Recycling Caustic from LAW Stream using NaSICON Membrane based Electrochemical Technology

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Outline

- Opportunity
- Technology Description
- Development Status
- FY09 Testing Results
- Evaluation in PEP simulant

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Opportunity

- **Problem:** DOE site at Hanford can use > 39,000 MT of caustic for sludge leaching and WTP pretreatment

- **Solution:** Ceramatec's NaSICON patented technology can remove sodium from LAW and make caustic for reuse on site.

- **Benefits:** (1) Potential to reduce handling, processing of waste and Time Schedule at DOE sites. (2) Potential cost savings for waste cleanup by lowering volume of waste
- The process regenerates the sodium in the form of "clean" sodium hydroxide for reused on site
- NaSICON ceramic membrane technology will directly make sodium hydroxide up to 50 wt% and prevents migration of Cs and other radionuclides to the sodium hydroxide stream.

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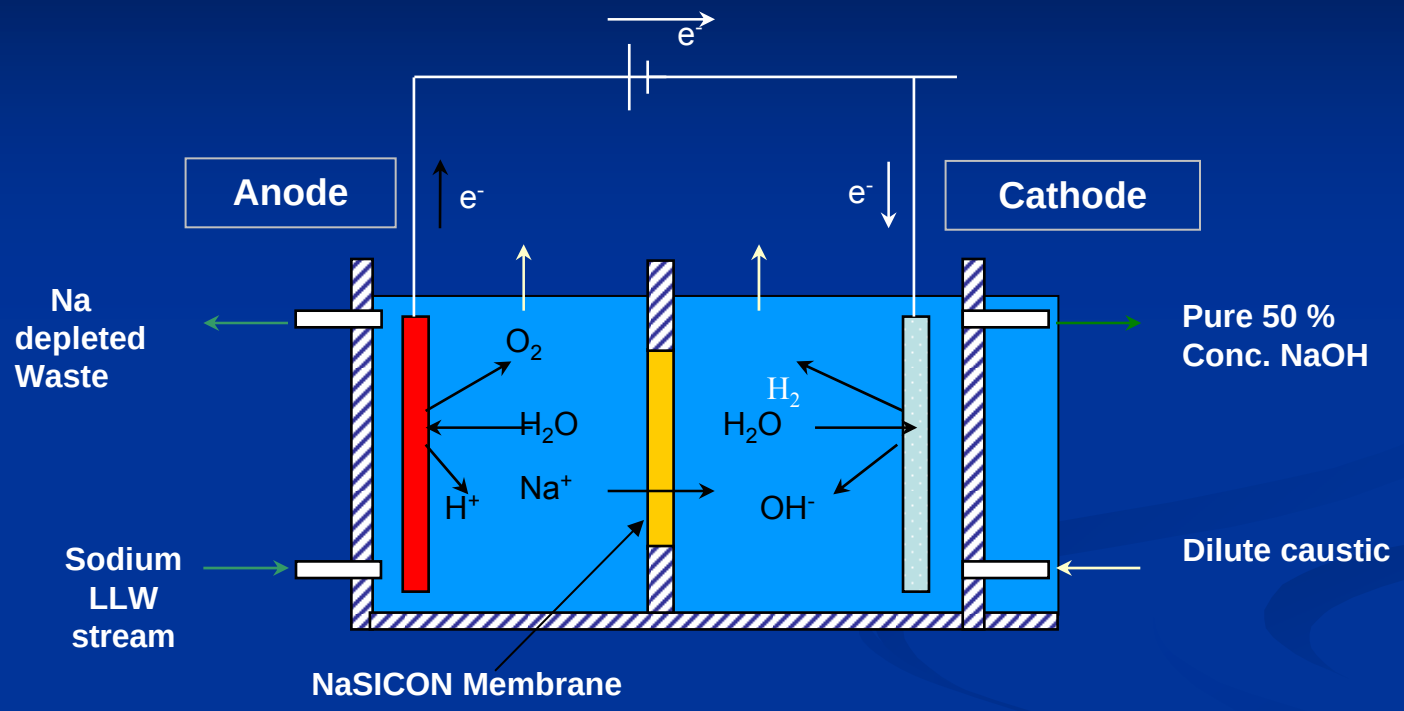
Principle of Operation: Electrolytic NaSICON Ceramic membrane cell



NaSICON Membrane

Na=Sodium

SI=Super Ionic

CON= Conductors

Electrode Reactions:

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

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

Overall: $2H_2O = 2H_2 + O_2$

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Technology Development and Maturation

- Energy efficient thin supported Planar NaSICON membranes Developed
  - 50% reduction in energy requirement
- Recycling of caustic from multiple simulant streams
  - Operational reliability in AP104, Group 5, PEP Effluate
  - simulants to produce up to 50 % strong caustic
  - Demonstrated 7.35 months of continuous cell operation to recycle sodium
- Bench scale demonstration of caustic recycling from simulant stream
  - Design scale up for high processing rates
- Dynamic testing and cell recovery from gelling and solid precipitation evaluated
  - Cell design modification eliminates flow restrictions
- Two actual waste tests conducted at PNNL
  - The Cs Decontamination Factor was 5585
  - No other radio nuclides in the catholyte solution above detection limits
- Planar technology design matured for pilot demonstration
  - Industrial size
  - Recycle and product feed up to 71.2 kgs per hour of 10 M caustic concentration

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Bench Scale Cell Testing

- Demonstrate higher throughput (55 gallons size) of feed stream
  - Multiple membrane housing scaffolds
  - Total active surface area 315 cm^2
  - 53 times increase in active area compared to laboratory size cells
- Demonstrated very successfully production of 50 wt % caustic product from AP104 simulant in continuous mode testing

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Planar Demonstration Unit in Operation

AP104 simulant NaOH

- 0.36 volts reduction in cell voltage compared laboratory size cell
- 307.2 moles of sodium transferred during the test
- Cathode current efficiency = 99.98%

- Demonstrate higher throughput of feed stream
- Successfully production of 50 wt % caustic product from AP104 simulant

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Group 5 Tank Waste Composition by ICP-OES

