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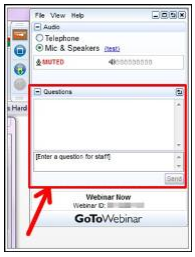

Type them into questions box!

"Why am I muted?"
Don't worry. Everyone is muted except the presenter and host. Thank you and enjoy the show.

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www.acs.org/covid-19

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Advancing ACS's Core Value of Diversity, Inclusion & Respect

We believe in the strength of diversity in all its forms, because inclusion of and respect for diverse people, experiences, and ideas lead to superior solutions to world challenges and advances chemistry as a global, multidisciplinary science.

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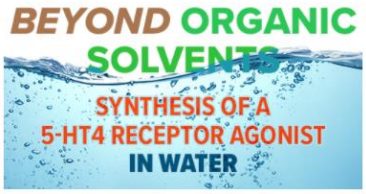
Free Upcoming ACS Webinars!



Thursday, September 17, 2020 at 2-3pm ET
Speaker: Dan Bailey, Takeda Pharmaceuticals
Moderator: John Tucker, Neurocrine Biosciences

Register for Free!

What You Will Learn

- Why we urgently need to reduce or eliminate organic solvent use in chemical manufacturing
- How Takeda process chemists adapted a manufacturing process to aqueous conditions
- Strategies for running reactions and isolating products under aqueous conditions

Co-produced with: ACS Green Chemistry Institute

Wednesday, September 23, 2020 at 3-4pm ET
Speaker: Christopher McCurdy, College of Pharmacy, University of Florida

Register for Free!

What You Will Learn

- Understanding of kratom products and their use in the traditional and Western populations
- The pharmacology and pharmacokinetics of the major alkaloid, mitragynine (and others)
- Some insights into the scientific hypotheses for therapeutic benefits as well as negative consequences

Co-produced with: ACS Division of Medicinal Chemistry, American Association of Pharmaceutical Scientists, and ACS Publications

Friday, September 25, 2020 at 10-11am ET
Speaker: Pamela Tadross, Organic Process Research & Development
Moderator: Kali Miller, ACS Publications

Register for Free!

What You Will Learn

- What editors look for when reviewing submissions
- Tips for responding to reviewer reports
- Qualifications to become a reviewer and strategies to evaluate a manuscript

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ACS Green Chemistry Institute

Engaging you to reimagine chemistry and engineering for a sustainable future!

We believe sustainable and green chemistry innovation holds the key to solving most environmental and human health issues facing our world today.

- Advancing Science
- Advocating for Education
- Accelerating Industry

ACS GCI convenes **companies in the chemical industries to advance the implementation of sustainable and green chemistry and engineering.**

Join our ACS GCI OCR Mission!

ACS Green Chemistry Institute
Chemistry for Life®

To integrate GC&E principles into the chemical supply chain for the oilfield industry.

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ACS Green Chemistry Institute Chemistry for Life®

Contact: gciroundtables@acs.org ; and/or Isamir Martinez, i_martinez@acs.org

www.acs.org/oilfield-chemistry

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Save the Date…ACS GCI Webinar Next Week!

ACS Chemistry for Life®

Dan Bailey
Process Chemist, Takeda Pharmaceuticals

Thursday. September 17, 2-3pm ET

"Beyond Organic Solvents: Synthesis of a 5-HT4 Receptor Agonist in Water"

2020 Peter J. Dunn Award Winner for Green Chemistry and Engineering Impact in the Pharmaceutical Industry

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THIS ACS WEBINAR WILL BEGIN SHORTLY...

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Grand Challenges and Opportunities for Greener Alternatives within the Oil and Gas Industry

Brian Price
Vice President of Technology & Completions Business Line, Rockwater Energy Solutions and Member, ACS GCI Oilfield Chemistry Roundtable

Dave Horton
Chief Technology Officer, CES Energy Solutions and Co-Chair, ACS GCI Oilfield Chemistry Roundtable

David Constable
Science Director, ACS Green Chemistry Institute, American Chemical Society

Presentation slides available now! The edited recording will be made available as soon as possible.

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This ACS Webinar is co-produced with ACS Green Chemistry Institute.

