On the Delayed Post-Fracture Souring of Shale Gas Production

UNIVERSITY OF CALGARY

Payman Pirzadeh, Shaunak Raval and Robert A. Marriott

November 6th, 2014

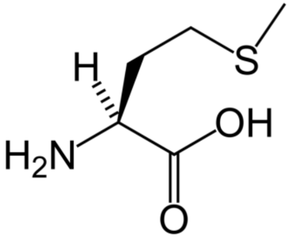
21st GPAC-PJVA Joint Annual Conference

Calgary, Alberta

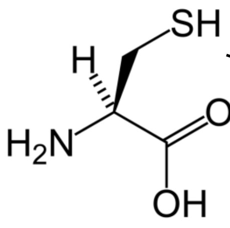
NSERC
CRSNG

What are the Sources of H_2S in a Conventional Gas Reservoirs?

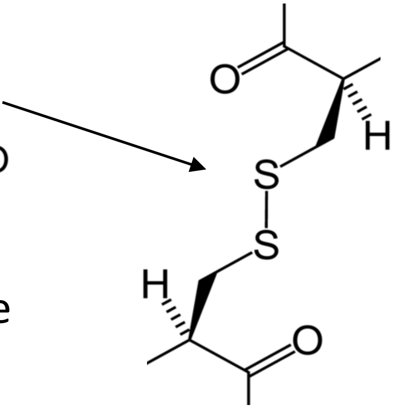
Sulfur combined in living precursor material (natural amino acids)



Methionine

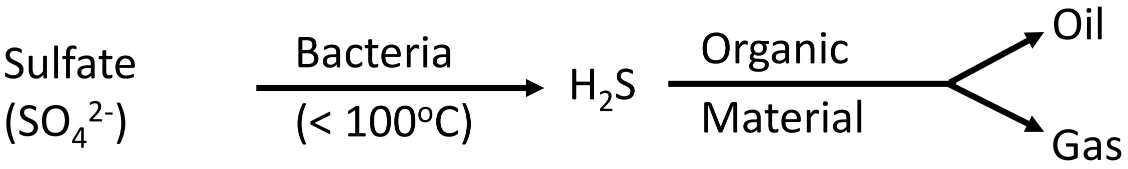


Cysteine



Reduction of Sulfates (*eg.*, $CaSO_4$)

Microbial (MSR)



Sulfate (SO_4^{2-}) $\xrightarrow[(< 100^oC)]{\text{Bacteria}}$ H_2S $\xrightarrow[\text{Material}]{\text{Organic}}$ Oil / Gas

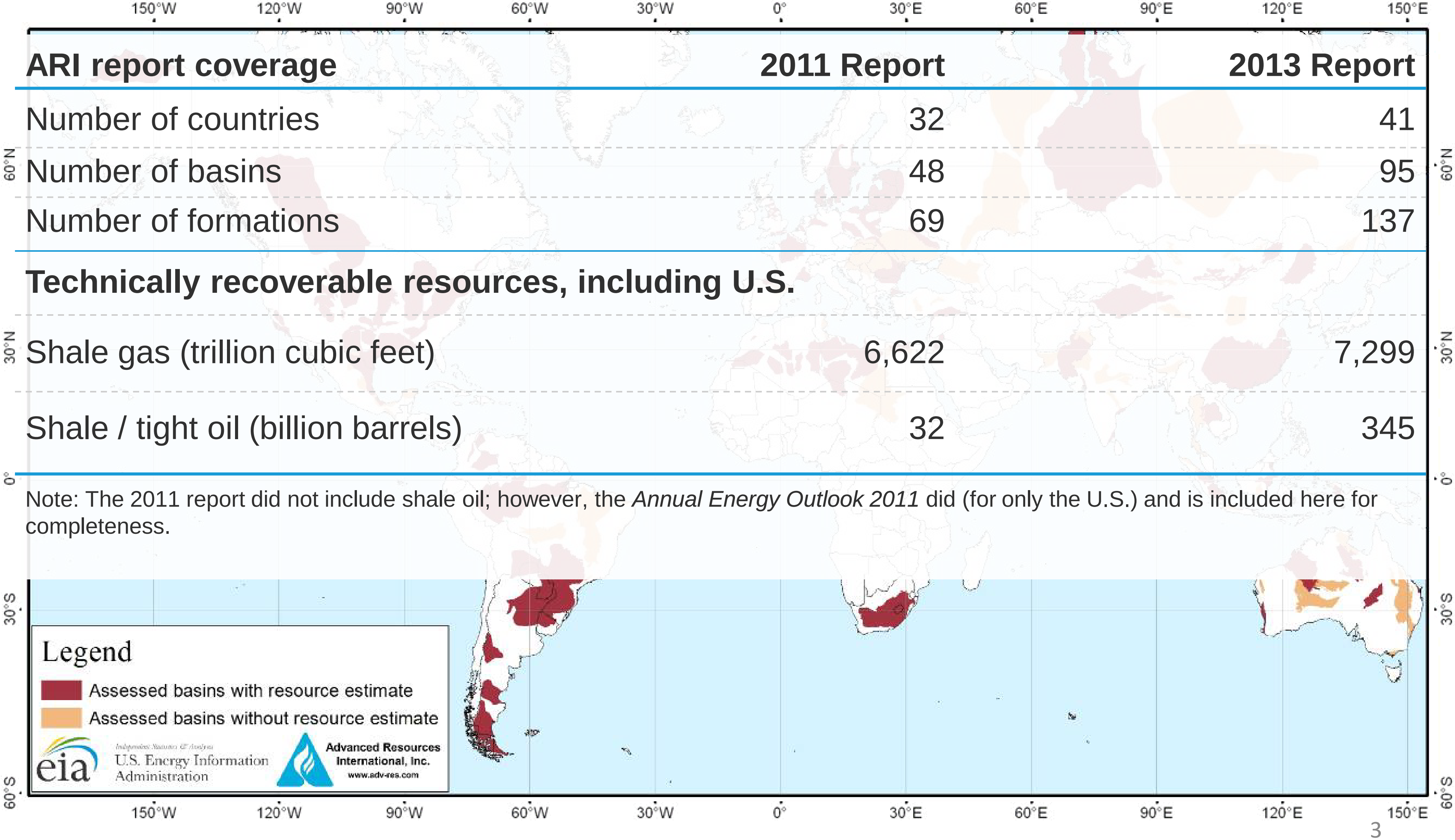
Thermal Sulfate Reduction (TSR)

