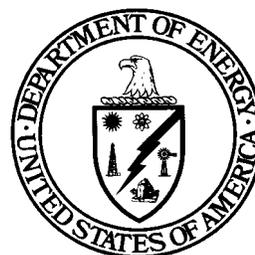


# **INNOVATIVE TECHNOLOGY**

Summary Report DOE/EM-0494

## **Caustic Recycle**

Tanks Focus Area and  
Efficient Separations and Processing  
Crosscutting Program



*Prepared for*  
U.S. Department of Energy  
Office of Environmental Management  
Office of Science and Technology

September 1999



# Caustic Recycle

OST/TMS ID 885

Tanks Focus Area and  
Efficient Separations and Processing  
Crosscutting Program

*Demonstrated at*  
Savannah River Site  
Aiken, South Carolina  
Pacific Northwest National Laboratory  
Richland, Washington



## ***Purpose of this document***

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine whether a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at <http://ost.em.doe.gov> under "Publications."

## TABLE OF CONTENTS

1. SUMMARY	page 1
2. TECHNOLOGY DESCRIPTION	page 4
3. PERFORMANCE	page 7
4. TECHNOLOGY APPLICABILITY AND ALTERNATIVES	page 10
5. COST	page 12
6. REGULATORY AND POLICY ISSUES	page 16
7. LESSONS LEARNED	page 18

### APPENDICES

A. REFERENCES	page 21
B. COST ANALYSIS DETAILS	page 23
C. ACRONYMS AND ABBREVIATIONS	page 33

# SECTION 1 SUMMARY

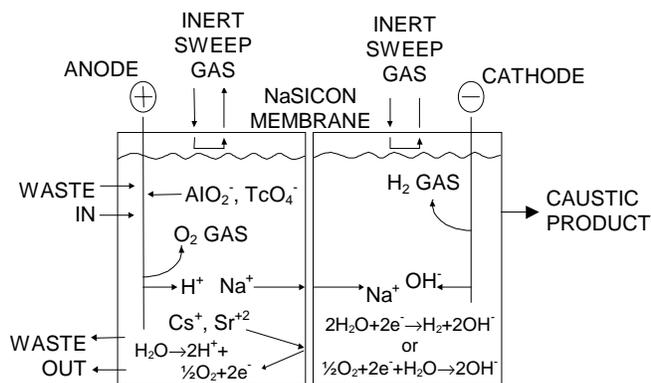
## Technology Summary

### Problem

High-level waste (HLW) tanks at the Hanford Site and the Savannah River Site (SRS) contain significant amounts of sodium nitrate, nitrite, and hydroxide salts. Sodium was added to the waste in the form of sodium hydroxide to change it from acidic, which would cause problems with the carbon-steel tanks, to basic, which would not. Pretreatment processes, such as enhanced sludge washing with sodium hydroxide, will introduce additional quantities of sodium to the waste stream. Sodium increases the volume of waste to be immobilized because the sodium concentration in HLW glass must be limited. One of the tank remediation challenges is how to handle this chemical. The Tanks Focus Area (TFA) and the Efficient Separations and Processing Crosscut Program (ESP-CP) demonstrated caustic recycle technology to recover and recycle the sodium hydroxide from the waste using an electrochemical-based process.

### How It Works

Highly selective membranes are capable of blocking the passage of unwanted ions while allowing others to pass through. Organic Nafion<sup>®</sup> Type 350 membrane and the ceramic Type NAS membranes made of **(Na) Super Ion Conductors (NaSICON)** allow the diffusion of sodium ions ( $\text{Na}^+$ ) while blocking other positively charged ions. With a NaSICON membrane in an electrolytic cell, sodium can be separated from other metals and recovered as a caustic product, as shown in Figure 1. Other ions, such as cesium ( $\text{Cs}^+$ ), remain in the waste stream.



**Figure 1. Schematic of an electrochemical process using the NaSICON membrane.**

Source: Kurath et al. 1997a.

### Potential Markets

Caustic recycling technology is applicable to the following sites:

- Hanford Site HLW tanks, with an estimated 68,000 metric tons (MT) of soluble sodium and an additional 11,000 MT from proposed sludge washing pretreatment
- SRS, with an estimated 48,000 MT of sodium from the decontaminated low-level waste (LLW) feed stream
- Tank wastes at the Idaho National Engineering and Environmental Laboratory (INEEL), containing about 165 MT of sodium

### Advantages over the Baseline

The baseline technology is defined as tank waste remediation without the use of caustic recycle technology. The advantages of caustic recycle technology over the baseline scenario are

- significant cost savings from the use of recycled caustic,
- significant volume reduction of LLW to be vitrified, and
- improved effectiveness of waste processing due to the removal of sodium salts from the waste stream.

## Demonstration Summary

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Pilot- and bench-scale demonstrations of caustic recycle technology were performed at three locations: Pacific Northwest National Laboratory (PNNL) in Richland, Washington; Ceramatec in Salt Lake City, Utah; and SRS in Aiken, South Carolina. These demonstrations were conducted during fiscal year 1995 (FY95) through FY98. They were sponsored by the U.S. Department of Energy (DOE) Office of Science and Technology (OST) ESP-CP and TFA.

Ceramatec conducted extensive testing of all ceramic membranes developed. These tests include longevity testing, conductivity testing, fracture strength, and corrosion testing. Membranes tested included dysprosium- (Dy-) NaSICON, neodymium- (Nd-) NaSICON, NaSICON (NAS) -D, NAS-E, NAS-G, and NAS-H. A single membrane disk was operated for over 1,000 hours (h) with various anolyte solutions.

At PNNL, bench-scale demonstrations were conducted using waste simulants from five tanks using two different electrochemical cells as follows:

### 1996

- A set of eight Dy-NaSICON membranes was tested for a total of 500 h.
- A set of four Nd-NaSICON disks was operated for a total of 650 h with various waste simulants.

### 1997

- A set of eight Nd-NaSICON disks was operated for a total of 1300 h with various waste simulants.

### 1998

- An organic-based Nafion Type 350 membrane was operated with two radioactive tank waste samples.
- A set of eight NAS-G disks was operated with two radioactive tank waste samples producing reasonably clean caustic.
- In preparation for radioactive testing at SRS, a bench-scale unit using the NAS-D membrane material was operated for more than 350 h.

In FY96 and FY97, five bench-scale tests with radioactive waste from Tank 50H were completed at the Savannah River Technology Center (SRTC). Each of these tests was 100 h.

- Three tests used an organic membrane, Nafion Type 350.
- Two tests used the NAS-D membrane.
- In two of the tests, the radioactive waste was first treated to electrolytically destroy the nitrate and nitrite, resulting in a high-hydroxide waste feed solution.

Four pilot-scale tests were conducted at SRTC using simulated SRS waste. Simulant runs, each 100 h long, were completed with the following membranes.

- The first pilot-scale test used a Nafion membrane and was successfully completed in May 1997.
- The second pilot-scale test was completed the week ending July 11, 1997. This test used a simulated waste solution high in hydroxide and low in nitrate and nitrite, which simulated decontaminated salt solution after electrolytic destruction of nitrate and nitrite. A Nafion Type 350 membrane was used.
- The third pilot-scale test was completed on July 23, 1997, using simulated waste with average flowsheet concentrations. A Ceramatec membrane was used.
- The fourth pilot-scale test began on July 25, 1997. This test used the Ceramatec membrane and a simulated waste high in hydroxide and low in nitrate and nitrite.

## **Key Results**

The key observations from the pilot- and bench-scale demonstrations are as follows:

- Pilot-scale testing demonstrated the feasibility of process operation.
- Bench-scale testing demonstrated that ceramic membranes could effectively block the transport of cesium, and gamma counting of the catholyte samples indicate that no <sup>137</sup>Cs was present.
- Membrane fouling was not observed in either bench- or pilot-scale demonstrations.

