Slide 2

SPE Webinar

A Critical Review of Hydraulic Fracturing Fluids over the Last Decade

Ghaithan A. Al-Muntasheri, PhD

Team Lead, Production Technology
Aramco Research Centers-Houston
Email: ghaithan.muntasheri@aramcoservices.com

SPE-169552 • A Critical Review of Hydraulic Fracturing Fluids over the Last Decade• Ghaithan A. Al-Muntasheri

COPYRIGHT

Poll Question

What is your job title?

Engineer
Geologist
Geophysicist
Consultant
Educator

Poll Question

Who is your employer?

E&P Company
NOC
Government
Academia
Consultant
Non-governmental Organization
Environmental Organization

Poll Question

How many years of experience do you have?

0-5
6-10
11-15
16-20
20+

Poll Question

What geographic region are you from?

North America
South America
Africa
Middle East
Europe
Asia
Other

ABOUT THE AUTHOR

- 2001-2004: Research Scientist, Saudi Aramco, Dhahran, Saudi Arabia
- 2004-2008: PhD Candidate, Delft University of Technology, The Netherlands
- 2012-present: Aramco Research Center-Houston, Houston, TX
- 2014-present: Adjunct Professor, Rice University, Houston, TX

King Fahd University of Petroleum & Minerals Dhahran, Saudi Arabia

- Website:
- https://msne.rice.edu/Content.aspx?id=2147483950

Slide 9

COMPONENTS OF THIS TALK

- Objectives & importance
- Brief introduction about fracturing
- Advancements in:
  - Polymers
  - Crosslinkers
  - High density brines
  - Re-use of produced water
  - Nanotechnology
- Conclusions

This material is protected by copy right. For questions, please email the author at: Ghaithan muntasheri@aramcoservices.com

SPE-169552 • A Critical Review of Hydraulic Fracturing Fluids over the Last Decade• Ghaithan A. Al-Muntasheri

Slide 10

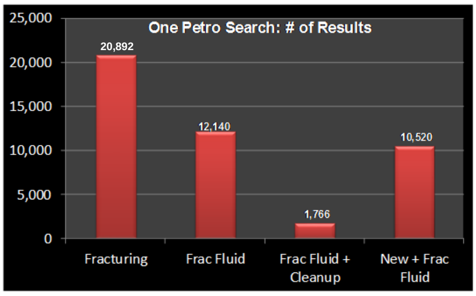
HYDRAULIC FRACTURING FLUIDS: WHERE DO WE STAND?

- Provide an overview of state-of-the-art fracturing fluids
- Discuss their different chemistries
- Cover the advancements in this subject over the last decade

SPE-169552 • A Critical Review of Hydraulic Fracturing Fluids over the Last Decade • Ghaithan A. Al-Muntasheri

Slide 11

IMPORTANCE OF THE SUBJECT



SPE-169552 • A Critical Review of Hydraulic Fracturing Fluids over the Last Decade • Ghaithan A. Al-Muntasheri

RESERVOIR STRESSES

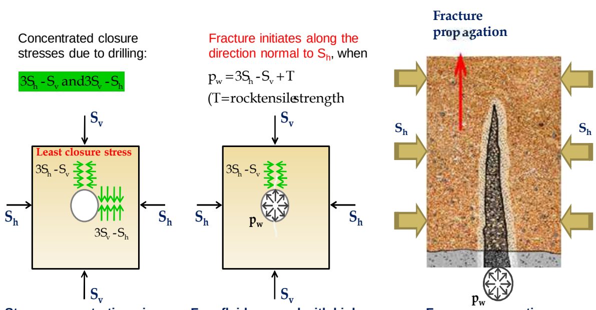
Concentrated closure stresses due to drilling:

$3S_h - S_v$ and $3S_v - S_h$

Fracture initiates along the direction normal to S_h, when

$p_w = 3S_h - S_v + T$

(T = rock tensile strength)



