

Pilot-Scale System for Recycling Caustic from LLW Simulant – 11342

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ABSTRACT

Ceramatec has successfully demonstrated the NaSelect™ (sodium super ionic conductor) ceramic membrane based electrolytic process to recycle sodium from several Low Activity Waste (LAW) simulants and actual wastes to generate “usable” sodium hydroxide for reuse onsite. This sodium recovery process allows for recycling of the caustic (NaOH) used to remove aluminum during sludge washing as a pretreatment step in the vitrification of radioactive waste. The sodium recovery process will decrease the LAW volume by as much as 39%. A technology demonstration scale unit (TDU) was successfully developed and demonstrated to process NTCR (Near Tank Cesium Removal) effluent feeding at 7 l/hr to make up to 30 wt% of sodium hydroxide. This process separated about 80% of sodium from the NTCR feed simulant before alumina precipitation was observed. Tens of thousands of hours of testing has been performed with the single and multiple prototypical cells to develop and scale up the design of the Caustic Recycling Unit to recycle sodium hydroxide from multiple simulant feed LAW compositions from Hanford site. The ability of the caustic recycling NaSelect™ membrane based process to recycle caustic from several simulant chemistries representative of actual wastes on site was successfully demonstrated. Based on testing with the single tubular membrane cell units, the prototype unit to configure multiple tubular membranes to handle higher feed throughput was developed. , A sub-pilot scale modular system was designed, built and operated to process higher through put of LAW simulant stream. Presently a Caustic Recycling Unit (CRU) is being built to recycle free sodium hydroxide from NTCR effluent as part of an integrated Near Tank Treatment System (NTTS) pilot demonstration with Continuous Sludge Leaching (CSL) and NTCR for reuse of caustic from the CRU process in the CSL process is in progress. The pilot scale system will process 16.6 liters per hour (4.4 gal/h) of NTCR effluent and generate 10M concentration of “usable” sodium hydroxide at 9.33 kilograms per hour.

INTRODUCTION

Electrochemical salt splitting technology for caustic recycle was investigated in the 1990s to treat the tank wastes at the Hanford, Savannah River and Idaho sites. Investigations, primarily funded by the EM-50 Efficient Separations and Processing Program, included testing of commercially available organic-based ion exchange membranes (e.g., Nafion) and ceramic-based NaSelect™ membranes developed by Ceramatec Inc. Both membrane types were tested with simulants at the laboratory scale with actual radioactive waste samples. The Nafion, polymer membranes were less efficient and selective than the ceramic membranes, transporting radioactive cesium at a higher rate than the sodium. Laboratory scale simulant and actual waste tests using NaSelect™ ceramic membranes were conducted to demonstrate the membrane performance. Tests with simulants showed that the process can generate up to 50 wt% caustic as a product. The radioactive test showed there was little to no transport of radioactivity across the ceramic NaSelect™ membranes or leaking through the seals. The ceramic membranes also have demonstrated better radiation resistance than the Nafion membranes¹. Therefore, the NaSelect™ ceramic membranes were selected for further development and use during late 90's for Waste

Treatment Plant (WTP) NaOH applications to Recovery and Recycle technology development project.

The ceramic membranes are from a family of materials known in the power sources industry as sodium (Na), super fast ionic conductors (NaSelect™). The NaSelect™ is unique in that sodium is mobilized along channels within the crystal structure for fast sodium ion conduction. Silica tetrahedral “rings” and sodium and heavy metal ions form the structure around these channels, which are filled with highly mobile sodium ions.

Ceramatec Inc. has developed a membrane based technology to recycle sodium from LLW streams at the Hanford site. The membrane based cells have been demonstrated both with a large range of simulants and actual LLW waste streams to recover sodium in the form of sodium hydroxide (caustic) very efficiently and safely. The technology has also been demonstrated to selectively remove sodium from a Hanford PEP (Pretreatment Engineering Platform) simulant.