## **Parties Involved in the Demonstration**

- PNNL, Richland, Washington
- SRTC, Westinghouse Savannah River Company, Aiken, South Carolina
- Ceramatec, Salt Lake City, Utah
- E. I. duPont de Nemours & Company, Inc., Wilmington, Delaware

## **Commercial Availability and Readiness**

The organic-based Nafion membrane is available from E. I. duPont de Nemours & Company, Inc. The ceramic NAS-D membranes are not commercially available, but are being developed by Ceramatec, Inc. Additional developmental work on ceramic membranes may be necessary with new compositions and the addition of dopants. Ceramic membranes can be incorporated into commercially available plate-and-frame cells. Further engineering development may be necessary with respect to scaffold design and O-rings.

## **Future Plans**

Bench-scale demonstrations of caustic recycle are completed. A pilot-scale unit is available for further testing at SRS.

## **Contacts**

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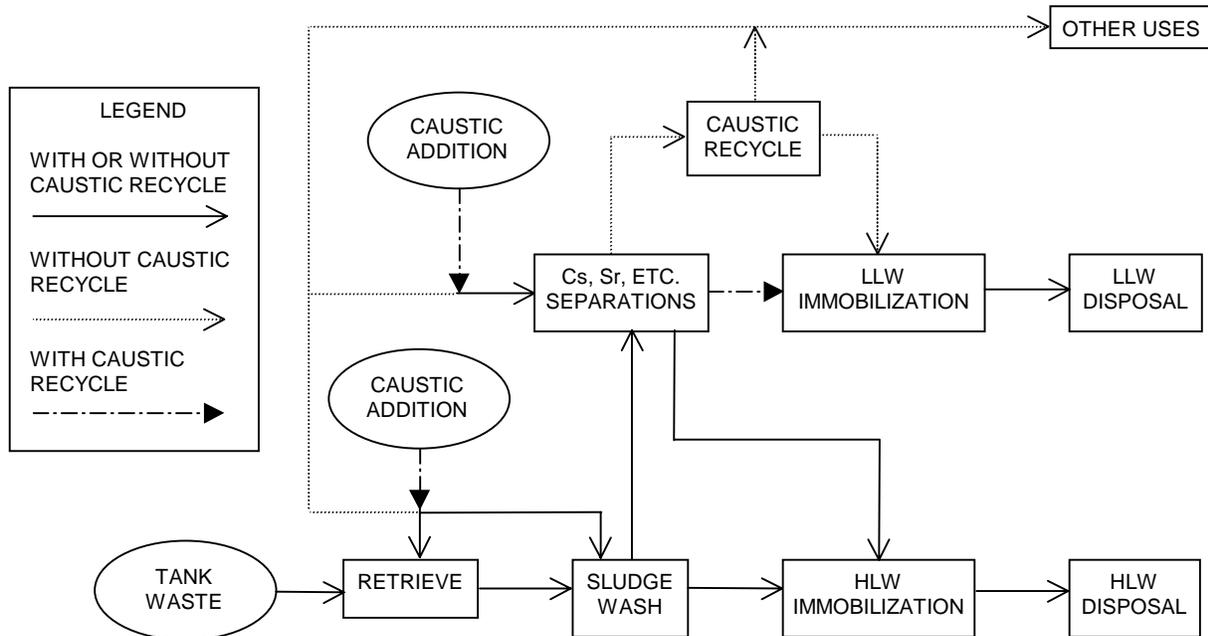
### **Other**

All published Innovative Technology Summary Reports are available on the OST Web site at <http://ost.em.doe.gov> under "Publications." The Technology Management System (TMS), also available through the OST Web site, provides information about OST programs, technologies, and problems. The OST/TMS ID for caustic recycle is 885.

## SECTION 2 TECHNOLOGY DESCRIPTION

### Overall Process Definition

Caustic recycle was demonstrated using commercially available, bench-scale electrochemical cells that incorporate highly selective ceramic membranes into a scaffold. The overall objective of the demonstrations was to determine the feasibility and performance of sodium removal from tank waste. The ceramic membranes evaluated allow the selective diffusion of sodium ions while blocking other positively charged ions. Figure 2 shows a flow diagram of tank waste remediation with the addition of the caustic recycle process.



**Figure 2. Tank remediation flow diagram with caustic recycle.**

### Description of Technology

Caustic recycle is based on an electrolytic process that selectively separates sodium ions from a waste stream. The sodium ions are recovered as a caustic product, which is recycled and used in a pretreatment process such as sludge washing or other purposes. The key feature of the process is an ion-selective membrane separating the electrodes in an electrolyzer. This membrane allows sodium ions to pass through but blocks most other cations, such as potassium (K), cesium (Cs), and strontium (Sr).

In this process, waste is added to the anode compartment, and an electrical potential is applied to the electrolytic cell. Sodium ions are driven through the membrane. The charge balance at the anode is maintained by generating hydrogen ions ( $H^+$ ) from the electrolysis of water. The charge balance at the cathode is maintained by generating hydroxide ( $OH^-$ ), either from the electrolysis of water or from oxygen and water. Sodium hydroxide (NaOH) builds up in the cathode compartment and is removed as a useful caustic product. Cations other than sodium ions remain in the anode compartment and are removed for further waste treatment, as shown in Figures 1 and 2.

## Major Elements of the Technology

Electrochemical salt splitting of radioactively contaminated sodium salt solutions uses the organic Nafion Type 350 membrane or the NAS membranes made of NaSICON.

- Nafion is organic polymer with a fluorocarbon backbone and small proportions of sulfonic or carboxylic ionic functional groups. As a result of electrostatic interactions, these ionic groups tend to aggregate to form tightly packed regions referred to as clusters. The clustered regions are the ionic exchange sites.
- NaSICON is a polycrystalline material with channels in the crystal structure for sodium ion conduction. This structure is key to the selective diffusion of sodium ions.

Several improved NaSICON compositions have been developed and include materials based on rare-earth ions (RE-NaSICON). Rare earth-based NaSICON membranes have higher conductivity and resistance to corrosion. The most effective membranes developed in this family (Dy-NaSICON and Nd-NaSICON) are based on the rare-earth elements dysprosium and neodymium. Additional improvements in membrane properties, especially in terms of ionic conductivity and durability, have been realized through the development of NaSICON with and without dopants. Dopants are deliberate impurities in the membrane material that tend to increase electrochemical stability against corrosion. Such compositions are proprietary and not yet commercially available.

## Specific DOE Application Demonstrated

Early investigations were directed at selecting and modifying membrane compositions compatible with the expected chemical and radioactive environment. FY96 work consisted of completing a preconceptual design of a ceramic membrane-based salt-splitting process for sodium separation and caustic recycle. Tests were conducted in FY96 and FY97 to demonstrate electrochemical salt splitting of radioactively contaminated sodium salt solutions.

## System Operation

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The following system requirements are based on a full-scale caustic recycle plant to meet the requirements of waste treatment at the Hanford Site. Depending on various case scenarios and using the specifications of the commercially available Nafion membrane, the membrane area required for the full-scale implementation of caustic recycle at Hanford is about 50–80 m<sup>2</sup>. Under these assumptions, system operational requirements for caustic recycle are as follows (DeMuth and Kurath 1998):

### Special Operational Parameters

- Due to the highly radioactive nature of the waste stream, caustic recycle is performed in a shielded facility.
- Using a sweep gas prevents potentially flammable gas mixtures in the electrochemical cells (oxygen at the cathode and hydrogen at the anode).
- Nafion membranes can be used when caustic recycle is deployed after cesium removal, and separation of sodium ions from cesium ions is not necessary.

### Estimated Annual Requirements of Materials, Energy, and Consumables

- Electric power 7,000 MWh
- Raw water 19,000 m<sup>3</sup>
- Demineralized water 400 m<sup>3</sup>
- Membrane replacement 67 m<sup>2</sup>

**Personnel Required**

- Plant operates for 12 years with a one-year start-up period.
- Five shifts will be required for complete coverage.
- Each shift requires five operating personnel.
- Total requirement is 25 operating personnel.