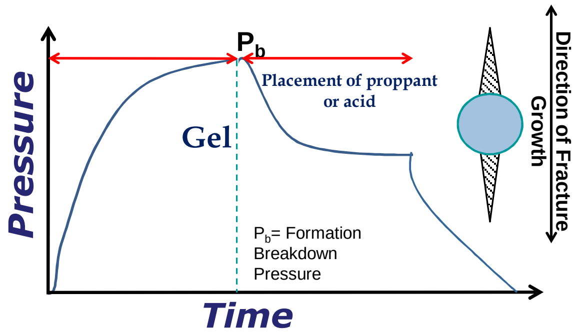
Stress concentrations in a section normal to wellbore

Frac fluid pumped with high pressure

Fracure propagation perpendicular to the Least In Situ Stress

Slide 13

PRESSURE PROFILE DURING FRACTURING



Slide 14

FRACTURING A FORMATION IS ONLY 1/3 OF THE STORY

- **How is the fracture created?**
  -Exceed the "fracture pressure"
- **What keeps the fracture open?**
  - Pressure you have on the well

Unless

- Physically maintain the channel by use of proppants

OR

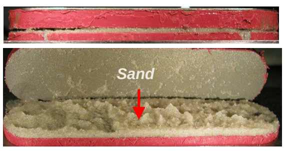
- Chemically create channels to increase flow by use of acids

Slide 15

ACID VS. PROPPANT FRACTURING

Acidized Fracture

Acidized Fracture



CRITICAL PARAMETERS FOR SUCCESS

Acid Frac
- Penetration depth of the acid
- Dissolution of the rock

Proppant Frac
- Fracture clean up
- Proppant placement
- Proppant strength

Slide 16

IDEAL FRACTURE FLUID: DEFINITION AND TARGETED PROPERTIES

- **A fluid employed to generate the fracture *and* transport the proppant/sand**
- **An ideal fracturing fluid should possess the following properties:**
  - ✓ **Adequate viscosity for proppant transport**
  - ✓ **Good fluid loss control**
  - ✓ **Low friction pressure**
  - ✓ **Easy preparation**
  - ✓ **Cost effective**
  - ✓ **Minimum damage**
  - ✓ **Shear stability**

KEY PARAMETER IS VISCOSITY BUT HOW MUCH?

Polymer Type	Concentration (pptg)	Measurement Conditions: Temperature [°F (°C)]	Measurement Conditions: Shear Rate (sec^{-1})	Viscosity (cp)	Reference
Guar	80	77 (25)	511	103	Ely (1989)
Guar	45	77 (25)	511	42	Harris and Heath (1998)
Guar	20	77 (25)	511	10	Ely (1989)
Guar	25	77 (25)	50	50	Fischer et al. (2001)
Guar	20	77 (25)	50	15	Fischer et al. (2001)
Guar/nonacetylyzed xanthan (NAX)	25 (with 4:1 ratio of guar to NAX)	77 (25)	50	110	Fischer et al. (2001)
Finely processed guar	37.6	150 (65.6)	170	>150	Qun et al. (2008)
Clean biopolymer	40 to 70	250 (121)	40	216	Walters et al. (2009)
Clean biopolymer	40 to 70	96 (35)	40	352	Walters et al. (2009)
Less residues polymer	25	150 (65.6)	100	580	Williams et al. (2012)
Less residues polymer	25	200 (93)	100	500	Williams et al. (2012)

Table 2—Viscosity data of linear gels reported in this paper.

CLEANER POLYMERS

Polymer Type	Polymer Loading (pptg)	Measurement Conditions: Temperature [°F (°C)]	Measurement Conditions: Shear Rate (sec^{-1})	Viscosity (cp)
High-yield guar/new borate crosslinker	25	150 (65.6)	100	580
Regular guar/regular borate crosslinker	30	150 (65.6)	100	440
High-yield guar/new borate crosslinker	25	200 (93)	100	500
Regular guar/regular borate crosslinker	30	200 (93)	100	420

Table 3—Effect of the use of high-yield guar and the new crosslinker on the viscosity of crosslinked gels (data extracted from Williams et al. 2012).