Near Tank Treatment System (NTTS)

Within the WTP, the High Level Waste (HLW) stream will require a processing step to remove non-radioactive hydrated aluminum oxides in the form of either Gibbsite or Boehmite sludge. Removal of this sludge is necessary to reduce the number of HLW canisters produced during vitrification operations and improve overall processing efficiencies in that operation. The sludge is removed from the HLW by a leaching process that utilizes large amounts of sodium hydroxide. The caustic requirements are still under study. As the amount of sodium added in the form of sodium hydroxide approaches the base sodium in the HLW inventory, a technology need to develop methods to allow for recovery and recycling of the available caustic inventory to reduce the overall sodium load to the LAW vitrification process was recognized.

The WTP project at Hanford has mentioned that vitrification of approximately one half of the waste is projected to be limited by aluminum through processing to remove it from vitrified feed. The baseline WTP flow sheet is designed to effectively remove aluminum. Separating the aluminum stream (boehmite) from HLW sludge would reduce the quantity of the HLW canisters by approximately one half.

As part of an overall plan to address WTP flowsheet deficiencies, we have designed and developed an electrochemical system technology to remove sodium from low-level radioactive waste. This concept employs a sodium super ionic conductor membrane (NaSelect™) to selectively remove sodium from low-level and supplemental waste streams. This allows for recycling of the caustic used to remove aluminum during sludge washing as a pretreatment step in the vitrification of radioactive waste which will decrease the LAW waste volume by as much as 39%. Caustic recycle may also reduce the life cycle cost and schedule for the tank waste treatment mission by minimizing the sludge leachate, lowering the cost of LAW immobilization. The addition of sodium to the tank waste treatment system increases the immobilized LAW volume, cost and schedule.

NTTS, an integration scheme of Advanced Remediation Technologies is proposed to combine Caustic Recycling, CSL and NTCR, integrated into a single demonstration system. The CSL will utilize a suitable Hanford simulant containing Boehmite, Gibbsite, sludge and supernate and would be operated to leach the Boehmite and Gibbsite by using the caustic leaching process. The clarified liquid from CSL process will be sent to the NTCR process for cesium (Cs) removal.

The cesium decontaminated effluent from NTCR process will then be sent to the caustic recycle process for recovery of the caustic which will be reused in another cycle of caustic leaching in the CSL.

The recycling process will recycle sodium in the form of pure sodium hydroxide. The 1/4 scale device, will produce 9.33 kilogram per hour of 10 M NaOH which will be fed to the CSL pilot process. The pilot size caustic system to recycle sodium will be integrated with the CSL and NTCR processes as part of NTTS demonstration. The caustic recycle system will minimize the addition of further sodium into the waste tanks. Such an integrated mobile technology demonstration will give Department of Energy (DOE) the options to insert this process for sodium management at the Hanford site. The system foot print was designed to fit on a flat bed trailer for mobile operation for integration with the CSL process.

The general integrated NTTS process shown in Figure 1 describes how the Caustic Recycling Technology will be integrated with CSL and NTCR technologies into a single overall demonstration system. The integrated technologies will demonstrate a system to minimize the addition of further sodium into the waste tanks.

