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CAUSTIC RECYCLING

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Outline

- Insertion Opportunities at Site
- Caustic Recycling Overview
- Pilot Scale Demonstration Phase
- Conclusions

Sodium Separation Technology Already Commercially Deployed!

- ✓ NaSelect Ceramic Membrane Technology Deployed
- ✓ Producing Sodium Methylate (SMO) for Archer Daniels Midland
- ✓ Technology is Scalable
  - ✓1500 lbs/day on a 100% basis of SMO
- ✓ Equivalent to production of 71.2 kgs per hour of 10 M NaOH concentration from Actual Waste

Biodiesel Facility in Mexico, MO

Modular revolutionary commercial technology applied to treat radioactive waste

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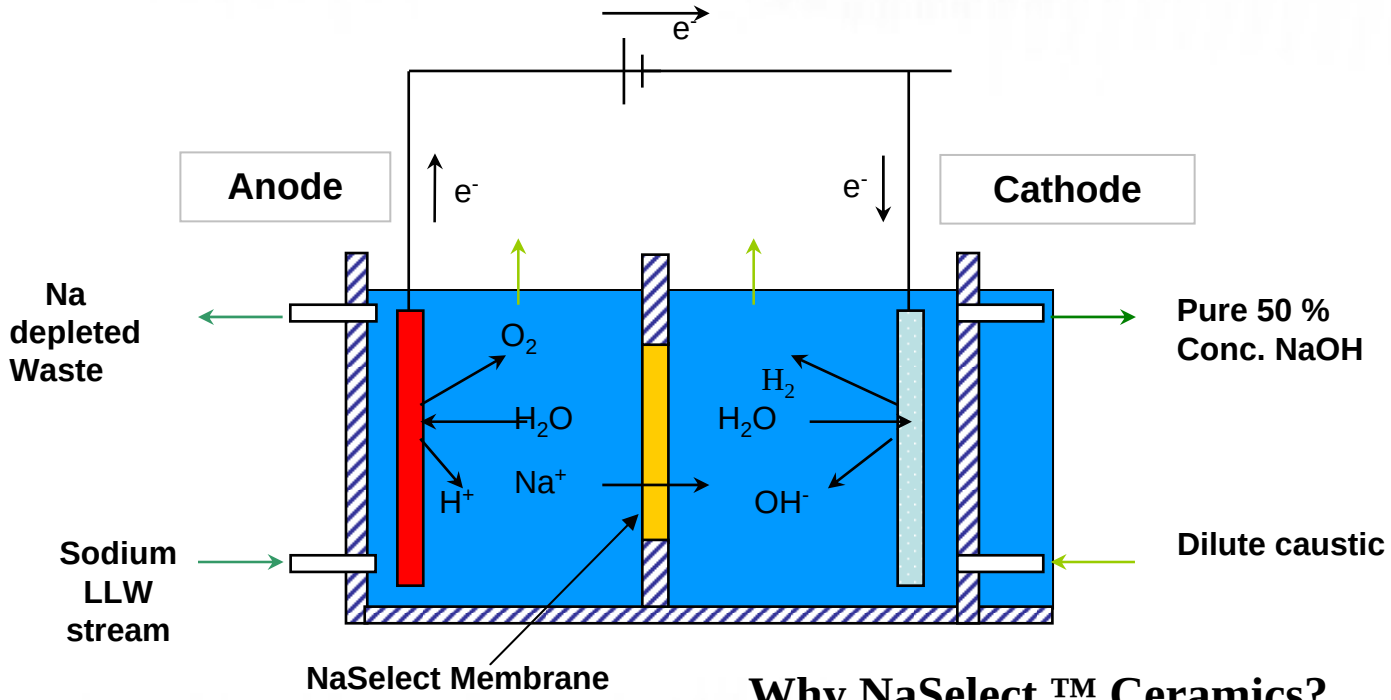
Principle of Operation: Electrolytic Ceramic Membrane Cell



Electrode Reactions:

Anode: $2H_2O = O_2 + 4H^+ + 4e^-$

Cathode: $4H_2O + 4e^- = 2H_2 + 4OH^-$

Overall: $2H_2O = 2H_2 + O_2$

Why NaSelect ™ Ceramics?

- Selective only to sodium ions
- Chemically stable to radioactivity- 10^9 Rads
- Electrochemical Efficiency Greater than 95%
- Operates at 40 C and lower

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Caustic Recycling Deployment at Hanford

The benefits of the Ceramatec Sodium Recovery System to Hanford:

- Avoid import of fresh sodium hydroxide for both Waste Treatment Plant and Tank Farm Operations
- Ease operating constraints caused by trying to minimize sodium usage for caustic leaching, sludge flushing and hard heel removal
- Reduce the volume of Immobilized Low Activity Waste (ILAW) produced by either Fluidized Bed Steam Reforming or Vitrification
- Increase the waste loading of ILAW
- Decrease duration of operations due to decreased volume of waste processed
- Decontaminate recovered sodium hydroxide to the extent it can be easily handled with minimal radioactivity concerns or can be disposed of as a VLLW stream

OPTION 1: DEPLOYMENT AT A DST (IN AP FARM WITH RMF AND SCIX)

