Sustainable Chemistry in Oil and Gas Water Treatment

Greg Bradley
Associate Director
Global Regulatory Sciences and Product Sustainability
Introduction

- Defining
  - Green Chemistry
  - Sustainable Chemistry
- Chemical Selection
- Differentiating Criteria for Gas and Oil Chemicals
- Hazard, Exposure and Risk
- Product Stewardship Practices
- Screening Evaluation Tools: Examples
Chemicals Used in Gas and Oil Production

- Friction reducer
- Gelling agent
- Breaker/aide
- Stabilizer
- Biocide
- Crosslinker
- Non-emulsifier
- Corrosion inhibitor
- pH adjusting agent
- Surfactant
Hydraulic Fracturing Fluids

- Water + Sand + Chemicals
- Composition varies based on conditions
“Greener Alternatives”

- Green Chemistry
- Sustainable Chemistry

While both reflect a journey to make something more desirable, from an environmental and safety perspective, there are important differences between the two terms.
Twelve Principles of Green Chemistry

- Prevention
- Atom Economy
- Less Hazardous Chemical Syntheses
- Designing Safer Chemicals
- Safer Solvents and Auxiliaries
- Design for Energy Efficiency
- Use of Renewable Feedstocks
- Reduce Derivatives
- Catalysis
- Design for Degradation
- Real Time Analysis for Pollution Prevention
- Inherently Safer Chemistry for Accident Prevention
Sustainable Chemistry

- Sustainable chemistry builds upon the principles of green chemistry by integrating economic viability and social benefits across the lifecycle for a given application.
- More sustainable products and processes must not only be more efficient in their use of materials and resources, but must also be profitable, scaleable and useful to society.
- This must be accomplished across the lifecycle of the product and in comparison to alternatives which could provide the same application or service.
Science Based Risk (HxE=R)

- Conduct Hazard Assessments
  - Understand potential for harm
- Exposure Assessment
  - Use scenarios
  - Dosage
- Risk Mitigation
  - Upper label limits minimize exposure
  - Lower label limits limit ineffective usage
Environment, Health and Safety Attributes

- Product Stewardship Principles
- Right chemical for the right use
- Ensure that products are used in a responsible/sustainable manner
- Socially responsible and Environmental Awareness
  - Disclosure of chemicals
  - Protection of water quality
  - Best practices and continuous improvement
Biocides

- Biocides are a common and necessary component in fracking fluids
- They are chemical agents used to control harmful microorganisms
  - Flow assurance
  - Protect process and product
  - Asset integrity
- Also known as antimicrobials, pesticides, algaecides, or bactericides
Physical Property Testing

- Many tests are performed to understand the physical properties of biocides
  - Stability, melting/boiling points, solubility, pH, chemical compatibility, partitioning behavior, etc.
- Data used in risk evaluations
Biocides Selection

Antimicrobial Efficacy

Minimally Effective
Extremely Effective

Compatibility

Increasing Length of Protection

Increasing Speed of Action
Data Requirements to Support Registration

- Biocides are thoroughly tested to meet regulatory requirements
- EPA requires over 100 different studies for registration
- Testing includes:
  - Physical properties
  - Environmental fate
  - Ecotoxicology
  - Mammalian toxicology
Chemical Selection: Criteria for Fracking

- Persistence
  - Readily biodegradable
- Bioaccumulation
  - Octanol / Water Partition Coefficient
- Toxicity
  - Aquatic
  - Avian
- Use Rate/Pattern
  - Efficacy / Efficiency
Ecotoxicological Testing

- Acute hazard testing determines a chemical’s effect on a variety of organisms
- Information gathered on a variety of terrestrial, aquatic, and marine organisms
- Data used in risk evaluations
Mammalian Toxicology Testing

- Provides information on how chemicals affect mammals
- Both acute (short term) and chronic (long term) data gathered to meet regulatory requirements
- Data used in risk calculations
The environmental fate of a chemical describes the processes by which it moves through and transforms in the environment.

