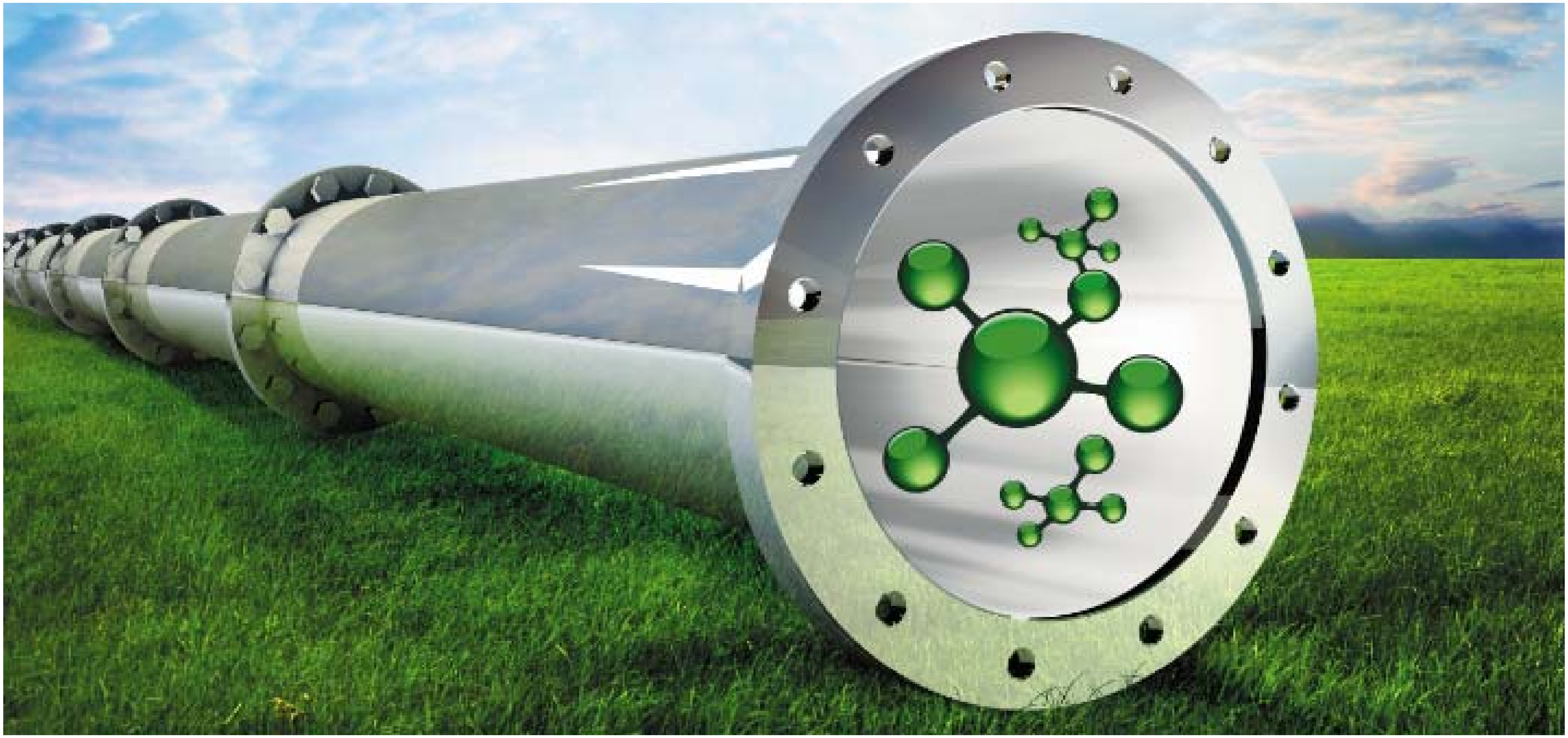


H_2S Control via Downhole Injection of a New, Non-Scale Forming H_2S Scavenger

Lonza South America

Patagonia – Oct. 2016

Presentation Outline

- Considerations for choosing the appropriate H_2S scavenger
  - Triazine vs New H_2S scavenger
- Modeling the H_2S scavenging reaction - the importance of understanding kinetics for optimization
- Field results

Desired Characteristics of a Chemical H_2S Scavenger

- Complete reaction with H_2S
- Known reaction rates – fast enough to react in the desired timeframe of the system
- Applicable to gas, oil, and / or co-produced fluids
- Scavenges over a wide pH and temperature range
- Non-corrosive chemical
- Does not form solids (e.g., scale deposits)

Triazine Derivatives
Performance Characteristics

- Rapid reaction with H_2S to form primarily mono- and dithiazines
- React to completion without re-release of H_2S
- Strong performance for gas sweetening applications
- Extensive field experience
- Potential to form Ca^{2+} and Ba^{2+} scale in aqueous / produced water applications
- Ineffective at low pH and low T
- Has potential to forms oligomeric dithiazine / polysulfide solids
  - Taylor, G.N., et al *Ind. Eng. Chem. Res.,* **2011**, *50*, 735
  - Madsen, H.T. "Investigation of Fouling Formation During H2S Scavenging with 1,3,5-tri-(2-hydroxyethyl)-hexahydro-s-triazine", Master's Thesis, Aalborg University, June 2011

Triazine Derivate

Reaction of Triazine with H_2S is Strongly pH-Dependent

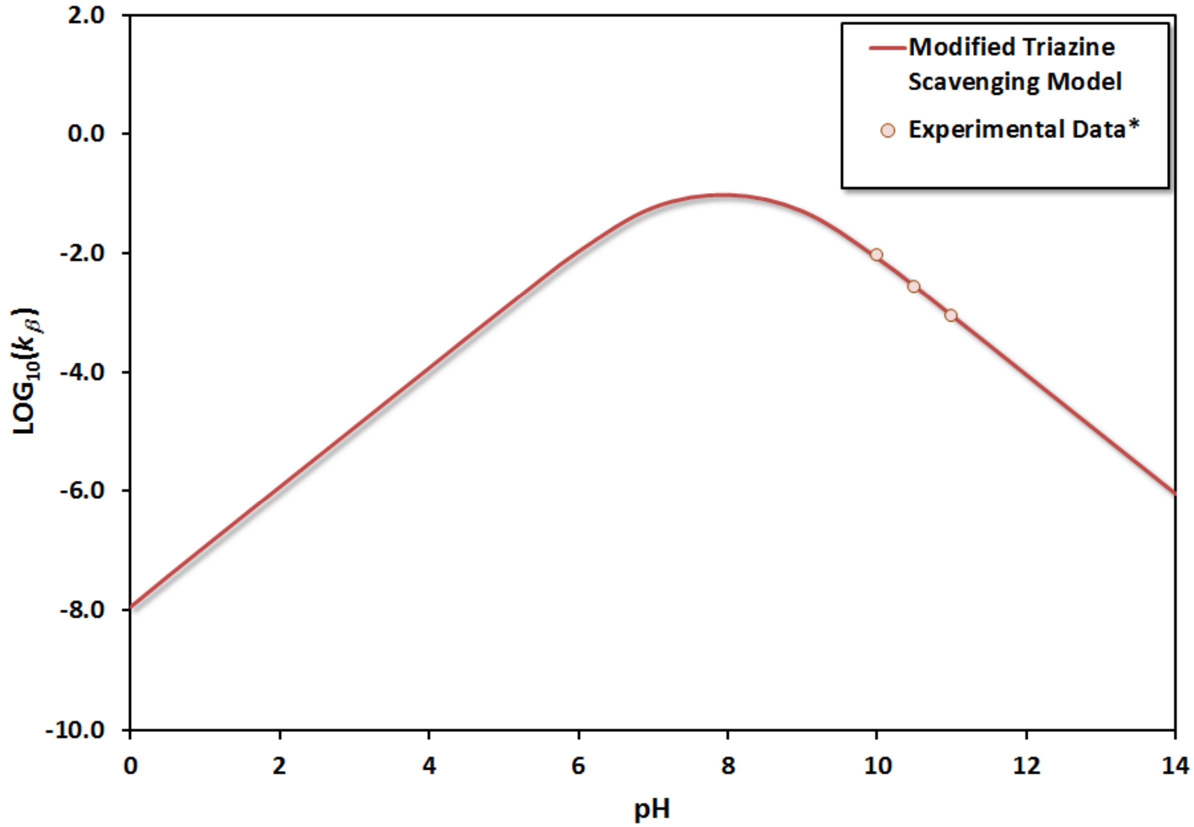
- Accounting for triazine pKa, scavenging rates decrease at lower pH

$$\{\text{Triazine-H}^+\} + HS^- \xrightarrow{k_\beta} \text{Thiazines}$$

$$H_2S \underset{}{\overset{K_{H2S}}{\rightleftharpoons}} H^+ + HS^-$$

$$\{\text{Triazine-H}^+\} \overset{K_a}{\rightleftharpoons} \text{Triazine} + H^+$$

$$k_\beta = k_{scav}\left(\frac{[H^+]}{K_a + [H^+]}\right)\left(\frac{K_{H2S}}{K_{H2S} + [H^+]}\right)$$