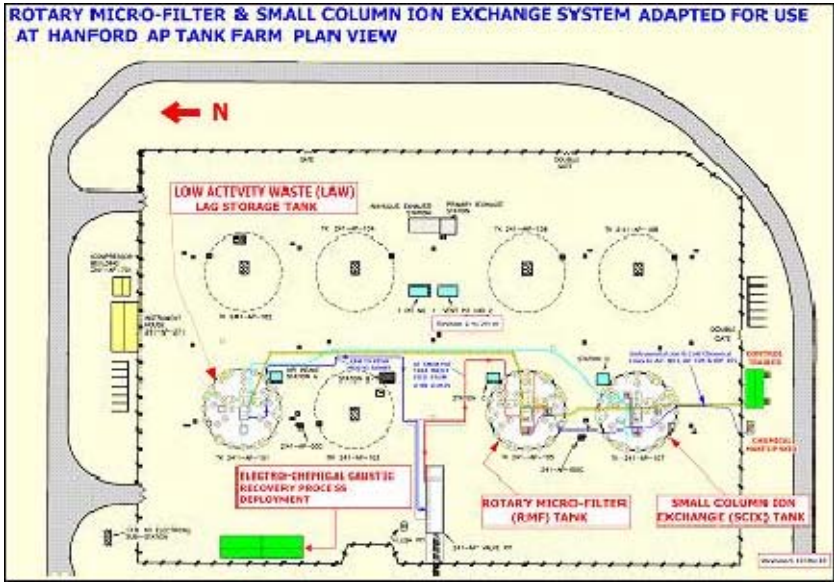

FIGURE 1. ECCR SYSTEM DEPOLYED IN AP TANK FARM

- Though this figure shows ECCR deployed with RMF & SCIX, it could be deployed with any ultra-filtration and ion exchange process. It could also be deployed with another part of the NTTS, i.e., Continuous Sludge Leaching (CSL). The recovered caustic could be used with CSL

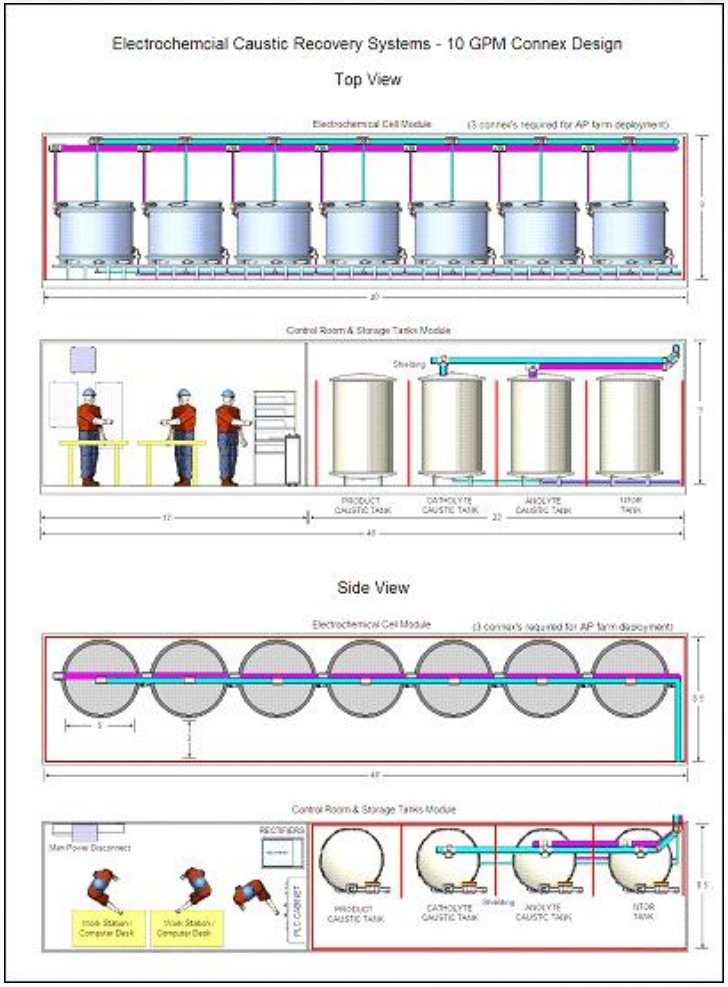

FIGURE 2. ECCR MODULES DIAGRAM

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OPTION 2: DEPLOYMENT AT AN SST (ECCR TECHNOLOGY ALONE)

OPTION 3: DEPOLYMENT AT A WRF

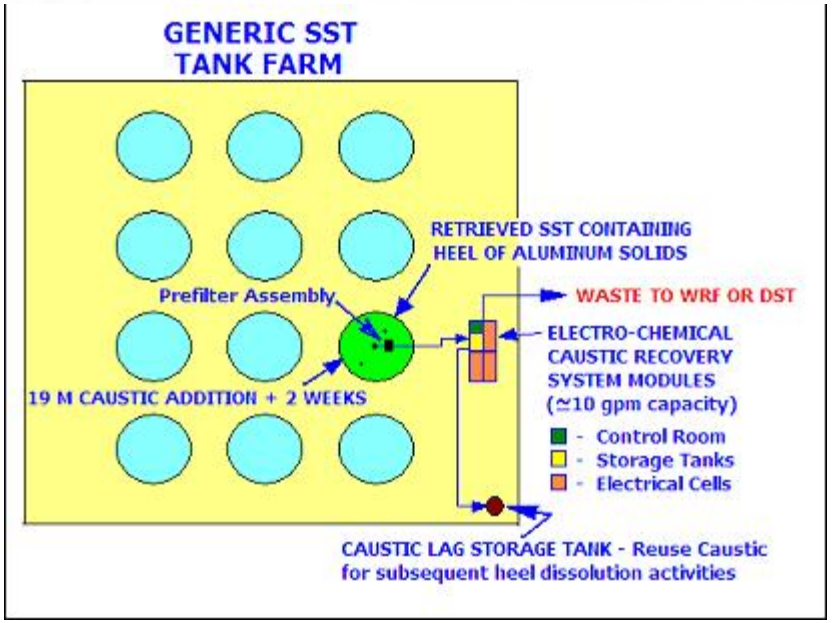


FIGURE 3. ECCR SYSTEM DEPLOYED AT GENERIC SST FARM (SAME SYSTEM AS USED IN DST FARM)

