The Chemistry of Produced Water

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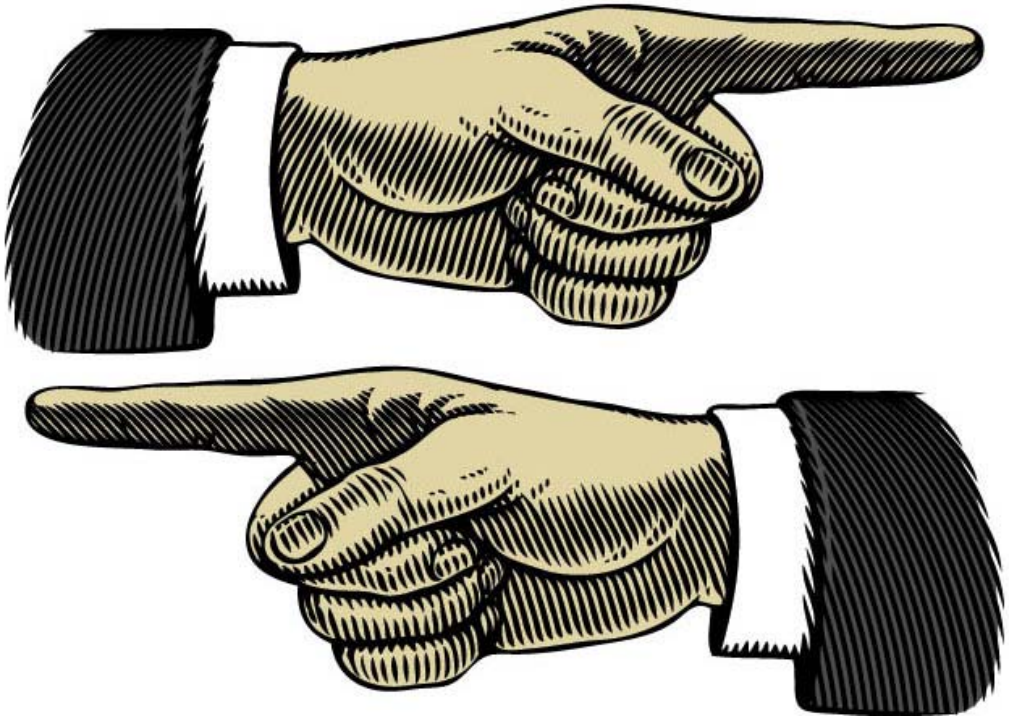
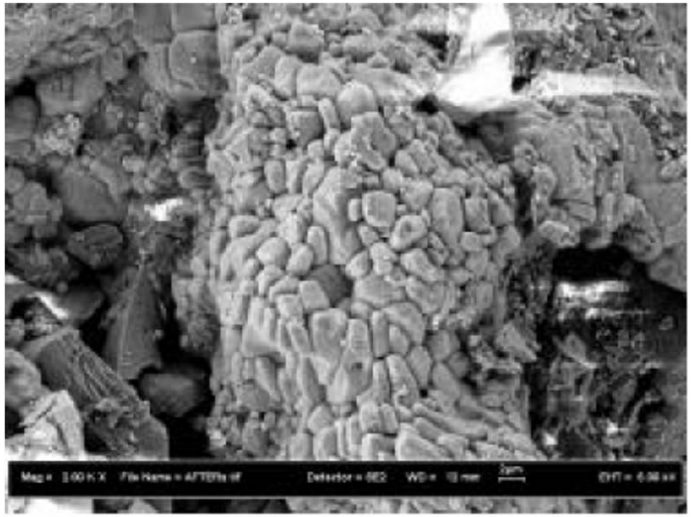
Produced Water Chemistry is Important

- Saltwater disposal
- Increasing use of produced water in fracturing
- What is causing the problem?
  - Pressure spikes
  - Rock won't fracture
  - Whose fault is it?
  - Why did this happen?