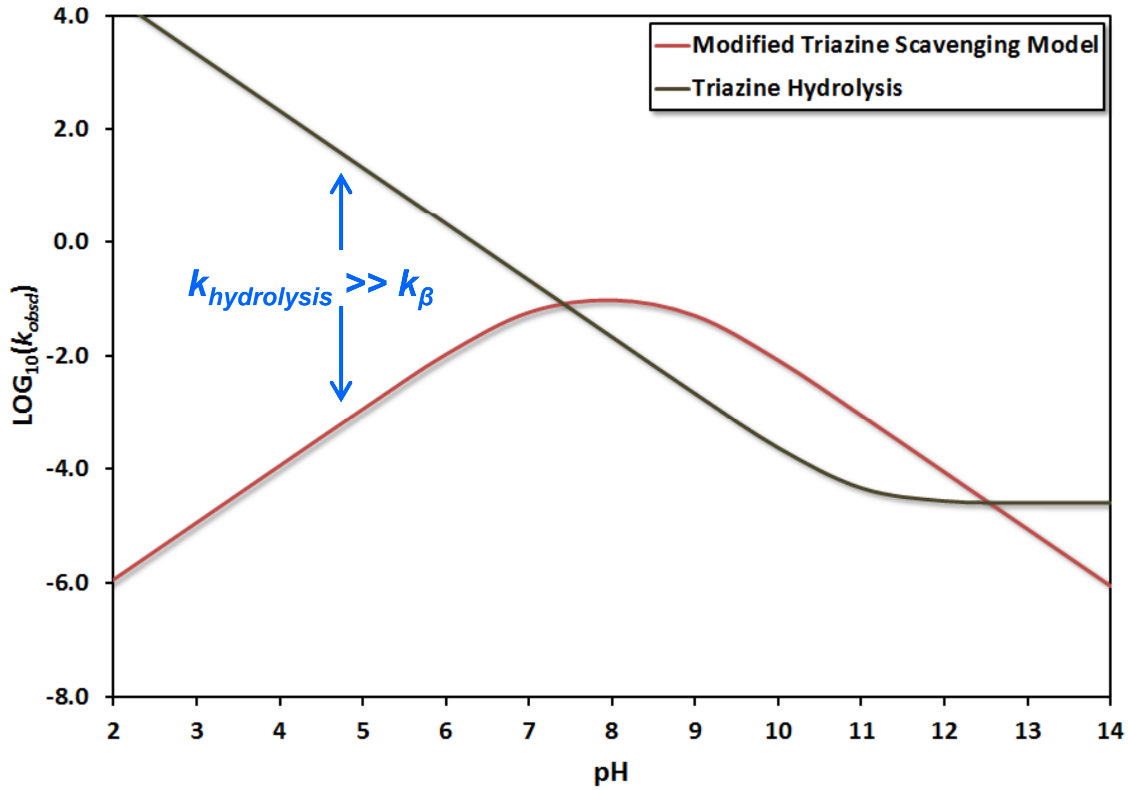


*Data fit according to experimental results in Buhaug, J.; Bakke, J.M. *AIChE Spring National Meeting* 2002, 151

Triazine Derivatives

Competitive Hydrolysis of Triazine at Lower pH Rationalizes Oligomer Formation of Triazines

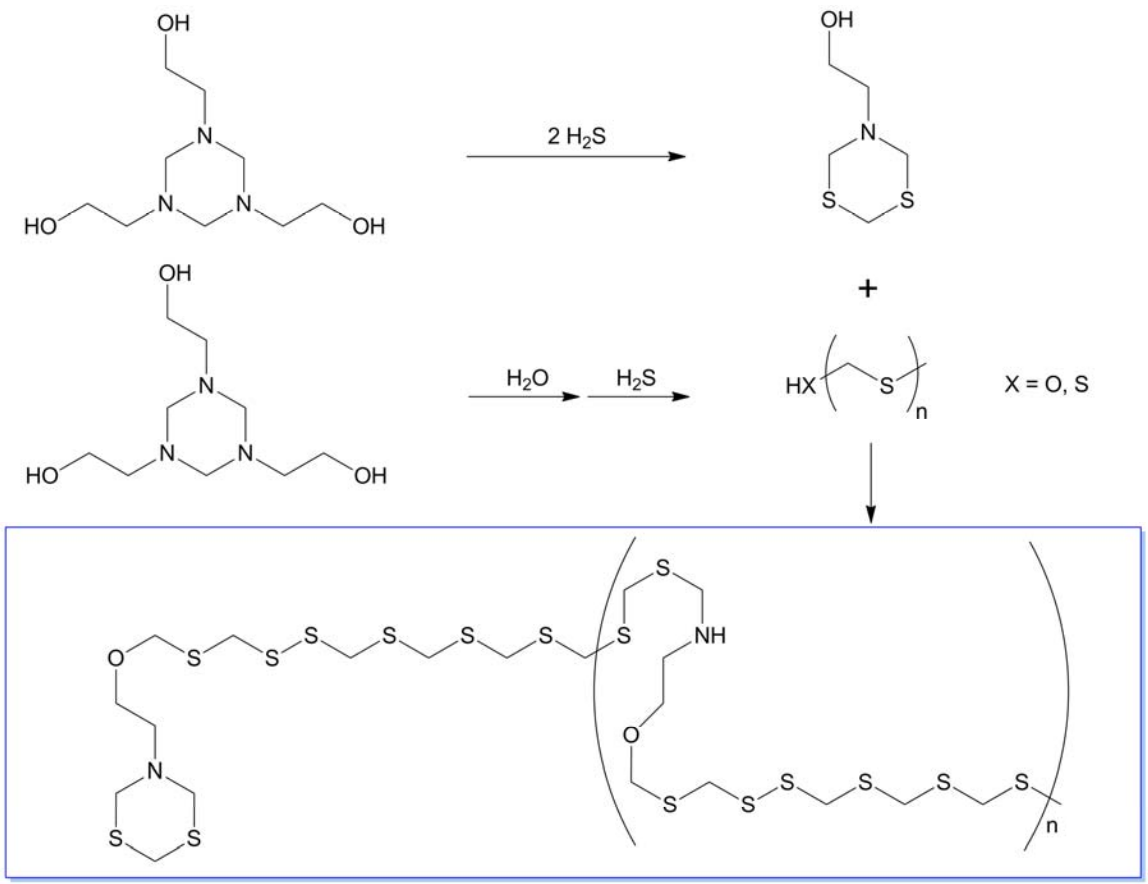
- At pH <7.4, hydrolysis is faster than scavenging
  - >100 times faster at pH <6.5



Triazine Derivatives

Competitive Hydrolysis of Triazine at Lower pH Rationalizes Oligomer Formation of Triazines

- General mechanism of oligomer formation is justified



Taylor, G.N., et al *Ind. Eng. Chem. Res.*, 2011, *50*, 735

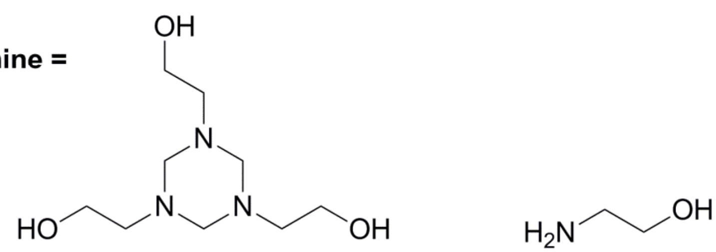
Triazine Derivatives
Amine Chemistry can Increase pH and Scale Potential

