EPA HF Study Technical Workshop: Chemical and Analytical Methods

Crosslinked and Linear Gel Composition

Richard Hodge

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

Polymer	***Concentration (by weight)***
Guar	*< 1%*
HPG	*< 1%*
CMHPG	*< 1%*
HEC	*< 1%*
CMHEC	*< 1%*
Synthetic Polymers	*< 0.05%*
Viscoelastic Surfactants	*< 2%*

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

General Class	Concentration Range
Borate	*< 150 ppm as Boron*
Titanate	*< 150 ppm as Titanium*
Zirconate	*< 100 ppm as Zirconium*

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

1. "Chapter 7: Fracturing Fluids and Additives", *Recent Advances in Hydraulic Fracturing - SPE Monograph Series Volume 12* ; Society of Petroleum Engineers, 2001.

2. "Chapter 7: Fracturing Fluid Chemistry and Proppants", *Reservoir Stimulation* – 3rd Edition; John Wiley and Sons, 2000.

3. "Chapter 7: Fracturing Fluids and Formation Damage", *Modern Fracturing* ; Energy Tribune Publishing Inc., 2007.


Questions ?