

Recycling Caustic from LAW Stream using NaSICON Membrane based Electrochemical Technology - 9127

S.H. Balagopal, R.M. Flinders, S.V. Bhavaraju, D.A. Clay, K.L. Schatten
Ceramatec Inc., 2425 South 900 West, Salt Lake City, UT 84119

M.S. Fountain, D.E. Kurath, G.J. Sevigny
P.O. Box 999 MSIN P7-27, Richland, WA 99325

ABSTRACT

Ceramatec Inc. has developed and demonstrated an efficient electrochemical technology to separate sodium from Low Activity Waste (LAW) streams using a NaSICON (Sodium Super Ionic CONductor) ceramic membrane based electrolytic process. The NaSICON membrane process separates sodium contained in LAW streams thereby significantly reducing the quantity of LAW glass to be produced. The separated sodium is regenerated in the form of “clean” sodium hydroxide and reused on site. Laboratory scale reliability and lifetime tests have been conducted at Ceramatec Inc. with multiple simulants representing baseline chemistries at site and have demonstrated the ability to recycle sodium from LAW streams. Three specific evaluations were conducted at Pacific Northwest National Laboratory (PNNL) to investigate the ability of NaSICON membrane based electrolytic cells to separate sodium from actual LAW streams. The average sodium transport efficiencies were 93% (non-radioactive test) and 99% (two radioactive tests). A maximum recoverable sodium quantity could be predicted by combining both an aluminate solubility model and a gibbsite crystal growth rate. Testing shows cell voltages were relatively stable until saturation ratios exceeded 9 and the cell was successfully operated at saturation ratios as high as 12. No transport of any cations or anions was detected except for Na and Cs-137. Decontamination factors on the order of 2000 were observed with respect to Cs-137.

INTRODUCTION

The DOE site at Hanford has contaminated sodium salts in 177 radioactive contaminated tanks. The site may require up to 28,000 metric tons of Na for Waste Treatment Plant (WTP) pretreatment. The use of electrochemical ceramic membrane electrolytic cell technology has been demonstrated to separate sodium from LAW streams. [1], [2], [3]. This process will reduce the volume of waste to be treated and disposed, and also produces caustic that can be on site for pretreatment needs at the WTP and requirements at the tank farms. Overall, the most significant benefits of this technology are:

- Reduction in the amount of Intermediate Level Radioactive Waste (ILW) leading to reduced costs associated with LAW vitrification, handling and disposal of the ILW product.
- Improved risk management due to the potential to reduce handling and processing of waste at DOE sites.
- Reduction in the volume of contaminated chemicals needed to be processed and transported.
- Caustic recycling for use on site and cost reduction for the amount of caustic required for waste processing on site

APPROACH

Ceramatec developed the electrolytic technology and successfully demonstrated an electrochemical approach for the separation of sodium from LAW. Through a designed effort several ceramic NaSICON (Sodium Super Ionic CONductor) membrane compositions denoted as NAS-D, NAS-E, NAS-G, NAS-GY, NAS-F and NAS-H were synthesized. Ionic substitution in the crystal structure and thermodynamic

modeling approaches were used to develop the membrane materials. Chemical, electrical and physical characterization methods were used to establish the chemical stability and sodium transport properties of the NaSICON membranes for sodium recycling application. The membrane compositions with the best combination of ionic conductivity and lifetime characteristics were evaluated in actual LAW stream at PNNL and simulant streams at Ceramtec.

Development of Optimal NaSICON Membranes

Several NaSICON chemistries were systematically synthesized by using conventional ceramic processing methods. Green parts were pressed by powder pressing techniques and heat treated at temperatures above 1200°C to make dense ceramic oxides. The densification of membranes is associated with shrinkage of the green pressed parts during the sintering cycle. X-ray diffraction analysis of the compositions was performed to identify the crystal structure and phase purity before they were used in chemical and electrochemical testing in simulant streams. The sintered membranes were machined by a surface grinding method to finish parts to specific dimensional requirements for electrochemical cell testing. Figure 1 shows the progression of membrane size over the course of development effort.

An advanced tape casting processing method was used to manufacture this NaSICON layer (< 250 micron) on a support, Large Area NaSICON Structure (LANS), to functionally enhance the performance characteristic of the membrane.

Quality Control of NaSICON Membranes

The membranes are inspected by Helium diffusion to establish the part as hermetic. The quality analysis (Q.A/Q.C.), on surface finished membranes, to meet defined physical and dimension specifications is carried out with inspection for visible contamination, surface pores and cracks using a light table and UV penetrant dye. The Scanning Electron Microscope (SEM) is used to image parts to qualitatively determine the bulk microstructure.

