Advanced Integrated Technologies for Treatment and Reutilization of Impaired Water in Fossil Fuel-based Power Plant Systems

Thursday April 21st, 2016

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Institute for Sustainable Energy and the Environment

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OHIO UNIVERSITY

Institute for Sustainable Energy and the Environment (ISEE)

Institute Facts

- Established in 2004
- Faculty: 3
- Staff: 5 (Engineers and scientists)
- Graduate Students: 12
- Undergraduate Students: 14
- Space: 14,000 ft^2

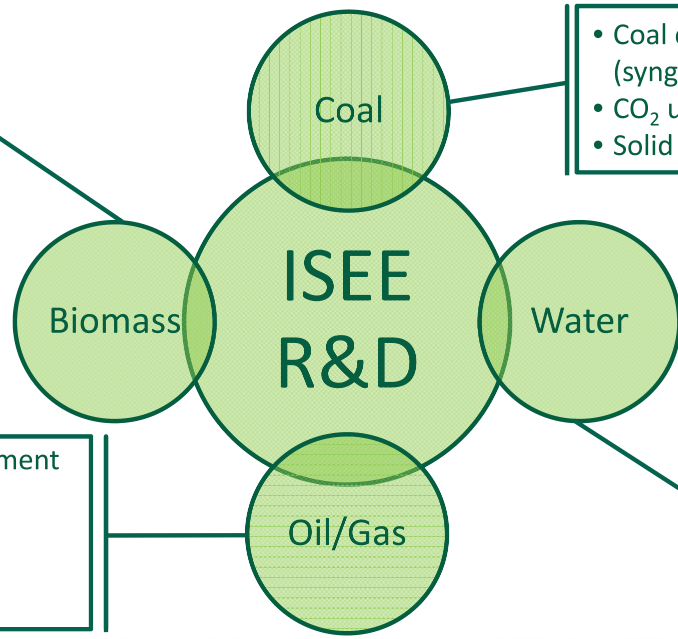
Core Capabilities

- Thermocatalytic Processes
- Process Engineering & Design
- Process Modeling & Simulation

Home to Two Ohio Third Frontier Technology Commercialization Centers

- Algae growth/conversion
- Thermocatalytic conversion

- Coal conversion (syngas & pyrolysis)
- CO_2 utilization
- Solid oxide fuel cells



- Wastewater management
- Electrochemical conversion
- SAGD operations
- Fracturing simulation

- Nutrient recovery
- Acid mine drainage
- NORM removal
- Hydrocarbon removal

Project Specifics and Team

OHIO Project Team

•Project Management

•Jason Trembly (OHIO)

•Process Development

•Xingbo Liu (WVU)

•David Ogden (OHIO)

•Wen Fan (OHIO)

•Shyler Switzer (OHIO)

•Graduate Student(s)

•Process Engineering

•Dora Lopez (OHIO)

•Matt Usher (AEP)

It is strongly recommended that application submission begin well in advance (at least 48 hours) of the Application Due Date.

NOTE: Applications in response to this FOA must be submitted through Grants.gov.

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Project Specifics

- DOE/NETL Cooperative Agreement No. DE-FE0026315
- DOE Project Manager: Barbara Carney
- Principal Investigator: Jason Trembly

