
IDEA2021
Powering the Future: District Energy/CHP/Microgrids
Sept. 27-29 | Austin Convention Center | Austin, Texas

Using Electrochlorination Systems to Produce Stabilized Bromine for Cooling Tower Disinfection Applications

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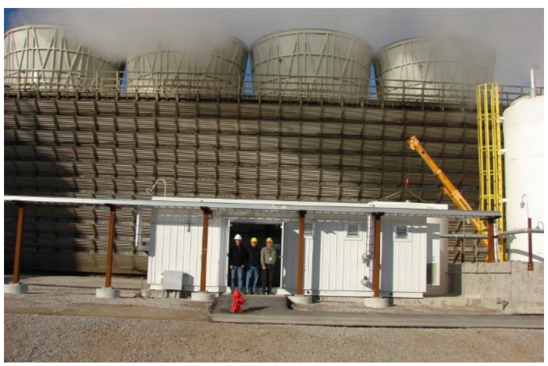
Water Treatment for Cooling Towers



Cooling water treatment programs require a three-prong approach

Corrosion prevention

- Corrosion prevention is needed to minimize damage to the structural elements of the tower

Scale prevention

- Scale inhibitors prevent the formation of calcium carbonate and other scales, which can reduce heat transfer and cooling capacity of the tower

Biocide

Cooling Tower Disinfection

Cooling towers present unique disinfection challenges

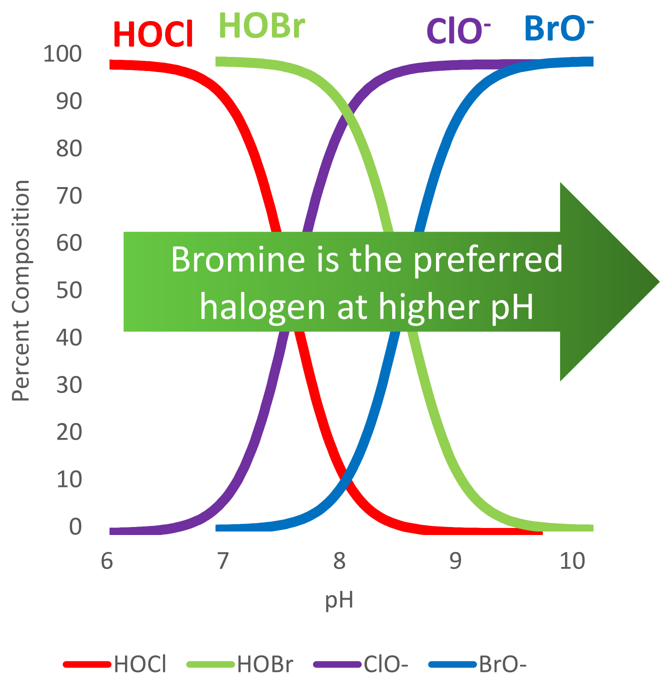
Disinfection is critical

- Eliminate pathogenic bacteria like legionella
- Control of biofilm, which negatively impacts heat transfer and can harbor pathogenic bacteria

Unique aspects of cooling waters

- Cooling towers typically operate at elevated pH which can impact the selection of oxidizing biocides, especially halogens

Halogen Chemistry

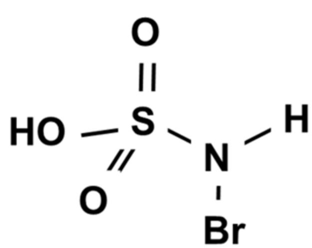


Chlorine and bromine are the most common oxidizing biocides in cooling towers

- In aqueous form, both chlorine and bromine exist as an acid (HOCl or HOBr) or a conjugate base (ClO- or BrO-)
- Distribution between these forms is driven by pH
- For both, the acid form is generally more active in terms of microbial inactivation
- Cooling towers generally operate at higher pH, often making bromine the preferred chemistry in conjunction with chlorine