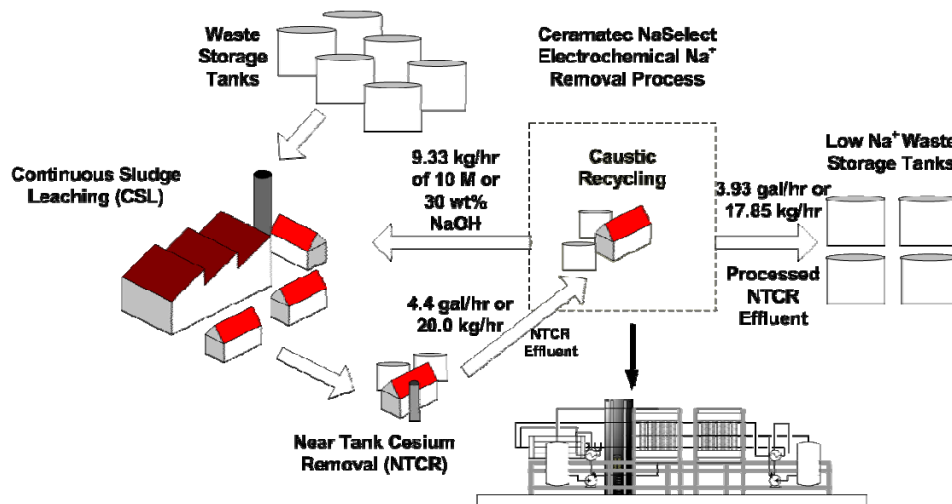


Figure 1: Integrated Pilot Scheme

The cesium decontaminated effluent (NTCR) stream will be sent to the caustic recycle process for recovery of the caustic to the level where sufficient sodium hydroxide is retained to keep aluminum saturated in the stream after sodium removal for downstream processing. The caustic produced from the NaSelect™ ceramic membrane based electrolytic process will be reused in another cycle of caustic leaching in the CSL process. This approach will provide a modular integrated system that minimizes the addition of sodium into the waste tanks while removing the aluminum and the cesium from the waste. This integrated system forms the basis for the Pilot Near-Tank Treatment System (PNTTS).

DESIGN AND TESTING OF PROTOTYPE AND TDU MODULES

The TDU modules were developed, built and tested as prototype units and sub-pilot scale with simulant chemistries representative of actual waste chemistries at site.

These modules recycle free sodium hydroxide from the NTCR effluent in a continuous fluid recycling process. In the process sodium is removed from the simulant by transporting it through NaSelect™ membrane into the NaOH fluid.

The NaSelect™ membranes are formed into a tubular shape in order to enhance the process efficiency and operation. There are 38 tubular membranes arranged in this particular design arranged in a vertical orientation. The electrolytic process is activated by passing current between two electrodes with the NaSelect™ membrane positioned between them. One electrode is a metal rod positioned in the center of the tubular membrane and the second electrode is a tubular configuration of metal mesh positioned around the outside of the membrane. Figure 2 illustrates the tubular membrane configuration with the electrode.

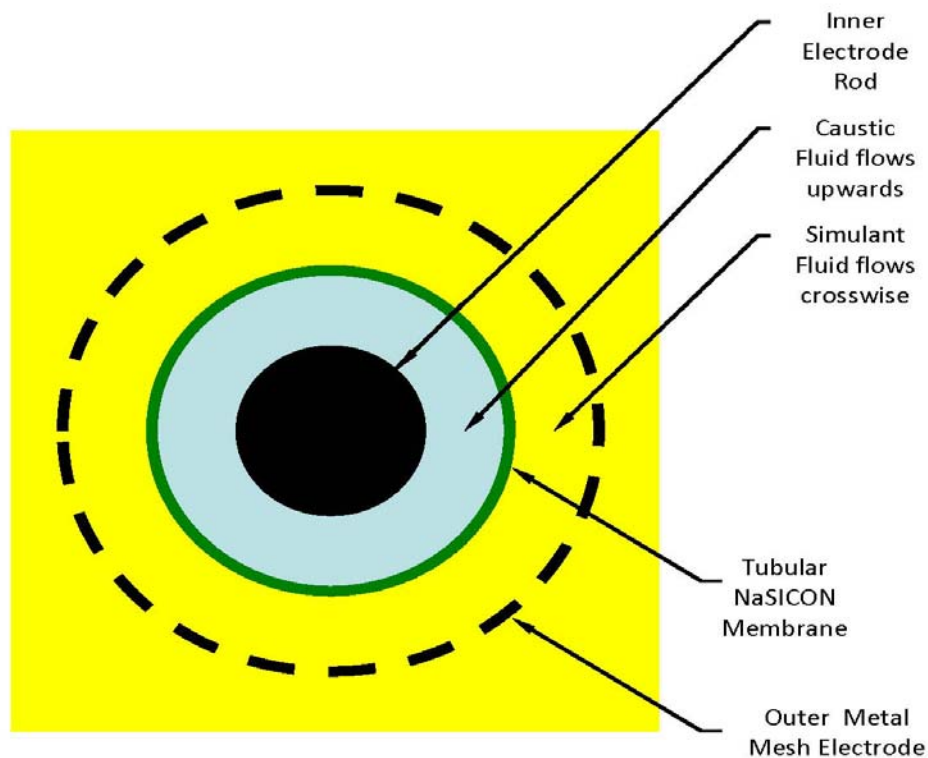


Figure 2: Top view of tubular membrane-electrode assembly

The NTCR fluid is shown in yellow in this diagram and it flows horizontally around the outside of the tubular membrane. The caustic fluid is shown in blue and it flows up through the inside of the membrane. When current passes between the electrodes and through the membrane, sodium

is transported through the membrane from the simulant into the caustic solution. The sodium then combines with the water in the caustic fluid thus concentrating the sodium hydroxide, thereby producing the sodium hydroxide at the desired strength.

