

Naselect MULTI-TUBULAR ELECTROLYTIC CELL FOR SODIUM REMOVAL FROM LOW LEVEL WASTE

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Abstract: Ceramatec Inc. has developed an efficient electrolytic process using a NaSelect ceramic membrane to separate sodium from Low Level Waste (LLW) stream. The process selectively removes sodium contained in LLW stream thereby significantly reducing the waste volume and quantity of LLW glass to be produced. The separated sodium is regenerated in the form of “usable” sodium hydroxide for reuse onsite. Combined laboratory scale cell testing for > 25,000 hours have been performed to demonstrate sodium recycling, validate the cell design and establish process reliability with several simulant chemistries. Successful tests with NaSelect ceramic membranes cell for sodium recycling from actual LLW wastes were conducted at PNNL and no discernable transport of non-Na cations was observed (based on inductively coupled plasma-optical emission spectrometry or “ICP-OES” analysis). The Cs-137 Decontamination Factor (DF) has a high value of 5585. GEA analysis showed no other radionuclides were transported and measured in the catholyte solution above detection limits.

Single tubular electrolytic cells were designed and tested to validate the operation reliability of the membrane seal and other cell components in LLW streams and caustic (> 35 wt.% NaOH). Seven and half months of continuous operation of the cell to recycle sodium from waste simulant was achieved. Recovery and recycling of 65-83% of sodium from several simulant chemistries such as AP-104, NTCR, PEP Leachate and Group 5 representative of baseline LLW streams was successfully demonstrated with single tube cell operations. The behavior of different sodium to alumina ratios in various LLW simulant chemistries on the performance of electrolysis cells during sodium recovery was studied. Long-term shelf stability of the different simulant chemistries after sodium separation and the nature of precipitates formed during storage has been evaluated. The changes in properties of anions such as NO₂, NO₃, F, Cl, SO₄, and PO₃ present in the LLW waste chemistries after exposure to anodic oxidation conditions were analyzed by Ion Chromatography (IC).

A geometrically scalable tubular electrolytic cell configuration has been designed to facilitate the use of multiple NaSelect tubular membranes to handle higher feed throughput. The solution flow characteristics through this multi tube cell have been modeled and the design is finalized. The multi-tubular unit will be tested to demonstrate the maturity of the NaSelect ceramic membrane based electrolytic process to recycle sodium from simulant and actual waste streams. The membrane technology design has been matured for pilot demonstration to produce up to 71.2 kg per hour of 10 M caustic concentration from LLW waste streams.

APPROACH

Ceramatec have developed the electrolytic ceramic membrane based process which operated at temperatures below 60°C to selectively separate sodium from low level contaminated stream (LLW). The process feeds the LLW waste or simulant containing sodium based salts into the anolyte chamber of a two compartment cell separated by the sodium ion conducting NaSelect® membrane. A low concentration sodium hydroxide solution is fed into the catholyte chamber. An electric field is applied across the anode and cathode to drive the electrolysis reaction and the sodium ions are specifically transferred from the anolyte solution across the ceramic membrane to combine with the hydroxide ions to form sodium hydroxide in the catholyte compartment. The performance of the solid ceramic membrane is not influenced by the presence of solid precipitants and organic and inorganic contaminants present in the feed chemistry.

Development of NaSelect ® Membranes

The membrane geometry was changed from planar to tubular configuration to support scalability requirements for the electrolytic process so as to allow handling of a higher processing throughput of feed stream. The membrane in tubular configuration provides structural reliability to withstand higher differential pressures across the membrane. The process to manufacture the ceramic membrane in tubular geometry (lengths of 8 inches and 0.9 inches in diameter) was developed. Minimal machining is required for this membrane fabrication, greatly reducing cost and increasing potential manufacturing yields. Figure 1 shows the tubular membranes manufactured for testing purposes.



Figure 1 shows the NaSICON tubes fabricated and sintered using a powder compaction technique.

The tubular membranes were inspected for surface defects such as pores and cracks using a high intensity light and UV penetrant dye. The goal of quality control is to establish structural and performance reliability of NaSICON membranes in electrolytic devices. The strength analysis of NaSICON membranes was conducted by an ASTM standard Compressed C-Ring method. Test ring specimens were prepared and ultimate strength analysis conducted by compressing the ring. Weibull statistics method was 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-parameters. Weibull equation is calculated:

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

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 value obtained for the tube fabrication using the C-ring testing method is 6.88.

Electrochemical testing of Tubular membrane cells

Electrochemical testing was conducted using NaSelect[®] (NAS-GY) tubular membranes in various simulant chemistries to separate sodium contained in LLW simulants and evaluate the ability to produce up to 19M (50 wt %) concentrations of NaOH. The following variables were studied in single tube cells:

Construction of Tubular Cells

The two compartments of the electrolytic cell configuration were accomplished by sealing the NaSelect[®] tubular membrane to the manifold. KOVAR and stainless steel were used as anode and cathode. Flow was maintained inside and outside the tubular configuration by regulating and adjusting the pressure gradient between the two chambers. Anolyte solution was pumped through the anolyte chamber, mesh electrode side, in a cross flow pattern, bottom to top. The flow inside the catholyte chamber was from bottom to top and flowing parallel to the NaSelect[®] tubular membrane. Figure 2 below shows the two cell configurations connected to the test setup.



Solid External Electrode



Mesh External Electrode

Performance tests were conducted in a flow through type of cell configuration. The anolyte and catholyte tanks with a 43.5 liter capacity. Two magnetically driven pumps were used to circulate the catholyte and anolyte solutions through their respective loops. The catholyte, caustic solution, was prepared using reagent-grade chemicals in de-ionized water (DI). The anolyte and catholyte solutions were heated to 40°C and pumped into the cell chamber at flow rates of 5.68 liters per minute. The solution loop and pressure across the membrane was monitored with corrosive service gauges capable of 0 to 15 psig.