Sources of Bromine

$$NaOCl + Br^- \downarrow NaOBr + Cl^-$$



N-bromosulfamic acid

In-situ production

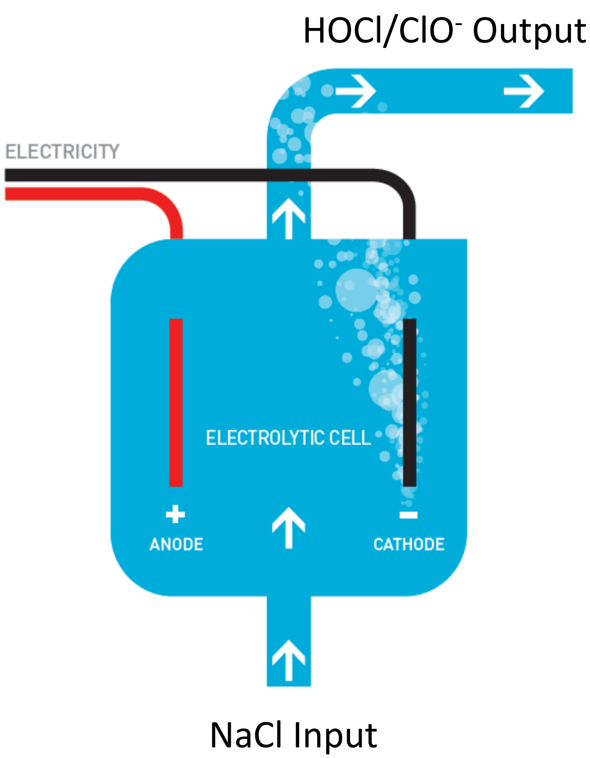
- Sodium bromide can be dosed into a cooling tower treated with aqueous chlorine (sodium hypochlorite or gas chlorine), generating aqueous bromine in situ in the tower

Delivered stabilized bromine

- Aqueous bromine can also be delivered in a concentrated product formulated with a stabilizer like sulfamic acid to preserve the bromine
- Alternatively, solid state stabilize bromine such as 1-bromo-3-chloro-5,5-dimethylhydantoin can be used

Is there a third option?

Brine Electrochlorination (Brine EC)



Electrolysis processes have long been used to produce chlorine-based oxidant solutions

- These systems require three inputs: salt (sodium chloride), fresh water, and electricity

Oxidant solutions are produced through the electrolysis of sodium chloride containing brines

- Anode- Oxidation of Chloride :

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

- Cathode: Reduction of water:

$$2H_2O + 2e^- \rightarrow 2HO^- + H_2$$

- Overall, electrolysis of NaCl produces a sodium hypochlorite-based oxidant solution

This technology has been extensively utilized in industrial cooling applications

Brine EC Replaces Delivered Biocides

Hundreds of Brine EC systems have been installed in cooling towers around the world

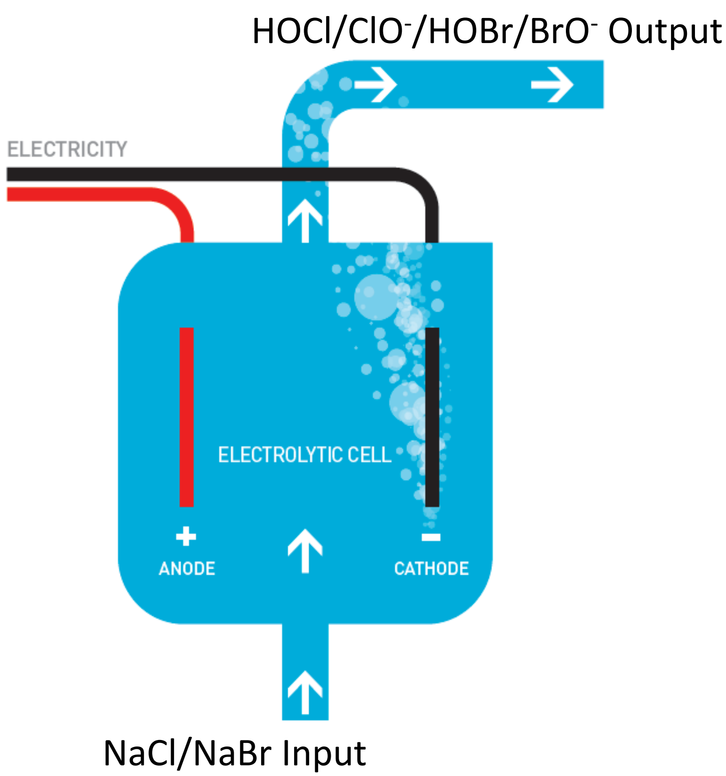
Brine EC treatment capacity

- Brine EC systems have the capacity to treat 50 ton towers all the way up to towers with flow rates of 200,000 GPM