**Secondary Waste Stream**

- Spent membrane is generated as low-level solid waste that can be encapsulated.
- About 4 m<sup>3</sup> of secondary waste will be generated annually.

**Potential Operational Concerns and Risks**

Remote handling will be required because of the presence of cesium in the waste stream.

## SECTION 3 PERFORMANCE

### Demonstration Plan

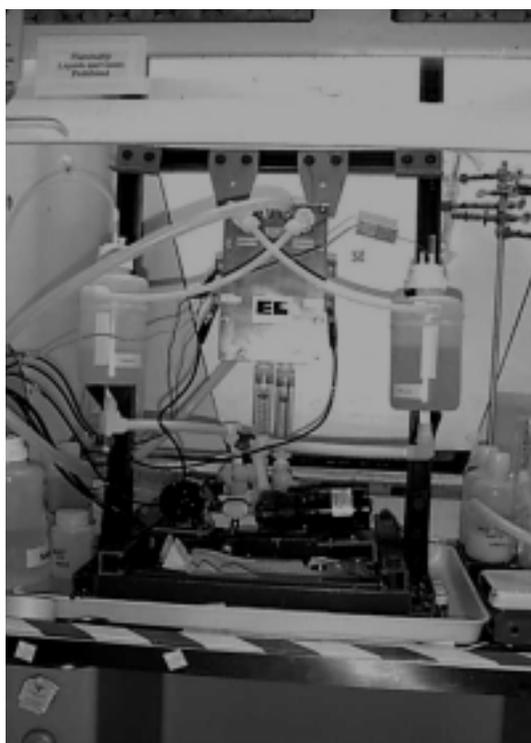
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During FY95 and FY96, ESP conducted scoping studies to evaluate the feasibility of electrochemical salt splitting for the recovery of caustic from SRS and Hanford wastes. During FY97 and FY98, TFA performed bench-scale testing of ceramic membranes at PNNL, Ceramatec, and SRS. Ceramic and organic-based membrane testing was conducted using actual waste from SRS tanks and five waste simulants:

- simple three-component simulant
- Hanford neutralized current acid waste simulant
- Hanford double-shell slurry feed simulant
- SRS simulant
- Hanford superblend simulant

At PNNL, several electrochemical cells were fabricated and installed in a fume hood laboratory. These bench-scale units were used to test a variety of tank waste simulants. The electrochemical cell was supplied by Electrosynthesis Co. and contained Pt/Ti anodes (lantern blades), Ni cathodes (lantern blades), and NaSICON or Nafion Type 350 membrane. Figure 3 shows a bench-scale test stand in a radioactive fume hood used for salt splitting for caustic recycle.

At SRTC, the bench-scale system consisted of an electrolyzer manufactured by ElectroCell AB, equipped with either a Ni or Pt/Ti cathode and a Pt/Ti anode. Membranes included Nafion Type 350 and NAS-D25 ceramic membranes. The ceramic membrane assembly consisted of eight circular membrane disks secured in a polyethylene scaffold with O-rings. The total available membrane area was 22 cm<sup>2</sup>. The pilot-scale system consisted of a scaffold used in an ICI FM-21 electrolyzer. The scaffold contained 58 NAS-D ceramic membranes, 5.1 cm in diameter and 1.4 mm thick. The total available membrane area was greater than 800 cm<sup>2</sup>.



**Figure 3. Salt-splitting test stand for caustic recycle in radioactive fume hood.**

### Major Objectives

The primary objectives of the testing were to

- evaluate membrane properties,
- develop and select optimum composition,
- test critical design features of the preconceptual design, and
- collect information on performance using nonradioactive simulants that would lead to testing with actual radioactive wastes.

### Major Elements of the Demonstration

The specific operations and performance criteria that were evaluated during the demonstration of the caustic recycle technology include the following:

- Sodium ion conductivity of NaSICON and Nafion membrane materials.
- Chemical stability of the electrochemical cell components, including the NaSICON and Nafion membranes. This criterion could be evaluated by conducting long-term testing (more than 1000 h) with complex waste simulants.
- Selectivity of the ceramic membranes for various waste components relative to sodium ions. Components of greatest interest include aluminum (Al), potassium, strontium ( $^{90}\text{Sr}$ ), technetium ( $^{99}\text{Tc}$ ), cesium ( $^{137}\text{Cs}$ ), and transuranic (TRU) components.
- Scaffolding design to preventing leakage between the anolyte and the catholyte solutions and design changes to the flat-plate concept, as required.
- Potential fouling of the ceramic membranes, both internal and external.
- Product purity as a function of operating conditions.
- Changes in the waste composition induced by the oxidizing environment that develops in the anode compartment.
- Processing parameters for various waste compositions as a function of operating conditions, (i.e., current, voltage, temperature, sodium concentration, and pH).

## Results

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Performance data for PNNL's bench-scale tests for various ceramic membranes are summarized in Table 1 (Kurath et al. 1997a). The performance data indicate that the NAS-D and NAS-D10 membranes have high sodium transport efficiencies ranged from 70–100% for NAS-D and 85–90% for NAS-D10. NAS-D10 displayed good selectivity towards Al, Cs, K, and Sr. NAS-D showed good selectivity towards Al and Cs. For the Nd- and Dy-NaSICON materials, the Na transport efficiency ranges 16–32%. However, corrosion was observed from ion exchange between ions in the waste and sodium in the membrane structure. Corrosion may limit durability of these materials and reduce the Na transport efficiency.

At SRTC, bench-scale radioactive tests were also performed to compare ceramic membranes with organic-based membranes (Hobbs 1998). The 100-h tests demonstrated that the NAS-D family of materials was nearly 100% selective for Na over Cs and that no detectable amounts of Cs were transported from the waste solution to the recycled caustic solution. Detailed performance data for these tests are not available and are not shown in Table 1. This commercially available membrane proved highly conductive; however, testing indicated that Cs was transported across the membrane into the caustic product. The tests were conducted at a current density of 400 mA/cm<sup>2</sup>. Sodium transport efficiencies ranged 70–80%; however, approximately 60% of  $^{137}\text{Cs}$  and 6% of  $^{90}\text{Sr}$  were transported into the caustic product. In contrast, the NAS-D ceramic membrane demonstrated the production of caustic with much lower levels of radioactivity ( $^{137}\text{Cs}$  activity was less than 51 disintegrations per minute per gram [dpm/g]). Detailed performance data for SRTC's pilot-scale scaffold are not available, because the tests were conducted using waste simulants.

Both organic and inorganic membranes can be used for caustic recycle operations. Ceramic membranes are resistant to radiation damage. Also, ceramic membranes are resistant to fouling due to their tendency to exclude di- and trivalent cations that can precipitate in organic membranes during salt splitting. Finally, ceramic membranes appear to have a higher selectivity for Na relative to other waste components such as Cs. When caustic recycle is deployed after Cs removal, separation of Na from Cs is not necessary.

**Table 1. Comparison of ceramic membrane performance in bench-scale tests**

Property	Membrane				
	Nd-NaSiCON <sup>a</sup>	Dy-NaSiCON <sup>a</sup>	NAS-D	NAS-D	NAS-D10
Test location	PNNL	PNNL	PNNL	Ceramatec	PNNL
Na transport efficiency <sup>b</sup> , %	16–29	24–32	85–100	70–100	85–90
Current density <sup>c</sup> , mA/cm <sup>2</sup>	59–178	43–68	15–25	25–35	20–23
Na conduction, kg NaOH/day/m <sup>2</sup> membrane area	5.5–12.8	2.1–4.5	3.06	4.5	3.8–3.9
Al selectivity <sup>d</sup>	68–4,871	5.3–13.6	1,073	Not available	180–infinity
Cs selectivity <sup>d</sup>	0.7–3	Infinity	Not available	Infinity	>19,700
K selectivity <sup>d</sup>	1.1–11	Not available	Not available	Not available	15
Sr selectivity <sup>d</sup>	Infinity	Not available	Not available	Not available	>4.5
Total duration of experiment, h	1,300	500	250	1,200	207
Comments	Observed ion exchange–induced corrosion	Observed ion exchange–induced corrosion	Incomplete due to scaffold design	Incomplete due to radial cracks	Incomplete due to circular cracks near O-rings

<sup>a</sup>Nd and Dy are the rare-earth metals neodymium and dysprosium, respectively.