Slide 19

FRACTURING FLUIDS

- Linear Gels
- Crosslinked Gels
- Surfactants
- Foamed Fluids
- Slickwater

- Each type has its operating conditions
- Selection of fluid depends on availability, reservoir permeability, temperature, required leakoff and suspension capabilities

Slide 20

SUMMARY OF SYSTEMS REVIEWED IN THIS WORK

Fluid Type	Polymer Concentration, lb/1000 gal	Crosslinker Concentration, lb/1000 gal	Working Temperature Range	Reference
PAM-Based/Zirconium	66	3	269- 449.6ºF (132-232ºC)	Holtsclaw and Funkhouser (2010)
PAM-Based/Zirconium and activator	87	3.4 to 3.7	100.4- 269ºF (38-132ºC)	Holtsclaw and Funkhouser (2010)
AMPS-vinylsolphonate/Zirconium	40	Not Available	425ºF (218ºC)	Gupta and Carman (2011)
Linear Biopolymer	40-70	-	<200ºF (93ºC)	Walters et al. (2009)
Low Molecular Weight HPG/Borate	Not Available	Not Available	200-275ºF (93-135ºC)	Weaver et al. (2002a and b)
Linear guar/SiO_2 particles	33	0	<175ºF (79ºC)	Fakoya et al. (2013)
Guar/ boronic acid-functionalized nanoparticles	30	0.0166	100ºF (37ºC)	Lafitte et al. (2012)

Slide 21

SUMMARY OF SYSTEMS REVIEWED IN THIS WORK CONTINUED

Fluid Type	VES Concentration, Vol%	Working Temperature Range	Reference
VES (Quaternary ammonium)	0.5 to 4	<180ºF (82ºC)	Samuel et al. (1999, 2000)
VES (Amidoamine oxide) + ZnO particles	4	<250ºF (121ºC)	Huang and Crews (2008)
VES Zwitterionic	3.5 to 6	<195ºF (90ºC)	Sullivan et al. (2006)
VES/CO_2 Emulsion	4 with 60% quality	230ºF (110ºC)	Chen et al. (2005)

*Not applicable = N/A

BIO-BASED POLYMERS

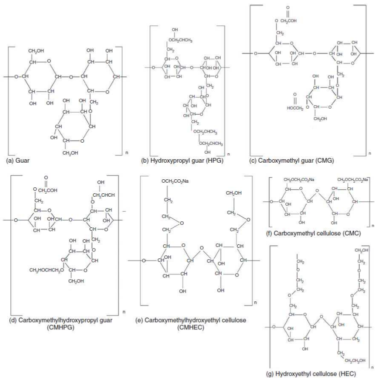
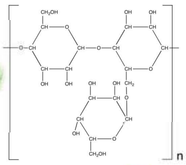


Fig. 1—Chemical structures of biopolymers used in hydraulic fracturing (Ely 1989; Montgomery 2013).

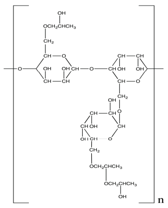
Slide 23

ENCHANED STABILITY VIA FUNCTIONALIZED POLYMERS

Guar-based polymers → most commonly used class of polymer in hydraulic fracturing



Fine-tuning properties: derivatization



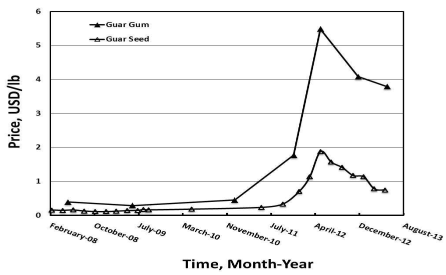
HPG (hydroxypropyl guar)

- Natural polymer
- Introduced to the petroleum industry in the 1960s
- Thermal stability: T < 200°F
- Potential for up to 10 wt% insoluble impurities
- Guar and its derivatives melt in the range of 360-375°F
- Fluctuating cost in recent years

SPE-169552• A Critical Review of Hydraulic Fracturing Fluids over the Last Decade• Ghaithan A. Al-Muntasheri

Slide 24

SHORTAGE OF GUAR: COST IS DRIVEN BY AVAILABILITY



http://www.cnbc.com/id/49263899

http://economictimes.indiatimes.com/commoditysummary/symbol-GUARSEED,type-fando,spotsymbol-SGUARSDBKN,keyword-Guarseed.cms?expiry=2013-06-20

SPE-169552• A Critical Review of Hydraulic Fracturing Fluids over the Last Decade• Ghaithan A. Al-Muntasheri

