Reuse of Produced Water for Electrolytic Oxidant Production: Challenges and Solutions

MIOX

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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

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What to do with Produced Water?

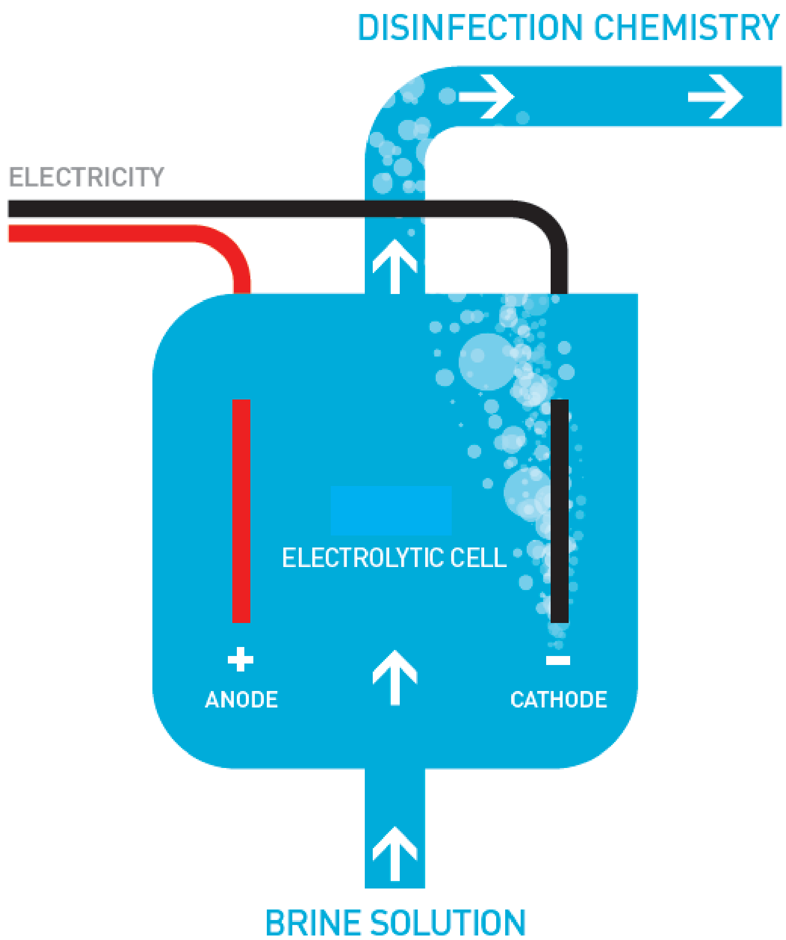
Disposal

- Surface discharge
- Deep injection well
- Commercial disposal

Reuse

- Injection for Enhanced Oil Recovery
- Recycling for hydrological fracturing
- Production of biocide?

Electrolytic Production of Biocide Solutions



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 : $2\ Cl^- \rightarrow Cl_2 + 2e^-$
- Cathode: Reduction of water: $2\ H_2O + 2e^- \rightarrow 2\ HO^- + H_2$
- 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

Constituent	Concentration Range (mg/L)

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 avilable, but there are a number of operational challenges to overcome