$$\tfrac{3}{4}xCaSO_4(s) + C_{x+1}H_{2x+4} \longrightarrow \tfrac{3}{4}xH_2S + \tfrac{1}{4}xCO_2 + \tfrac{1}{4}xH_2O + \tfrac{3}{4}xCaCO_3 + CH_4$$

Global Shale Gas and Shale Oil

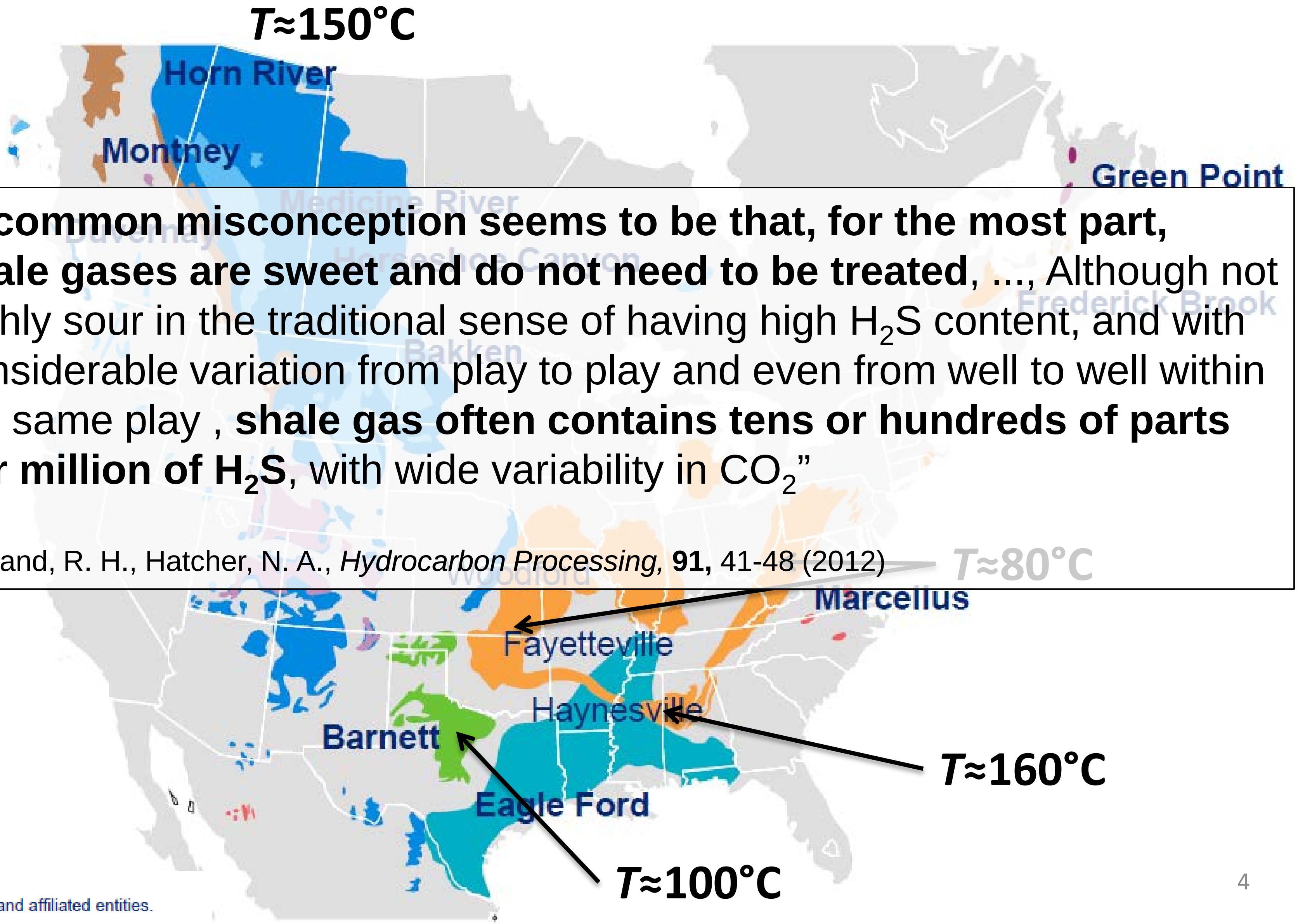
ARI report coverage	**2011 Report**	**2013 Report**
Number of countries	32	41
Number of basins	48	95
Number of formations	69	137
Technically recoverable resources, including U.S.		
Shale gas (trillion cubic feet)	6,622	7,299
Shale / tight oil (billion barrels)	32	345

