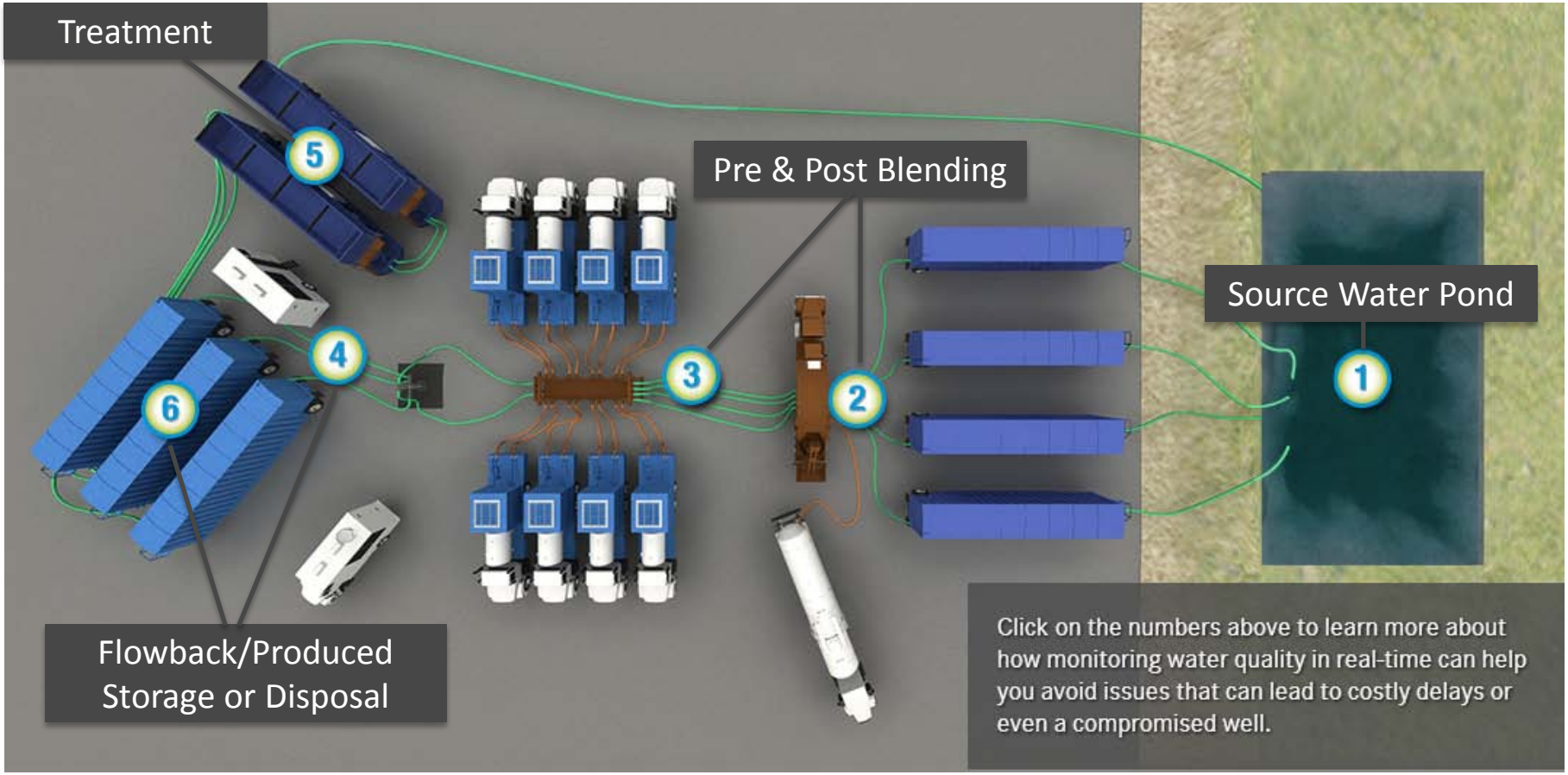
ANALYTICAL PROTOCOLS FOR OIL FIELD WATERS

Johnny Robinson
July 10th, 2013
Hach Company

HYDRAULIC FRACTURING WATER ANALYSIS



A comprehensive, on-site water analysis program is critical to success

HACH
Be Right™

SOURCE WATER MONITORING

- Key Questions
  - It costs $400K to $700K to transport water to site, how do I validate the product to avoid costly issues?
  - How is my source water quality changing over time?
- Role of Water Quality
  - Provide selection/acceptance criteria of purchased water prior to a frac job
  - Maximize compatibility with fracturing additives and avoid interferences

Understanding source water quality in real-time can help ensure that you are meeting spec and mitigating issues early in the process

HACH
Be Right™

EXAMPLE: BACTERIOLOGICAL EFFECTS

- Source water may contain large populations of microorganisms
- Injecting this water can cause:
  - Microbiologically influenced corrosion (MIC)
  - Well souring due to hydrogen sulfide-producing bacteria
  - Clogging due to slime-forming bacteria