<sup>b</sup>Na transport efficiency, or Na current efficiency, is a relative measure of the amount of Na (in moles) transferred through the membrane relative to the total amount of electrons transferred through the electrochemical cell.

<sup>c</sup>Current densities were achieved under current potential of 4.5–5 V.

<sup>d</sup>Selectivity of the membranes with respect to a nonsodium metal was determined using the following ratio:

$$\text{Selectivity} = (\text{Na transferred}/\text{initial Na concentration}) / (\text{metal transferred}/\text{initial metal concentration})$$

“Na transferred” and “metal transferred” in the formula are based on catholyte concentrations. Since the nonsodium metal concentrations are very low compared to those of Na, both the Na and the nonsodium metal ions transferred are normalized to their initial concentrations.

## SECTION 4 TECHNOLOGY APPLICABILITY AND ALTERNATIVES

### Competing Technologies

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The baseline technology is defined as remediation of tank waste without the addition of the caustic recycle process. In other words, the baseline assumes that sodium salts are not removed from the waste stream. Caustic recycle uses sodium-selective membranes to remove sodium from tank waste. A number of organic-based ion exchange membranes are available; however, ceramic membranes offer the following advantages:

- high resistance to radiation damage,
- superior resistance to fouling, and
- higher selectivity to sodium.

In particular, radiation effects on organic membranes would lead to failure and higher maintenance costs.

Table 2 shows the advantages and disadvantages of the caustic recycle using ceramic membrane technology over the baseline.

**Table 2. Advantages and disadvantages of caustic recycle ceramic membrane technology**

Advantages	Disadvantages
Significant cost savings may be realized at Hanford and SRS (see Section 5)	Technological risks associated with an innovative technology may persist until there is operating experience in the field
Disposal volumes of LLW are reduced through caustic recycle	Additional developmental work on ceramic membranes may be necessary with new compositions including dopants
Durability of final waste forms such as glass are enhanced by the removal of sodium from the waste stream	Further engineering development may be necessary with respect to scaffold design and O-rings
Waste treatment processes such as cesium ion exchange, sludge washing, and calcination are more efficient and less expensive when sodium concentrations are reduced in the waste stream	The application of the technology may be limited to the DOE complex at the Hanford and Savannah River Sites
Procurement of additional caustic for waste pretreatment is avoided	Additional evaluation is needed of changes in waste composition induced by the oxidizing environment in the anode compartment

### Technology Applicability

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Application of the caustic recycle technology resides mainly within the DOE complex. Potential deployments could occur at Hanford, SRS, and INEEL. Applications of the technology include the following:

- caustic recycling for sludge leaching, regenerating ion exchange resins, inhibiting corrosion in carbon steel tanks, and retrieving tank wastes;
- reducing the disposal volume of LLW; and
- removing sodium from acidic wastes to facilitate calcining

## Patents/Commercialization/Sponsor

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Ion-selective membranes have been developed for a variety of industrial electrochemical processes. Organic-based membranes, such as the commercially available perfluorinated Nafion 350 membrane, have been used extensively in the chloralkali industry. Ceramic membranes have potential application in the aluminum industry. Ion-selective, inorganic-based membranes have not been developed as extensively as organic-based membranes and are not as widely available.

Within DOE, OST funded the development of caustic recycle using a ceramic membrane salt-splitting process. Participating institutions include PNNL, SRTC, and Ceramatec, Inc. Both Hanford and SRS have participated in the program by supplying information on waste simulants, actual wastes for membrane testing, and site facilities for bench- and pilot-scale tests.

Ceramatec, Inc. developed the ceramic membranes used in the demonstrations and holds patents associated with the ceramic membrane compositions. Ceramatec, Inc. supported the project under a subcontract with PNNL. The Nafion organic-based membrane is available from E. I. duPont de Nemours & Company, Inc.

## SECTION 5 COST

### Methodology

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Los Alamos National Laboratory researchers developed the caustic recycle cost analysis in conjunction with PNNL (DeMuth and Kurath 1998). The costs are evaluated for both Hanford and SRS. Two cases are evaluated. Case 1 presumes that caustic recycle is used to recover the sodium required to meet all identified caustic needs for the entire site. Case 2 presumes that maximum amounts of sodium are extracted from LLW without precipitation of  $Al(OH)_3$ .

Capital and operating costs for the caustic recycle are based on estimates of sodium mass and waste volumes derived from published data. Electrosynthesis Co. supplied the electrochemical plant costs (DeMuth and Kurath 1998). For Hanford, the caustic recycle facility is assumed to be part of a waste treatment plant that is necessary for treatment and immobilization of the wastes. Capital and operating costs are developed as incremental costs to this facility. A stand-alone facility is used at SRS. The impact of LLW immobilization and disposal costs are also estimated. Retrieval and HLW vitrification costs are not considered because they are not affected by caustic recycle.

The cost analysis is for using caustic recycle technology to supplement the baseline. Figure 2 (see Section 2) shows a flow chart of tank remediation with and without the use of the caustic recycle technology.

### Cost Analysis

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This section presents capital and operating costs for the caustic recycle facility, scale-up considerations, and a cost benefit summary of potential cost savings for Hanford and SRS. The cost analysis is based on the parameters and assumptions discussed in DeMuth and Kurath 1998.

#### Capital, Operating, and Decontamination and Decommissioning (D&D) Costs

For Hanford, two cost savings estimates were made based on two different estimates of remediation costs: Tank Waste Remediation System Environmental Impact Statement (TWRS EIS) and Raytheon/BNFL trade studies. For Hanford, the Tank Waste Remediation System Operation and Utilization Plan (Kirkbride et al. 1997) was used for the assumptions. Revision 9 of the HLW System Plan (Davis 1998) was the basis for SRS estimates.

#### *Hanford Site*

Capital and operating costs for the implementation of caustic recycle at Hanford were developed using the following assumptions. Detailed assumptions are provided in Appendix B.

- The capital cost of the electrochemical cell is estimated based on the area of electrodes to be installed and the overall cost per unit area.
- The installed nonradioactive electrochemical plant capital cost is estimated by applying a factor of 5 to the cost of the electrochemical cell plant. A cost factor of 5 is then applied to estimate the cost of an installed radioactive plant of similar capacity.
- The plant will operate for 12 years, which is currently allocated for operations in Phase II of the River Protection Project (RPP) Privatization, with one year allowed for start-up.

Tables 3 and 4 present the capital and operating costs for the Hanford Site. The driving parameter is the design membrane area in the electrochemical plant needed to handle the capacity of sodium removal under cases 1 and 2. For Hanford tank remediation, it was determined that 55 and 83 m<sup>2</sup> of membrane

area would be required for cases 1 and 2, respectively (DeMuth and Kurath 1998). These membrane requirements were based on process operating parameters discussed in Appendix B.

**Table 3. Incremental capital costs for an electrochemical plant at the Hanford Site**

Case	Membrane area (m <sup>2</sup> )	Unit cost (\$/m <sup>2</sup> )	Cell cost (\$)	Installed plant cost (nonradioactive) (\$ million)	Installed plant cost (radioactive) (\$ million)
1	55	17,750	976,250	4.88	24.4
2	83	16,500	1,369,500	6.85	34.2

**Table 4. Incremental operating costs for caustic recycle at the Hanford Site**

Case	Annual operating costs (\$)	Total operating costs (\$ million)
1	1,691,000	21.6
2	2,129,000	30.1

D&D costs are based on capital costs. The ratio of D&D to capital costs was assumed to be 0.227, which is equal to that of the RPP LLW immobilization facility. Based on the installed radioactive plant costs in Table 3, the D&D costs are \$5.5 million for Case 1 and \$7.7 million for Case 2.