In this process hydrogen gas is formed at the cathode electrode. Since the membranes are positioned vertically and the fluid flow is directed upwards the hydrogen gas is easily carried up out of the membrane and subsequently out of the TDU module where it is separated from the fluid safely. The caustic fluid is recirculated back from the tank through the TDU module to increase the concentration of sodium hydroxide .

The sodium level in the simulant is constantly being reduced concurrently with the caustic fluid's increase in concentration. When the sodium concentration in the batch of simulant fluid reaches the desired level the system is shut down. Both fluids are removed and replaced with another batch to be treated.

Prototype Baseline Performance Testing In Group 5 and NTCR Simulants

Initial testing with the 22 tubular membrane prototype cell unit was conducted to determine the baseline performance of the multi-tubular membrane unit. By testing under a continuous flow of feed, a steady voltage from the cell under a constant operating current was used to show stable performance. Short-term testing under these conditions also allowed for qualification of the seal design to house the ceramics and separate the waste simulant from product caustic.

Testing was performed for 40 hours to evaluate if the unit was showing stable performance to recycle sodium hydroxide. During testing, both 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 tank and deionized (DI) water to the catholyte tank. After 40 hours of testing, the unit showed steady performance at a stable 3.4 volts and showed no signs of external leaks.

To determine the prototype unit's potential for use in a variety of caustic concentrations, further testing was done to determine how the cell unit performance was affected by the sodium hydroxide concentration in the catholyte feed tank, which in turn could affect the gas void fraction present in the cell. The unit voltage and catholyte caustic concentration data was then compared with the results achieved using single tubular membrane cells to ensure the unit operated at or above previously established performance targets. This performance comparison was especially important to establish because the prototype unit was designed to use lower catholyte and anolyte flow rates, which were identical to flow rates that were to be used for operation of the TDU.

This testing was performed for 90 hours to provide time for the catholyte solution to increase from roughly 16 to 30.5 wt% NaOH. During this time the process was operated in a semi-batch mode where the anolyte was continuously recharged, but not the catholyte side. Titrations of the catholyte sodium hydroxide concentration were taken daily to correlate cell voltage with sodium hydroxide concentration. After 90 hours of unit testing, the catholyte concentration was manually increased to 37 wt% and 50 wt% and run briefly at both concentrations to establish operating voltages at higher catholyte concentrations.

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 which decreases the conductivity of the solution.

At this point in testing, the prototype unit was pressurized with air to certify the unit was leak tight, showing no signs of leaking through either the seals or membrane manifolds. Visual inspection of both the insides and outsides of the tubular unit was conducted which also showed no visible fouling of the membranes over short-term testing period.

Final testing of the 22 tubular membrane prototype unit was performed in full batch mode using NTCR simulant. The prototype unit was tested for 83 hours at an operating voltage in the range of 3.47V to 3.73V (see Figure 3). Variations in cell voltage are primarily due to temperature fluctuations during testing or starting and stopping the cell, as the cell was only run for 5 to 8 hours a day. During this time the NTCR feed anolyte compartment had removed roughly 71% of the sodium, while the catholyte caustic had increased its catholyte concentration from 35 to 44wt%.