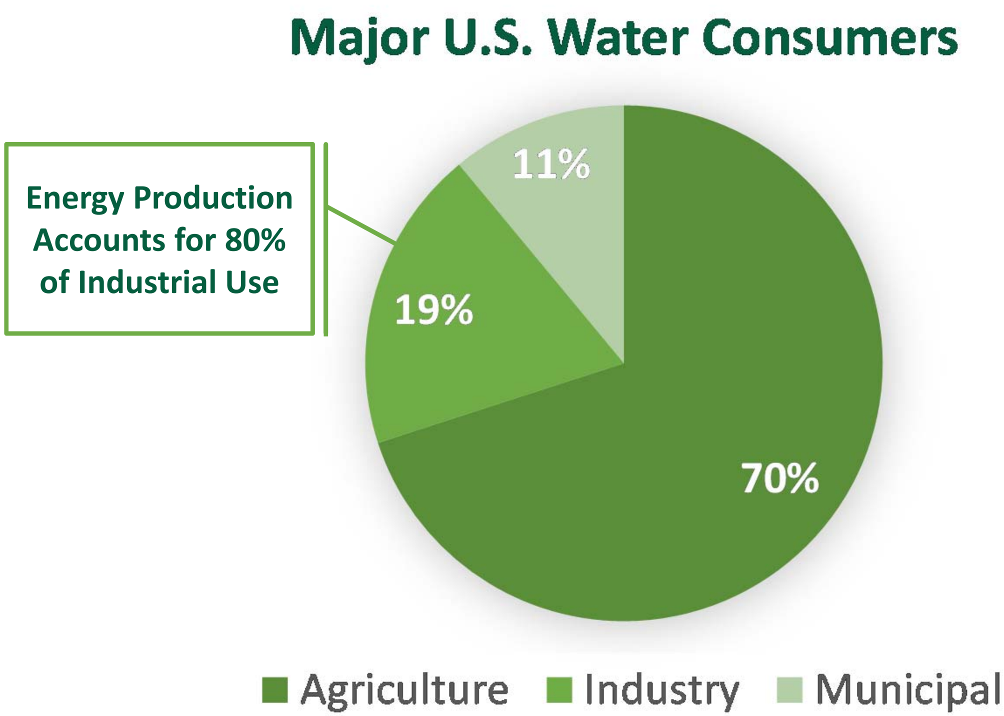
Project Funding

- DOE Funding: $750,000
- Cost Sharing: $187,500

Period of Performance

- September 1, 2015 to February 28, 2017

Water-Energy Constraints



U.S. Water Supply

- Critical to U.S. energy/economic security
- Major constraints
  - Increasing population
  - Increasing energy production
  - Competing demands
  - Climate change
- Power generation
  - Withdraws 950-2,700 M/bbl daily
  - Consumes 45-90 M/bbl daily
  - Fresh water supply geographically dependent
    - East of Mississippi River: Surface water
    - West of Mississippi River: Ground water
  - Contributes to stress on nearly 100 U.S. watersheds

Power Plant Water Requirements

Cooling Tower

FGD Installation

Power Plant Makeup Water Requirements[1]

Unit Operation	Subcritical PC	Supercritical PC
Cooling Tower	-440 gal/MWh	385 gal/MWh
Flue Gas Desulfurizer (FGD)	~70 gal/MWh	~60 gal/MWh
Boiler Feedwater	~10 gal/MWh	~10 gal/MWh
Total	**~520 gal/MWh**	**~455 gal/MWh**

1. NETL, 2009.

- **Advanced Cycles**
  - IGCC (Slurry fed): 310 gal/MWh
  - NGCC: 190 gal/MWh

CCS Addition Increases Water Makeup Requirements by 50-90%

Power Plant Makeup Water

Makeup Water Quality Guidelines

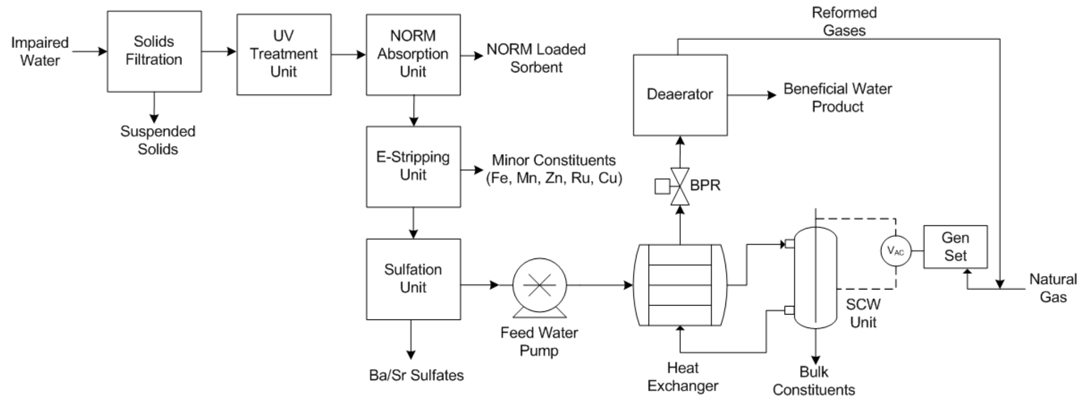
Constituent	FGD	Circulation Water	Boiler Feedwater
pH	6.0-9.0	6.8-7.2[1]	9.3-9.6
SO_4^{2-} (mg/L)	300	147,200	0
Cl^- (mg/L)	100-110	-	0
Fl^- (mg/L)	2	-	0
Fe_{total} (mg/L)	2	<0.5	<.01
Ca^{2+} (mg/L)	100-150	900	0
Mg^{2+} (mg/L)	30-50	-	0
Na^+ (mg/L)	75-125	-	0.003-0.005
HCO_3^- (mg/L)	150-200	30-250[1]	0
Mn^{2+} (mg/L)	-	<0.5	0
Al^{3+} (mg/L)	-	<1	0
Cu^{2+} (mg/L)	-	<0.1	<0.002
NH_4^- (mg/L)	-	<2	<0.02
SiO_2 (mg/L)	10-50	150	0
TDS (mg/L)	500-1,000	70,000	<.05
Mg x SiO_2	-	35,000-75,000	0
TSS (mg/L)	200-300	100-300	0
Turbidity (NTU)	200-2,000	-	0
Conductivity (µS/cm)	500-1,000	-	0.5, Max.
Hardness (mg_{CaCO3}/L)	200-300	500,000	0
Oil & Grease	0	0	0

Makeup Water Considerations

- Water chemistry
- Volume
- Process considerations
  - Scaling
  - Corrosion
  - Biofouling

Proposed Impaired Water Treatment Process

- **Technologies**
  - UV Treatment
  - NORM Absorption (Produced water)
  - Electrochemical Removal
    - Minor constituent removal (Fe^{2+}/Fe^{3+}, Mn^{2+}, Ru^{2+}, Zn^{2+}, and Cu^{2+})
  - Selective precipitations
    - Minor constituents (Ba^{2+} and Sr^{2+})
  - SCW Treatment
    - Bulk constituents



