impossible to avoid
- Controlling the elements that dictate corrosion will usually manage corrosion rates unless your plant is in the sweet spot
- Although not absolute, total iron field data and filter element changeout frequency can be useful for secondary monitoring

ACKNOWLEDGMENTS



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