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Review of Ceramtec's Caustic Recovery Technology

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EXECUTIVE SUMMARY

In May 2007, the Department of Energy Environmental Management Office of Waste Processing (EM-21) requested a Technology Assessment of a potential sodium hydroxide recovery technology under development by Ceramatec, Inc., Salt Lake City, Utah. This electrochemical process utilizes a novel inorganic membrane technology to recover concentrated sodium hydroxide from alkaline wastes typical of decontaminated ion exchange effluents from the Hanford Waste Treatment Plant (WTP). A successfully developed technology could be used to reduce the overall sodium demands to the Low Activity Waste (LAW) vitrification process at WTP by recycling the sodium hydroxide for use in aluminum leaching. The consensus of the Technology Review Team was that the NaSICON electrochemical process for recovering sodium hydroxide is a viable technology at its current state of development. Additional work is needed to determine if this Ceramatec technology or other caustic recovery technologies could be successfully integrated into the WTP mission.

A summary of the key technical issues include:

- The need to reduce the overall sodium burden to the Low Activity Waste (LAW) vitrification process is well established. This sodium burden is worsened by the need to perform aluminum leaching of High Activity Waste sludge. Recovering sodium hydroxide to be recycled within this process would offer significant advantages. However, the ability to recover sufficient caustic from WTP LAW vitrification feed without adverse impacts is not well established. Key to this recycling is the stability of supersaturated aluminate solutions produced during the caustic recovery process. Additional research is needed to establish the parameters to allow recovery of caustic and avoid aluminum precipitation.
- Insufficient data exist at high catholyte caustic levels (50 wt %) to ensure NaSICON electrochemical cell operability and reliability at high catholyte caustic level
- Integration of any caustic recovery technology into WTP mission is needed to ensure success. Currently, caustic recovery is not included in the baseline flowsheet for WTP. The DOE is investing in caustic recovery development via several technologies. To date, a close arrangement between the Ceramatec development and project staff to integrate the technology into the flowsheet does not exist.

The Technology Assessment Team observed three technical issues listed above that require resolution prior to implementation of the technology. In addition, the Team identified seven areas of concern and five opportunities for improvement which are detailed in this report.

Table of Contents

Executive Summary 4

1.0 Introduction..... 6

1.1 Description of the Sodium Hydroxide Recovery and Recycle System 7

1.2 Alternate Caustic Recovery Technologies..... 9

2.0 Technology Review Process..... 9

3.0 Technology Assessment results and Observations..... 10

3.1 Technical Issues 10

3.1.1 Ability to reduce the overall sodium burden to the LAW vitrification process is not well established..... 11

3.1.2 Insufficient data exists at high catholyte caustic levels (50 wt %)..... 11

3.1.3 Improvement in integration of caustic recovery technology with the WTP mission is needed to ensure success. 12

3.2 Areas of Concern 12

3.2.1 Ceramtec’s role with respect to technology deployment not well defined...... 12

3.2.2 Understanding the caustic management throughout the whole of River Protection Project (RPP)...... 13

3.2.3 Systems Engineering Evaluation versus other technologies for caustic recovery has not been performed. 13

3.2.4 Development and testing of system flowsheet is insufficient to proceed with design. 14

3.2.5 Commercialization of the production of ceramics to meet full scale facility requirements. 14

3.2.6 Additional characterization of aqueous bi-products and offgas is needed. 15

3.2.7 Electrodes may not meet requirements due to corrosion performance. 16

3.3 opportunities for improvement 16

3.3.1 Movement of contract oversight from Idaho to Office of River Protection 16

3.3.2 Need to identify an Architectural and Engineering Point of Contact 16

3.3.3 Improved Electrochemical Cell Design 17

3.3.4 On-Line instrumentation for hydroxide and aluminate concentrations..... 18

3.3.5 Coupling Aluminum/Chromium leaching pilot and actual waste testing to examine varying simulant composition 19

4.0 CONCLUSIONS 19

5.0 Bibliography 20

Attachment 2. Committee qualifications 24

Attachment 3. Lines of Inquiry 26

Programmatic 26

Na Recovery Technology 26

Electrochemistry..... 26

Membrane and Corrosion Technology 27

WTP Applicability and Implementation..... 28

1.0 INTRODUCTION

The Department of Energy (DOE) Office of River Protection (ORP) was chartered to provide safe storage, retrieval, treatment and disposal of over 53 million gallons of highly radioactive mixed waste in 177 underground storage tanks at the DOE's Hanford site near Richland, Washington. Currently, the Waste Treatment Plant (WTP) is being designed to separate the Low Activity Waste (LAW) from the High Level Waste (HLW) fraction. Each waste stream will be vitrified into suitable waste forms for near surface disposal (LAW) and deep geologic disposal (HLW).

Within the Waste Treatment Plant, the 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 non-radioactive component of sludge is necessary to reduce the number of HLW canisters produced during vitrification operations and improve overall processing efficiencies in that operation. The aluminum is removed from the HLW by a sludge leaching process that utilizes large amounts of sodium hydroxide. The additional caustic requirements are still under study. Current projections 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.

As part of an overall plan to address WTP flowsheet deficiencies, Ceramatec, Inc. was funded to design and develop a full scale electrochemical system technology to remove sodium from low-level radioactive waste. This concept employs a sodium super ionic conductor membrane (NaSICON) 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, thereby lowering the cost of low activity waste immobilization. The addition of sodium to the tank waste treatment system increases the immobilized low activity waste volume, cost and schedule. Figure 1 shows a proposed conceptual process for implementation of a caustic recovery and recycle for use in the Waste Treatment Plant.