The goal of quality control is to establish structural and performance reliability of NaSICON membranes in electrolytic devices for LAW treatment applications. The strength analysis of NaSICON membranes is conducted by the ASTM standard 4-point flexure method. Test bars are prepared and flexure testing is done on a standard 4-point test fixture.

It is often useful to take a statistical approach to describe the mechanical properties of ceramics. To this end, a tool known as Weibull statistics is used to characterize the strength and reliability of a ceramic. Using this method, the probability of failure of a ceramic as a function of applied tensile stress, $P(\sigma)$, is predicted by the following two-parameter Weibull equation:

$$P(\sigma) = 1 - \exp\left\{-\left(\frac{\sigma}{\sigma_0}\right)^m\right\} \quad (\text{Eq.1})$$

Where, m is the *Weibull modulus* and σ_0 is the *characteristic stress* of the material. The higher the Weibull modulus, the more tightly distributed the probability of failure is and the more reliable the material. This translates physically as a more uniform flaw size population. In general, a Weibull modulus below 5 is considered poor for a ceramic, a modulus in the range of 8-12 is average, while Weibull modulus values above 20 are considered outstanding.

The strength data for a representative membrane composition (NAS-GY) is summarized in Table I below. The results show an increase in mechanical reliability of the ceramics, primarily due to improved processing techniques through the course of the development work.

Table I. Strength and Weibull data on several lots of NAS-GY parts fabricated.

Lot	Strength (MPa)		Weibull Modulus	Characteristic Strength, σ_0 (MPa)
	Mean	Std. Dev.		
1	93.0	11.6	8.70	98.4
2	85.7	13.2	7.78	91.1
3	84.9	10.9	9.16	89.6
4	79.7	4.0	23.70	81.5
5	95.2	5.6	20.09	97.8
6	91.7	7.9	15.51	95.8

Chemical Stability of NaSICON type membranes

Several different NaSICON membrane compositions were exposed to LAW simulant chemistry and caustic NaOH solutions without the influence of an electric field.

Exposure tests were conducted at 60°C for 168 hr (1 week) in three different solutions: a 4.36M (15 wt. %) NaOH aqueous solution (the composition of the baseline catholyte solution), a stock simulant “AP104” solution with a Na: K ratio of roughly 50:1, and the same “AP104” solution with enough KOH added to bring the Na: K ratio to 7:1 simulating the highest K concentration that the membranes may be exposed to in the actual LAW. The results are presented in Table II below, which shows that in most cases, the corrosion level, which is minimum, was notably lower in the 50:1 solution when compared to the 4.36M NaOH, due primarily to the increase in mass as K exchanged for Na offsetting the mass removed during corrosion.

Table II. Corrosion rates on baseline NaSICON materials.

NaSICON Material	Corrosion Rates (mg/cm ² /100hr)		
	4.36M NaOH	“AP104”, 50:1 Na:K	“AP104”, 7:1 Na:K
NAS-D	0.97 ± 0.10	1.29 ± 0.62	3.11 ± 0.16
NAS-H	3.05 ± 0.30	0.47 ± 0.04	0.55 ± 0.02
NAS-E	4.64 ± 0.78	0.45 ± 0.07	0.77 ± 0.13
NAS-F	2.74 ± 0.11	0.52 ± 0.06	0.38 ± 0.11
NAS-GY	0.80 ± 0.06	0.19 ± 0.02	0.28 ± 0.03

Overall, the best material was NAS-GY composition, which is the current baseline composition used in this program. The NAS-GY material was tested in exposure experiments in LAW simulant for over three months without any noticeable impact on chemical stability.

Electrochemical Testing

Electrochemical testing was conducted using NaSICON (NAS-GY) membrane in simulant chemistry to evaluate the performance, membrane lifetime and ability to produce up to 19M (50 wt%) concentration of NaOH from sodium containing LAW simulant and actual waste.

The NaSICON membrane (LANS geometry) is sealed in a plastic scaffold and then retrofitted into a commercially available plate and frame cell. The electrodes for the tests were platinized titanium (anode) and nickel (cathode). Turbulence promoters are inserted between the scaffold and the electrode to promote solution mixing.

The anolyte and catholyte reservoirs are polypropylene (PP) based tanks with a 43.5 liter capacity. Two caustic-resistant, magnetically driven centrifugal pumps were used to circulate the catholyte and anolyte solutions through their respective loops. The anolyte and catholyte solutions are heated to 40°C and pumped into the cell chamber at flow rates of 5.68 L per minute. Solution loop and pressure across the membrane are monitored with corrosive service gauges capable of 0 to 15 psig. The experiment setup for cell testing is shown in Figure 1.



Figure 1: The laboratory size experimental setup

The anolyte chemistry is a complex sodium based simulant salt solution identified as AP104. Table III identifies the primary constituents and concentrations in the simulant.

