Non-Fouling, Low-Cost, Electrolytic Coagulation & Disinfection for Treating Flowback and Produced Water (FPW) for Reuse

Award No. DEFE0031854

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U.S. Department of Energy

National Energy Technology Laboratory

Resource Sustainability Project Review Meeting

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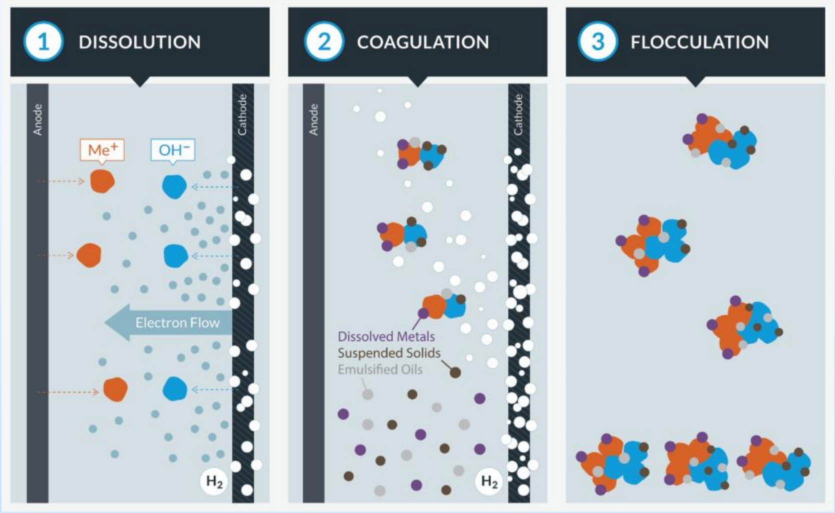
Project Overview

- **Funding**: DOE $935,254   Matching $234,725
- **Original**: January 1, 2020 through December 31, 2021
- **Modified**: January 1, 2020 through June 30, 2023
- **Participant**s: University of Arizona, Water Tectonics (Everett, WA) and Franklin Mountain Energy (Jal, NM)
- **Objective**: Develop a more effective and lower cost process for treating flowback and produced water (FPW)

Background: Current State of the Art FPW Treatment

- Coagulation-flocculation processes remove particulates and emulsified oil
- 15 of 16 commercialized FPW treatment use coagulation-flocculation processes
- Commercialized electrocoagulation processes: Halliburton CleanWave®, Origin Clear Clean-Frac®, BakerCorp-Kaselco, Bosque MWR®, Veolia ShaleFlow™



- **Coagulation-flocculation processes add Fe^{2+}/Fe^{3+} or Al^{3+} ions into the water**
- Reactions with water form high specific surface area (>30 m^2/g) precipitates that adsorb particulates, bacteria and emulsions

$$Fe^{3+}_{(aq)} + 3\,H_2O \rightarrow Fe(OH)_{3(s)} + 3\,H^+$$
$$Al^{3+}_{(aq)} + 3\,H_2O \rightarrow Al(OH)_{3(s)} + 3\,H^+$$

Background: Electrocoagulation

- Iron or aluminum sheet metal anodes are dissolved into the solution via electrochemical oxidation

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$$
$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-$$

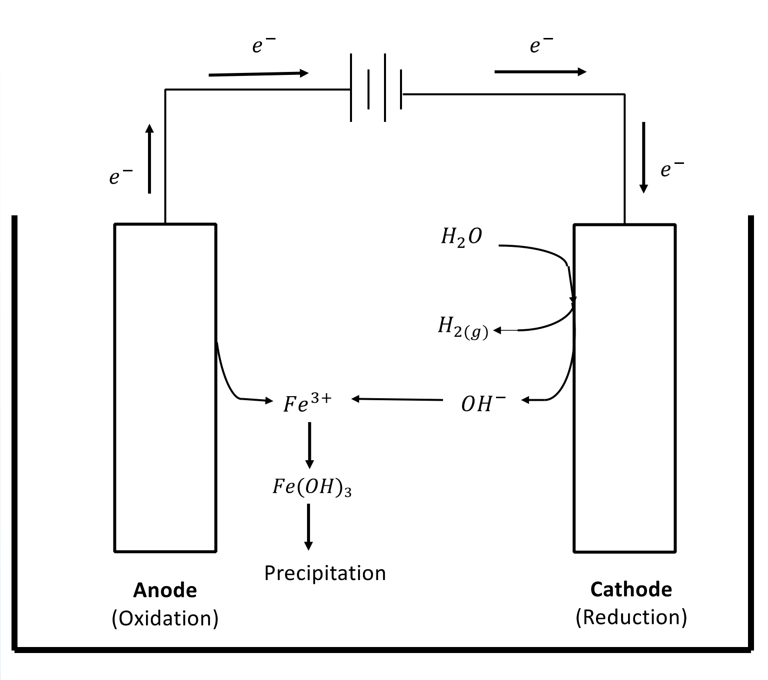
- Acid produced via precipitation reactions

$$Fe^{3+}_{(aq)} + 3\,H_2O \rightarrow \ Fe(OH)_{3(s)} + 3\,H^+$$
$$Al^{3+}_{(aq)} + 3\,H_2O \rightarrow \ Al(OH)_{3(s)} + 3\,H^+$$

is removed at the cathode via electrochemical reduction

$$2H^+ + 2e^- \rightarrow H_{2(g)}$$

- Process does not change the pH of the solution



Problems with electrocoagulation:
1) high cost of sheet metal anodes
2) low current densities require very large anode surface area
3) dissolved O_2 concentrations limits maximum iron coagulant dose to ~1 mM