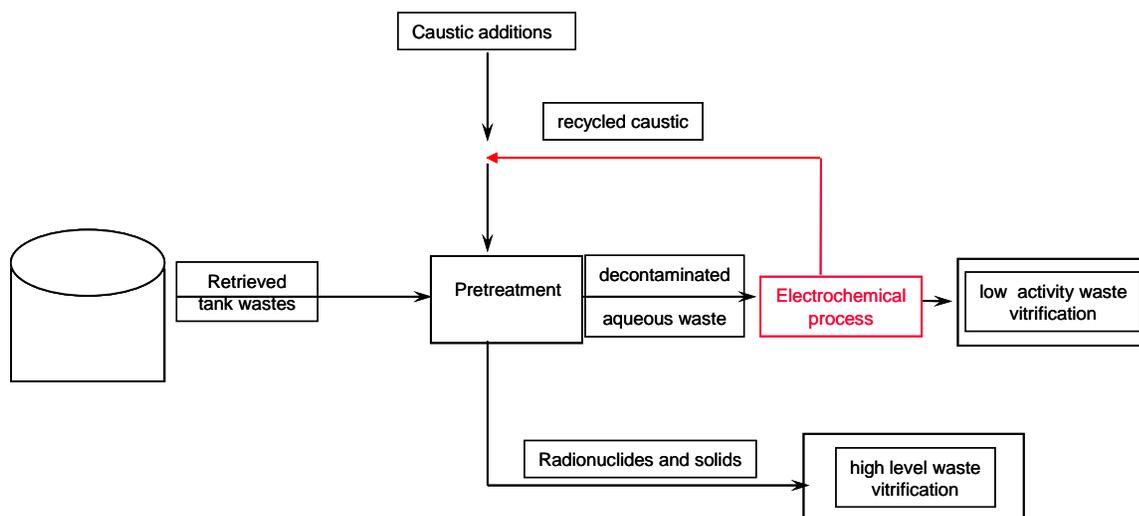


Figure 1. Conceptual Process for Caustic Recovery and Recycle

1.1 DESCRIPTION OF THE SODIUM HYDROXIDE RECOVERY AND RECYCLE SYSTEM

Electrochemical salt splitting technologies for caustic recycle were investigated in the 1990s for applications to the treatment of tank wastes at the Hanford, Savannah River and Idaho sites. These investigations, which were primarily funded by the EM-50 Efficient Separations and Processing Program, included testing of commercially available organic-based ion exchange membranes (e.g., perfluorosulfonic acid (PFSA) class of membranes offered by DuPont as Nafion[®] series of membranes) and ceramic-based NaSICON membranes developed by Ceramatec Inc.

Both membrane types were tested with simulants at the pilot scale and with actual radioactive waste samples at the bench scale. The Nafion[®] polymer membranes exhibited very good performance and chemical stability. However, due to water transport, these type of membranes are limited to producing caustic having a NaOH concentration of ≤ 35 wt%. Furthermore, these membranes transport other cations such as potassium and cesium. In fact, cesium transport is favored over sodium transport and, therefore, the product caustic solution contains most of the radioactive cesium present in the initial waste.

In contrast to the PFSA membranes, the NaSICON membranes demonstrated the ability to produce 50 wt% caustic as a product. Furthermore, the radioactive test showed that no measurable transport of radioactive cesium across the membranes or leaking through the seals. The ceramic membranes also exhibit much better radiation resistance than the Nafion[®] membranes. Given these results, NaSICON ceramic membranes were selected for evaluation in the WTP Sodium Hydroxide Recovery and Recycle technology development project.

The Ceramtec membranes are from a family of materials known in the power sources industry as sodium (Na), super fast ionic conductors (NaSICON). The NaSICON membrane 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. The primary NaSICON compositions that have been investigated for separation purposes are based on rare earth (RE) ions (i.e., Na₅RESi₄O₁₂). These membranes separate the anolyte and catholyte compartments, allowing only sodium to move through the membrane to the catholyte.

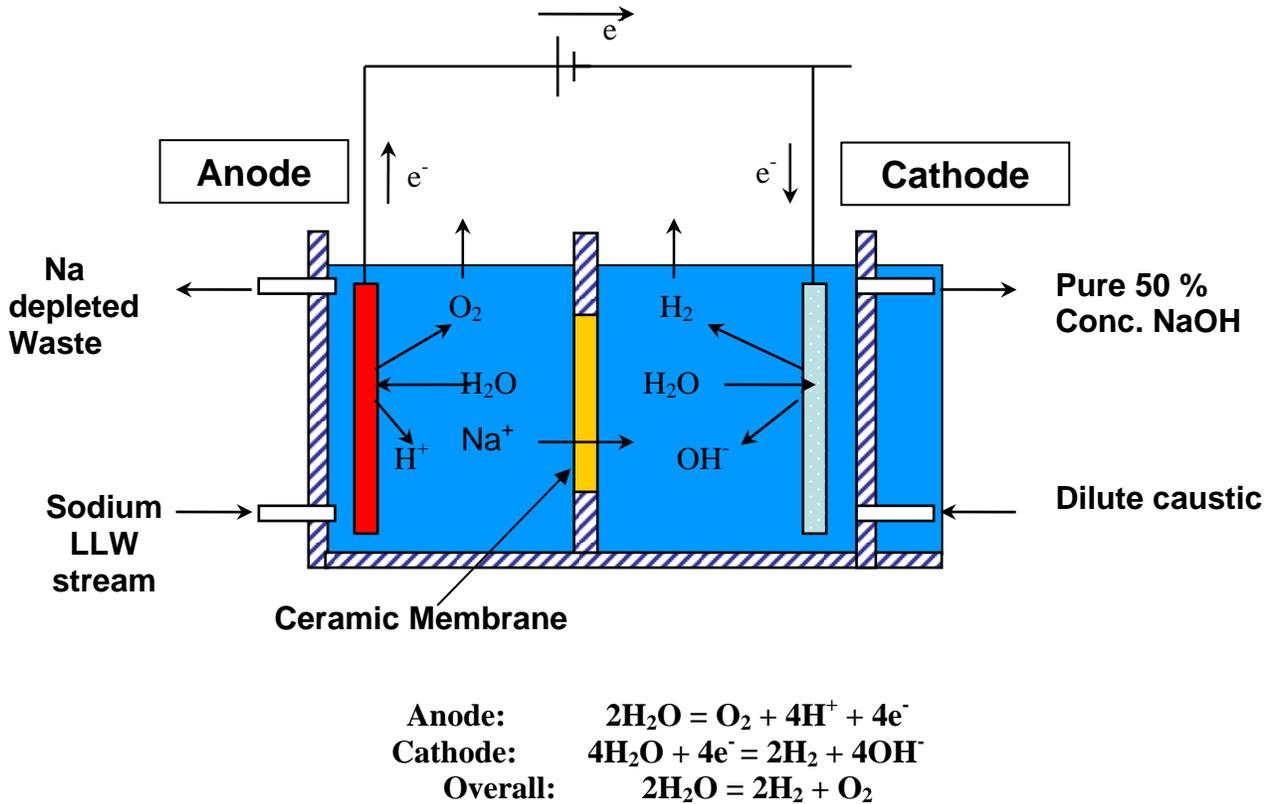


Figure 2. Schematic of a two-compartment Electrochemical Process Using the NaSICON Membrane.