Long Term operation of Tubular membrane cells

The anolyte chemistry of complex sodium based simulant salt solution identified as Group 5 which represents LLW chemistry was developed. Table 1, identifies the primary constituents and concentrations in the simulant.

Table 1: 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			

NaSelect® tubular membranes at 500 micron in wall thickness, 4" long and 0.9" in diameter (active membrane area of 56 cm²) were used in for testing. The single tubular membrane cells were operated in a continuous feed mode, where the sodium concentrations of the anolyte and catholyte were held constant by replenishing the sodium hydroxide and water in the anolyte and catholyte respectively. These tests were conducted with independent membrane cells to assess long-term performance and to establish reliability and robustness of device operation.

Two tests were conducted for up to 4000 hours of continuous operation after which the tests were stopped. The performance of one of the two cells is shown in Figure 3. This cell operated at an average voltage of ~ 3.07 volts. Sodium titrations were performed periodically during the testing period and the sodium transfer current efficiency in all the tests was near 100% within measurement tolerances. The cell consumed 1.75 kWhr of energy for every kilogram of sodium hydroxide produced.

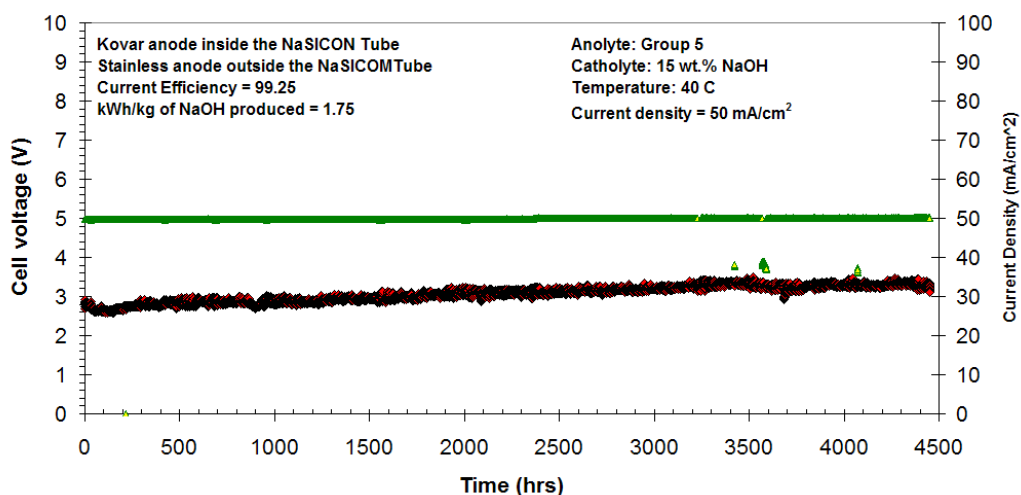


Figure 3: Long-Term Continuous Mode Operation in Group 5

Establish sodium removal limits of PEP Leachate and CSL-NTCR simulants

A single tubular membrane cell was tested with the PEP leachate (sample received from PNNL) and CSL-NTCR simulants in batch mode operation where the anolyte and catholyte sodium concentrations are allowed to decrease and increase respectively. The test performance with PEP leachate is presented in Figure 4 where the cell was operated for 86.5 hours at a current density of 50 mA/cm². Figure 4 shows the cell was operated even after aluminum hydroxide has precipitated from the solution. 70 % of sodium hydroxide present in the anolyte initially was transferred to the catholyte at nearly 100% current efficiency. The cell was operated at lower than 3.6 V at 2.12 kWhr to produce a kg of sodium hydroxide. The final concentration of catholyte of 47.2% NaOH was reached at the end of testing.

The samples collected at 40° C after 65% of sodium separation from the simulants shows precipitation of alumina as alumina hydroxide (Figure 5). The precipitated sample was recovered, dried and analyzed by SEM/EDX and X-ray diffraction (XRD) analysis. XRD

analysis (Figure 6) clearly showed two aluminum hydroxide phases. XRD analysis identified the phases as Bayerite $\text{Al}(\text{OH})_3$ and Gibbsite $-\text{Al}(\text{OH})_3$. A Rietveld refinement using crystal structure information from the AMCSD estimated the Bayerite and Gibbsite amount at 61.2% and 38.8% respectively.

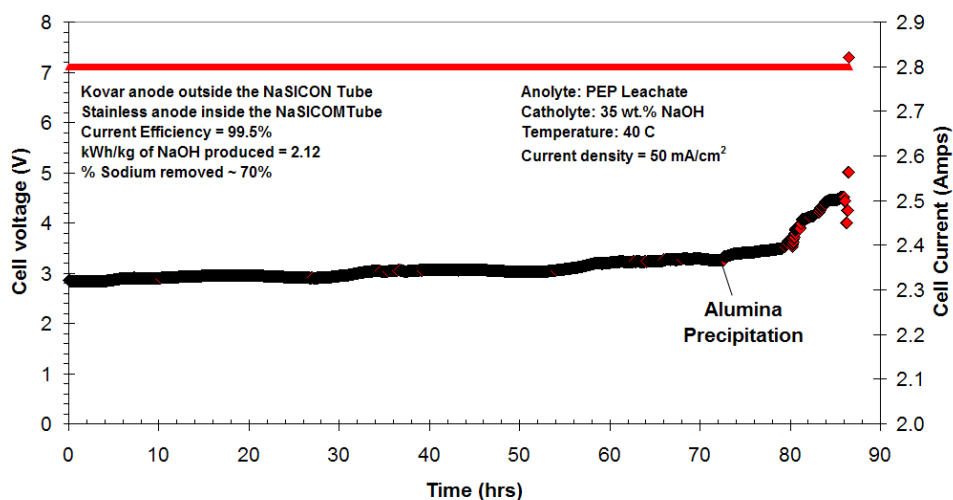


Figure 4: Batch mode operation of a tubular cell in PEP Leachate simulant at 50 mA/cm²

