Produced Water

Produced water is extracted from wells at a rate far greater than hydrocarbon extraction:

- ~8 bbl produced water per bbl of onshore oil
- ~260 bbl produced water per Mmcf of onshore gas

Produced water is typically highly saline and also contains high concentrations of metal ions, organics, and ammonia.

Produced water management is an important aspect of oil and gas production.
What to do with Produced Water?

**Disposal**
- Surface discharge
- Deep injection well
- Commercial disposal

**Reuse**
- Injection for Enhanced Oil Recovery
- Recycling for hydrological fracturing
- Production of biocide?
On-Site Generation (OSG) processes have long been used to produce chlorine-based oxidant solutions. These solutions are produced through the electrolysis of sodium chloride containing brines.

- Anode: Oxidation of Chloride: $2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
- Cathode: Reduction of water: $2 \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2 \text{HO}^- + \text{H}_2$

Combined, these produce sodium hypochlorite (NaOCl) as the primary oxidant product. OSG-produced oxidant solutions can be used in place of delivered halogens for a variety of applications.
Mobile OSG Systems

Mobile OSG systems can be built to deploy electrolytic technology for remote O&G applications.

Oxidant production currently requires the input of both freshwater as well as sodium chloride, which must be trucked into remote production locations.
Successful Application of Electrolytically Produced Oxidants

Millions of barrels of produced water have been treated for over 3 years using electrolytically produced oxidant at a water recycling facility in Arkansas.

Technology has been successfully deployed on numerous other O&G jobs throughout Arkansas, Texas, and California.
Is Freshwater Really Needed for Electrolysis?

Due to transportation and acquisition costs, freshwater can be a significant OPEX component in remote locations.

Can produced water replace freshwater in electrolysis processes?

Reuse of produced water in electrolysis processes would have a number of benefits, including:

- Decreased water transportation
- Decreased disposal volumes
- Eliminate delivery and reduce handling of hazardous biocides on location
Composition of Produced Water

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration Range (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>0 - 250,000</td>
</tr>
<tr>
<td>Bromide</td>
<td>0 – 1,149</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0 – 300</td>
</tr>
<tr>
<td>TOC</td>
<td>0 – 1,700</td>
</tr>
<tr>
<td>H₂S</td>
<td>0 - 216</td>
</tr>
<tr>
<td>Iron</td>
<td>0 – 1,100</td>
</tr>
<tr>
<td>Calcium</td>
<td>0 – 75,000</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0 – 46,656</td>
</tr>
<tr>
<td>Barium</td>
<td>0 – 850</td>
</tr>
</tbody>
</table>

**GOOD!** – Can be used to produce oxidants through electrolysis

**ACCEPTABLE** – Reacts with produced oxidants to make chloramines

**BAD!** – Reacts with produced oxidants, resulting in undesired consumption of oxidant product

**WORSE!!** – Can cause scale in the electrode and downstream system components

Overall, the opportunity to reuse produced water in electrolytic oxidant generation processes is available, but there are a number of operational challenges to overcome.
Challenge 1: Variable Chloride Content of Produced Water

Chloride content is the primary driver of oxidant production

- Oxidant production can be assessed through Free Available Chlorine (FAC) or Total Chlorine (TC) measurement

All electrolytic cells have a maximum FAC production that cannot be increased through additional chloride ion content
Produced waters with low chloride ion content can be boosted through supplying additional chloride.

Extensive laboratory testing has been conducted to understand optimal chloride boost levels.

While supplemental chloride is a deliverable to the site, freshwater deliveries are still eliminated.

Boosting of Chloride Ion Content

Oxidant FAC Content (mg/L)

0 1000 2000 3000 4000 5000 6000

Boosting Chloride Ion Content with Sodium Chloride Brines
Challenge 2: Electrode Scaling

Scales can form from a variety of components of produced water:

- Calcium Carbonate ($\text{CaCO}_3$)
- Magnesium Hydroxide ($\text{Mg(OH)}_2$)
- Iron Oxides ($\text{Fe}_x\text{O}_y$)
- Manganese Oxide ($\text{MnO}_4$)
- Barium Sulfate ($\text{BaSO}_4$)

Scaling in electrolytic OSG systems can cause several issues:

- Blinding the electrolytic cell, eventually inhibiting oxidant production and destroying the cell
- Clogging components such as valves, lines, and injection pumps downstream of the electrolytic cell
Scale Formation

CaCO₃ is highly soluble in acidic solutions, pH < 3 needed for effective dissolution.

In the high pH range typically seen during electrolysis, CaCO₃ is extremely insoluble and produces scales.

Scales are mainly formed in the high pH environment near the cathode:

- Primary cathode electrochemical reaction: \( 2 \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\ \text{HO}^- + \text{H}_2 \)
- Typically, the pH at and near the cathode surfaces is very high, resulting in the perfect environment of the precipitation of calcium, magnesium, and iron based scales.

Some scales can also form on anodes, but these are much less common.
Most scales are usually removed through acid washing of the cell

- Typically ~25% hydrochloric acid is used

Some scales can also form on anodes, but these are much less commonly encountered

Extremely high Ca/Mg/Fe composition of produced water would require several acid wash cycles per day
One potential solution to this challenge is to use *in situ* acid washing.

- In this approach, the produced water would be acidified with HCl prior to electrolysis, keeping both the inlet and outlet of the electrolytic cell acidic.
- This would, in theory, prevent scales from forming and accumulating in the OSG system.

In aqueous chlorine solutions, molecular chlorine is present at pH~4 and becomes the dominant chlorine species at pH <2. Under typical electrolysis conditions, this would result in the evolution of substantial amounts of Cl\(_2\) gas.
Use of sulfamic acid in place of hydrochloric acid is a potential resolution to this challenge.

Electrolysis of sulfamic acid containing NaCl brines results in the production of Stabilized Oxidant Solution (SOS).

- Sulfamic acid combines with halogens produced during electrolysis to give N-halosulfamates or N-halosulfamic acids.
- Importantly, these compounds are active biocides but not volatile, even from highly acidic solutions.

SOS has been produced previously using freshwater and used to successfully disinfect a variety of produced waters.
Electrolysis of sulfamic acid/NaCl brines results in very rich chemistry.

- At low sulfamic acid concentrations in the precursor brine, the pH of the oxidant solution initially increases.
- Once sufficient amounts of sulfamic acid have been incorporated in the brine, very acidic oxidant solutions are produced.
- The pH of these solutions (< 3) is low enough to ensure that scales such as calcium carbonate are effectively dissolved.
Electrolysis of Sulfamic Acid Containing Brines

Increasing sulfamic acid also increases SOS in product solutions.

Extensive testing has demonstrated that SOS is preferable over free halogens for the disinfection of produced water.

- SOS is less chemically reactive than free chlorine, therefore, more of the chemistry added to produced water remains to inactivate bacteria.
Bringing it all Together....

Bench testing was used to validate this process

- Brines contained 50 g/L chloride ion and 1.5 g/L calcium with and without sulfamic acid
- Electrodes were operated for 20 minutes

Brine with no sulfamic acid produced substantial carbonate scale

Sulfamic acid prevented scale build up

- While the oxidant solution was very acidic, no chlorine odors were detected
Field Trials are Underway

- Preliminary field testing of this technology is being carried out at a salt water disposal well.
- Preliminary testing demonstrated the produced water conditioned with sulfamic acid can effectively be electrolyzed.
- Next generation prototype electrolysis system is currently being designed and built for deployment in early 2017.
Thank You Very Much for Your Time and Attention!

Any Questions?