Silver Electrolysis for Disinfection of Spacecraft Potable Water: 2024 Update

ICES-2024-045

P. Hicks, R. Garcia Fernandez, N. Adam

Background

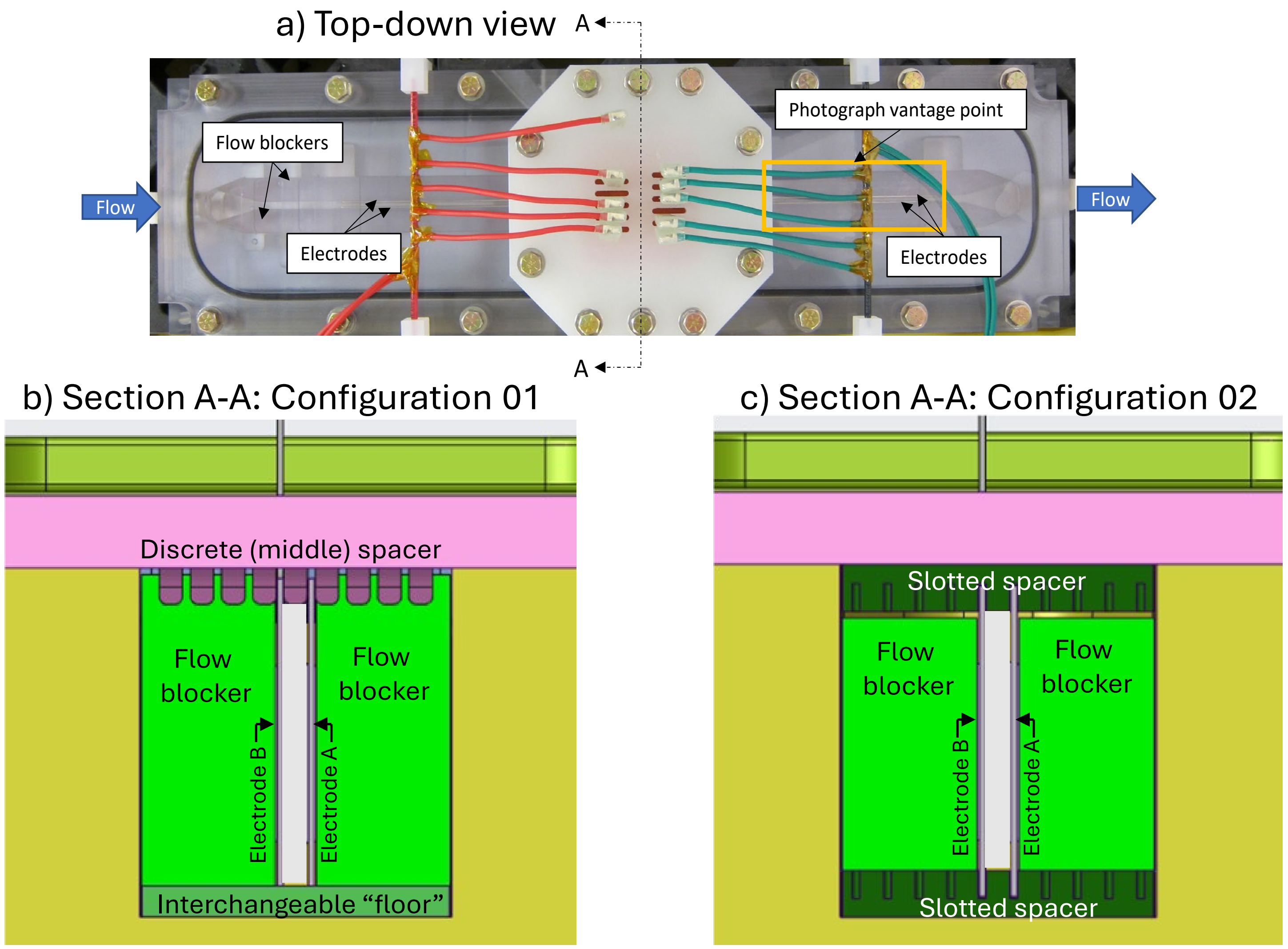
- Goal to implement ionic silver as residual biocide in water recovery systems
  - Requires inline method for silver ion introduction
  - Silver electrolysis (anodic dissolution of silver) is a promising candidate
- Previous testing (see ICES-2022-20 and ICES-2023-41)
  - Demonstrated feasibility and advantages of technology
  - Uncovered fault condition that occurs in certain reactor configurations/modes of operation: "electrode bridging"
  - Demonstrated strategies for preventing bridging fault:
    - polarity reversal (with increased frequency: 1-min half-cycles)
    - masking of electrode edges (proof of concept with electroplating tape)
  - Assessed impact of influent DO on reactor performance (cathode reaction)
- The past year's efforts focused on:
  - Determining whether alternate interelectrode material mitigates bridging
  - Demonstrating combination of polarity reversal with edge masking
    - and use of permanent coating rather than tape
  - More robust testing of cathode reaction (including dissolved hydrogen sensor)
  - Determination of reactor performance at significantly higher silver concentration output

Agenda

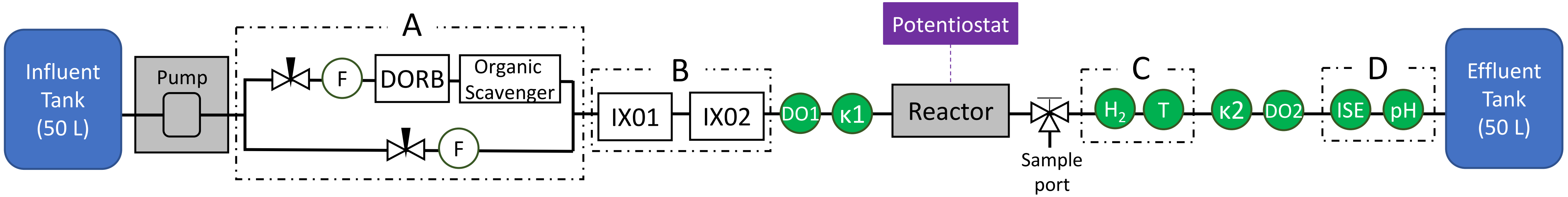
- Test Article/Test Rig description
- Tests performed
  - Alternate Interelectrode Material Test
  - Coated Edge Test
  - Cathode Reaction Test
  - Elevated Concentration Test
- Conclusions

Test Article (Silver Electrolysis Reactor)

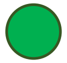
- Removable electrodes
- Variable spacing/# of electrodes
- View into electrode channel
- Configurations:
  - Config 01 for testing alternate interelectrode materials
  - Config 02 for all other testing



Test Rig



 = resin bed
DORB = DO removal bed
IX = ion exchange

 = sensor
DO = dissolved oxygen
κ = conductivity
H2 = dissolved hydrogen
T = temperature

ISE = silver ion-selective electrode
pH = pH electrode

F = analog flow meter (rotameter)

(Optional hardware shown in dashed boxes)

Dashed Box	Description	Purpose
A	Dissolved oxygen removal / bypass	Control influent dissolved oxygen from 0 – 8.7 mg/L
B	Ion exchange beds	Remove dissolved CO_2 -> high purity influent
C	Dissolved hydrogen / temperature sensor	Measure effluent dissolved hydrogen concentration
D	Ag+ ISE and pH sensor	Measure effluent silver concentration and pH