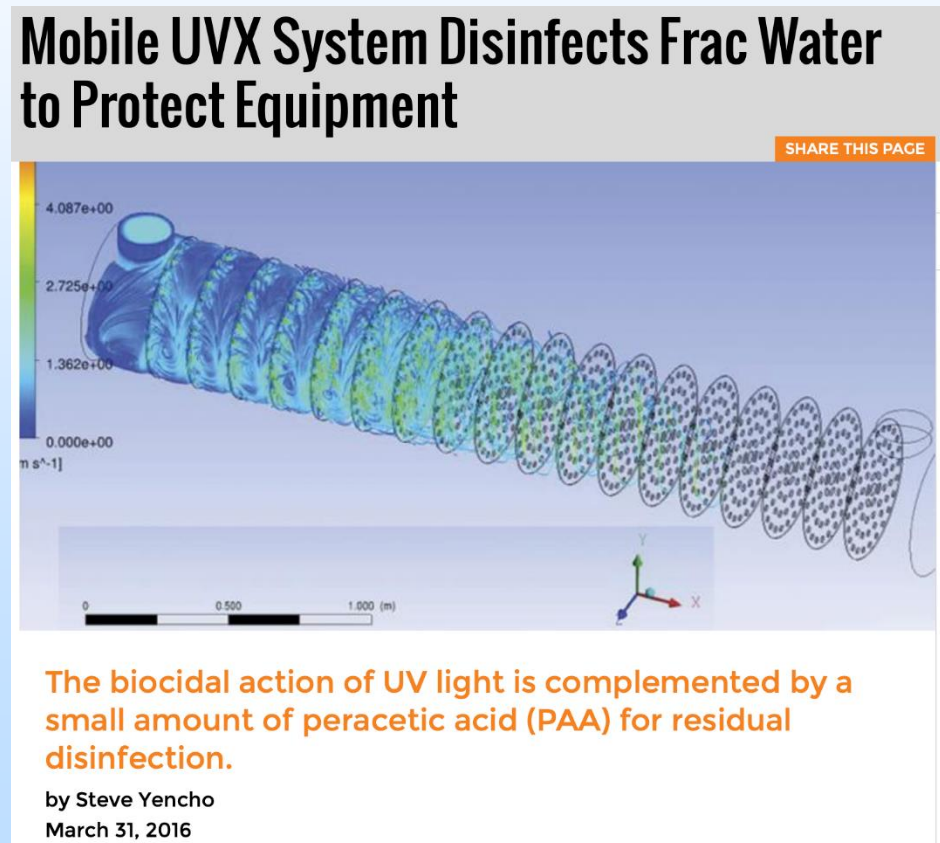
$$2\ \mathrm{Fe}^{2+} + \ 2\ \mathrm{H}^+ + 0.5\ \mathrm{O}_2 \rightarrow 2\ \mathrm{Fe}^{3+} + \mathrm{H}_2\mathrm{O}$$

Background: Current State of the Art FPW Disinfection

- Disinfection using UV radiation, onsite generated hypochlorite (HOCl) or ozone
- Oxidation of Cl^- ions produces HOCl disinfectant:

$$2Cl^-_{(aq)} \rightarrow Cl_{2(aq)} + 2e^-$$

$$Cl_{2(aq)} + H_2O_{(l)} \rightarrow HOCl_{(aq)} + H^+{}_{(aq)} + \ Cl^-_{(aq)}$$



Technical Approach: Electrolytic Coagulation & Disinfection (ECD)

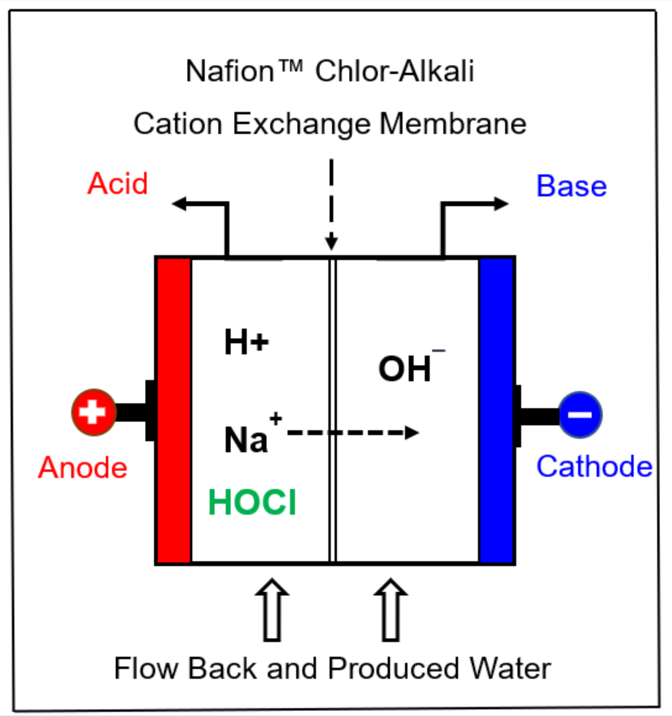
An electrochemical cell is used to split water into acid and base.