Scale

- Scaling indexes
  - Based on inorganic ion incompatibility
  - Must know both the pumping water chemistry and the formation water chemistry
    - Using seawater to pump
  - Scaling in the formation can cause permanent damage

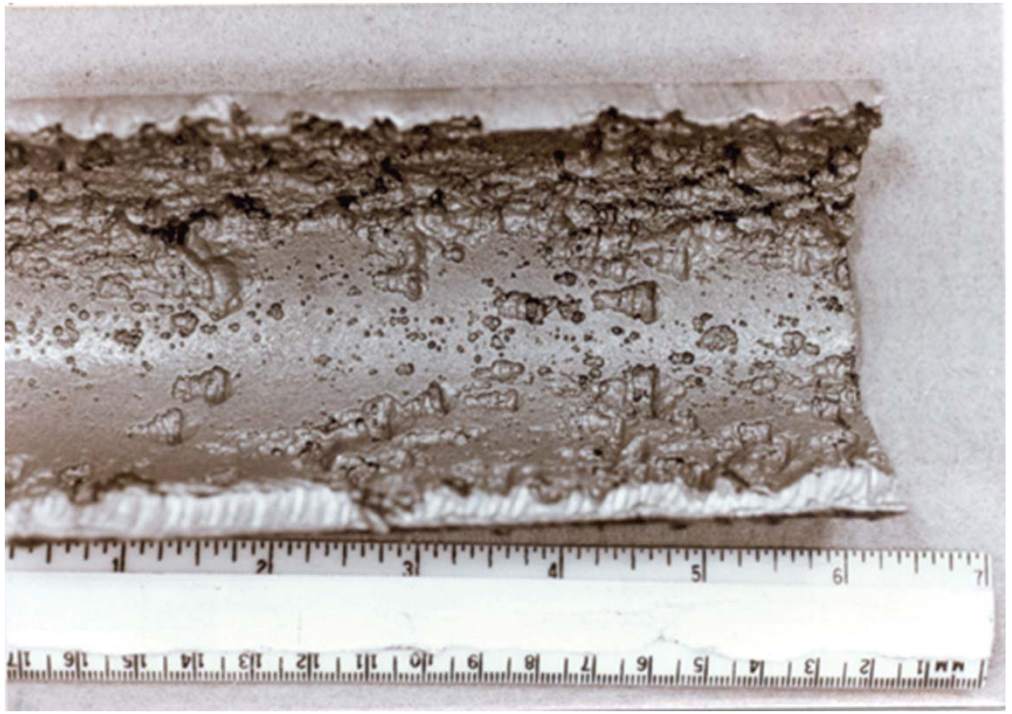


Two types of scaling

- Mixing of incompatible waters
  - Injection of brines incompatible with formation water
  - Damages to the formation
- Self scaling
  - Scale deposits form as formation water is brought to the surface
  - Changes in temperature and pH
  - Little effect on formation

Corrosion

- "Aggressive" water composition
  - Protective scale erosion
  - Acidic conditions
  - Corrected by corrosion inhibitors

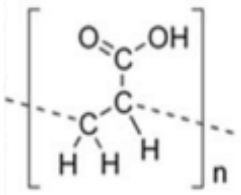


Membrane Fouling

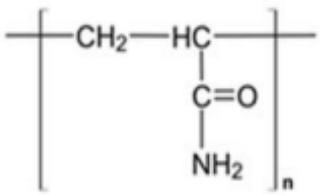
- Membranes for produced water treatment
  - RO
  - Particulate
  - Highest concentrations at membrane surface
- Deposition on the surface of the membrane
  - Suspended solids
  - Microorganisms
  - Mineral scale

Friction Reducers

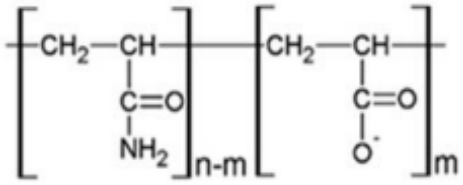
- Required to make "slickwater" for fracs
- Cationic and anionic
  - Cation/anion levels affect performance, cause precipitation
  - Harder anions/cations affect more



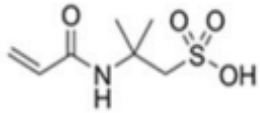
Polyacrylic acid (PAAc)



Polyacrylamide (PAAm)