Test Methods

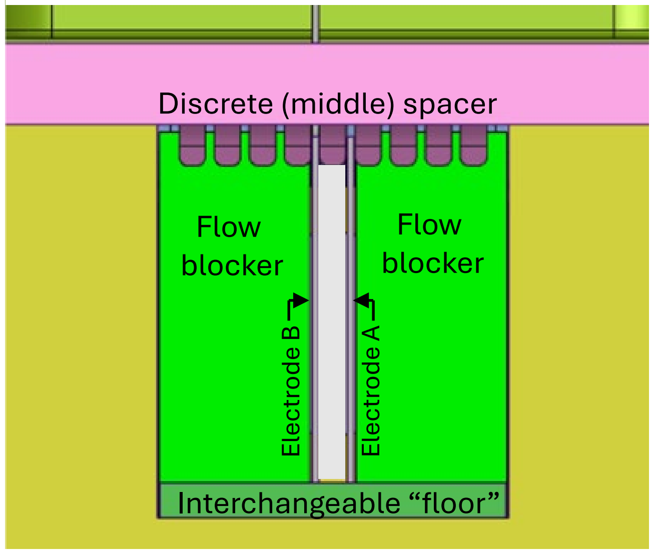
Test*	Spacer Config	# Electrodes	Electrode Mask	Test Rig Includes	Flowrate (mL/min)	Current (mA)	Polarity Reversal
Alt. Intelec. Matl. 01	01	2	None	B,D	33	0.33	None
Alt. Intelec. Matl. 02	01	2	None	B,D	33	0.7	1 min
Coated Edge	02	2	Parylene-C	B,D	33	0.5	1 min
Cathode Reaction 01	02	10	Electroplating tape	A,B,C	100	0.75	See text
Cathode Reaction 02	02	10	Electroplating tape	A,B,C	100	3	See text
Cathode Reaction 03	02	2	Electroplating tape	A,B,C	100	0.75	See text
Elevated Conc. 01	02	10	Electroplating tape	B,D	100	1.5 - 9.0	See text
Elevated Conc. 02	02	10	Electroplating tape	D	100	1.5 - 9.0	See text

*The number after a test name indicates the test case. Note that some test cases had several steps or iterations, as described in Section IIC.

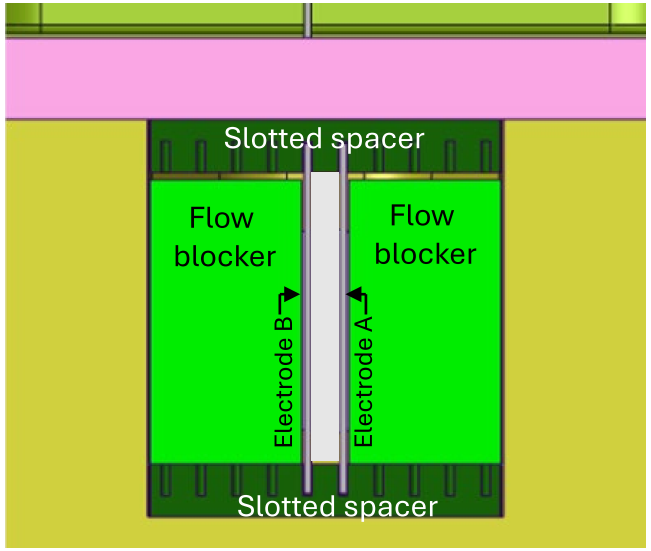
Alternate Interelectrode Material Test: Methods

- Materials
  - Polycarbonate (PC) – baseline
  - Quartz – low porosity
  - PTFE – low surface energy
- Configurations
  - 01 – used for testing alternate materials
  - 02 – was used with PC in prior testing; included for comparison
- Test cases
  - Constant polarity; tested to failure
  - Polarity reversal every minute; tested for cumulative operating time of 24 hours