Studies performed under controlled, standard conditions:
- Partitioning behavior
- Chemical degradation
- Biodegradation
- Photodegradation
- Transport phenomena
Risk Analysis

- Attempts to model real-world conditions
- Evaluates the risk of using a specific chemical in a specific application
- Uses physical property, environmental fate, and toxicology data from chemical
- Applies safety factor to worst-case scenarios
- When properly used, biocides can effectively control microbial contamination without adversely affecting the environment
Risk Assessment Methods – North Sea

- Chemical Hazard and Risk Management Model (CHARM)
  - Predicted environmental concentration (PEC)
    - application-specific
    - “realistic worst case”
  - Hazard quotient (HQ)
    - ratio of PEC to predicted no-effect concentration

<table>
<thead>
<tr>
<th>Hazard Quotient Bands</th>
<th>HQ range</th>
<th>Band Color</th>
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</thead>
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<tr>
<td></td>
<td>0-1</td>
<td>Gold</td>
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<td></td>
<td>100-300</td>
<td>Blue</td>
</tr>
<tr>
<td></td>
<td>300-1000</td>
<td>Orange</td>
</tr>
<tr>
<td></td>
<td>&gt;=1000</td>
<td>Purple</td>
</tr>
</tbody>
</table>
Sustainability Footprint Tool

A qualitative tool developed for Sustainable Chemistry/Life Cycle Analysis experts with grounding through a common review system.

Addressing 6 dimensions of sustainability:
- Economic
- Social
- Life Cycle – Environment
- Greenhouse Gas Emissions
- Water
- Resource Use
  - Energy, Raw Material
A Sustainable Chemistry Screening Tool

- Based on ACC Sieve tool
- Initial Screening
  - Hazard Ranking = Higher Score from Environmental and Human Health Hazards
  - Exposure Ranking = Based on Sum (Use rates + PB + Use patterns)
- Purpose: to differentiate sustainable chemistry endpoints of chemicals
HAZARD
Environment and Human Health Classifications based upon GHS

Environmental:
From GHS classification guidance document:

Persistence:
- Volatile substance (VP > 1000 Pa): Not Persistent if air half life < 2 days
- Nonvolatile (VP < 1000 Pa): Not Persistent if:
  a) ready biodegradability (OECD 301)
  b) inherent biodegradability (OECD 301, 302, 306)
  c) read across from measured data on a related substance.
  d) equivalent degree of degradation (i.e., >20% in 28 days) via an abiotic degradation mechanism such as photolysis (OECD 316) or hydrolysis (OECD 111)

Bioaccumulation:
A substance is not bioaccumulative if:
- measured TMF < 1 (field study)
- measured fish BMF < 1 (lab study)
- measured fish BCF < 5000 (lab study)
- predicted BCF < 5000 using the BCFBAF model included in EPIWIN 4

NOTE -- P&B CRITERIA ARE FOR ORGANICS

Human Health:
As above, based upon GHS

EXPOSURE
Use Elements - based upon IUR
- intermediate consumed during industrial processing
- industrial (not intermediate) - used in an industrial setting
- commercial occupational use in nonindustrial setting
- consumer general population residential use

Persistence:
- evaluation of simulation data from transformation in soil, marine water/sediment, brackish water/sediment, surface water/sediment, oceanic water die away (e.g., OECD 308/309) have half lives below 180 days.
- if data are lacking:
  - evaluation via BIOWIN model (EPIWEB 4)

Bioaccumulation:
A substance is not bioaccumulative if:
- measured TMF < 1 (field study)
- measured fish BMF < 1 (lab study)
- measured fish BCF < 5000 (lab study)
- predicted BCF < 5000 using the BCFBAF model included in EPIWIN 4

Tonnage - based upon IUR reporting ranges
- < 25,000 lbs (below IUR site reporting limit)
- 25,000 - <1 MM lbs national aggregate
- 1MM - <100 MM lbs national aggregate
- ≥100 MM lbs national aggregate
# Sustainability Chemistry Screening Tool