#### **Savannah River Site**

Capital and operating costs for the implementation of caustic recycle at the SRS were developed using the following cost elements and assumptions (detailed operating costs are provided in Appendix B):

- The estimated capital cost of the electrochemical cell is based on the area of electrodes to be installed and overall cost per unit area. The cost of an evaporator facility is \$35 million.
- The installed nonradioactive electrochemical plant capital cost is estimated by applying a factor of 5 to the cost of the electrochemical cell plant. A cost factor of 5 is then applied to estimate the cost of an installed radioactive plant of similar capacity.
- The plant will operate for 25 years, with one year allowed for start-up.

Tables 5 and 6 present the capital and operating costs for the SRS. The driving parameter is the design membrane area in the electrochemical plant needed to handle the capacity of sodium removal under cases 1 and 2. It was determined that 9.6 and 37.4 m<sup>2</sup> of membrane area would be required for cases 1 and 2, respectively (DeMuth and Kurath 1998). These membrane requirements were based on process operating parameters discussed in Appendix B.

**Table 5. Incremental capital costs for an electrochemical plant at the Savannah River Site**

Case	Membrane area (m <sup>2</sup> )	Unit cost (\$/m <sup>2</sup> )	Cell Cost (\$)	Installed plant cost (nonradioactive) (\$ million)	Installed plant cost (radioactive) (\$ million)	Evaporator facility cost (\$ million)	Caustic recycle and evaporation cost (\$ million)
1	9.6	19,950	191,500	0.96	4.79	35	39.8
2	37.4	18,250	682,550	3.41	17.1	35	52.1

**Table 6. Incremental operating costs for caustic recycle at the Savannah River Site**

<b>Case</b>	<b>Annual operating costs (\$)</b>	<b>Total operating costs (\$ million)</b>
1	5,793,000	144.8
2	7,862,000	196.4

D&D costs are based on capital costs. The ratio of D&D to capital costs was assumed to be 0.227, which is equal to that of the RPP LLW immobilization facility. Based on the installed radioactive plant costs in Table 5, the D&D costs are \$9.0 million for Case 1 and \$11.8 million for Case 2.

**Scale-Up Costs**

The cell costs were based on the use of ICI FM-21 cells containing Pt/Ti anodes, Ni cathodes, a Nafion 350 membrane, and ethylene-propylene-diene monomer (EPDM) gasketing flexible electrode connections to the busbars and all cell busbars. The Nafion Type 350 membrane was used in cost estimating because the ceramic membranes were not yet commercially available. The installed plant cost for a nonradioactive service plant was estimated by applying a factor of 5 to the cost of the electrochemical plant, which is typical of small salt-splitting applications. The installed plant cost includes any pretreatment, gas handling, caustic concentration, and the rectifier. The installed cost of a plant for radioactive service was determined by applying a factor of 5 to the installed cost of a nonradioactive service plant. While these cost estimates have a large degree of uncertainty, they provided estimates in line with preconceptual design estimates (Hobbs 1997).

**Cost Benefit**

Table 7 shows the cost savings for Hanford. More detailed calculations are shown in Appendix B. The caustic recycle process provides cost savings by reducing the volume of LLW that must be handled and the amount of caustic that must be procured for pretreatment. Immobilization costs from the Tank Waste Remediation System Environmental Impact Statement (TWRS EIS) and Raytheon/BNFL trade studies (Raytheon/BNFL 1995) were inflated from 1995 to 1998 dollars by using a discount rate of 3.5%/year. Estimated unit costs for LLW immobilization (1998\$) are \$1,609/MT of glass in the TWRS EIS and \$1,344/MT of glass using Raytheon/BNFL estimates. The estimated unit cost for LLW disposal is \$1,784/MT of glass. Assuming caustic sells for an average of \$300/MT, cost savings from avoiding procurement of caustic were estimated at about \$5.7 million for the 19,130 MT required. This saving is identical for both cases because the caustic requirement is the same.

**Table 7. Cost savings basis for Hanford**

<b>Item</b>	<b>Baseline (Phase II)</b>	<b>Case 1</b>	<b>Case 2</b>
LLW immobilization, MT of glass produced	396,000	319,000	279,000
Caustic recycle costs, \$ million	0	(51.5)	(72.0)
LLW immobilization and disposal cost savings—Total, 1998\$ million	0	240–261	363–394
Caustic cost savings, \$ million	0	5.7	5.7
Caustic recycle savings, \$ million	0	194–215	297–328

Table 8 shows that at SRS the caustic recycle process results in cost savings by reducing the volume of saltstone produced and reducing the amount of caustic that must be procured. The variable cost of producing saltstone has been estimated at \$4.88/gal (or \$1,290/m<sup>3</sup>). Assuming caustic sells for an average of \$300/MT, cost savings from avoiding procurement of caustic were estimated at about \$2 million for the 6,500 MT required. These savings are identical for both cases because the caustic requirement is the same.

**Table 8. Cost savings basis for Savannah River Site**

Item	Baseline	Case 1	Case 2
LLW immobilization and disposal volume, m <sup>3</sup>	769,000	478,000	356,000
Caustic recycle and evaporation costs, \$ million	0	(193.5)	(260.2)
LLW immobilization and disposal cost savings, 1998\$ million	0	376	534
Caustic cost savings, \$ million	0	2	2
Caustic recycle savings, \$ million	0	184	276

## Cost Conclusions

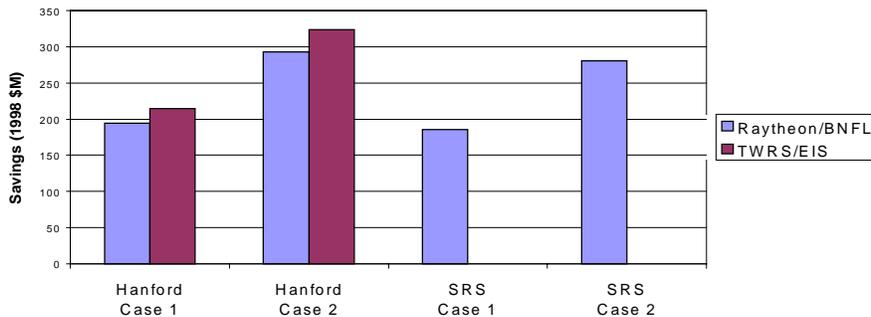
Projected cost savings that may result from implementing caustic recycle for cases 1 and 2 at Hanford and SRS are summarized in Table 9 and Figure 4. The cost analysis conducted in DeMuth and Kurath 1998 and presented in this report clearly shows that potential cost savings are significant when caustic recycle is introduced in the remediation process of tank wastes at Hanford and SRS. Potential cost savings at Hanford and SRS are as follows:

- Cost savings at Hanford are estimated at \$194–215 million for Case 1 and \$293–324 million for Case 2, depending on different estimates for the baseline scenario.
- Cost savings at Savannah River are estimated at \$186 million for Case 1 and \$281 million for Case 2.

**Table 9. Projected cost savings resulting from the use of caustic recycle at Hanford and Savannah River Site**

Site	Case	Costs <sup>a</sup> (\$ million)	Savings (\$ million)
Hanford, based on Raytheon/BNFL estimates	Baseline	1,244	0
	Case 1	1,050	<b>194</b>
	Case 2	951	<b>297</b>
Hanford, based on Tank Waste Remediation System EIS estimates	Baseline	1,349	0
	Case 1	1,134	<b>215</b>
	Case 2	1,025	<b>328</b>
Savannah River Site	Baseline	994	0
	Case 1	808	<b>184</b>
	Case 2	713	<b>276</b>

<sup>a</sup>Costs include pretreatment, immobilization, and disposal with (cases 1 and 2) or without (baseline) caustic recycle. Costs for cases 1 and 2 do not include posttreatment of caustic product to remove <sup>137</sup>Cs and other radionuclides associated with the use of organic-based membranes.