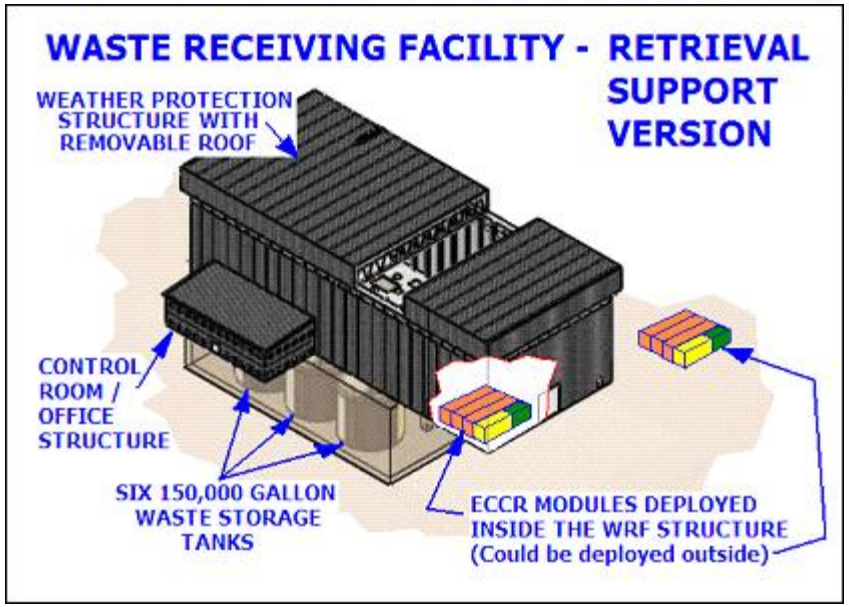
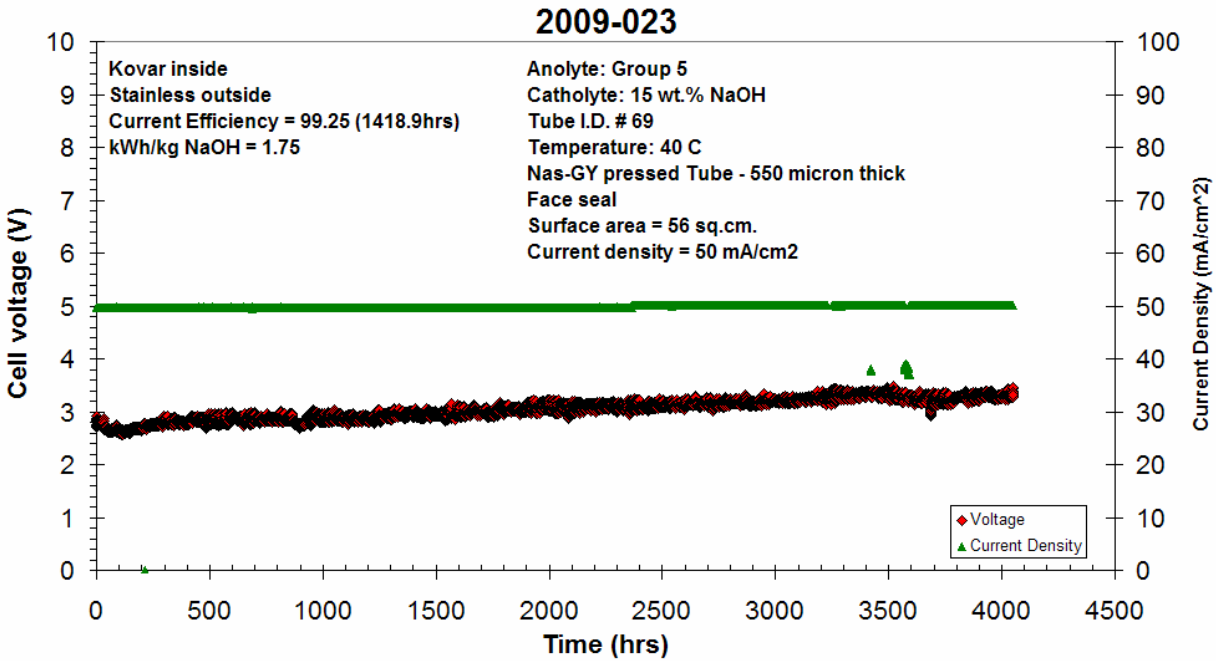


FIGURE 4. ECCR SYSTEM DEPLOYED AT WRF

- Figure 3: This type of deployment would be used to support retrieval of the aluminum bearing heels from SST that have been retrieved to the limits of the retrieval technology but still have aluminum heels larger than allowed, i.e., greater than 360 cubic feet or 2,700 gallons. The reclaimed caustic could then be used to dissolve aluminum heels in other nearby SSTs.

Long Term Success: Testing in Group 5 Simulant



- **Demonstrated** Long term test: Steady cell operation in continuous mode (Approx 6 months)
- **Low** power consumption-1.75 kWh/kg of NaOH produced
- **Demonstrated** continuous production up to 50 wt% caustic from Group 5 simulant
- >25,000 hours of testing with multiple simulants performed to recycle NaOH

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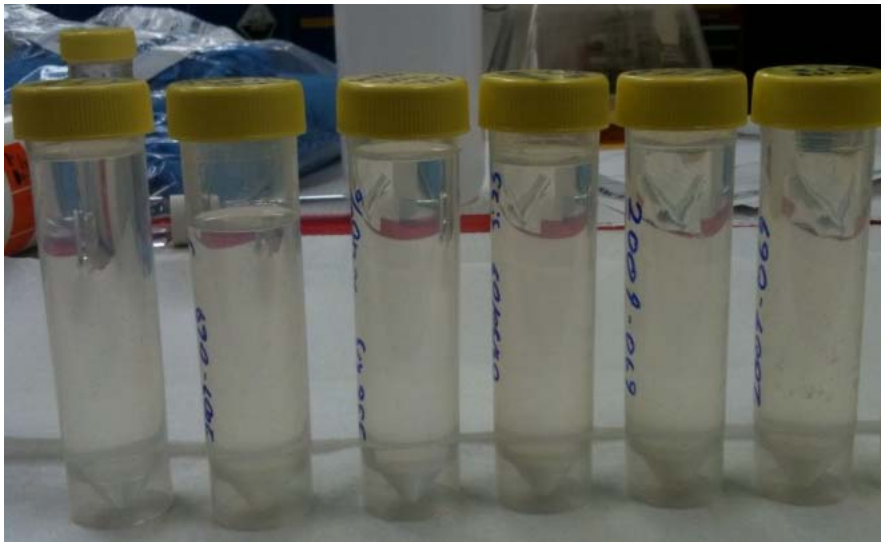
Testing and Analysis: Single Tubular Membrane Tests in Waste Simulants