**Use Pattern**
- **intermediate**
- **not intermediate**
- **commercial**
- **consumer**

**Use Score**
- 1
- 2
- 3
- 4

**Persistence / Bioaccumulation (PB)**
- not P, not B
- P & not B OR B & not P
- P & B

**PB Score**
- 1
- 2
- 3
- 4

**Tonnage**
- <25,000 lbs (below IUR site reporting limit)
- 25,000 - <1MM lbs IUR aggregate
- 1MM- <100MM lbs IUR aggregate
- >100MM lbs IUR aggregate

**Tonnage Score**
- 1
- 2
- 3
- 4

**Hazard Ranking** = Higher Score from Environmental and Human Health Hazards

## Environmental Hazard
- Not carcinogen/mutagen/repro/develop; OR Repeat Dose >1000 mg/kg/day (oral); >2000 mg/kg/day (dermal); >1000 ppm/6hr/day (gas inhalation); >5.0 mg/l/6hr/day (vapour inhalation); >1.0 mg/l/6hr/day (dust mist fume inhal).

## Human Health Hazard
- Not carcinogen/mutagen/repro/develop;OR Repeat Dose 100 - 1000 mg/kg/day (oral); 200 - 2000 mg/kg/day (dermal); 250 - 1000 ppm/6hr/day (gas inhalation); 1.0 - 5.0 mg/l/6hr/day (vapour inhalation); 0.2 - 1.0 mg/l/6hr/day (dust mist fume inhal).

## Exposure Ranking = Based on Sum (Use + PB + Tonnage Scores)

<table>
<thead>
<tr>
<th>Hazard Ranking</th>
<th>Environmental Hazard</th>
<th>Human Health Hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 low</td>
<td>Not classified</td>
<td>Not carcinogen/mutagen/repro/develop; OR Repeat Dose &gt;1000 mg/kg/day (oral); &gt;2000 mg/kg/day (dermal); &gt;1000 ppm/6hr/day (gas inhalation); &gt;5.0 mg/l/6hr/day (vapour inhalation); &gt;1.0 mg/l/6hr/day (dust mist fume inhal).</td>
</tr>
<tr>
<td>2 medium</td>
<td>Acute III OR Chronic III/IV ; [not acutely toxic and no chronic data]</td>
<td>Not carcinogen/mutagen/repro/develop;OR Repeat Dose 100 - 1000 mg/kg/day (oral); 200 - 2000 mg/kg/day (dermal); 250 - 1000 ppm/6hr/day (gas inhalation); 1.0 - 5.0 mg/l/6hr/day (vapour inhalation); 0.2 - 1.0 mg/l/6hr/day (dust mist fume inhal).</td>
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<tr>
<td>3 med-high</td>
<td>Acute II or Chronic II</td>
<td>GHS CMR Cat 2; OR GHS Repeat Dose Cat 2: Repeat Dose 10 - 100 mg/kg/day (oral); 20 - 200 mg/kg/day (dermal); 50 - 250 ppm/6hr/day (gas inhalation); 0.2 - 1.0 mg/l/6hr/day (vapour inhalation); 0.02 - 0.2 mg/l/6hr/day (dust mist fume inhal).</td>
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<tr>
<td>4 high</td>
<td>Acute I OR Chronic I OR insufficient information to classify</td>
<td>GHS CMR Cat 1a, 1b; OR GHS Repeat Dose Cat 1; Repeat Dose &lt;= 10 mg/kg/day (oral); &lt;= 20 mg/kg/day (dermal); &lt;= 50 ppm/6hr/day (gas inhalation); &lt;= 0.2 mg/l/6hr/day (vapour inhalation); &lt;= 0.02 mg/l/6hr/day (dust mist fume inhal). OR insufficient information to classify</td>
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## Exposure Elements

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<th>Use Pattern</th>
<th>Exposure Elements</th>
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<tbody>
<tr>
<td><strong>intermediate</strong></td>
<td><strong>industrial</strong> not <strong>intermediate</strong></td>
</tr>
<tr>
<td><strong>commercial</strong></td>
<td><strong>consumer</strong></td>
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## SIEVE RANKING = Hazard + Exposure Rankings

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## Exposed Ranking = Based on Sum (Use + PB + Tonnage Scores)

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