Use of a biocide prior to injection may be necessary to avoid costly issues– popular methods include UV, chlorine dioxide, or ozone

HACH
Be Right™

BEFORE AND AFTER BLENDING

- Key Questions
  - How consistent is the water quality in my working/storage tanks?
  - How do I combine multiple sources of water in a way that allows me to still meet spec?
  - How do I verify that the blending process is working correctly
- Role of Water Quality
  - Early warning system to potential issues with the frac fluid
  - Optimize blending of multiple sources of water prior to the blender to meet specifications
  - Provide traceability to root cause performance issues

Understanding the make up of the water in your storage tanks and final blend can help identify and protect yourself from potential formulation issues

EXAMPLE: CATION EFFECTS

- Fluids that are crosslinked are gels that are used to carry the proppant (sand) downhole
- Elevated levels of naturally occurring calcium inhibit the crosslinking from occurring.
- Iron in the formation can prevent the crosslinking breakers from working after transporting the sand downhole.

Understanding calcium and iron levels prior to frac fluid formulation is critical to optimal performance

HACH
Be Right™

REUSE & TREATMENT DECISIONS

- Key Questions
  - How do I determine if the water is acceptable for reuse?
  - What is the best method for treating the water?
  - How do I avoid over/under treating?
  - When should I try to treat vs. dispose and what are my disposal options?

- Role of Water Quality
  - Optimize blending and onsite treatment
  - Avoid interferences with friction reducers –TDS (Chloride)
  - Prevent down hole plugging – TSS, Bacteria
  - Minimize formation of precipitates – Barium, Iron, Hardness, Silica, Strontium, Sulfates
  - Protect capital equipment from corrosion – Bacteria, Dissolved Oxygen

Measuring before and after the treatment process allows you to make important economic determinations that result in time, chemical, and energy savings

HACH
Be Right™

EXAMPLE: SCALING AND CORROSION EFFECTS

- Scaling Agents
  - Ba, Ca, Sr, SO_4 can produce fouling precipitates of $BaSO_4$, $SrSO_4$ and $CaSO_4$. These ions are naturally occurring from shale formation reservoirs

$BaSO_4$ Scale

- Corrosive Agents
  - Iron oxides – naturally occurring; Acids (HCl) – by product of the drilling process, helps dissolve minerals and initiate cracks in the rocks

A knowledge about the ions in your water is needed to evaluate risk and avoid unnecessary damage to capital equipment

HACH
Be Right™

WATER ANALYSIS CHALLENGES

- Flowback and produced water properties vary
  - From region-to-region & within regions
- Challenging sample matrix
  - Suspended solids, dissolved solids, color, bacteria, oil, polymers, etc
- Delays, complexity, and cost in obtaining reliable results
  - Significant time delay to receive results from 3rd party lab, plus hassle to collect, preserve, and ship sample

Without accurate, reliable, and timely information, water will become the weakest link in the process

Approximate Flowback Water Contaminant Ranges*

Parameter	Concentration Range (ppm)
Alkalinity	100 – 600
Calcium	500 – 12,000
Magnesium	50 – 2,000
Barium	50 – 9,000
Strontium	50-6,000
Sodium	4,000 – 40,000
Iron	50 – 300
Silica	50 – 300
Sulfate	10 – 400
Chloride	5,000 – 80,000
TDS	1,000 – 150,000
TSS	1,000 – 7,000

*Source: Shramko, Andrea. Analytical Characterization of Flowback Waters in the Field. IPEC, Houston, November 3-5, 2009.

HACH Be Right™

PROBLEM STATEMENT

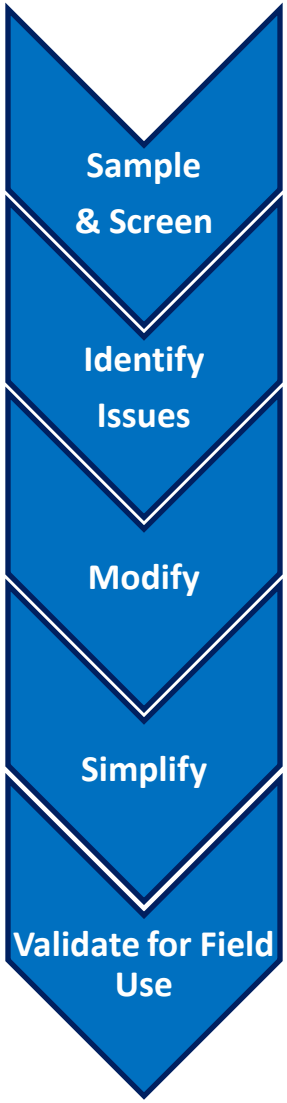
- Existing methods only cover ranges adequate for source water
- Limited number of viable portable parameters available (i.e. pH, conductivity, etc)
- No easy, portable methods for the other key parameters of interest in hydraulic fracturing waters

Parameter	Current methods (ppm)	Target (ppm)
Barium	2 – 100	2 – 9,000
Chloride	10 – 8,000	10 – 12,000
Hardness	10 – 4,000	10 – 14,000
Sulfate	2 – 70	2 – 400
Iron	0.02 – 3.0	0.01 – 300
Boron	0.2 – 14	0.2 – 50

Challenge: Create methods that can easily be conducted by operators onsite, which cover the entire range needed to test source, fracturing fluid, flowback, and produced water.