The two compartment cell configuration is shown in Figure 2. The waste solution is pumped to the anode compartment, and an electrical potential is applied to the cell transporting sodium ions through the membrane to the catholyte solution where caustic is concentrated. The membrane rejects most other mono-valent cations (e.g., K⁺, Cs⁺) because of their larger size and multivalent ions due to electro-neutrality constraints. The charge balance in the anode compartment is maintained by electrolyzing water to oxygen gas and protons (H⁺). The charge balance is balanced in the catholyte by electrolyzing water to hydrogen gas and hydroxide ions (OH⁻). As protons are generated in the anode compartment, the pH drops and the waste stream becomes less alkaline. Production of hydroxyl ions in the cathode compartment results in a rise in pH as the sodium hydroxide product is recovered.

1.2 ALTERNATE CAUSTIC RECOVERY TECHNOLOGIES

Two other possible technologies for the recovery of caustic from alkaline waste solutions include fractional crystallization and solvent extraction. Fractional crystallization has been studied at the Hanford site by Herting, et. al as a means to decontaminate a large fraction of the sodium salts from the bulk of the radioactivity. After successive crystallizations the remaining waste solution is enriched in both caustic and radioactivity. In principle this product solution could be used as a source of caustic. Although, this solution is rich in caustic it also contains other sodium salts (e.g., sodium nitrate, aluminate, etc.) that carry through the sequential crystallization stages of the process. Due to the much higher radioactivity content, largely due to the high solubility of cesium in alkaline solutions, considerable shielding would likely be required to handle this caustic solution for reuse. Thus, this technology is not particularly attractive in producing caustic for reuse at the Hanford site

Moyer, et. al have demonstrated a solvent extraction based process that extracts sodium from waste solutions. In this system sodium is exchanged for the proton of a weakly acidic organic compound and extracts into the organic solvent. The sodium is then recovered by contacting the organic solvent with water which protonates the organic compound and releasing the sodium into the aqueous phase as sodium hydroxide. This solvent extraction process has been tested with both simulated and actual radioactive waste solutions. Due to solubility limitations, this process produces relatively dilute NaOH, which must then be concentrated by evaporation to provide sufficiently concentrated caustic solution for reuse. The additional unit operation (i.e., evaporation) required to produce concentrated caustic solution and likely radioactive contamination in the caustic product makes this technology less attractive than the electrochemical separation process that employs a ceramic membrane.

2.0 TECHNOLOGY REVIEW PROCESS

The Technology Review Team was chartered to evaluate two main aspects to the Ceramatec Caustic Recovery project. The review focused on the technical maturity of the electrochemical recovery technology and the programmatic applicability of the technology to the DOE complex in particular to the Hanford Waste Treatment Plant. The members of the Technology Review Team divided the review into five areas. These areas were:

- Programmatic Applicability
- Sodium Recovery Technology
- Electrochemistry
- Membrane and Corrosion Technology
- WTP Applicability and Implementation

The Technology Review Team has defined four categories of observations. These categories are:

- Findings – These are observations that would prevent the technology from being deployable or render the technology from being fully developed to meet WTP mission needs.

- Technical Issues – Observations that require resolution to ensure that the technology will successfully meet mission needs.
- Areas of Concern – These observations may require design modifications to the technology deployment or additional testing to resolve a technical concern.
- Opportunities for Improvement - Areas that would improve the ability to meet WTP mission needs or offer alternative solutions to technical problems

3.0 TECHNOLOGY ASSESSMENT RESULTS AND OBSERVATIONS

The technology assessment consisted of reviews of documents provided by Ceramtec, Inc. and in-depth technical presentations along with mutual discussion in the Salt Lake City, Utah facilities of Ceramtec. The Technology Assessment Team appreciated the receptiveness of the Ceramtec personnel in support of this review. The overall impressions of the team are that Ceramtec, Inc. is progressing with the development of the NaSICON technology for caustic recovery from WTP waste streams. The technology has high promise to meet mission needs but additional research and development is needed to ensure the viability of process. The Team noted that initial implementation strategies have been developed including initial facility design. Additionally, Ceramtec staff and facilities are well equipped to complete the scope of work successfully. During the performance of this project, Ceramtec has completed a significant number of accomplishments including:

- Established the tape casting/lamination manufacturing process to make large area co-fired NASICON structures (LANS)
- Completed the design of a bench-scale modular unit, manufacturing, design, validation and performance evaluation in several simulant compositions including actual waste testing
- NaSICON ceramic membrane processing has been scaled up from 1.5 kilograms per batch up to 12 kilogram per month
- Selected two preferred membrane compositions and membrane manufacturing technologies
- Demonstrated greater than 2000 hours of continuous operation of NaSICON membrane-based electrolytic cells to separate sodium from a typical Hanford simulant composition
- Demonstrated that a 5 scaffold stacked modular bench scale cell operation at 100 mA/cm²/scaffold was successful
- Completed initial scoping of a facility design for a full scale operable unit capable of processing up to 39,000 MT sodium over the lifetime of the facility

3.1 TECHNICAL ISSUES

Listed below is a summary of the technical issues, areas of concern and areas of improvement as defined in section 2.0 of this assessment report.

3.1.1 Ability to reduce the overall sodium burden to the LAW vitrification process is not well established

The throughput of the LAW vitrification process at the WTP is limited by the amount of sodium contained in the decontaminated waste solution. This sodium burden is negatively affected by the need to reduced aluminum contained in the HLW sludge. The aluminum leaching process will utilize sodium hydroxide to dissolve the aluminum from the HLW sludge and send the aluminum to the LAW melter along with the sodium. Estimates of the amount of sodium added to the waste from the leaching process almost double the total sodium inventory.

