Electrochemical Process to Recover Sodium from Radioactively contaminated Alkaline Wastes

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Presentation Outline

- **Project Description**
- **Technical Strategy/Approach**
- **Technical Results and Status**
- **Impact on High Risk/Cost Reduction or Avoidance**

Opportunity

Hanford Site

Problem:

- 53 million gallons of highly radioactive mixed waste are stored in 177 storage tanks.
- HLW is processed to remove aluminum oxides in the form of Gibbsite or Boehmite sludge with sodium hydroxide

Solution:

- A technology for recycling caustic to reduce overall sodium load to LAW vitrification is required

Result:

- Successfully developed technology will reduce overall sodium demand for Low Activity Vitrification process at WTP by recycling the sodium hydroxide for use in aluminum leaching

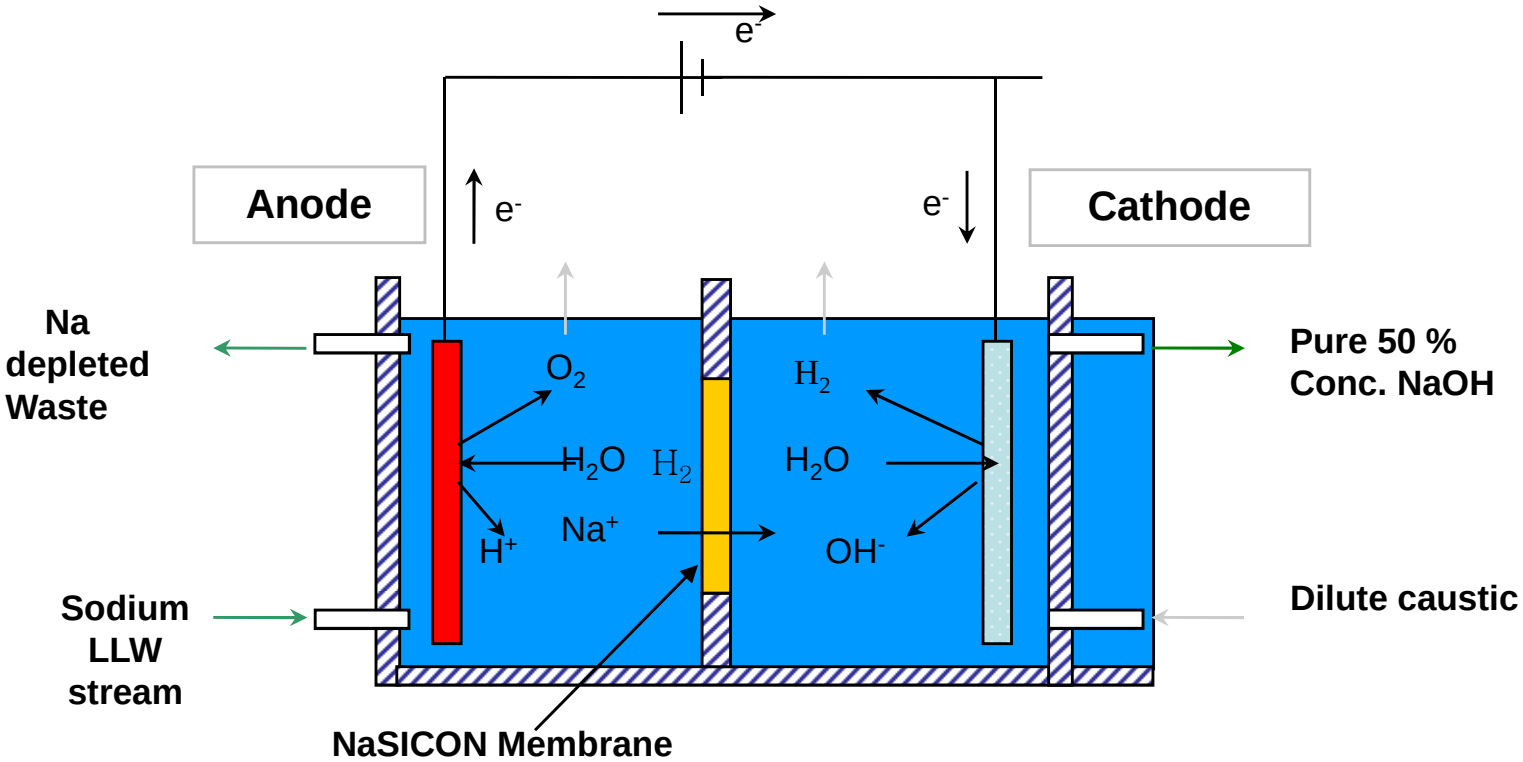
Project Description

- As part of WTP flow sheet process-Ceramatec, Inc. is developing an NaSICON electrolytic membrane based technology to recover sufficient caustic from WTP LAW vitrification feed
- The process also regenerates the sodium in the form of “clean” sodium hydroxide for reuse on site
- Ceramic membrane technology will separate sodium from LAW waste stream and reduces the quantity of LAW glass to be produced
- Allows for direct sodium hydroxide generation up to 50 wt% and prevent migration of Cs or radionuclides to the sodium hydroxide stream

Technical Strategy/Approach

- Scale up ceramic membrane process to efficiently recycle sodium from LAW for use as sodium hydroxide in down stream processes
- Complete qualification of NaSICON Cells at lab scale in simulant and real wastes
- Establish robust operation in multiple feed streams
- Complete cycling and cell recovery operations
- Evaluate feed stability after sodium recovery to meet downstream processing requirements on site
- Complete a safety evaluation of electrolytic system-process controls
- Scale up and demonstrate a successful larger system for caustic recycling- up to 250 gallons batch size
- Conceptual design of a full size system for caustic recycling

Principle of Operation:
Electrolytic NaSICON Ceramic membrane cell



NaSICON Membrane

Na=Sodium

SI=Super Ionic

CON= Conductors

Electrode Reactions:

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

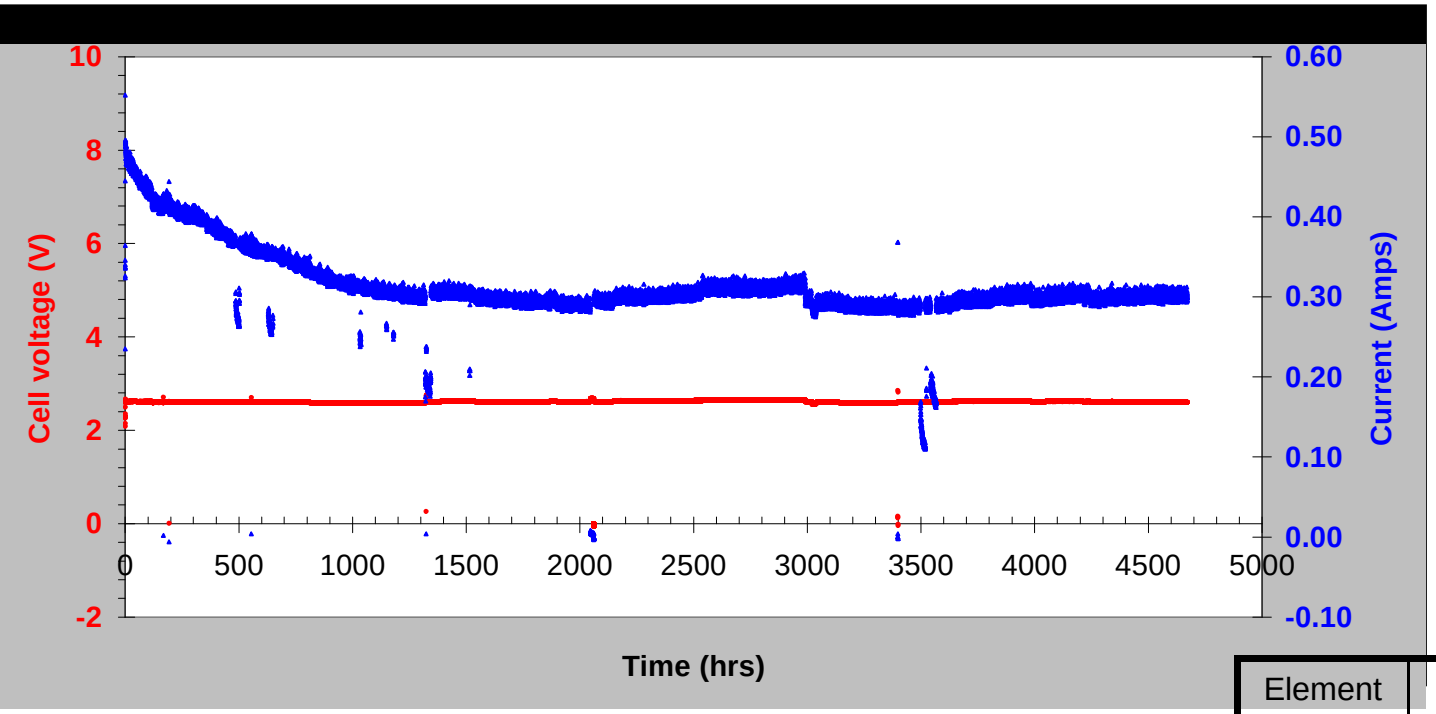
Cathode: $4H_2O + 4e^- = 2H_2 + 4OH^-$

Overall: $2H_2O = 2H_2 + O_2$

Technical Status and Results

- Validated technology at lab. scale with non-radioactive waste simulants and actual waste
  - 6.5 months of continuous operations of cell to recycle sodium from AP 104 simulant- 12 gallons batch size
  - Made 50 wt % caustic product from simulant stream
  - Demonstrated efficient (> 95%) separation of sodium from actual waste
  - Performance reliability for robust operation demonstrated in AP104 simulant
  - Cell recovery tests in the event of gelling and precipitation is in progress
- Ceramic manufacturing scale up in progress to make statistically reliable and quality ceramic
  - Production Partner Indentified-CoorsTek
- Design and demonstration of bench scale unit to recycle caustic starts in fiscal 2009 - up to 250 gallons simulant batch size

Process Optimization Highlights

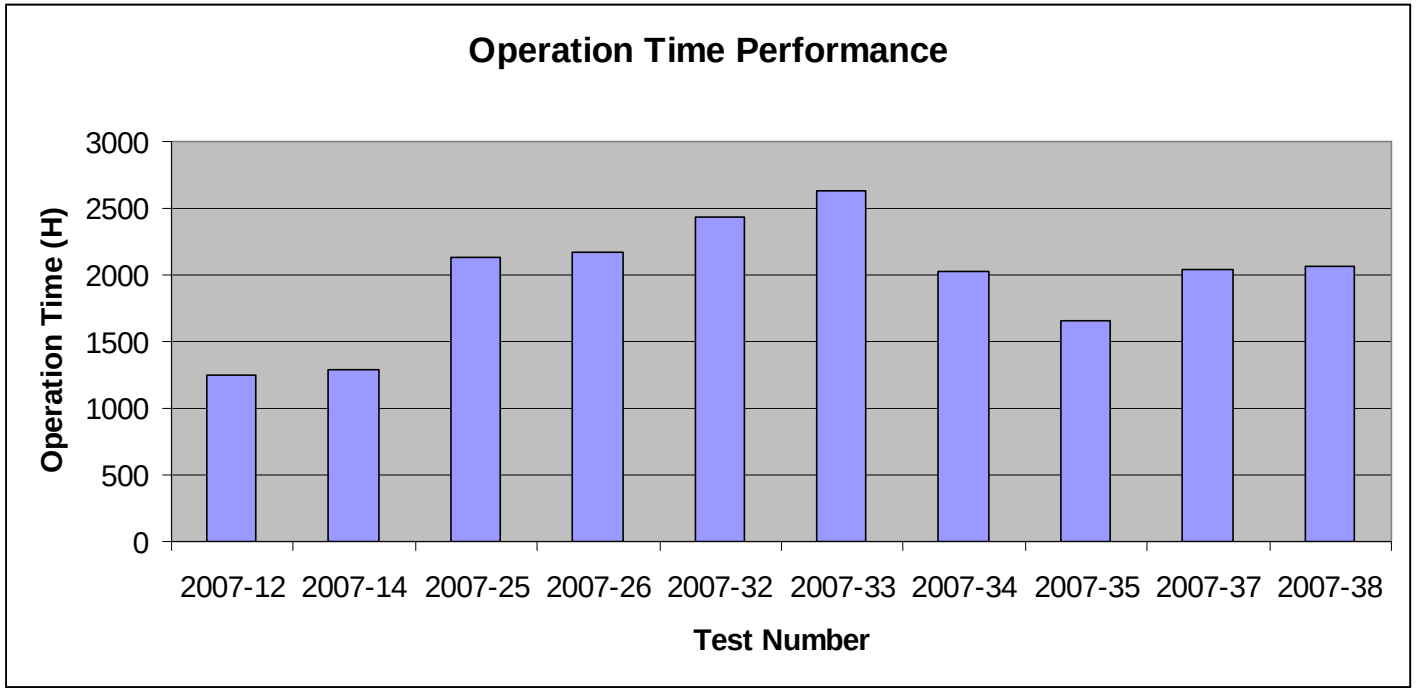


Element	ICP detection limits mg/L	Initial Concentration, mg/L	Final Concentration, mg/L
Ba	0.02	< 0.02	< 0.028
Cd	0.04	< 0.04	< 0.04

- Demonstrated 6.5 months of continuous cell operation at 50 mA/cm^2
- Recycled sodium from AP104 Simulant
- Low cost Anode- 15 wt.% NaOH catholyte, 2.6 volts
- Established reliable operation