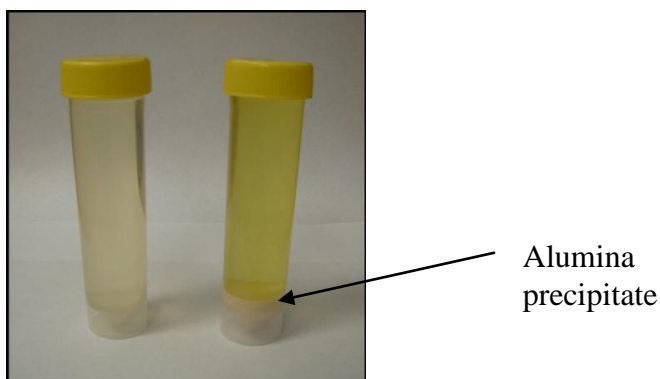


Figure 5: PEP Leachate anolyte before (left) and after 65% sodium removal (right) at 40° C

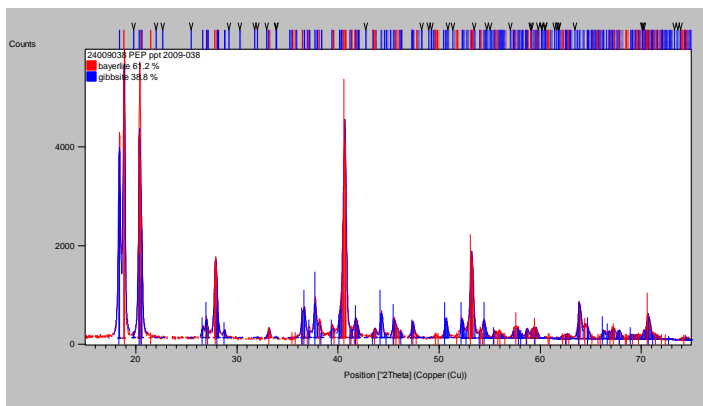


Figure 6: Reitveld refinement of aluminum hydroxide precipitate collected after 65% sodium removal from PEP-leachate.

To determine the stream stability at various sodium removal values, intermediate anolyte samples were collected, cooled to room temperature and examined after a period of time for precipitation. Table 1 shows the samples collected after a certain percent sodium removed and the hours after which they are examined.

Table 2: Intermediate samples collected during sodium removal process and hours of storage of the samples

Sample	Na Removal	Hrs since the sample was taken.
1	0	1488
2	29%	912
3	30%	888
4	46.5%	552
5	50%	504
6	64%	216

After storing for the hours shown in Table 2, the samples were examined for precipitates. Figure 7 shows that precipitates were noticed in the room temperature stored samples with 46.5% and higher sodium removal. The conclusion is that while precipitates may not form at the cell operating temperature (40°C), they will form when the solution cools for specific intermediate solutions.

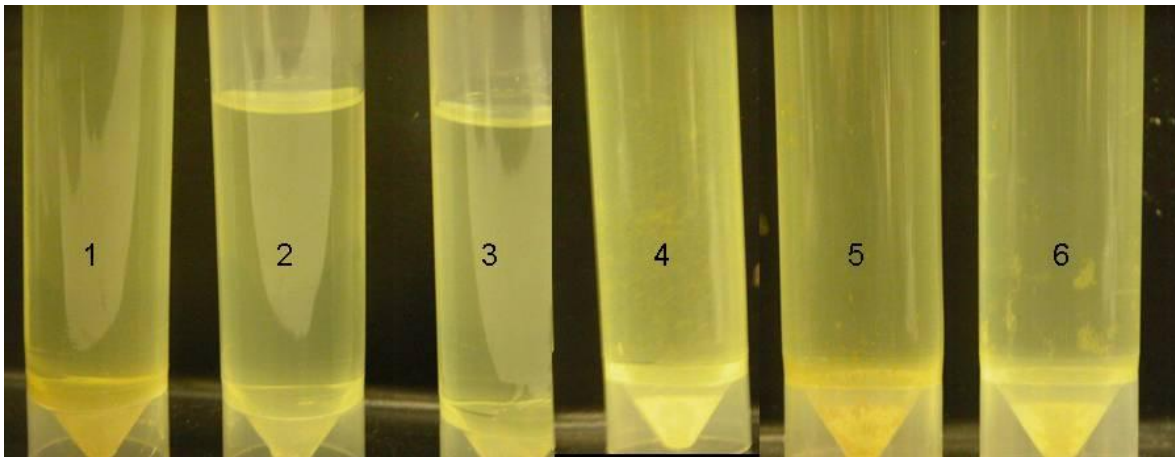


Figure 7: Reitveld refinement of alumina precipitate collected after 65% sodium removal from PEP-leachate.

The batch mode testing data for CSL-NTCR simulant is shown in Figure 8. The cell was operated for 700 hours at 75 mA/cm², even after aluminum hydroxide has precipitated from the solution. 83% of sodium from the original simulant testing anolyte batch was transferred to the catholyte at nearly 100% current efficiency. The cell operated at less than 3.6 V before alumina precipitation. The cell used 2.34 kWhr to produce a kg of sodium hydroxide. The test used an initial catholyte NaOH concentration ~35% and the catholyte NaOH concentration at the end of the test 46.7 wt%).