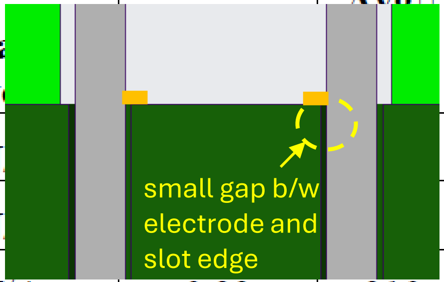
Configuration 01

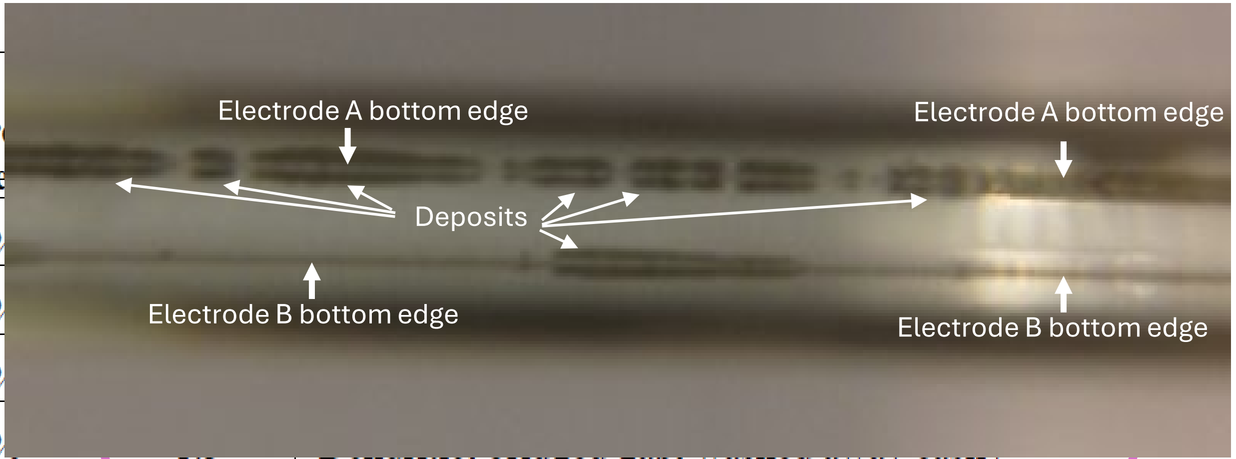


Configuration 02



Alternate Interelectrode Material Test: Results



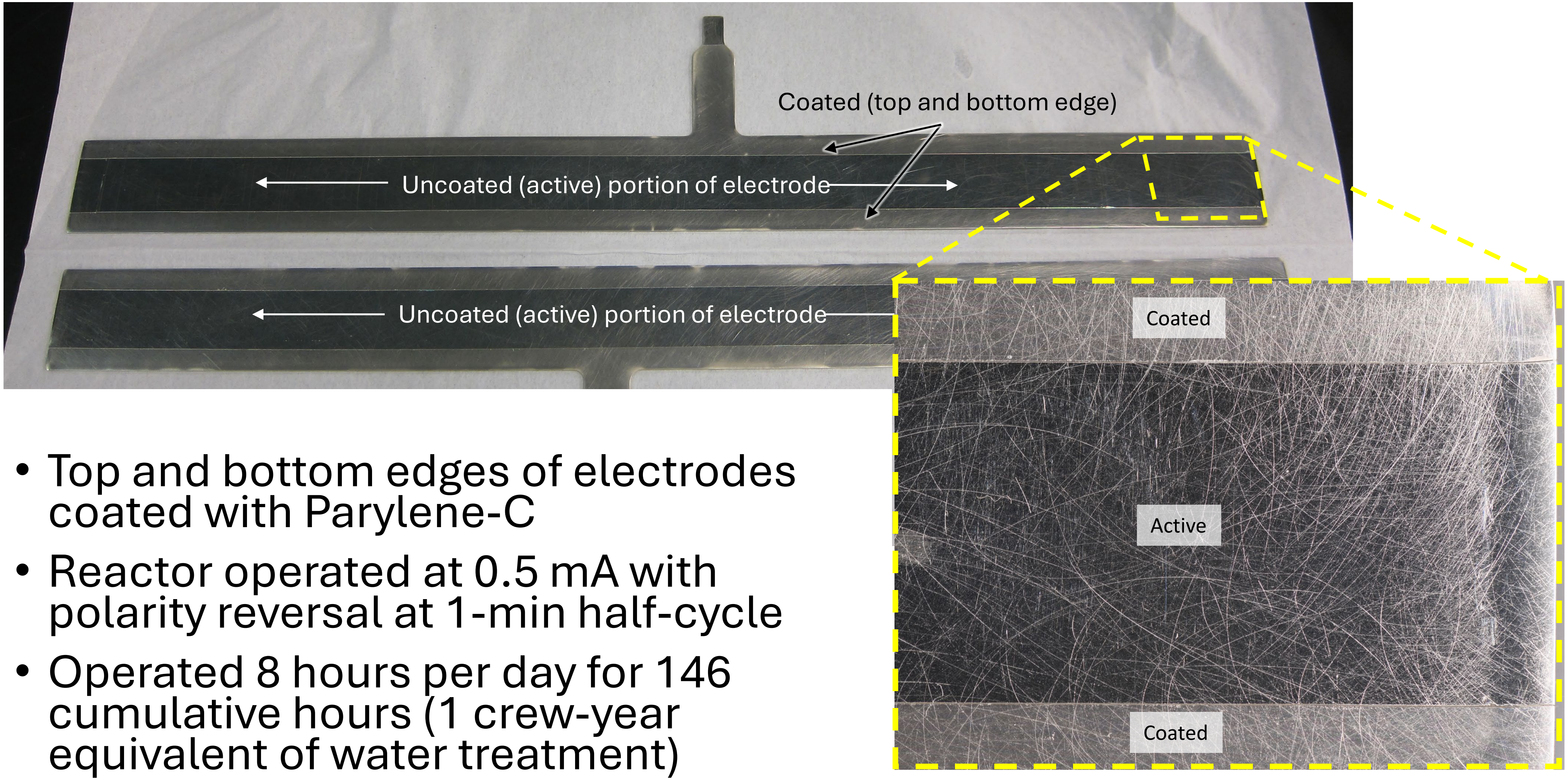


Material	Spacer Config	Pola Rev	[illegible]	Avg††	Curr Efficie	[illegible]	[illegible]
PC*†	02	N	[illegible]	[illegible]	48%	[illegible]	[illegible]
PC†	01	N	[illegible]	[illegible]	64%	[illegible]	[illegible]
Quartz†	01	N/A	0.33	310	46%	[illegible]	[illegible]
PTFE	01	N/A	0.33	240	36%	[illegible]	[illegible]
PC*	02	1 min	0.70	420	N/A	N/A	Along electrode interface only; see Ref. 2
PC	01	1 min	0.70	320	N/A	N/A	Very minor; almost imperceptible
Quartz	01	1 min	0.70	410	N/A	N/A	Very minor; almost imperceptible
PTFE	01	1 min	0.70	460	N/A	N/A	Very minor; almost imperceptible

*From prior testing; included for comparison
†Results listed are the average of three replicates; all other cases were a single replicate
††Average silver concentration is an estimated average of the steady-state concentration throughout the test case

- Material change alone not sufficient to prevent bridging fault
- Polarity reversal prevented bridging in all cases
- In Config 02, gap b/w electrode and spacer allows buildup of electrolysis products

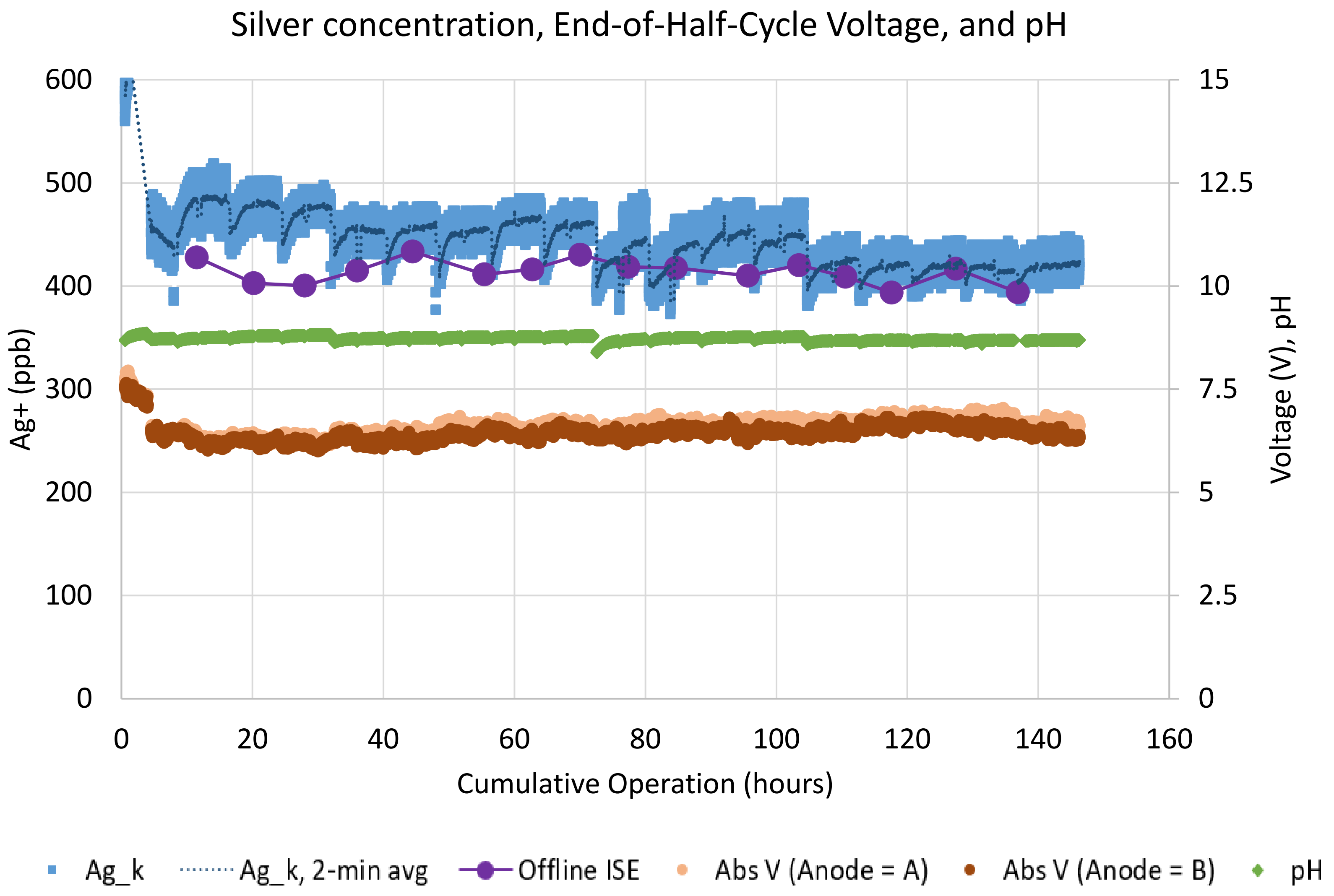
Coated Edge Test: Methods



- Top and bottom edges of electrodes coated with Parylene-C
- Reactor operated at 0.5 mA with polarity reversal at 1-min half-cycle
- Operated 8 hours per day for 146 cumulative hours (1 crew-year equivalent of water treatment)

Coated Edge Test: Results

- Reactor provided Ag^+ near target value of 400 ppb for ≥ 1 crew year
- Reactor output was consistent
  - Gradual decrease in Ag^+ and pH; gradual increase in V
  - Magnitude of change not a concern
  - To be monitored in full lifetime (12 crew-year) testing