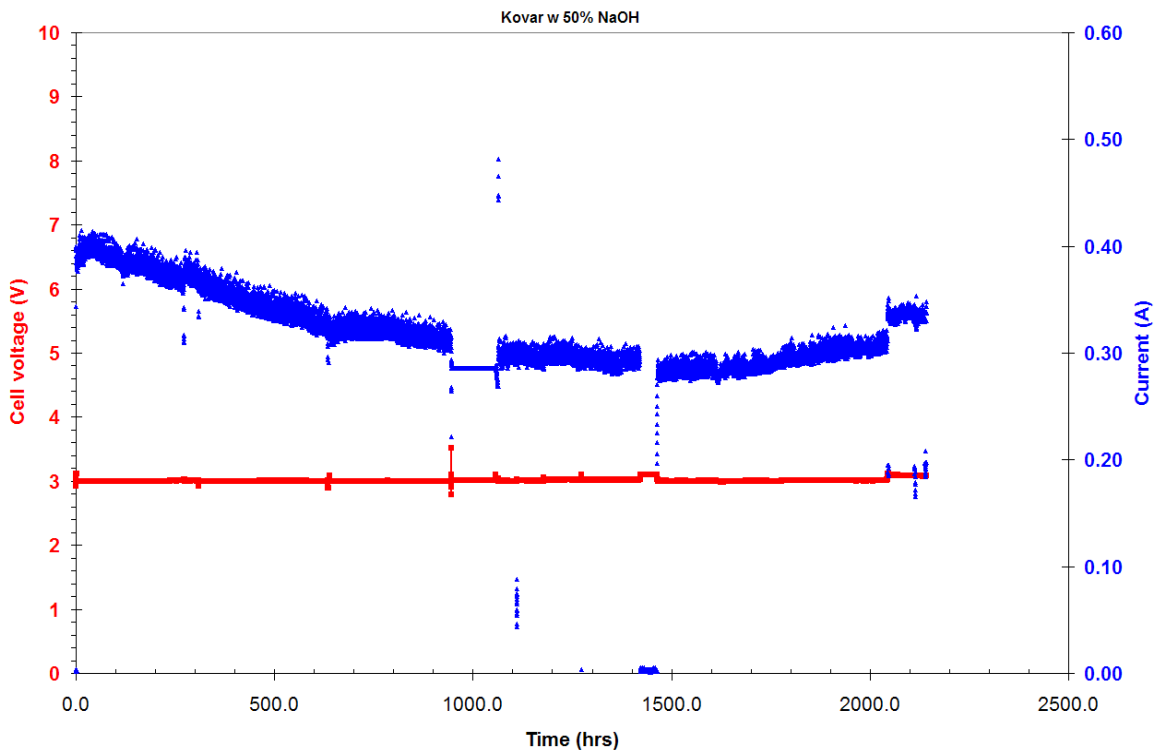
Statistical Performance Highlights

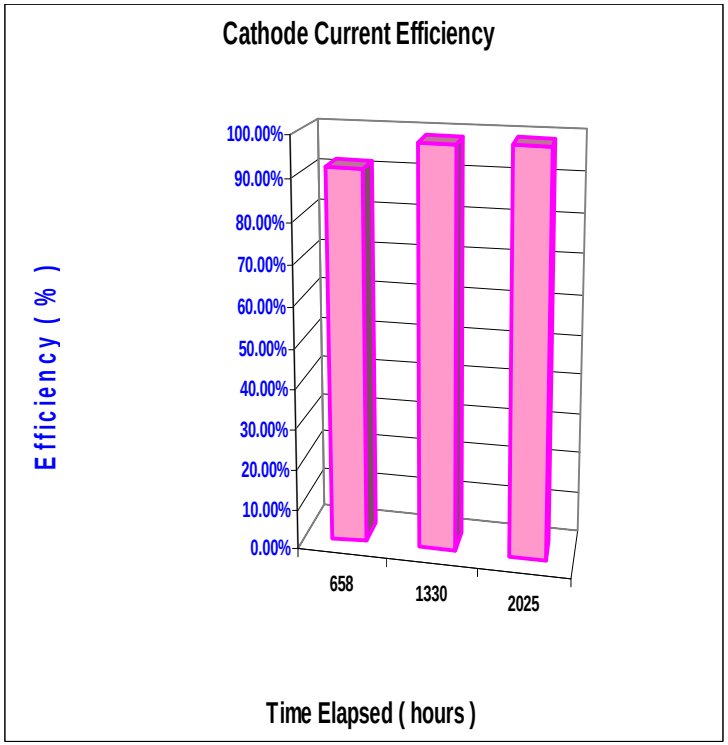
Pt/Ti-Anode, 15 wt.% NaOH catholyte 2.6V, 10 separate tests in AP104 simulant



- 3 months of reliable performance at 2.6 volts
- 51.227 mA/cm^2 average current density- Std. Dev. = 8.41
- Tighter distribution anticipated with use of final set of operation conditions