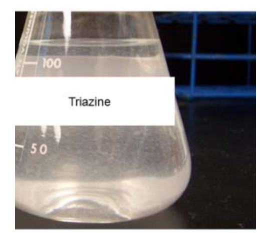
- An Amine source can cause a jump in pH at the point of injection, giving a high, localized pH
  - High pH will dramatically increase the Saturation Index and can cause nucleation – the big issue in scale control
    - Impacted by high alkalinity and M^{2+} content (e.g., Ca^{2+})
- The Amine can be the *scavenger or the by-product amines*

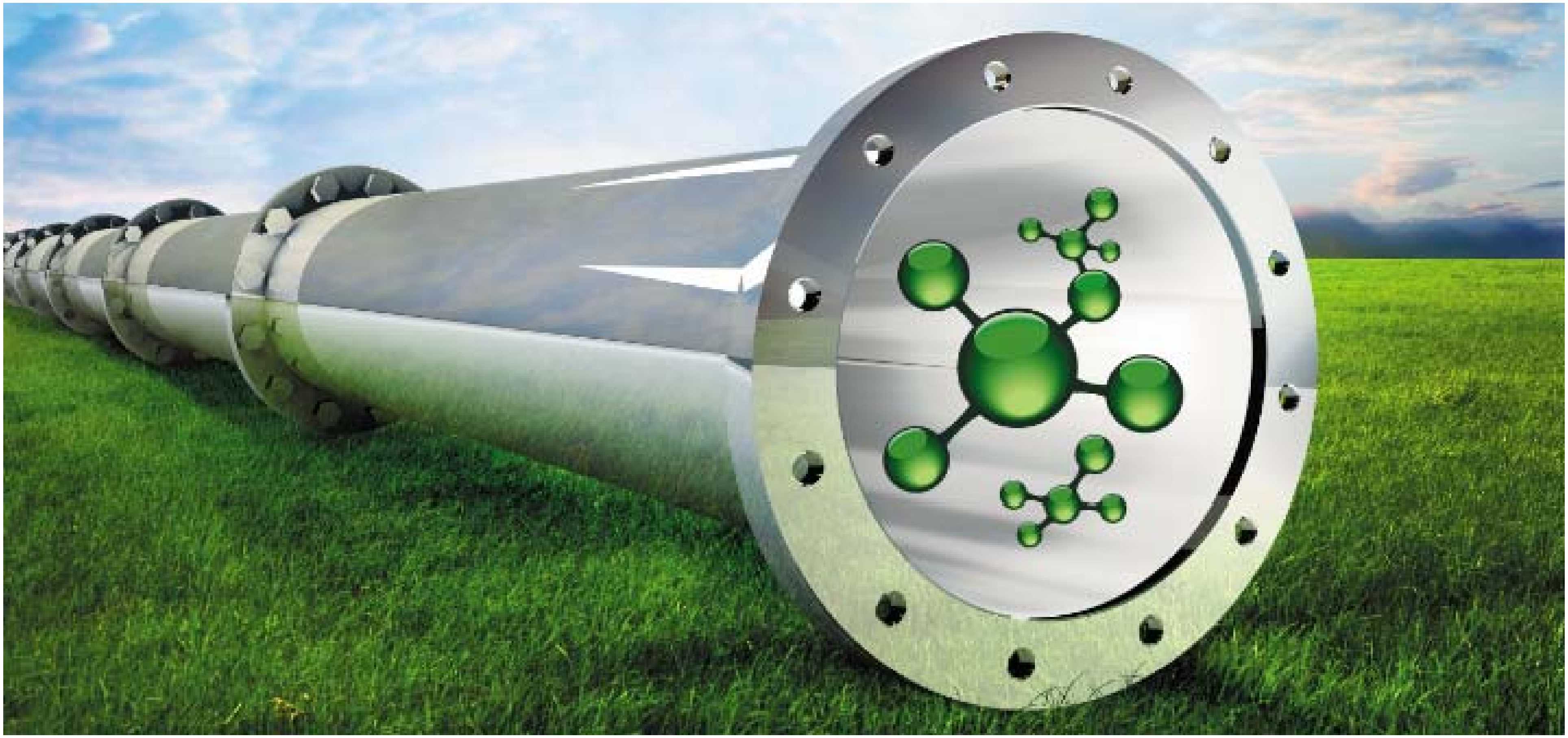
$$HCO_3^-{}_{(aq)} + \text{Amine} \longrightarrow CO_3^{2-}{}_{(aq)} + \overset{\oplus}{\text{H}}\text{-[Amine]}$$

$$CO_3^{2-}{}_{(aq)} + Ca^{2+}(aq) \longrightarrow CaCO_{3(s)} \downarrow$$

Amine =







New H_2S Scavenger

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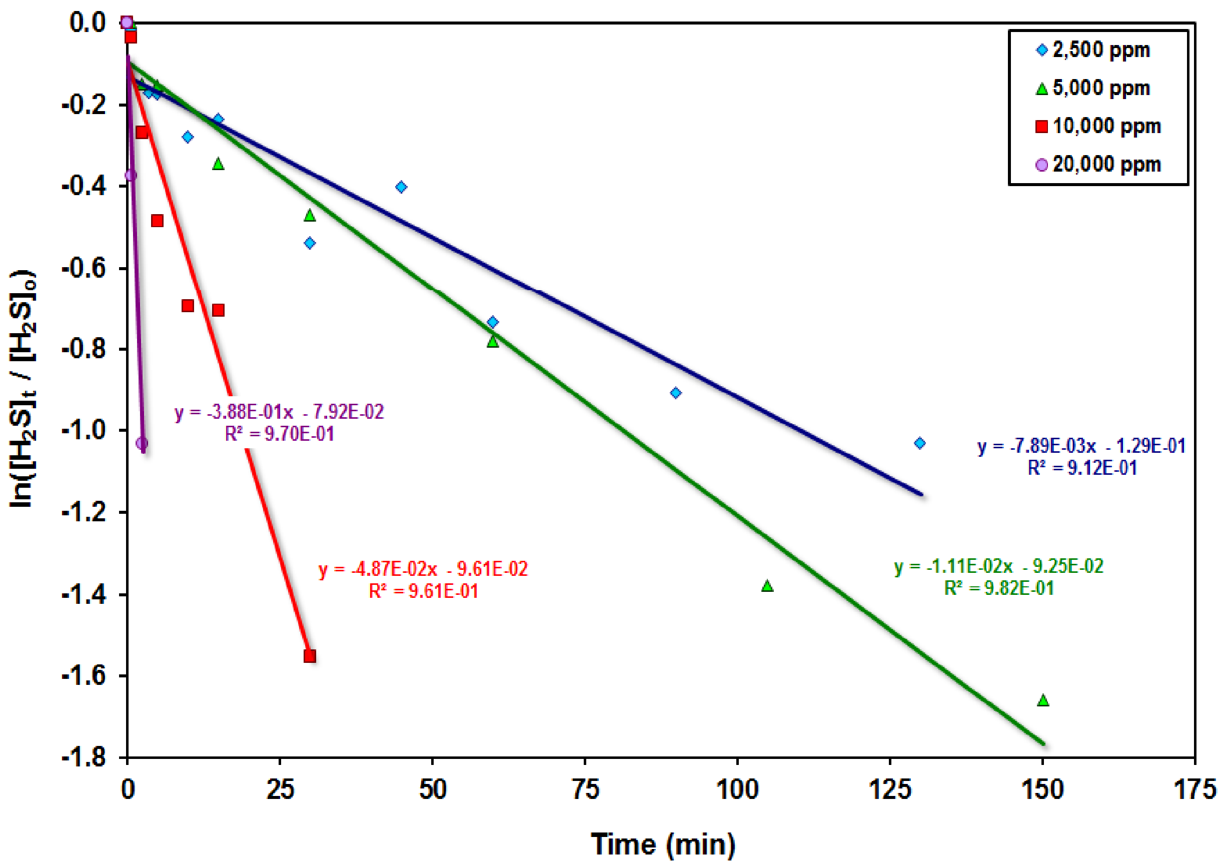
New H_2S Scavenger
Performance Characteristics