Table III: AP104 Tank Waste Simulant Composition

Item	Formula	%	Item	Formula	%
1	H ₂ O	64.11	15	H ₃ BO ₃	0.0091
2	NaOH	12.49	16	MoO ₃	0.0092
3	NaCH ₃ CO ₂	0.064	17	NaCl	0.223
4	HCOONa	0.31	18	NaF	0.342
5	Na ₂ C ₂ O ₄	0.11	19	NaH ₂ PO ₄	0.254
6	Al(NO ₃) ₃ -9H ₂ O	8.25	20	Na ₂ SO ₄	1.455
7	Ba(NO ₃) ₂	0.00004	21	NaNO ₃	1.268
8	Cd(NO ₃) ₂ -4H ₂ O	0.00045	22	KOH	0.372
9	Ca(NO ₃) ₂ -4H ₂ O	0.014	23	WO ₃	0
10	Fe(NO ₃) ₃ -9H ₂ O	0.00075	24	Na ₂ SiO ₃ -9H ₂ O	0.046
11	Pb(NO ₃) ₂	0.00096	25	Na ₂ CrO ₄	0.134
12	LiNO ₃	0.00072	26	NaNO ₂	6.815
13	Ni(NO ₃) ₂ -6H ₂ O	0.0041	27	Na ₂ CO ₃	3.712
14	Zn(NO ₃) ₂ -6H ₂ O	0.00059			

The catholyte caustic solutions are prepared using reagent-grade chemicals in deionized, distilled water (DDI).

Performance tests were conducted in a dynamic flow through type of cell set up. The main goals for these preliminary tests are as follows:

- 1.) Evaluate energy and performance benefits of LANS for recycling sodium from LAW simulant stream
- 2.) Demonstrate up to 2000 hours of continuous testing at an operating current density of 50 mA/cm².
- 3.) Establish statistical performance reliability through multiple cell testing
- 4.) Evaluate the lifetime performance of membranes for caustic recycling with long-term testing to make from 4.36M to 19M NaOH product in the catholyte.

LANS membranes at 3.556 cm (1.4") in diameter (active membrane area of 5.89 cm²) were used in the majority of tests. The cells were operated in continuous feed mode, where the sodium concentrations of the anolyte and catholyte were maintained constant by replenishing the sodium hydroxide and water in the anolyte and catholyte respectively. Ten separate tests were conducted with independent membrane cells to assess statistical significance in performance and to establish reliability and robustness of device operation.

The performance of the ten tests is shown in Figure 2. Seven out of ten cells were operated close to 2000 hours in continuous testing. These cells operated at an average current density ~ 51.2 mA/cm² with a standard deviation of 8.4. Sodium mass balance was conducted periodically during the testing period. The sodium transfer current efficiency in all the tests was greater than 95%.

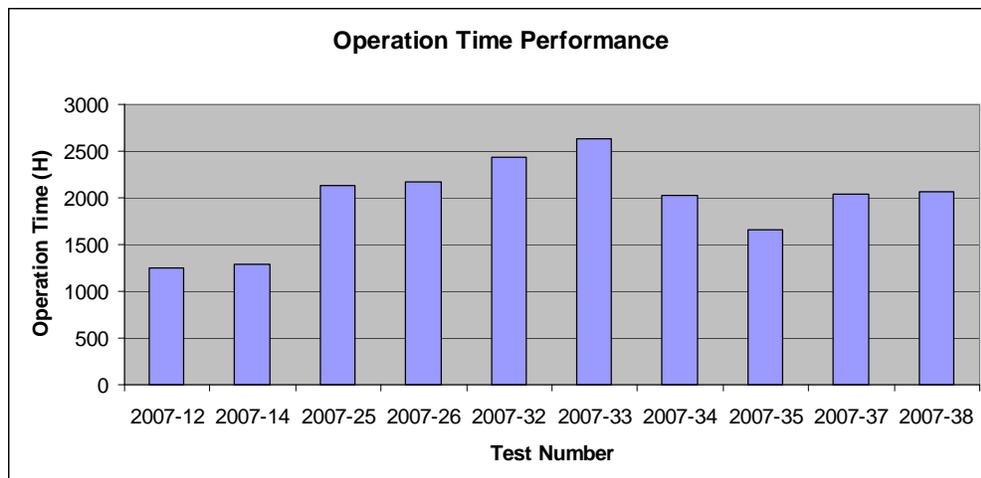


Figure 2: The operational life time performance tests conducted with 10 LANS membrane cells

A 4000 hour long term single membrane based cell was operated with a low cost anode to replace Pt/Ti electrode. This test was conducted using the optimized process operating conditions based on statistical testing, Ceramatec performed research to develop a specific anode that meets the desired cost and performance goals for caustic recycling applications. Figure 3 shows the operation of cell with the alternate anode. The cell was operated for a total duration of 4700 hours at an average current of 0.31 amps corresponding to a current density of $\sim 52.6 \text{ mA/cm}^2$. A total of 66.7 moles of sodium was transferred across the membrane.