Composition	Group 5	PEP	CSL/NTCR
Na (M)	4.42	7.39	5.01
Al (M)	0.26	0.75	0.25
Starting Na/Al	16.89	9.85	20
% sodium removed at 40°C before precipitation	45 %	65%	80%

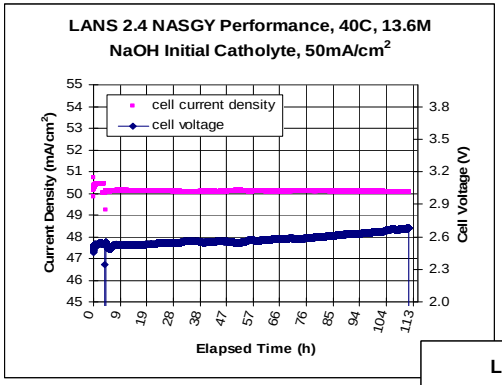
NTCR Sample Analysis

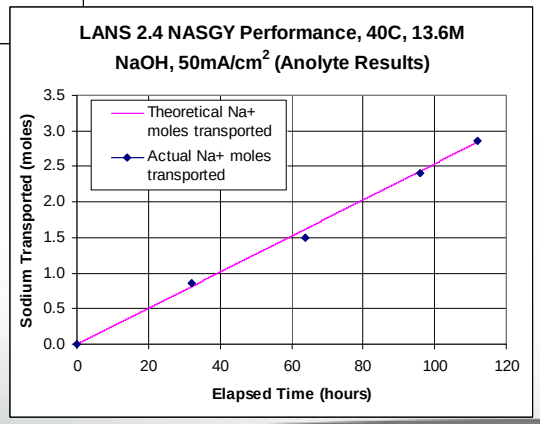


- NTCR Samples after 10, 30, 40, 50, 65, and 80% sodium removal from left to right
- Alumina precipitation observed in the 80% sodium removed sample

Sodium Recycling from Actual Waste

- ✓ Four Successful Tests performed
  - 2 tests at PNNL
  - 1 test at SRNL
  - 1 test with HLW at JGC Corp. for JAEA





Group 5 Waste

- ➢Good agreement between theoretical Na transport based on applied current
- ➢Na transport based on OH^- titration results.
- ➢Average Na transfer rate of 10.2 kg/day/m^2
- ➢*99% sodium transport efficiency*
- ➢ Cs-137 Decontamination Factor = 5585- GEA analysis)
- ➢ No other radionuclides were transported and measured in the catholyte solution above detection limits

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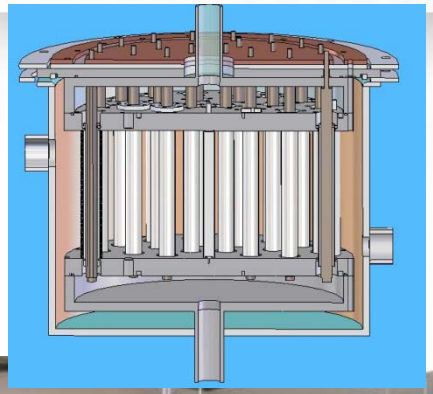
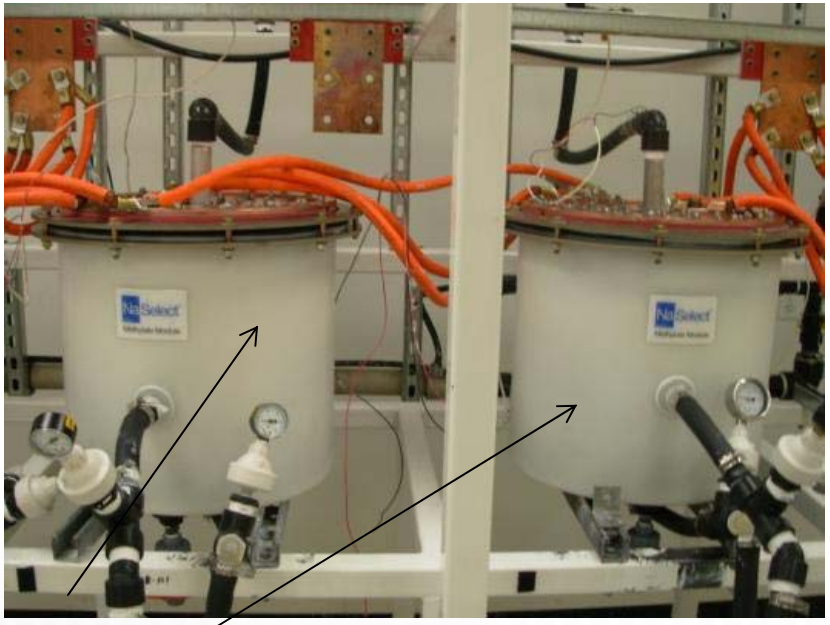
Technology Demonstration Unit (TDU): Caustic Recycling

Inside Core of Module





Modules
38 NaSelect™ tubular membranes (0.5 m^2 per module)