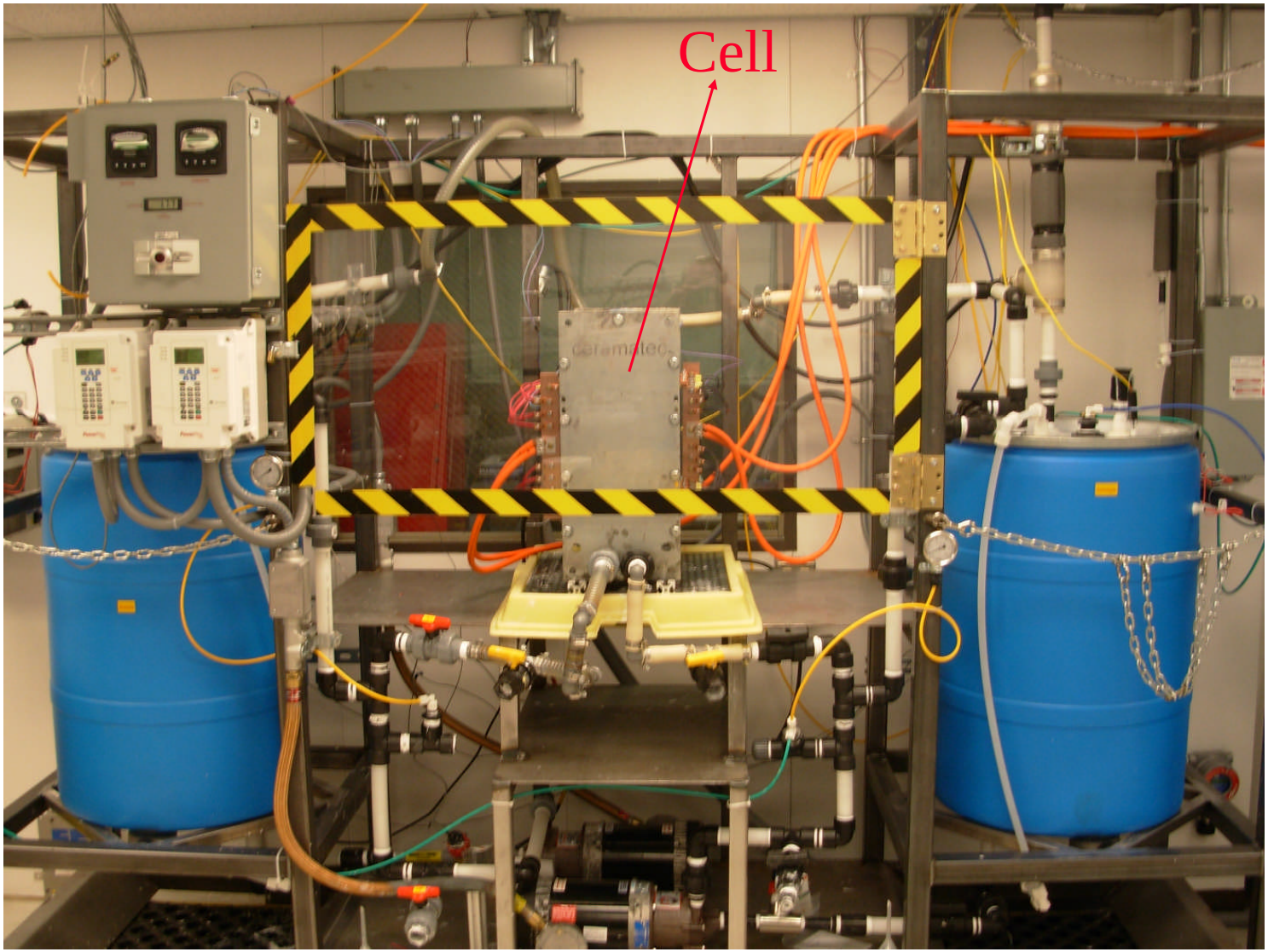
Performance Optimization Highlights





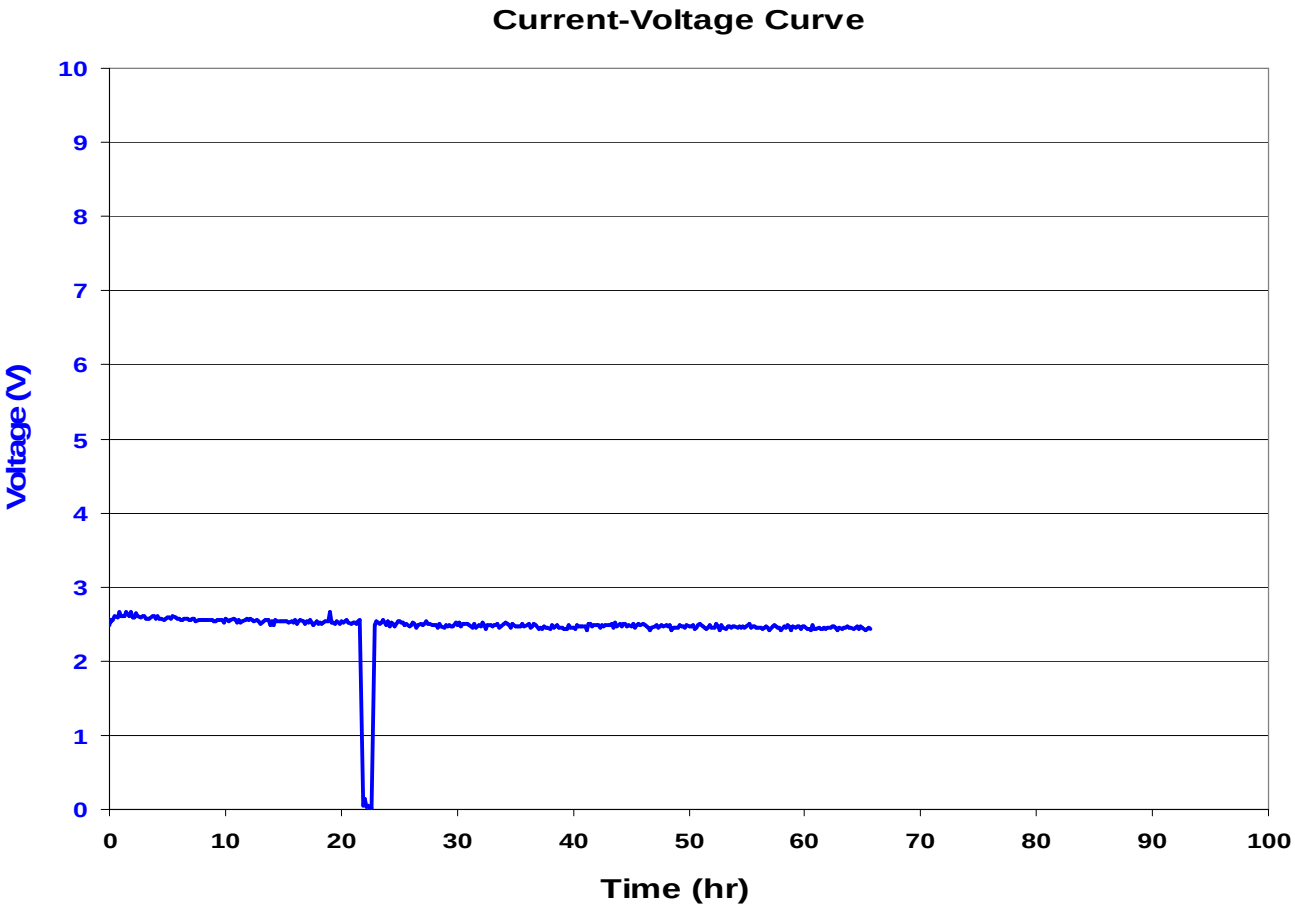
- Demonstrated production of 50 wt% caustic from AP104 simulant
- 3 months continuous operation with Kovar electrode at high sodium transfer efficiency
- Unit Operated in semi continues mode

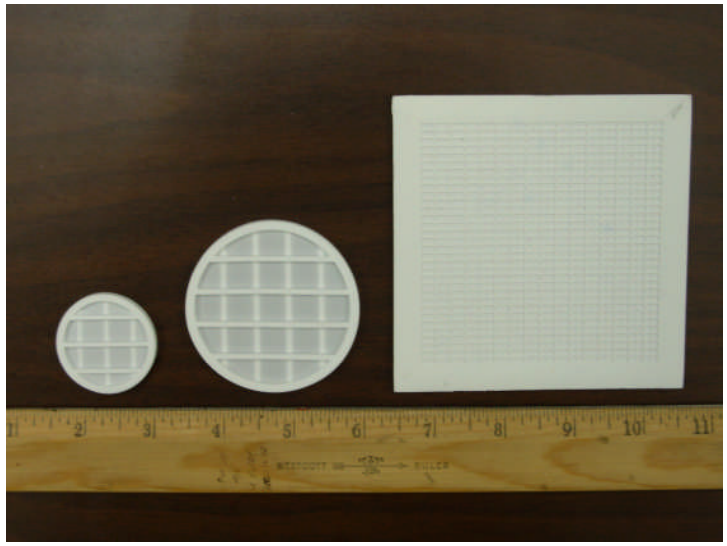
Bench Scale Cell Validation Test:



- Validation of multiple ceramics housing and seals

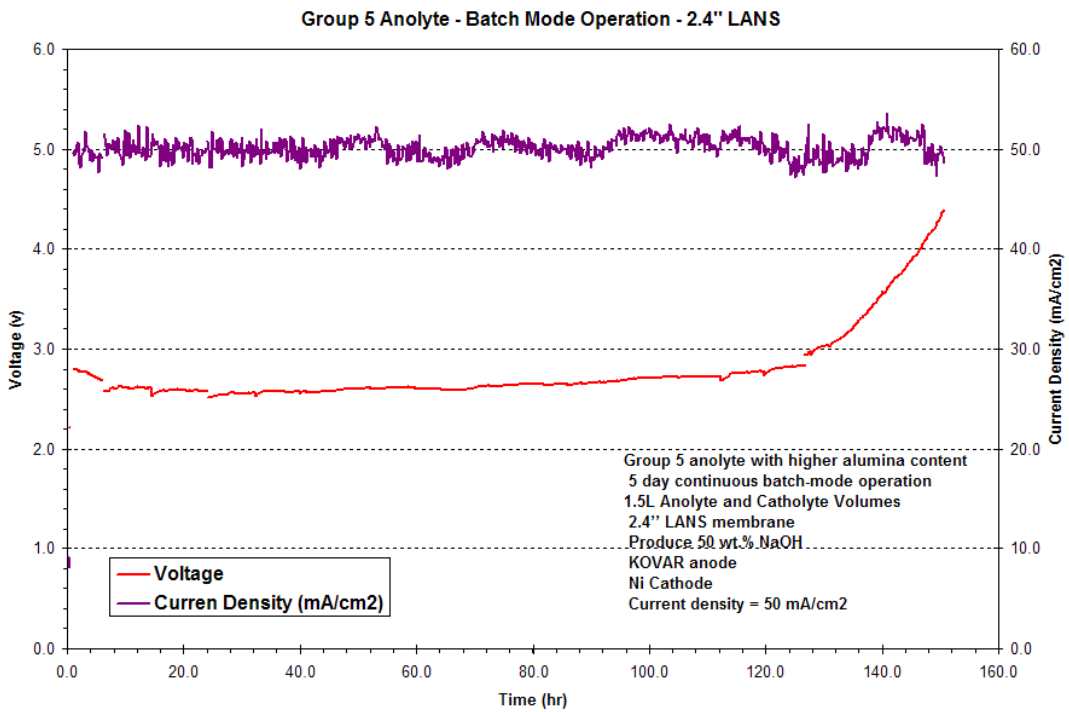
Operation of Single Cell- Scaffold with 8 Ceramics





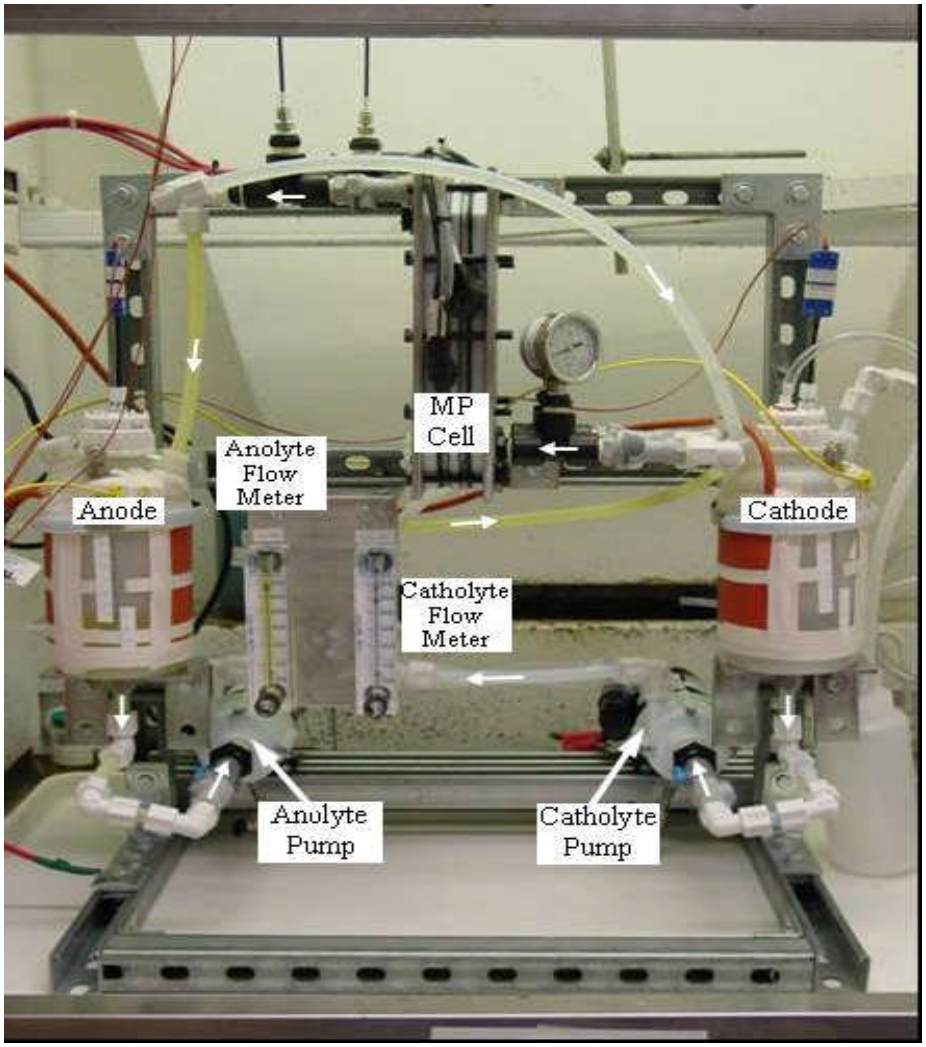
- Tank Feed: 55 gallons of caustic
- 3 GPM flow-Batch mode
- Cell Operated at 100 mA/cm^2 current
- Cell size- 14 X scale up from Laboratory size

Batch Mode Testing- 2.4" LANS



- 5 identical tests conducted with Group 5 simulant
- In preparation for 120 hours (5 days) actual waste testing at PNNL- August 2008