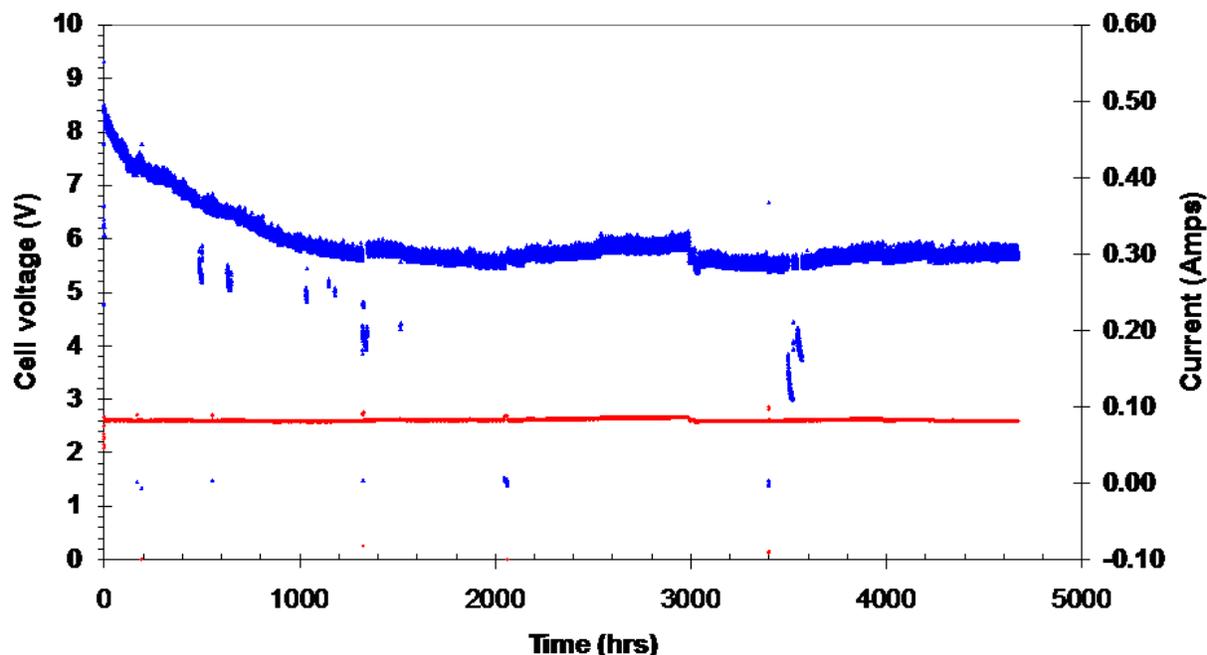


Figure 3: Performance of a cell with a Fe-Ni-Co alloy anode

The catholyte solution was analyzed to look for specific elements from anolyte to establish the selectivity and cell operation efficiency. The results before and after the test are presented in Table IV. The data shows no transfer of preferred elements across the membrane and seal during the 6 months of cell operation.

Table IV. Elemental Analysis of Catholyte Before and After 4700 hours Test

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

The next step in the evaluation phase of a LANS membrane cell was to produce 19M NaOH from LAW stimulant. This test was performed to demonstrate the operation of a LANS membrane cell to make 19M NaOH from the AP104 simulant containing sodium salts. Figure 4 shows the operation characteristics of a cell to make 19M NaOH. The cell was operated at constant voltage of 3.0 volts for 3 months in continuous mode at operation current density of 87 mA/cm².

Ceramtec also investigated the performance of NaSICON membrane cells in simulants other than AP104 such as Group 5 chemistry. The composition of Group 5 simulant is shown in Table V.