Constituent	µg/mL	Constituent	µg/mL
Al	7047	Sn	34
As	11	Sr	0
B	19	Ti	2
Ba	0	V	1
Ca	30	W	57
Cd	2	Zn	2
Cr	511	Zr	2
Cs	0	U	0
Fe	1	Cl	1610
Hg	1	CO_3 as Carbon	5555
K	3079	F	1842
Li	1	NO_2	59815
Mo	73	NO_3	66399
Na	104810	OH	14241
Ni	10	PO_4	2297
Nd	3	SO_4	11661
P	779	Oxalate	871
Pb	7	Acetate	544
Pd	13	Citrate	0
Rh	7	Formate	2465
Ru	34	Gluconate	0
Se	6	Glycolate	0
Si	54		
Concentrations less than 0.5 were rounded to zero			

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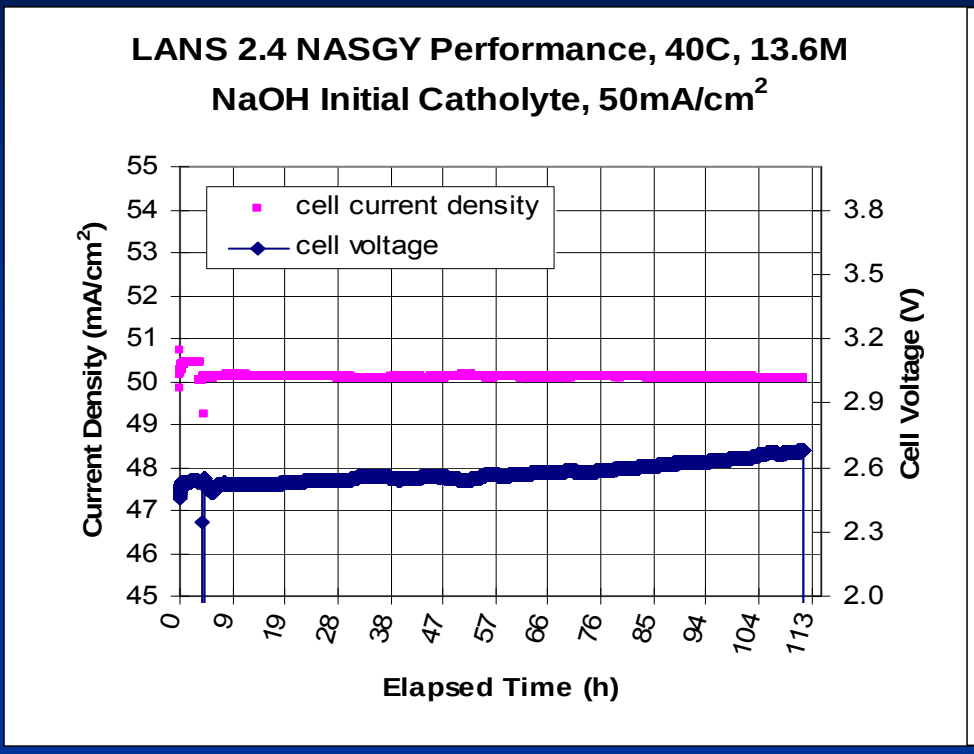
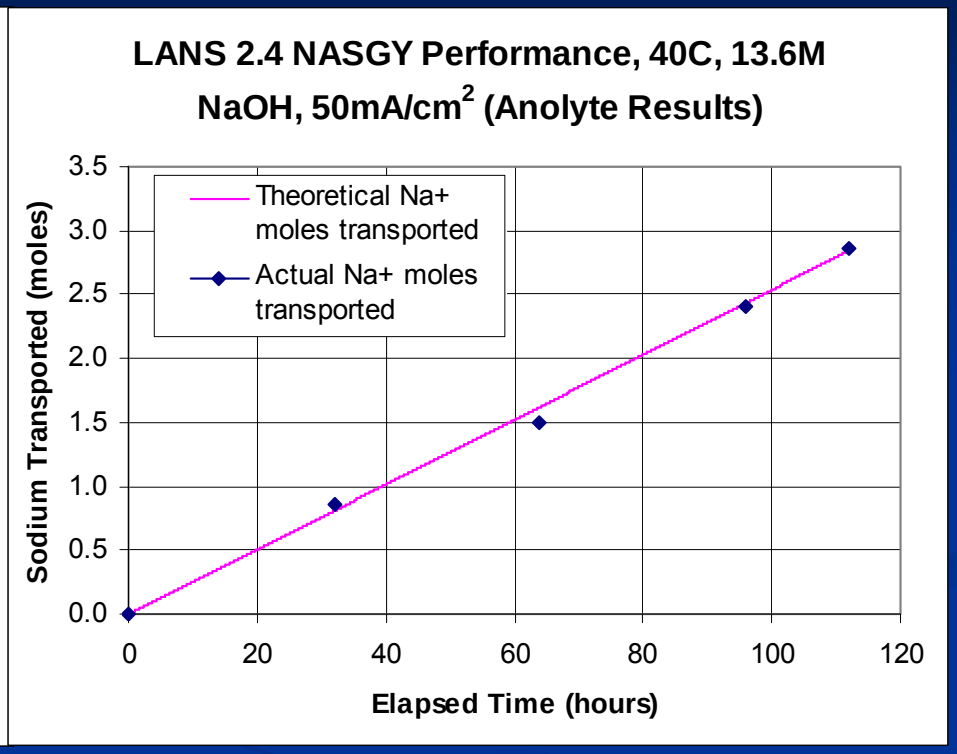
Voltage and Current Behavior- Na Transport Anolyte Results in Actual Waste





- 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.

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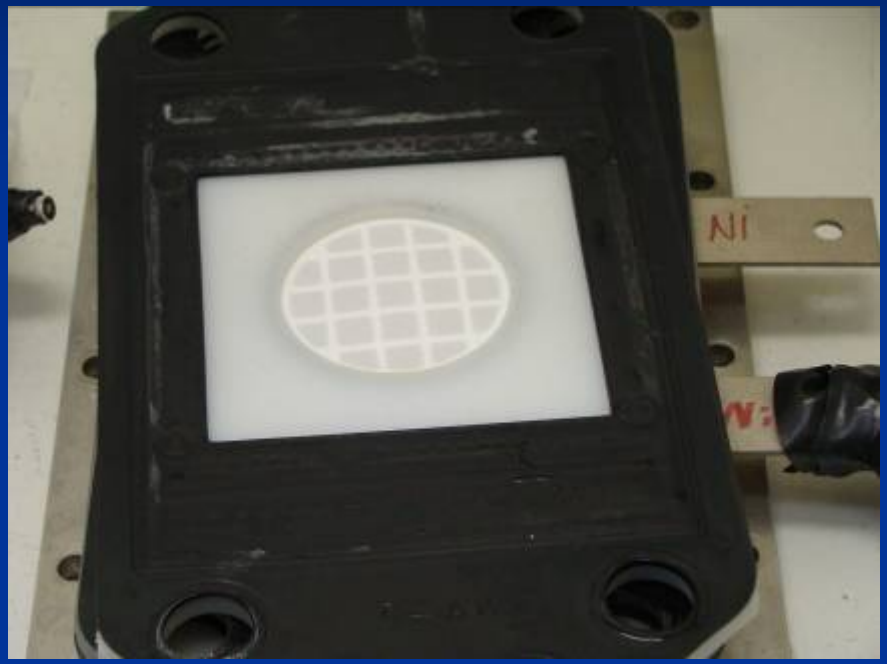
Post Experimental Investigation of Cell



- Post experimental visual inspection of the membrane shows no membrane degradation.