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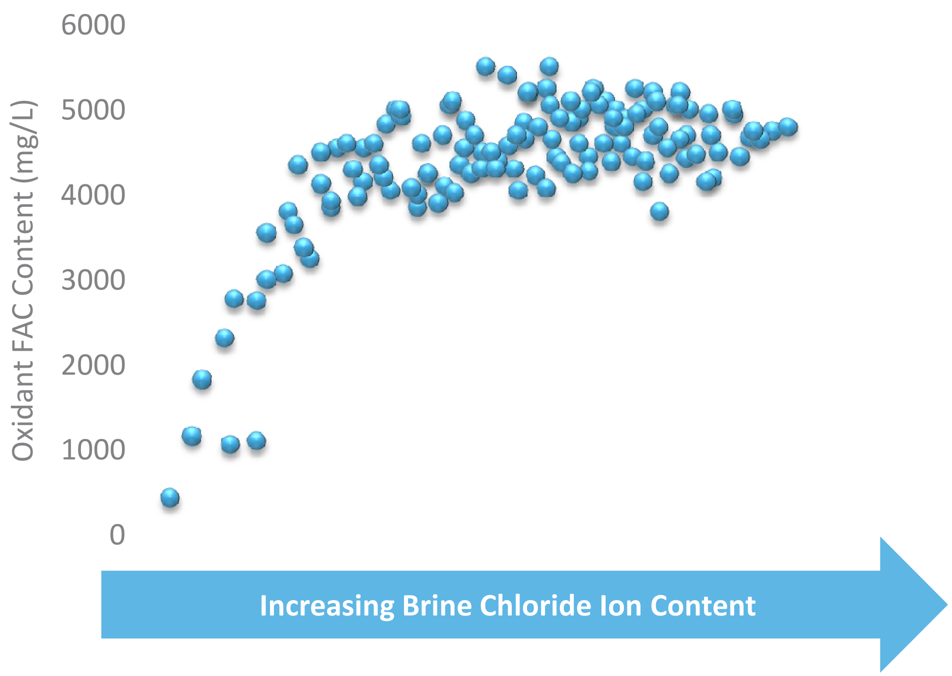
Challenge 1: Variable Chloride Content of Produced Water