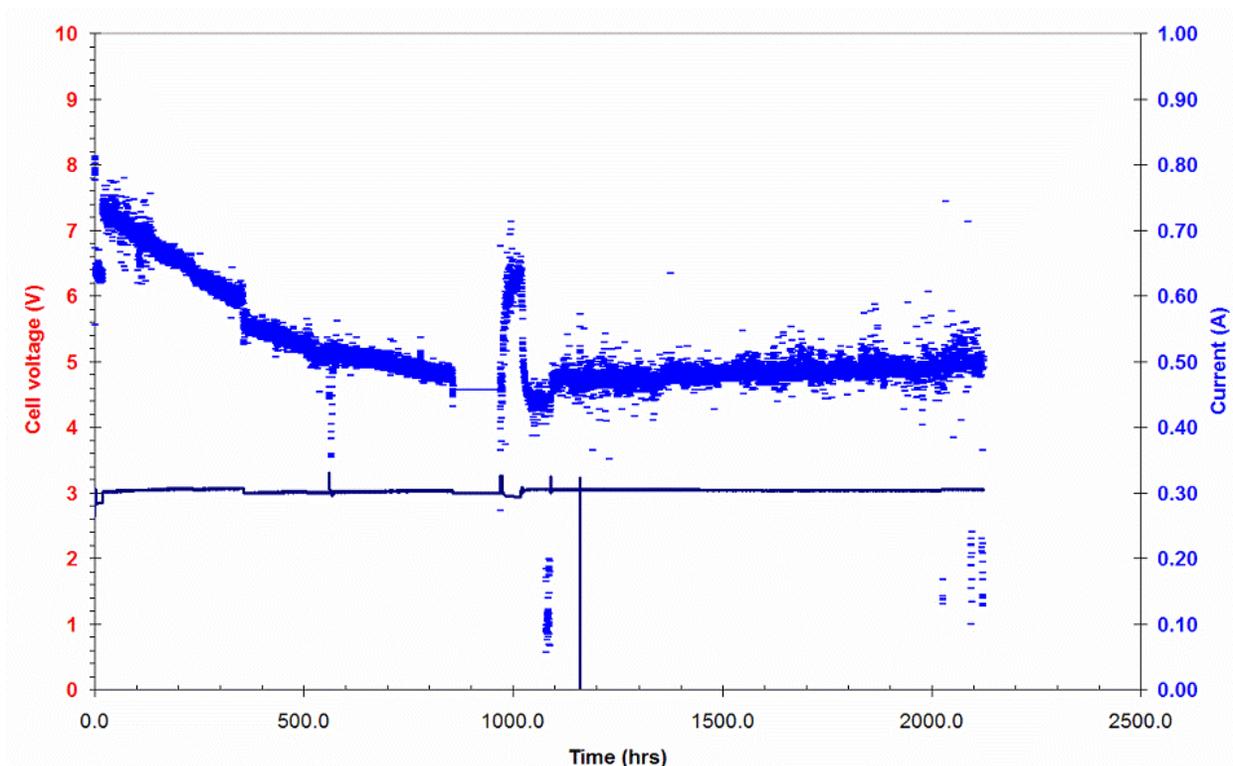


Figure 4: Operation of a LANS membrane cell in 19M NaOH at 3.0 volts

Table V: Group 5 Tank Waste Simulant Composition

Item	Formula	%	Item	Formula	%
1	H ₂ O	62.43	10	Na ₂ SO ₄	0.264
2	NaOH	22.0179	11	NaNO ₃	1.4278
2	Na ₂ C ₂ O ₄	0.56	12	WO ₃	0.00215
4	Al(NO ₃) ₃ -9H ₂ O	11.072	13	Na ₂ SiO ₃ -9H ₂ O	0.02511
5	H ₃ BO ₃	0.0072	14	Na ₂ CrO ₄	0.17773
6	MoO ₃	0.00129	15	Na ₂ CO ₃	1.808
7	NaCl	0.223	16	KNO ₃	0.08
8	NaF	0.00779	17	Al(OH) ₃	0.20116
9	NaH ₂ PO ₄	0.2354			

Larger size LANS membranes at 6.096 cm (2.4") in diameter were used (active membrane area of 13.6 cm²) for the Group 5 simulant tests. The tests were conducted in batch mode where the sodium concentrations in the anolyte and catholyte are allowed to respectively decrease and increase. Six separate tests were conducted with independent membrane cells to establish reliability and robustness of device operation. A representative test performance is presented in Figure 5 shows the cell operation for 142.5 hours at 50 mA/cm². The cell continued to operate even after aluminum hydroxide had precipitated from the solution. A total of 2.23 moles of sodium hydroxide out of 2.82 moles present in the anolyte was transferred to the catholyte to make caustic at nearly 100% sodium current efficiency.