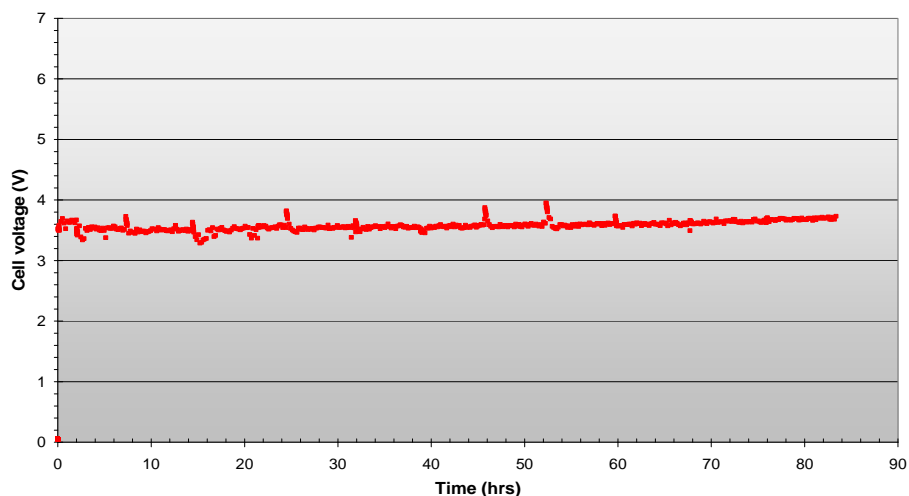


Figure 3: Operating voltage of 22 tubular membrane cell with NTCR simulant

The 22 tubular membrane cell prototype unit performed at a steady voltage range over the concentration range of the feed NTCR simulant. Similarly, no precipitation was observed from any of the anolyte samples taken during testing from 0 to 71% of the sodium removed, which suggests similar batch operation with the multi-tubular design should pose no additional operation reliability issues from testing with NTCR effluent simulant chemistry in the defined range for recycle sodium hydroxide.

Testing of Sub-Pilot Scale TDU Modules (0.5 and 1.0 m²)

Initially, a single TDU of 0.5 m² of membrane area (**Error! Reference source not found.**) was run for 3 batch cycles to validate the electrode, membrane, manifold, and seal design, as well as establish the operating voltage of the scale up design for comparison with the prototype unit.

Finally, two units were combined (1.0 m² of membrane area) and tested for two batch cycles to demonstrate separation of at least 60% of sodium from NTCR simulant. The results from this testing was used for design and build the pilot scale unit for integrated NTTS demonstration. Overall, sub-pilot scale TDU module testing was conducted over 5 anolyte simulant batch cycles, totaling over 175 hours, to demonstrate the maturity of the caustic recycling technology to recycle sodium from NTCR simulant. The operational parameters for TDU testing are shown in Table 1. Testing showed good performance of the TDU, similar to the previously tested single tubular and prototype units.



Figure 4: A single TDU test skid

A new batch of NTCR was made for the first batch cycle, after which the solution was simply recharged with pure sodium hydroxide for two additional batch cycles. During each batch cycle the anolyte solution was processed until 60% of the sodium was removed. The catholyte solution was maintained at approximately 30 wt% sodium hydroxide by continuous addition of DI water. This caused a buildup of 30 wt% caustic solution in the catholyte tank which was removed, weighed, and titrated to ensure the concentration remained constant and to be used for indirect current efficiency calculations through verification of a 100% efficient mass balance on the system. Final operating conditions of the unit are shown in Table I.

Table 1: Operational parameters for sub-pilot scale TDU modules

| Operation Parameter | Value or Specification |
|------------------------------|-------------------------------|
| Current density | 75 mA/cm ² |
| Solution temperatures | 40°C |

| | |
|----------------------------------|---|
| Anolyte | NTCR Batch with objective to separate 60% Na removal |
| Catholyte | Continuous production of 10M or 30 wt% NaOH |
| Number of test cycles | 5 |
| Batch operating time | 42.2 hours and 21.1 hours (for 0.5 and 1.0 m ² respectively) |
| Orientation of electrodes | Catholyte – Outside of tubular membrane Anolyte – Inside of tubular membrane |
| Anode | Iron, Nickel, Cobalt alloy |
| Cathode | Iron, Nickel, Cobalt alloy |
| Processing rate | 8.7 L/hr, based on 60% Na ⁺ removal |
| Production rate | 3.74 kg/hr or 2.87 L/hr of 10M NaOH in the catholyte |

Two additional batch tests were conducted with freshly made simulant solutions and using the two module combined units (1.0 m² of membrane area). The samples after sodium was separated from the NTCR simulant samples were collected and sent out for analysis.

Figure 5 shows the cell voltages during testing, which held constant during testing and are slightly lower than, but similar to, the 22 tubular prototype unit previously developed. Variations in cell voltages near the end of testing, seen in Figure 5, are due to daily temperature fluctuations while running two units simultaneously. Overall, the modules operated with stable and reliable performance over the course of testing.

