Tutorial on Produced Water Quality and Analysis and Chemical Selection for Water Treatment
Typical Water Quality Specs
and Untreated Water Analysis
### Typical KPIs vs Typical Untreated Produced Water Analysis

<table>
<thead>
<tr>
<th>Typical KPI</th>
<th>Units</th>
<th>Untreated Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Fe</td>
<td>&lt;= 10 mg/L</td>
<td>0 - 50</td>
</tr>
<tr>
<td>H₂S</td>
<td>&lt;= 0.5 mg/L</td>
<td>0 - 100+</td>
</tr>
<tr>
<td>Bacteria</td>
<td>&lt; 100 pg/ml (cATP)</td>
<td>2,000 - 20,000</td>
</tr>
<tr>
<td>TSS</td>
<td>&lt; 100 mg/L</td>
<td>400 - 1,000</td>
</tr>
<tr>
<td>Turbidity</td>
<td>&lt; 100 NTU</td>
<td>100 - 200</td>
</tr>
<tr>
<td>TPH</td>
<td>&lt; 100 mg/L</td>
<td>40 - 250</td>
</tr>
<tr>
<td>pH</td>
<td>6.0 - 8.0</td>
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Some produced water has little H₂S or iron
Producers using a non-oxidizing biocide at the frac blender may not be concerned with bacteria in frac water before it arrives at the well pad
Solids in produced water are low compared to industrial waste streams so removal is not difficult, but it adds to the cost
Since solids can be introduced via wind blown dust, fines in frac sand, dirty tanks and formation fracturing, tight solids specs upstream may be undone downstream
Overly tight solids and oil & grease specs are costly and slow the throughput of treated water

Conclusion:
Produced water is not difficult to treat, but overly tight specs can be costly – want to strike the proper balance
Chemical Selection for Water Treatment
Oxidizing Biocides

- Common Oxidants – Oxygen, Sodium Hypochlorite (bleach), Sodium Chlorite, Chlorine Dioxide, Peracetic Acid, Hydrogen Peroxide, Ozone

- Attributes –
  - Oxidants kill bacteria and remove metals, $\text{H}_2\text{S}$, other oxidizable water constituents
  - Broad spectrum - kill a broad array of bacteria
  - Fast-acting (chemical reactions last minutes or hours then cease)
  - Biodegradable
  - Can be used to break up emulsions and improve oil separation
  - Relatively inexpensive

- Drawbacks –
  - Hazardous to handle but have the advantage of fast action with essentially no lingering unreacted chemicals and are biodegradable
  - Could be incompatible with frac chemicals
  - Oxidants are corrosive

- Chemical mechanism:
  - oxidation-reduction (redox) reaction
  - Attack microorganisms by oxidizing the cell structure, disrupting nutrients from passing across the cell wall
Non-Oxidizing Biocides

- Common non oxidizing biocides – Glutaraldehyde (Glut), Quaternary Ammonium Compounds (Quat), Tetrakis Hydroxymethyl Phosphonium Sulfate (THPS), Tributyl Tetradecyl Phosphonium Chloride (TTPC), Isothiazolone (Iso), Dibromonitriloproprionamide (DBNPA)
- Attributes: Effectively kill bacteria, microorganisms over a long period
- Drawbacks:
  - Act slowly and require high dosages
  - Can be deactivated by presence of H₂S, especially gluteraldehyde
  - Generally insoluble in water; quats help solubilization but have deleterious effect on friction reducers
  - May not kill a broad array of bacteria; some bacteria become resistant
  - Active and persistent for long time vs oxidizing biocides (good & bad)
  - Do not remove metals, H₂S and other water constituents
  - Hard to measure effectiveness in real time, so treatment performance cannot be verified and dosages adjusted to changes in water conditions
  - Generally more expensive than oxidizing biocides
- Chemical mechanism
  - Often work on a distinct metabolic pathway
  - May crosslink polypeptide chains or change cell membrane permeability
Oxidation-reduction potential (ORP) is a millivolt measurement of water’s tendency to release or accept electrons.

• Serves as a measure of how much oxidation or reduction takes place.
• Negative ORP indicates the presence of oxidizable constituents in water.
• Positive ORP indicates a diminished quantity of oxidizable matter.
• A meaningfully positive ORP (say, >100 mV) is desirable for treated water.

• ORP is a subjective, relative, indicative measurement; not an absolute, definitive, highly repeatable measurement that is standard across all water samples.
• Therefore the use of inline ORP meters to automatically adjust chemical dosage can lead to over or under dosage.
  • Best to use multiple water analysis tests, including a test for a residual amount of unreacted oxidant.
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<th>Cost</th>
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<td>Moderate cost</td>
<td>Effective biocide and oxidant</td>
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<td>Hydrogen Peroxide (H₂O₂)</td>
<td>Low cost</td>
<td>Most effective for H₂S control</td>
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- Selection of an oxidant is dependent on water chemistry
- Customer specifications drives cost/performance decision on which oxidant to use
• Chemical selection depends on the customer’s treatment criteria/KPIs, water quality, water pre-treatment, whether a non-oxidizing biocide will be used downhole, and other factors
• Chemical demand study on representative water sample helps select
• If a non-oxidizing biocide is used, may want to focus on iron and H₂S and choose a less expensive oxidant such as hydrogen peroxide
• If bacteria control is the main priority, ClO₂ and PAA are good choices
  • If bacteria is a priority due to concern about microbially induced corrosion (MIC), note that microbes may be only a minor contributor, with naturally occurring amounts of oxygen and other factors having a greater impact
• H₂S removal requires more oxidant than does metals removal, so removal of H₂S is an indication metals and bacteria likely have also been mitigated
  • Sodium chlorite is an excellent H₂S and sulfide scavenger
  • Hydrogen peroxide is also highly effective and less expensive
• ClO₂, sodium chlorite, or PAA can be effectively used for on-the-fly treatment
• ClO₂ is commonly used, but ....
  • ClO₂ is less effective than other oxidants for iron and H₂S removal
  • After the downturn in 2015-2016, water treatment prices have come down, forcing treatment companies to abandon large, enclosed ClO₂ trailers for smaller ones and 2 man crews for 1 man
  • For safety, chemicals should not be placed in an enclosed trailer, and only experienced lead operators should be used on a 1 man crew
  • ClO₂ eduction must occur +/- quarter of a mile from water transfer pump
• Water chemistry is highly complex and differs with each situation
• Water treatment technology is based on science but also plenty of trial-and-error learning
• Lab testing is not enough; field experience is critical
• The industry is still learning and evolving, with little definitive data available in the public domain
• No one chemical or piece of equipment will do it all
• KPIs and water quality determine treatment process selection
  • Tight KPIs and low quality water increase water treatment cost
  • Each operator selects its own optimal balance of cost and performance
• Treated produced water can compete with fresh, but trade-offs exist
• \( \text{H}_2\text{S} \) and iron removal are a high priority
• SRB is the enemy... most important bacteria to control
• It is best to remain open-minded and flexible
For addition information, contact:

Joe Abell
(713)-202-1053
jabell@artesia-ecoscience.com