- Reacts to completion with H_2S over a wide T range
  - Even at lower T (< 25 ^oC)
- Predictable H_2S Scavenging rate – no pH dependence
- Scavenging rate unaffected by CO_2
- Does not increase water pH
  - reduced scale risk relative to Triazines
- Non-hazardous, non-corrosive chemical

New H_2S Scavenger

Reaction with H_2S Proceeds to Completion in Aqueous Solution

- Pseudo-1st Order Reaction Rates at pH 5, T = 22 °C



New H_2S Scavenger
Reaction with H_2S is Independent of pH

- Pseudo-1st Order Reaction Rates and ½ lives

pH	Temp (°C)	Scavenging Rate Constant k_{obsd} (min^{-1})	Half-life (min)
5.0	22	1.11×10^{-2}	62
7.2	22	1.30×10^{-2}	53
8.4	22	1.56×10^{-2}	44
9.4	22	1.24×10^{-2}	56
5.0	40	4.68×10^{-2}	15
6.1	40	4.77×10^{-2}	15

near zero slope indicates that *the reaction of H2S with the new scavenger product is not pH dependent, in contrast with the reaction of H2S with triazines*

The lack of dependence on pH suggests that H2S scavenging the new scavenger product could be more versatile for a variety of applications

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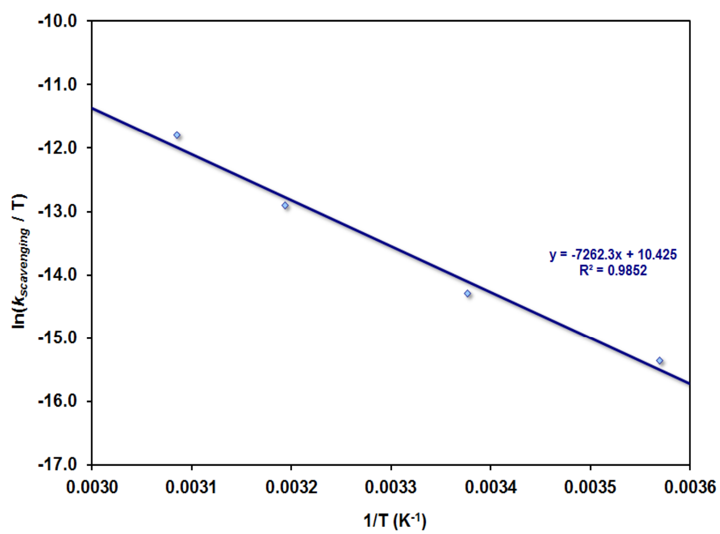
New H_2S Scavenger
Temperature Dependence of the Reaction with H_2S

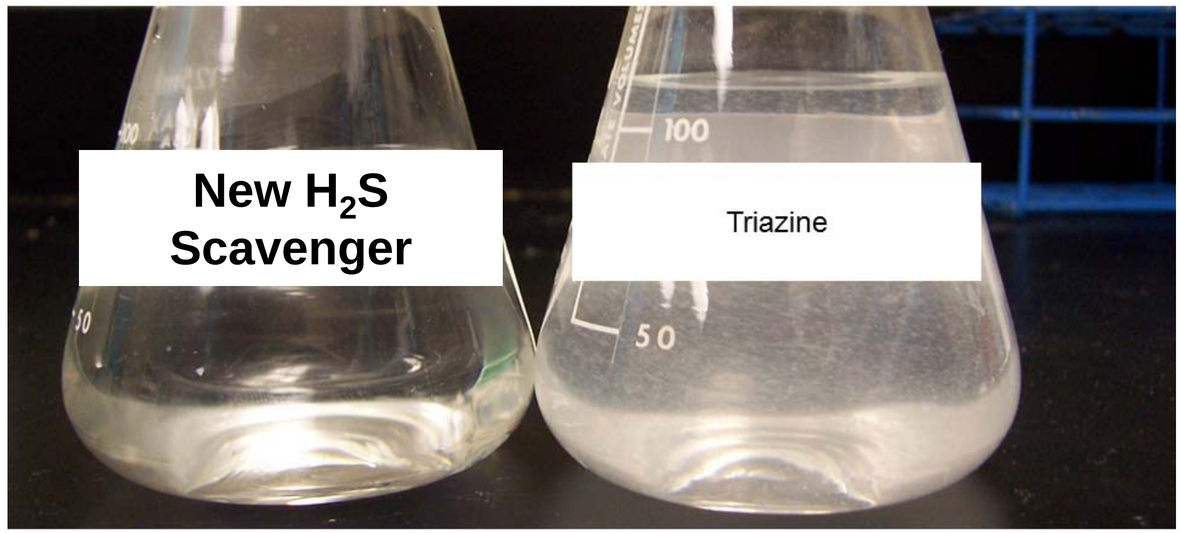
- Pseudo-1st Order Reaction Rates at pH 5, T = 22 °C
- Negative entropy is consistent
  - indicates that the rate is very temperature dependent.
  - allows for additional prediction of H2S scavenging rates over a broader range of temperatures.
  - H2S scavenging rate increases dramatically with increasing temperature……. But
  - ……The scavenging rate is still rapid even at lower temperatures



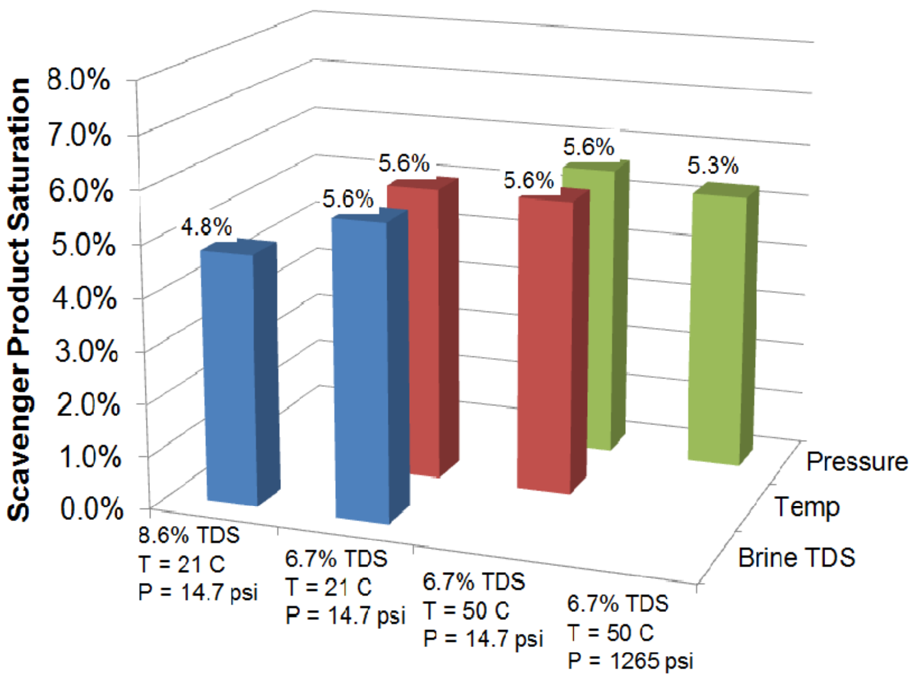
Temp (°C)	Scavenging Rate Constant k_{obsd} (min^{-1})	Half-life (min)
-5	1.00×10^{-3}	691
10	4.42×10^{-3}	157
25	1.69×10^{-2}	41
40	5.67×10^{-2}	12
55	1.71×10^{-1}	4.1
70	4.69×10^{-1}	1.5
85	1.18	0.6

New H_2S Scavenger is
Not Amine Based and Does Not Generate Scale Deposits like Triazine