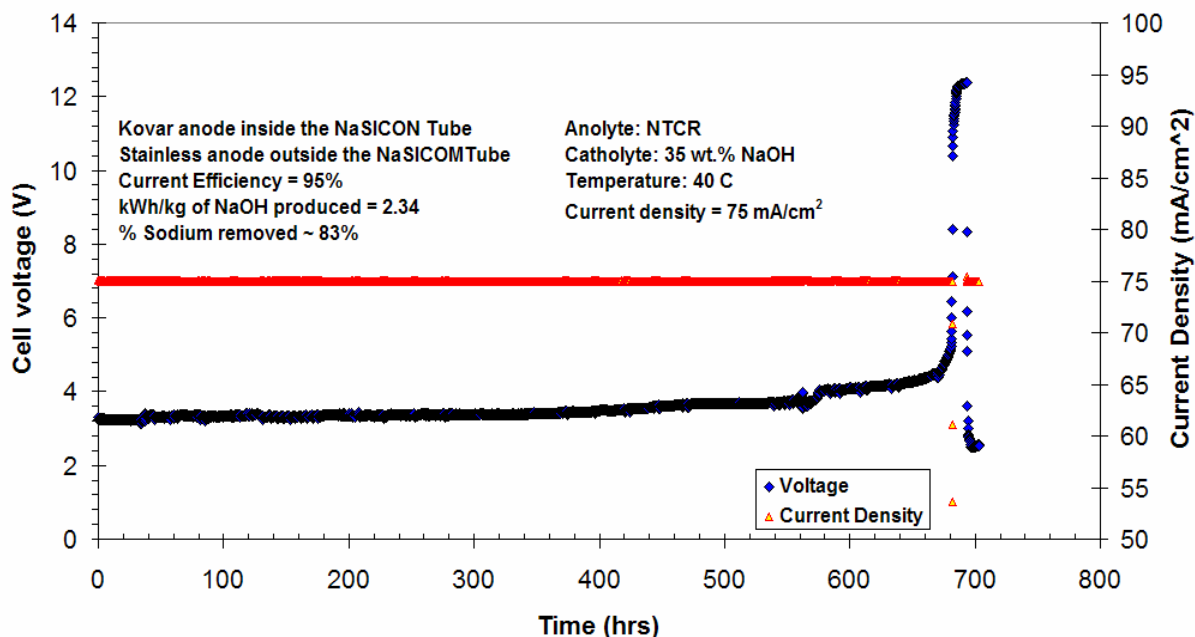


Figure 7: Batch mode operation of a tubular cell in CSL-NTCR simulant at 75 mA/cm²

The alumina precipitation behavior of the three different simulants during batch mode testing using NaSICON tubular cells is shown in Table 3.

Table 3. Alumina precipitation for different simulants during sodium removal process using NaSelect[®] tube cells

	Group 5	PEP	NTCR
Na (M)	4.425	7.39	5
Al (M)	0.262	0.75	0.25
Starting Na/Al molar ratio	16.89	9.85	20
Na/Al molar ratio when Alumina precipitates	TBD	3.449	4

Demonstration of device performance in actual Group 5 tank waste at PNNL

The performance of electrolytic process to recycle caustic from simulants were compared by conducting an independent field test during December 2008 at PNNL using actual radioactively contaminated LLW at PNNL. Ceramtec and the PNNL teamed together to accomplish the goal to demonstrate the applicability of the NaSelect[®] technology to recycle caustic from real tank waste samples. Unlike the first actual waste test conducted in Fall of 2007 at PNNL this test was performed for a longer duration with the objective to qualify the cell components and reliability of cell unit to operate in actual waste. The setup for testing at PNNL is shown in Figure 8. The anolyte and catholyte reservoirs consisted of polypropylene (PP) tanks with a 2 liter capacity.

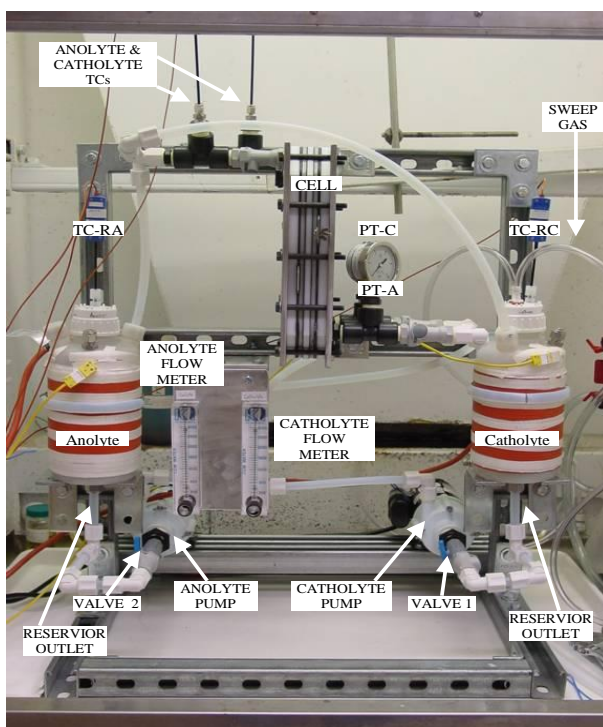


Figure 8: NaSICON electrolytic cell set up for conducting caustic recycling test

The system was operated in a batch recycle mode with initial feedstock volume of 1.5 L. The flow rate of the recirculating solutions ranged from 108 to 156 L/h. The starting catholyte solution was 1.4 M NaOH. The catholyte solution was prepared using reagent-grade 19 M NaOH and deionized, distilled water (DDI). The anolyte solution was a composite sample of Group 5 and 6 tank waste. Table 4 and Table 5 identify the estimated constituent and radionuclide concentrations, respectively, of Group 5 anolyte used in the test.