The current constraint for the Waste Treatment Plant caustic leaching process is to produce a solution that is stable with respect to aluminum precipitation (and in particular the formation of gibbsite crystals in equipment downstream of the filtration system). The primary rationale for preventing aluminum precipitation is to ensure stable operation of the ion exchange system. It is recognized that the ion exchange system will not likely operate as designed if there is a significant quantity of solids in the feed stream to the columns. Since the current design basis operating temperature for the ion exchange system is 25°C, the target product leaving the filtration system would be saturated (or near saturation) with respect to aluminum precipitation.

The proposed caustic leach process would increase the existing stream temperature to 40 °C to provide additional aluminum solubility then recover the NaOH to the point where the Al is saturated at 40 °C. This affords the ability to recover a significant quantity of caustic. However, when upon cooling the stream to 25 °C, a supersaturated stream with respect to Al precipitation of gibbsite is produced.

Additional testing needs to be performed to assess the stability of these supersaturated streams and to identify the process limits for this system. In particular, testing needs to be done to determine the point at which spontaneous crystallization occurs and the point at which amorphous – non crystalline solids form. The amorphous solids – which form when significant excess caustic is removed – would be significantly more difficult to mitigate. However, it is very likely that appropriate process limits can be established which either for-stall precipitation altogether or which at a minimum render the production of amorphous solids improbable.

3.1.2 Insufficient data exists at high catholyte caustic levels (50 wt %)

Insufficient data exist at high catholyte caustic levels (50 wt %) to ensure that NaSICON electrochemical cell will operate reliably at high caustic levels. In meeting the defined milestones for the project, Ceramatec personnel have performed extensive testing of the electrochemical cell design under continuous operations for over 3000 hours. These data have been used to project cell lifetimes and have been included in economic analyses for

project validation. The Technical Issue resides in that electrochemical cell operation durability may be adversely affected at very high hydroxide concentration. Ceramatec personnel provided data showing that the process has operated for 1000 hours at 50% caustic catholyte. Subsequent post-mortem analyses indicated there was no degradation of the membrane or seals. This single test, while demonstrating that the technology may well provide the 50% caustic product necessary for successful implementation in the Hanford WTP flowsheet, does not provide the level of confidence that would be required to plan technology deployment. Additional tests at 2000+ hours, generating enough data for reliable statistical analysis, are in progress.

3.1.3 Improvement in integration of caustic recovery technology with the WTP mission is needed to ensure success.

The opportunity to utilize a caustic recovery flowsheet would benefit the overall operation of the Waste Treatment Plant by reducing the total amount of sodium being fed to the Low Activity melter. Currently, the Ceramatec work is being managed through the Idaho DOE field office as a research and development project. Ceramatec has the responsibility to design an implementation of the electrochemical recovery technology. Without complete integration with the Office of River Protection, key interfaces will be difficult. A decision on where the caustic recovery system will be inserted into the WTP flowsheet will have a significant influence on the numerous design aspects of an operable unit for caustic recovery. Such a decision can best be made through collaboration between Ceramatec and the WTP staff. One point could be in a diversion box between the Pretreatment building and the Low Activity Waste Vitrification facility. This access point offers several advantages. However, another point where the process could be fed is directly after the ion exchange columns and prior to the downstream evaporator. Without key interface between the WTP project and the Ceramatec project, the electrochemical recovery process could be designed to work in a non-conservative control point. Management of the Ceramatec project under the auspices of the Office of River Protection would afford Ceramatec personnel better access to the WTP project personnel to ensure successful development of the caustic recovery flowsheet and subsequent design and construction.

3.2 AREAS OF CONCERN

3.2.1 Ceramatec's role with respect to technology deployment not well defined.

Under the current contractual arrangement, Ceramatec, Inc. has scope defined to develop and complete a preliminary design of a caustic recovery technology. To that end, Ceramatec has contracted with the Pacific Northwest National Laboratory to conduct radioactive waste testing and initiate flowsheet development and conceptual design. Ceramatec has the capability, staffing and design services to produce an operable production-scale electrochemical unit. However, with respect to developing a DOE-compliant project to implement the electrochemical recovery of caustic, the team does not believe that Ceramatec has the capabilities to accomplish that complex of a task. Ceramatec's role with respect to

the project should be limited to the development of the caustic recovery production cell technology, manufacture of ceramic membranes and cell modules (with possible assistance from a large ceramic manufacturing partner) and technical support to an architectural and engineering firm for the design, construction and start-up of the caustic recovery facility.

3.2.2 Understanding the caustic management throughout the whole of River Protection Project (RPP).

In addition to the caustic requirements identified associated with WTP in section 3.1.3, the role of caustic through out the entire RPP is also required. Most of the sodium currently stored in the Hanford tank farm is associated with the salt-cake fraction of the waste. However, because of the differing solubilities of nitrate/nitrite and hydroxide, these salt-cakes are typically enriched in nitrate/nitrite relative to hydroxide. Also, with continuing exposure to air (and by corollary, CO₂), the caustic concentration decreases. Thus, maintaining corrosion control (which relies upon periodic additions to maintain sufficient caustic to inhibit tank corrosion) places an additional burden on the caustic requirements for the RPP. Any process developed to manage caustic should also consider both methods (aluminum leaching and corrosion control) to decrease the quantity of additional sodium added to maintain corrosion control and should avoid exacerbating the current caustic deficiencies in the tank farm system.

3.2.3 Systems Engineering Evaluation versus other technologies for caustic recovery has not been performed.

The electrochemical recovery of sodium hydroxide shows promise as a technology that could be implemented at the Waste Treatment Plant to reduce the overall sodium demand on the Low Activity Waste vitrification. The project has been funded by the DOE for the last couple of years. However, this process technology is not the only DOE investment in sodium recovery. Researchers at Pacific Northwest National Laboratory and Oak Ridge National Laboratory have been funded through a DOE-BER Environmental Remediation Sciences Project to explore an ion recognition approach to separate sodium salts from alkaline wastes. This solvent extraction-based technology has been investigated for the past five years or so. Significant work has been accomplished and this technology also shows promise. The Department of Energy should perform a downselection at either conceptual design-1 or -2 (CD-1 or CD-2) systems engineering evaluation to determine the best technology to apply to sodium recovery at WTP.