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Actual Waste Testing Results

Operational Parmeter	Range or Value
Membrane Type	NAS GYR6-152 (2.4" LANS)
Membrane Thickness (mm)	250 micron
Membrane Diameter (cm)	
Current Density (mA/cm^2)	50
Applied Current (Min-Max Amps)	0.68-0.69
Applied Current (Min-Max Volts)	2.45-2.68
Temperature (^{o}C)	40-45
Active Membrane Area (cm^2)	13.6
Anolyte Flow Rate (L/min)	2.6
Catholyte Flow Rate (L/min)	1.8-2.0
Catholyte (M NaOH)	14
Operating HP (psig)	2.1
Na Transport Efficiency (%)	93-106
Avg. Na Transport Rate (kg/day/m^2)	10.2
Operating Time (h)	112

- 99% sodium transport efficiency
- 2.86 moles of sodium transferred from anolyte to catholyte

- No discernable transport of non-Na cations was observed (Based on ICP-OES analysis)
- 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 Phase

- Ceramic tubular configuration device scale up
  - → smaller foot print, minimize seal area- reliability
- Process development to meet site needs
  - → Caustic recycling economics to recycle sodium for near term use
  - → Based of sodium flow sheet requirements for CSL and NTCR processes
  - → Impacts of stream stability and maximum sodium separation
- Engineering Scale Up- Technology Demonstration unit (TDU) plan
  - → Maturity of process
  - → Risk assessment

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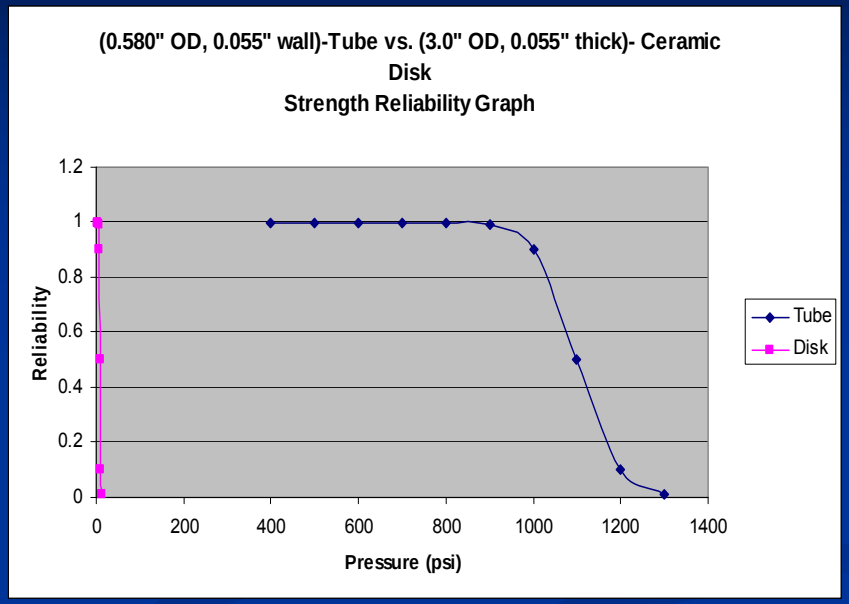
Tubular membrane reliability and Weibull Statistical Analysis



- 250 times increase in burst strength reliability compared to planar membrane

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NaSICON Manufacturing Activities

- July 2007 DOE Independent Assessment Report
  - Concern over Ceramatec's ability to support large scale manufacturing
  - ✓ Solved by CoorsTek acquisition of Ceramatec
- Working with CoorsTek to determine the most optimum method for low cost NaSICON planar and tube manufacturing
  - CoorsTek investing significant internal resources to evaluate different methods
  - Example: tube excursion, aqueous spray drying, iso-pressing, bag pressing, tape casing, and uni-axial pressing
  - CoorsTek NaSICON tubes and planar already delivered for evaluation
- Expect to determine most cost effective method by Fall of 2009

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Sodium Recycling from PEP Leachate and Group 5 Simulants

March 09 → **June 09**

I
500 micron
15 wt.% NaOH
50 mA/cm2
AP104
Life Time
2 Tests

II
500 micron
35 wt.% NaOH
50 mA/cm2
Group 5
Life Time
In/Out Configuration
2 Tests

III
500 micron
35 wt.% NaOH
50 mA/cm2
PEP Leachate
Life Time
Batch Mode
1 Test

IV
800 micron
35 wt.% NaOH
50 & 100 mA/cm2
PEP Leachate
Life Time
Batch mode
2 Tests

V
35 wt.% NaOH
50& 100 mA/cm2
Sodium removal
Optimization
Batch mode
2 Tests

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Evaluation Conditions

- Ability of NaSICON Tubular membrane cells to recycle sodium for near term applications (S and SX waste tanks)

  → Evaluate the amount sodium removal from Group 5 and PEP Leachate simulants before solid precipitation

  - Cell operation in Batch mode vs. Continuous mode
  - Effect of Operating Temperature: 45°C and 65°C
  - AP104, Group 5 and PEP leachate simulants
  - Batch mode vs. continuous mode operation
  - 1 gallon versus 20 gallon tank size
  - 1-1.5 gpm flow rate of feed
  - Operational current density: 50 and 100 mA/cm^2