Installation sites

- Heavy manufacturing (eg. nitrogen production and pulp&paper)
- Power generation plants
- District cooling facilities

Adapting Brine EC to Produce Bromine



Electrolysis with bromide in place of or addition to chloride

- Formulate brines that contain bromide ions in place of or in addition to chloride ions

Direct or indirect production of bromine

- Direct production through electrolytic oxidation of bromide ions:

$$2Br^{-} \rightarrow Br_2 + 2e^{-}$$

- Indirect production through oxidation of bromide by hypochlorite:

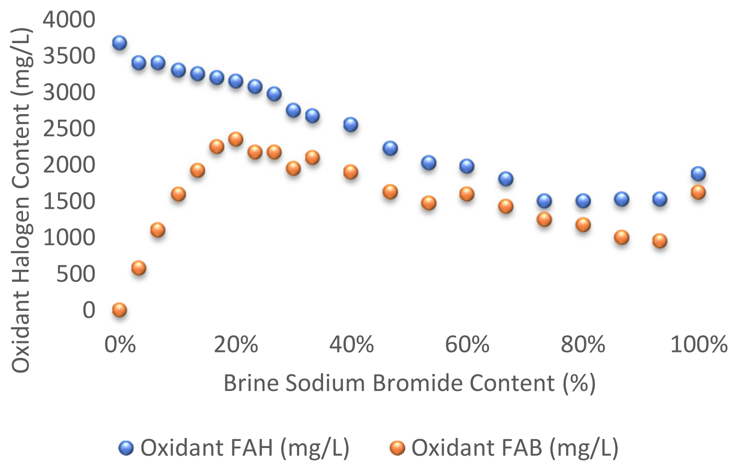
$$Br^{-} + ClO^{-} \rightarrow Cl^{-} + BrO^{-}$$

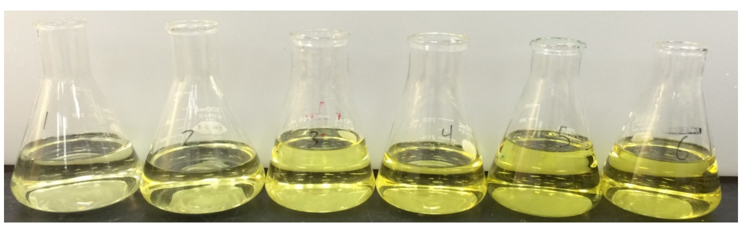
Laboratory Testing

Process chemistry testing is being conducted using small capacity benchtop Brine EC systems

- Electrolysis was carried out using a benchtop electrochlorination system
- Brines were formulated with NaCl, NaBr, and sulfamic acid
- Several parameters of the bromine solutions were characterized:
  - Free Available Chlorine (FAC)
  - Free Available Bromine (FAB)
  - Total Halogen (TH, includes FAC, FAB and haloamines)

Production of Mixed Halogen Solutions





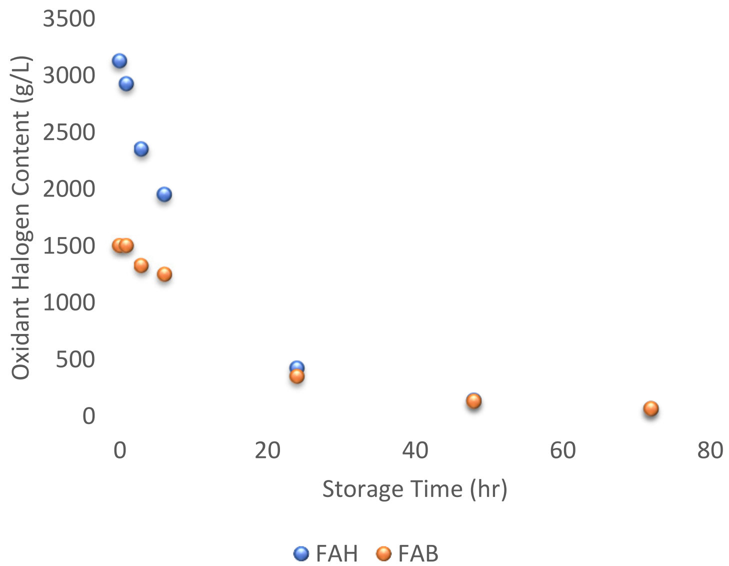
Brine formulations

- Total of 30 g/L salt by weight with varying amounts of NaCl and NaBr

Testing outcomes

- Increasing bromide content of brine resulted in an increase of aqueous bromine in the product solution
- Maximal bromine production occurs with a brine that is ~20% bromide
- Increasing bromide content over 20% resulted in a slow decrease in the halogen content of the oxidant solution