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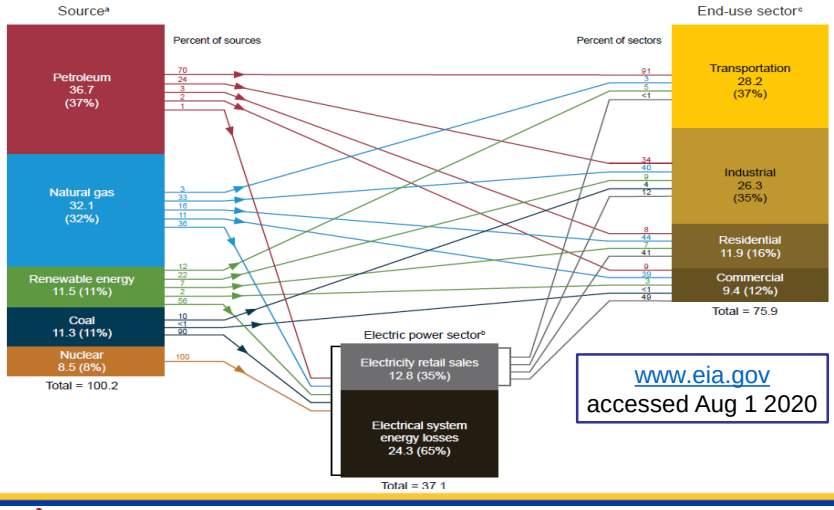
Meeting the Energy Needs of Today's World

ACS Green Chemistry Institute
Oilfield Chemistry Roundtable

U.S. energy consumption by source and sector, 2019
(Quadrillion Btu)



www.eia.gov
accessed Aug 1 2020

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ACS GCI & Oil/Gas Industries Collaboration

ACS Green Chemistry Institute
Oilfield Chemistry Roundtable

ACS Green Chemistry Institute
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Common ground: To fulfill today's energy needs minimizing environmental impact.

Pre-competitive scientific collaboration within a non-profit organization, where research innovations could be driven and all companies could benefit.

Working together, brainstorming new ideas, creating tools and sharing best practices.

Why? *Green chemistry & engineering is a driver to sustainability.*

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ACS GCIOR Mission & Strategic Priorities

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To systematically integrate GC&E principles into the chemical supply chain for the oilfield industry.

- **Develop scientific information.**
- **Provide a scientific framework and tools.**
- **Identify, assess and prioritize chemicals** to find sustainable **alternatives**
- **Promote effective communication and collaboration.**
- **Advocate for scientific approaches & innovative additive technology.**

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Recent ACS GCIOR Perspective Publication!

ACS Green Chemistry Institute
Oilfield Chemistry Roundtable

energy&fuels

Energy Fuels 2020, 34 (7), 7837-7846

pubs.acs.org/EF Review

Grand Challenges and Opportunities for Greener Chemical Alternatives in Hydraulic Fracturing: A Perspective from the ACS Green Chemistry Institute Oilfield Chemistry Roundtable

David Harry, David Horton, Danny Durham, David J. C. Constable,* Simon Gaffney, Joseph Moore, Bridget Todd, and Isamir Martinez

Cite This: *Energy Fuels* 2020, 34, 7837–7846 Read Online

ABSTRACT: Formulated products used in hydraulic fracturing are designed to address specific subsurface challenges during oil and gas well completion and are intended for the treatment of a myriad of issues in a wellbore; however, there are public concerns regarding the use of certain chemical ingredients in hydraulic fracturing. Public perception of hydraulic fracturing and concerns regarding water and chemical usage provide the industry with a unique opportunity to review current chemistries and water management practices with the aim being to identify more environmentally acceptable alternatives or replacements. Herein, we describe what the industry considers to be the greatest challenges, what is currently being done, and potential opportunities to provide alternatives that lead to a more sustainable industry.

DOI: 10.1021/acs.energyfuels.0c00933

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Fracturing Process Overview

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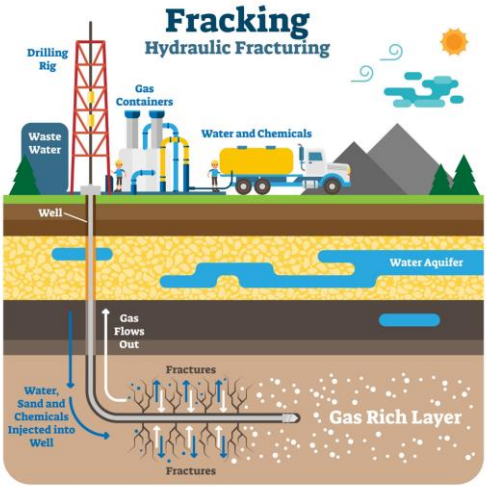

- **"Frac,"** term used for hydraulic fracturing.
- After an oil and gas well is drilled in a shale reservoir, this stimulation method is used to create fracture networks in the shale that allow for the flow of oil and gas from the reservoir.
  - **Fracs** allow for release of oil and gas and improve harvest from the shale.
  - **Frac fluid** is pumped at high rates and high pressure to fracture the shale.
- **Frac Fluid** is a combination of water, proppant and additives specifically formulated for application in a **specific shale**.
- Shale reservoirs, isolated from the surface.
- **Frac fluids** are contained within the reservoir and associated well infrastructure.