**Figure 4. Projected cost savings compared to two estimates of baseline costs at Hanford and Savannah River.**

## SECTION 6 REGULATORY AND POLICY ISSUES

### Regulatory Considerations

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All DOE HLW and TRU waste is also hazardous waste. The hazardous waste is subject to the Resource Conservation and Recovery Act (RCRA). The following issues should be addressed:

- The tank waste may be classified as U.S. Environmental Protection Agency Hazardous Waste Code D002 on the basis of its corrosivity if its pH is  $\leq 2$  or  $\geq 12.5$  (see Code of Federal Regulations 261.22 for the definition of D002).
- The caustic recycle product would not be classified as a hazardous waste because it is reused as a product in the tank waste treatment system.
- National Environmental Policy Act review may be required in conjunction with tank waste remediation.
- Radioactive materials license may be required.
- An air permit may be required if a sweep gas is utilized to remove hydrogen and oxygen produced at the electrochemical cell electrodes.

### Secondary Waste Streams Regulatory Considerations

The technology generates a caustic product. It is possible to reuse this caustic in the pretreatment process; however, on-site uses are not large enough to consume all of the caustic that may potentially be recovered. A significant number of commercial nonradioactive applications could use decontaminated caustic; however, there are regulatory and institutional barriers for unrestricted release of materials derived from the treatment of radioactive wastes. One of the most significant is that there is no *de minimus* level specified that would allow the designation of formerly radioactive materials as nonradioactive. Spent membrane will also be generated. This membrane will be encapsulated for permanent disposal.

### CERCLA Considerations

The technology may also be used to treat wastes regulated by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), which governs remediation of tanks removed from service at some sites. The remedial response must ensure that health and environment are protected at the site. CERCLA considerations are discussed below.

- Human Health and Environment—The technology does not pose further risk to human health or the environment.
- Compliance with applicable or relevant and appropriate requirements (ARARs) can be met.
- Long-Term Effectiveness—The technology supports permanent treatment and disposal of radioactive tank waste.
- Reduction of Volume—The technology reduces the volume of LLW for permanent disposal.
- Short-Term Effectiveness—Some hypothetical incidents associated with operation of a caustic recycle plant could cause inadvertent escape of contaminated material to the environment.

- **Implementability**—Membranes are incorporated into polyethylene scaffolds for implementation in commercially available plate-and-frame electrochemical cells. The technology is implementable, and adding more scaffolds can increase scale of operation.
- **Costs**—Costs to build and operate the caustic recycle are discussed in Section 5.
- **State Acceptance**—State acceptance should be favorable towards this technology; however, off-site use of the caustic product may require approval.
- **Community Acceptance**—Community acceptance should be favorable towards this technology; however, local use of the caustic product would require negotiation.

## **Safety, Risks, Benefits, and Community Reaction**

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### **Worker Safety Issues**

The following considerations shall be addressed to ensure worker safety when working with, producing, or handling caustic materials:

- Caustic products are harmful and require careful handling. They can cause severe burns to the skin and extreme damage to the eyes.
- Precautions for worker safety are necessary and include the use of goggles, gloves, and rubber boots in conjunction with Level B or C personnel protection, as required.
- During operation of the recycle process, shielding will be required for worker protection in radioactive environments.
- It is anticipated that the caustic recycle process will be remotely operated and monitored, thus minimizing the potential for worker contact with caustic products.

### **Community Safety**

The risk to the community is low. Although accidental releases of caustic are possible, secondary containment for piping and storage tanks will reduce the potential for accidental releases to the environment.

An off-gas system is required if sweep gas is used to remove hydrogen from the anode. The hydrogen may be destroyed by catalytic oxidation resulting in harmless gaseous effluents.

### **Benefits**

Caustic recycle clearly benefits the community and the environment from both reduced risk of exposure to tank waste and cost savings of the overall tank waste remediation. Caustic recycle can potentially reduce the volume of tank waste to be treated by removing a significant amount of sodium from the waste stream and reusing it as a caustic product in the pretreatment process.

## SECTION 7

# LESSONS LEARNED

### Design Issues

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The following outstanding design and development issues were identified and will require consideration before the technology can be deployed on a full-scale basis:

- Additional developmental work on ceramic membranes may be necessary with new ceramic compositions and dopants.
- Further engineering development may be necessary with respect to scaffold design and O-rings.
- The testing with actual radioactive waste was limited to bench-scale tests at SRS and Hanford. A pilot-scale demonstration with actual radioactive waste may be needed before a full-scale plant design can be completed.
- An off-gas system design for hydrogen removal and destruction may be needed if sweep gas is used to remove hydrogen from the anode.

### Implementation Considerations

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Implementation of caustic recycle technology should be made with full consideration of the following:

- Higher current density is achieved when thinner membranes are used. Newly developed membrane materials can maintain a current density up to 200 mA/cm<sup>2</sup>. Higher current densities allow an increase in sodium conductivity and thus would result in lower cost for building and operating a caustic recycle plant.
- Additional development work on ceramic membranes with dopants is needed.
- Additional evaluation of changes in waste composition induced by the oxidizing environment in the anode compartment should be completed to reveal the impacts on waste treatment systems design.
- A pilot-scale demonstration of the caustic recycle technology with actual radioactive waste may be required to fully demonstrate the technology and obtain the operating parameters for a full-scale engineering design.

### Technology Limitations and Needs for Future Development

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The recently developed ceramic membrane compositions with dopants have the potential to significantly reduce the cost of building and operating a caustic recycle plant. Initial results indicate that the new family of materials have high sodium-transport efficiencies (90–100%) and can maintain current densities of 200 mA/cm<sup>2</sup> at applied current potentials less than 10 V. The increase in sodium transport and conductivity would result in cost reduction of the treatment plant. The size of the electrochemical plant is a direct function of the required waste processing rate and the sodium ion conduction rate.

Adding dopants to the membrane composition has the potential to extend their lifetime to thousands of hours, thus reducing the replacement frequency and maintenance requirements. Performance of these new materials still needs to be demonstrated with respect to the following criteria:

- membrane lifetime,
- selectivity of sodium relative to key waste components such as Cs and Sr, and
- extended operation at high current densities with complex simulants and actual wastes.

## **Technology Selection Considerations**

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The main technology selection consideration is the need for further development of the ceramic membranes. This will involve all the steps required to develop, design, and test such membranes at the bench scale as well as at the pilot scale. Furthermore, a pilot- or full-scale demonstration of the caustic recycle technology with actual radioactive waste may be required to fully demonstrate the technology and obtain the operating parameters for scale-up engineering design. The commercial availability of the ceramic membranes combined with remediation schedule constraints may be a barrier to the near-term deployment of the caustic recycle technology.

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## APPENDIX B COST ANALYSIS DETAILS

### Hanford—Basis for Caustic Recycle Costs

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The electrochemical facility is assumed to be part of a waste treatment plant that is necessary for the treatment and immobilization of tank wastes. The caustic required for treatment of the tank waste (Case 1) could be recycled within the plant. Caustic in excess of that required for pretreatment is assumed to be trucked elsewhere for use or disposal (Case 2). For the cost estimates it is assumed that the excess is used in grout for backfilling tanks. The capital and operating costs for Hanford are developed as incremental costs to the waste treatment facility.

The number of electrochemical cells is determined by the rate at which sodium must be transported and the process operating characteristics as shown in Table B-1. The process operating parameters are based on pilot-scale testing with simulants, bench-scale testing with simulants, and actual wastes. The total operating efficiency (TOE) of 60% is based on the historical performance of Hanford plants.