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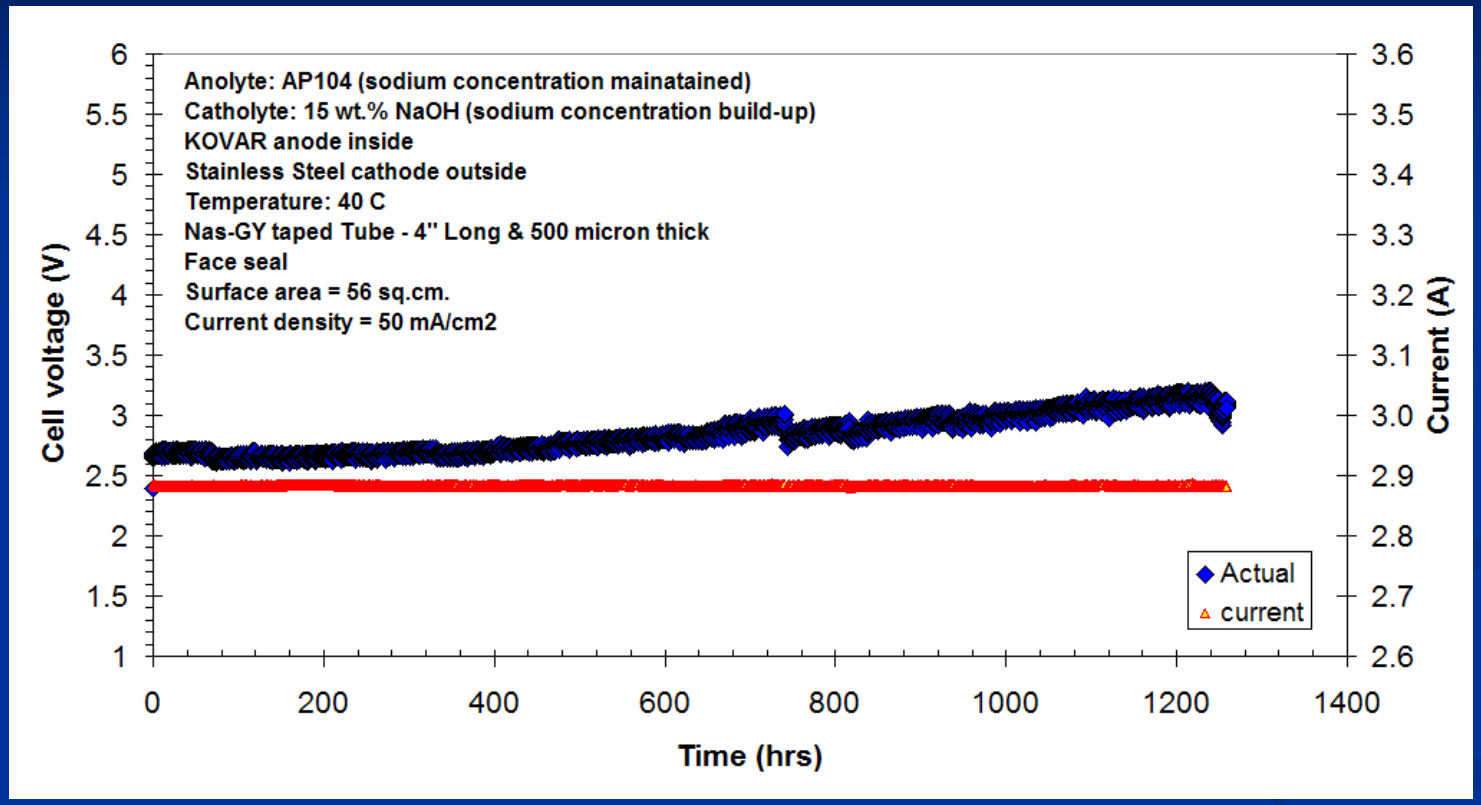
Tube cell performance in AP104



- Test operated at an average voltage of 2.88V
- > 50% sodium separation from AP104 Waste simulant
- No observation of precipitation

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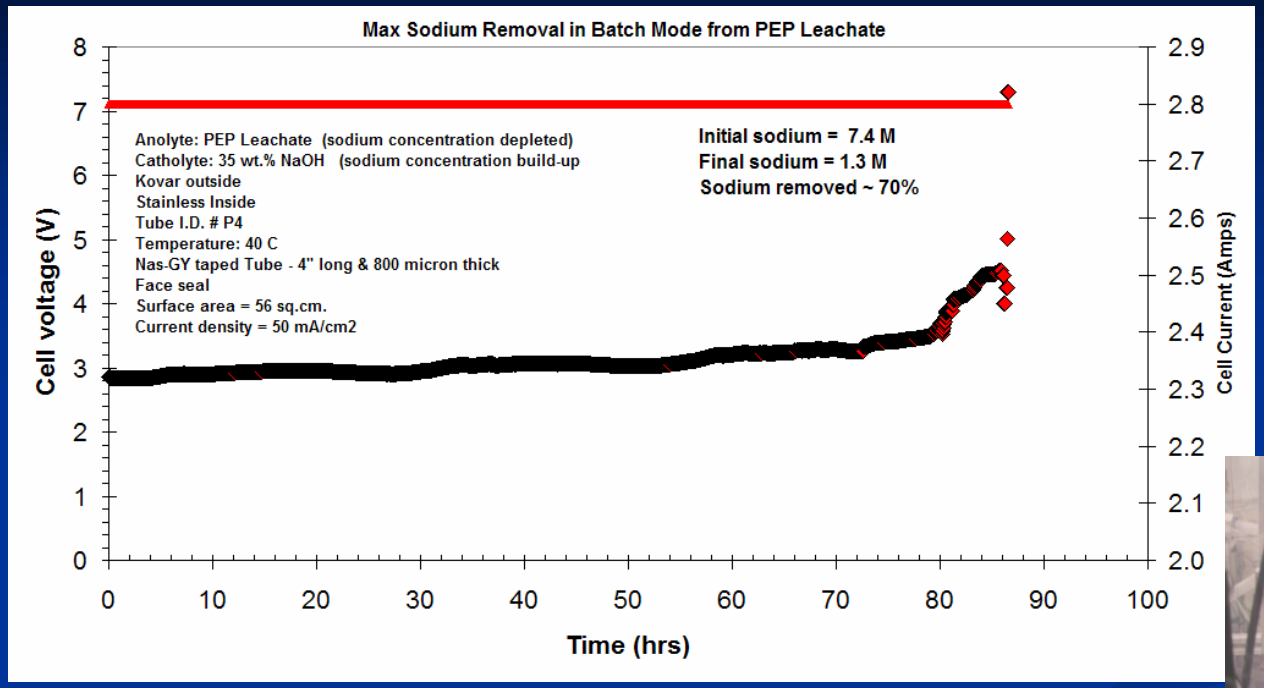
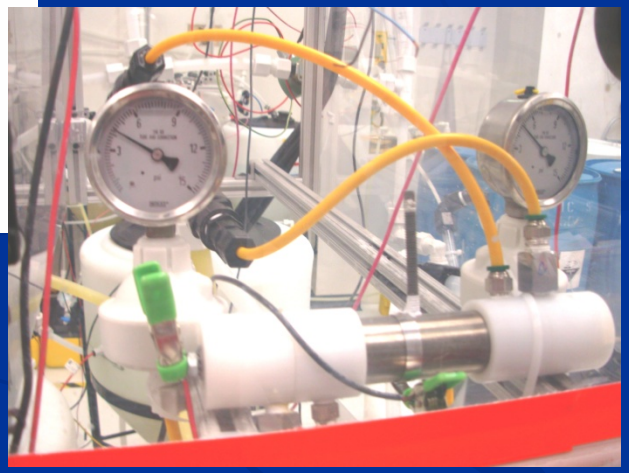
Batch Mode: Tube cell performance in PEP Leachate