HACH
Be Right™

OUR APPROACH



- Collect representative samples from key shale plays
- Characterize samples with electrochemical parameters

- Create laboratory experiments to identify interferences with existing field methods

- Explore opportunities to overcome interferences through method modification
- Validate test results against 3rd party laboratory results

- Explore opportunities to simplify procedures for easier field use
- Create step-by-step procedures that can be performed by an operator

- Confirm performance through field testing

HACH
Be Right™

METHOD ADAPTATIONS FOR HYDRAULIC FRACTURING

Parameter	Impact	Before (mg/L)	After (mg/L)
Barium	Scaling	2 to 100	2 to 8000
Chloride	Scaling/Corrosion/ Interferences	10 to 8,000	100 to 200,000
Hardness	Scaling/Corrosion	10 to 4,000	100 to 200,000
Sulfate	Scaling	2 to 70	2 to 7000
Iron	Corrosion	0.02 to 3.0	0.1 to 300
Boron	Crosslinking	0.2 to 14	2 to 50
Hydrogen Sulfide	Corrosion/ Biofouling	0.005 to 0.7	0.005 to 70

Extended ranges made easy for all key hydraulic fracturing parameters

HACH
Be Right™

METHODS MADE EASY

- Step-by-step procedures and detailed explanations for the non-technical user in a “Hydraulic Fracturing Water Analysis Handbook”

- Dilutions that are “invisible” to the user and are performed directly in sample cell:
  - User selects low range (LR), mid-range (MR), or high range (HR) by pressing the ‘conc’ key
  - Adds corresponding sample volume: LR = 10 mL, MR = 1.0 mL, or HR = 0.1 mL
  - Dilution factors calculated automatically by colorimeter

- Titration methods are simplified through:
  - An expanded concentration range using smaller sample volumes
  - A digital titrator (i.e. no glass pipettes)

Methods can now be performed quickly and easily in the field by non-technical operators

HACH
Be Right™

HYDRAULIC FRACTURING WATER ANALYSIS KIT

- Includes instruments, reagents, and methods to support parameters critical to hydraulic fracturing applications:
  - Alkalinity
  - Bacteria: Sulfate-reducing (SRB), Iron-related (IRB), Slime-forming (SLYM)
  - Barium
  - Chloride
  - Conductivity
  - Hardness
  - Iron
  - pH
  - Sulfate

- Provides real-time, on-site results
  No need to spend the time and money to send samples to a regional lab!
- Supports analysis of:
  - Source water
  - Produced water
  - Frac fluid
  - Flowback water
  - Water treatment
  - Drilling fluids
  - Enhanced oil recovery

- *Additional parameters may be added as needed*
- *Guar – polyacrylamide – H2O2, etc.*

The newly developed methods can provide real-time field results for key hydraulic fracturing waters via a portable kit

HACH
Be Right™

OTHER KEY LAB & FIELD PRODUCTS

Instruments

- 2100Q Portable Turbidimeter

- DR 2800 Portable Spectrophotometer

- DR 3900 Benchtop Spectrophotometer

- TSS Portable Probe

- MP-6 Meter

HQd IntelliCAL™ Probes

- Chloride ISE
- Dissolved Oxygen
- ORP

Chemistries

- Boron
- Bromine
- TPH
- Chlorine / Chlorine Dioxide
- Manganese
- Phosphate
- Ferrous Iron
- BARTS (Heterotrophic Bacteria)

HACH
Be Right™

CONTINUOUS MONITORING

Robust Online Analyzers

- Mount directly into the treatment process for continuous analysis of:
  - Chlorine
  - Conductivity
  - Dissolved Oxygen
  - Oil in water
  - pH
  - Suspended Solids
  - Total Organic Carbon
  - Turbidity
  - UV transmittance
  - And many more

Monitor continuously for better process control or the capture of historical data

HACH
Be Right™

TRAINING

- Training encompasses everything necessary to train operators to complete a test and get a correct answer in lab or on-site
- Hands-on training, small class sizes, combine technical discussion with practical exercises
- Experienced trainers available globally
- Customized classes – field or lab setting – HTTC brings the class to you

HTTC
Hach Technical Training Center

A commitment to educating our customers

HACH
Be Right™

ADDITIONAL RESOURCES

Additional information is available at the Hach website:

- Watch the methods in action
- Request your electronic copy of the ‘Hydraulic Fracturing Water Analysis Handbook’
- Access application notes and datasheets
- Order products and services

hach.com/fracwater

Be Right™