Radioactive Bench-scale unit installed in fume hood @ RPL

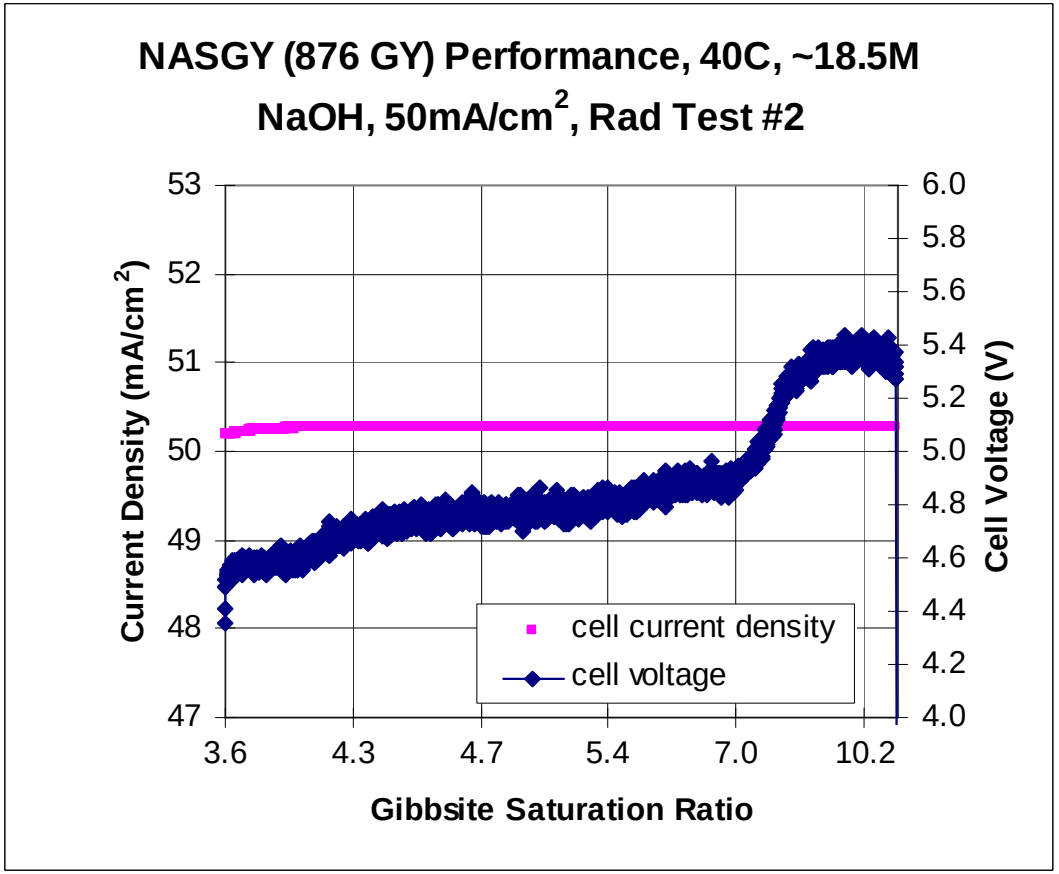


Experimental Conditions

Experimental Conditions

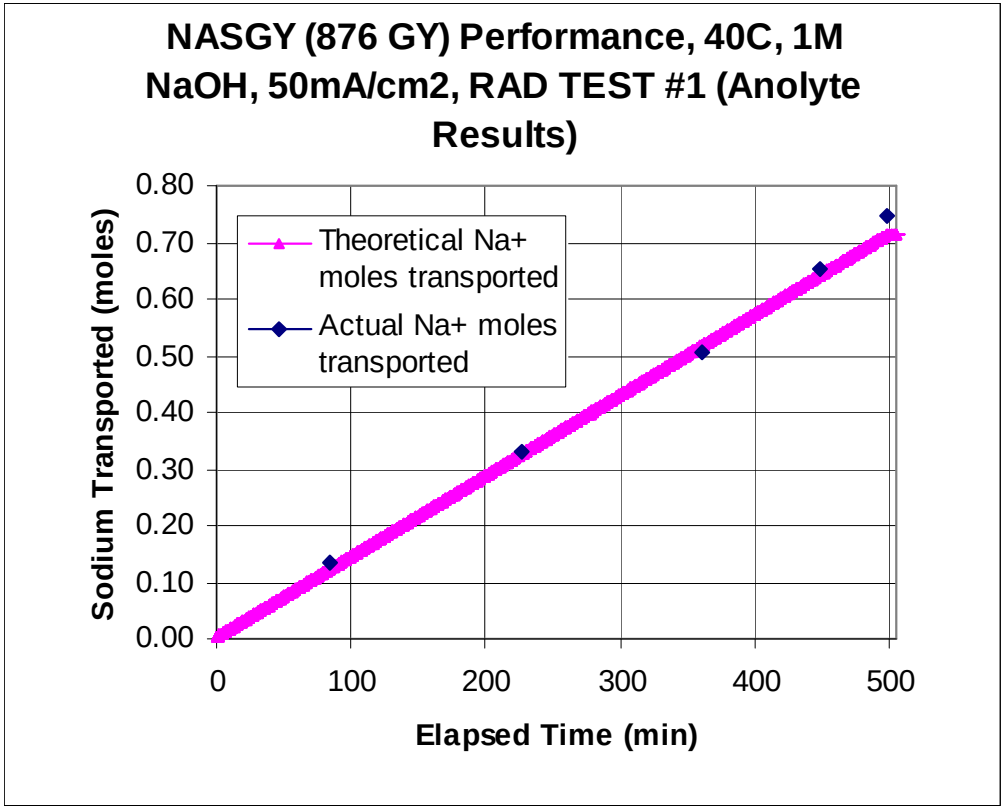
Membrane Type	NASGY (876 GY)
Membrane Thickness	1.4 mm
Membrane Diameter	7.62 cm
Current Density	50 mA/cm^2
Applied Current (Min-Max)	2.24-2.29 amps
Applied Voltage (Min-Max)	4.12-5.44 volts
Temperature	37-43°C
Active Membrane Area	45.6 cm^2
Anolyte Flow Rate	2.4-2.5 L/min
Catholyte Flow Rate	1.9-2.7 L/min
Scaffold Configuration	S3 edge seal with EPDM o-ring
Catholyte	1M & 19M NaOH
ΔP *max*	$\leq$ 0.25 psig
Operating ΔP	1.6–1.9 psig