- Nearly 70 % of sodium removed from PEP leachate
- Cell operated at 50 mA/cm^2 at less than 3.6 V before alumina precipitation
- Final catholyte NaOH concentration = 47.2%
- Current efficiency = 99.5%
- Power consumption = 2.12 kWh/kg of NaOH generated

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PEP leachate Characterization: Before and After sodium Removal

As received PEP

Alumina Precipitate

- Alumina precipitation started to appear after 65 % of sodium was separated
- Precipitation in the cell at end of the test- 70% separation

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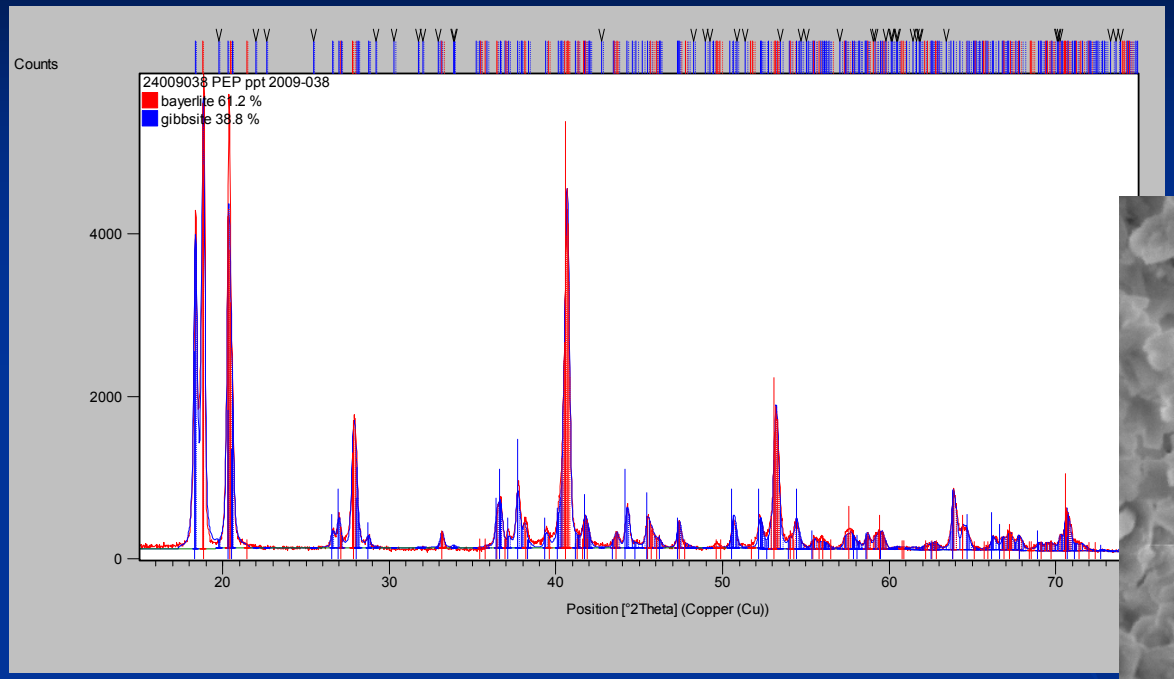
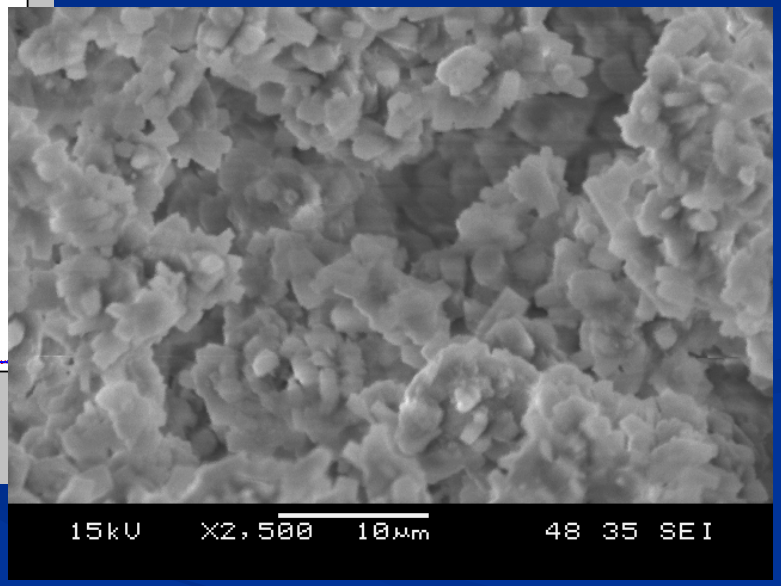
XRD analysis of the Precipitate: After 70% Sodium Removal from PEP





- Two aluminum hydroxide phases were present in the precipitate analyzed from recovered and dried sample after test.
- XRD analysis identified the phases as Bayerite $Al(OH)_3$ and Gibbsite - $AL(OH)_3$
- A Rietveld refinement using crystal structure information from the AMCSD estimated the Bayerite and Gibbsite amount at 61.2% and 38.8% respectively.