Table 4. Group 5 Tank Waste Composition by ICP-OES

Constituent	µg/mL	Constituent	µg/mL
Al	7294	Rh	[1.8]
As	<5.82	Ru	[1.9]
B	16.3	Se	<8.72
Ba	[0.42]	Si	31.4
Ca	[5.33]	Sn	<3.52
Cd	<0.42	Sr	<0.010
Cl	1070	Ti	<0.05
Cr	726	V	[0.54]
Cs	0	W	[22]
F	45.6	Zn	[3.83]
Fe	[1.37]	Zr	<0.17
Hg	0	U	<4.5
K	390	TIC	370
Li	[0.65]	TOC	2650
Mo	11.13	NO ₂	12700
Na	103400	NO ₃	43200
Ni	<0.36	OH	14241
Nd	0	PO ₄	2410
P	796	SO ₄	2310
Pb	<3.99	Oxalate	479
Pd	<0.87		

Concentrations less than 0.5 were rounded to zero.

Analyte uncertainties were typically within ±15%; results in brackets indicate that the analyte concentrations were greater than the minimum detection limit (MDL) and less than the estimated quantitation limit (EQL), and uncertainties were >15%.

Table 5. Group 5 and 6 Tank Waste Radionuclide Composition by GEA (Pre-spike)

Constituent	µCi/mL	Constituent	µCi/mL
¹³⁷ Cs	<8.0E-05	²³⁸ Pu	1.13E-05
⁶⁰ Co	<9.3E-05	²³⁹⁺²⁴⁰ Pu	7.40E-05
²⁴¹ Am	<2.8E-04	⁹⁰ Sr	1.52E-04

Note that ^{137}Cs , ^{60}Co , and ^{90}Sr concentrations are below detection limits in the initial Group 5 tank waste feedstock. A radioactive spike was added to the feedstock waste bottle since one objective of these tests was to monitor any radionuclide transport across the membrane.

Table 6 provides the radionuclide composition for the post-spike Group 5 and 6 tank waste feed.

Table 6. Group 5 and 6 Tank Waste Radionuclide Composition by GEA (Post-spike)

Constituent	$\mu\text{Ci/mL}$	Constituent	$\mu\text{Ci/mL}$
^{137}Cs	7.26E-02	^{238}Pu	<3.15E-01
^{60}Co	8.14E-05	$^{239+240}\text{Pu}$	<7.01E-01
^{241}Am	<1.39E-04	^{90}Sr	-

“-“ = radionuclide was not analyzed for

The period of testing was set at approximately 120 hours based on the current density target (50 mA/cm^2) and the OH^- concentration of the anolyte. As OH^- concentrations decrease during Na^+ transport, $\text{Al}(\text{OH})_3$ (Gibbsite) precipitates because of a drop in solubility as the anolyte solution becomes depleted of free OH^- , and the pH approaches 12. Solution pH levels are typically monitored with Hydrion microfine pH paper, but pH monitoring was deemed unnecessary in this case. In addition, since adequate levels of Na^+ and OH^- were predicted to exist during this test, no water, waste, or NaOH was added during testing. The temperature of the system was normally controlled at 40°C ($-1/+5^\circ\text{C}$).

Sample volumes of approximately 5 mL were taken by disposable pipette at least every 8 hours from both the catholyte and anolyte reservoirs. It was important to minimize the sample volume since a substantial amount of Na^+ could be removed from the system over the course of the experiment.

For major cation analysis, the process samples were analyzed with ICP-OES on an Optima 3300DV ICP-OES instrument (Perkin Elmer, Waltham, MA). For ICP-OES analyses, high-purity calibration standards were used to generate calibration curves and to verify continuing calibration during the analysis.

Hydroxide analyses were completed using a Model 295 Multi-Function Auto Titrator (Denver Instrument Company, Denver, Colorado). A volume of standardized sulfuric acid was added to the sample to an endpoint of pH 4.5 to measure total alkalinity. The contributions of carbonate and bicarbonate were removed from the reported alkalinity data, which is reported in terms of meq of NaOH .

Select samples were also analyzed by gamma energy analysis (GEA) to investigate radionuclide concentrations. The analyses were made using 60% efficient intrinsic-germanium gamma detectors. All germanium counters were efficiency calibrated for distinct geometries using mixed gamma standards traceable to the National Institute of Standards and Technology (NIST). Spectral analysis was conducted using libraries containing most mixed-fission products,

activation products, and natural decay products. Control samples were run throughout the analysis to ensure correct operation of the detectors.

A single experiment using a 2.4-inch Large Area NaSICON Structure (LANS) NAS-GY membrane was completed using the laboratory size cell . The cell was operated in the batch mode, at 40°C, with no material additions during testing. The current density was maintained at 50mA/cm² based on the exposed membrane area equal to 13.6 cm². Both the anolyte and catholyte reservoirs were sampled at 8 hour intervals. Current, temperature, flow rate, and voltage were monitored and recorded throughout the experiment.

A Group 5 and 6 radioactive tank waste charge of 1799.2 g (~1.5 L) was placed into the anolyte reservoir and 2052.0 g (~1.5 L) of 14 M NaOH was charged to the catholyte reservoir. No system breach or other modifications were performed on the electrochemical cell received from Ceramatec. Experimental conditions are provided in Table 7.

Table 7: Summary of Experimental Conditions

Operational Parameter	Range or Value
Membrane Type	NAS GYR6-152 (2.4-in. LANS)
Membrane Thickness (mm)	0.2 to 0.25
Membrane Diameter (cm)	6.1
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 (°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)	13.6
Operating ΔP (psig)	2.1
Na Transport Efficiency (%)	93-106
Avg. Na Transport Rate (kg/day/m ²)	10.2
Operating Time (h)	112

Figure 9, displays current density and applied voltage over the course of the LANS membrane experiment. The current density remained relatively steady, varying less than 0.46 mA/cm² from 50mA/cm² while the voltage rose from an initial minimum of 2.46 V to a maximum of 2.68 V just before stopping the experiment. Note that the power and fluid flow to the electrochemical cell was halted at the elapsed time between 4.0 and 4.2 hours in an attempt to correct a small leak

at the anolyte inlet fitting. No significant material loss was recorded, and no impact on the experimental results was expected.