anode reactions

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-$$
$$2\,Cl^-_{(aq)} \rightarrow Cl_{2(aq)} + 2e^-$$

hydrolysis of Cl_2

$$Cl_{2(aq)} + H_2O \rightarrow$$
$$HOCl + H^+ + Cl^-$$



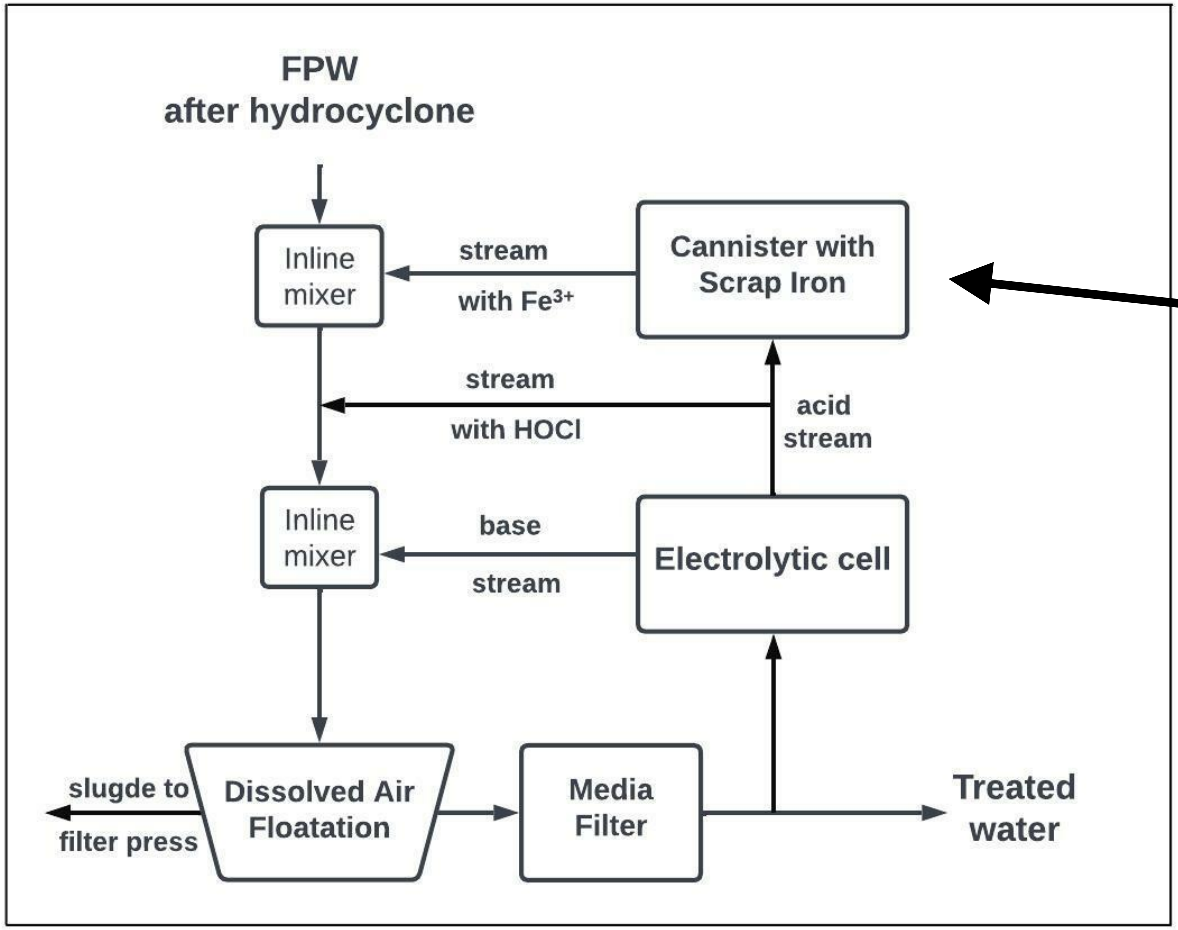
cathode reaction

$$4\,H_2O + 4\,e^- \rightarrow 2\,H_2 + 4\,OH^-$$

Technical Approach: Electrolytic Coagulation & Disinfection (ECD)

ECD uses acid to dissolve iron scrap metal to produce Fe^{3+} coagulant.