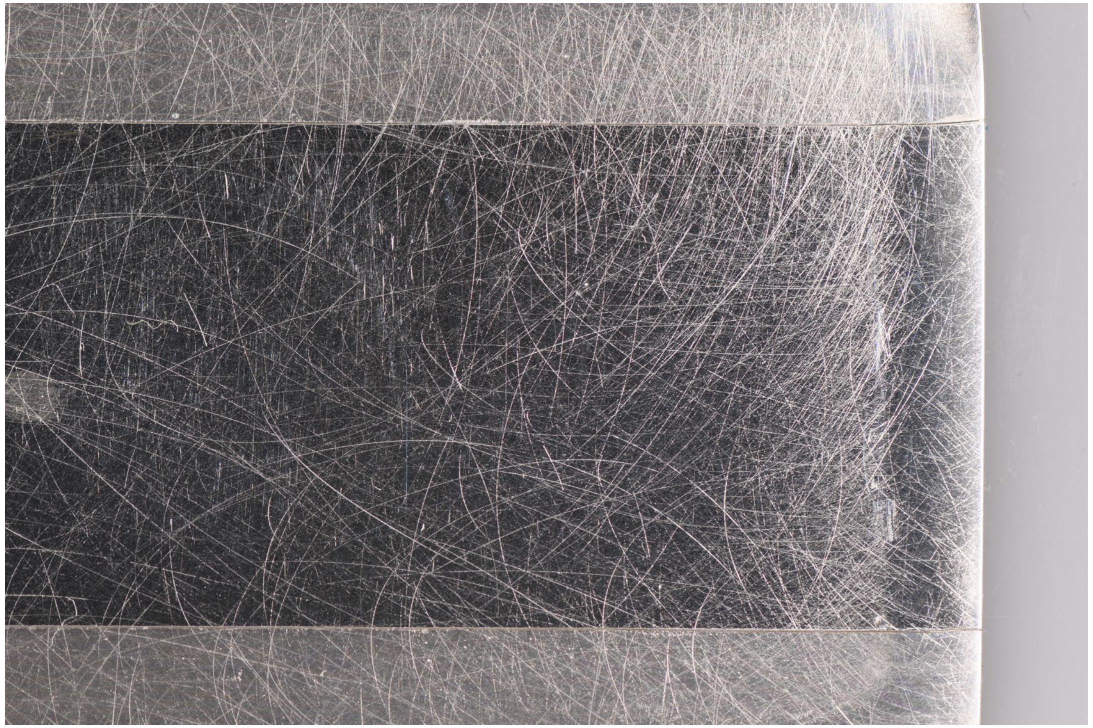


Coated Edge Test: Results

Combination of edge masking and polarity reversal provides long operation with no deposits or flakes

Coated Edge Test: Results

Pretest



Posttest

- Coating did not release any detectable organic nor ionic contaminants
- No macroscopically observable delamination or degradation of coating

Cathode Reaction Test: Background

Electrode	Reaction	Description	Abbreviation
Anode	$Ag \rightarrow Ag^{+} + e^{-}$	Silver dissolution	Ag+
	$Ag + OH^{-} \rightarrow \frac{1}{2}Ag_2O + \frac{1}{2}H_2O + e^{-}$	Oxide formation	Ag2O
Cathode	$\frac{1}{4}O_2 + \frac{1}{2}H_2O + e^{-} \rightarrow OH^{-}$	Oxygen reduction	O2
	$H_2O + e^{-} \rightarrow \frac{1}{2}H_2 + OH^{-}$	Hydrogen evolution	H2
	$Ag^{+} + e^{-} \rightarrow Ag$	Silver deposition	Ag_dep

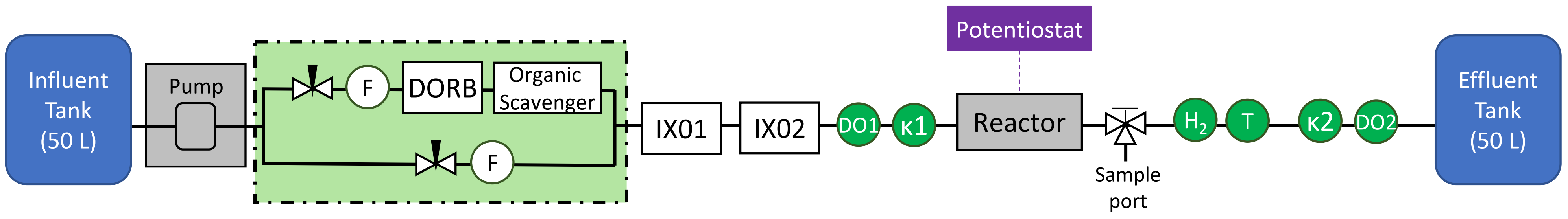
- Primary cathode reaction is oxygen reduction, but hydrogen evolution possible
  - hazards associated with hydrogen are easily controlled, but even easier if we avoid hydrogen evolution to begin with
- Secondary reactions reduce reactor efficiency
  - anodic oxide formation competes with silver dissolution
  - cathodic silver deposition depletes dissolved silver

Cathode Reaction Test: Methods

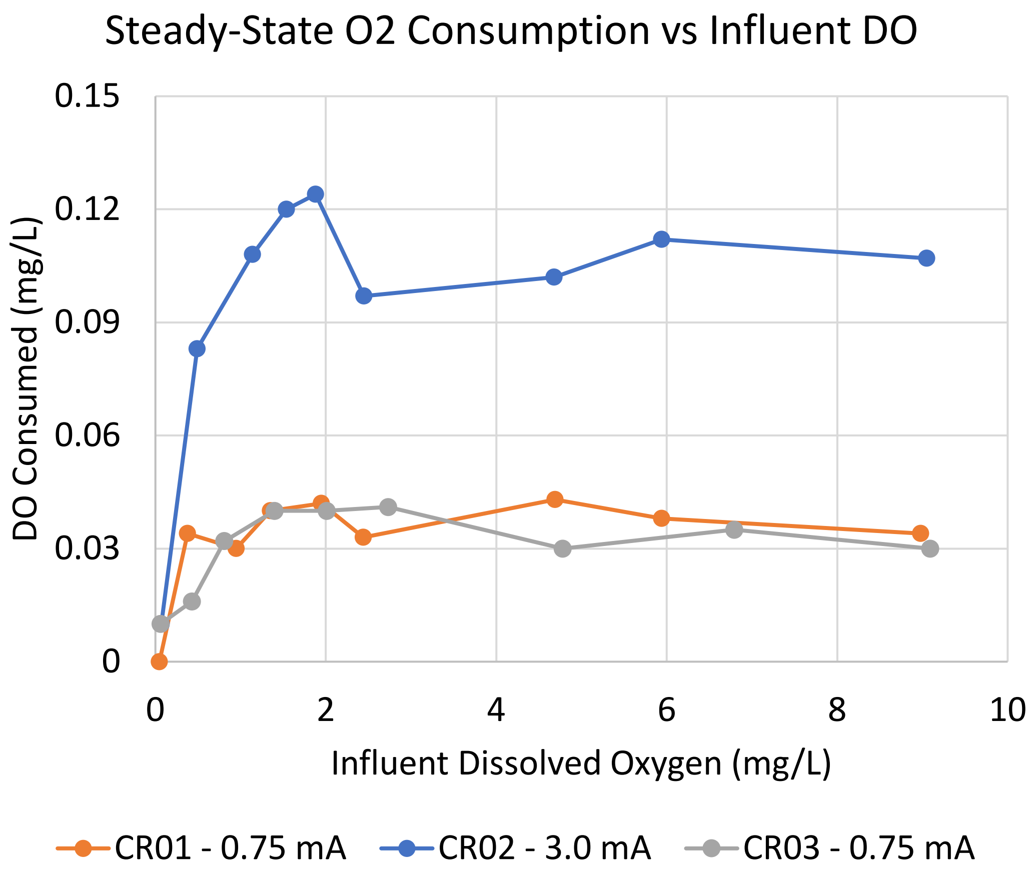
Test*	Spacer Config	# Electrodes	Electrode Mask	Test Rig Includes	Flowrate (mL/min)	Current (mA)	Polarity Reversal
Cathode Reaction 01	02	10	Electroplating tape	A,B,C	100	0.75	See text
Cathode Reaction 02	02	10	Electroplating tape	A,B,C	100	3	See text
Cathode Reaction 03	02	2	Electroplating tape	A,B,C	100	0.75	See text