19M NaOH Catholyte Test

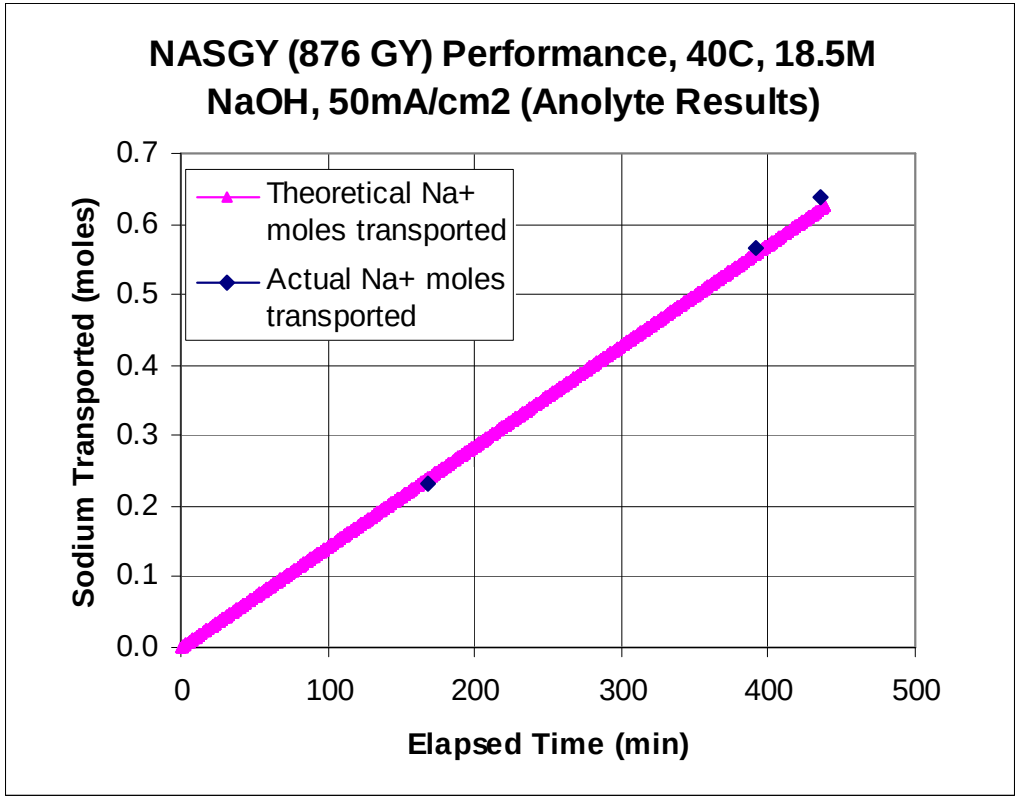


Na Transport Results

Anolyte (1M NaOH)



Anolyte (19M NaOH)



- Both sets of results are in good agreement with theoretical Na transport based on applied current (varied 95-103% of theoretical based on anolyte results). Na transport based on OH^- titration results.

Radionuclide Transport

	Test 1			Test 2		
	Anolyte Initial (μCi/ml)	Catholyte Final (μCi/ml)	Df (initial/final)	Anolyte Initial (μCi/ml)	Catholyte Final (μCi/ml)	Df (initial/final)
Total β	1.75E+00	4.66E-05	37446	6.11E-01	7.04E-05	8679
Sr-90	7.14E-01	<4.0E-5	>17850	2.44E-01	<4.0E-5	>6100
Co-60	1.53E-03	<2E-6	>765	1.48E-03	<2E-6	>740
Sb-125	2.01E-03	<5E-6	>402	1.84E-03	<5E-6	>368
Sn/Sb-126	1.71E-03	<2E-6	>855	1.30E-03	<2E-6	>650
Cs-137	3.00E-02	1.28E-05	2344	3.06E-02	1.85E-05	1654
Eu-154	6.17E-04	<5E-6	>123	1.11E-04	<5E-6	>22
Eu155	2.37E-04	<6E-6	>39.5	3.90E-05	<7E-6	>6
Am-241	7.09E-04	<1E-5	>70.9	9.78E-05	<3E-5	>3

- Cs^+ Selectivity = > 2330 (1M NaOH)
- Cs^+ Selectivity = > 1640 (19M NaOH)
- Al, K, and Sr were not detectable in the catholyte ICP data.

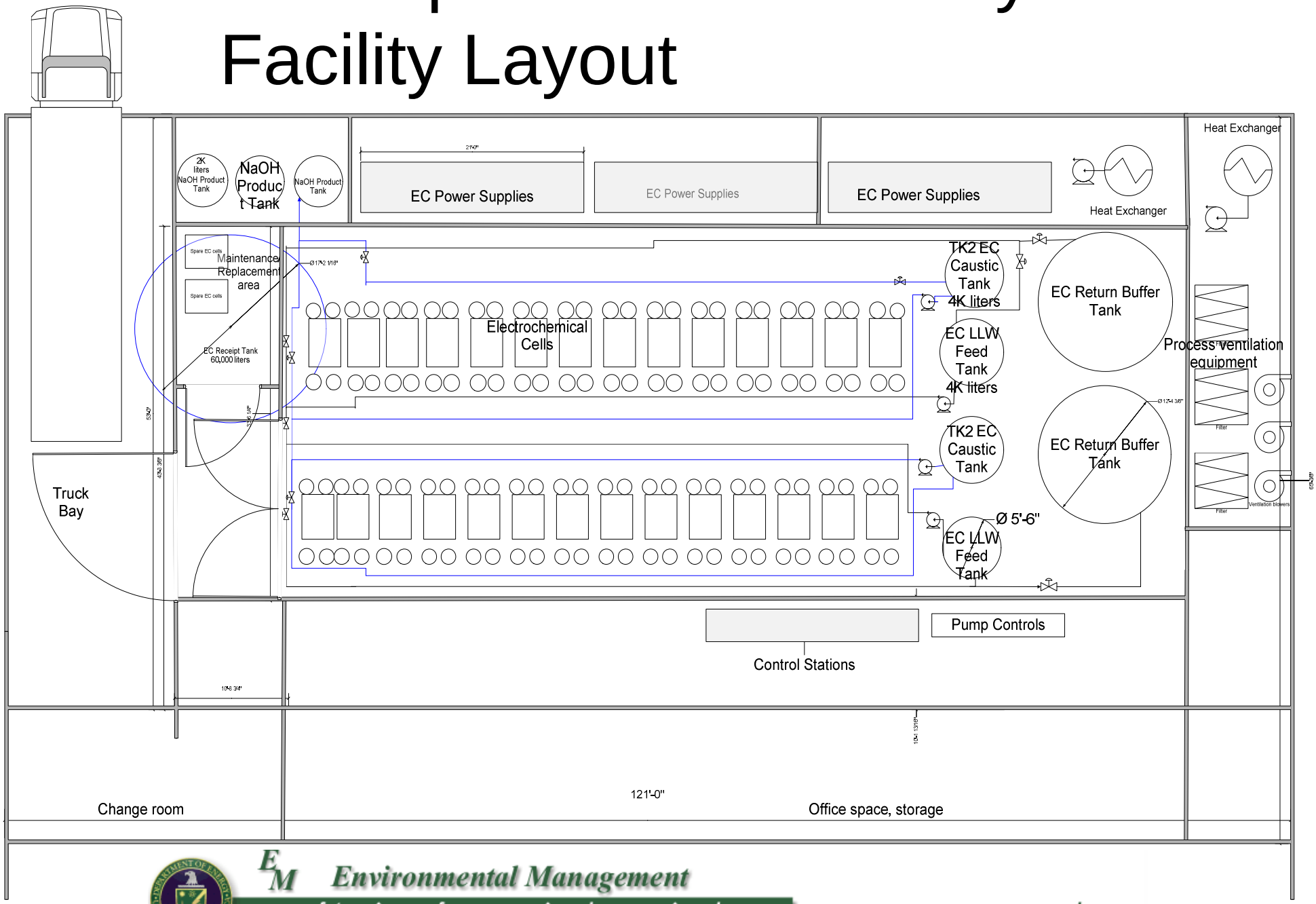
Project Impact

- Ceramatec's NaSICON patented technology can recycle sodium from low level radioactive waste for uses on site

- **Result:** (1) High potential to reduce handling, processing, of waste and Time Schedule at DOE sites.