Note: The 2011 report did not include shale oil; however, the *Annual Energy Outlook 2011* did (for only the U.S.) and is included here for completeness.



U.S. energy Information Administriation, Technically Recoverable Shale Oil and Shale Gas Resources (2013).

North American Shale Plays



“**a common misconception seems to be that, for the most part, shale gases are sweet and do not need to be treated**, ..., Although not highly sour in the traditional sense of having high H_2S content, and with considerable variation from play to play and even from well to well within the same play , **shale gas often contains tens or hundreds of parts per million of H_2S**, with wide variability in CO_2”

Weiland, R. H., Hatcher, N. A., *Hydrocarbon Processing,* **91,** 41-48 (2012)

© Deloitte LLP and affiliated entities.

Can Shale Gas Production go Sour?

- There have been informal communications regarding production of shale gas that starts sweet, but **goes sour after a few months**

  - **What can potentially cause a sweet reservoir go sour over time?**

  - **What may delay surfacing the H_2S in an initially sour reservoir?**

- Unpredicted souring may result in efficiency issues in processing units and affect the economy of production (metallurgy of construction and treatment of the products)

Possible Sources of H_2S in a Dry Shale Gas

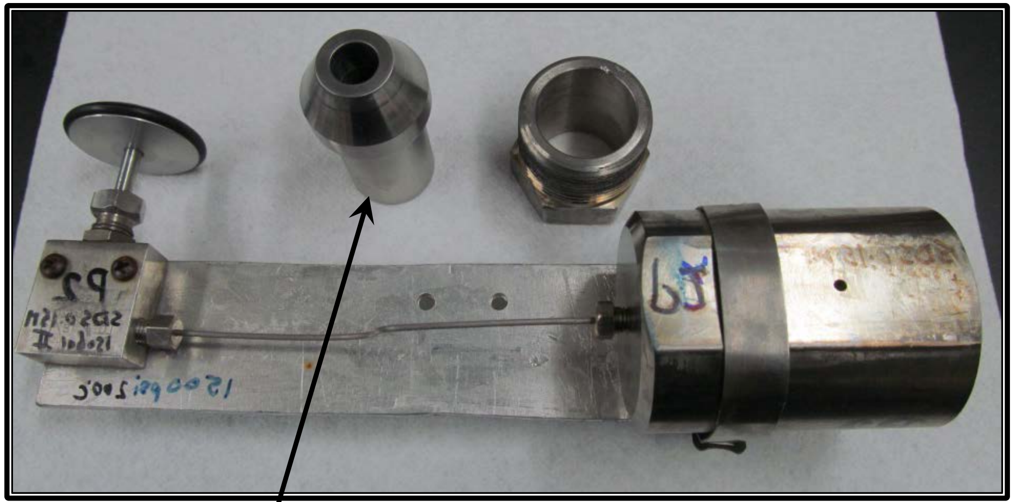
- Aquathermolysis of Kerogen (non-native H_2S)
  - Why doesn't the H_2S drop-off after flowback?
  - Unless we heated the reservoir (similar to SAGD), why was there no initial H_2S?
  - maturity?
- Late desorption of native H_2S
  - Why does initial testing show no H_2S?
  - Shouldn't the H_2S level continue to rise?
- Bacterial reduction of sulfate (non-native)
  - Would this occur for $T > 150°C$ and after biocide was used?
  - Where did the sulfate come from (HFF)?
- Ingress from another sour zone
  - Why wouldn't the H_2S continue to rise?
- **Thermal sulfate reduction**
  - May be the source of native H_2S, but is a geologically slow reaction, especially with mature gas
  - High reaction rate requires larger hydrocarbons.
- **Delayed production of H_2S due to *in situ* scrubbing with chemical additives**

Possible Scenarios

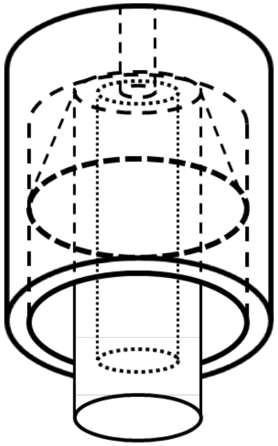
- It appears that hydraulic fracturing fluid may have introduced new species into the shale well
- Two scenarios are conceivable:
    - The shale reservoir is completely sweet and goes sour by time
    - The shale reservoir was sour, and hydraulic fracturing fluid may make the well appear sweet

Experimental

- Reactants are loaded at room temperature.
- N_2 pressure is added through a HP sampling manifold.
- Vessel is thermostated for *t* = 40, 132 or 168 hours before quenching.
- The sample is opened to the sampling manifold and blown down to GC (PFPD, FID, TCD).
- Liquids are removed for GC/MS, IC, ICP and pH.



