EPA HF Study Technical Workshop: Chemical and Analytical Methods

Crosslinked and Linear Gel Composition

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## Fracturing Fluid Composition

### Fluid Types

- **Water-based Fluids**
  - Linear Polymer Solution
  - Crosslinked Gel
  - Viscoelastic Surfactants

- **Oil-based Fluids**

- **Acid-based Fluids**

- **Multiphase Fluids**
  - Emulsions
  - Foams
  - Energized

### Additives

- **Gelling Agents**
- **Crosslinkers**
- **Breakers**
- **Fluid Loss Additives**
- **Biocides**
- **Thermal Stabilizers**
- **Surfactants**
- **Clay Control Additives**
Gelling Agents

• Increase Fluid Viscosity for Improved Proppant Transport
  – Into perforations
  – Along fracture

• Reduce Fluid Loss to Reservoir
  – Deposit filtercake
  – Viscous resistance in porous media

• Create/Maintain Desired Fracture Geometry

• Reduce Friction Pressure Loss in Wellbore
  – Slick Water applications
Common Frac Fluid Gelling Agents

- **Guar**
- **Guar Derivatives**
  - Hydroxypropyl Guar (HPG)
  - Carboxymethyl Guar (CMG)
  - Carboxymethyl Hydroxypropyl Guar (CMHPG)
- **Cellulose**
  - Hydroxyethyl Cellulose (HEC)
  - Carboxymethyl Hydroxyethyl Cellulose (CMHEC)
- **Synthetic Polymers**
  - Polyacrylic Acid (PAc)
  - Polyacrylamide (PAm)
  - Partially Hydrolyzed Polyacrylamide (PHPA)
  - Acrylamido-methyl-propane sulfonate (AMPS)
- **Viscoelastic Surfactants**
  - Cationic
  - Anionic
  - Amphoteric
## Typical Usage Rate of Frac Fluid Gelling Agents

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Concentration (by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guar</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>HPG</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>CMHPG</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>HEC</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>CMHEC</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>Synthetic Polymers</td>
<td>&lt; 0.05%</td>
</tr>
<tr>
<td>Viscoelastic Surfactants</td>
<td>&lt; 2%</td>
</tr>
</tbody>
</table>
Crosslinkers

- Increase Effective Molecular Weight by Chemically Linking Polymer Chains
- Create 3D Structure – Increases Elasticity and Suspension Properties
- React w/ Specific Sites (Functional Units) on Polymers
- Each Crosslinker Has Unique Reaction Requirements and Behavior
Common Crosslinker Compounds

Metallic (Ti & Zr)
- Chelated Compounds
  - Retard Oxide Formation
- Crosslinking Rate Controlled by Complex Stability and Ligand Concentration
- Non-reversible
- Shear Degraded

Borate
- Simple Salt ($H_3BO_3$ & Borax)
- Slowly Soluble Salts (Ca and Mg Salts)
- Borate Esters
- Polyborates
### Typical Usage Rate of Common Crosslinker Compounds

<table>
<thead>
<tr>
<th>General Class</th>
<th>Concentration Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borate</td>
<td>&lt; 150 ppm as Boron</td>
</tr>
<tr>
<td>Titanate</td>
<td>&lt; 150 ppm as Titanium</td>
</tr>
<tr>
<td>Zirconate</td>
<td>&lt; 100 ppm as Zirconium</td>
</tr>
</tbody>
</table>
Breakers

• **Purpose**
  - Improve Flowback & Maximize Conductivity

• **Mechanism**
  - Reduce Polymer Molecular Weight
  - React with Specific Sites in Polymer Chain
  - Reverse Crosslinking (Borate Only)

• **Common Types**
  - Oxidizers
    - Persulfate
    - Perborate
    - Hypochlorite
    - Mg & Ca Peroxide
  - Enzymes
  - Acids
    - Esters of hydroxycarboxylic acids
References


Questions ?