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Fracturing Process Overview

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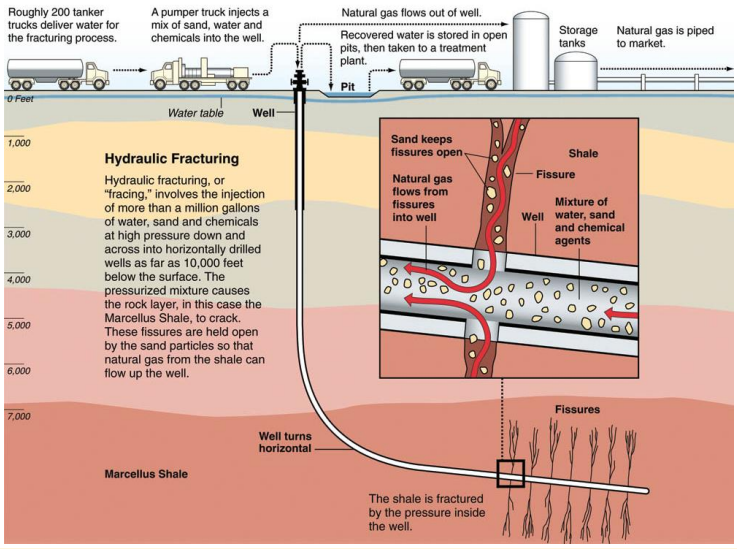

- Frac methods and frac fluid recipes vary depending on the shale basin.
- Each region can have different characteristics that require unique pumping and fluid designs.

This depiction is from the Marcellus Shale in the U.S.

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Global Shale Basins

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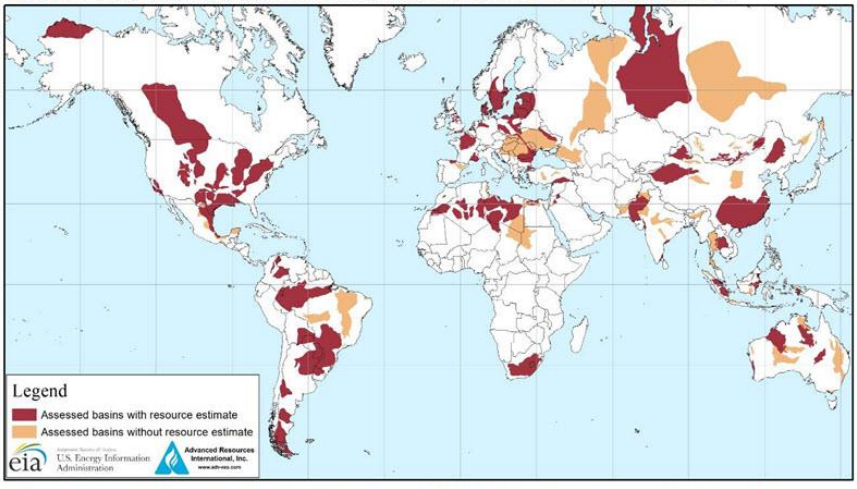
Figure 1. Map of basins with assessed shale oil and shale gas formations, as of May 2013



Source: United States basins from U.S. Energy Information Administration and United States Geological Survey; other basins from ARI based on data from various published studies.

- Shale basins across the globe account for a significant portion of harvestable oil and gas reserves.

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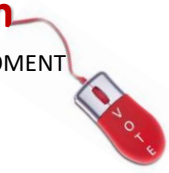
Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



Approximately what portion of the world's technically recoverable oil and gas lies in oil shale?