3.2.4 Development and testing of system flowsheet is insufficient to proceed with design.

A detailed process model of the caustic recovery system is required to provide further evaluation of the benefits of the proposed process. This process model would address a number of issues. Currently the process is proposed as a semi-batch operation, a detailed process model would provide the anticipated operating parameters for this semi-batch process. It would also address the impact of integration of batch sizes with the WTP. This integration is also significantly impacted by the point of implementation.

Currently two points of integration are envisioned. The first point of insertion would be between the WTP ion exchange columns and the WTP Treated LAW evaporator. This insertion point provides a solids free feed to the caustic recovery system but would require significant integration with the WTP process flowsheet. The second insertion point would be between the Treated LAW evaporator and the WTP LAW facility. This insertion point has the advantage of being staged between two WTP facilities, and thus having a lesser impact on the WTP process flowsheet. However, this insertion point would result in a more dilute feed to the LAW facility (with respect to Na concentration) and thus would increase the evaporative water load on the LAW facility – and a concomitant decrease in LAW production rate (though it would not change the LAW glass loading).

3.2.5 Commercialization of the production of ceramics to meet full scale facility requirements.

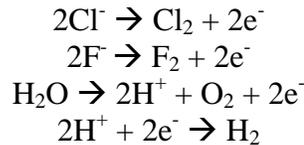
The current capacity at Ceramatec, Inc. for producing membranes may be able to meet full-scale requirements. The team understands from Ceramatec, Inc. that in July 2007 the company added an additional 38,000 sq.ft. of floor space to their existing Salt Lake facility. A portion of this addition is dedicated to the NaSICON cell production, testing and validation.. To fabricate the large number of membranes needed for implementation, alternative processing techniques will be required. Tape casting, which is used in the fabrication of Large Area NaSICON Structure (LANS) membranes, is an easily scalable process. However, difficulties may appear in processing of the powder precursors. For example, attritor mill processing is being investigated to replace the ball milling preparation currently used. To maintain the current particle size distribution, shorter processing times may be used with the attritor mill. However, with shorter processing time, inhomogeneity may occur in large scale production of the powder. A non-homogenous powder may cause significant chemical differences in the membrane during fabrication, which would affect its performance. Additional research is necessary to ensure that the implementation of attritor mills does not significantly affect the end product. This research may include looking at implementing powder circulators in large scale attritor mills and other techniques to ensure the powder quality.

In order to meet the large capacity requirement, membrane fabrication may need to be outsourced. If alternative facilities are utilized, a quality control plan needs to be initiated to ensure that the membranes meet defined acceptance criteria. A plan also needs to be

initiated to determine the capacity requirements and alterations that will be needed by WTP and other Ceramtec clients. This plan should also include recommendations for meeting these requirements.

3.2.6 Additional characterization of aqueous bi-products and offgas is needed.

Initial testing on radioactive simulant has been successfully completed at Ceramtec. The composition of the simulant can be found in Table 1. While the concentration of sodium hydroxide is constantly monitored, further on-line analysis is needed on operational by-products and emissions that occur with the use of simulants. Potential emission reactions, in addition to CO₂ and NO_x production, include:



Projected levels of halide and hydrogen formation have been calculated by Ceramtec. However, a direct comparison to WTP acceptability and operating limits needs to be completed. In addition, on-line analysis, such as gas chromatography, needs to be completed to determine experimental emissions levels. This testing will help determine if hydrogen production will be above 1% (25% of LFL). If so, methods for control, such as surge gases, need to be determined and investigated.

Table 1: Composition of PNNL simulant used in electrochemical evaluation.

Constituent	Wt %
H ₂ O	68.0460
NaOH	8.5777
Sr(NO ₃) ₂	0.0021
NaCl	0.1056
NaF	0.0513
Na ₂ HPO ₄	0.0989
Na ₂ C ₂ O ₄	0.1569
Na ₂ CO ₃	1.3832
Na ₂ SO ₄	1.6212
NaNO ₂	3.3748
NaNO ₃	6.9556
KNO ₃	0.1237
Ca(NO ₂) ₂ *4H ₂ O	0.0004
CsNO ₃	0.0016
Ba(NO ₃) ₂	0.0021
SiO ₂	0.0186
Al(NO ₃) ₃ *7H ₂ O	9.4793

There is also the potential to have organic contaminants in the electrolyzer feed. The impact of the organics on cell operation and downstream processes needs to be determined. Organics have the potential to be volatile in caustic solutions. This volatility would cause excess emissions and pressure generation in the reactor, which may impair cell performance.

3.2.7 Electrodes may not meet requirements due to corrosion performance.

The lack of understanding of electrode failure modes may impact safety. Ceramatec has proposed the use of a new variety of anode which will allow the caustic recover cell to operate with a 17% improvement in power efficiency. While this innovation is a worthwhile achievement, Ceramatec has not presented enough data to allow a reliability assessment. Failure of an electrode during operation may cause a serious solution (process or caustic) leak. Electrodes such as DSA and platinum on titanium routinely used in aqueous electrolytic and Chloro Alkali processes have been evaluated and optimized for this application at Ceramatec. A new variety of low cost and highly catalytic electrodes are also being developed.

3.3 OPPORTUNITIES FOR IMPROVEMENT

3.3.1 Movement of contract oversight from Idaho to Office of River Protection

As mentioned in Technical Issue 3.1.3, management of the Ceramatec project through the Office of River Protection offers several advantages over the current oversight. The advantages reside in the improvement in technical input to Ceramatec. This change will result in improved understanding of the potential interface issues between the internal operations of the Waste Treatment Plant and the caustic recovery process, increase the interaction between WTP project personnel and Ceramatec, and reduce research and development costs and durations. The Office of River Protection personnel involved in this review welcomed the concept of this transition.

3.3.2 Need to identify an Architectural and Engineering Point of Contact

Currently, much of the design support is provided by PNNL. However, many of the design issues associated with the layout and design of the proposed facility would be better addressed by an Architectural and Engineering (A&E) contractor. For example, maintenance integration in current facility layout would be better addressed by an A&E firm.