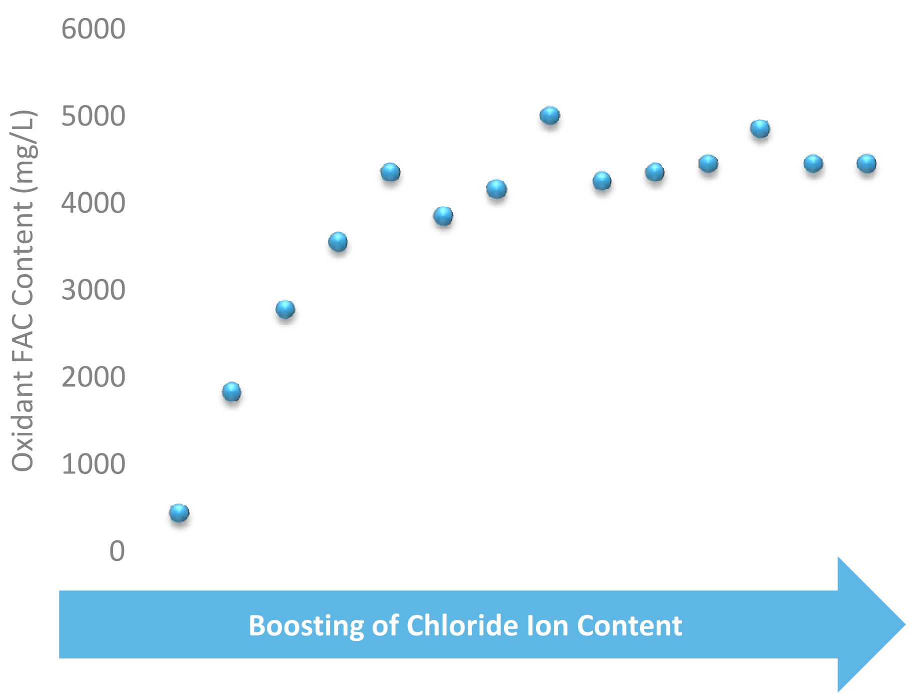


Chloride content is the primary driver of oxidant production

- 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

Boosting Chloride Ion Content with Sodium Chloride Brines

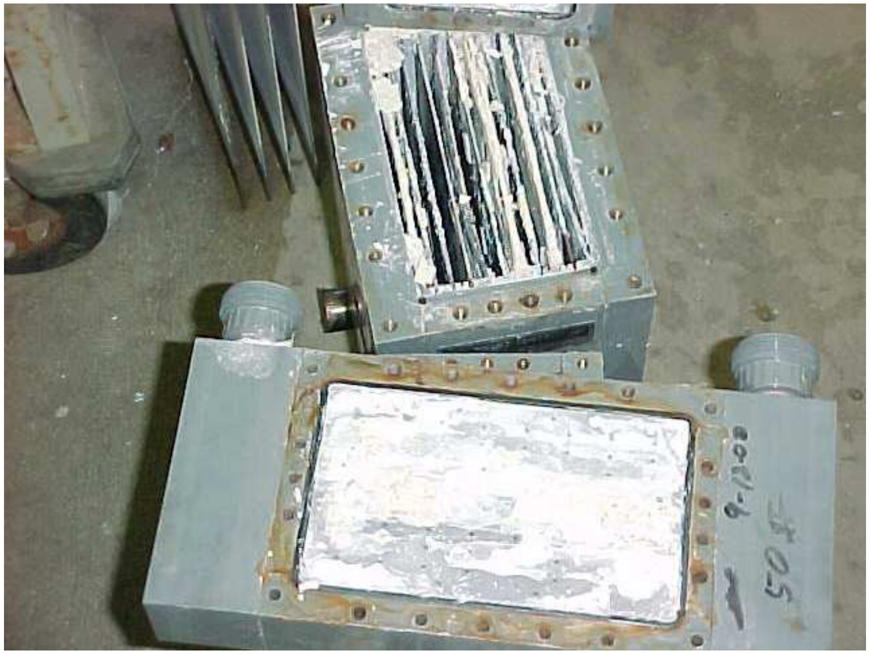


Produced waters with low chloride ion content can be boosted through supplying additional chloride

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

Challenge 2: Electrode Scaling



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

- Calcium Carbonate ($CaCO_3$)
- Magnesium Hydroxide ($Mg(OH)_2$)
- Iron Oxides (Fe_xO_y)
- Manganese Oxide (MnO_4)
- Barium Sulfate ($BaSO_4$)

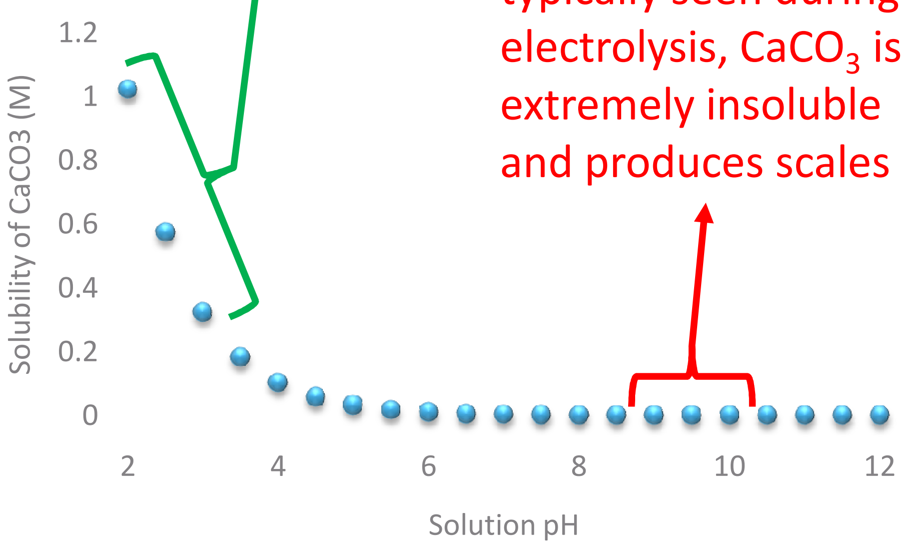
Scaling in electrolytic OSG systems can cause several issues:

- 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

$CaCO_3$ is highly soluble in acidic solutions, pH < 3 needed for effective dissolution

In the high pH range typically seen during electrolysis, $CaCO_3$ is extremely insoluble and produces scales



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

- Primary cathode electrochemical reaction: $2\ H_2O + 2e^- \rightarrow 2\ HO^- + H_2$
- 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