- Less than 10 percent
- Less than 30 percent, but greater than 10 percent
- Between 40 to 70 percent
- Other (tell us more in the chat)

** If your answer differs greatly from the choices above tell us in the chat!*

Average U.S. Shale Frac Fluid Composition

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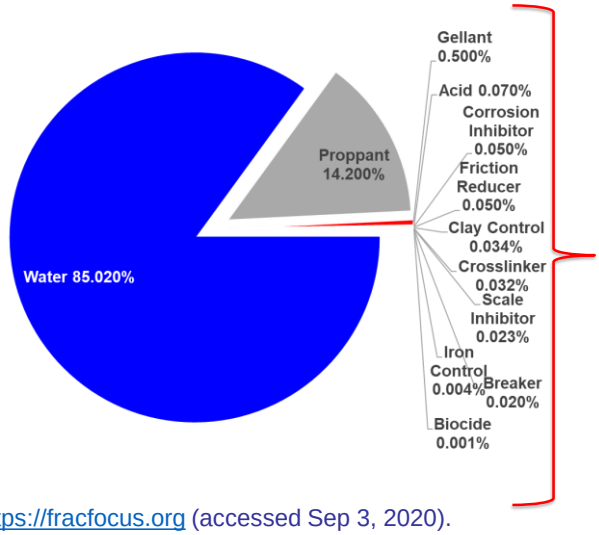

Composition:
- Water: 85.02%
- Proppant:14.2%
- Additives: 0.78%

https://fracfocus.org (accessed Sep 3, 2020).

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Water- Challenges and Opportunities

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- Finding a suitable source of water
- Suitability of the water for use in a frac fluid
- Reuse and recycling of water

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Creating a Frac Fluid

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Composition, determined from detailed analysis and application of engineering principles:

- Shale composition
- Source water composition
- Proppant loading requirement
- Stimulation design
- Productivity Results

Examples of Frac Fluid Additives Components in Society

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Compound	Purpose	Common Application
Acids	Helps dissolve minerals and initiate fissure in rock (pre-fracture)	Swimming pool cleaner
Ammonium bisulfite	Removes oxygen from the water to protect the pipe from corrosion	Cosmetics, food and beverage processing, water treatment
Polyacrylamide	Minimizes the friction between fluid and pipe	Water treatment, soil conditioner
Borate Salts	Maintains fluid viscosity as temperature increases	Laundry detergent, hand soap, cosmetics
Sodium/Potassium Carbonate	Maintains effectiveness of other components, such as crosslinkers	Washing soda, detergent, soap, water softener, glass, ceramics
Glutaraldehyde	Eliminates bacteria in the water	Disinfectant, sterilization of medical and dental equipment
Guar Gum	Thickens the water to suspend the sand	Thickener in cosmetics, baked goods, ice cream, toothpaste, sauces
Citric Acid	Prevents precipitation of metal oxides	Additive in food and beverages

Source: DOE, GWPC: Modern Gas Shale Development in the United States: A Primer (2009).

Green Frac Fluid Initiatives

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- Increased activity and volumes have placed **focus on chemistries** used
  - Oil & Gas companies are incentivized to **reduce chemical usage** and **meet ESG objectives**
  - Suppliers of frac additives have been challenged to **provide green alternatives**
- **Frac fluids optimization** has been a primary driver in reducing chemical usage in frac fluids.
- **New chemistries** from a broader supply chain have found their way into oil and gas.

Type of Chemicals Used in Hydraulic Fracturing

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- Friction Reducers (FRs)
- Surfactants
- Scale Inhibitors
- High Viscosity FRs (HVFRs)
- Solvents
- pH Adjusting Agents
- Biocides
- Acid Additives
- Breakers
- Chelating Agents
- Guar Slurries
- Clay Control Additives & Formation Stabilizers

- Each chemical has a specific purpose.
- We will review current chemistry being used in these areas and opportunities for improvement.

Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

Fluids used in Fracturing Fluids typically display?

(Select all that apply)

- Shear thickening behavior
- Shear thinning behavior
- Newtonian behavior
- Other (tell us more in the chat)

** If your answer differs greatly from the choices above tell us in the chat!*

Friction Reducers & High Viscosity Friction Reducers
(FR and HVFR)

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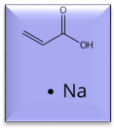
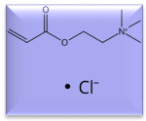
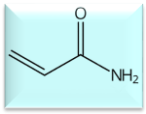
- Added to water to make "slickwater"
- Current technology: acrylamide co-polymers
  - Supplied in three polymeric forms
    - dry, emulsion, slurried
  - Anionic, cationic and zwitterionic polymers

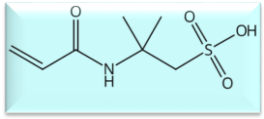
- Compatibility with the water source is paramount in selection of the chemistry.