Skid Operation

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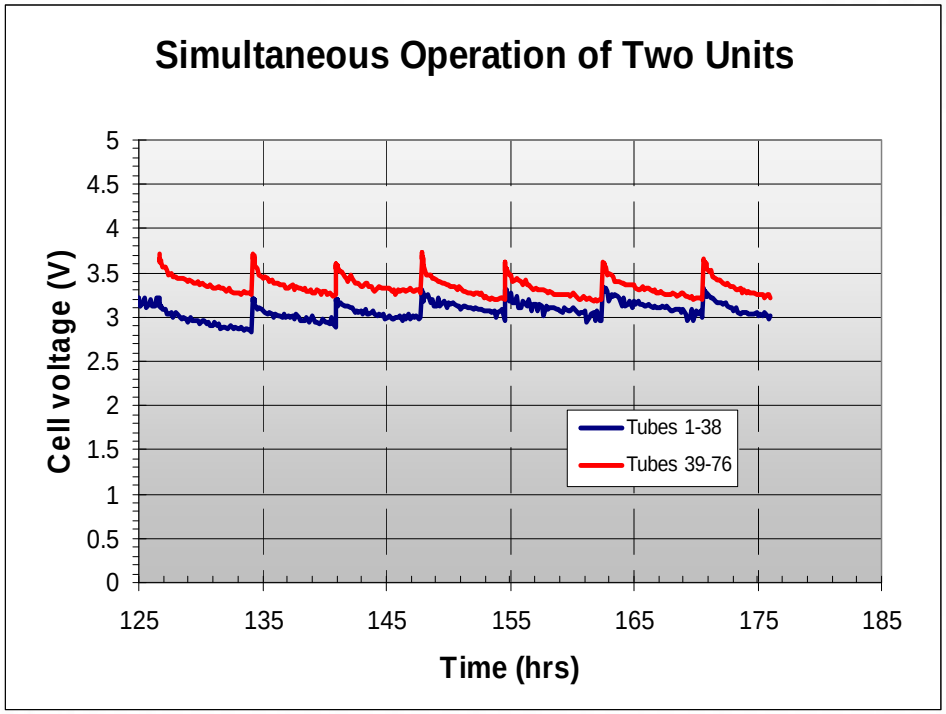
Caustic Recycling: Technology Demonstration Unit (TDU) Operation

- Five batch tests with fresh NTCR effluent simulant to recycle sodium were conducted for a total of 176 hours of testing
- Performance of the unit to recycle sodium validated the TDU design
- 60% sodium was removed from NTCR stream without solid precipitation in the simulant after sodium separation
- TDU testing proved capability to recycle 80% sodium hydroxide
- Process current efficiency remains >95%
- Demonstrated continuous production of 30 wt% caustic from the NTCR effluent simulant chemistry



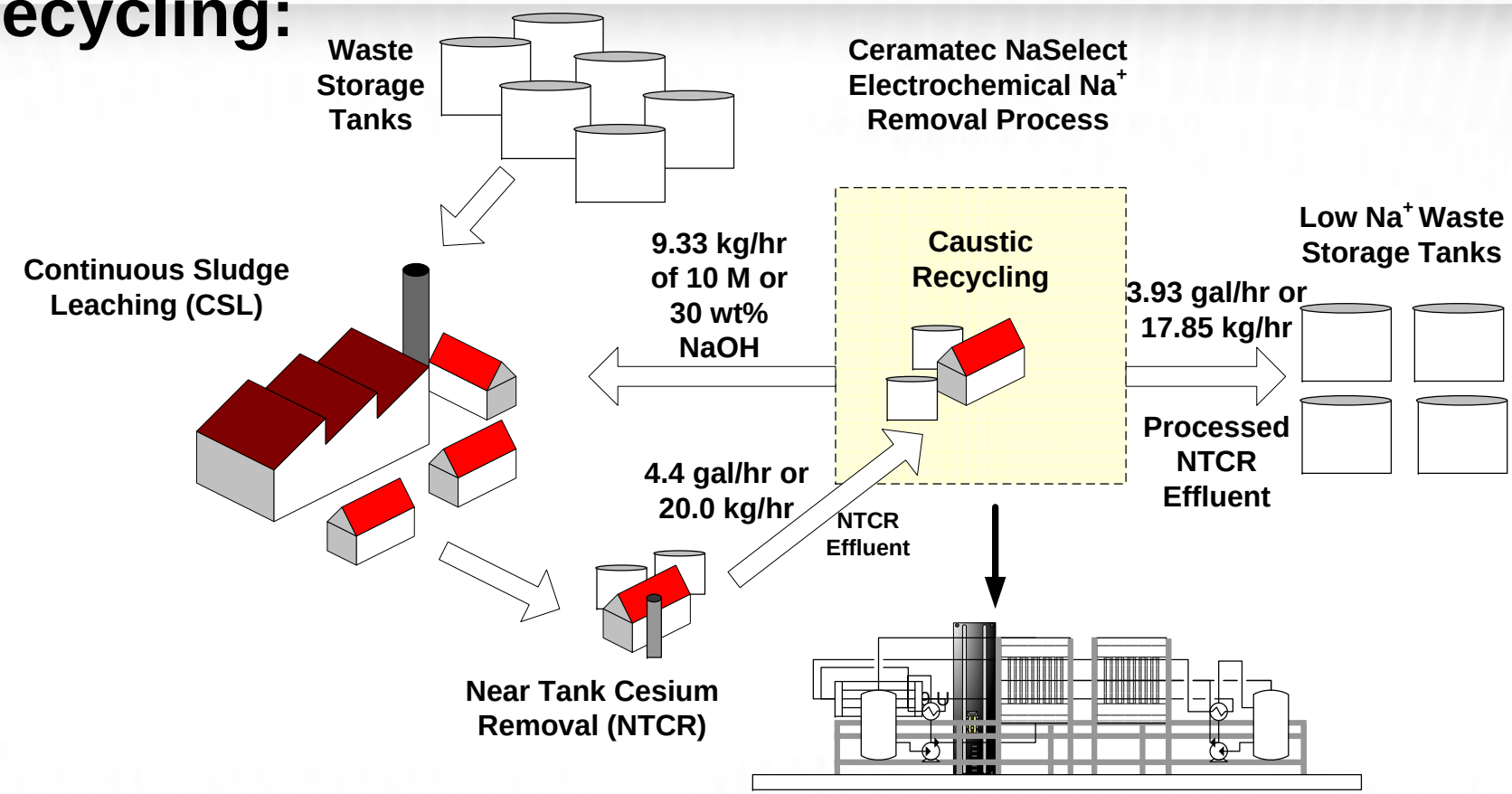
Technology Readiness

SYSTEM	CTE	TRL
CSL	Continuous Dissolution	3
NTCR	Resin Chemistry	4
CR	Electrochemical Cell: Electrodes and Membranes	4

Independent PARSONS review with Battelle

- **Caustic Recycling (CR)**: The Electrochemical Cell was assigned a TRL4. The technology meets the technical and manufacturing requirements for TRL5 as a stand-alone technology element.
- However, additional integration with the other NTTS components needs to be demonstrated as the primary technical TRL5 requirement.