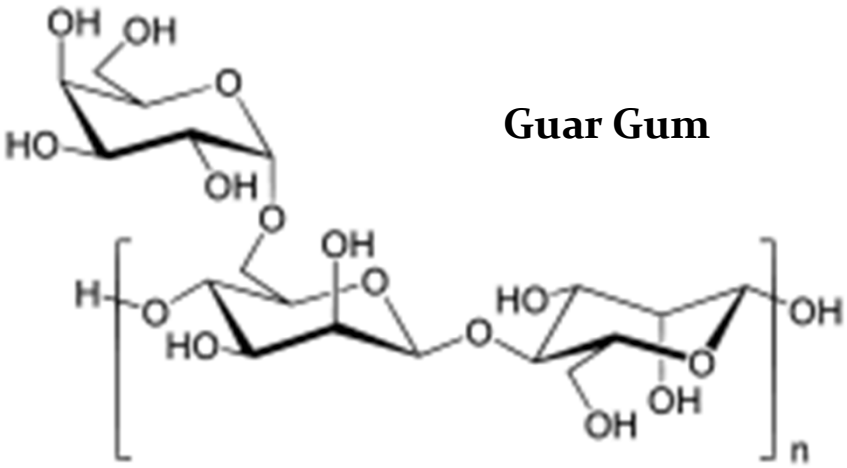
Hydrolyzed Polyacrylamide (PHPA)



AcrylamidoMethylPropane Sulfonate (AMPS)

Gelling Agents

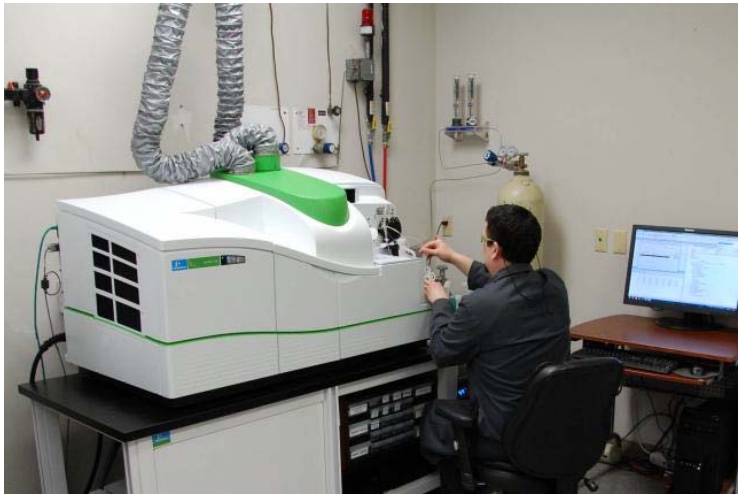
- Used in gel fracs
- Must be broken down for cleanup
- Guar gum, derivatives (crosslinked)
  - Temperature, pH, cross-linkers
  - Hardness (Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+})



Guar Gum

Current Laboratory Tests

- AA & ICP-MS/OES
  - Measures each ion's absorbance, emission, and/or mass
  - Low LOD
  - Susceptible to high TDS, interferences
  - Often limited to cations
  - Difficult to deploy in the field
- Ion Chromatography (IC)
  - Measures ion's elution times out of a selective column
  - Tests anions and cations and polyatomic anions
  - Higher LOD, smaller scope than ICP
  - Susceptible to interferences from co-eluting ions