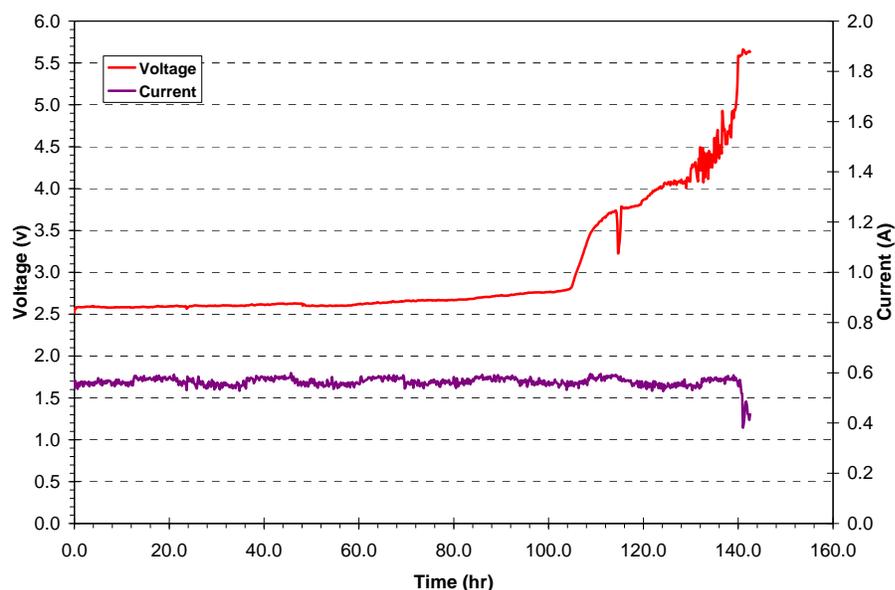


Figure 5: Batch mode operation of a LANS membrane cell in Group 5 simulant at 50 mA/cm²

Based on testing performed in simulant solutions at Ceramatec, an actual waste test was conducted at Pacific Northwest National Laboratory (PNNL) to recycle sodium. A new cell equipped with 2.4" membrane was shipped to PNNL. The test at PNNL was focused on specific test objectives presented below:

- Determine the selectivity of membrane to sodium versus various elements present in AP104/SY101/AZ101 waste simulant. Components of interest included aluminum, potassium, and the radionuclides (Sr-90, Tc-99, Cs-137, etc.).
- Compare the performance in simulants versus real waste of NaSICON membrane based cell
- Analyze any changes in waste composition induced by oxidizing environment in the anode compartment.
- Validate the AP104/SY101/AZ101 simulant behavior with actual AP104/SY101/AZ101 tank waste after sodium separation.

The setup for testing at PNNL is shown in Figure 6. The anolyte and catholyte reservoirs consisted of polypropylene (PP) tanks with a 2 liter capacity.

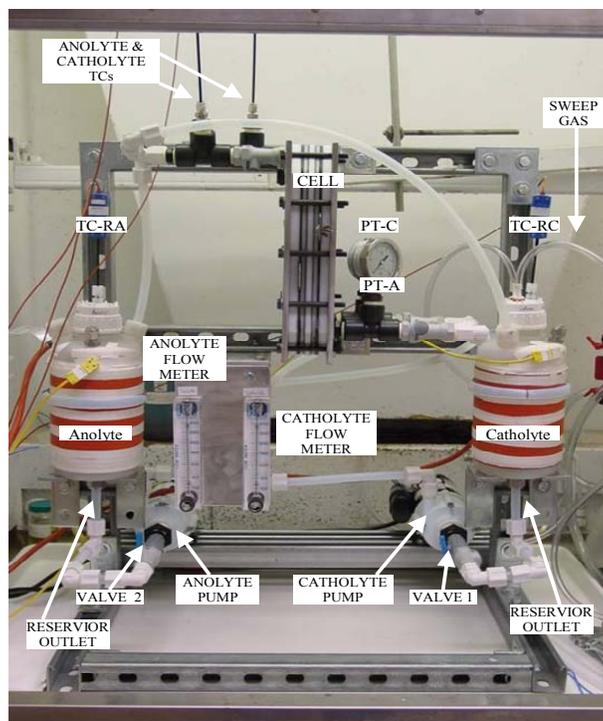


Figure 6: NaSICON electrolytic cell set up for conducting caustic recycling test

The system was operated in a batch recycle mode with initial feedstock volumes ranging from 0.8 to 1.2 L. The flow rate of the recirculating solutions ranged from 138 to 156 L/h. In the case of the stimulant and first actual tank waste test, the starting catholyte solution was 1 M NaOH. The second test with actual tanks waste used ~18.6 M NaOH as the initial catholyte solution. The anolyte simulant and actual waste composition was AP104/SY101/AZ101.

Sample volumes of 5 to 10 mL (depending on the analytical requirements) were taken at least every 30 minutes during simulant testing and 45 minutes during radioactive testing. The testing duration was primarily dictated by the start of $\text{Al}(\text{OH})_3$ (Gibbsite) precipitation in the anolyte solution as pH approached 12 from depletion of sodium hydroxide. Experiments with actual wastes were terminated when solids started to precipitate.