Proposed Impaired Water Treatment Process

Project Schedule and Tasks

Task	Start Date	End Date	Phase I																	
			BP1												BP2					
			Sep '15	Oct '15	Nov '15	Dec '15	Jan '16	Feb '16	Mar '16	Apr '16	May '16	Jun '16	Jul '16	Aug '16	Sep '16	Oct '16	Nov '16	Dec '16	Jan '17	Feb '17
Task 1.0 - Project Management and Planning	9/1/2015	2/28/2017		A	C															
Task 2.0 - Small Scale Impaired Water Treatment Testing	9/1/2015	2/28/2017																		
Sub-task 2.1 - Electrochemical Stripping of Minor Constituents	9/1/2015	2/28/2017									D									
Sub-task 2.2 - Corrosion Resistant Coatings Testing	9/1/2015	2/28/2017																		
Sub-task 2.3 - Evaluation of Scalable SCW Unit for Impaired Water Treatment	9/1/2015	2/28/2017		B										E						
Task 3.0 - Process Modeling and Techno-Economic Assessment	9/1/2015	2/28/2017															F			
Task 4.0 - Pilot Scale Scoping Study	9/1/2015	2/28/2017																		
Milestone Log				A,B	C						D			E			F			
Reporting				Q		Q			Q			Q			Q			Q		FR

Vertical arrows indicate interdependencies between tasks

Q: Quarterly reports; FR: Final report due three months after project's end

Milestones (as indicated by diamond markers): A: Updated project management plan; B: Complete SCW Test Unit Modifications C: Kickoff meeting; D: Determine preliminary E-stripping minor constituent removal efficiency; E: Determine new SCW unit design major constituent removal efficiency; F: Identify best suited power plant make-up water application(s)

Project Objectives

Overall

- Develop a site deployable cost-effective technology for treating impaired water generated from CO_2 storage operations

Small Scale Testing

- Validate technical and commercial feasibility of new internally heated SCW treatment methodology for removal of major constituents from impaired water
- Determine effectiveness of electrochemical stripping to remove minor constituents from impaired water
- Determine effectiveness of corrosion resistant coatings to improve SS performance in high chloride content water

Process Engineering

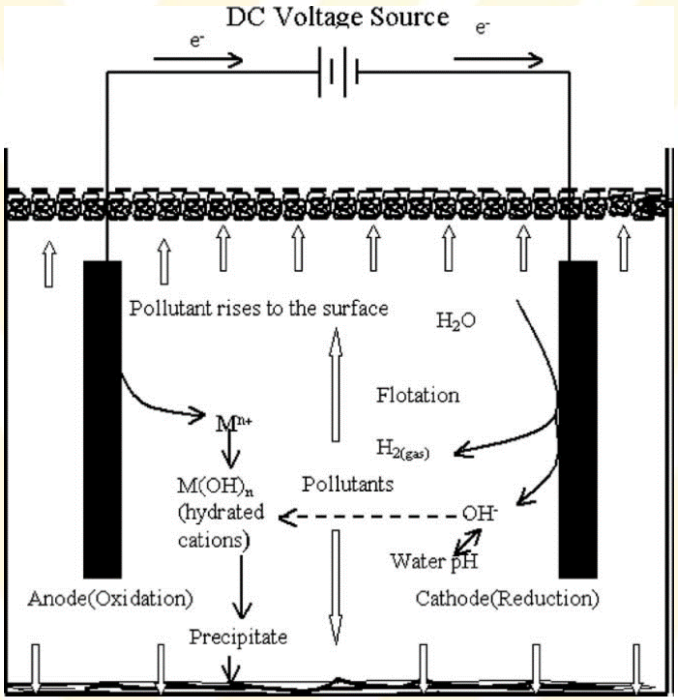
- Identify process configurations which maximize constituent removal, optimize heat integration, and minimize water treatment costs
- Prepare scope for implementing the SCW-based impaired water treatment for a pilot scale effort
- Identify best suited power plant makeup water applications for treated water product

Preliminary Electrocoagulation Results

Electrocoagulation Process

Major steps:

1) Anodic oxidation and cathodic reduction;
2) Generation of coagulants;
3) Precipitation of pollutants on coagulants;
4) Separation by flotation with generated H_2.



Electro-Coagulation Process

Major Objectives

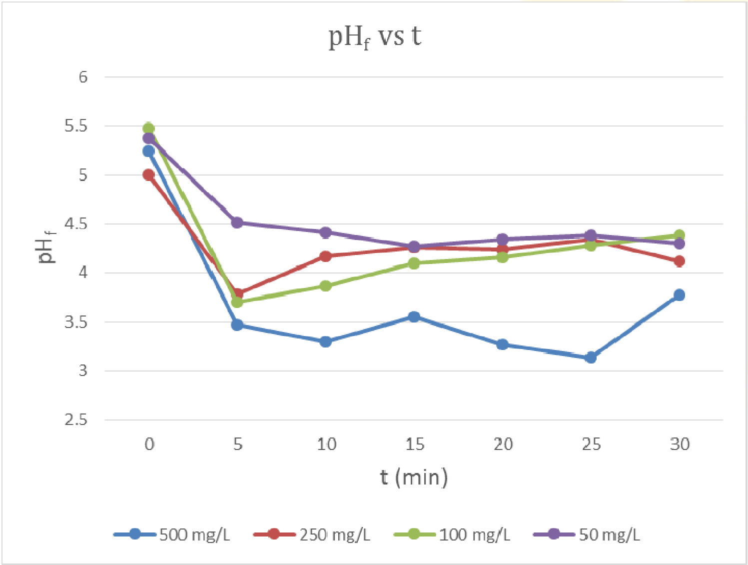
- Maximize removal efficiency
- Kinetic assessment: minimize energy consumption while maintaining higher removal efficiency
- Assess EC process mechanism: (absorption, co-precipitation, surface complexation or electrostatic attraction)