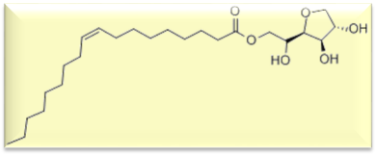
FR & HVFR: Chemistries











" slick the water" to minimize friction and reduce surface treating pressure at the wellhead.

CAS 64742-47-8 Distillates (petroleum), hydrotreated light

- Complex combination of hydrocarbons
- Obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst.
- Consists of hydrocarbons in the range of C9 through C16 and boiling in the range of approximately 150°C to 290°C (302°F to 554°F).

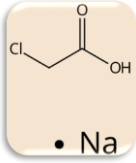
FR and HVFR: Challenges & Opportunities

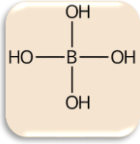
- Monomers from non-renewable feedstocks
  - renewable feedstocks / high molecular weight biopolymers?
- HVFR's are sensitive to ionic strength.
  - Higher usage required in high TDS brines.
    - Can chemistry solve this?
- Dry polymers require hydration units prior to application.
  - Dry HVFR can be challenging to hydrate on the fly.
    - Improvements to the powdered polymer to enhance **dispersibility**.

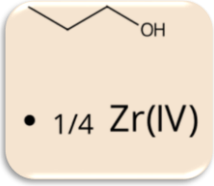
Guar Gum

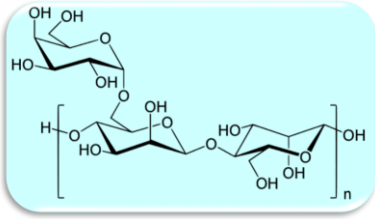
- Until early 2010's most common viscosifier
  - displaced by FR and HVFR
  - Guar gum, hydroxypropyl guar (HPG) and carboxymethyl hydroxypropyl guar (CMHPG) are materials of commerce in fracturing
- Provide little friction reduction, mainly used due to sand transport / suspension characteristics.
- Cross-linked with a variety of inorganic compounds
- Viscosities in range of 10^2 cP (@ 100/sec shear rate)
- Two forms: powder form or slurried in mineral oil for ease of application

Guar Gum: Chemistries









CAS 64742-47-8
Distillates (petroleum), hydrotreated light

➢ Increases viscosity making high-pressure pumping and fracturing process more efficient

Guar Gum: Challenges & Opportunities

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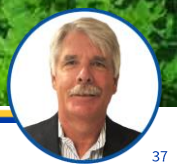
- Renewable solvent sources
- Mechanical Improvements



Breakers

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- To **reduce viscosity** and clean viscosifier off formation face
- Examples:
  - **Oxidizers** (e.g. ammonium persulfate, peroxide etc.)
    - randomly attack backbone of polysaccharides – degradation products may have lower viscosity but may not be water soluble.
  - **Enzymes**, to break guar systems (e.g. hemi cellulase and mannanase)
    - Fragments from hydrolysis are water soluble.
    - Sensitive/specific to temperature and pH
    - Higher temperature and/or higher pH range enzymes present the greatest need / opportunity

Clay Stabilizers

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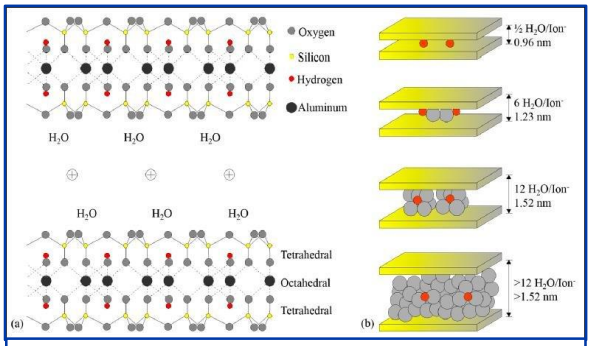
- Swelling / dispersion will impair rock permeability
- Osmotic swelling occurs due to potential differences of the water in the clay interstitial spaces
- Hydrocarbon bearing formations frequently contain **inclusion of swellable / migratable clays** – *e.g.* illites and smectites