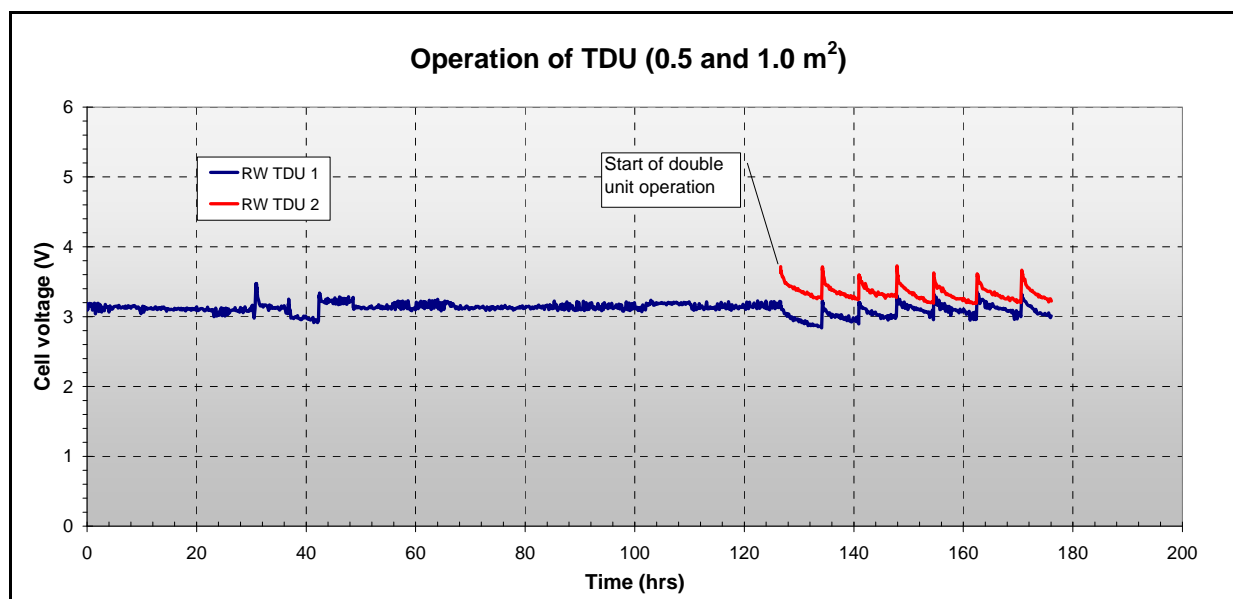


Figure 5: Test data for a single TDU unit over the course of three batch cycles

Inductively coupled plasma (ICP) analysis of initial and final of the feed and product samples was performed to evaluate reliability of seal and membrane performance to recycle sodium hydroxide from NTCR effluent. Results of this analysis are shown in Table II and show no major signs of electrode degradation or internal seal leakage over the course of testing. Visual observation of the samples suggested no noticeable quantities solids had formed in the anolyte during testing. Preliminary solids analysis of the samples taken during testing also showed no appreciable increase in the quantity of solids present in the anolyte solution.

Table 2: Metal analysis of solutions used in testing

| | Element | Reporting Limit (mg/L) | Results (mg/L) |
|-------------------|-----------|------------------------|----------------|
| Initial Anolyte | Iron | 10 | <10 |
| | Nickel | 0.004 | 0.034 |
| | Potassium | 100 | <100 |
| Final Anolyte | Iron | 10 | <10 |
| | Nickel | 0.004 | 0.011 |
| | Potassium | 100 | <100 |
| Initial Catholyte | Aluminum | 10 | 27 |
| | Potassium | 100 | 200 |
| Final Catholyte | Aluminum | 10 | 51 |
| | Potassium | 100 | 210 |

CAUSTIC RECYCLING INTEGRATED PILOT

As part of the DOE sponsored Advanced Remediation Technologies initiative, a scheme is proposed to combine Continuous Sludge Leaching (CSL), NTCR, and Caustic Recycling using the present technology, into a single system know as the Pilot NTTS. Ceramatec is responsible for providing the Caustic Recycling component of the system, while CSL and NTCR will be developed and provided by other organizations.