No visual observations of solids precipitation were made during the experiment or up to 2 weeks after testing was completed. Comparing ICP samples of the anolyte, the initial Al concentration (6610 $\mu\text{g/mL}$) and final Al concentration (6540 $\mu\text{g/mL}$) were equivalent within analytical uncertainty, and this suggests that gibbsite remained soluble in the solution. The Electro MP cell was disassembled layer-by-layer and photographed to investigate any abnormal corrosion, damage, and possible solids precipitation.

Testing was stopped based on a pre-determined plan to operate close to 120 hours. The actual sodium transport time was 112 hours. Samples were obtained every 8 hours for both the catholyte and anolyte. A representative group of the samples were then submitted for analysis, which included OH^- titration, ICP-OES (cations), and radionuclide identification by GEA.

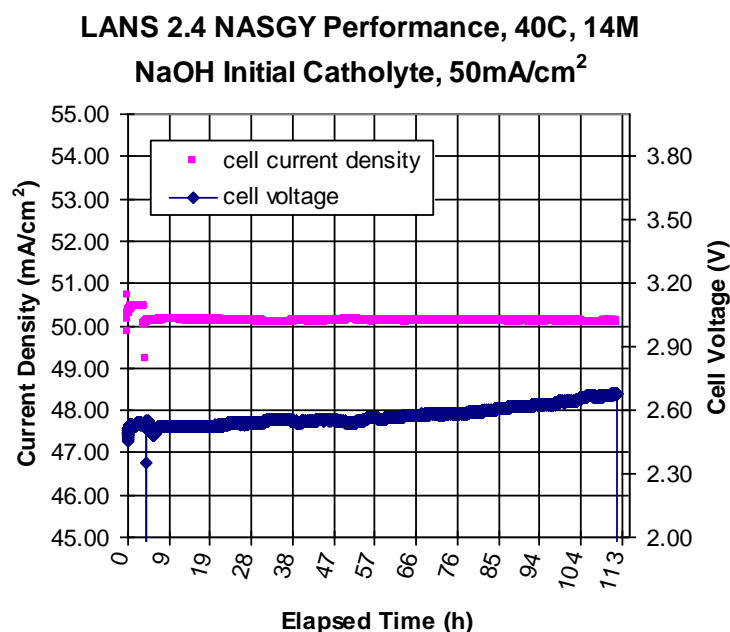


Figure 9: Voltage and current density during LANS testing

Figure 10 provides a comparison between the theoretical sodium transport and the actual sodium transport determined by OH^- titration analyses of the anolyte solution. Figure 11 illustrates good agreement between theoretical and the actual sodium transport rate. The theoretical transport rate assumes that all applied current was involved in electron transfer.

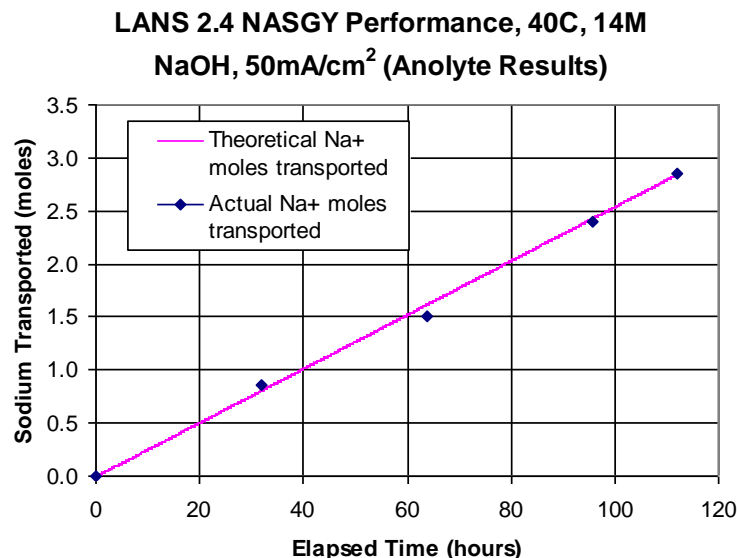


Figure 10: Sodium Transport Rate Comparison During LANS Testing (Anolyte Results)

The sodium transport efficiency was determined through OH⁻ titration results on the anolyte samples. The calculated sodium transport efficiencies varied between 93 and 106% while the average was 99%. The uncertainty for this OH⁻ titration was estimated at + 5% based on calibration check standards and assuming a 3 standard deviation range. The average sodium transfer rate was 10.2 kg/day/m² and is consistent with transfer rates obtained with 3.5-inch diameter NAS-GY membranes tested in early 2008 (Fountain et al. 2009).

The selectivity of the LANS NAS-GY membrane towards sodium is an important performance parameter in the tank-waste treatment process because membrane selectivity towards undesirable cations and radionuclides degrades the purity of the recycled material (19 M NaOH) and can increase dosing (?) to operators. Based on ICP-OES analysis of the catholyte and anolyte, no discernable transport of non-Na⁺ cations was observed. GEA indicated that roughly 0.02% of the initial ¹³⁷Cs 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 ¹³⁷Cs was 2823. Both ICP and GEA results demonstrate that the LANS NAS-GY membrane was several thousand times more selective to Na than ¹³⁷Cs and verified that o-ring and membrane integrity were maintained.

A Df value is frequently used in the radiological protection arena and represents the effectiveness of a decontamination process. Df values generally >1,000 are excellent while <10 are poor. The only radionuclide detected in the catholyte was ¹³⁷Cs, and a Df value of 5585 was calculated. The extremely high Dfs observed during the present testing indicate that the caustic recycle process will generate a very-high-purity caustic product with dose rates approximately 5500 times less than the initial waste stream.