Integrated Project NTTS Demonstration- Caustic Recycling:



- NTCR effluent feed to caustic recycling and processed NTCR effluent volumes are close to 1:1 based off preliminary flow sheet information from PARSONS
- 1/4th Scale: Pilot PFD for Caustic Recycling from (NTTS) flow sheet

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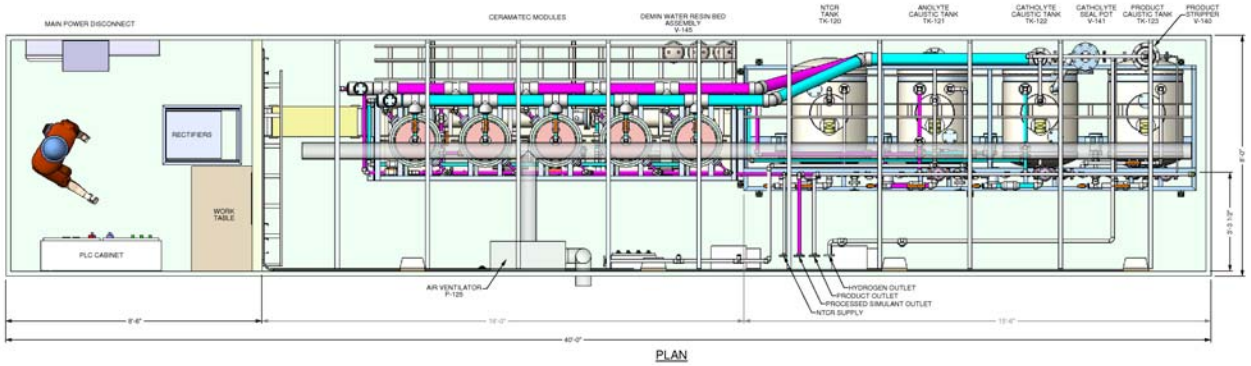
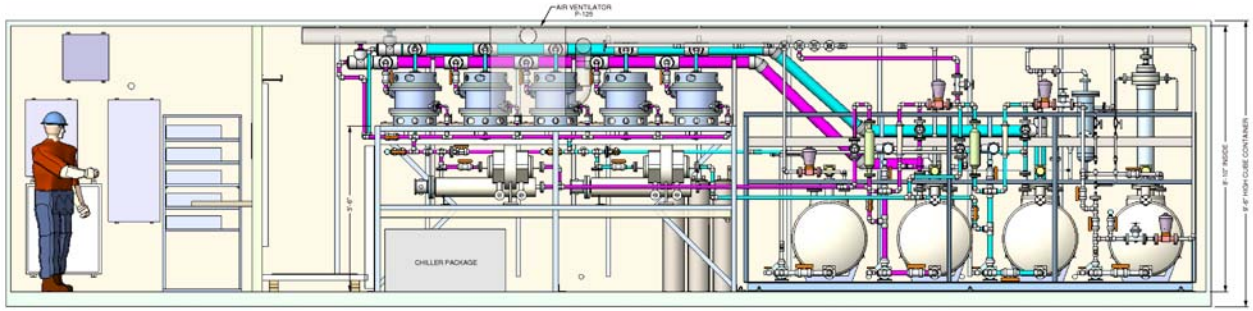
NTTS: Skid Layout for Integrated Caustic Recycling Pilot: Process NTCR Effluent

Control Center

Processing Area





Process flow rates:

- NTCR Effluent – 4.27 gal/hr
- 10M NaOH Production 9.33 kg/hr
- Recirculation flow rate: 2 gal/min
- Ventilation flow rate: 250 + cfm

- Modular cell design and mobile footprint
- Operation at PASCO facility April 2011

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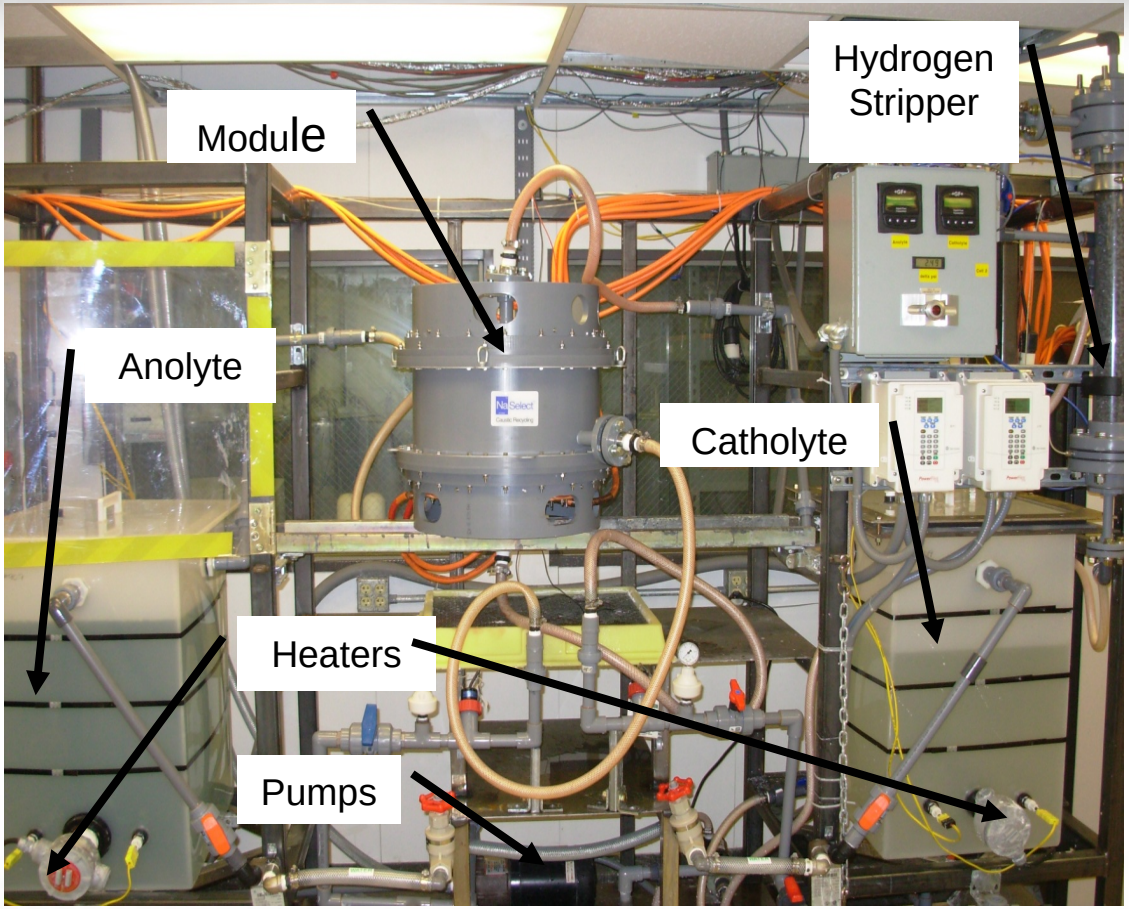
Module Certification for Pilot Skid