The process samples were analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES), which provided concentrations of the important cations. Hydroxide analyses were completed using acid/base titration method. Selected samples were also analyzed with total organic carbon (organic content), total inorganic carbon (carbonate), ion chromatography (anions), and hydroxyl ion titration to obtain information on the changes in waste chemistry. For the tests with actual waste, gamma energy analysis (GEA) was used to determine the concentrations of Co-60, Ru/Rh-106, Sn/Sb-126, Cs-137, Eu-154, Eu-155, and Am-241. The Tc-99 concentration was determined by liquid scintillation counting after a combination of ion exchange and solvent extraction. The Sr-90 concentration was determined using extraction chromatography followed by liquid scintillation counting.

Simulant testing was completed before conducting radioactive testing. The left portion of Figure 7 displays current density and applied voltage over the course of the experiment. The current density remained relatively steady. No solids precipitation was observed, and testing was stopped just before reaching hydroxide levels approaching pH 13.6 in the anolyte. A good agreement between theoretical and

the actual sodium transport rate was obtained for this test. The theoretical transport rate assumes that all applied current was involved in sodium transfer.

Treatment of the radioactive AP104/SY101/AZ101 tank waste sample was completed after the successful simulant test. Center portion of Figure 7 displays current density and applied voltage over the course of the tank waste sample experiment. At roughly 390 minutes, an increase in the rate of voltage was observed at a pH of approximately 13.2. A sharp change in current density can be observed at approximately 397 minutes. The experiment was ended at the first visual indication of solids precipitation, and a final sample was taken.

The sodium-transport efficiency was determined through OH^- titration results on the catholyte samples. Efficiencies varied from 94 to 101% over the course of the experiment while the average efficiency was 99%. The average sodium transfer rate was 10.3 kg/day/m^2 . A good agreement between theoretical and the actual sodium transport rate was obtained for this test. Based on ICP-OES analysis of the catholyte, no discernable transport of non-Na cations was observed. GEA indicated that about 0.04% of the initial Cs-137 in the anolyte was transported to the catholyte. No other radionuclides were transported and measured in the catholyte solution above detection limits. The sodium selectivity with respect to Cs-137 was 384.

A second radioactive test was completed using the sodium-depleted anolyte solution from the previous (Rad Test #1) experiment. To replenish the anolyte reservoir of depleted sodium hydroxide, an addition of 19 M NaOH was made. The anolyte solution was recirculated through the anolyte loop for 7 minutes to re-dissolve the precipitate into solution before shutting down. The catholyte solution was drained from the previous experiment (Rad Test #1) and replaced with 18.6 M NaOH.

Right portion of Figure 7 displays current density and applied voltage over the course of the experiment. At 335 minutes, a sharp increase in voltage was recorded and continued until roughly 375 minutes when the voltage started approaching a level value. Precipitated/suspended solids were observed immediately in the anolyte sample obtained at 438 minutes. The experiment was ended at the first visual indication of solids precipitation, and a final sample was taken. As in the earlier tests, there was a good agreement between theoretical and the actual sodium transport rates.