Efficiency Considerations

- Electrode materials and arrangement
- Distance of the electrodes
- Conductivity of wastewater
- Initial pH
- Current density and EC time

A.K. Golder, A.N. Samanta, S. Ray. Journal of Hazardous Materials 141 (2007) 653–661

Preliminary Results



- Generally, the solution pH (pH_f) increased at the end of EC process due to OH^- generation.
- Metals ions still consuming OH^-.

Note: If water electrolysis is the only favorable reaction, the bulk pH would remain constant, due to equimolar production of H+ and OH^-.

Preliminary Results

Table1 Initial and residual metal concentration, metal removal (%), residual concentration of anode ion after Al EC and Fe EC process. Control sample (marked with red lines) was obtained after 30 min of Al EC at initial pH 4.6, electrode distance of 10mm.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
Electrode material	Al	Al	Al	Al	Al	Al	Fe
Initial concentration of Zn (mg/l)	500	500	500	500	500	500	500
Current density (mA/cm^{-2})	4.1	4.1	4.1	4.1	4.1	4.1	4.1
Electrodes distence (mm)	10	10	10	10	20	10	10
EC time (min)	30	15	30	60	30	30	30
Concentration of NaCl (mol/l)	0	0.1	0.1	0.1	0.1	0.1	0.1
Initial pH	5.2	4.5	4.7	4.5	4.5	3.2	4.5
Final pH	3.8	4.5	4.5	4.5	4.5	4.3	4.5
Residual concentration of Zn (mg/l)	355.5	363.3	349.3	255.2	334.7	310.9	294.6
Removal (%)	29	27	31	49	33	38	41
Residual concentration of Al/Fe (mg/l)	24.4	6.7	5.4	2.2	5.5	43.4	106.5

Preliminary Results

Table 2 Metal removal (%), residual concentration of anode ion after 30 min Al EC and Fe EC process. With electrode distance of 10 mm.

Metal ions	Samples	Current density (mA/cm^{-2})	pH		Removal (%)				Residual anode ions (mg/l)
			pH_i	pH_f	Ba^{2+}	Ca^{2+}	Mg^{2+}	Sr^{2+}	Al^{3+}
Ba^{2+},Ca^{2+},Mg^{2+},Sr^{2+} Al electrode	Sample 1	4.2	5.8	4.63	5.9	9	36	0	18.44
	Sample 2	8.4	5.75	4.77	4.7	5.8	25	0.5	38.32
Ba^{2+},Ca^{2+},Mg^{2+},Sr^{2+} Fe electrode	Sample 3	4.2	pH_i	pH_f	Ba	Ca	Mg	Sr	Fe
			5.75	4.46	11.2	4.7	11.7	0	6.2

Preliminary Results – Conclusions

1) The optimum current density for this case is not located in the range of 0.1-0.2A;
2) Acceleration of EC process is possibly unfavorable for the removal of these metal ions.
3) In this case, Fe-electrode is more efficient than Al-electrode.
4) Different removal mechanisms for Ba^{2+}, Ca^{2+}, Mg^{2+}, and Sr^{2+} during EC process.

Future Work – Improving Removal Efficiency

- Optimum characteristics of EC reactor.

  -$d_{a\text{-}c}$: 0.5-2 cm;

  -conductivity: concentration of NaCl

- Key factors– $pH_{initial}$, CD, t_{EC}

  pH=3-7; I= 0.05-0.2 A, 0.5-1A; t=0-60 min

Preliminary TDS Removal Results

Small Scale Testing: Internally Heated SCW Treatment

Goal: Determine technical and commercial feasibility of Joule-based heating for SCW treatment of brines

- **Methodology**
  - Utilize lab prepared and field derived brine solutions
  - Analyze products using ICP, IC, and GC/MS
- **Experimental Parameters**
  - Inlet temperature: 340-380 °C
  - Pressure: 22.1-25.0 MPa
  - Flow rate: 50-200 mL/min
  - Power flux
  - Impaired water composition