$$iron\ reaction \quad 3\,H^{+} + \ Fe \rightarrow Fe^{3+} + 1.5\,H_2$$



Process Description: ECD Advantages

1. lower cost for coagulant than conventional EC
2. high current density allows for significantly smaller system
3. high Fe doses can be delivered (ECD not limited by dissolved oxygen)
4. eliminates significant labor for changing electrodes
5. disinfectant is produced

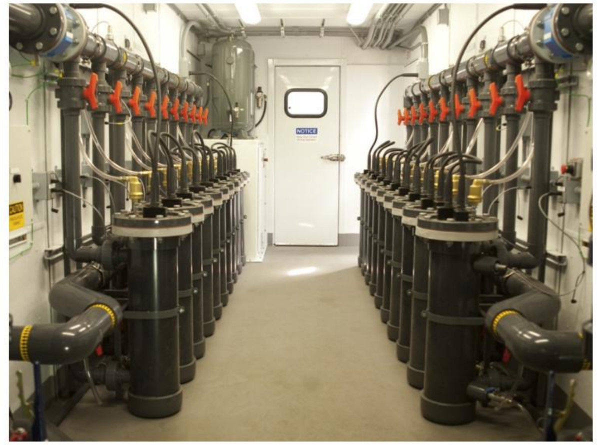


Figure 18. Picture of Halliburton Clean Wave® process utilizing cylindrical electrochemical cells and metal disk electrodes. (1) Note there are only 20 cells per container box and >100 cells are needed to treat 1 MGD.

Figure 19. Commercial electrochemical cells from Electro Cell North America. Left: ElectroSyn Cell® used in this study with 0.04 m^2 per electrode. Right: ElectroProd Cell® with 0.4 m^2 per electrode. A single ElectroProd Cell® operating at 100 mA/cm^2 is sufficient for treating 1 MGD of FPW.

Project Scope

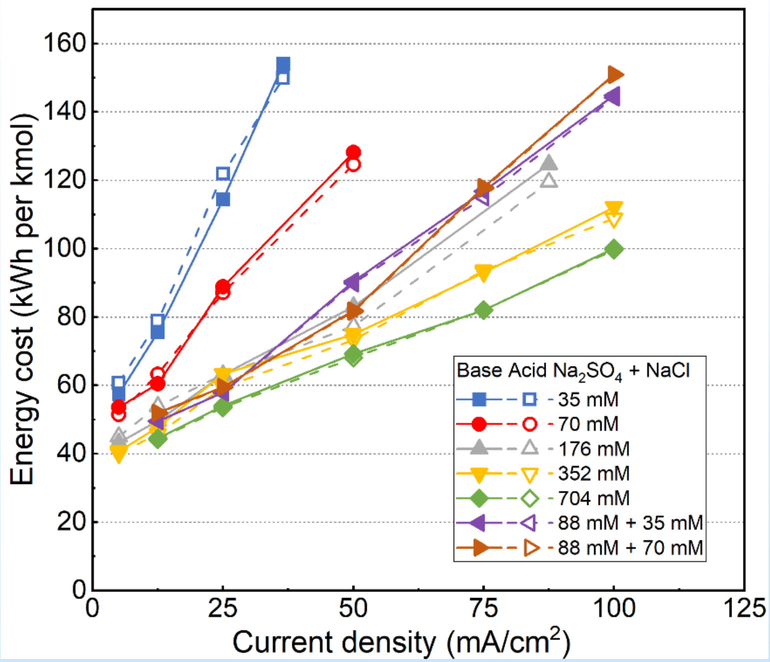
- Develop and test a new method for delivering a Fe^{3+} coagulant and disinfectant
- System will remove: suspended solids, emulsified oil, H_2S, microorganisms and some scale-forming cations
- Target cost savings of at least 50% compared to current practices
- Design, construct and test an automated treatment system for use in pilot demonstrations with FPW flow rates of 25 gallons per minute
- Laboratory testing to determine system outcomes from simulated FPW
- Test the treatment system at oil and gas production facilities in New Mexico
- Develop specifications for operating the treatment system for different water qualities
- Write operations and maintenance manual for scale-up of the technology