Bromine Solution Stability



Free bromine solutions were found to be extremely unstable

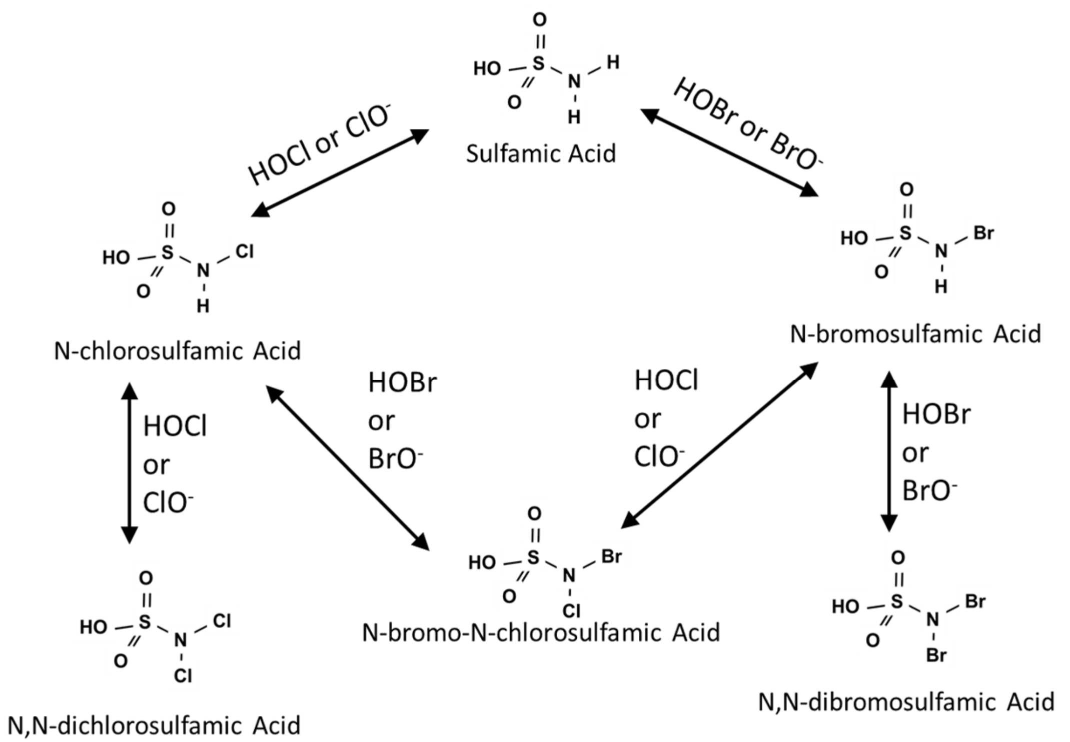
Both the bromine and total halogen rapidly decayed

- Significant degradation was seen within hours
- The majority of the halogen degraded within 24 hours
- Solution pH was observed to drop from 9.77 to 8.06 over 72 hours

Rapid degradation prevents being able to store bromine solution in a day tank

Bromine Stabilization

Sulfamic acid is commonly used to stabilize bromine solutions



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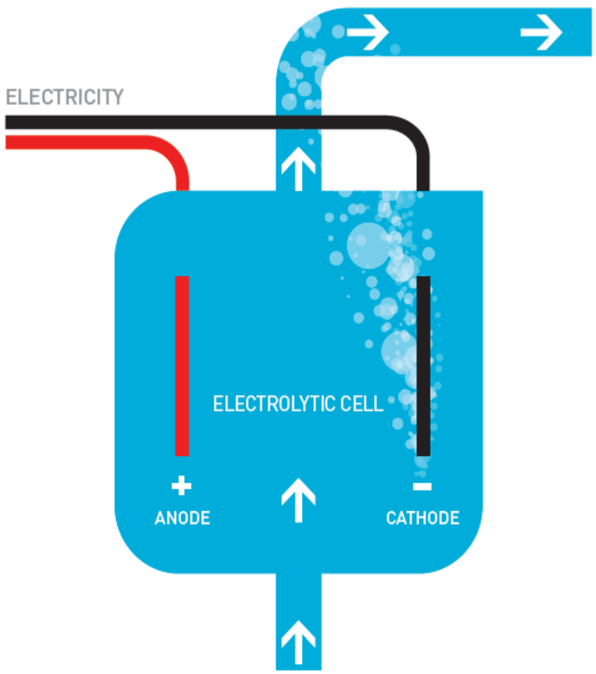
Incorporating Sulfamic Acid as a Stabilizer