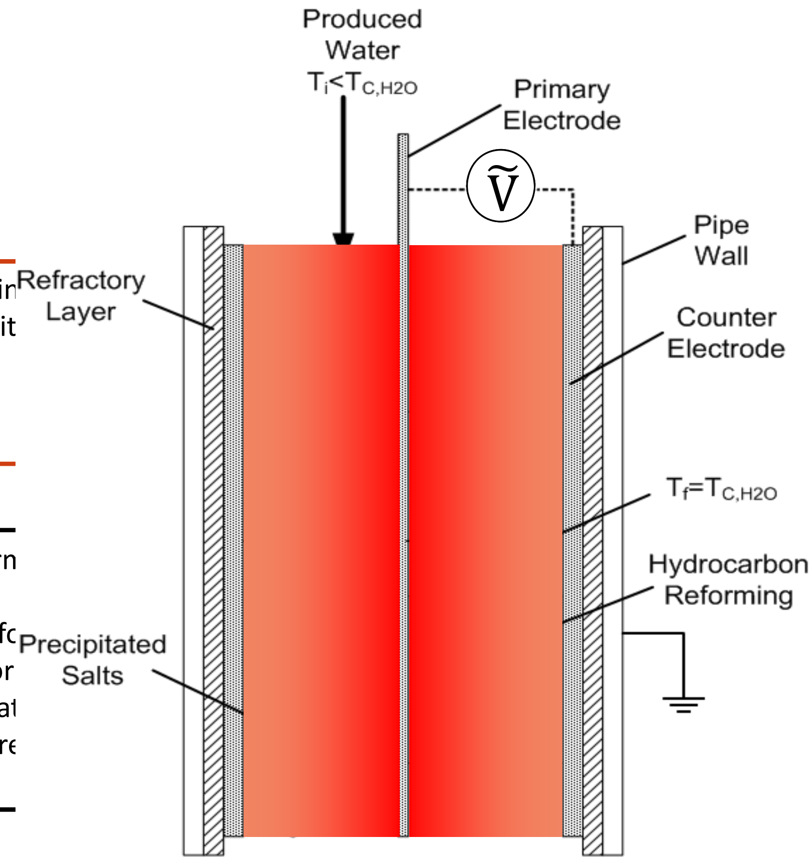
OHIO Prototype Internally-Heated SCW Reactor

Comparison of SCW Reactor Types

- **Reverse Flow Reactor**
  - Externally heated
  - Inlet turbulence results in mixing and critical transition
  - Flow regime prevents internal wall scaling
- **Internally Heated Reactor**
  - AC power provides heating between primary/counter electrodes, rapid heat transfer
  - Creates homogeneous salt nucleation preventing surface scaling
  - Results in significantly cooler reactor wall temperature leading to higher throughput and small footprint

- Inlet feed swirlin sub- to supercrit transition
- Results in TDS precipitation

- Precipitates forn of reactor
- Prevents scale fc on inner reactor
- Solids accumulat removed from re bottom



OHIO Reverse Flow SCW Reactor
OHIO Internally Heated SCW Reactor

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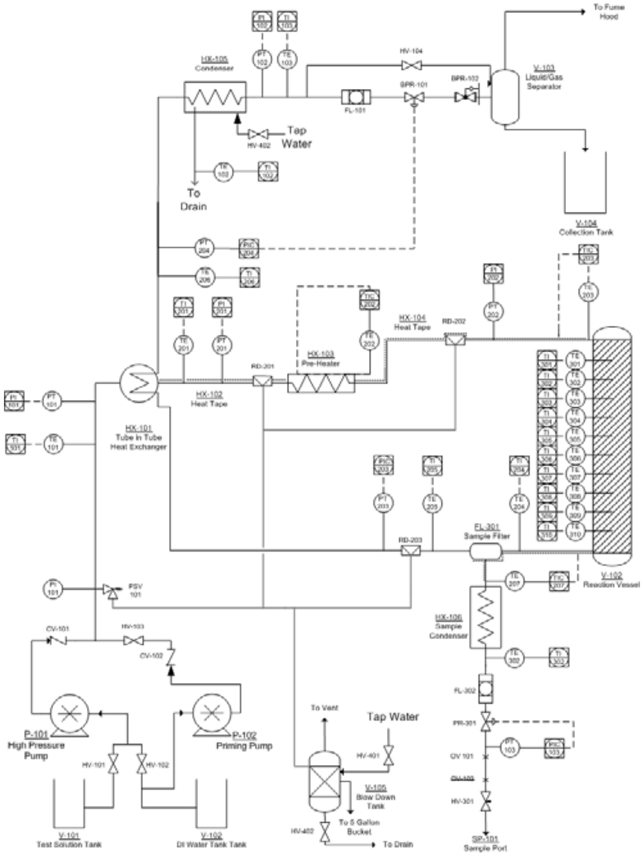
Prototype Overview

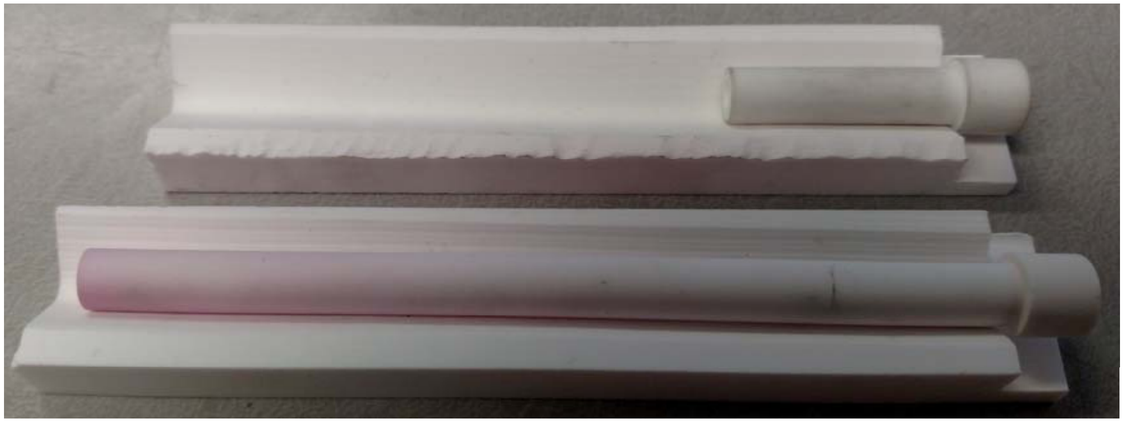
Design Criteria	Design Specifications
Pressure	29 MPa
Temperature	400 °C
Flowrate	10-200 mL/min
Current Supply	140 A (max)
Reactor Power	7.0 kW