  (2) Significant cost savings for waste cleanup by lowering volume of waste and costs associated with procurement of 50 wt % of caustic

Conceptual-Sodium Recycle Facility Layout



DESIGN: Progression Plan of Electrolytic unit

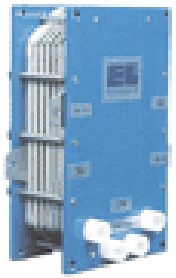
Nov 2009

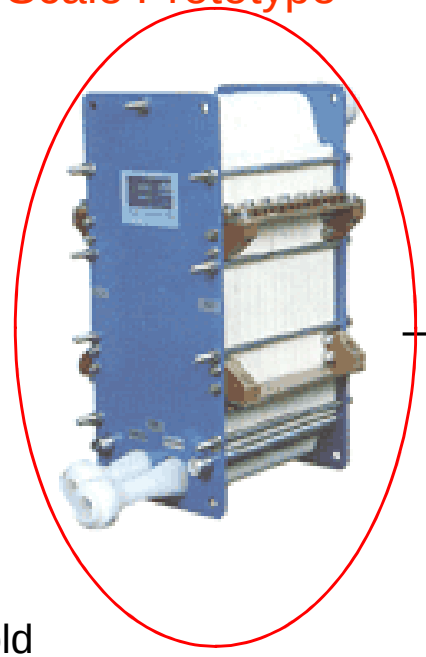
Production full size

Bench Scale Prototype

Laboratory cell

Concept-Microflow Cell





3.29 g_{Na^+}/day/scaffold

Up to 39 g_{Na^+}/day/scaffold

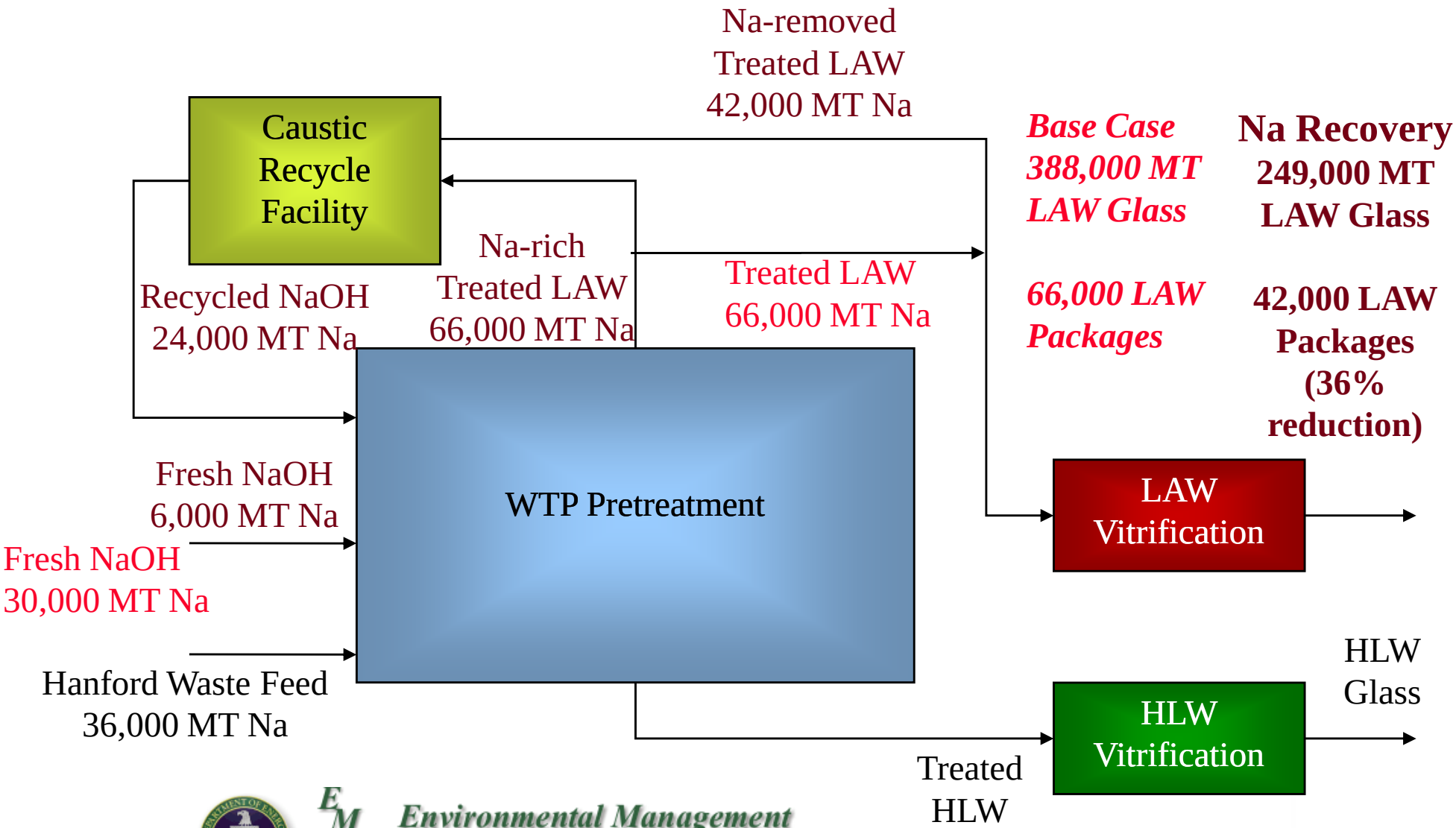
313 g_{Na^+}/day/scaffold

> 1.4 kg_{Na^+}/day/scaffold

- **Device scales linearly**
- **Design and hydrodynamics established**
- **Retrofit and process engineering of ceramic scaffold**

Commercial Cells-Figures are not to scale

Project Impact: WTP Only- Nominal Case with and without Sodium Recovery and Recycle



Summary

- Caustic recycling with NaSICON technology proven with simulant and actual waste
- Evaluated up to 5 different simulant chemistries to recycle caustic
- Demonstrated to make 50 % caustic from AP104 simulant
- Successfully operated a cell for 6.5 months
- Statistical performance established with operation of multiple laboratory cells
- Planning a 120 hour real waste test with an optimized cell design and low cost reliable components
- Pre conceptual design for caustic recycling plant and cost estimates completed
- On target to scale up to bench scale demonstration unit