The cell was disassembled after the test and the components were examined. Post experimental visual inspection of the membrane shows no membrane degradation (Figure 11).



Figure 11: Post test optical image of the membrane: Anolyte side (left) and catholyte side (right)

Electrolytic Tubular Cell Design

The progression of NaSelect[®] tubular technology began with using planar ceramic disks as the separator in an electrolytic cell. The tubular technology provides device scale up benefits compared to planar ceramics. Larger size tubular ceramics compared to planar ceramics can be packed more efficiently in an electrolytic cell, increases active area of membrane with relation to electrode area, membrane areas, and potentially eliminates gelling of waste and precipitation of solids during the process. The configuration scheme for a tubular cell configuration is shown in Figure 12.

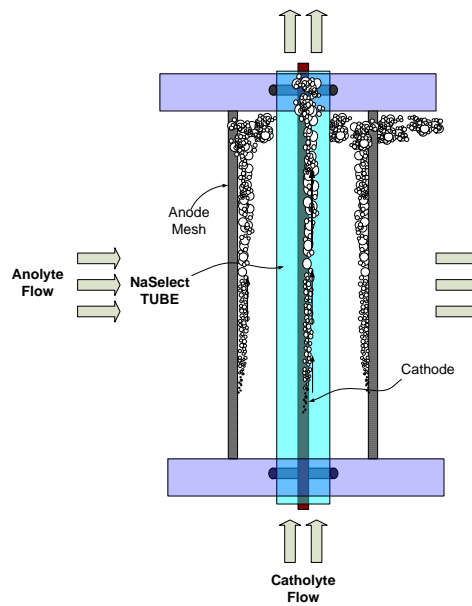


Figure 12: Schematic of a NaSelect[®] tube as a separator in an electrolytic reactor

General cell and electrode configuration work was done to ensure suitable fluid and gas flow through the cell while meeting shape, uniformity and other tubular cell design requirements. Due to ceramic geometry, the inner electrode design was limited to a rod-like cylindrical shape, while work on the outer electrode involved both solid shell and mesh designs.

To analyze turbulence flow patterns through various cell designs both FEA modeling work, and laboratory bench-scale testing was performed. Basic fluid flow modeling through cell designs was performed for the inner and outer chambers of a single tube cell, which included an inner rod electrode and an outer shell or mesh electrode. This modeling work helped to determine whether or not the cell was receiving uniform flow over all portions of the membrane and electrodes and what kind of flow rates should be present throughout the cell.

Figure 13 shows a cross section of the modeling results of the inner electrode-membrane gap of a multi-tube cell design. Each tube shows uniform inner flow and comparable flow rates to neighboring tubes suggesting that the initial header and tubular geometries provided consistent and uniform flows across all active membrane surfaces.

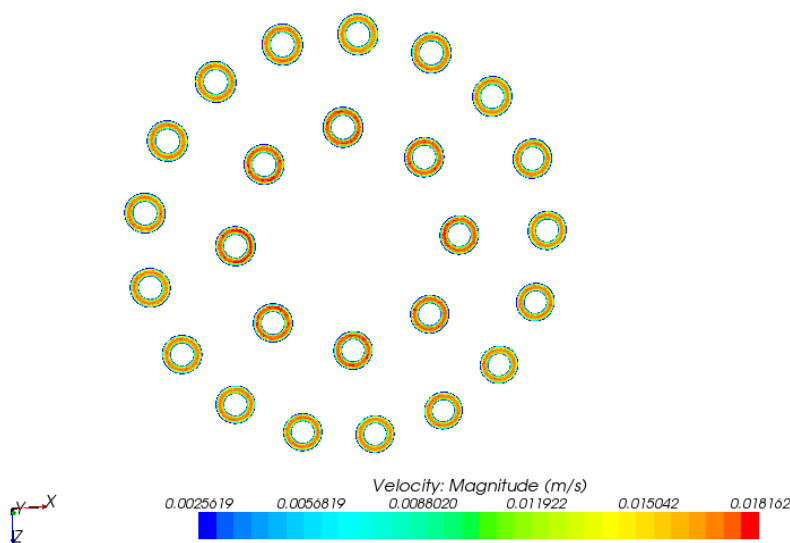


Figure 13: Inner electrode-membrane flow modeling results using Star-CCM+

Due to software modeling limitations the true flow patterns within a cell could not be modeled due to large quantities of gas evolved on the electrodes; therefore, this modeling work was coupled with bench-scale testing to determine how gas evolution might influence cell performance. A special Void Fraction Cell (VFC) was designed to study the affects of gas evolution within the shell electrode cell design on performance and testing was performed over a variety of current densities and flow rates to simulate different levels of void fraction within the cell due to gas evolution.

Testing with the VFC showed no significant changes in conductivity across the cell over the range of flow rates estimated to be applicable for commercial scale development of this

technology, suggesting gas evolution within the closed cell design would not affect cell performance. The mesh electrode was assumed to be significantly less affected, and possible aided, by gas evolution from the electrolytic process and laboratory testing was therefore determined to be unneeded.

Evaluation of Multi-Tubular Cells

A scaled up electrolytic cell (0.3 m^2 active area) was tested in Group 5 simulated waste. The cell was run under conditions similar to those used to test single tube cell to compare general operating performance in continues mode operation. The test conditions were as follows:

Current density: 75 mA/cm^2
Anolyte/catholyte temperature: $40 \text{ }^\circ\text{C}$
Anolyte/catholyte flow rate: $0.5\text{-}1.5 \text{ gpm}$

The anolyte and catholyte compartments were recharged daily/semi-daily to maintain the sodium hydroxide concentrations in each compartment. This meant adding solid 100% sodium hydroxide to the anolyte side and de-ionized water to the catholyte side keeping the concentrations steady. Figure 14, shows the prototype cell with test setup and operation.