Akpe & al./ Appl. J. Envir. Eng. Sci. 4 N°3(2018) 337-351

- Imperfections in the crystal lattice where Mg substitutes for Al, and Al substitutes for Si.
- In clay interstitial spaces, labile ions are coulombically bound to the surface of the platelet.
- If these labile ions are sodium, then swelling can occur due to ion hydration

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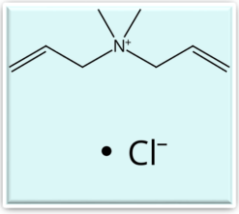
Clay Stabilizers Chemistries – Ion Exchange

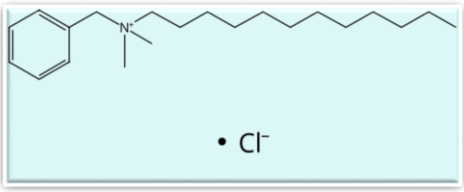
ACS Green Chemistry Institute
Oilfield Chemistry Roundtable

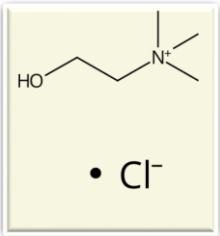
$Al_2Si_4O_{10}(OH)_2$

$M^+_{(x+y)}Mg_xAl_{2-x+y}Si_{4-y}O_{10}(OH)_2$

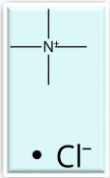
➢ Prevent migration or swelling







Choline Chloride
Vitamin B4



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Stabilizers: Challenges & Opportunities

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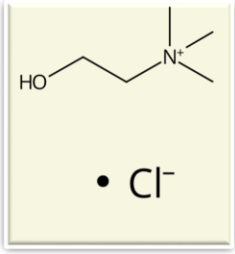
- Currents chemistries relies in Vitamin B4
  - Manufacturing methods from petrochemicals feedstocks
  - Potential Biosource (e.g. biochemical reaction pathway)



Choline Chloride
Vitamin B4

Biocides

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- Designed to:
  - Control populations of bacteria and other microorganisms.
  - To eliminate
    - sulfate reducing bacteria – formation souring / corrosion
    - acid producing bacteria – corrosion
    - slime forming bacteria – microbially induced corrosion
- For these chemistries to work they need to be inherently toxic
  - amount vs. toxicity considerations

Biocides Chemistries

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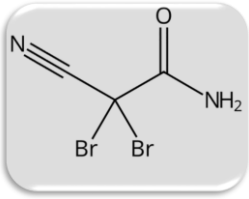
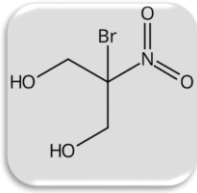
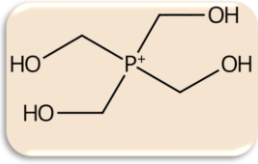
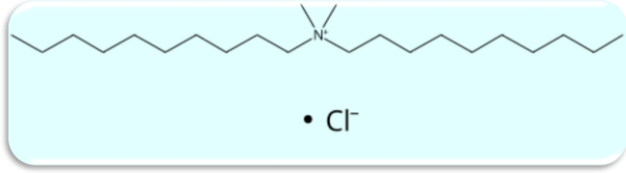
Oilfield Chemistry Roundtable



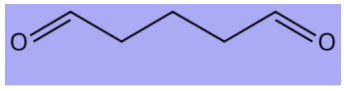


To control populations of bacteria and other microorganisms





Bleach, peroxide – other oxidizers



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Biocides: Challenges & Opportunities

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- Potential for synergy with enzymes that disrupt biofilms
  - ACS GCIOCR engaged a collaboration with MSU to use enzymes to reduce the biofilm formation
- Potency – does reduced toxicity require increased dosage?
- Regulatory – will require EPA registration.

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Scale Inhibitors

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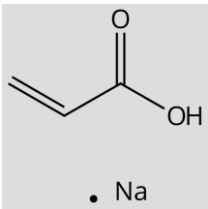
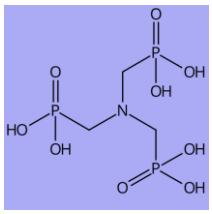
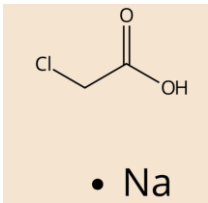
- **Prevent scaling** from incompatible waters (e.g. sulfate / barium)
  - Chemistries are crystal modifiers, not chelants
  - Work at sub stoichiometric concentrations
  - Must be compatible with other additives, typically the friction reducer