6 cm^3 Titanium plug



Scenario (I): Starting with a sweet reservoir
Can Additives Sour a Reservoir via TSR

Frac Focus
Chemical Disclosure Registry

	Additive Type	Chemical	Purpose
	surfactant	sodium dodecyl sulfate	friction reduction, emulsion inhibition
	surfactant	isopropanol, ethanol, methanol, 2-butosyethanol	formulation stabilizer, winterizer
➡	biocide	gluteraldehyde, ammonium chloride, hydroxymethyl phosphonium sulfate	eliminate bacteria
➡	gel breaker	ammonium persulfate, magnesium peroxide, magnesium oxide	delays breakdown of gel polymer until after propant is deposited
➡	oxygen scavenger	ammonium bisulfate	removes oxygen
➡	scale inhibitor	ethylene glycol	prevents deposits within wellbore and pipelines
	friction reducer	polyacrylamide, mineral oils, SDS	interfacial friction reduction (slick water)
	Gel	Guar gum, hydroxyethyl cellulose	viscosity modification for carrying propant
	iron controller	Citric acid	chelating of metal oxides
	pH adjusting agent	sodium or potassium carbonate	maintains the effectiveness of some compounds, such as crosslinkers
	crosslinker	borate salts	viscosity modification for carrying propant (high-temperature)
	propant	silica and quartz sand	props fractures open for gas migration after fracture fluid has been recovered
	diluted acid	hydrochloric acid	mineral dissolution for some acid stimulation

Scenario (I): Starting with a sweet reservoir
Can Additives Sour a Reservoir via TSR

- Sodium dodecyl sulfate (SDS) is also known sodium lauryl sulfate (SLS)
- Common surfactant in chemical industry and biology
- It hydrolyses into 1-dodecanol and bisulfate anion at room temperature:

$$H_2O + C_{12}H_{25}SO_4^-{}_{(ads)} + Na^+ \longrightarrow C_{12}H_{25}OH + HSO_4^- + Na^+$$

- Will 1-dodecanol participate in a TSR reaction?

TSR Reaction of 1-dodecanol in 40 hours

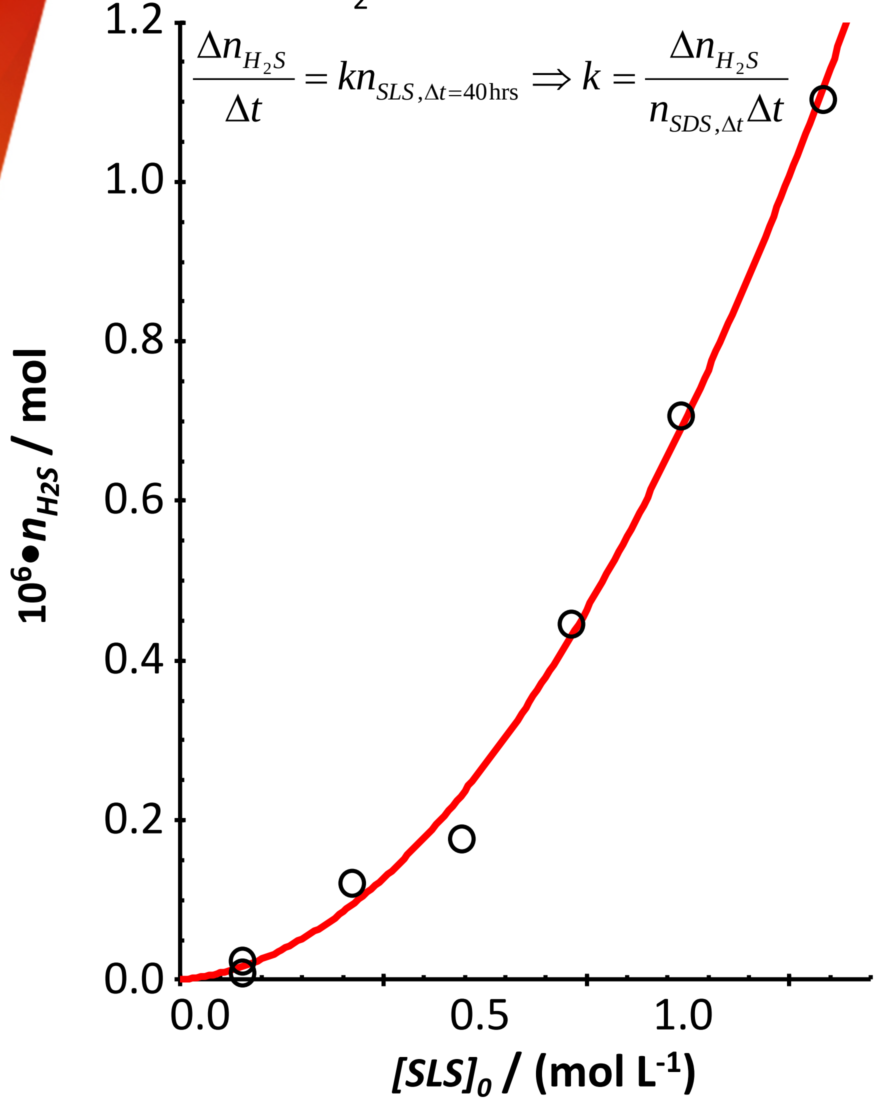
				Initial	Final			
Oxidant	***T* / °C**	***p* / MPa**[a]	***t* / hrs**	**$10^3 \bullet SO_4^{2-}$ / mol**	**$10^3 \bullet SO_4^{2-}$ / mol**	**$10^5 \bullet H_2S$ / mol**	**$10^5 \bullet CO_2$ / mol**	**% recovery**[b]
$MgSO_4$(*aq*)	300	6.5	40	5.06	3.60	0.47	0.30	71
$MgSO_4$(*aq*)	300	15.7	40	5.06	3.95	0.52	0.75	78
$NaHSO_4$(*aq*)	200	36.9	40	4.68	4.01	3.0	0.18	86
H_2SO_4(*aq*)	200	71.2	40	4.68	--	121	0.090	26
H_2SO_4(*aq*)	200	36.9	40	4.68	0.37	136	0.30	65
$(NH_4)_2S_2O_8$	200	20.9	40	4.98	4.73	0.0006	1.4	95