3.3.3 Improved Electrochemical Cell Design

Use of an Air Cathode to remove generated hydrogen and reduced voltage

The current design of the Ceramatec caustic removal cell generates hydrogen gas at the cathode. The cell will generate one mole of hydrogen for every mole of caustic produced. The wide flammability range of hydrogen gas in air (4-74%) dictates a serious consideration of safety issues with respect to disposal of the gas. It would be much safer if the cell were adapted to reduce or eliminate this hazard. The addition of a fuel cell at the cathode end of an electrolysis scaffold would “burn” the hydrogen gas in a safe manner and generate power that would reduce the voltage of that scaffold/cell. Power savings on the order of 20% could be realized with this modification.

Evaluation of cell design (tubular versus plate and frame) to better handle solids formation

The filter-press cell design currently used by Ceramatec is somewhat sensitive to the generation (e.g., precipitation) of solids in either compartment (anolyte or catholyte) of a scaffold due to the flow patterns and hardware contained in each compartment. A tubular cell design with the process solutions passing through the center of a large number of parallel cells would be more resistant to solids precipitation/fouling. The catholyte would be in the outer annulus of such a cell design. Since there is essentially a zero probability of generating solids in the catholyte solutions, there should be no impact on the operation of such a cell design. Preliminary design has been completed for the tubular concept. Testing and validation of single and stacked assembly of tubes with waste simulant and ceramic tube manufacturing will be proposed.

Take cell to failure and determine recovery methods

As was discussed at the Salt Lake meeting, there has been no abuse testing, per se, of the Ceramatec cell design. Abuse testing of equipment is necessary to determine the operating envelope available to process operation and to provide plant operating personnel with guides for recovery of equipment operated beyond design basis. This testing may well prove to be critical for safe plant operation and upset recovery. Preliminary tests were conducted by taking ceramic to failure with operation at current densities from 50 mA/cm² to greater than 400 mA/cm² and at voltages higher than 8 volts. The process conditions envelope for operation will be optimized.

Individual scaffold power supply versus full bipolar operation

This is a configuration which should be tested. Individual power supplies for each module scaffold would allow an individual scaffold to be “cut off” of the operating loop should it fail in a variety of ways. For a module which is gang-wired in parallel as currently design at the Ceramatec facility, a shorted cell would pop the circuit breakers for the entire model with no indication of which scaffold caused the upset. With the relatively inexpensive availability of small, rack-mounted power supplied with parallel control circuitry, a single scaffold failure will not shut down the entire module and plant operation can continue with a slight loss of capacity. Design changes to cell configuration to distribute separate flow to each scaffold in the event of a single scaffold failure will be evaluated to ensure safe shutdown.

Addition of reference electrode on/at each side of membrane to use cell as process instrument

The design of the Ceramatec cell with its ion-selective membrane would allow the cell to be used as an indicator for process health indication (e.g., membrane fouling) or possibly process control. With a passivated or noble electrode fabricated as part of the separator hardware included in the cell design, a high-impedance potential-measuring instrument could determine the sodium activity and conductivity of the anolyte and catholyte solutions while operating. This data could be calibrated for indications of a variety of operating conditions of the cell and used to monitor process operating conditions.

Complete development of membrane as Ion-Selective electrode

The use of the ion-selective membrane as a component of a sodium-ion activity detector could be used to determine the nature of the process solution being processed and a “look-up table” could be developed to allow cell parameter settings to optimize operation for that particular batch of process solution.

Implementation of new electrode materials could reduce power demand by reducing voltage drop across cell

The new anode electrode material developed by Ceramatec indicated that it would decrease cell operating voltage by about 17%. This material change is a worthwhile improvement in the cell design and should be pursued by Ceramatec. The electrode should be abuse-tested to assure that it will perform satisfactorily in the solutions expected from WTP.

3.3.4 On-Line instrumentation for hydroxide and aluminate concentrations

Several factors complicate the solution composition of the decontaminated salt solution coming from ion exchange within the Waste Treatment Plant. These factors include whether aluminum leaching is in operation, the exact retrieved waste composition as well as the composition of recycles within the plant. Therefore, estimating the aluminate and hydroxide concentration in the feed to the caustic recovery process will be difficult. This difficulty in estimating concentrations coupled with the need to recover the maximum caustic as practical leads to the need for on-line instrumentation to provide process information. Otherwise, the caustic recovery would have to recover only a conservative fraction of the available caustic or risk recovering too much caustic leading to aluminum gel formation or gibbsite precipitation. Either of these outcomes would not be desired. Ceramatec does not have a current process plan on how to determine the amount of caustic that could be recovered during a continuous process.

3.3.5 Coupling Aluminum/Chromium leaching pilot and actual waste testing to examine varying simulant composition

Current plans are for the WTP process to be demonstrated in both pilot-scale simulant tests and small scale actual waste tests under a number of process conditions. These tests will produce prototypic product streams that would need to be process through the caustic recovery technology. Therefore, these prototypic process streams would be excellent candidates for demonstration of Ceramatec's caustic recovery process.

4.0 CONCLUSIONS

The Technology Assessment Team completed an evaluation of the Ceramatec electrochemical caustic recovery project. Details of the technical issues, areas of concern and opportunities for improvement have been detailed in this report. At a summary level, the team addressed the two requested areas as outlined in the review charter, namely,

- Assess the Technical Merit of the technology as it currently exists

The Technology Assessment Team did not identify any Findings indicating that the technology could not be developed in a manner which would meet mission needs. However, the team did identify two main areas where additional work is needed to underpin the technical basis for the caustic recovery flowsheet. In particular, development of the understanding of the stability of supersaturated aluminate solutions is needed to determine how much caustic can be recovered for use in aluminum leaching without adverse downstream impacts. Additionally, the Team identified a need for further testing of the electrochemical cells at high caustic concentrations in the cathode compartment to better assess the life of the electrochemical cell.

- Ascertain the Programmatic Applicability of the technology for applications within the DOE Complex in particular the Hanford-WTP.