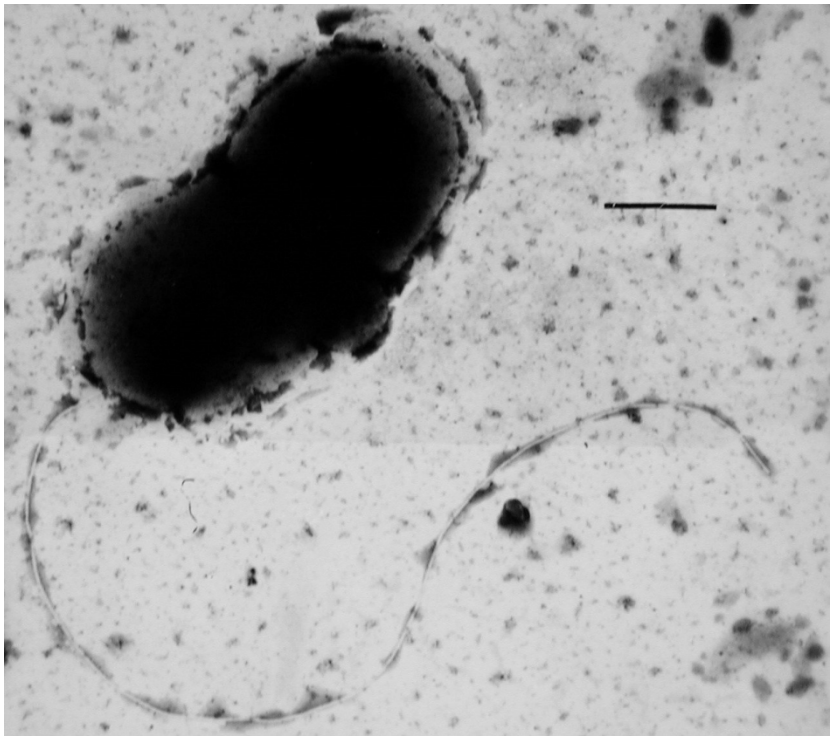
Conductivity and TDS

- Assumes NaCl solution
  - Tends to overshoot
- Equation breaks down over ~100,000 TDS
  - Overshoots very strongly
- Results may correlate well by chance alone
  - Presence of polymer (FR, gel, etc) will justify the overshoot
  - Purely by luck
  - Always overshoots when polymer is absent

To Acidize or Not To Acidize?

- Acid "Preservation" (Filter, then acidify)
  - Keeps things in solution at their original concentration
  - Fights action of carbonate precipitation
  - Mg, Ca, Sr, Ba, Fe, etc.
- Acid "Digestion" (Acidify, then filter)
  - Yields total mineral content
  - Changes many insoluble species into soluble species
- BOTH will give complete picture, but also change key parameters

Biological Agents



Desulfovibrio vulgaris

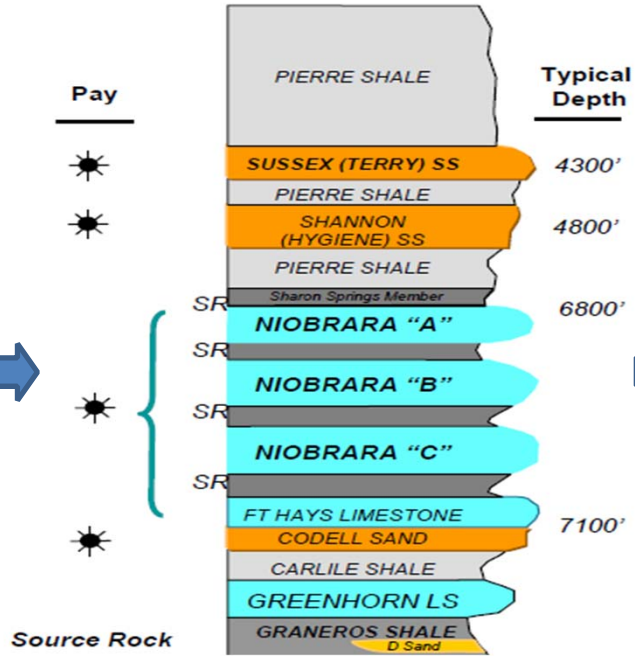
- Acid producing bacteria (APB)
  - Corrosive to pipes and equipment
- Sulfate reducing bacteria (SRB)
  - Hydrogen Sulfide

Current Bacteria Tests

- Classification and Quantification
- ATP Tests ("Bug Bottles")
- DNA Tests (PCR)
- Chemical Tagging
- Live vs. Dead Bacteria
  - Sample Location
  - ATP/DNA concentration changes from point of treatment and with time
  - Determine biocide effectiveness

Changing Water Chemistry

***Frac fluid* in (mg/L)**	
K	3,200
Na	1,215
Ca	130
B	125
Fe	10
Mn	0



Frac fluid out (mg/L)	
K	3,250
Na	1,500
Ca	**900**
B	124
Fe	12
Mg	**1,700**
Mn	**10**

- Used for predictive measures
  - Ca increase may mean corrosion inhibitors are ineffective
  - Mg increase may mean frac job tagged dolomite interval
  - Mn increase indicates corrosion in pipes