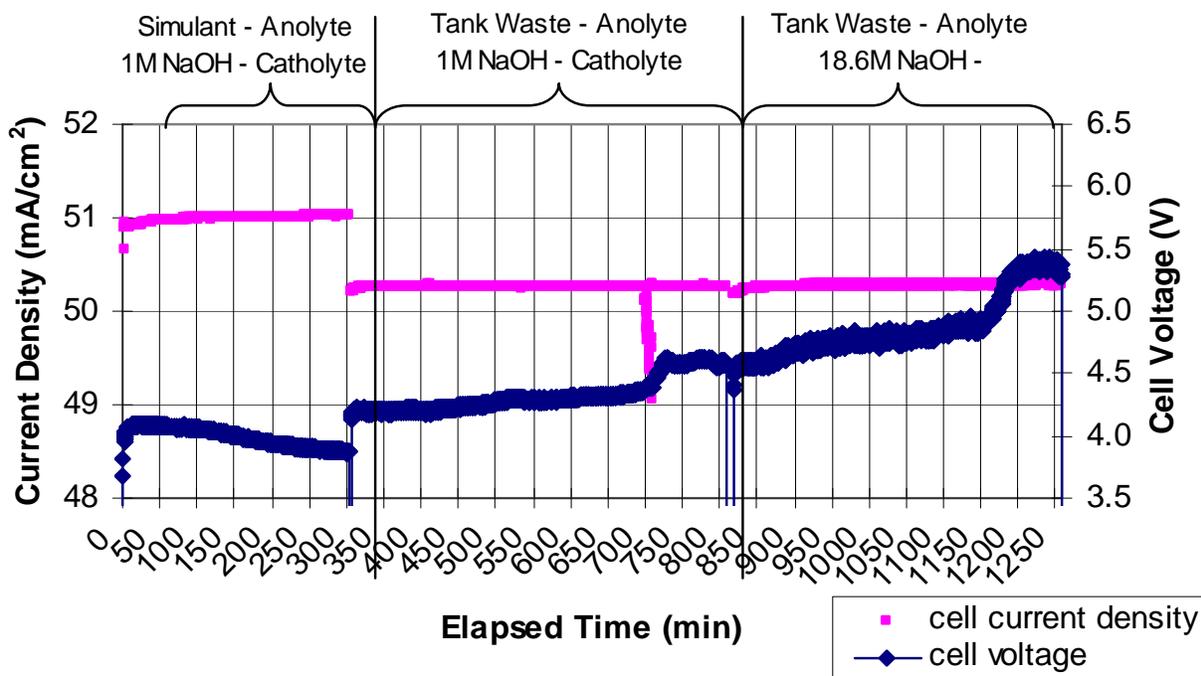


Figure 7: Voltage and Current Density During Radioactive Test #2

The sodium-transport efficiency was determined through OH⁻ titration results on the anolyte samples. Efficiencies varied from 95 to 102% over the course of the experiment while the average efficiency was 99%. The average sodium transfer rate was 10.3 kg/day/m². Based on ICP-OES analysis of the catholyte, no discernable transport of non-Na cations was observed. GEA indicated that about 0.06% of the initial Cs-137 in the anolyte was transported to the catholyte. No other radionuclides were transported and measured in the catholyte solution above detection limits. The sodium selectivity with respect to Cs-137 was 250.

A summary of process parameters for the three experiments is provided in Table VI. With few exceptions, little variation in operating conditions existed between experiments. The sodium transport efficiency values were consistently high, indicating good reproducibility and effective power usage. Sodium transport rates, summarized in Table VI, were relatively consistent throughout testing and offer a basis for scaling up Na production processes to the industrial level to meet throughput requirements of the Waste Treatment Plant.

Table VI: Summary of Process Parameters For All Experiments

Operational Parameter	Test ID		
	Simulant	RAD Test #1	RAD Test #2

Membrane Type	NAS-GY (876 GY)	NAS-GY (876 GY)	NAS-GY (876 GY))
Membrane Thickness (mm)	1.4	1.4	1.4
Membrane Diameter (cm)	7.62	7.62	7.62
Current Density (mA/cm ²)	51	50	50
Applied Current (min-max amps)	2.32–2.33	2.24-2.29	2.29
Applied Voltage (min-max volts)	3.86–4.10	4.12–4.62	4.36–5.44
Temperature (°C)	39–41	37–43	41–43
Active Membrane Area (cm ²)	45.6	45.6	45.6
Anolyte Flow Rate (L/min)	2.3–2.4	2.4–2.5	2.4–2.5
Catholyte Flow Rate (L/min)	2.5–2.6	2.5–2.7	1.7–.9
Catholyte (M NaOH)	1	1	18.6
Operating DP (psig)	1.5–1.75	1.6-1.9	1.9
Na Transport Efficiency (%)	88-95	95-101	95–102
Na Transport Rate (kg/day/m ²)	9.6	10.3	10.3
Operating Time (h)	5	8.2	7.3

The selectivity of NAS-GY membrane towards sodium is an important performance parameter in the tank-waste treatment process because membrane selectivity towards undesirable cations and radionuclides degrade the purity of the recycled material (19M NaOH) and can increase dose to operators. In both radiological experiments, no cations or anions except Na and trace quantities of Cs⁺ were transported through the membrane. Na membrane selectivity with respect to Cs-137 was 384 in radiological test #1 and 250 in radiological test #2. These results demonstrate the NAS-GY membrane was several hundred times more selective to Na than Cs-137, and verify that o-ring and membrane integrity were maintained. Visual analysis of the membrane after the testing showed it was in a pristine nature.

The performance results from the testing, which include caustic purity, transport efficiency, power consumption, and mass balance results were used to complete preliminary electrochemical process analysis for this project. Also estimated are the process costs and benefits to implement the NaSICON membrane technology for remediation of low level waste at the Hanford facility.

FUTURE WORK

1. As part of WTP flow sheet process-Ceramatec, Inc. will establish economics for the NaSICON electrolytic membrane based process to recover sufficient caustic from WTP LAW vitrification feed
2. Establish robust operation in multiple feed streams
3. Complete lifetime cycling and cell recovery operations
4. Evaluate feed stability after sodium recovery to meet downstream processing requirements on site
5. Complete a safety evaluation of electrolytic system-process controls
6. Scale up and demonstrate a successful larger system for caustic recycling- up to 250 gallons simulat batch size
7. Complete a conceptual design of a full size system for caustic recycling at Hanford site

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