The primary goal of this work package is to design, fabricate, and test a caustic recycling unit at as part of the integrated demonstration with the CSL and the NTCR unit, designed and fabricated by other organizations, to form the PNTTS. This pilot system operation will be conducted at the Technology Development and Fabrication Complex (TDFC) facility in Pasco, WA.

Integration of a caustic recycling system into a proposed NTTS will substantially minimize the addition of further sodium hydroxide into waste tanks. This scope of work covers the

development work required to design, fabricate, and test a Caustic Recycling demonstration unit for incorporation into an integrated testing platform with capabilities for CSL and NTCR. This integrated platform is referred to as the Pilot NTTS. The CRU will be capable of operating in a continuous mode to separate sodium from the output of the NTCR demonstration module and feed caustic to the CSL system. The CRU will operate in a batch mode and is designed to receive the NTCR effluent feed in continuous mode.

CONCLUSIONS

1. Successfully demonstrated an engineering scale system to process higher throughput of feed NTCS effluent stream. Also demonstrated a safe operation of the multi-tubular NaSelect™ membrane based modular unit to recycle sodium in the form of sodium hydroxide to make up to 30 wt% in concentration. The performance of seal and membrane reliability was established through independent components validation and operation of the single and multiple membrane units in various testing conditions to simulate wider process parameters such as temperature of operation, pressure conditions, and chemistry changes.
2. Tubular ceramic configuration provides several benefits from larger size of membranes (3.5 times planar membrane), ability to withstand up to 250 PSI pressure drop across the membrane compared to planar membrane configuration, lowers the number of seal enhancing seal reliability and improved performance with reduction in cell operation voltage. The tubular membrane design improves the cell's ability to cope with aluminum precipitation compared to the planar design.
3. The design of a tubular membrane based TDU was developed and matured. The unit was manufactured, and the reliability and performance of the components and equipment was evaluated and validated in NTCR simulant. The design basis was to focus on ability to efficiently package multiple tubular membranes to support size and achieve footprint scalability of modular cell arrangement for processing higher throughput of LLW feed. The modular nature of the tubular cell configuration design will allow an economy of scale sizing by adding additional modules to the foot print based on the processing, production and feed rate requirements for full-scale production system. The scalability and design maturity of tubular caustic recycling technology was successfully demonstrated by operation of a TDU unit in several simulant chemistries such as Group 5, Pre Engineering Platform (PEP) Leachate, CSL and NTCR LLW simulant chemistries.
4. The TDU was successfully operated at 75 mA/cm² operating current density resulting in heating the anolyte and catholyte solutions to as high as 44°C when the set point was 40°C compared to performance matrix established with single cell testing to show ability of the process to recycle sodium in the form of sodium hydroxide. The cell operation efficiency was near 100% for sodium transfer across the membrane. This indicates that cooling the solutions during operation may not be necessary with the piping and stainless steel process equipment acting as heat exchange medium with air. Even slight fluctuations in the ambient air temperature within the laboratory tests resulted in noticeable changes in the equilibrium temperature without direct heating or cooling to the system. This suggests that the entire system, as designed and operated in the laboratory setup is capable of maintaining the temperature constant between 40 and 44°C during testing.
5. No indications of leaking through membranes or around internal membrane seals were detected. The external seals to the modules with piping to the holding tanks also showed no

leaks and are robust for extreme operating process conditions. The cell component, membrane and anode and cathode electrode materials were stable and showed no sign of corrosion.

6. In the 1.0 m² TDU modular cell unit test, 189.3 liters of NTCR simulant was processed in 21.1 hours which is equivalent to processing 8.7 l/hr, for continuous 60% sodium removal, while at the same time producing approximately 3.74 kg/hr or 2.93 l/hr of 10M NaOH in the catholyte.

7. With the successful demonstration of the TDU operation, the design maturity has been demonstrated for the caustic recycling technology and is ready to scale up the size of the caustic recycling unit for a Pilot Phase Integrated testing with CSL and NTCR to recycle sodium in the form of sodium hydroxide from the NTCR effluent to be fed into the CSL process.

REFERENCES

[1] Caustic recovery from alkaline nuclear waste by an electrochemical separation process . **D. T. Hobbs*** Westinghouse Savannah River Company, Savannah River Technology Centre, Aiken, SC 29808, USA SDep Purif. Technology.