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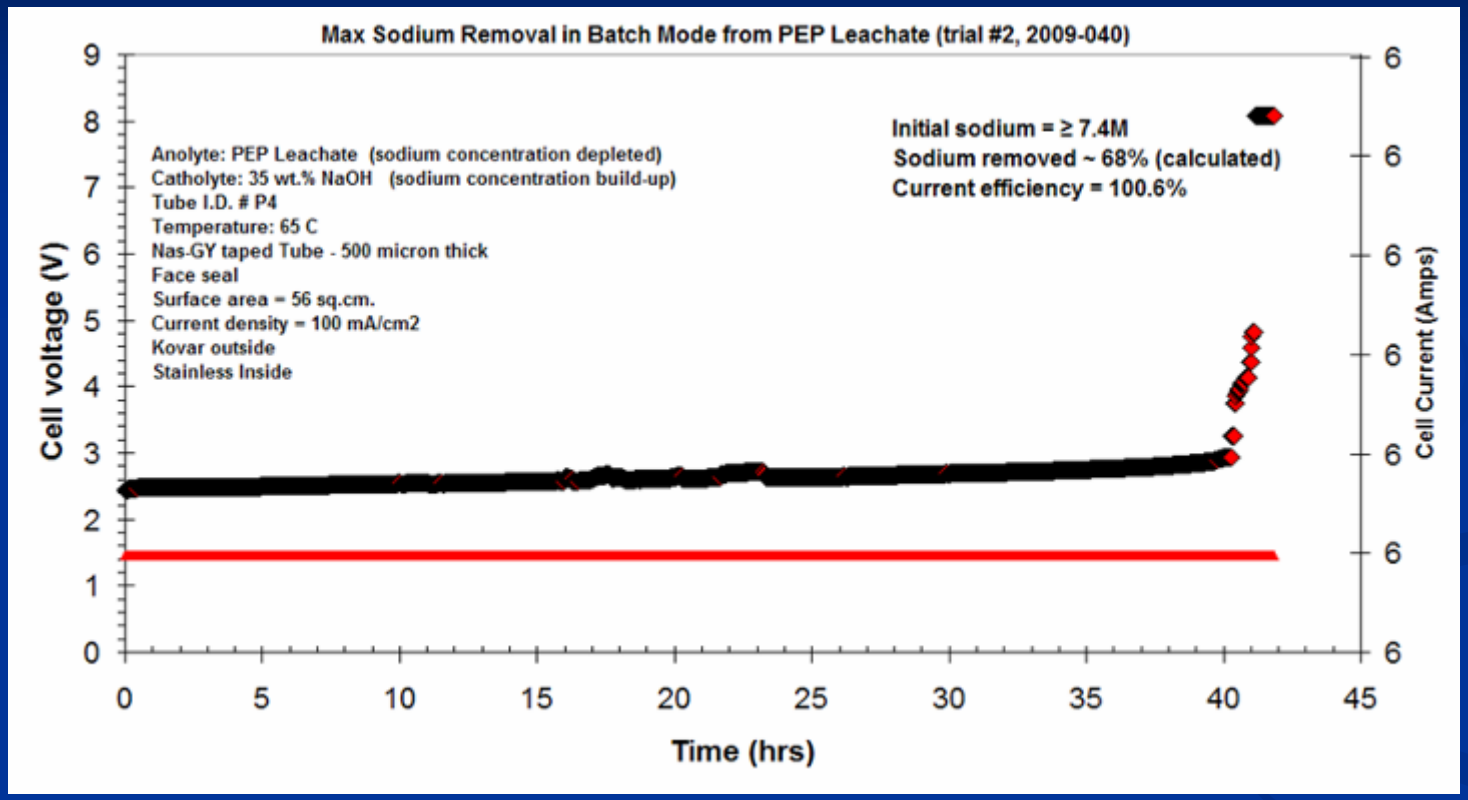
Batch Mode: Cell performance in PEP Leachate at 65°C



- 68% of sodium removed from PEP Leachate Cell Operated at 100 mA/cm^2 at less than 2.95V before alumina precipitation
- Final Catholyte NaOH concentration = 47.2%
- Sodium transfer current efficiency = 100.6%
- Power consumption = 1.84 kWh/kg of NaOH generated

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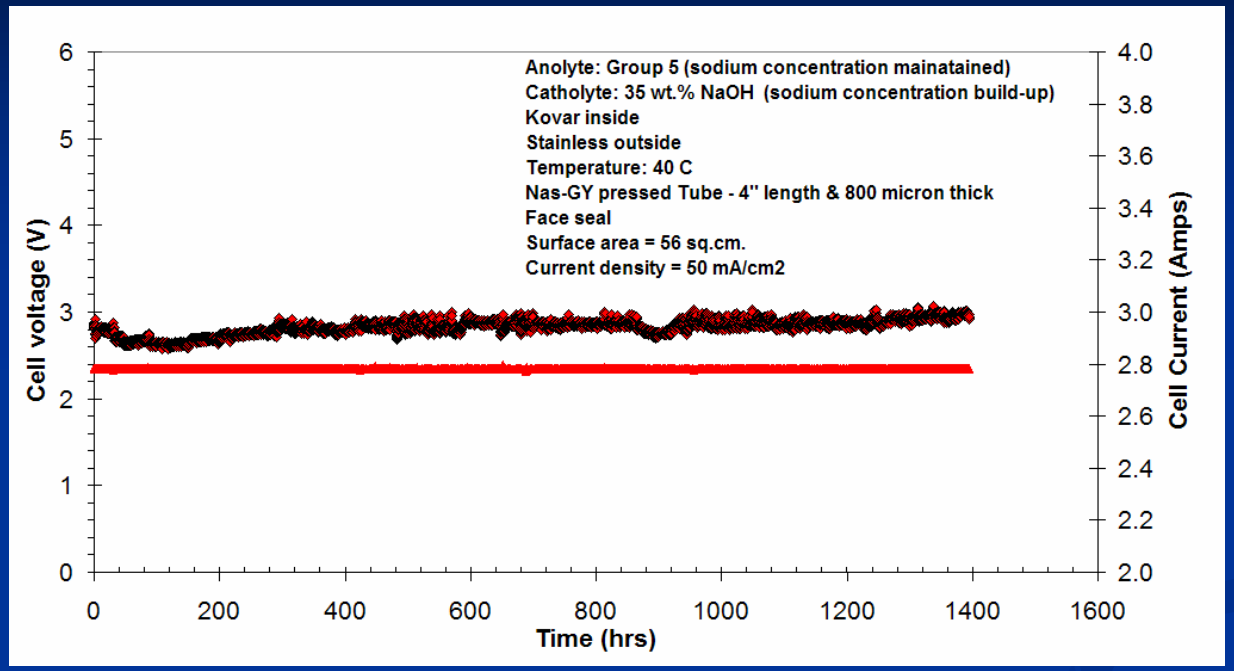
Continuous Mode: Tube cell performance in Group 5