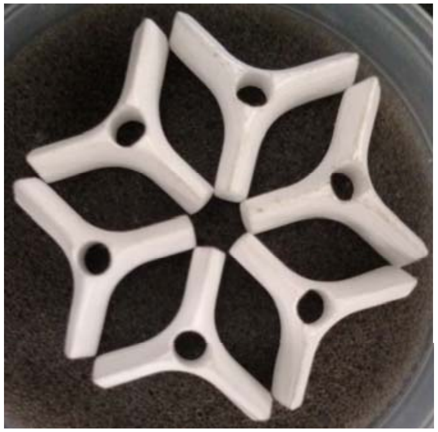


OHIO Prototype Brine Treatment Reactor and System P&ID

Prototype Modifications

- Electrode Arcing and Overheating
  - Extended insulators
  - Alternative electrode materials
  - Electrode centering spacers
- Filter Plugging
  - Flow through sintered metal filters

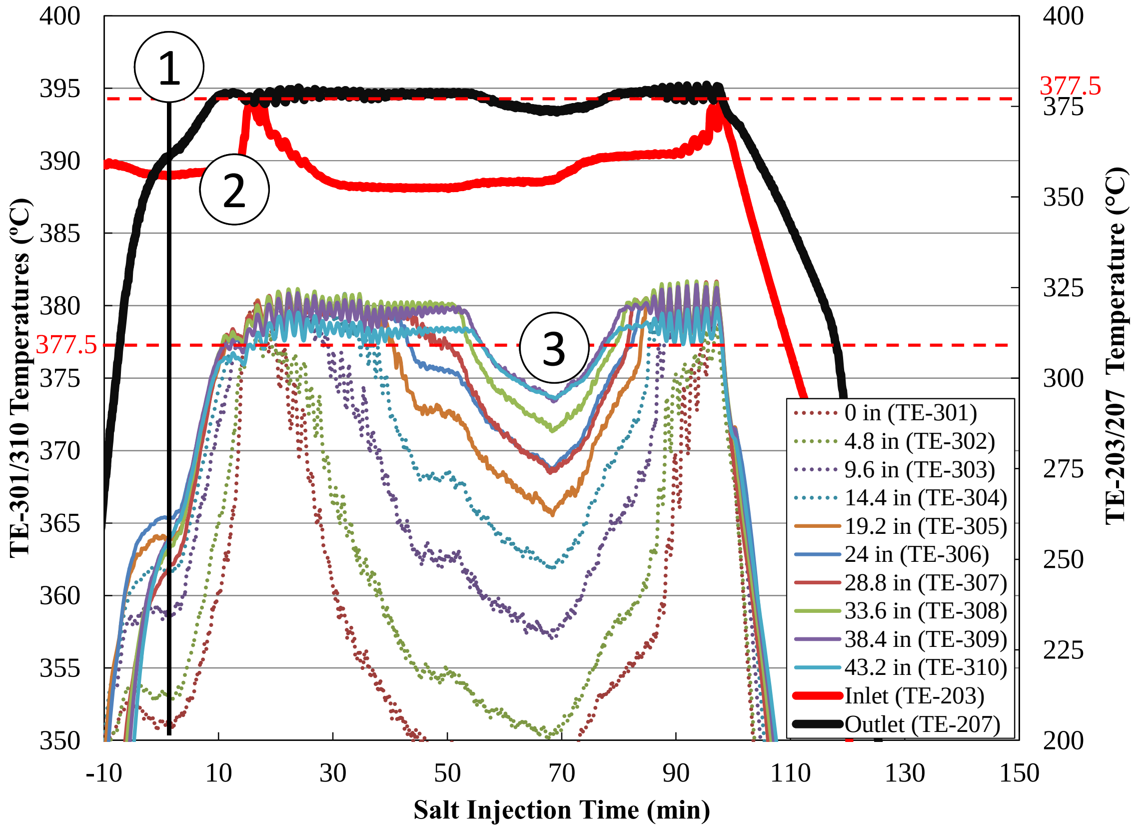


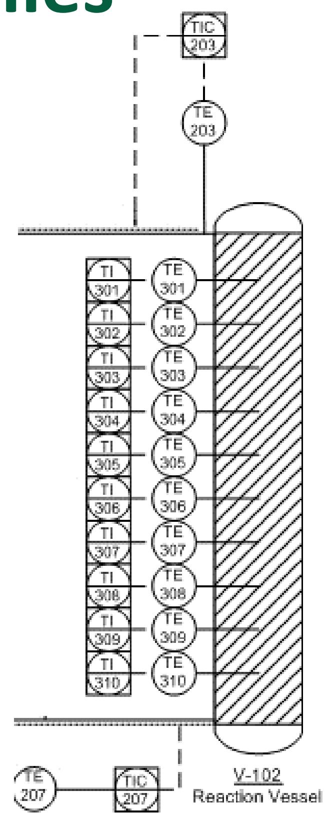


Experimental Results: Reactor Temperature Profiles