Progress: System Construction

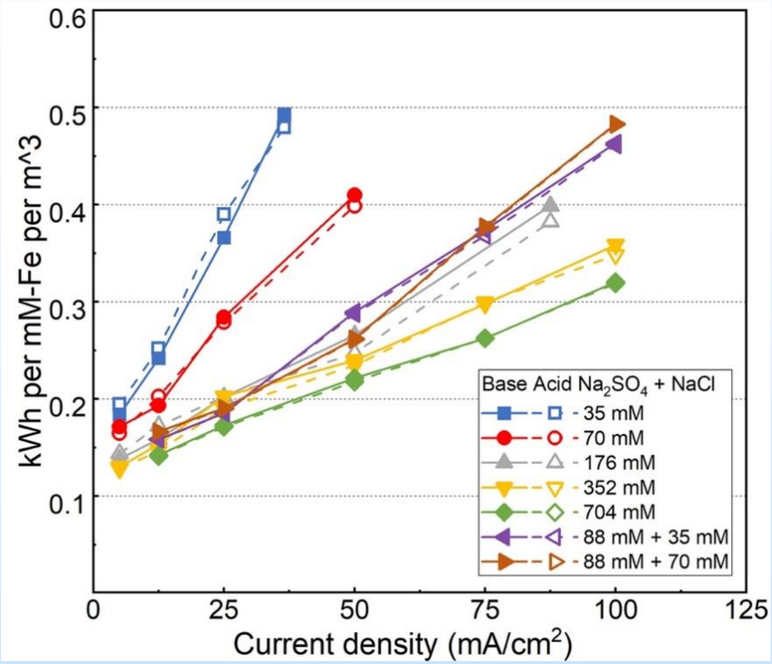
- System designed by UA and constructed by Water Tectonics (Everett, WA)

- System delivered to UA on 12/3/2020

Progress: Electrochemical Experiments



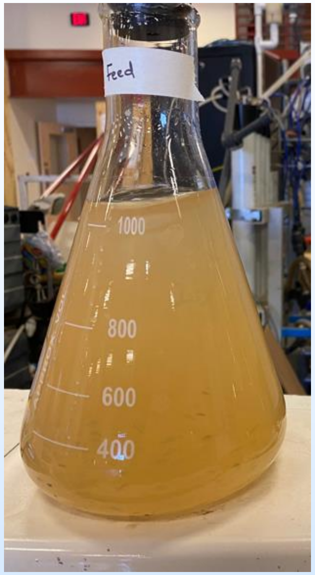
Energy requirements per kmol of acid or base produced for different electrolyte solutions



Electrical energy in kWh required for delivering a 1 mM Fe^{3+} dose per cubic meter of water as a function of current density