Stabilized Halogen Output



NaCl/NaBr/Sulfamic Acid Input

Operational concept

- Utilize brines containing sodium chloride, sodium bromide, and sulfamic acid
- Electrolyze the combined brine to produce a stabilized halogen solution: electrooxidation will produce halogens which will then combine with the sulfamic acid to produce N-halosulfamic acids

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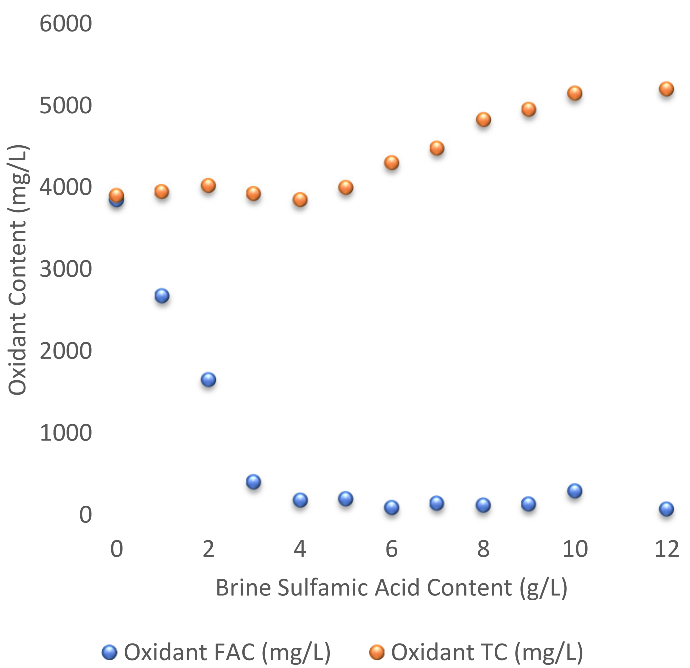
Electrolysis of NaCl/Sulfamic Acid Brines



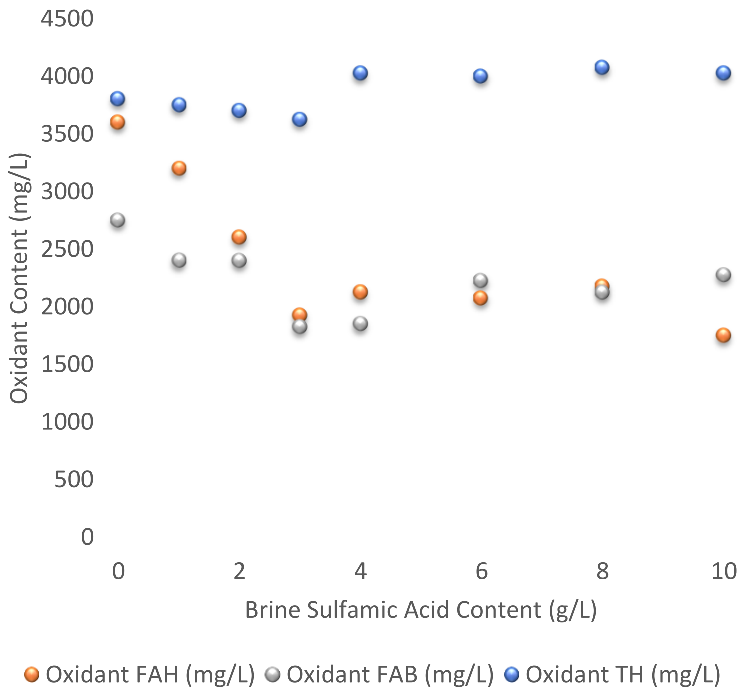
Brine formulation

- 30 g/L sodium chloride with varying amounts of sulfamic acid

Testing outcome

- Free halogen rapidly disappeared but total halogen content stayed the same or increased, indicating the production of N-chlorosulfamic acid compounds
- Increased total halogen production possibly due to the increased conductivity of the brines