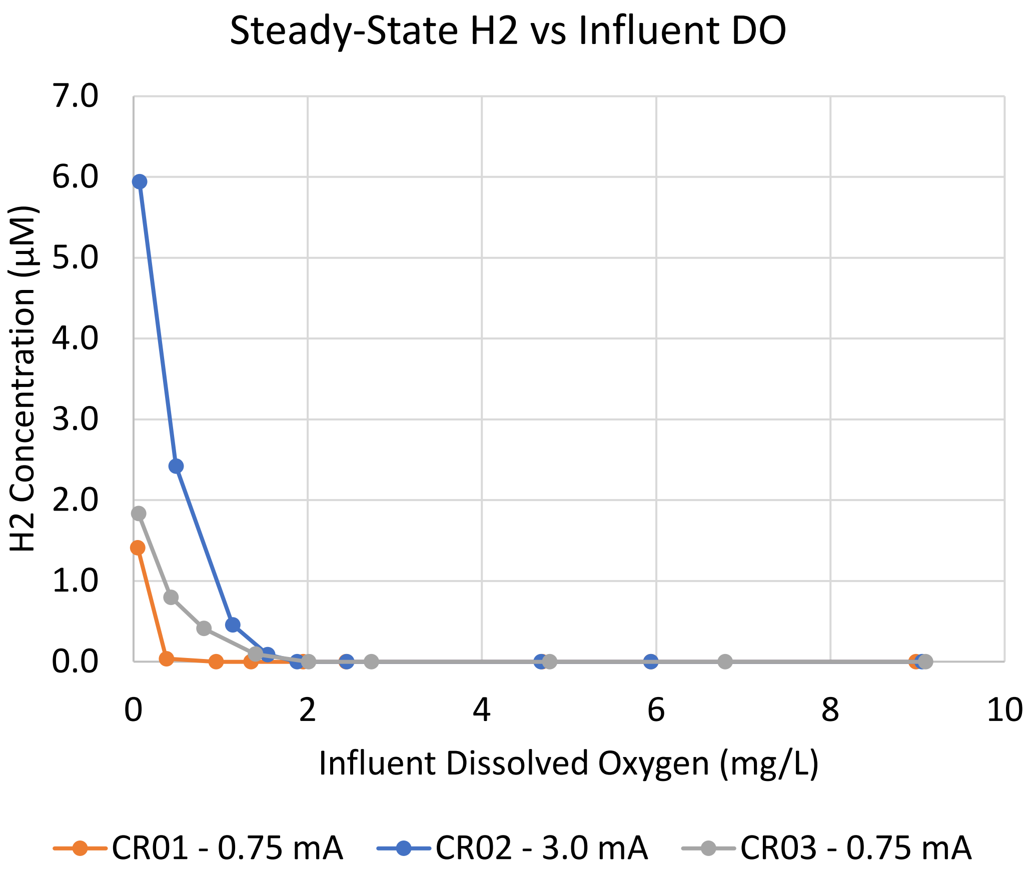
*The number after a test name indicates the test case. Note that some test cases had several steps or iterations, as described in Section IIC.

Dissolved oxygen removal hardware used to control influent DO.
Each test case included 9 steps of decrementing influent DO concentration, from saturated down to ~0.



Cathode Reaction Test: Results





Current Fractions

$$\varphi_i = \frac{I_i}{I_T}$$

Cathode: $\varphi_{O2} + \varphi_{H2} + \varphi_{Ag\_dep} = 1$

Anode: $\varphi_{Ag2O} + \varphi_{Ag+} = 1$

$$\varphi_{Ag+,meas} = \varphi_{Ag+} - \varphi_{Ag\_dep}$$

Faraday's law: $\dot{n}_i = \frac{I_i}{\nu_i F} = \frac{\varphi_i I_T}{\nu_i F}$

Mass balance: $\dot{n}_i = C_i \not V$

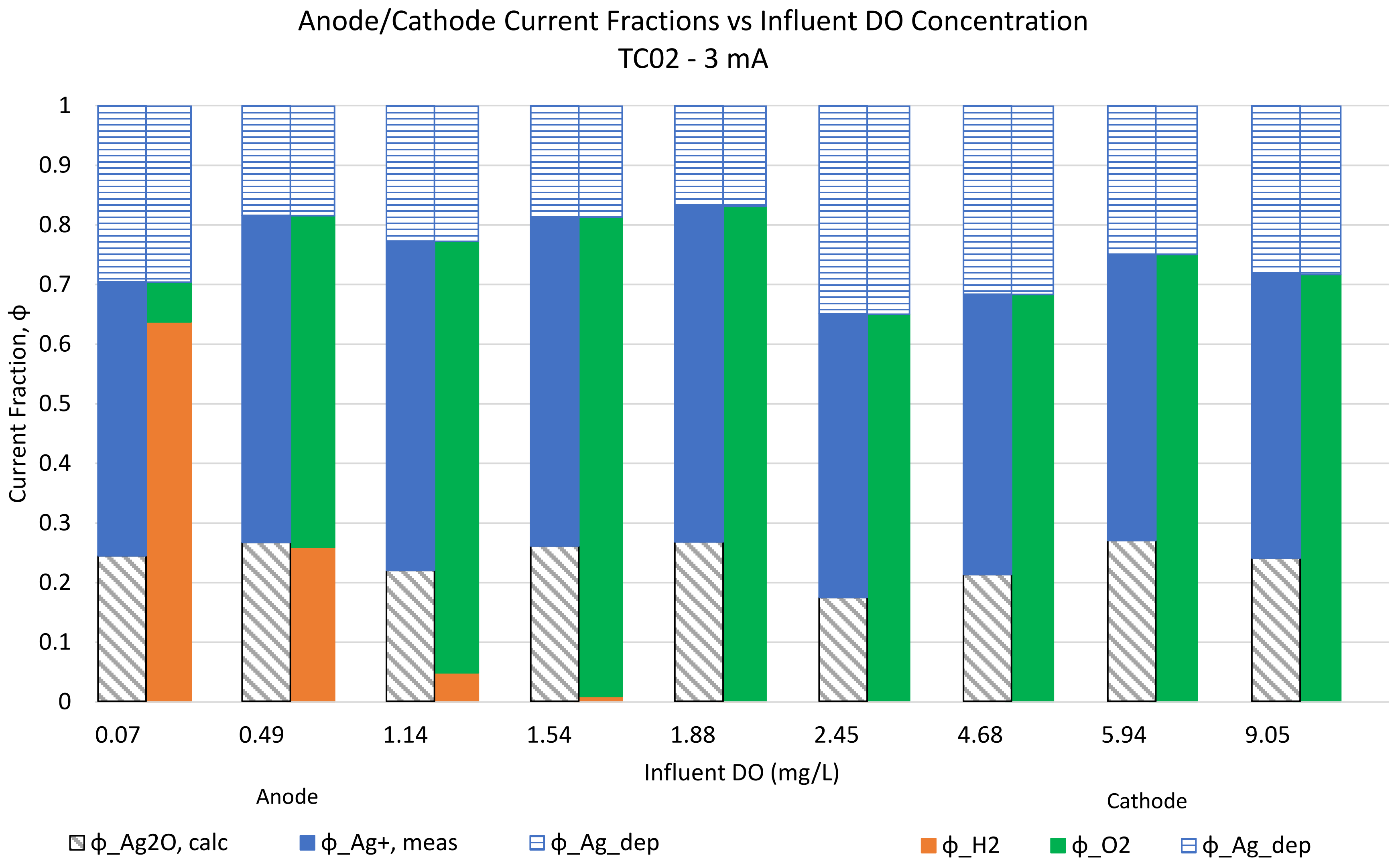
$$C_i \not V = \frac{\varphi_i I_T}{\nu_i F}$$

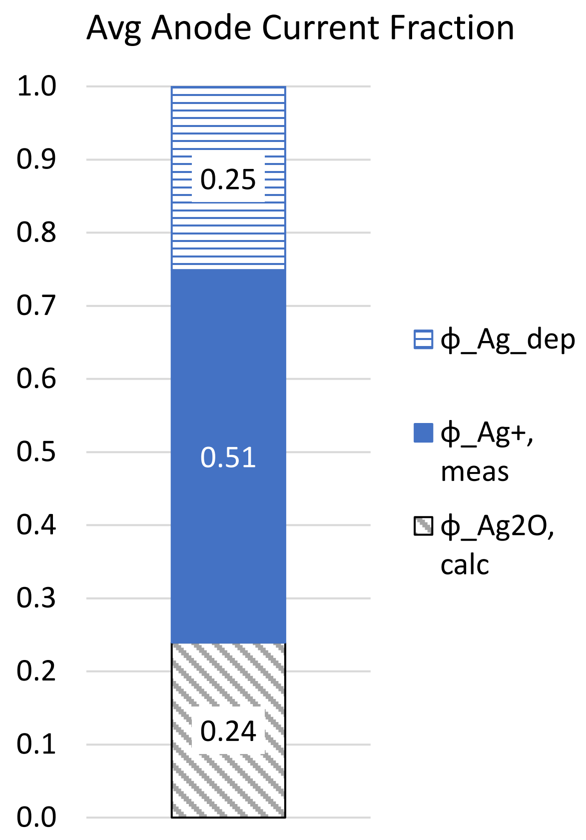
$\dot{n}_i$ is species rate of production/consumption
I_i is current of relevant reaction
ν_i is stoichiometric ratio of electrons to species
F is Faraday's constant