**Table B-1. Hanford process operating parameters based on Nafion membranes**

Parameter	Value
Current density, mA/cm <sup>2</sup>	400
Voltage, V	8
Process operating time, years	12
Sodium transport efficiency, %	90
Total operating efficiency, %	60
Area available for ionic transport, %	100

The electrochemical cell and membrane area requirements shown in Table B-2 are based on sodium transport capacity and the process operating parameters given in Table B-1. The ICI FM-21 cell has a projected membrane area of 0.42 m<sup>2</sup> per electrode pair. Each cell stack can contain up to 60 electrode pairs for a total membrane area of 25 m<sup>2</sup> per cell stack for Nafion.

**Table B-2. Hanford electrochemical cell requirements for ICI FM-21 cells with Nafion membranes**

Case	Number of electrode pairs	Number of cell stacks	Membrane area (m <sup>2</sup> )	Unit cost (\$/m <sup>2</sup> )	Cell cost (\$)	Installed plant cost (nonradioactive) (\$ million)	Installed plant cost (radioactive) (\$ million)
1	131	3	55	17,750	976,250	4.88	24.4
2	197	4	82.9	16,500	1,367,850	6.84	34.2

The operating and maintenance costs are shown in Tables B-3 and B-4. The costs are based on the following assumptions:

- The operating plant lifetime is 12 years, which is currently allocated for operations in Phase II of the River Protection Project (RPP) Privatization, with one year allowed for start-up.
- A total operating efficiency of 60% was used based on historical performance of radioactive processing plants.
- Labor costs are based on five shifts, each with two operators and one supervisor. The fully burdened cost is \$60,000/year for an operator and \$75,000/year for a supervisor.

**Table B-3. Incremental operating costs for caustic recycle at the Hanford Site—Case 1**

Item	Unit	Unit cost (\$)	Quantity per year	O&M cost (\$/year)	# of yrs	Total cost (1998\$)	Basis/comments
Operating years including one-year start-up	Year				13		Baseline
Operating hours	Hour		5,256		12		Raytheon/BNFL trade study
Number of shifts			5				
Additional operating personnel	Each		5				Raytheon/BNFL trade study
Staff (base salary + 40% overhead)	Man-year	100,000	5	500,000	13	6,500,000	Typical salary + benefits
Working space	Ft <sup>2</sup> -year	17	100	1,700	13	22,100	Raytheon/BNFL trade study
Supplies and misc. expenses @ 10%	Man-year	7,143	5	35,714	13	464,295	Raytheon/BNFL trade study
Electric power	MWh	48	7,013	336,624	12	4,039,488	Unit cost from Waste Integration Team
Raw water	M <sup>3</sup>	0.25	18,750	4,688	13	60,944	Volume from trade study; unit cost from Waste Integration Team
Demineralized water	M <sup>3</sup>	9	420	3,780	13	49,140	Unit cost and volume from Raytheon/BNFL trade study
Membrane replacement	M <sup>2</sup>	800	66.7	53,360	13	693,680	Unit cost per Electrosynthesis Co. one-year lifetime assumed
<i>Maintenance for balance of process</i>							
Labor	Man-hour	50	2,500	125,000	13	1,625,000	Raytheon/BNFL trade study
Equipment @ 2.25% of capital facility/year	\$/year			610,150	13	7,931,950	Annual cost assumption, TWRS EIS, p. G11-20
Low-level solid waste	m <sup>3</sup>	5,000	4	20,000	13	260,000	Raytheon/BNFL trade study and PNNL disposal costs
<b>Totals</b>				<b>1,671,016</b>		<b>21,646,597</b>	

**Table B-4. Incremental operating costs for caustic recycle at the Hanford Site—Case 2**

Item	Unit	Unit cost (\$)	Quantity per year	O&M cost (\$/year)	# of yrs	Total cost (1998\$)	Basis/comments
Operating years including one-year start-up	year				13		Baseline
Operating hours	hour		5,256		12		Raytheon/BNFL trade study
Number of shifts			5				
Additional operating personnel	each		5				Raytheon/BNFL trade study
Staff (base salary + 40% overhead)	man-year	100,000	5	500,000	13	6,500,000	Typical salary + benefits
Working space	ft <sup>2</sup> -year	17	100	1,700	13	22,100	Raytheon/BNFL trade study
Supplies and misc. expenses @ 10%	man-year	7,143	5	35,715	13	464,295	Raytheon/BNFL trade study
Electric power	MWh	48	10,467	502,416	12	6,028,992	Unit cost from Waste Integration Team
Raw water	m <sup>3</sup>	0.25	18,750	4,688	13	60,944	Volume from trade study; unit cost from Waste Integration Team
Demineralized water	m <sup>3</sup>	9	420	3,780	13	49,140	Unit cost and volume from Raytheon/BNFL trade study
Membrane replacement	m <sup>2</sup>	800	99.6	79,680	13	1,035,840	Unit cost per Electrosynthesis Co. one-year lifetime assumed
<i>Maintenance for balance of process</i>							
Labor	man-hour	50	2,500	125,000	13	1,625,000	Raytheon/BNFL trade study
Equipment @ 2.25% of capital facility/year	\$/year			855,950	13	11,127,350	Annual cost assumption, TWRS EIS, p. G11-20
Low-level solid waste	m <sup>3</sup>	5,000	4	20,000	13	260,000	Raytheon/BNFL trade study and PNNL disposal costs
Transportation of excess caustic 50% by weight	m <sup>3</sup>	211	1,173	247,503	12	2,970,036	Transportation and packaging evaluation
<b>Totals</b>				<b>2,376,432</b>		<b>30,143,697</b>	

- Electric power is based on an operating voltage of 8 V and current efficiency of 90%. The unit cost of power is estimated at \$57/MWh.
- One lot of support utilities is included at an annual cost of \$60,000.
- Membranes will be replaced once a year at a cost of \$800/m<sup>2</sup>.
- The annual process maintenance is estimated at 5% of capital cost.
- The cost for low-level solid waste disposal is \$5,000/m<sup>3</sup>, based on disposal costs at a commercial site (Raytheon/BNFL 1995).
- The evaporator operating costs of \$1.50/gal were obtained from the preconceptual evaporator cost study.
- It is assumed for both cases that the caustic must be transported by truck to another location. It was further assumed that the caustic is concentrated to 50% by weight and transported in a 5,000-gal cargo tank at \$4,000/trip.

D&D costs are based on the ratio of D&D to capital costs. This ratio is assumed to be 0.227, which is equal to that of the RPP LLW immobilization facility. Based on the installed radioactive plant costs in Table B-2, the D&D costs are \$5.5 million for Case 1 and \$7.7 million for Case 2.

## **Hanford—Cost Savings of Caustic Recycle**

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The caustic recycle process allows users to save costs by

- reducing the volume of LLW that must be handled,
- reducing the amount of caustic that must be procured, and
- reducing the costs of vitrification of final waste.

The potential cost savings at Hanford for cases 1 and 2 have been estimated as shown in Tables B-5 and B-6. Estimated unit costs for LLW immobilization (1998\$) are \$1,609/MT of glass in the TWRS EIS and \$1,344/MT of glass using Raytheon/BNFL estimates. (Raytheon/BNFL 1995) The TWRS EIS and Raytheon/BNFL immobilization costs were inflated from 1995 to 1998 dollars by using a discount rate of 3.5% per year. Cost savings shown in Table B-5 are based on the TWRS EIS immobilization costs; those shown in Table B-6 are based on Raytheon/BNFL immobilization costs. The cost of handling and disposal of LLW packages after they are returned from the contractors is assumed to be \$3,800/m<sup>3</sup>, according to the Waste Integration Team (WIT). This translates to a cost of \$1,784/MT of glass waste.

The costs for LLW immobilization and disposal are dependent on the total amount of LLW produced. It was assumed that the LLW production rate would be constant but that the length of processing time would be reduced for cases 1 and 2. This assumption implied that LLW immobilization and disposal capital costs would not change. Assuming that caustic is selling at an average of \$300/MT, the cost saving from avoiding procurement of caustic is estimated at \$5.7 million for the 19,130 MT of NaOH (11,000 MT of Na) that is required. These savings are identical for both cases since the caustic requirement is constant.