Scale Removal

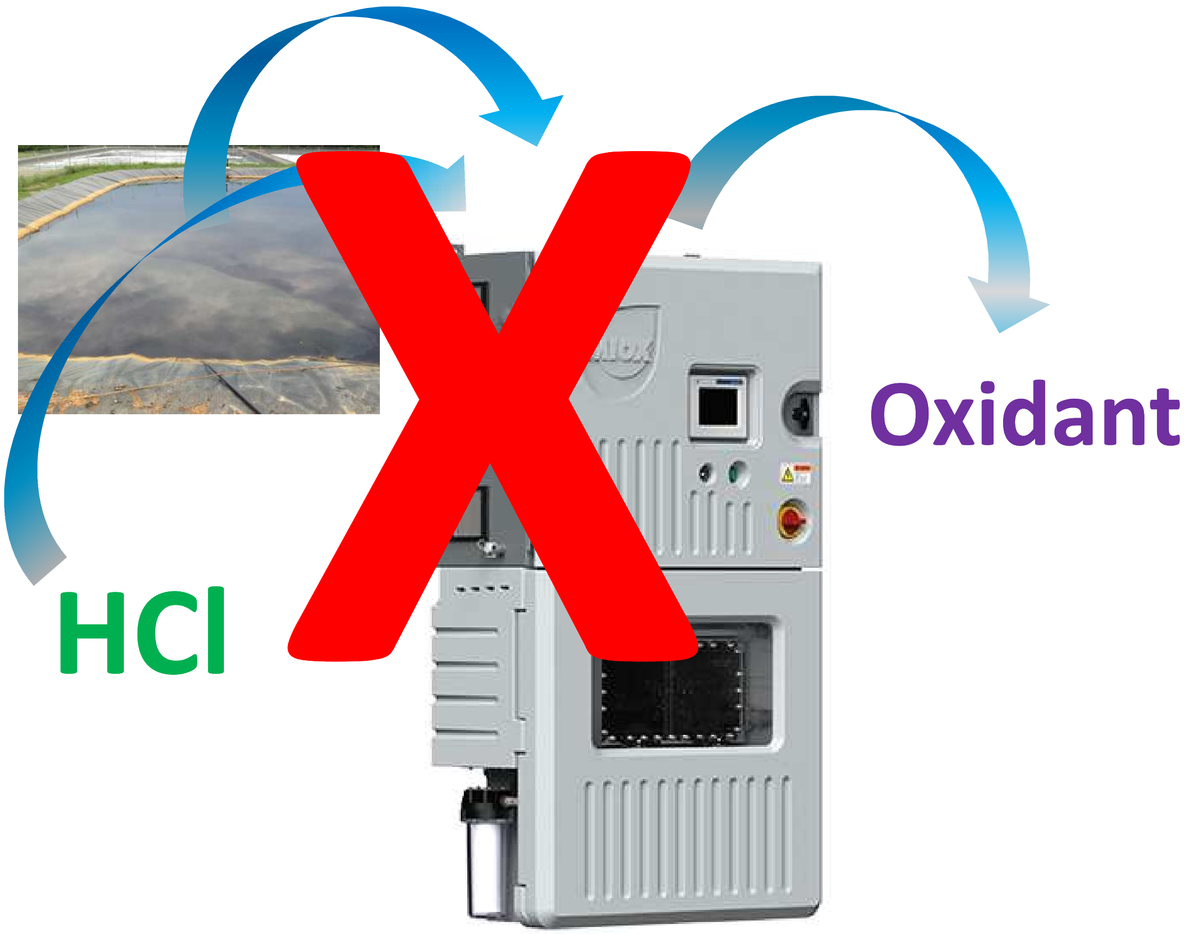
Most scales are usually removed through acid washing of the cell