Batch Process Conditions:

- 70% Na^+ removal
- 42 gallons of NTCR processed per batch
- 43.08 hours per batch
- Catholyte production – 1.86 kg/hr (30wt% Caustic)

Components validated:

- CPVC/PVC valves/piping/unions
- PVC/Tygon braided tubing (alternate)
- H_2 Stripper (including pump)

- Qualification in NTCR effluent per test plan
- Parametric tests on chemistry variations
- Lifetime qualification

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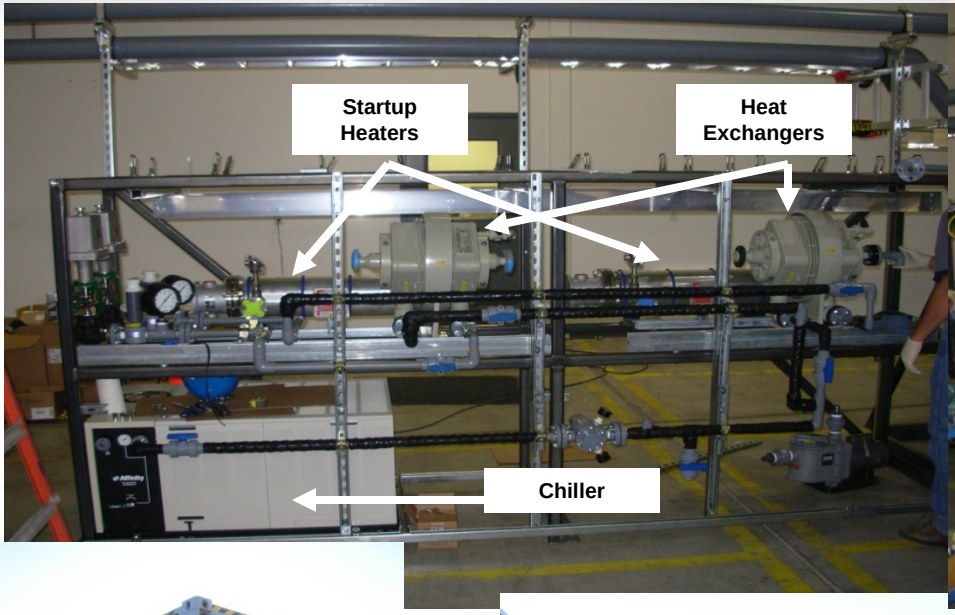
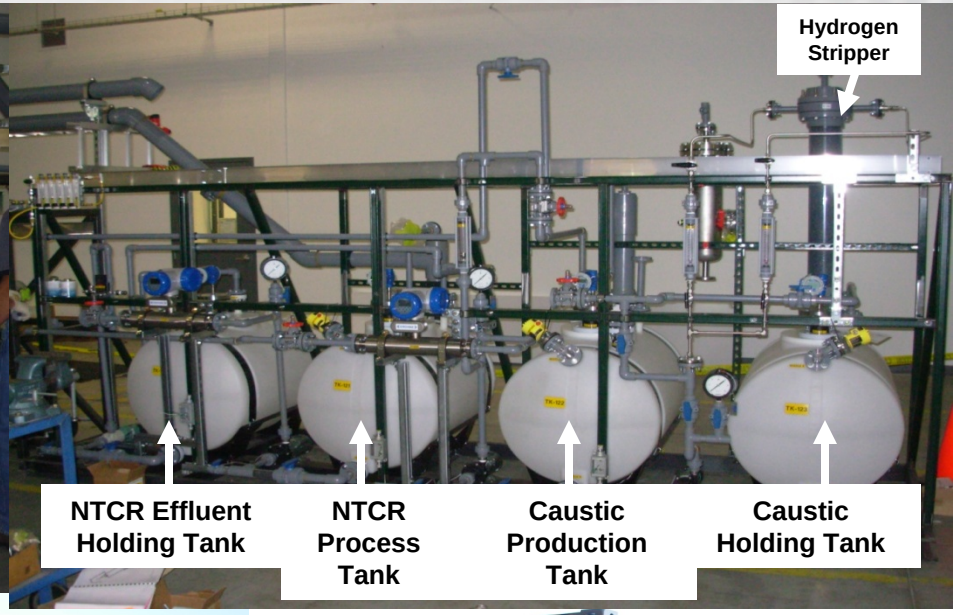
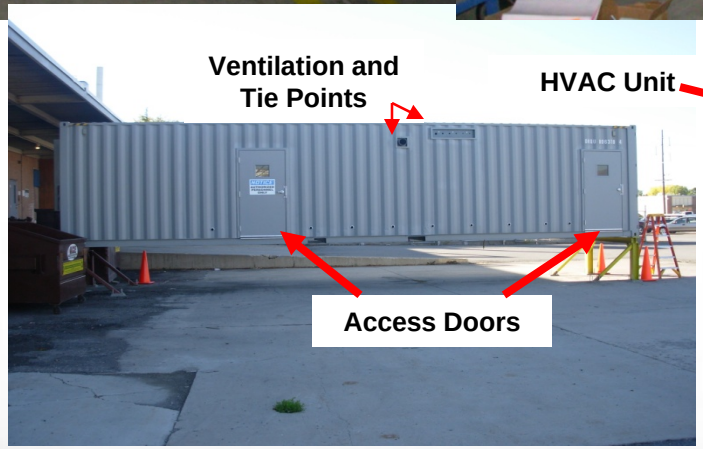
Pilot Unit: Container-Skid Construction Underway