Figure 14: Prototype tubular cell testing

It was verified that after 40 hours of testing the cell showed no signs of operational issues. The cell operated at a stable 3.4 volts throughout testing at 50 mA/cm^2 which is shown in Figure 15. The spikes in voltage is due to start up charging of cell prior to the catholyte and anolyte solutions reaching their set point temperatures, and does not reflect high cell resistance which subsides during the course of cell operation.

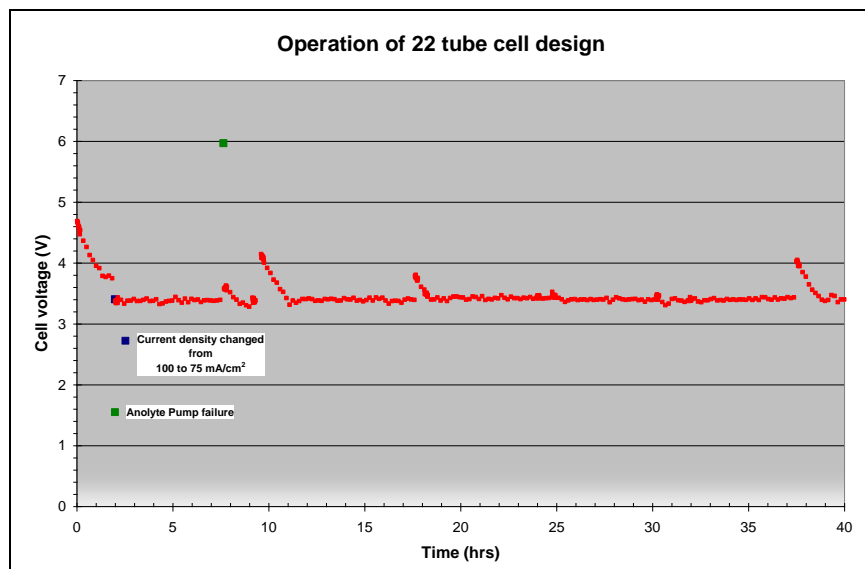


Figure 15: Voltage vs. time data over 40 hours of testing under continuous mode operation

The next phase of testing was focused on evaluation of this unit to perform in a wide range of catholyte NaOH concentrations. This test was operated at a current density of 75 mA/cm^2 . Testing was performed for an additional 90 hours to provide time for the catholyte solution to increase from roughly 16-50 wt% NaOH. This allowed for determination how catholyte concentration affects cell performance. During this time the process was operated in a semi-batch process where the anolyte was continuously recharged, but recharging was halted on the catholyte side. Titrations of the catholyte sodium hydroxide concentration were to be taken daily to correlate cell voltage with sodium hydroxide concentration. Periodically, testing was to be paused after steady state had been reached within the cell so that the dispersion rate of H_2 bubbles in the catholyte solution could be measured and correlated to catholyte sodium hydroxide concentration.

Testing of the prototype unit under semi-batch conditions showed comparable results to previous test data. The voltage slowly increased over time, which was expected due to the increasing sodium hydroxide concentration in the catholyte tank. Figure 16 shows voltage versus time during testing. Again, the sharp spikes and drops in voltage are due to starting the cell before the catholyte and anolyte solutions were heated to their set points, and from recharging the anolyte solution with sodium hydroxide which increased the solution temperature. The prototype 22 tube cell is able to perform as well, if not better, than previously tested single tube cells in Group 5 simulat over the course of short term testing.

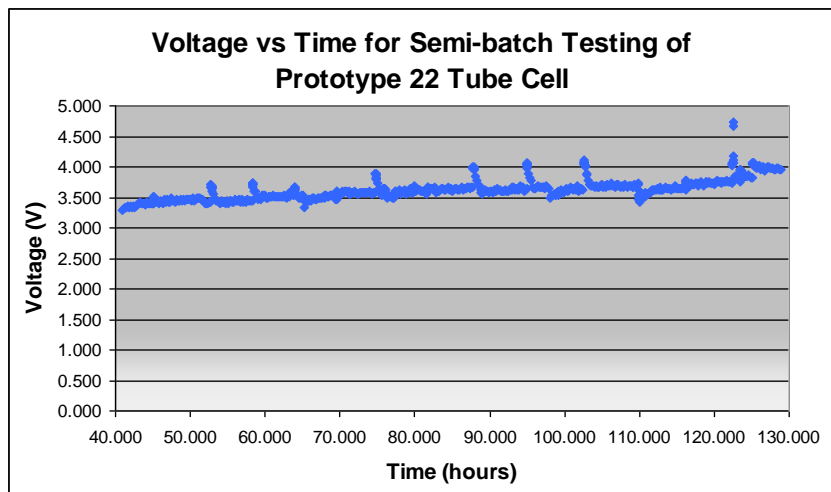


Figure 16: Voltage vs. time during semi-batch testing

A proposed technology demonstration unit (1 m² size) to demonstrate the engineering benefits of a tubular membrane based configuration, scalability and operation reliability of the electrolytic process to efficiently recycle sodium from simulant stream at up to 3 gallons minute to make sodium hydroxide product is planned as part of a project deliverable in 2010.

Conclusions:

An energy efficient electrolytic process to recycle has been demonstrated and matured with > than 25,000 hours of cell testing conducted to recycle sodium from multiple simulant chemistries and validate the cell design and establish process reliability. Successful tests were conducted for sodium recycling from actual wastes which duplicates the performance with simulant chemistries. Tubular ceramic configuration offers scale up advantages over planar configuration. 65%-75%-80% removal of sodium from CSL-PEP and NTCR type waste simulants demonstrated before precipitation of Alumina occurs in tests conducted at temperatures below 50°C. Multi-tube cell module design successfully demonstrated. Technology Demonstration Unit (TDU with multi-tubular membrane based modular cell design is being fabricated for validation and operation.

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