- 50 ppm as H_2S
- pH_o = 7.4
- 800 ppm Hardness (as $CaCO_3$)
- 1% TDS



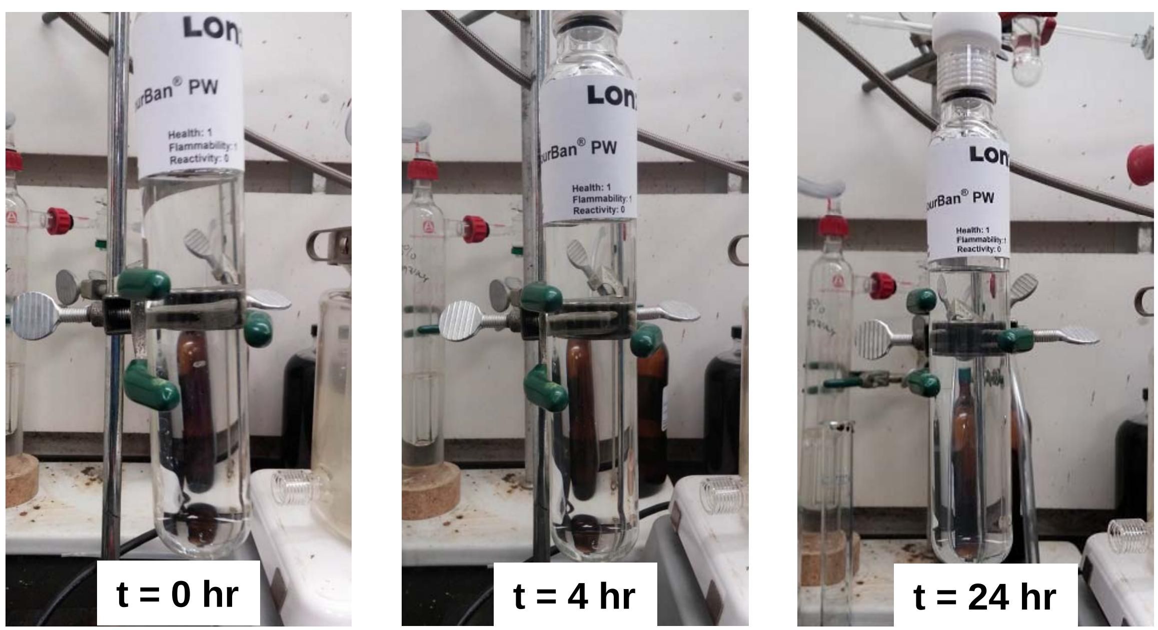
New H2S Scavenger
Solubility Profile of the Reaction Product



- By product solubility
  - Decrease with increase TDS
  - Non change to T
  - Moderately sensitive to P

New H_2S Scavenger
Scavenging by-products are water soluble

- Experiment #1 – Static Test
  - No water insoluble products generated during typical treatment residence times (4 – 24 hr)
    - 300 ppm as $H_2S(aq)$
      - Equates to1,350 ppm $H_2S(g)$ at pH_o = 8.2
    - 1,000 ppm New H_2S Scavenger



Lonza Internal Data

New H_2S Scavenger
Scavenging by-products are water soluble

- Experiment #2 – Purge Test
  - No water insoluble products generated during typical treatment residence times (4 – 24 hr)
    - 100 ppm as $H_2S(g)$ gas purge through a 500 ppm New H_2S Scavenger Solution

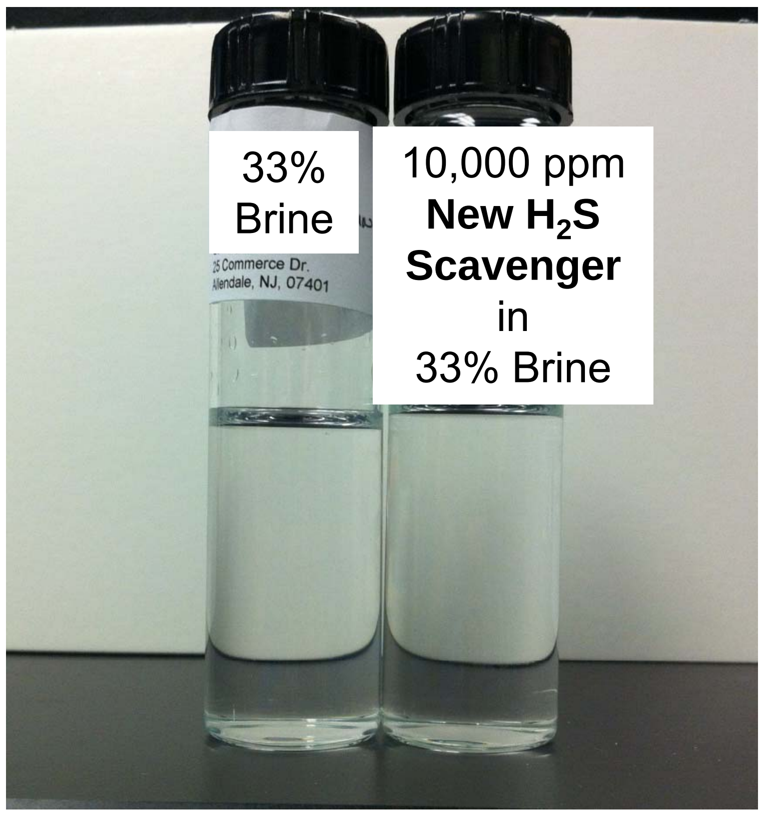
t = 0 hr

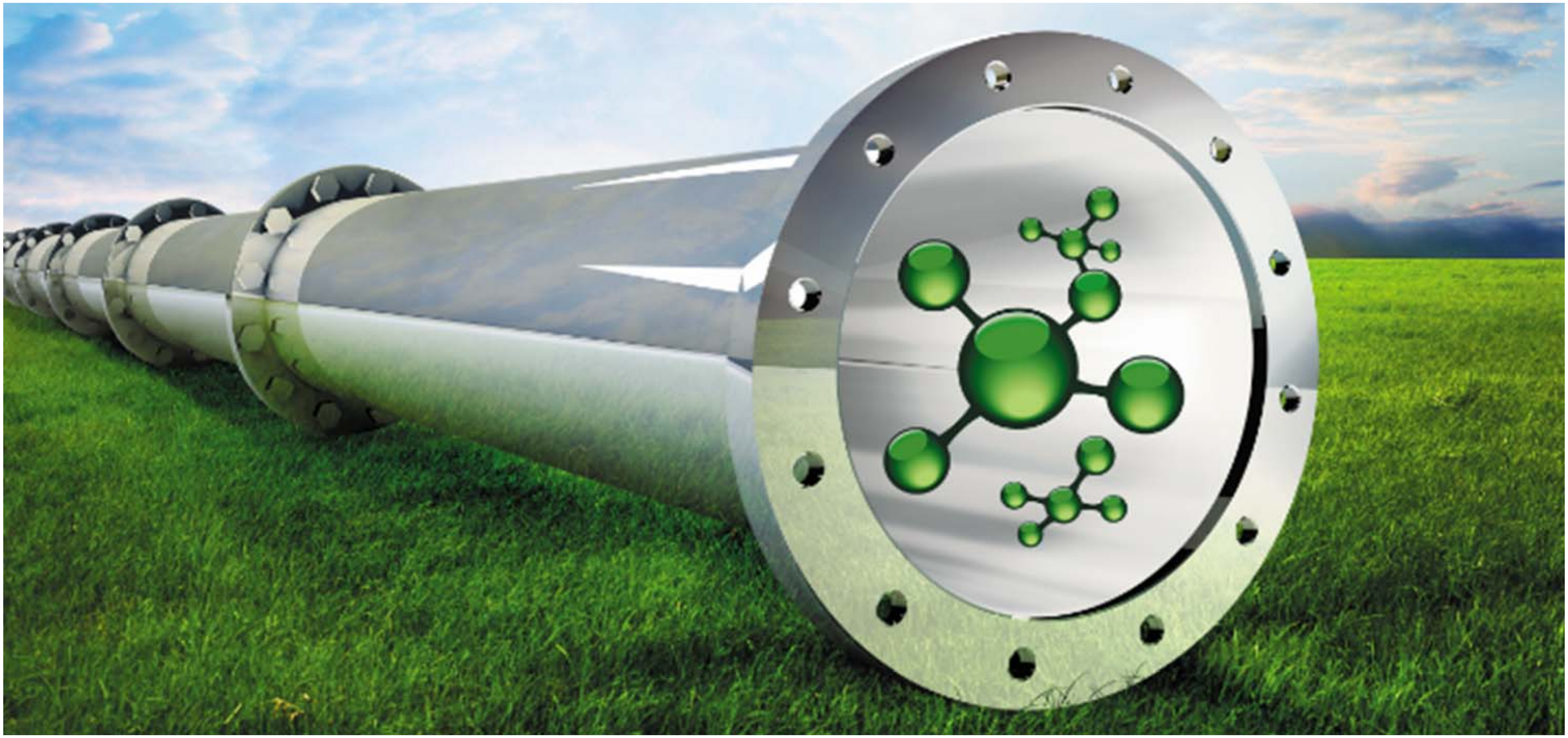
t = 4 hr

t = 24 hr

New H_2S Scavenger
Brine Compatibility

- New H_2S Scavenger is highly soluble in brines, even up to 33% (330,000 ppm)