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Gas Handling

- H_2 separation from NaOH at atmospheric pressure – 0.01 in/s
- Distillation Packing 'Pro-Pak' 0.24" Protruded Metal
- Volume of Packing – 16.7 L

- Prevents air entering the system
- Hydrogen is ventilated to a vent stack that is connected with a thermocouple.
- Hydrogen vent stack is grounded to dissipate static buildup

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Process Instrumentation/Controls

- Effluent Transfer pump – pumps NTCR solution into recirculation/process tank
- Anolyte & Catholyte pump tank level transmitter – reports liquid level
- Anolyte & Catholyte pump tank temperature transmitter – Controls and monitors solution temperatures via PLC
- Anolyte & Catholyte pump tank level switch - Shuts down process if tank overflows
- Anolyte & Catholyte mass flow transmitter – Coreolis flow meter used to measure Density and flow rate of solutions. Used as a sodium sensor based on calibration curve of density vs. Na+ concentration
- H_2O volumetric flow controller – Controls water makeup to catholyte process tank to make NaOH. Feed rate based on total DC current to modules
- Ambient H_2 LEL sensors – monitors environment in and outside the process lines and tanks
- O_2 sensors – monitors environment in catholyte tank and Hydrogen vent line
- H_2 0 to 100 ppm sensor – determines when all of hydrogen has been removed from the product 10M NaOH
- N2 Purge – maintains positive pressure of nitrogen in piping, tanks, and process equipment
- Cell line low ventilation flow switch – Maintains air ventilation in skid. Shuts off process if flow drops

Caustic Recycling Summary

✓ Several Caustic Recycling Points at WTP and Near Tank

✓ Technology is Scalable as demonstrated by commercial application

✓ Currently the caustic recycling technology at TRL 4, expected to reach TRL 6 after Pilot Integrated NTTS Operation

✓ 25,000 hours of testing in simulated waste chemistries to recycle sodium hydroxide with multiple simulants to design and establish process reliability

- 65%-75%-80% removal of sodium from CSL-PEP and NTCR waste simulants demonstrated before precipitation of Alumina occurs

✓ Four successful tests in actual waste at Hanford and SRS
Japanese Atomic Energy Agency (JAEA)

✓ NTTS Pilot Skid system commissioning and operation February-April 2011

✓ Full size deployment system design and schedule will be focused starting April 2011

Acknowledgement

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Gary Peterson

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- Nick Machara- DOE EM
- Terri Sams, David Swanberg, Rebecca Robbins, (WRPS)

✓**Large Scale Manufacturing Method in Place**

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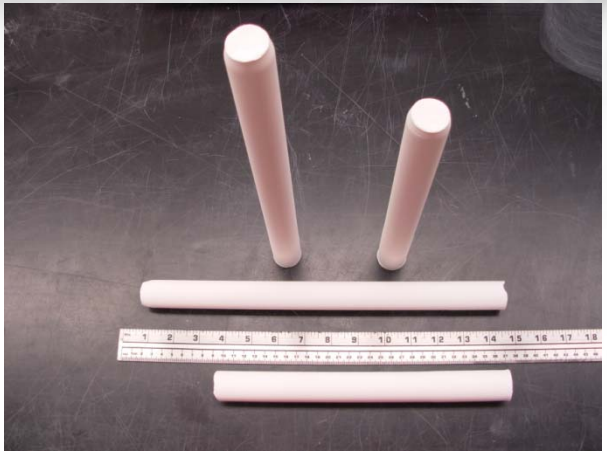
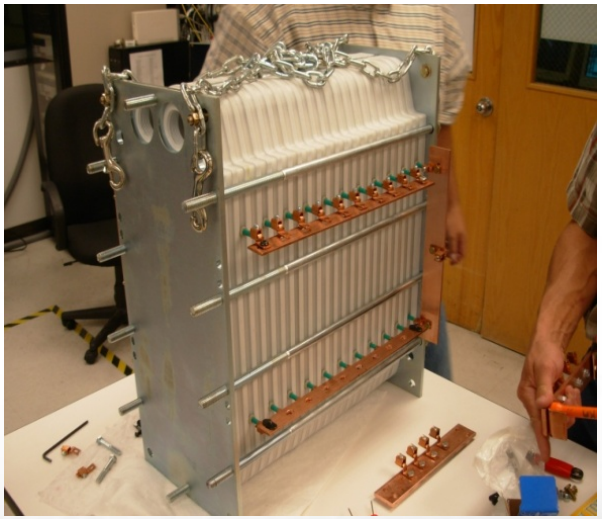
Ceramatec Overview



- ***Subsidiary Company* of CoorsTek**
  - **Privately Owned by Coors Family**
  - **CoorsTek the worlds largest tech ceramic company**
  - ***100 years old American Company***
  - ***Global Presence***
- **Concept to commercialization**
  - **R&D --> prototype --> pilot scale fabrication -->**
- **Core competencies:**
  - **electrochemistry, ionic conducting ceramics, & advanced materials**
- **Customers**
  - **60% Fortune 100/500 Companies**
  - **40% Govt.**



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