Reactor Phenomena

1. Salt Injection
2. Inlet temp increase
3. Temperature dynamic due to inlet temp change

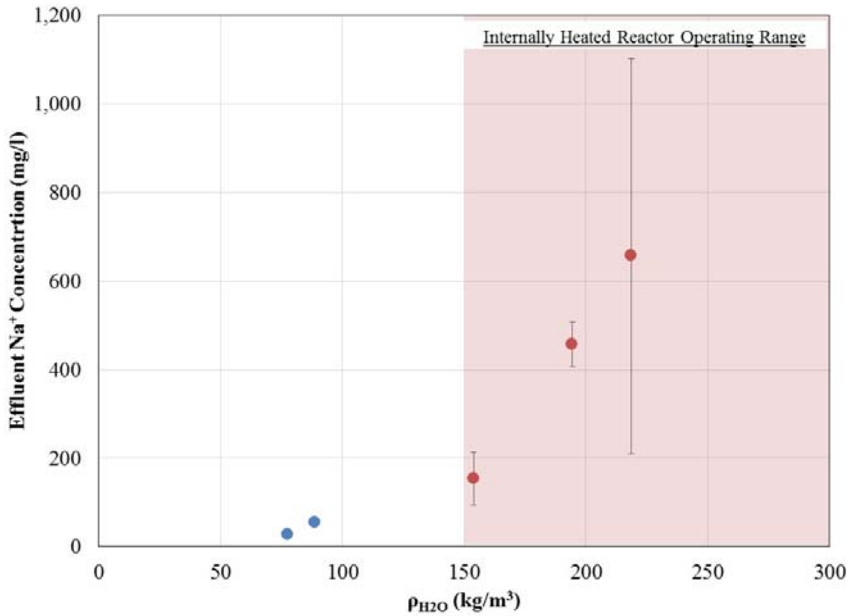




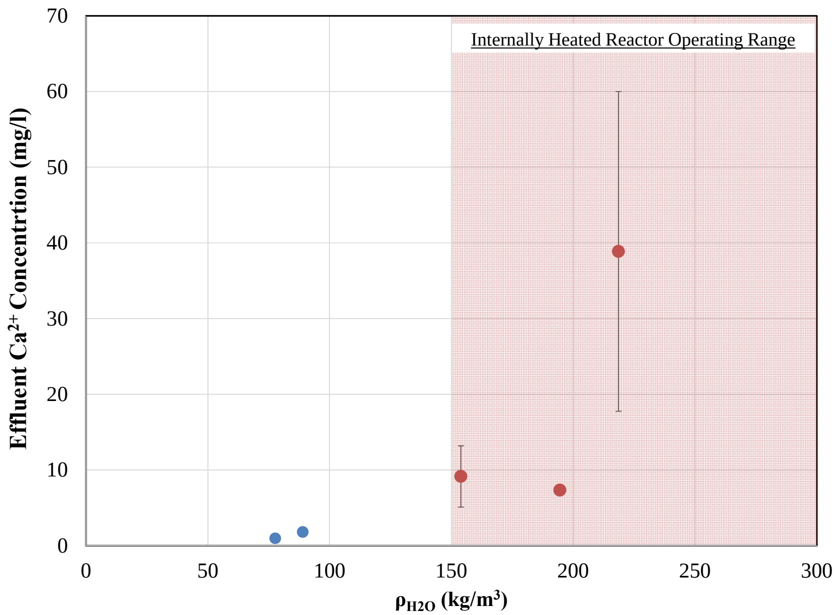
Reactor Temperature Profiles After Injection of 50 mL/min Brine Solution at 23 MPa and 500 W. Pseudocritical temperature is 377.5 °C.

Experimental Results (Cont.)

a)



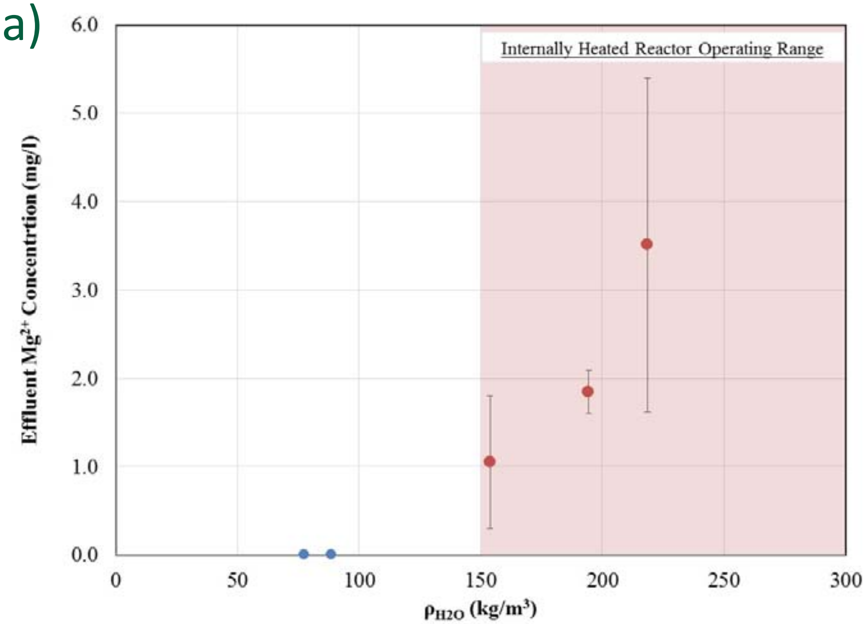
b)