Progress: Suspended Solids Removal

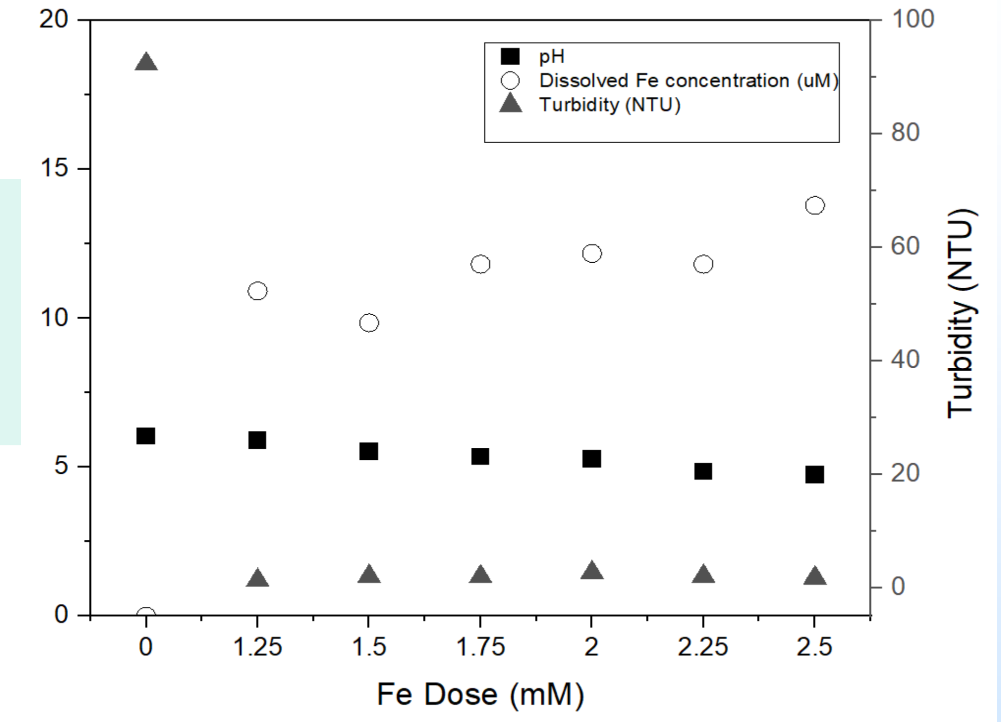
Feed Water



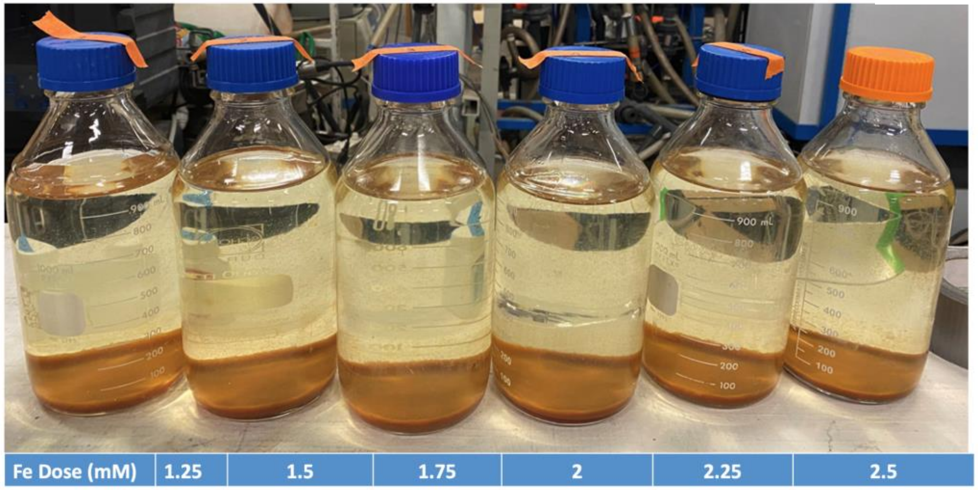
pH

or

[Fe]



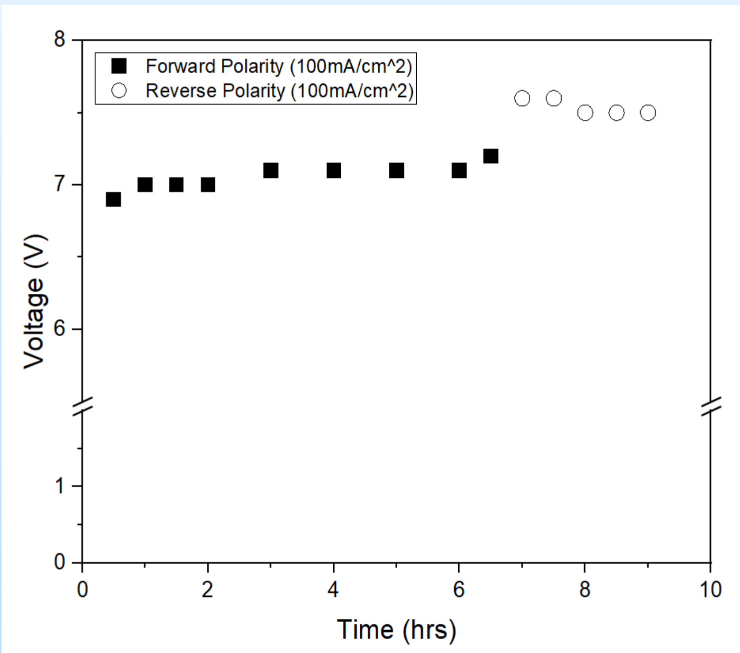
Treated Water



- turbidity reduced to 2-4 NTU, below guideline of 10 NTU
- dissolved Fe^{3+} <0.75 mg/L, below guideline of 10 mg/L

Progress: No Electrode Fouling

Parameter	Jal Well	Experiment
pH	7.3	7.6
Ca^{2+}	4247 mg/L	4240 mg/L
Mg^{2+}	727 mg/L	730 mg/L
HCO_3^-	2867 mg/L	3050 mg/L
Na^+	42,720 mg/L	36,800 mg/L
Cl^-	65,800 mg/L	56,800 mg/L



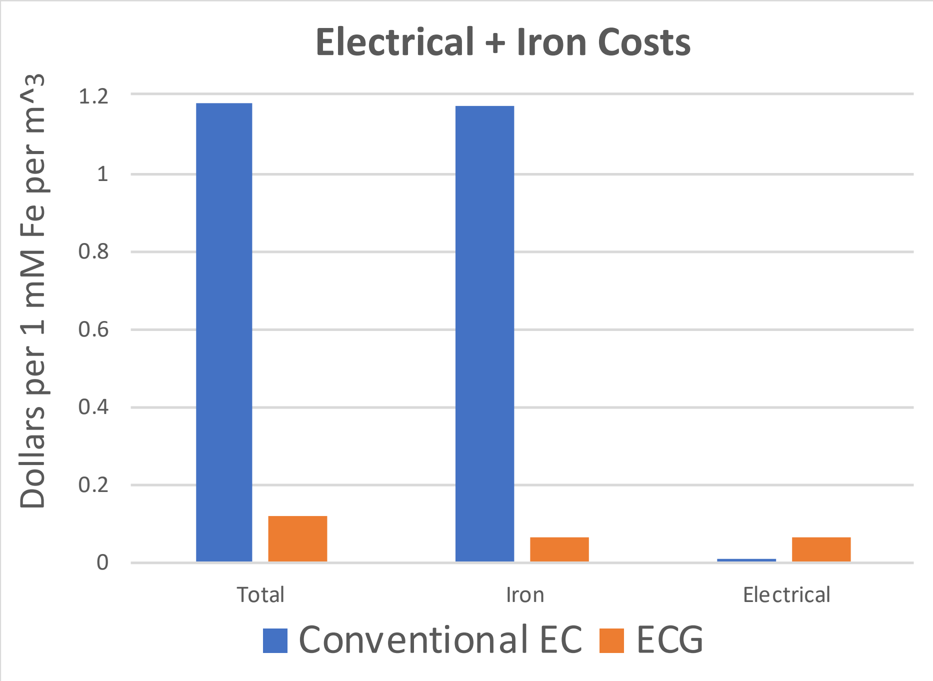
Cathode and cathode facing membrane after 2 hours of operation at a current density of 100 mA/cm^2 without cleaning cycle.