(a) The total pressure at the reaction temperature was calculated based on the measured pressure and temperature upon opening the vessel (see methods); **(b)** small quantities of S^{2-}(*aq*), SO_3^{2-}(*aq*) and $S_2O_3^{2-}$(*aq*) were found, but omitted from the table for clarity. '% recovery' is the fraction of sulfur species accounted for after all analyses, *i.e.*, the % sulfur mass balance.

Hydrolysis + TSR Reaction of SLS

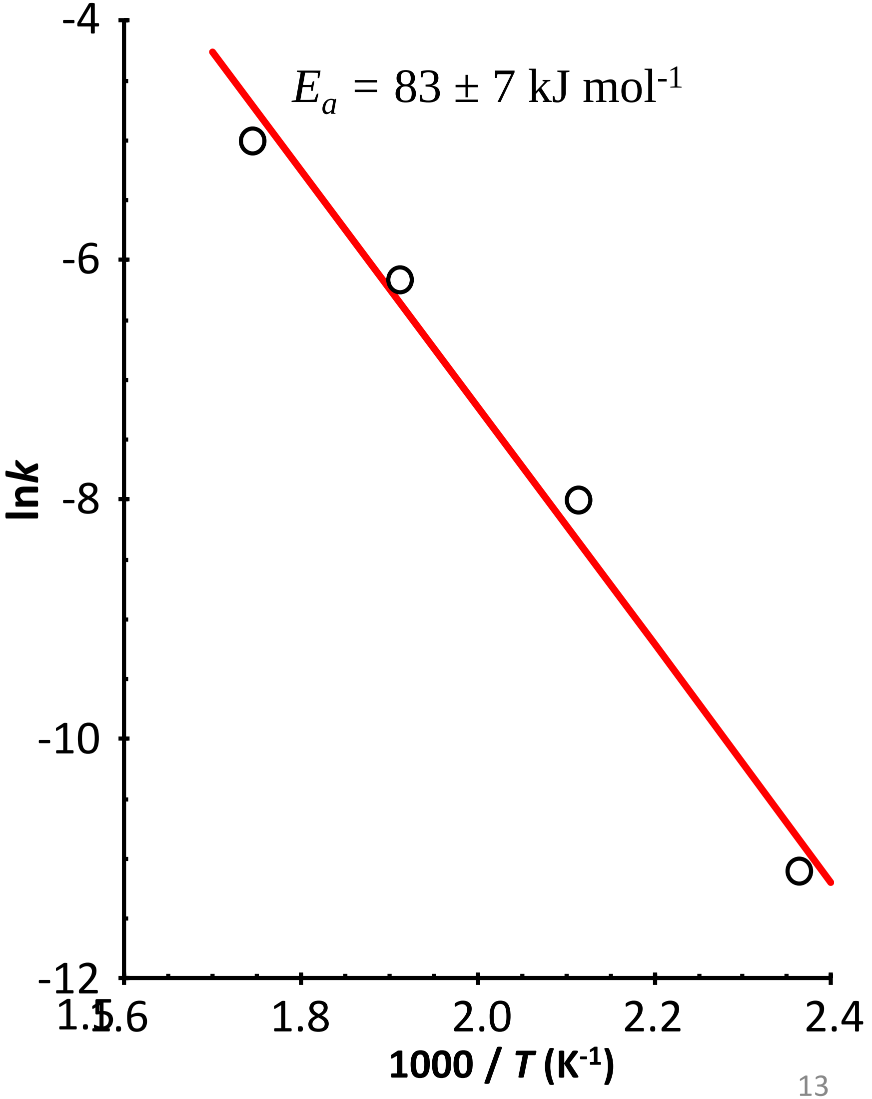
			Initial	Final				
T / °C	*p* / MPa	*t* /hrs	10^3•SLS /mol	10^3•SO_4^{2-} /mol	10^5•H_2S /mol	10^5•CO_2 /mol	10^3•*k* /h^{-1}	% recovery
300	15.1	40	6.32	2.95	69	90	5.08	60
250	20.9	40	6.38	4.31	16	4.9	1.92	71
200	26.2	40	6.34	5.77	0.38	3.8	0.17	91
200	17.0	40	6.35	5.32	0.20	3.4	0.05	84
200	27.6	40	6.35	5.51	1.1	5.2	0.33	87
150	28.7	40	6.35	4.92	0.084	4.0	0.02	77
150	37.2	40	6.35	4.76	1.7	3.9	0.26	75
150	16.7	40	6.33	4.69	0.13	3.6	0.02	74
200	18.5	132	4.92	4.28	0.71	3.7		87
200	19.0	132	3.84	3.48	0.45	2.4		91
200	19.6	132	2.76	2.53	0.18	1.8		92
200	18.4	132	1.68	1.61	0.12	1.1		96
200	16.2	132	0.634	0.51	0.009	0.61		81
200	16.9	132	0.634	0.53	0.024	0.50		86