Prediction of Chemical H_2S Scavenger Use in a Production System

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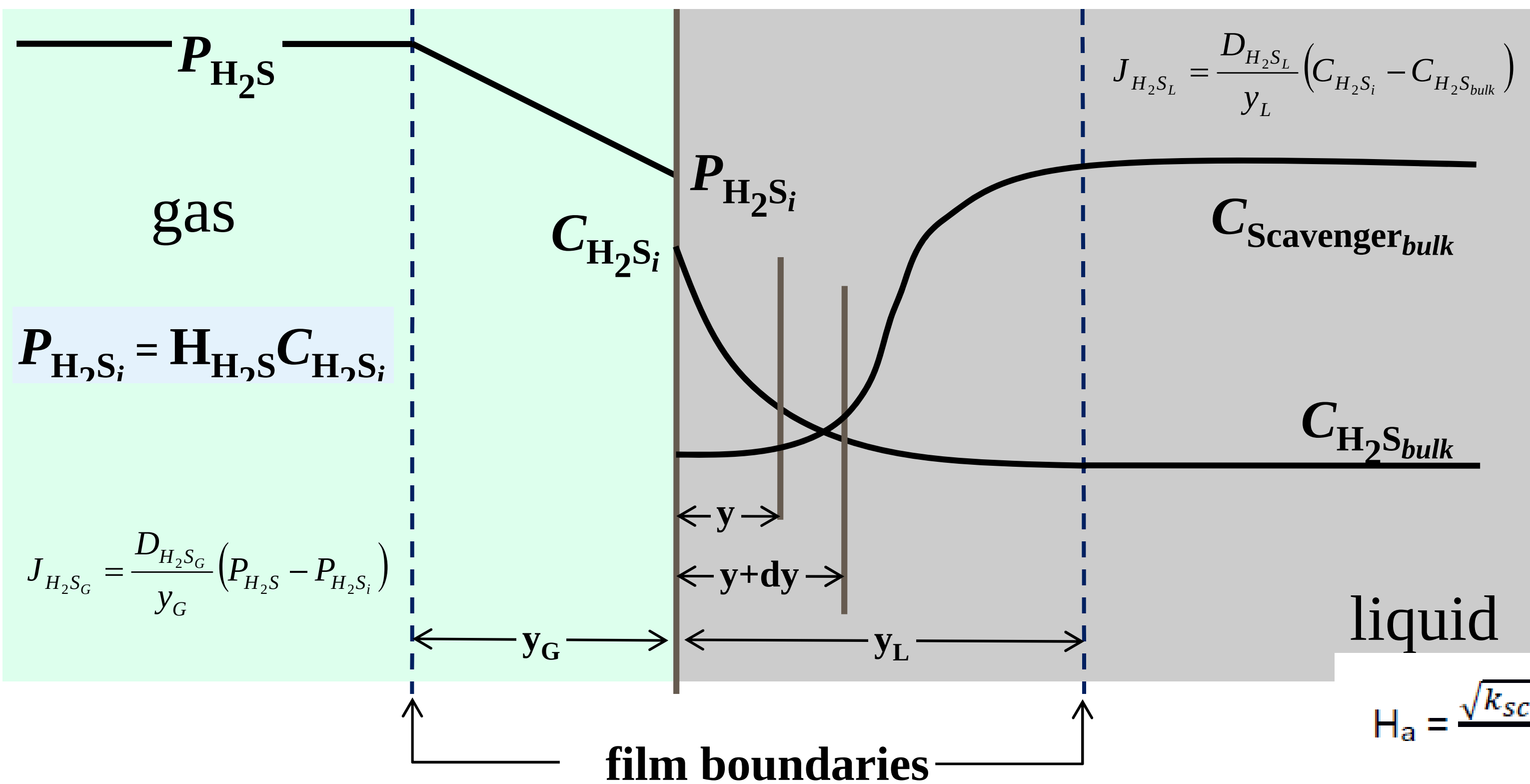
System Modeling for H_2S Scavenging

- Scavenging is a Function of:
  - Overall H_2S within the system
  - System Parameters
    - Production levels – Gas (MSCF), Oil (BOPD), Water (BWPD)
    - Flow velocity
    - Mixing Dynamics

- Modeling Requires a Few Inputs & Assumptions
  - Gas / Water and Oil / Water Partitioning
  - Reaction rate of the scavenger within each / the appropriate phase
  - Estimate of the boundary layer thickness between the gas and liquid

Basic Mass Transfer Model Utilized

- Physical Mass Transfer followed by Irreversible Reaction
  - Diffusion to the boundary layer
  - Mass transfer across the layer
  - Reaction with the scavenger in the layer and in the bulk solution



$$H_a = \frac{\sqrt{k_{scav} D_{H2S}}}{k_l}$$

Modeling Scavenging Under Field Conditions

- Thermodynamic Parameters for Partitioning of H_2S
  - K_{gw} = 428 (Kgw = χ H2Sg / χ H2Saq)
  - K_{ow} = 17, (Kow = χH2Soil / χ H2Saq)
  - K_{go} = 25 (Kgo = χH2Sg / χ H2Soil)
    - Where χH2S*i* = mole fraction of H2S in phase *i*. *
  - First-order reaction with scavenger in the layer and in the bulk solution

- Kinetic Parameters for Scavenging
  - Diffusion of H_2S – 1.60 x 10^{-5} cm^2/sec in water
  - Equation and reaction rates with scavenger in the layer and in the bulk solution

- Fluid Velocity and Distance

*E.D. Burger, G. E. Jenneman, J. J. Carroll "On the Partitioning of Hydrogen Sulfide in Oilfield Systems", Paper No. 164067, SPE 2013