φ_i is current fraction
I_T is total current
C_i is species concentration
$\not V$ is volumetric flowrate

- Sum of currents for each reaction at electrode equals total current passed through electrode
- Current fraction defined as ratio of current of specific reaction to total current
- Current fractions sum to 1
- Measurement of effluent concentrations enables determination of $\dot{n}_i$ and φ_i

Cathode Reaction Test: Results





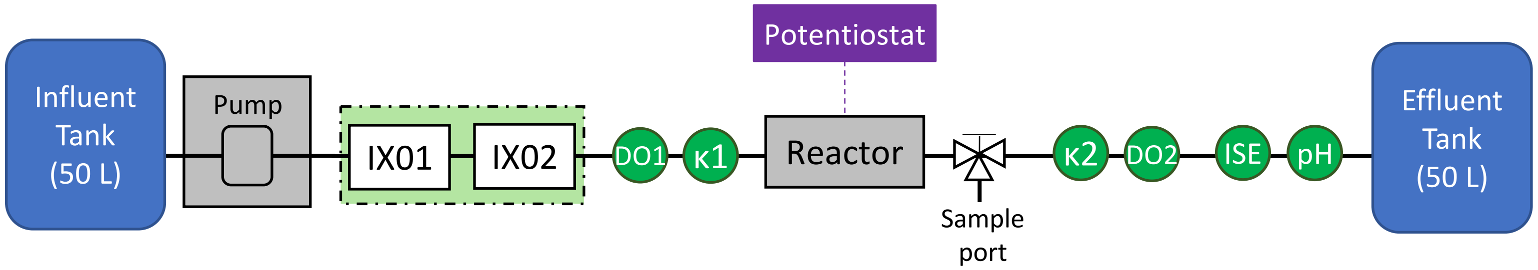
Elevated Concentration Test: Methods

Motivation: determine reactor performance at higher concentration

- Potentially useful for microbial shock and/or dormancy prep

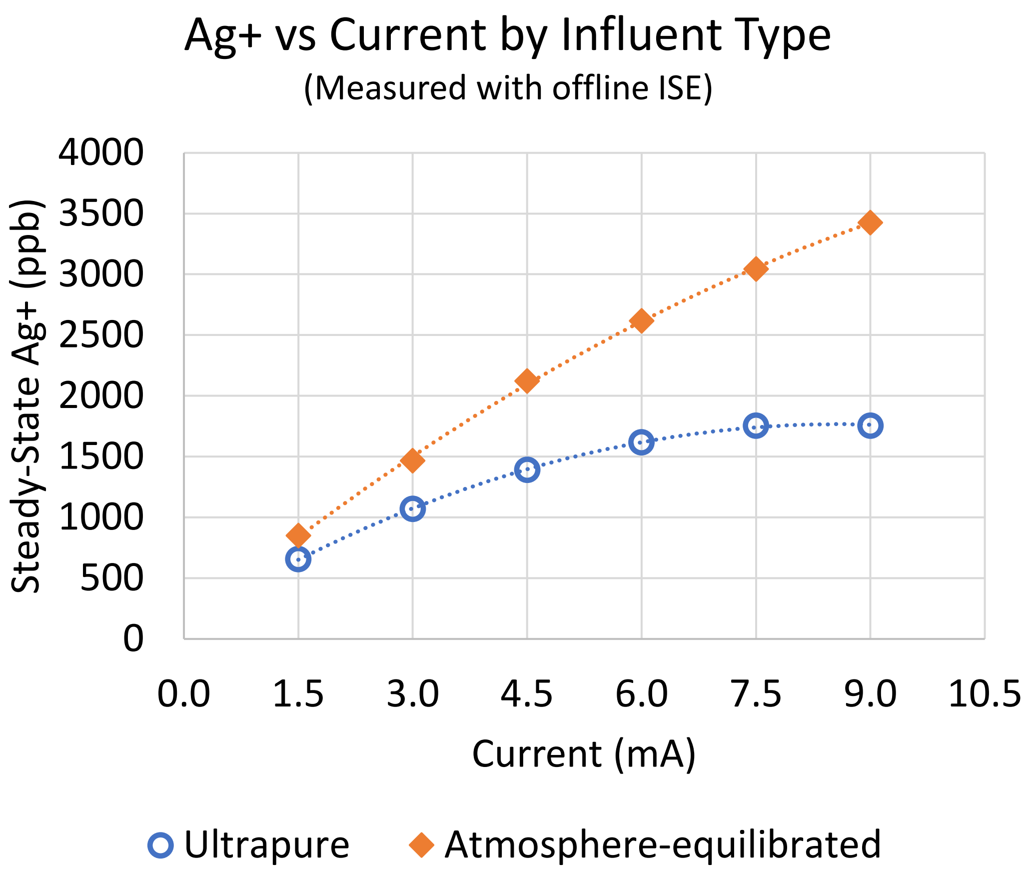
Method

- Increment current by 1.5 mA every 30 minutes
- Obtain effluent sample 25 minutes into each current step
- Perform one test case with IX included and another with IX omitted
  - When included, reactor influent is ultrapure water
  - When omitted, reactor influent is equilibrated with atmosphere (contains CO_2)



Elevated Concentration Test: Results

- For case with ultrapure influent, silver concentration approaches a maximum of ~1800 ppb for the reactor configuration used for this test
- For case with atmosphere equilibrated influent, silver concentration reaches nearly 10x nominal and has not yet peaked
- Lower pH in atmosphere-equilibrated water (from carbonic acid) discourages silver oxide formation and thus increases efficiency
- Either case enables significant increase in output silver concentration above nominal concentration of 200-400 ppb
    - Could be increased through reactor design optimization



Conclusions

- Interelectrode material properties do not have significant enough effect on silver deposit formation to serve as mitigation strategy
- Coupling electrode edge masking with polarity reversal is very effective for ensuring long-lasting reactor performance
- Parylene-C is an effective and appropriate coating for edge masking
- Hydrogen is only evolved at very low influent DO
- Full characterization of cathode reaction provides insights on optimization of reactor current efficiency
- Reactor can achieve significantly higher than nominal concentration
- This knowledge can be applied to design of next-generation prototype and ultimately a flight unit for long-duration space missions

Acknowledgements

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- Invaluable assistance, feedback, analysis, etc. was provided by:
  - Mike Callahan
  - Stacey Marshall
  - Dean Muirhead
  - Leopoldo Romero
  - Chris Carrier
  - Stuart Pensinger
  - Otto Estrada