Slide 25

BIO-POLYMERS AT A GLANCE: ADVANCEMENTS IN THE FIELD

- **Improved optimization on guar concentrations at low temperatures**
  - ✓ Nimerick et al. 1997; Harris and Heath 1998
- **Low molecular weight guars**
  - ✓ Weaver et al. 2002
- **Use of linear polymers for proppant transport**
  - ✓ Walters et al. 2009
- **Use of non-guar based polymers**
  - ✓ Loveless et al., 2011
- **Development of cleaner guars with analogous viscosity properties**
  - ✓ Qun et al. 2008; Williams et al. 2012

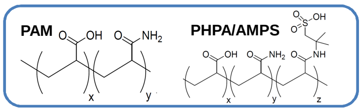
Slide 26

ADVANCEMENTS IN POLYMER-BASED FLUIDS

Polymer Type	Concentration, lb/1000 gal	Measurement Conditions		Viscosity, cp	Reference
		Temperature, ºF (ºC)	Shear Rate, 1/s		
Guar	80	77 (25)	511	103	Ely (1989)
Guar	45	77 (25)	511	42	Harris & Heath (1998)
Guar	20	77 (25)	511	10	Ely (1989)
Guar	25	77 (25)	50	50	Fischer et al. (2001)
Guar	20	77 (25)	50	15	Fischer et al. (2001)
Guar/Nonacetylyzed Xanthan (NAX)	25 (4:1 – guar:XAN)	77 (25)	50	110	Fischer et al. (2001)
Finely Processed Guar	37.6	150 (65.6)	170	>150	Qun et al. (2008)
Clean biopolymer	40-70	250 (121)	40	216	Walters et al. (2009)
Clean biopolymer	40-70	96 (35)	40	352	Walters et al. (2009)
Less residues polymer	25	150 (65.6)	100	580	Williams et al. (2012)
Less residues polymer	25	200 (93)	100	500	Williams et al. (2012)

Slide 27

DEVELOPMENT OF SYNTHETIC POLYMERS



- Increased cost coupled with the need to fracture wells having temperatures exceeding 375ºF (190ºC) → *development of synthetic polymers as alternative frac fluids (e.g. polyacrylamide, PAM).*
- PAM - a drag reducer - typically added at concentrations ranging from 1.25 to 2.5 pptg (Gaillard et al. 2013)
- PAM-based polymers are crosslinked with zirconium

Slide 28

SYNTHETIC POLYMER TESTING: VISCOSITY MEASUREMENTS

Polymer Content, gal/1000 gal	Crosslinker Content, gal/1000 gal	Measurement Conditions		Viscosity, cp	Reference
		Temperature, °F (°C)	Shear Rate, 1/s		
40	Data Not Available	400 (204.4)	100	1,020	Gupta and Carman (2011)
40	Data Not Available	425 (218.3)	100	1,000	Gupta and Carman (2011)
50	Data Not Available	450 (232.2)	100	200	Gupta and Carman (2011)
66	0.5	399 (203.9)	100	200	Holtsclaw and Funkhouser (2010)
66	1.5	399 (203.9)	100	450	Holtsclaw and Funkhouser (2010)

Slide 29

SYNTHETIC POLYMER TESTING: CONDUCTIVITY

Polymer/ Crosslinker Type	Polymer Content, lb/1000 gal	Breaker Content, gal/1000 gal	Closure Stress, psi	Shut-in Time, hours	Temp.	Regained Conductivity, %	Reference
PAM-Based/Zr	87	4	5,000	48	399°F (204°C)	68	Holtsclaw and Funkhouser (2010)
PAM-Based/Zr and activator	87	0.3 to 1.5	2,500	42-72	449.6°F (232°C)	34 to 100	Holtsclaw and Funkhouser (2010)
PAM-Based/Zr	66	5	4,000	71	399°F (204°C)	43-73	Holtsclaw and Funkhouser (2010)
PAM-Based/Zr	66	5	8,000	118	399°F (204°C)	39-47	Holtsclaw and Funkhouser (2010)
PAM-Based/Zr	66	5	10,000	165	399°F (204°C)	37	Holtsclaw and Funkhouser (2010)
AMPS-vinylsolphonate/Zr	40	NA	3,000	24	425°F (218°C)	64-69	Gupta and Carman (2011)
AMPS-vinylsolphonate/Zr	40	NA	3,000	24	385°F (196°C)	83	Gupta and Carman (2011)