SLS Reduction Kinetics for *T* ≥ 150°C



Produced H_2S versus initial SLS *T* = 200°C

$$\frac{\Delta n_{H_2S}}{\Delta t} = k n_{SLS,\Delta t=40\,\mathrm{hrs}} \Rightarrow k = \frac{\Delta n_{H_2S}}{n_{SDS,\Delta t}\Delta t}$$



First order Arrhenius Fit

E_a = 83 ± 7 kJ mol^{-1}

Scenario (I): Starting with a sweet reservoir
Can Additives Sour a Reservoir via TSR

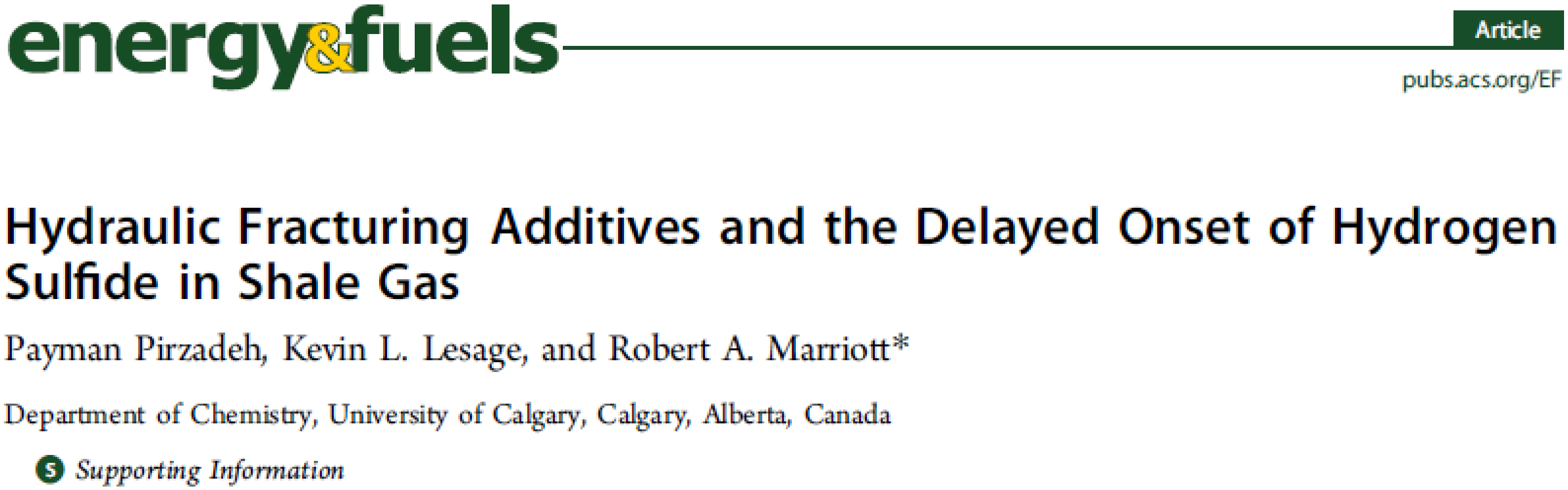
- SLS was found to undergo hydrolysis and thermal sulfate reduction to form H_2S.
- H_2S generation *via* SLS degradation was more rapid than expected from normal reservoir hydrocarbons.