- Test ongoing
- Current Desnity-50 mA/cm^2- average voltage of 2.83V
- Catholyte NaOH concentration building during the test (presently 42.1%)
- Sodium transfer current efficiency current efficieny = 99.25%
- Power consumption = 1.89 kWh/kg of NaOH generated

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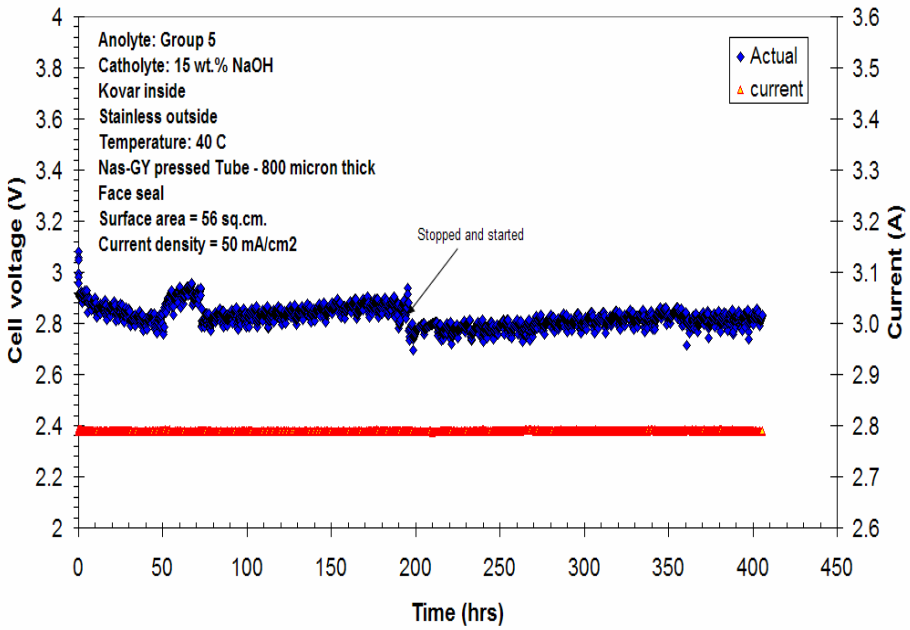
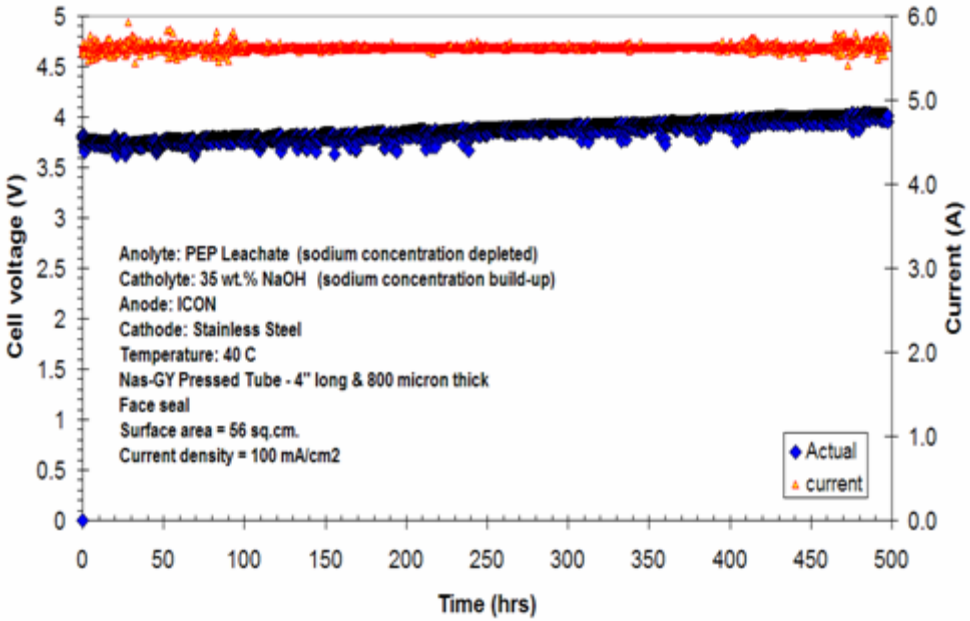
Continuous mode: Tube cell performance in Group 5 / PEP Leachate





- **Test ongoing**
- **Cell operation at 100 mA/cm²** at an average voltage of 3.86 V
- **ICON anode**
- **Catholyte NaOH concentration building during the test (presently 42.83%)**
- **sodium transfer current efficiency = 97.44 %**

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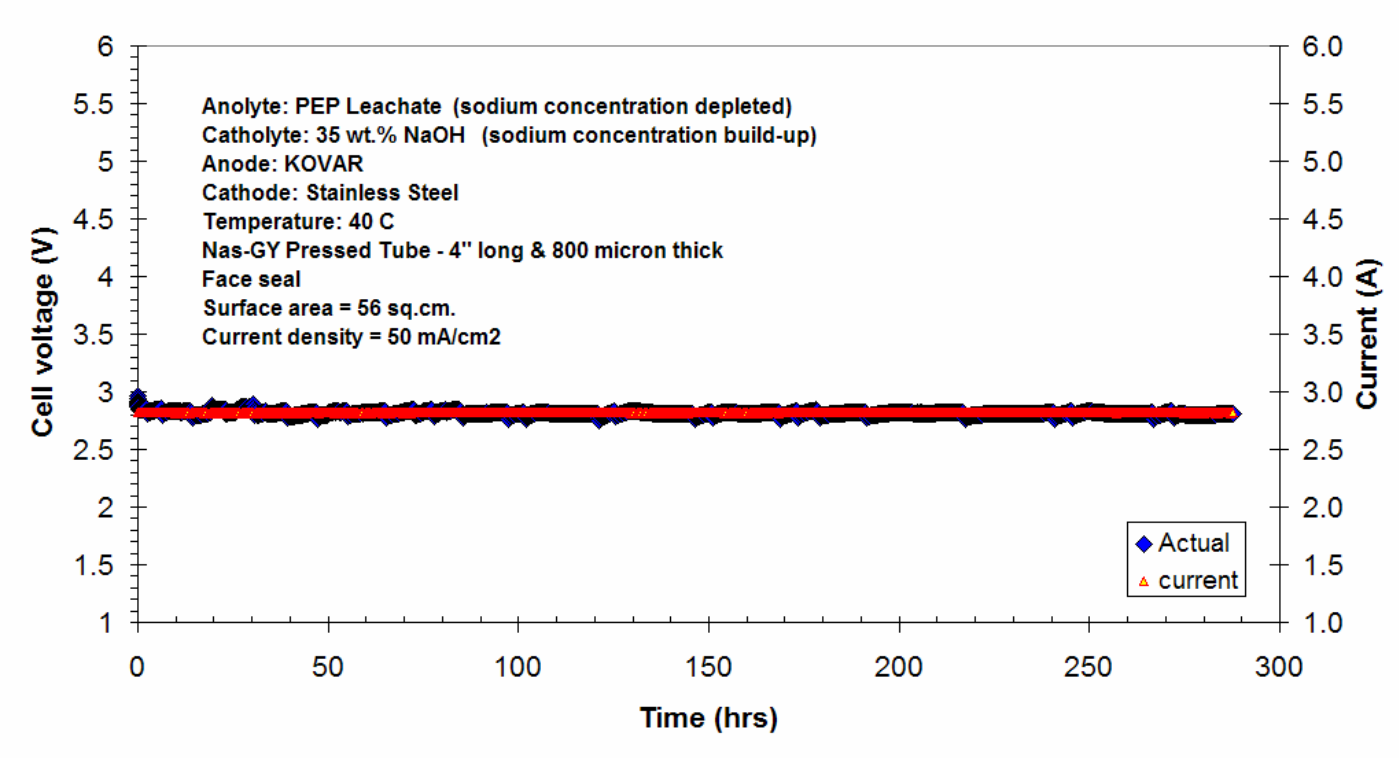
Continuous mode: Tube cell performance in PEP Leachate