- 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

In Situ Acid Washing



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

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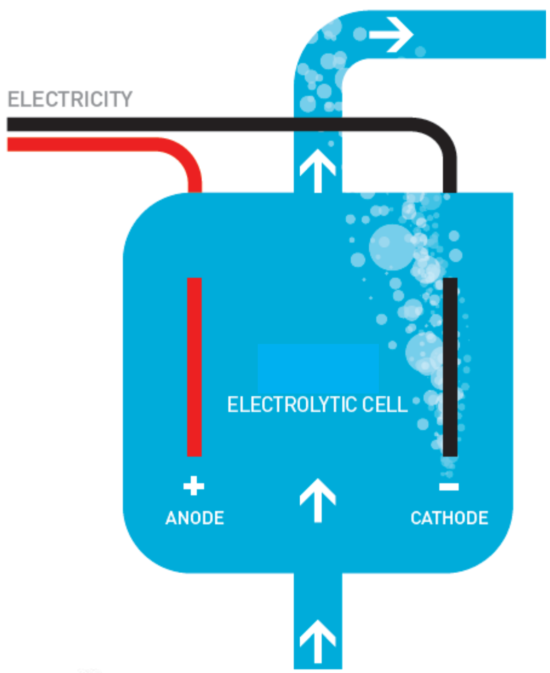
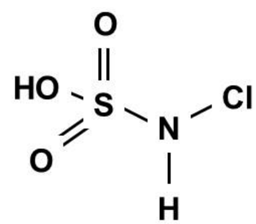
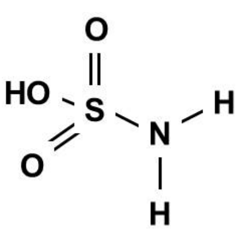
Sulfamic Acid





N-chlorosulfamic Acid
(*N*-chlorosulfamate)



Sulfamic Acid

+ NaCl

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

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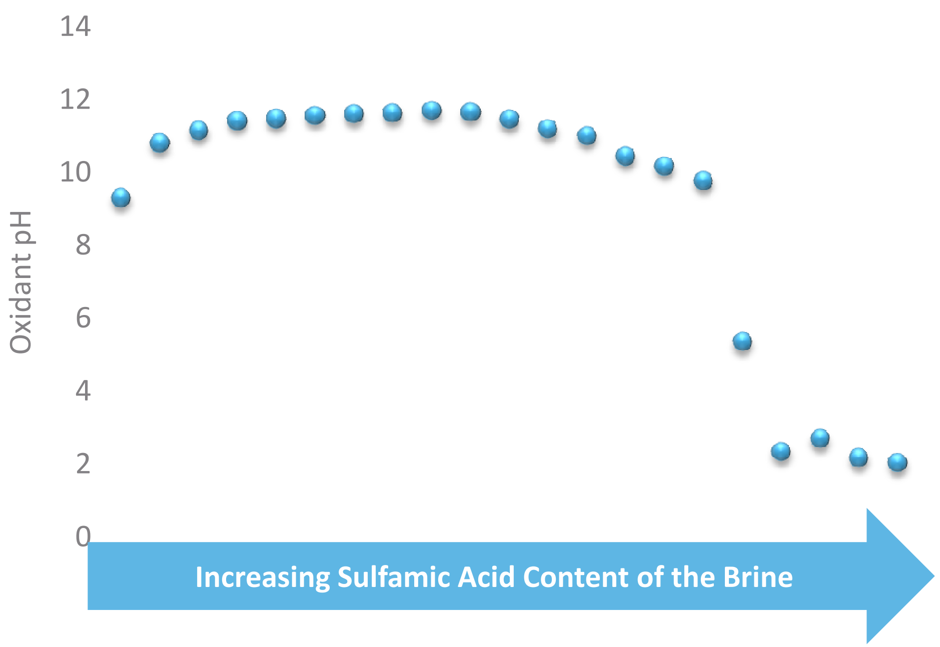
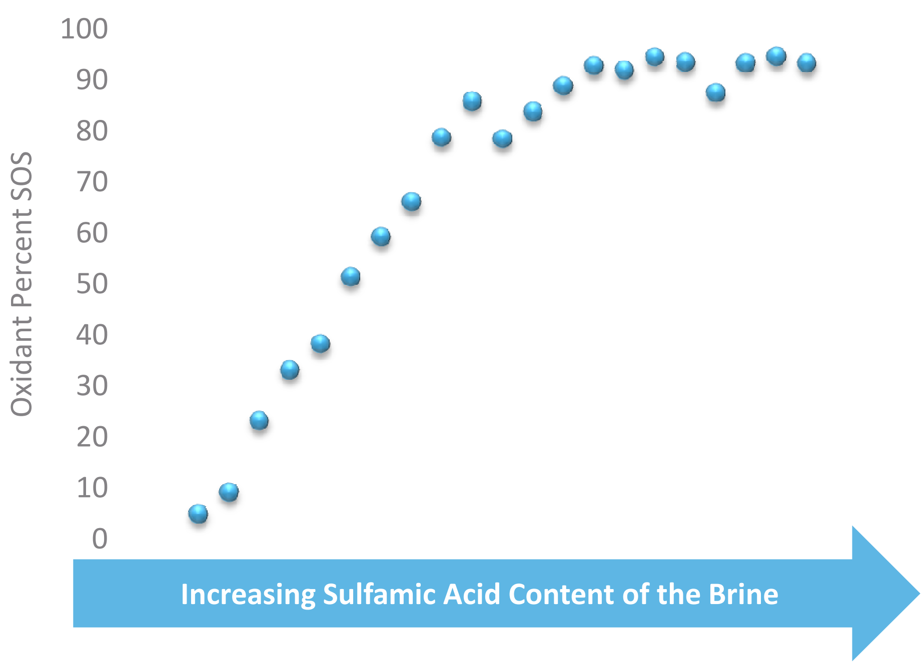
Electrolysis of Sulfamic Acid Containing Brines