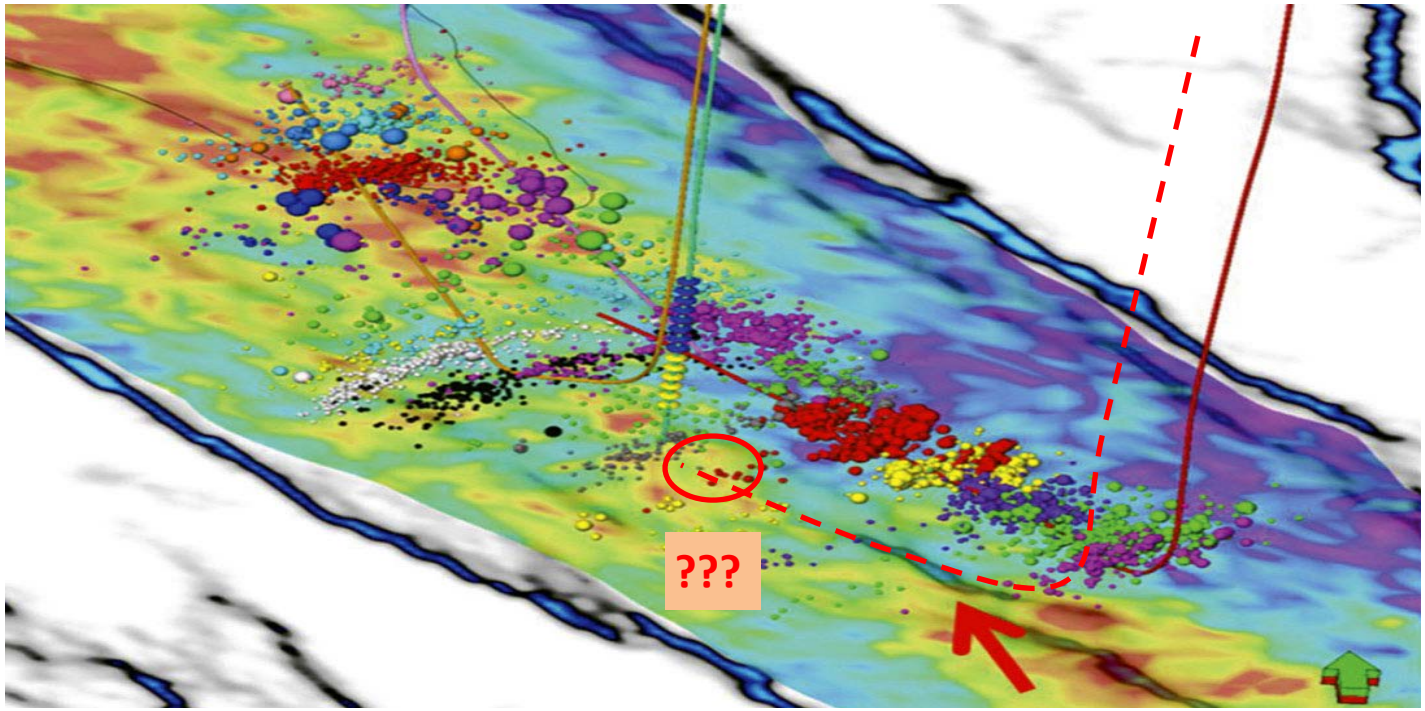
Switching from Flowback to Production

- When is the water coming back to the surface ready for production?
  - Free from fracturing additives
  - High dispersed oil content
  - Most common to flow back "X" number of barrels
- Use water chemistry data to determine switching point
  - Monitor flowback for changes in water chemistry
  - Plot trends to determine when to switch
  - Save on crew time

Conclusion

- Water chemistry must be consistently monitored
  - Preventative measures
  - Predictive measures

Predictive Accuracy in Future Frac Fluid Make-Up



- Tie flowback water chemistry to 3D seismic
- Use correlations to predict geology

Proppants

- Deposition of "filter cake" in gel fracs
- Coated proppants have chemical requirements
  - Decreased rate of formation scaling
  - Timed release of scale inhibitors
  - Sensitive to hard cations

Produced Water

- Natural water released from the formation
- Flowback vs Produced Water
  - When to switch?
- Dispose or Recycle
  - Land based operations
  - Offshore

Recycling of flowback and produced water

- Save money
- Prevent environmental concerns
- Monitor microbial contamination
- Requires chemical additives for compatibility

Events and Trends

- Changing water chemistry
- Steady or sudden
- Monitor drilling fluid for feedback