This material is protected by copy right. For questions, please email the author at: Ghaithan.muntasheri@aramcoservices.com

SPE-169552 • A Critical Review of Hydraulic Fracturing Fluids over the Last Decade• Ghaithan A. Al-Muntasheri

Slide 30

HIGH DENSITY BRINES: PATHWAY TO REDUCE SURFACE PUMPING PRESSURE

$$P_{Surface} = P_{Bottom\ Hole} + P_{Friction} - P_{Hydrostatic}$$

- **Approach 1:** Increase hydrostatic pressure - Bartko et al. (2009) and Bukhamseen et al. (2010)
  - Substitution of KCl brine (8.7 lb/gal) for NaBr (density of 12.3 lb/gal)
  - *41 % increase*
- **Approach 2:** Use salt-sensititive polymers – Gupta et al. (2012)
  - Use of polyampholyte, which interacts with salts (e.g. $CaCl_2$, NaBr, NaCl)
  - Field applications using CMHPG/Zr^{+4} at 375°F in a gas reservoir

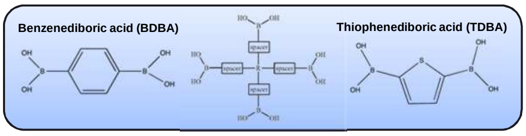
This material is protected by copy right. For questions, please email the author at: Ghaithan.muntasheri@aramcoservices.com

SPE-169552 • A Critical Review of Hydraulic Fracturing Fluids over the Last Decade• Ghaithan A. Al-Muntasheri

Slide 31

ADVANCEMENTS IN CROSSLINKERS

GOAL → Produce adequate viscosities while reducing the polymer concentration



Sun & Qu (2011), SPE 140187

Loveless et al. (2012) US Patent application, 2/0000659 A1

STRATEGY → Alter the size/molecular weight of the crosslinker

Slide 32

VISCOSITY DATA OF SYSTEMS UTILZING NEW CROSSLINKERS

Crosslinker Type	Polymer Concentration, lb/1000 gal	Viscosity, cp
Boric acid (BA)	24	510
Thiophenediboronic aid (TDBA)	16	580
Benzenediboronic acid (BDBA)	17	650
Biphenyldiboronic acid (BPDBA)	16	550

Sun & Qu (2011), SPE 140187

Slide 33

RECYCLYING OF PRODUCED WATER

Motivation

- Water conservation
- Environmental regulations, processing and disposal of produced water (0.75 to 1 USD/gallon) (Lebas et al. 2013)
- Scarcity of water in some parts of the world

Challenges

- *Produced water contains*: salts, suspended solids, bacteria and potentially hydrocarbons
- Bacteria produces enzymes that degrade guar-based polymers

Slide 34

RECYCLYING OF PRODUCED WATER: STRATEGIES

- Use of organo zirconium compounds (e.g. sodium zirconium lactate)
  - Li et al. (2009)
- Use of electrocoagulation methods
  - LeBas et al. (2013)
- Use of glutaraldehyde to suppress bacterial growth
  - Huang et al. (2005)

Slide 35

FRAC FLUID VISCOSITY: EFFECT OF BACTERIA

Sample	Viscosity after 2 hours, cp	Shear Rate, 1/s	Temperature, ºF(ºC)	Comments
1	740	100	125 (52)	Guar/borate gel prepared in distilled water
2	50	100	125 (52)	Same as sample 1 but with an enzyme breaker
3	600	100	125 (52)	Same as sample 2 but with a stabilizer
4	320	100	135 (93)	Guar/borate gel treated with stabilizer and then prepared in produced water
5	50	100	135 (93)	Guar/borate gel treated with prepared in produced water (Same as sample 4 but with no stabilizer)

Li et al. (2009) SPE 124212

Slide 36

USE OF SODIUM ZIRCONIUM ORGANO COMPOUNDS

Component, mg/L	Produced Water Type	
	Offshore Oilfield (California)	Oilfield (New Mexico)
Sodium	9,930	11,100
Potassium	230	150
Magnesium	970	450
Calcium	260	1,160
Chloride	18,400	20,740
Bicarbonate	100	170
Sulfate	> 1,600	<400