Experimentally determined effluent a) Na^{+} and b) Ca^{2+} concentrations based upon water density

Experimental Results (Cont.)

a)



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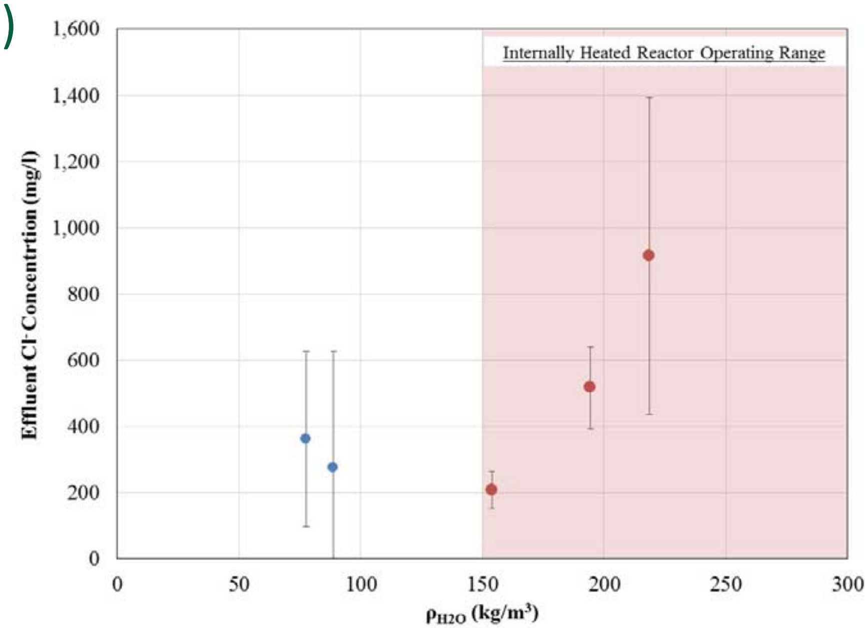

Experimentally determined effluent a) Mg^{2+} and b) Cl^- concentrations based upon water density

Summary

Preliminary Conclusions

1. Internally heated reactor design is capable of heating brine solution to critical condition.
2. Minimal heating occurs beyond the critical point due to precipitation of dissolved solids and resulting decrease in solution conductivity.
3. Water density is major factor controlling TDS removal level.
4. TDS removal greater than 99.5% from solutions containing greater than 100k ppm TDS.
5. Internally heated reactor design shows capability of producing water product with multiple beneficial reuse applications.

Power Plant Makeup Water Quality Guidelines and Preliminary OHIO Water Product Results

Constituent	FGD	Circulation Water	Boiler Feedwater	Preliminary Product Quality
pH	6.0-9.0	6.8-7.2[1]	9.3-9.6	6.2
SO_4^{2-} (mg/L)	300	147,200	0	BDL
Cl^- (mg/L)	100-110	-	0	200-850
Fl^- (mg/L)	2	-	0	DNT
Fe_{total} (mg/L)	2	<0.5	<.01	DNT
Ca^{2+} (mg/L)	100-150	900	0	7-38
Mg^{2+} (mg/L)	30-50	-	0	1-3.8
Na^+ (mg/L)	75-125	-	0.003-0.005	180-700
HCO_3^- (mg/L)	150-200	30-250[1]	0	BDL
Mn^{2+} (mg/L)	-	<0.5	0	DNT
Al^{3+} (mg/L)	-	<1	0	DNT
Cu^{2+} (mg/L)	-	<0.1	<0.002	DNT
NH_3^- (mg/L)	-	<2	<0.02	DNT
SiO_2 (mg/L)	10-50	150	0	DNT
Mg x SiO_2	-	35,000-75,000	0	DNT
TSS (mg/L)	200-300	100-300	0	0
Turbidity (NTU)	200-2,000	-	0	DNT
Conductivity (µS/cm)	500-1,000	-	0.5, Max.	DNT
Hardness (mg_{CaCO3}/L)	200-300	500,000	0	DNT
Oil & Grease	0	0	0	0

BDL: Below detectable limit
DNT: Did not test to date

Upcoming Work

OHIO

- Continue prototype testing to evaluate TDS removal efficiency and evaluate reactor operability (Ongoing)
- Update existing techno-economic analyses using newly generated experimental data (Starting mid-May)

WVU

- Continue evaluating electrocoagulation and electrochemical stripping techniques to remove high-value trace elements (Ongoing)
- Begin evaluating corrosion resistant cladding materials for low-cost steels (Starting June)


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