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

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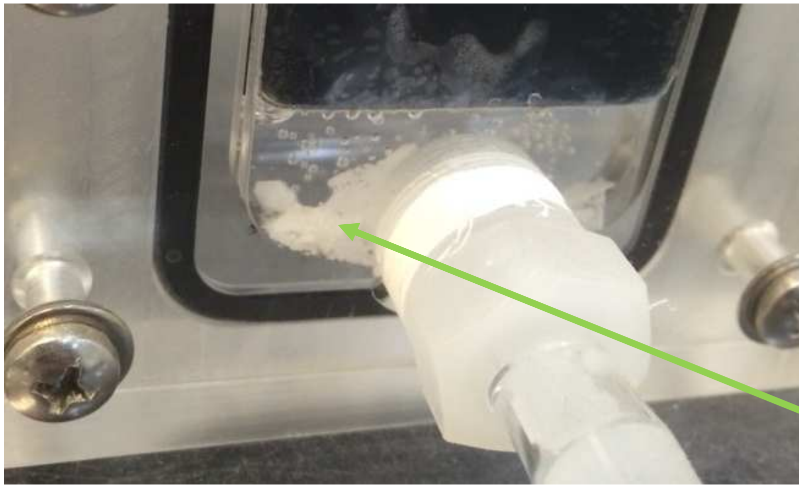
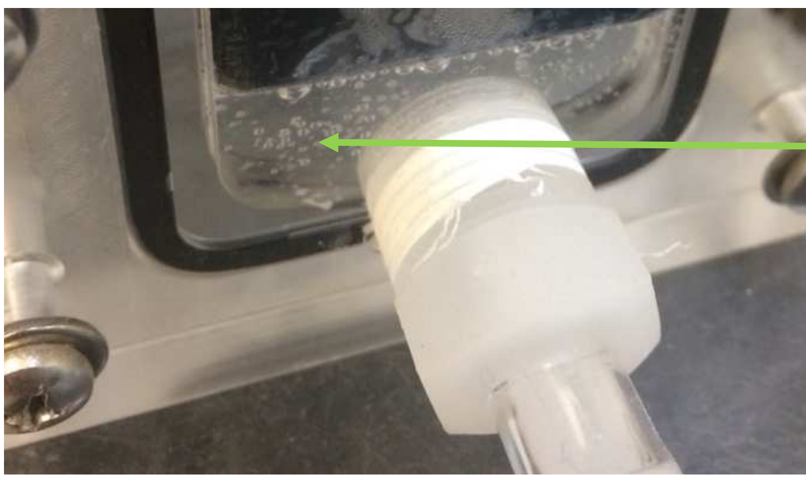
Bringing it all Together....





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

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Thank You Very Much for Your Time and Attention!

Any Questions?

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