Scale Inhibitors Chemistries

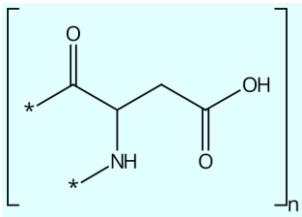
ACS Green Chemistry Institute
Oilfield Chemistry Roundtable

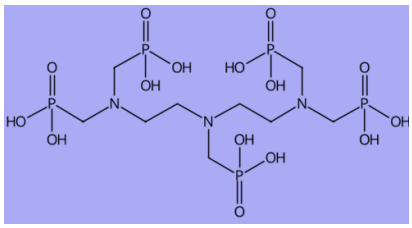


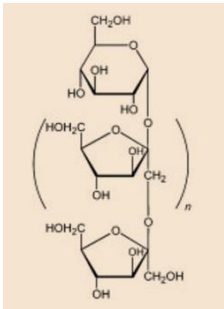




Prevents scaling from incompatible waters







Surfactants

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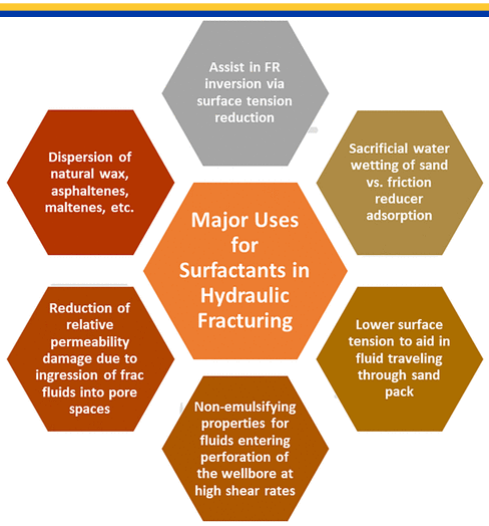

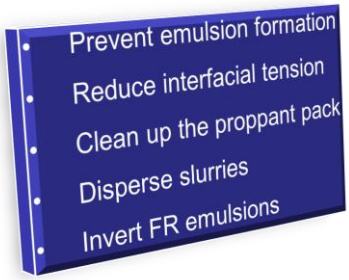

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Surfactant Chemistries

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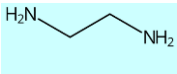
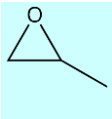
Oilfield Chemistry Roundtable

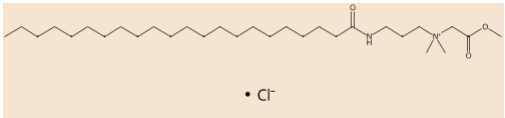
Reduce the surface tension, detergent effect

Non-emulsifiers





Surfactant Gels



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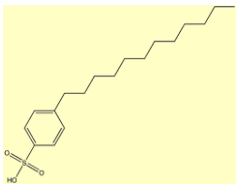
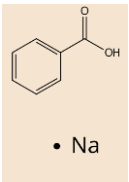
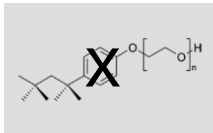
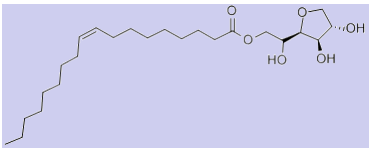




Inverting Surfactants



Emulsifiers



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Surfactants: Challenges & Opportunities

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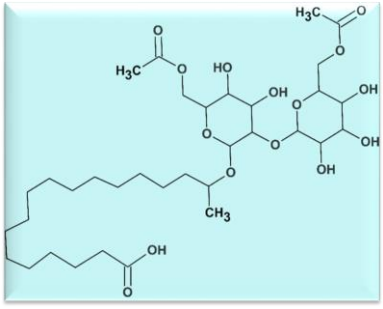
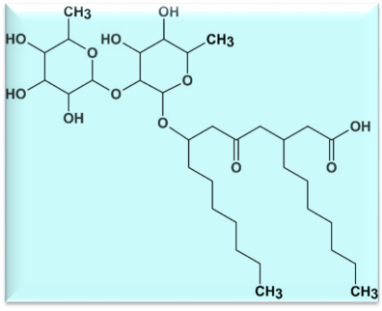
- Non-renewable resource
- Biodegradable – e.g. branched alkylbenzene sulphonates
- Biosource