Fit of Model to Field Trial Data with the New Scavenger – Example A

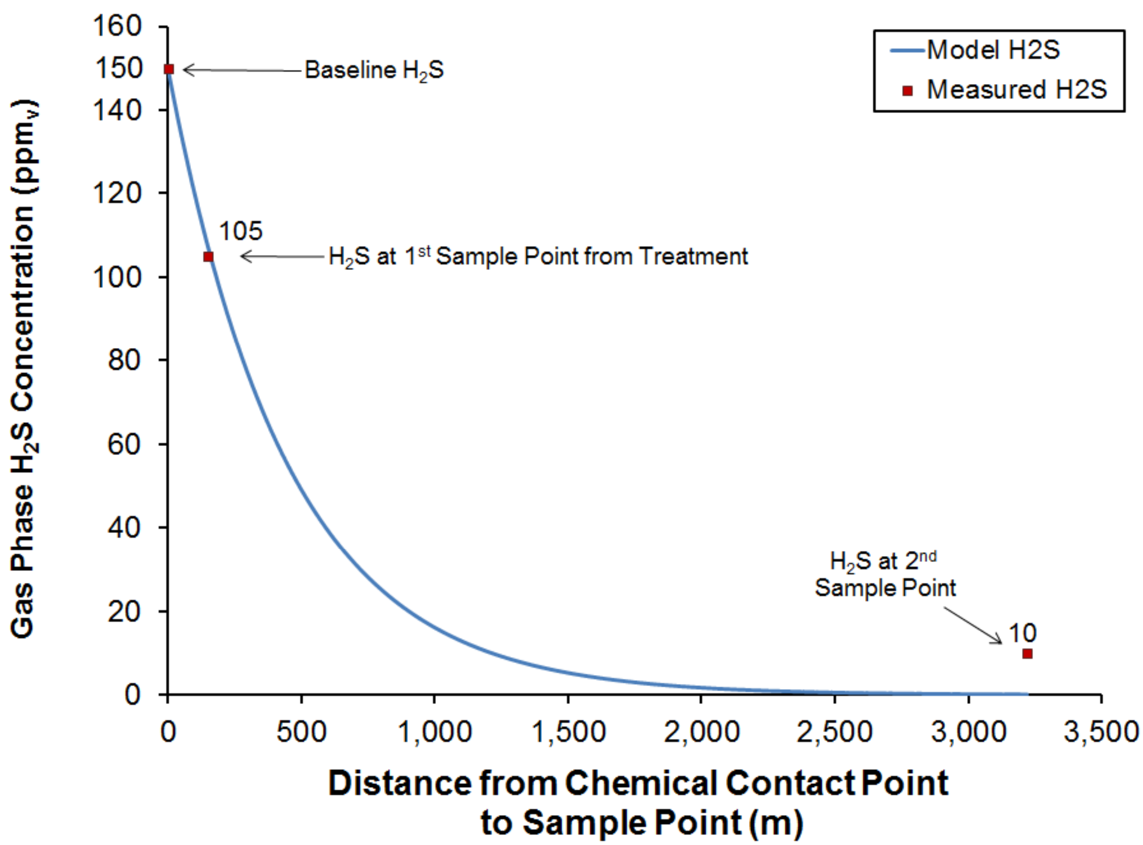
- Kinetic Parameters
  - Pseudo first-order reaction with scavenger in the layer and in the bulk solution

- Production Levels – Field A
  - 250 MSCF / day
  - 40 BWPD
  - 415 BOPD
  - 150 ppm_v H_2S baseline level

- Reduced to 10 ppm_v H_2S with 18 gpd Scavenger

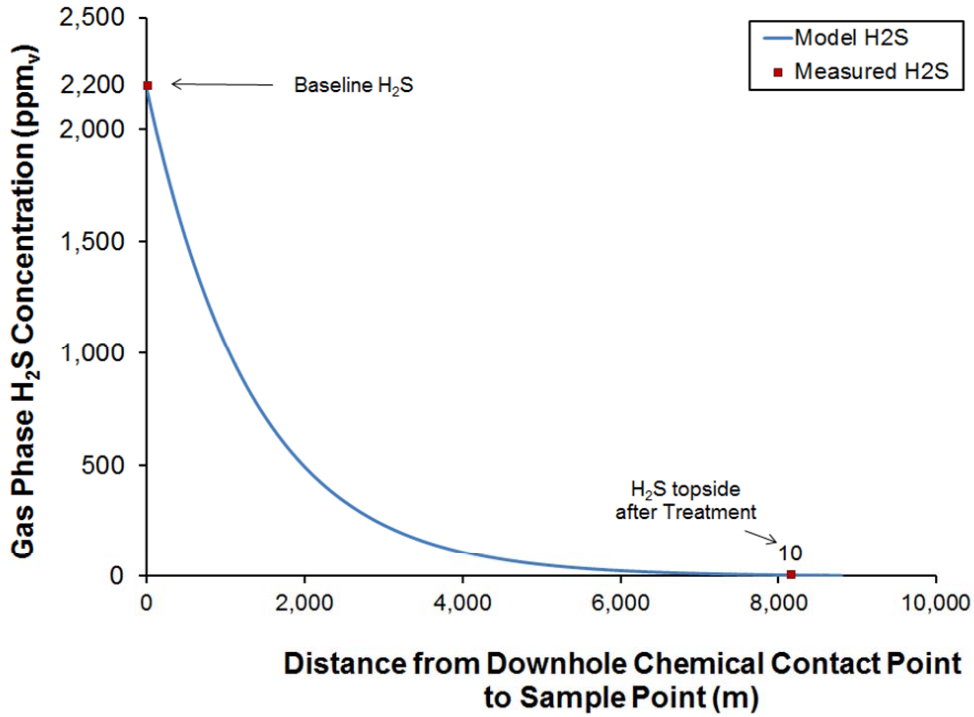
Fit of Model to Field Trial Data with the New Scavenger – Example A

- Model shows a reasonable fit to the measured data
  - Overall mass transfer is slower than reaction
  - Reaction increase mass transfer slightly
    - Hatta number (H_a) ~ 1.49



Fit of Model to Field Trial Data with the New Scavenger – Example B

- Production Levels – Field B
  - 240 MSCF / day
  - 90 BWPD
  - 240 BOPD
  - 2200 ppm_v H_2S baseline level
- Reduced to 10 ppm_v H_2S with 30 Scavenger
  - Downhole injection utilized
- Hatta number (Ha) ~ 1.20



Comparison of the Model and Field Performance

- Model provided a recommended dose rate consistent with actuals

System	Initial H_2S_g (ppm_v)	Target H_2S_g (ppm_v)	Final H_2S_g (ppm_v)	Scavenger Dose Rate (model)	Scavenger Dose Rate (actual)
Oilfield A Ha ~ 1.49	150	<20	10	1.5 gpd (5.7 lpd)	2 gpd (7.6 lpd)
Oilfield B Ha ~ 1.20	2,200	<20	10	19 gpd (72 lpd)	26 gpd (99 lpd)

- **Typically Ha > 2 = scavenging reaction = near the gas liquid phase**
- **Tipically Ha < 0.2 = scavenging reaction = within the water phase**

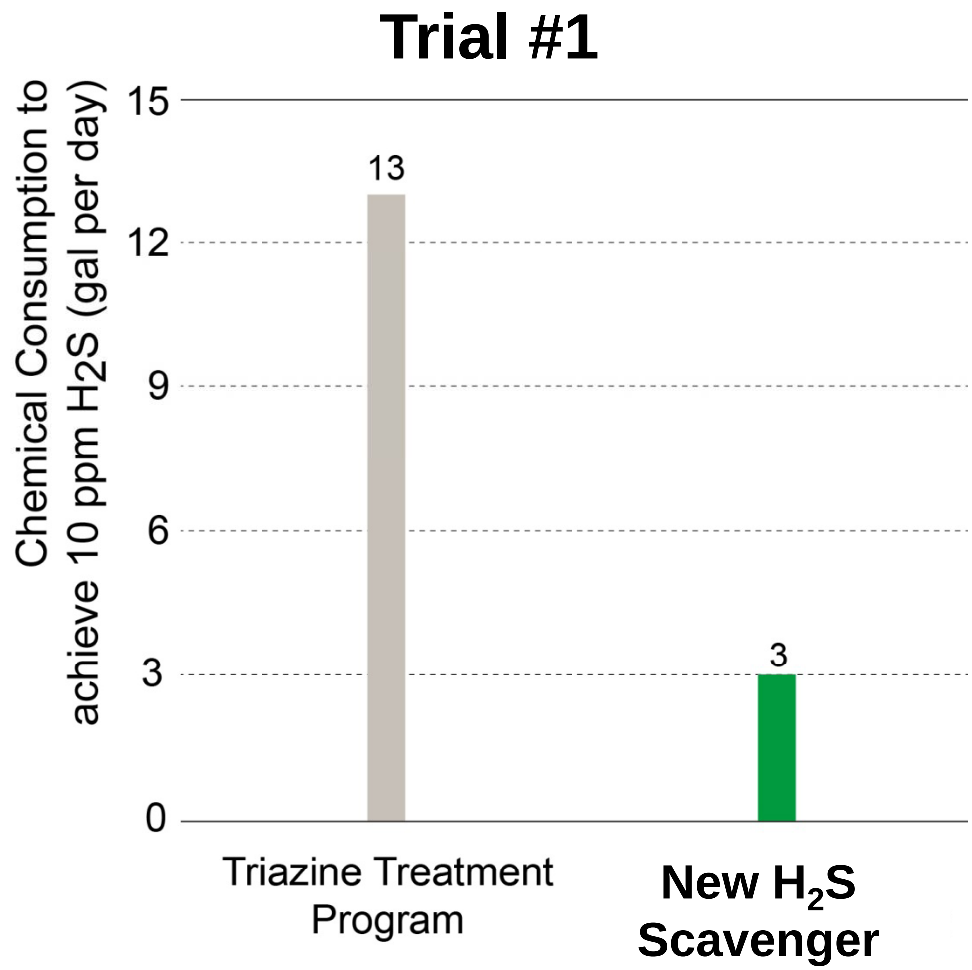
=

This shows that the chemical dose effectively creates a pseudo-first order reaction rate within the water phase that makes the scavenging reaction competitive with mass transfer of H2S from the gas or oil phase to the water phase.