T / °C	$t_{1/2}$ / days
300	4
250	14
200	85
150	2000 (5.6 years)

❖ **In a initially sweet shale reservoir, SLS and other fracture fluid additives can sour the production via TSR.**

❖ **The degree to which SLS participates in souring profile (*i.e.* its kinetics) requires further work, which incorporate minerals and additives**

Scenario (I): Starting with a sweet reservoir
Can Additives Sour a Reservoir via TSR



energy&fuels

Article

pubs.acs.org/EF

Hydraulic Fracturing Additives and the Delayed Onset of Hydrogen Sulfide in Shale Gas

Payman Pirzadeh, Kevin L. Lesage, and Robert A. Marriott*

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada

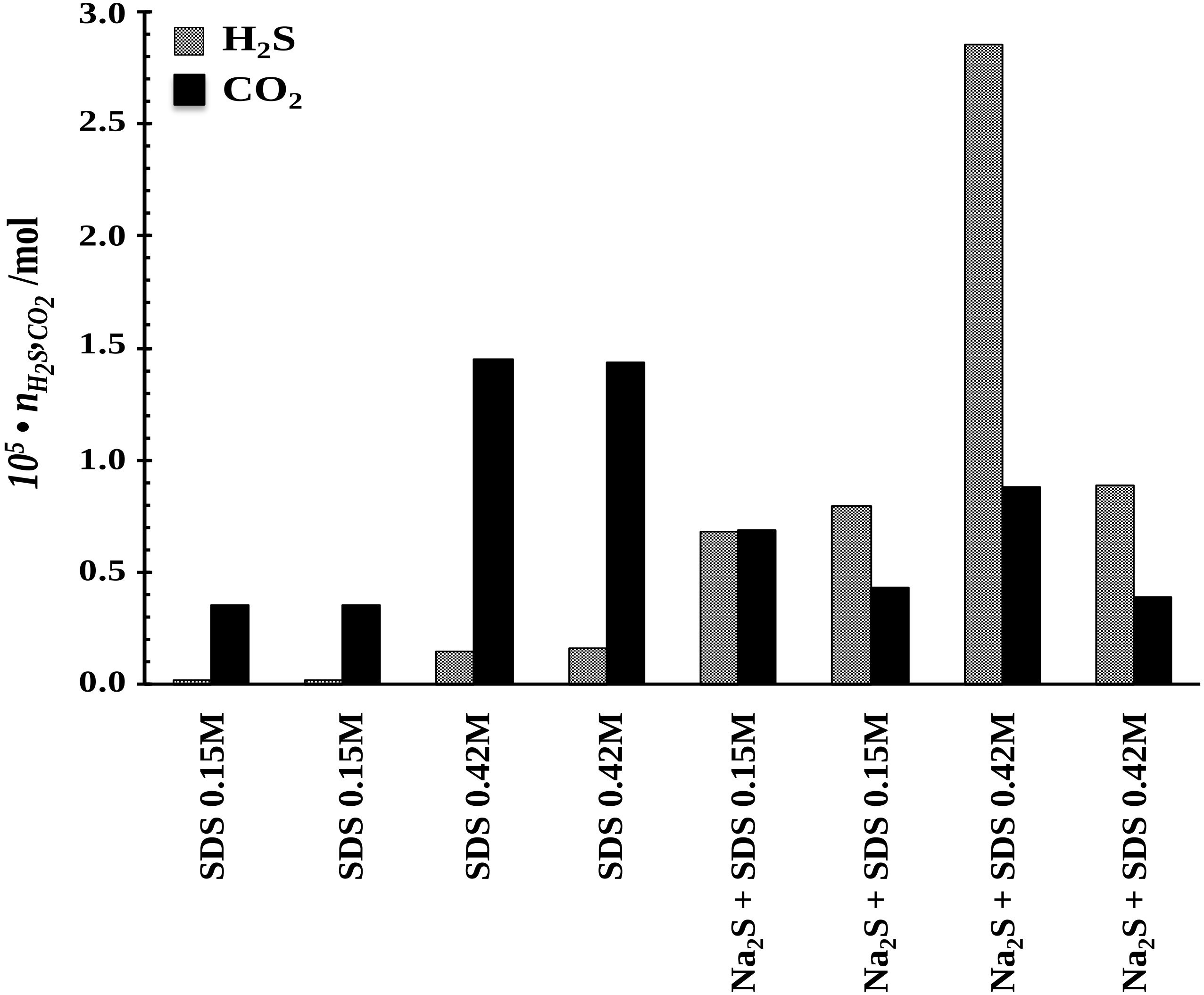
Ⓢ *Supporting Information*

dx.doi.org/10.1021/ef501059k| *Energy Fuels* 2014, 28, 4993 - 5001

Scenario (II): Starting from a Sour Reservoir
Delayed Appearance of H_2S at Surface

Role of H_2S: Experimental results without/with initial sulfide

- T = 200˚C
- p = 17 MPa (2500 psi)
- Experiments in duplicates
- H_2S is represented by Na_2S



Scenario (II):Starting From a Sour Reservoir Delayed Appearance of H_2S at Surface

A Simplified Mechanism for SDS degradation, scavenging H_2S and re-release of H_2S

$H_2O + C_{12}H_{25}SO_4^-(ads) + Na^+ \longrightarrow C_{12}H_{25}OH + HSO_4^- + Na^+$ Frac / post flowback