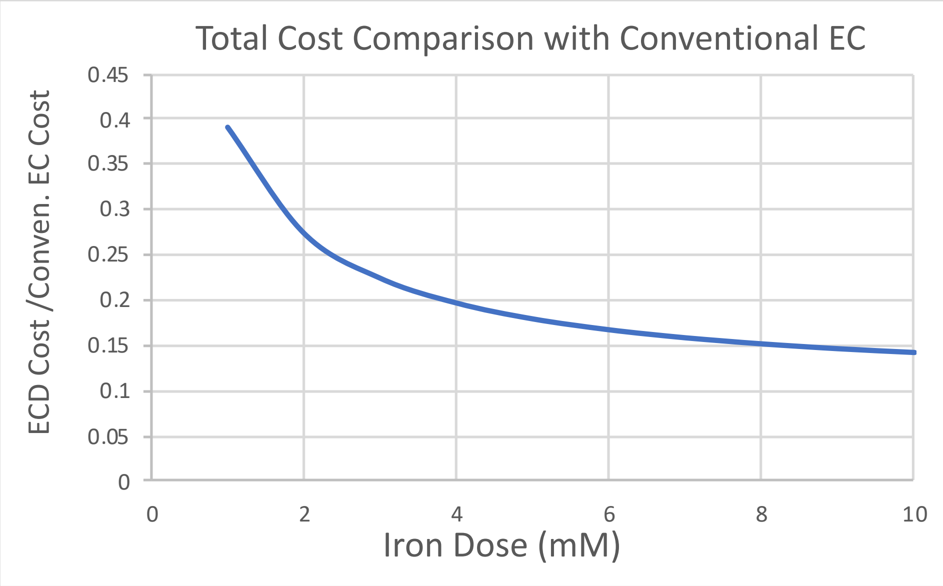
Electromagnetic water conditioner to reduce precipitation on surfaces.

Progress: Economic Analysis

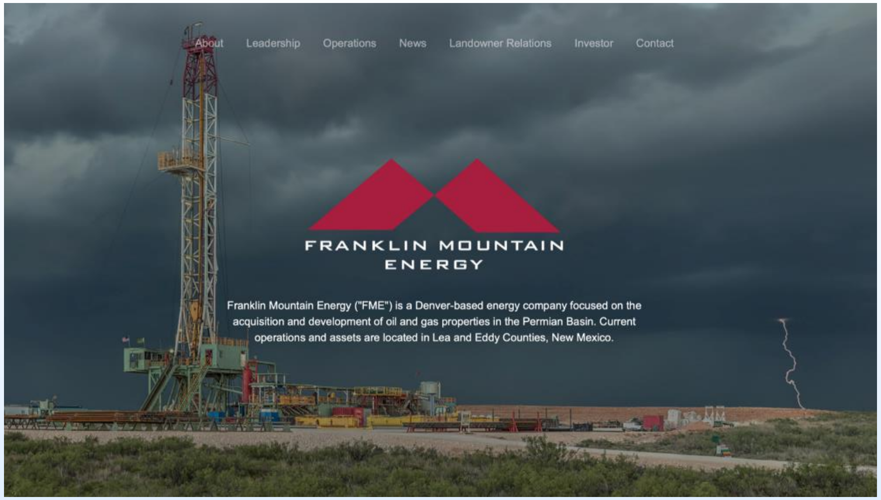
Treatment costs for operating the system at 50 gpm over a 10-year period with a coagulant dose of 2 mM-Fe^{3+}.

Item	**Amount**
Capital Cost (actual cost from this project)	\$368,750
Interest Expense @ 5%/yr	\$184,375
Capital plus Interest	\$553,125
Operational Expense @\$0.12/mM-Fe/m^3	\$238,575
Total Cost for 10 years	\$791,700
Volume of FPW Treated @ 50 gpm	994,064 m^3
Cost per m^3 FPW Treated	\$0.80/m^3
Cost per bbl FPW Treated	**\$0.13/bbl**





Future Plans – Field Test in Jal, NM



Critical Properties of FPW available at Franklin Mountain Energy production site in Lea County, NM (Jal, NM).