Electrolysis of NaCl/NaBr/Sulfamic Acid Brines

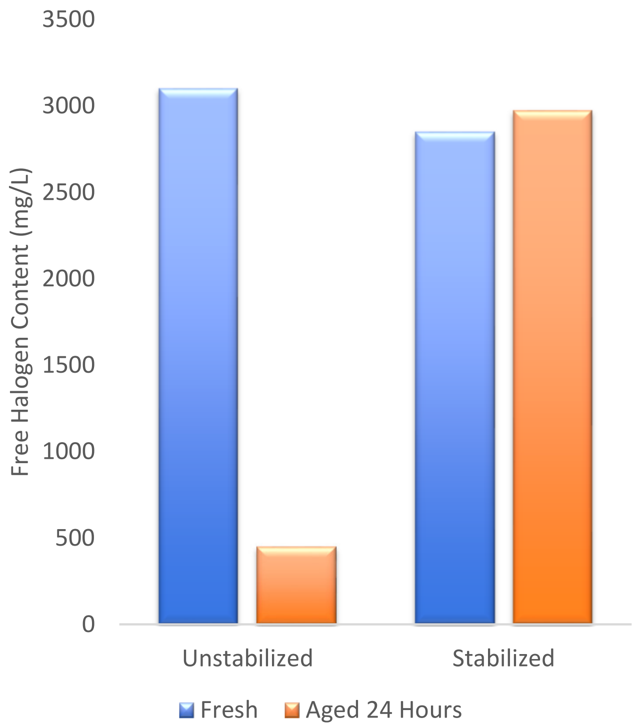


Brine formulation24 g/L NaCl and 6 g/L NaBr with varying amounts of added sulfamic acid

Testing outcome

- Increasing sulfamic acid resulted in decreased free halogen but total halogen stayed the same
- Higher amounts of free halogen observed at high sulfamic acid content for bromine as compared to chlorine likely related to relative strength of Cl-N and Br-N bonds

Impact of Sulfamic Acid on Solution Stability



Stabilized and unstabilized bromine solutions stored under ambient conditions for 24 hours

As observed previously, unstabilized bromine solutions rapidly decayed with near complete loss of halogen within 24 hours

Essentially no decay was observed for bromine solutions prepared with added sulfamic acid, verifying that the solution was stabilized

MIOX-Br Pilot System

Pilot testing is being used to validate this technology in real world cooling towers

Pilot system overview

- Built in 40’ toy-hauler style trailer
- Can be deployed to a variety of locations
- Plug-and-play installation only requires inputs for power and water with an output for oxidant produced by the system
- Can be operational within hours of arrival on location
- Has the capacity to treat as much as 30,000 gal/min

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MIOX-Br Pilot System

Pilot system capabilities

- Incorporates three MIOX-60 Brine EC systems
- All supplemental equipment (filters, tanks, etc.) are on board
- Injection pumps to transfer produced bromine solutions to the point of treatment
- Master control board for all equipment
- Laboratory space for on-site analysis of water samples
- Standard hydrogen venting system
- Multiple emergency stop mechanisms

Pilot Testing Plans

Pilot testing is scheduled to start Q4 2021

Protocol

- MIOX-Br unit to be deployed at the test facility and integrated into treatment process
- Test will involve monitoring location for 12-18 weeks including periods before, during, and after treatment with MIOX-Br system

Evaluation criteria

- Bacteria control
- Corrosion
- Bromine production cost

Field data will be used to further optimize technology

Additional tests will be conducted in 2022

Next Steps

Process Chemistry
Optimize brine formulations to maximize efficacy and minimize process costs

Pilot Testing
Deploy MIOX-Br pilot unit to multiple cooling tower locations to validate technology

Productization
Finalize technical specifications for a full MIOX-Br product launch in 2022

Summary

- Lab testing has successfully demonstrated the production of bromine using Brine EC technology
- Brines are comprised of sulfamic acid, sodium chloride, and sodium bromide to produce sulfamic acid stabilized bromine
- Pilot system has been developed to test and validate the MIOX-Br technology in the field, testing in Q4 2021
- MIOX-Br pilot platform incorporates three Brine EC systems and can treat up to 30,000 gpm
- Ongoing R&D efforts are focused on chemistry optimization and field validation

Q&A

Thank You!

Andrew K. Boal