Although test data suggests that the NaSICON electrochemical recovery process is capable of producing 50 wt % sodium hydroxide for use in aluminum leaching within the Waste Treatment Plant, testing has not shown under prototypic conditions, i.e., varying aluminum and free hydroxide concentrations, that the electrochemical process will work efficiently and cost effectively. The Team encourages closer collaboration between Ceramatec and the Waste Treatment Plant. Additionally, a comparison between this technology and others under development would allow for a down select to a primary technology. This comparison would afford one to undertake an economic analysis as to the viability of caustic recovery for the WTP.

In conclusion, the NaSICON electrochemical recovery of sodium hydroxide is a technology that could benefit the Waste Treatment Plant at Hanford. For its stage of development, the technology appears to hold promise. Additional research is needed to ensure safe and efficient implementation at WTP. No significant issues were identified that would prevent this technology from meeting mission needs. The team believes that the technical issues identified in this review need to be addressed in the near term.

The Technology Assessment Team appreciated the assistance of the Ceramatec project personnel for their help in this review. Additionally, the team acknowledges that Ceramatec has already initiated several actions to address issues identified in this review.

5.0 BIBLIOGRAPHY

Below are listed a short list of documents reviewed by the team.

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Attachment 1. Review Team Charter and Membership

**SODIUM HYDROXIDE RECOVERY PROJECT
INDEPENDENT TECHNICAL REVIEW****1. CHARTER**

Ceramatec, Inc. is funded through FY07 to develop, design and build a full-scale electrochemical system to remove sodium from low-level radioactive waste. Under this concept, sodium super ionic conductor membranes (NASICON) will be used to selectively remove sodium from low-level and supplemental waste streams. This removal will allow for recycling of the caustic used to remove aluminum during sludge washing as a pretreatment step in the vitrification of radioactive waste. Thus, the life cycle cost and schedule for the tank waste treatment mission will be greatly reduced by minimizing the addition of sodium hydroxide which lowers the cost of low activity waste immobilization.

The project has is near completion of Phase I through III of a four-part project to develop and deploy the technology at the Department of Energy's Hanford site in Washington state. Phase I was the Proof-of-Concept of technology and lab scale testing with non-radioactive simulants. Phase II included scale-up of membranes for testing sub-scale membrane modules and design and engineering of a sub-scale system and test it at PNNL using radioactive waste and completed pre-conceptual design and preliminary cost estimates for full scale membrane modules. Phase III is to scale-up the membrane fabrication process; evaluate the sub-scale system; and team with PNNL to evaluate the technology and develop an implementation plan. The Team will develop a conceptual design for a full scale system. Complete an economic analysis of a skid mounted, full-scale system. The final phase is to implement the membrane technology at the Hanford Waste Treatment Plant.

2. SCOPE OF THE REVIEW

The scope of this review is to include the work performed by Ceramatec, Inc. for the caustic recovery from High Level Waste. The main focus of this review is to determine:

- The Technical Merit of the technology as it currently exists;
- Ascertain the Programmatic Applicability of the technology for applications within the DOE Complex in particular the Hanford-WTP.

3. TEAM MEMBERSHIP

The team will comprise expertise and extensive experience in design, engineering and management of chemical processing and radioactive waste management systems. The team will

include five or more independent experts whose credentials and experience align with the specific lines of inquiry (LOIs) and who collectively provide to the team sufficiently broad capability and flexibility to address the full range of issues that may emerge in this review. The experts will be independent of any corporate accountability or responsibility for managing the sodium recovery technology and will be free of any conflict-of-interest with respect to potential benefit from the selection of any specific technology. Attachment A is a matrix which lists of the candidates and illustrates the applicability of their education and experience to the LOIs for this review.

Each team member is responsible for conducting a thorough, professional and independent review, for supporting the identification and resolution of technical issues, for participating in the development of draft and final reports, of supporting resolution of comments and any points of disagreement. Collectively, the team is responsible to produce a high quality review report that is responsive to this charter, that includes unambiguous conclusions regarding the identified LOIs, and that presents clearly any dissenting viewpoints. All team members will sign the final report.

4. PERIOD OF PERFORMANCE

This review is expected to begin in early May 2007 and be completed by the end of June 2007 including a final report that documents the team's results and recommendations. The review shall include a combination of interviews with key project personnel, information gatherings sessions and independent document reviews. The two primary deliverables for this review team are:

- Briefing on Preliminary Results during week of June 4, 2007
- Final Report approved by June 30, 2007

5. LINES OF INQUIRY

The review team will conduct their review pursuant to the scope outline above. The review team will utilize a set of lines of inquiry (LOIs). Attachment B contains the LOIs to be used for this review.

ATTACHMENT 2. COMMITTEE QUALIFICATIONS

Team Lead: Dr. William R. Wilmarth, Savannah River National Laboratory

Dr. Wilmarth is currently a Group Leader of the Advance Characterization and Process Research Group of the Savannah National Laboratory. In this capacity, research into the treatment of high level waste resulting from nuclear processing is conducted. Dr. Wilmarth has made significant contributions in the physiochemical understanding of high level waste and has led in the development of several process flowsheets for the removal of strontium, cesium and the actinides. Dr. Wilmarth has served as technical lead for the deployment of ion exchange materials for removal of cesium from wastes stored at Savannah River and Hanford. Other endeavors included the examination of caustic side solvent extraction of cesium removal from Savannah River wastes. Additionally, Dr. Wilmarth and his co-workers developed a strontium and actinide removal flowsheet for use in the River Protection Program at the Hanford reservation. His research interest included actinide solvent extraction and ion exchange supporting the F-canyon and FB-Line plutonium processing mission. Dr. Wilmarth and others performed research into the pyrochemical processing of plutonium leading to a product acceptable for purification at Savannah River. Dr. Wilmarth has also served as the SRNL Regulatory manager. In this capacity, Dr. Wilmarth managed the implementation and oversight programs for safety analysis, chemical hygiene, environmental compliance, radiation protection and waste certification activities.

Team Members:

Sodium Recovery Technology: Dr. David T. Hobbs, Savannah River National Laboratory

David Hobbs is an Advisory Scientist at the Savannah River Technology Center (Aiken, SC). He obtained his B.S. in Chemistry from the University of North Carolina at Chapel Hill (1974) and Ph.D. in Inorganic Chemistry at Vanderbilt University (1979). Professional affiliations include the American Chemical Society, Electrochemical Society, Sigma Xi and Alpha Chi Sigma. David has been employed at the Savannah River Site since 1984.