Water Source	Ca^{2+} (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	TDS (mg/L)	Supersaturated Species
SeaWolfFreshwater	359	78	1122	4784	none
Pilot Water	3025	1098	71953	121544	$BaSO_4$, $SrSO_4$, FeS $FeCO_3$, $CaCO_3$, $CaSO_4$
Ross SWD (038)	4102	366	54600	87790	$BaSO_4$, FeS, $FeCO_3$, $CaCO_3$,
Ross SWD (036)	850	1208	58700	96398	$BaSO_4$, FeS, $FeCO_3$, $CaCO_3$
Tatanka Federal 1H	3671	976	63763	108715	$BaSO_4$, $SrSO_4$, FeS $FeCO_3$, $CaCO_3$, $CaSO_4$
Parade 001H	4080	264	79541	131607	$CaCO_3$
Tatanke 001H	2240	476	55395	93799	$CaCO_3$
Proxy 001H	4080	332	86643	144036	$CaCO_3$
County Fair 001H	5200	215	92325	152455	$CaCO_3$

Arial photograph of field test site located in Lea County, NM. Approximate coordinates are 32.166285, -103.338411.

Outreach and Workforce Development

Outreach

- License technology to Water Tectonics
- Field Test with Franklin Mountain Energy

Workforce Development – Training Activities

- Post Doctoral Researcher: Jiale Xu (Asst. Prof. N. Dakota St. U.)
- Graduate Student, M.S.: Truc Vo (Engineer, Arizona Water Co.)
- Graduate Student, Ph.D.: Tenzin Phakdon (graduation, June 2023)

Summary

Key Findings (laboratory experiments)

- system performance similar to conventional EC
- treated water properties (suspended solids, dissolved Fe, etc.) satisfy guidelines for reuse in hydraulic fracturing and secondary oil recovery
- total cost is < 25% of that for conventional EC

Field Testing

- needed to validate technology in complex water matrices
- begins November 2022

Appendix: Organization Chart

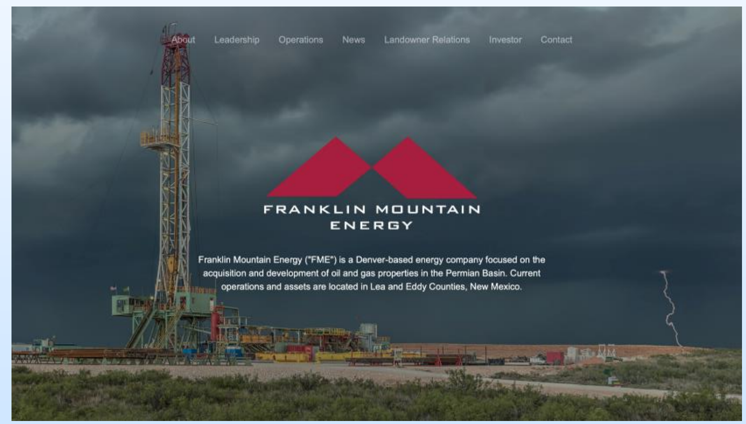
Water Tectonics, Everett, WA
Project Lead: Jason Mothersbaugh, VP

- construct treatment system
- pilot test at field site

University of Arizona, Tucson, AZ
Project Lead: James Farrell
Research Team: Jiale Xu (post-doc)
Tenzin Phakdon (PhD candidate)
Truc Vo (MS candidate)

- design treatment system
- laboratory testing
- assist in pilot test at field site

Franklin Mountain Energy, Jal, NM
Project Lead: Mark Hinaman



- host field test

Appendix: Gantt Chart

Task	Assigned Resources	Jan 22	Feb 22	Mar 22	Apr 22	May 22	Jun 22	Jul 22	Aug 22	Sept 22	Oct 22	Nov 22	Dec 22	Jan 23	Feb 23	Mar 23	Apr 23	May 23	Jun 23
1.0 Project Management & Reporting	Farrell / Mothersbaugh																		
1.1 Prepare Project Management Plan	Farrell / Mothersbaugh																		
1.1 Milestone Date = 2/25/20	completed																		
1.2 Prepare Technology Management Plan	Farrell / Mothersbaugh																		
1.2 Milestone Date = 9/21/20	completed																		
1.3 Prepare Data Management Plan	Farrell / Mothersbaugh																		
1.3 Milestone Date = 4/20/20	completed																		
Prepare Continuation Application	Farrell / Mothersbaugh		DP																
Milestone Date = 2/28/2022	completed																		
1.4 Prepare Final Report & Dev Strategy Plan	Farrell / Mothersbaugh																		
1.4 Milestone Date = 6/30/23																			
2.0 Order Equipment & Construct Treatment System	Farrell / Mothersbaugh																		
2.0 Milestone Date = 12/3/2020	completed																		
3.0/4.0 Cell and Dosing System Testing	UA PD#1 / UA PD#2																		
3.0/4.0 Milestone Date = 11/30/21	completed																		
5.0 Test system performance on simulated FPW	UA PD#1 / UA PD#2																		
5.0 Milestone Date = 8/31/22	completed																		
6.1 Test system at FME Field Site	Water Tectonics Team																		
6.1 Milestone Date = 4/30/23	UA/Water Tectonics																		
7.0 Develop Design & Operations Manual	Farrell / Mothersbaugh																		
7.0 Milestone Date = 6/30/23	UA/Water Tectonics																		

DP= Decision Point