$HSO_4^- + 3H_2S + H^+ \rightleftharpoons 4S^\circ + 4H_2O$ Frac / post flowback

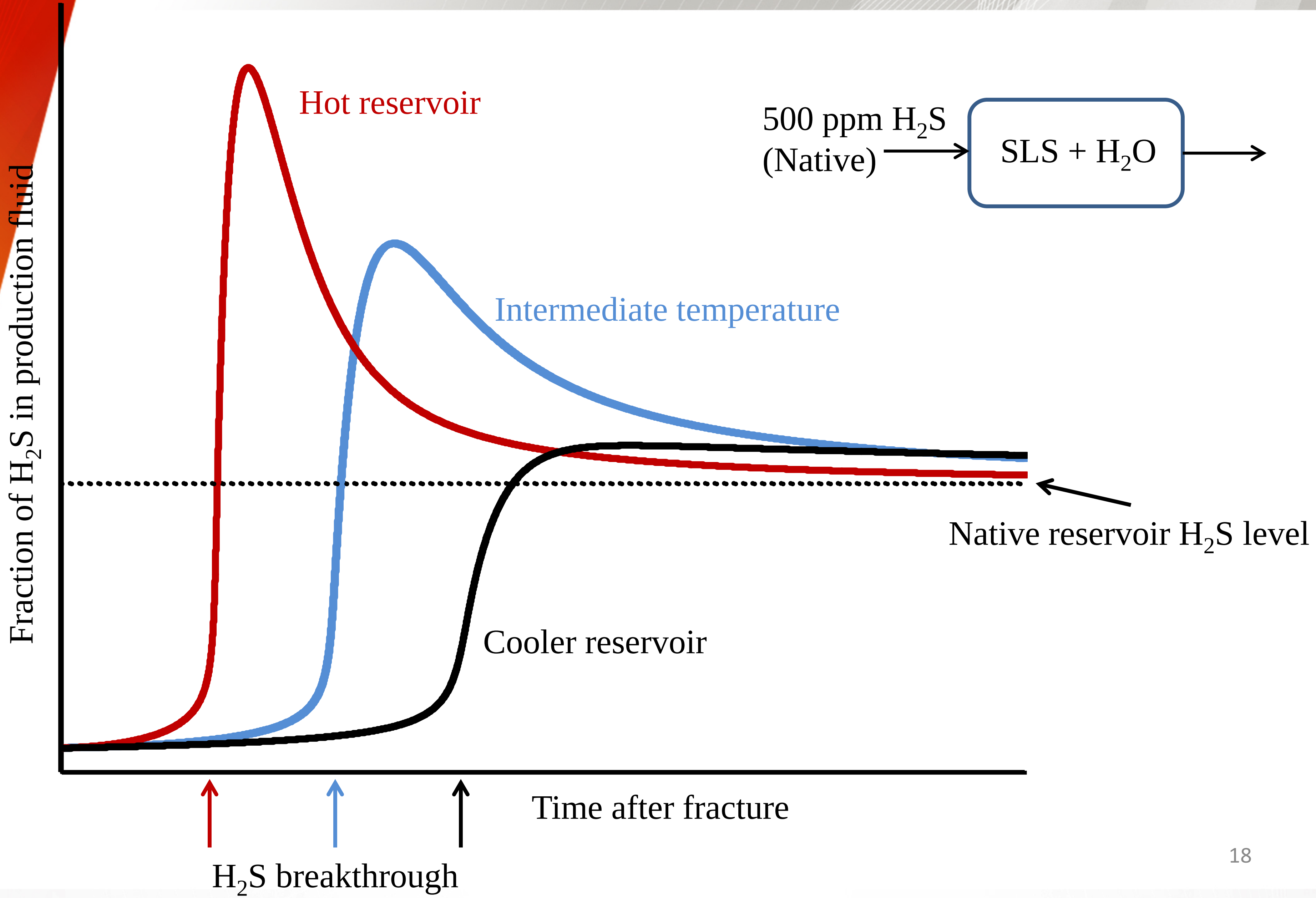
$3S^\circ + C_{12}H_{25}OH + 2H_2O \longrightarrow 3H_2S + CO_2 + C_{11}H_{23}OH$ Slow

$S^\circ + \frac{1}{3}C_{11}H_{23}OH + \frac{2}{3}H_2O \longrightarrow H_2S + \frac{1}{3}CO_2 + \frac{1}{3}C_{10}H_{21}OH$ Slow

$Na^+ + CO_2 + H_2O \rightleftharpoons NaHCO_3 + H^+$

$$NaC_{12}H_{25}SO_4 + \frac{2}{3}H_2O \longrightarrow NaHCO_3 + H_2S + \frac{1}{3}CO_2 + \frac{2}{3}C_{11}H_{23}OH + \frac{1}{3}C_{10}H_{21}OH$$

Scenario (II): Starting From a Sour Reservoir Delayed Appearance of H_2S at Surface



Summary

- In a sweet reservoir, the aqueous additives of hydraulic fracturing fluid can undergo TSR reactions under hydrothermal conditions
- In a sour shale reservoir, the fracturing fluid may scrub the H_2S and result in false negative test
- The scrubbed H_2S cab be re-released later during production
- Formation of thiols and acid-attack corrosions may be observed

Acknowledgment & Contacts

INNOVATION.CA
CANADA FOUNDATION FOR INNOVATION | FONDATION CANADIENNE POUR L'INNOVATION

NSERC
CRSNG

Payman Pirzadeh
E-mail: ppirzade@ucalgary.ca
Tel: +1-403-220-3146

Robert A. Marriott
E-mail: rob.marriott@ucalgary.ca
Tel: +1-403-220-3144