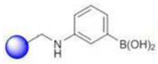
- Water was treated by 70 to 270 ppm of stabilizer for 20 minutes
- California Wells (31): CMHPG/Zr^{+4} system, 54ºC (130ºF)
- New Mexico wells (9): 197 to 225ºF (92 to 107ºC)

Li et al. (2009) SPE 124212

Slide 37

ADVANCEMENTS IN NANOTECHNOLOGY

- Nanotechnology provides a window of opportunity due to unique properties:
  - ✓ Large surface to volume
  - ✓ Small size and
  - ✓ Well-designed shapes
- SiO_2 particles (20 nm) were used to increase viscosity of guar-based gels (Fakoya et al. 2013)
- Nanolatex silica synthesized with boronic acid (Lafitte et al. 2012)
  - ✓ Reduce boron concentration and
  - ✓ produce adequate viscosities with guar gels
  - ✓ 30 nm with 300 m^2/g
  - ✓ 2 ppm of Boron → gel viscosity was 800 to 1,200 cp



Slide 38

CONCLUSIONS

Development of an 'ideal' frac fluid is a grand challenge and research is continuously evolving!

- The realm of a zero-damaging fluid remains non-existent.
- **Polymer-based systems:**
  - Guar-based polymers are still being used despite old introduction to the oil and gas industry.
  - Fracturing hot reservoirs (i.e. 400ºF) -- polyacrylamide-based polymers are suitable ***but*** appropriate cleanup methods are questionable.
- **Nanoparticles:**
  - Improvements in leak off of VES-based fluids
  - Production of high viscosities at lower concentrations of polymers
- **Re-use of Produced Water:**
  - Address environmental concerns → *water preservation*
  - Increased importance in shale reservoirs where millions of gallons of water are required
  - Proven to be effective by use of chemicals to treat produced water

Slide 39

ACKNOWLEDGMENTS

- Dr. David Loveless
- Mr. Jim Crews
- Mr. Ahmad AlSarraj
- Dr. Satya Gupta
- Dr. Hisham Nasr-El-Din
- Dr. Amy Cairns
- Aramco Services Company & Saudi Aramco

OPERATING WINDOWS

Fluid Type	Polymer Concentration (pptg)	Crosslinker Concentration (pptg)	Working Temporary Range	Reference
PAM-based/zirconium	66	3	269–449.6°F (132–232°C)	Holtsclaw and Funkhouser (2010)
PAM-based/zirconium and activator	87	3.4 to 3.7	100.4–269°F (38–132°C)	Holtsclaw and Funkhouser (2010)
Linear biopolymer	40 to 70	—	<200°F (93°C)	Walters et al. (2009)
CMHPG/zirconium	30	3	<300°F (<149°C)	Huang et al. (2005); LeBas et al. (2013)
Low-molecular-weight HPG/borate	Not available	Not available	200–275°F (93–135°C)	Weaver et al. (2002a, b)
AMPS-vinyl phosphonate/zirconium	40	Not available	425°F (218°C)	Gupta and Carman (2011)
Linear guar	33	0	<175°F (79°C)	Fakoya and Shah (2013)
Guar/boronic acid-functionalized nanoparticles	30	0.0166	100°F (37°C)	Lafitte et al. (2012)
VES (quaternary ammonium)	Not applicable	Not applicable	<180°F (82°C)	Samuel et al. (1999, 2000)
VES (amidoamine oxide)	Not applicable	Not applicable	<250°F (121°C)	Huang and Crews (2008)
VES zwitterionic	Not applicable	Not applicable	<195°F (90°C)	Sullivan et al. (2006)
VES/carbon dioxide emulsion	Not applicable	Not applicable	230°F (110°C)	Chen et al. (2005)

Legend:
PAM = polyacrylamide.
CMHPG = carboxyymethylhydroxypropyl guar.
HPG = hydroxypropyl guar.
AMPS = 2-acrylamido-2-methylpropanesulfonic acid.
VES = viscoelastic surfactant.

Table 1—Summary of fracturing fluids reviewed in this paper.