Other Areas of Interests

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- **Solvents**
  - Replacements:
    - Useful solvent interactive tool (free to use):

    https://www.acsgcipr.org/tools-for-innovation-in-chemistry/solvent-tool
  - Biobased, Cost-effective
- **Acid Additives** – corrosion inhibitors
- **Chelating Agents** – Citric / acetic, THP
- **pH Adjusting Agents** – sodium / potassium hydroxides, sodium / potassium carbonates, organic acids

Chemical Reduction Strategies in HF

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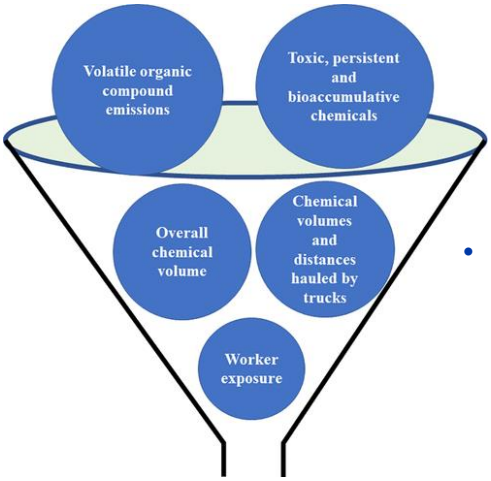

- To adopt strategies to enable a reduction in each area.
  - To reduce environmental, safety, and health impact.

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Summary

ACS Green Chemistry Institute
Oilfield Chemistry Roundtable

- Efforts to provide greener alternatives in hydraulic fracturing are ongoing.
  - Chemistries' environmental footprint have been improved; more could be done.
  - Finding new alternatives/replacements
    - collaboration among academia, chemical manufacturers, end users, and nonindustrial members **is imperative**.
- **Innovation is essential** for green chemistry, a driver for ***sustainability***!
- **ACS GCI OCR, pre-competitive scientific** collaboration has been established to accelerate greener alternatives.

Thank you to our Members! Questions?

ACS Green Chemistry Institute
Oilfield Chemistry Roundtable

Brian Price

BPrice@rockwater.com

Dave Horton

Dave.Horton@ceslp.ca

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Contact: gciroundtables@acs.org; and/or Isamir Martinez, i_martinez@acs.org

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Thursday, September 17, 2020 at 2-3pm ET
Speaker: Dan Bailey, Takeda Pharmaceuticals
Moderator: John Tucker, Neurocrine Biosciences

Register for Free!

What You Will Learn

- Why we urgently need to reduce or eliminate organic solvent use in chemical manufacturing
- How Takeda process chemists adapted a manufacturing process to aqueous conditions
- Strategies for running reactions and isolating products under aqueous conditions

Co-produced with: ACS Green Chemistry Institute

Wednesday, September 23, 2020 at 3-4pm ET
Speaker: Christopher McCurdy, College of Pharmacy, University of Florida

Register for Free!

What You Will Learn

- Understanding of kratom products and their use in the traditional and Western populations
- The pharmacology and pharmacokinetics of the major alkaloid, mitragynine (and others)
- Some insights into the scientific hypotheses for therapeutic benefits as well as negative consequences

Co-produced with: ACS Division of Medicinal Chemistry, American Association of Pharmaceutical Scientists, and ACS Publications

Friday, September 25, 2020 at 10-11am ET
Speaker: Pamela Tadross, Organic Process Research & Development
Moderator: Kali Miller, ACS Publications

Register for Free!

What You Will Learn

- What editors look for when reviewing submissions
- Tips for responding to reviewer reports
- Qualifications to become a reviewer and strategies to evaluate a manuscript

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Grand Challenges and Opportunities for Greener Alternatives within the Oil and Gas Industry

Brian Price
Vice President of Technology & Completions Business Line, Rockwater Energy Solutions and Member, ACS GCI Oilfield Chemistry Roundtable

Dave Horton
Chief Technology Officer, CES Energy Solutions and Co-Chair, ACS GCI Oilfield Chemistry Roundtable

David Constable
Science Director, ACS Green Chemistry Institute, American Chemical Society

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Save the Date…ACS GCI Webinar Next Week!

Dan Bailey

Process Chemist, Takeda Pharmaceuticals

Thursday. September 17, 2-3pm ET

"Beyond Organic Solvents: Synthesis of a 5-HT4 Receptor Agonist in Water"

2020 Peter J. Dunn Award Winner for Green Chemistry and Engineering Impact in the Pharmaceutical Industry

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