- **Long Term Test (ongoing)**
- **Cell Operation at 50 mA/cm2 and average voltage of 2.814V**
- **Anode outside configuration**
- **Catholyte NaOH concentration building during the test**

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Comparison of Sodium Removal Performance in Group 5/PEP Leachate

	Group 5	PEP
Na (M)	4.425	7.390
Al (M)	0.229	0.750
Starting Na/Al molar ratio	19.318	9.853
Na/Al molar ratio when Alumina precipitates	TBD	3.449

- 65 % of sodium removal before Alumina precipitation is visible

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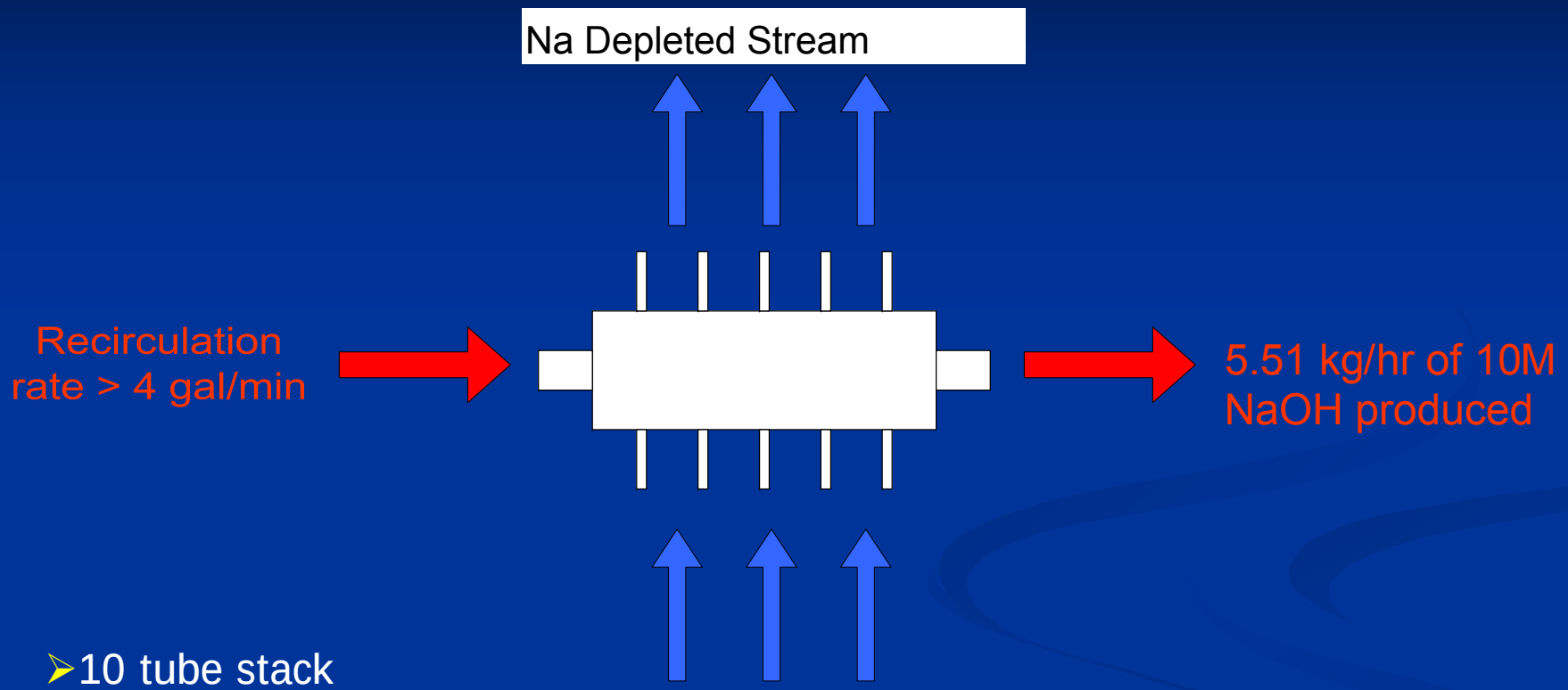
Technology demonstration Unit: Oct 2009



- 10 tube stack
- 8 stacks arranged in Modular configuration

2.5 kg/hr process rate of PEP

Recirculation rate > 4 gal/min

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Summary

- Designed, built and validated cell configuration for planar and tubular ceramics
- Demonstrated 7.35 months of continuous operation to separate sodium from LLW simulant to make 50 wt % caustic
- Successfully demonstrated a bench scale unit (Multi Stack-24 membrane cell)
- Two successful actual waste tests were conducted
- Performance reliability established with multiple LANS planar membrane cells
- Recycle up to 65 % of sodium from PEP simulant represents CSL and NTCR processes) without affecting the chemical and physical properties of the simulant using tubular configuration ceramic membrane cells

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Q/A

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