New H_2S Scavenger

Successful with 77% - Less Chemical vs. Triazine Treatment

- **New H_2S Scavenger** field results
  - Offshore production system
  - Reduced from 36 ppm to 10 ppm H_2S
  - 5.42 lbs (2.46 kg) H_2S removed per day
- Production
  - 370 BOPD
  - 1,800 BWPD
  - 22,400 MCF gas/day

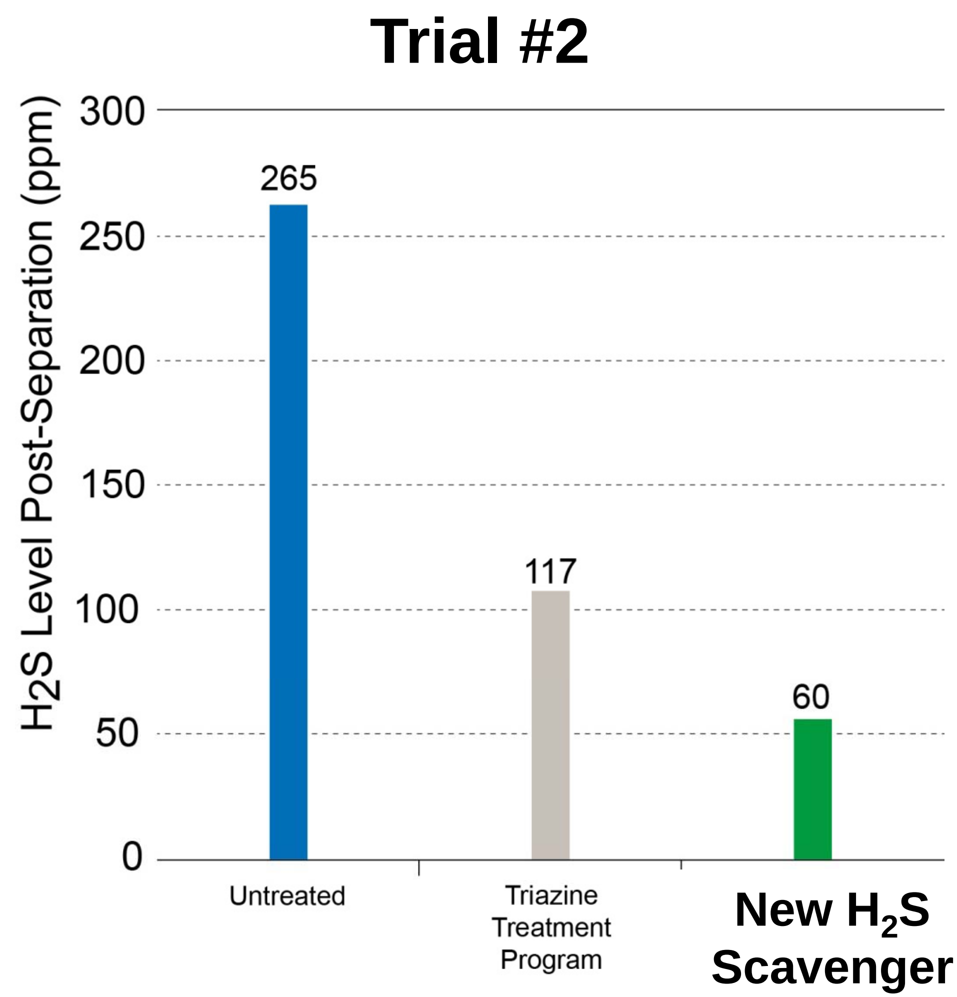


3rd Party Data

New H_2S Scavenger

Reduced the H_2S Level by ~50% vs. Triazine Treatment

- **New H_2S Scavenger** field results
  - 0.37 lbs (0.17 kg) H_2S removed per day
- Production
  - 12 BOPD
  - 120 BWPD
  - 12MCF gas/day
- Double the performance at equivalent cost



3rd Party Data

New H_2S Scavenger
Temperature Stability as Product

Temperature	Shelf-life
25 ^oC (77 ^oF)	> 2 yr
50 ^oC (122 ^oF)	> 2 yr
150 ^oC (302 ^oF)	> 6 hr

New H_2S Scavenger
Miscible with a Wide Range of Solvents

Solvent	Miscibility
Methanol	Complete
Ethanol	Complete
Isopropanol	Complete
Ethylene Glycol	Complete
Propylene Glycol	Complete
Monoethylene Glycol Monobutylether	Complete
Diethylene Glycol Monobutylether	Complete

Lonza Internal Data

New H_2S Scavenger
Chemical Additive Compatibility

Additive	New H_2S Scavenger Impact or Effect
Corrosion Inhibitors	
Cationics / water soluble	None
Phosphonates	None
Anionics	None
Dimer / Trimer Acid	None
Anti-scalants	None
Oxygen Scavengers	
Sodium / Ammonium Bisulfite	Incompatible
Erythorbate / Erythorbic Acid	Compatible

New H_2S Scavenger
Material Compatibility

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Material	Rating
Ethylene Propylene (EPDM)	A-Excellent
HDPE	A-Excellent
Neoprene (CR)	A-Excellent
Polypropylene (PP)	A-Excellent
PVC	A-Excellent
CPVC	A-Excellent
Teflon (PTFE)	A-Excellent
Viton	A-Excellent
Buna-N	B-Good
Hypalon	B-Good
Nitrile (NBR)	B-Good

A = Excellent

B = Good – Minor effect, slight discoloration

C = Fair – Moderate **effect**, not recommended for continuous use. Softening, loss of strength, swelling may occur

D = Severe Effect, not recommended for ANY use

New H_2S Scavenger
Metal Compatibility

Material	Corrosion Rate (mpy) at 50 ºC	Rating
Stainless Steel (304SS)	<0.1	A-Excellent
Stainless Steel (316SS)	<0.1	A-Excellent
Carbon Steel (C1018)	0.96	B-Good
N80	1.02	B-Good

A = Excellent, no corrosion (0 – 0.1 mpy)

B = Good – Minor corrosion (0.1 – 2.0 mpy)

C = Fair – Moderate corrosion (2.0 – 5.0 mpy)

D = Severe corrosion (>5.0 mpy)

Lonza Internal Data

New H_2S Scavenger vs.Triazine
Summary

	New H_2S Scavenger	**Triazine**
High Temperature Stability (>85º C)	Yes	No
Non-scaling	Yes	No
Scavenging is pH independent	Yes	No
Non-corrosive	Yes	Yes
Downhole injection	Yes	No

Summary of Mass Transfer Model and Prediction

- New Scavenger Effectively Reduced H_2S in Production Systems
  - Downhole injection preferred for maximum benefit
    - Increased contact time

- H_2S Scavenging Model Indicated Mass Transfer is Rate-Determining
  - Hatta numbers and Enhancement Factors show an intermediate scavenging scenario
    - Some scavenging in the film
    - Additional scavenging in the bulk water

- Scavenging Model can Assist in Predicting Performance Efficacy
  - Similar values for different well conditions are fit reasonably
  - Production Rates required
  - Injection points to analysis point distance is required (reasonable approximation)

- Further….
  - simplified reaction model and algorithm has been developed to model and predict the scavenging efficiency and predictably optimize chemical dose rate…..

- in order to…..
  - understanding the phenomenological kinetic equations for the scavenger of choice is required and, in particular, the rate in the phase or phase(s) it scavenges is important. This will dictate the complexity of the model used and the role mass transfer has on each of the potentially competing rates

Thank you

- **Acknowledgement**
  - Dr. Kevin Janak – Application Technology Manager

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