Dr. Hobbs' research focuses on high-level nuclear waste chemistry including the areas of corrosion, criticality, energetic compounds, waste retrieval, and waste pretreatment. Dr Hobbs' also leads research into developing improved membranes and catalysts for the electrochemical production of hydrogen. Since 1993 he has lead research programs with budgets in excess of \$500K/year for the development of electrochemical processes to destroy nitrate, nitrites and organic compounds, remove radionuclides and RCRA metals, recover process chemicals (e.g., caustic) from liquid waste streams, develop improved inorganic-based ion exchange materials for the separation of strontium and actinides from alkaline waste solutions and understand the chemistry of aluminum under conditions that pertain to the storage, evaporation, retrieval and pretreatment of high-level nuclear wastes.

Electrochemistry: Dr. William Averill, Los Alamos National Laboratory

Dr. Averill is currently Team Leader, Process Development, Planning & Analysis which provides technical expertise and support for manufacturing operations at LANL. He is currently principal investigator for the Rare Earth Electrochemistry Project to develop a process for pit manufacturing using electrochemical forming of plutonium and uranium from non-aqueous electrolyte systems. Previously, Dr. Averill was Pyrochemical Operations Technical Support at the Rocky Flats Plant. He was in charge of providing support to the plutonium electrorefining operations at the Rocky Flats Plant and technical support for residue stabilization and disposal, RCRA compliance, TOSCA compliance. Prior to Rocky Flats, Dr. Averill was at Sandia National Laboratories and was a member of Technical Staff working on the development of electrochemical power sources—thermal & room-temperature, test instrumentation and control systems for Sandia-developed weapons systems. Dr. Averill has also taught at the Colorado School of Mines: Assistant Professor, Metallurgical Engineering Department.

Membranes and Corrosion: Dr. Elise B. Fox, Savannah River National Laboratory

Dr. Elise Fox received her BS in Chemistry from the College of Charleston in 2001. She then went on to study the properties of glass fibers and the purification of hydrogen feedstreams at the Pennsylvania State University. She received her MS (2004) and PhD (2006) in Materials with a minor in Energy and Geo-Environmental Engineering. Elise joined SRNL in 2006 as a Senior Engineer. Current research topics include: hydrogen isotope recovery using PEM electrolysis, irradiation effects on materials, elucidating hydrogen generation in nuclear waste, and electrochemical corrosion of waste storage materials. She currently has over 15 relevant publications, technical reports and conference proceedings.

WTP Implementation: Dr. Reid A. Peterson, Pacific Northwest National Laboratory

Dr. Peterson has nearly 20 years of successful experience with technology development projects of similar complexity, including the development of separation technologies. Over the past 11 years, he has worked specifically in the area of nuclear waste treatment. Over that time period, he has had experience both as an individual Principal Investigator and as a manager of technology development activities associated with nuclear waste treatment and in particular HLW. Dr. Peterson was a lead author for the development of the Waste Treatment Plant Research and Development Plan that provided the technical and performance baseline for the all of the research and development performed in support of the WTP. Subsequently, Dr. Peterson has supported the development of the Issue Response Plan for the WTP External Flowsheet Review Team issue M-12 associated with caustic leaching.

ATTACHMENT 3. LINES OF INQUIRY

Programmatic

- What is the level of confidence that the technology can be deployed successfully? Is this supported by available test data?
- What is the degree to which this technology offers advantages over the baseline in terms of life cycle, capital and operating costs?
- Is there adequate empirical scientific and engineering information to support a conclusion that the process is deployable? Have other technologies been examined?
- Is the mass balance of sodium in the WTP sufficiently understood to determine caustic recovery needs from both concentration and throughput?

Na Recovery Technology

- What lab tests have been completed to confirm proof-of-principle for the technology?
- What scale were these tests performed at and how does that scale relate to plant implementation?
- What are the controlling and optimum process parameters? How are they inter-related?
- How do the waste compositions compare to planned waste compositions? Have bounding conditions been tested? Have thermodynamic modeling been performed on the waste stream return to ILAW to ensure post precipitation does not occur?
- What are the chemical and slurry limitations of a feed spec to the recovery process?
- How does the counter-current design work?

Electrochemistry

- How effective are the electrode design and electrode material of construction for this application?

- Are all possible electrochemical reactions of the waste matrices understood?
- Are the electrochemical by-products safely handled in the design (e.g., H₂, organics, etc.)?
- Are the materials of construction of the electrochemical cell stable to the chemical and radiolytic exposures?
- What are the power requirements for each cell module? Is the process continuous or batch?
- How sensitive is the applied potential to sodium recovery efficiency?
- How does one control the rate and amount of caustic recovered to avoid unwanted precipitation?
- Will pitting occur on electrodes leading to failure?
- What is anticipated lifetime of production cells and what is the basis?

Membrane and Corrosion Technology

- How does the membrane allow Na transport? What is the chemical composition?
- What are the ceramic properties of the membrane relative to chemical, thermal and radiolytic stability?
- What are the mechanisms of membrane fouling and have they been examined in testing to date? What solids loading can they take?
- What are the material properties of the ceramic membrane with respect to field application, e.g. tensile strength, rigidity, compressibility, etc.?
- What is the main limitation on the extended use of the membrane, e.g. membrane fouling, physical degradation, etc.? Has this been validated with testing?
- How has membrane production been examined in terms of scale of production, membrane size and costs of production? How does sodium ion selectivity perform at large production material?
- Are any new corrosion regimes introduced by the caustic recovery process?

WTP Applicability and Implementation

- To what extent has Ceramatec interacted with the DOE contractor to develop a conceptual design?
- Is the operation inherently safe due to production of flammable gases? Has a conceptual safety basis strategy been developed?
- What is the conceptual design of the full-scale process? Have operational, maintenance and ALARA considerations been integrated into the design? What are the maintenance strategies and disposal pathways?
- Can this process be added to the WTP flowsheet without perturbing other WTP systems or components?
- Has post-precipitation of aluminum-containing phases in vessels and pipelines been examined sufficiently?
- What process upsets could impact overall WTP HLW and ILW throughput?