Questions

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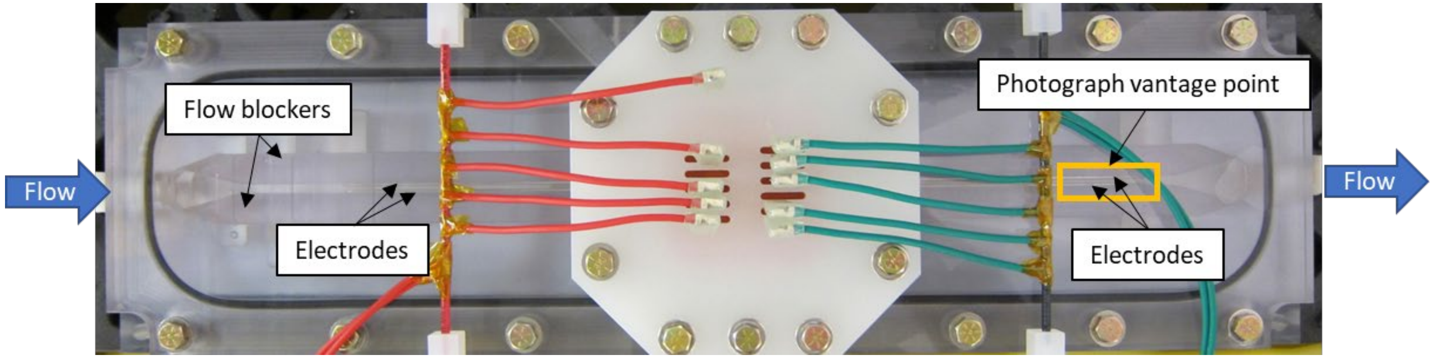
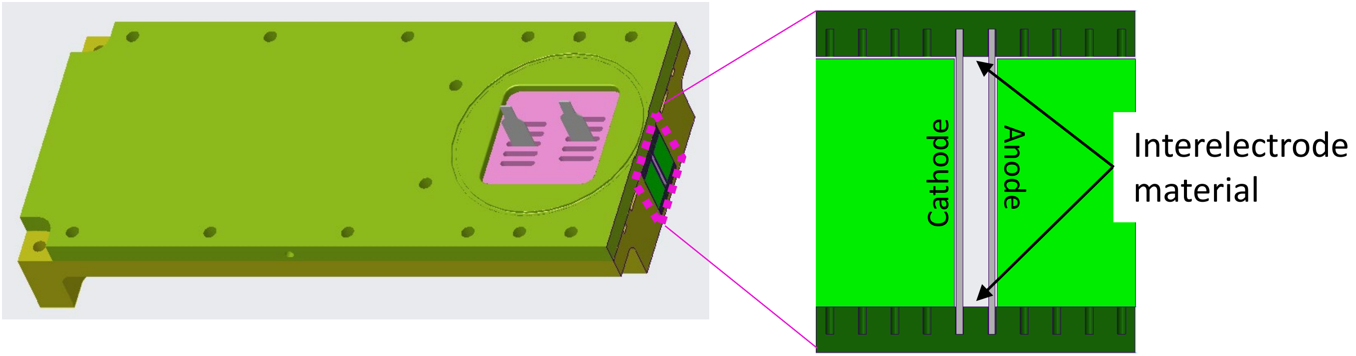
Backup

Test Article (Reactor) and Test Rig

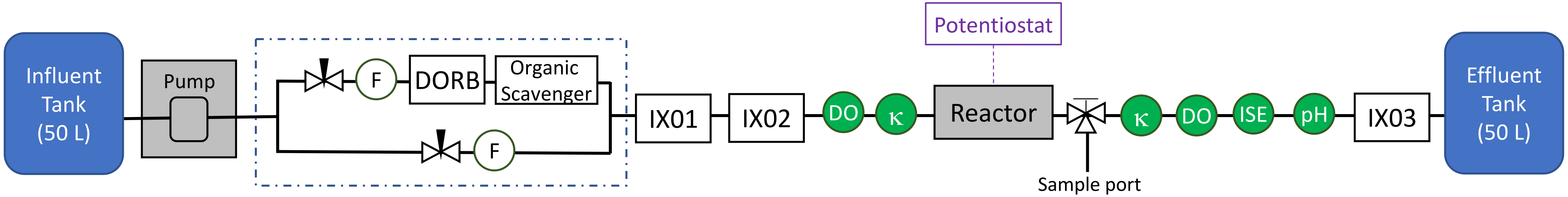
- Reactor enables:
  - Removable electrodes
  - Varied # of electrodes/spacing
  - View into electrode channel(s)
- Test Rig provides:
  - Water quality expected of spacecraft potable water
  - Control of dissolved oxygen (DO) concentration (dashed box)
  - Inline sensors and sample port

Reactor top view





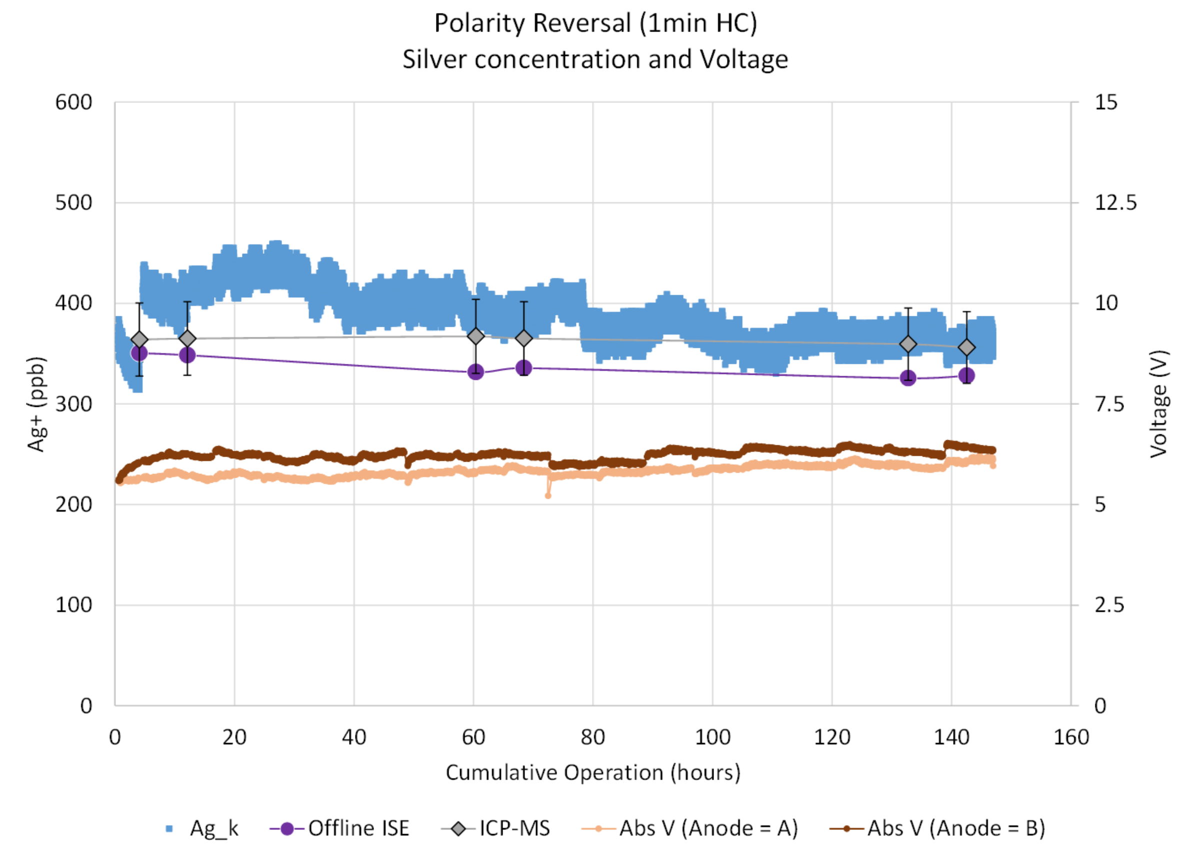
Test Rig Schematic

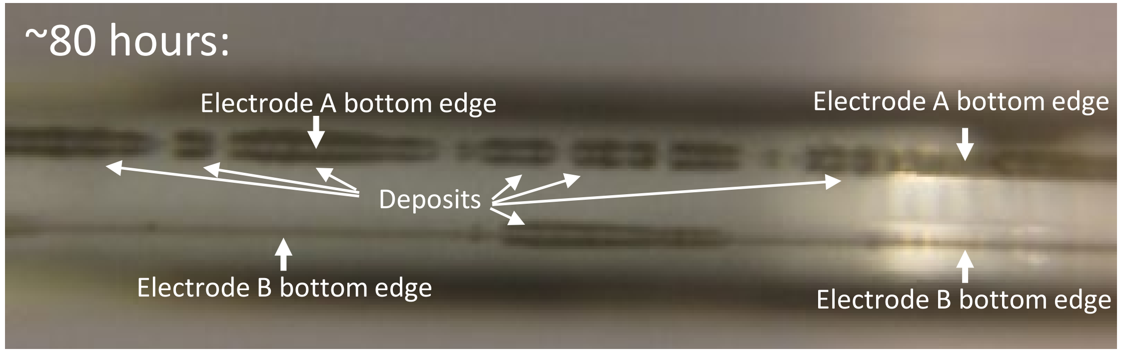


Baseline Test Case:

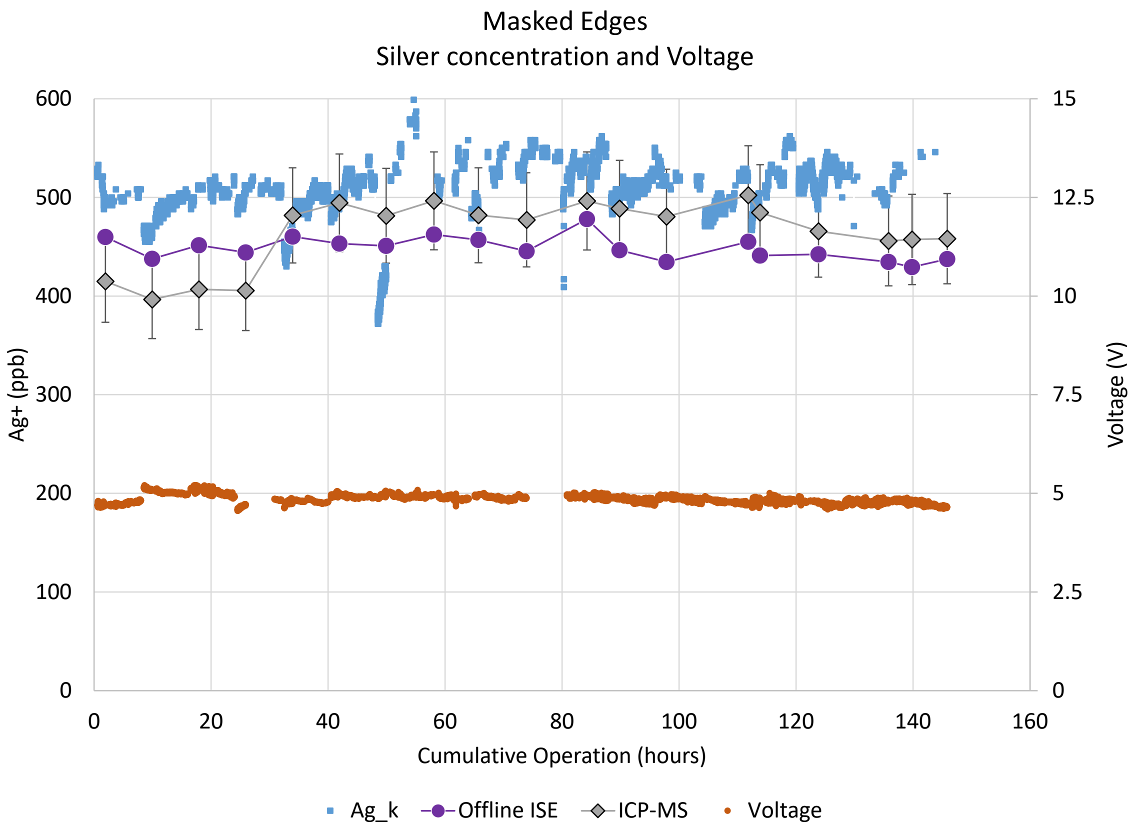
Polarity Reversal

- Polarity Reversal key points:
  - On a regular interval (every "half-cycle", HC), the direction of current is reversed; anode becomes cathode, vice versa
  - Keeps electrodes clean and prevents electrode bridging by re-dissolving fringes of silver deposits
  - Easy to implement in any design scheme
  - Previous testing ("Feasibility Test") used a 30min HC, which was too long; this test used a 1min HC
- System operated for 1 crew-year (146 cumulative hours) with no indication of bridging or other performance degradation
- Polarity reversal prevented deposits from growing perpendicular to electrodes. Deposits formed along electrode edges, but did not grow across gap and reached steady-state at ~80hrs
  - Deposits had no impact on performance or water quality
  - Could possibly be eliminated by increased reversal frequency and/or use of alternate interelectrode material
  - Can be eliminated by combining with other technique

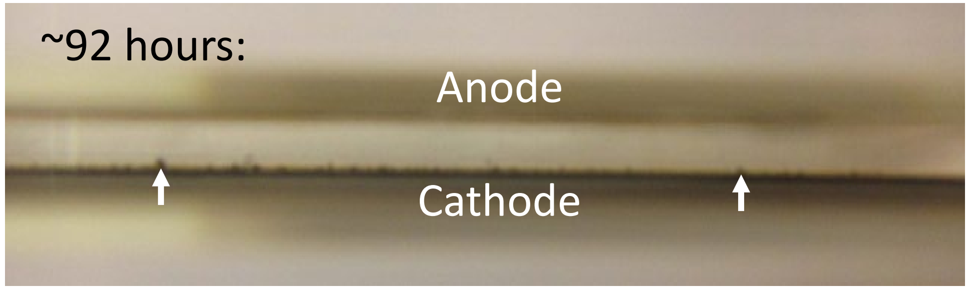


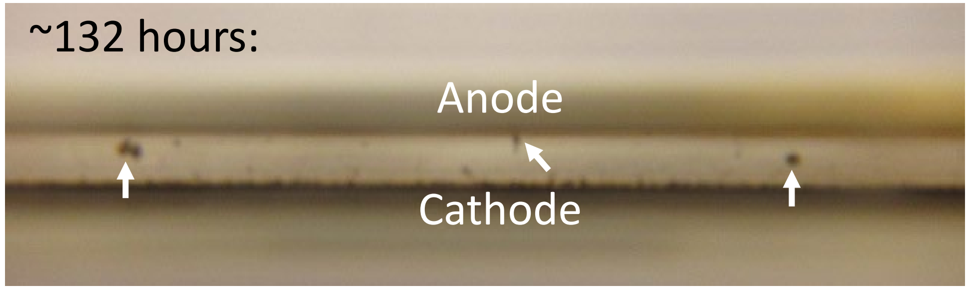


Masked Edges



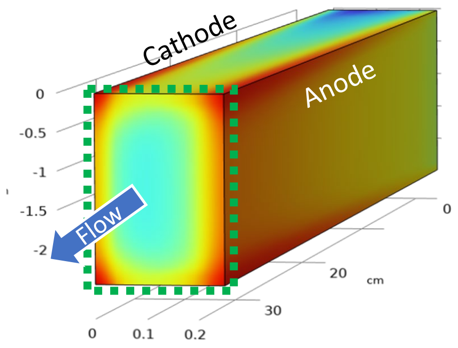
- Masked edges:
  - Prevent high silver concentration in corners of fluid channel
  - Separate active surface of electrode from interelectrode material and from regions of low fluid velocity
- Operated in constant polarity (no reversal)
- System operated for 1 crew-year (146 cumulative hours) with no indication of bridging or other performance degradation
  - 25% increase in current efficiency over baseline test case
- Flakes observed at cathode
  - Silver dendrites that break off/settle
  - First hint of flake formation at ~36hrs
  - Undesirable, but fully preventable with polarity reversal



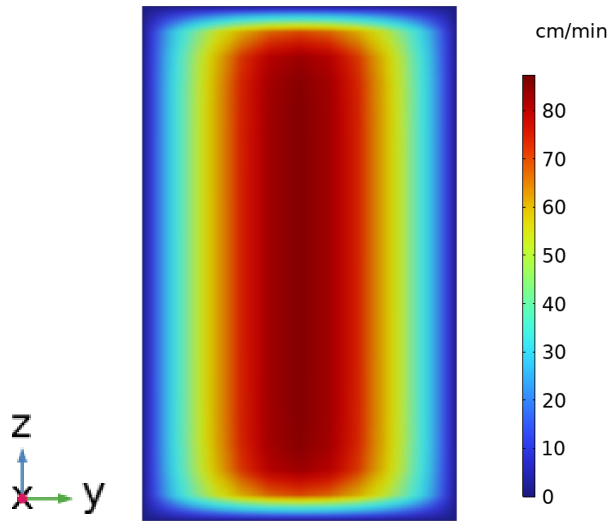


Preliminary Modeling

Steady-State [Ag+] Distribution in Alternate Configurations



Fluid Velocity Magnitude



Silver Concentration