**Table B-5. Cost savings basis for Hanford using RPP/TWRS EIS-EDP immobilization costs**

Item	Baseline (TWRS/ EIS Phase II)	Caustic recycle (Case 1)	Caustic recycle (Case 2)
LLW immobilization, MT glass	396,000	319,000	279,000
LLW immobilization, unit cost, 1998\$/MT glass	1,609	1,609	1,609
Subtotal—LLW immobilization, 1998\$ million	637	513	449
LLW disposal, unit cost, 1998\$/MT glass	1,784	1,784	1,784
Subtotal—LLW disposal, 1998\$ million	706	569	500
Caustic recycle capital, \$ million	0	24.4	34.2
Caustic recycle operating, \$ million	0	21.6	30.1
Caustic recycle D&D, \$ million	0	5.5	7.7
Subtotal—Caustic recycle, \$ million	0	51.5	72.0
Caustic cost, \$ million	5.7	0	0
Total cost, \$ million	1,349	1,134	1,021
<b>Caustic recycle savings, \$ million</b>		<b>215</b>	<b>328</b>

**Table B-6. Cost savings basis for Hanford using Raytheon/BNFL immobilization costs**

Item	Baseline (TWRS/ EIS Phase II)	Caustic recycle (Case 1)	Caustic recycle (Case 2)
LLW immobilization, MT glass	396,000	319,000	279,000
LLW immobilization, unit cost, 1998\$/MT glass	1,344	1,344	1,344
Subtotal—LLW immobilization, 1998\$ million	532	429	375
LLW disposal, unit cost, 1998\$/MT glass	1,784	1,784	1,784
Subtotal—LLW disposal, 1998\$ million	706	569	500
Caustic recycle capital, \$ million	0	24.4	34.2
Caustic recycle operating, \$ million	0	21.6	30.1
Caustic recycle D&D, \$ million	0	5.5	7.7
Subtotal—Caustic recycle, \$ million	0	51.5	72.0
Caustic cost, \$ million	5.7	0	0
Total cost, \$ million	1,244	1,050	947
<b>Caustic recycle savings, \$ million</b>		<b>194</b>	<b>297</b>

### Savannah River Site—Basis for Caustic Recycle Costs

The electrochemical facility for SRS is assumed to be a stand-alone facility combined with an evaporator for concentrating the saltstone feed. The evaporator consists of three skid-mounted evaporators, each processing 8.3 gpm of distillate (total capacity of 25 gpm) from a total feed flow rate of 72 gpm (24 gpm per skid). The evaporator building was assumed to be 60 ft wide by 140 ft long with a ceiling height of 30 ft, erected on a concrete slab. A total of four 35,000-gal underground tanks are included, two for feed to the evaporator and two for the concentrate. A single aboveground 35,000-gal tank is included for condensate storage. A rough order-of-magnitude cost estimate for this facility was \$35 million. This evaporation capability appears to be larger than required for the purposes of this study, in which a distillate rate of 4.9–8.2 gpm is sufficient with a total operating efficiency (TOE) of 60%.

The number of electrochemical cells is determined by the rate at which sodium must be transported, and the process operating characteristics are shown in Table B-7. The process operating parameters are based on pilot-scale testing with simulants, bench-scale testing with simulants, and actual wastes. The TOE of 60% is based on the historical performance of radioactive processing plants. The electrochemical cell and membrane area requirements shown in Table B-8 are based on sodium transport capacity, and the process operating parameters given in Table B-7. The ICI FM-21 cell has a membrane area of 0.42 m<sup>2</sup> per electrode pair. Each cell stack can contain up to 60 electrode pairs for a total membrane area of 25 m<sup>2</sup> per cell stack for Nafion. The fractional quantity of cells is determined by

dividing the number of electrode pairs by the maximum number of electrode pairs per cell stack, which is 60. The number of cell stacks is determined by rounding this number up to the next greater integer.

**Table B-7. SRS salt-splitting process operating parameters**

Parameter	Value
Current density, mA/cm <sup>2</sup>	400
Voltage, V	8
Process operating time, years	25
Sodium transport efficiency, %	90
Total operating efficiency, %	60
Area available for ionic transport, %	100

**Table B-8. SRS electrochemical cell requirements for ICI FM-21 cells with Nafion membranes**

Item	Case 1	Case 2
Number of electrode pairs	23	80
Number of cell stacks (fractional quantity)	1 (0.4)	2 (1.3)
Membrane area, m <sup>2</sup>	9.6	37.4
Unit cost, \$/m <sup>2</sup>	19,950	18,250
Cell cost, \$	191,520	682,550
Installed plant cost (nonradioactive), \$ million	0.96	3.4
Installed plant cost (radioactive), \$ million	4.8	17.1
Evaporator facility cost, \$ million	35	35
Caustic recycle and evaporation cost, \$ million	39.8	52.1

Operating and maintenance costs are shown in Tables B-9 and B-10. Assumptions used to estimate operating costs are listed below.

- A plant will operate for 25 years with one year for start-up.
- A total operating efficiency of 60% was used based on historical performance of radioactive processing plants.
- Labor costs are based on five shifts, each with two operators and one supervisor. The fully burdened cost is \$60,000/year for an operator and \$75,000/year for a supervisor.
- Electric power is based on an operating voltage of 8 V and current efficiency of 90%. The unit cost of power is estimated at \$57/MWh.
- One lot of support utilities is included at an annual cost of \$60,000.
- Membranes will be replaced once a year at a cost of \$800/m<sup>2</sup>.
- The annual process maintenance is estimated at 5% of capital cost.
- The cost for low-level solid waste disposal is \$5,000/m<sup>3</sup>, based on disposal costs at a commercial site (Raytheon/BNFL 1995).
- The evaporator operating costs of \$1.50/gal were obtained from the preconceptual evaporator cost study.

- It is assumed for both cases that the caustic must be transported by truck to another location. It was further assumed that the caustic is concentrated to 50% by weight and transported in a 5,000-gal cargo tank at \$4,000/trip.

D&D costs are based on the ratio of D&D to capital costs. This ratio is assumed to be 0.227, which is equal to that of the RPP LLW immobilization facility. Based on the installed radioactive plant costs in Table B-2, the D&D costs are \$8.9 million for Case 1 and \$11.7 million for Case 2.

**Table B-9. Incremental operating costs for caustic recycle at the Savannah River Site—Case 1**

Item	Unit	Unit cost (\$)	Quantity per year	O&M cost (\$/year)	# of yrs	Total cost (1998\$)	Basis/comments
Operating years including one-year start-up	year				25		High-Level Waste System Plan, Rev. 8
Operating hours	hour		5,256		25		60% TOE. Note that 70% is assumed in WSRC-OS-97-00008.
Number of shifts			5				Four shifts were assumed in WSRC-OS-97-00008. Increased to five to ensure complete coverage due to vacations and other leave.
Additional personnel—operators	each		10				2/shift assumed in WSRC-OS-97-00008
Additional personnel—supervisors	each		5				1/shift assumed in WSRC-OS-97-00008
Direct labor (fully burdened)—operators	man-year	60,000	10	600,000	25	15,000,000	WSRC-OS-97-00008
Direct labor (fully burdened)—supervisors	man-year	75,000	5	375,000	25	9,375,000	WSRC-OS-97-00008
Electric power	MWh	57	1,210	68,970	25	1,724,250	Unit cost from WSRC-OS-97-00008
Support utilities—HVAC, lighting, potable water, sewer	1 lot	60,000	1	60,000	25	1,500,000	Quantity and unit cost from WSRC-OS-97-00008. May overestimate cost as the nitrate destruction plant in WSRC-OS-97-00008 is much larger (10 electrochemical cells vs one).
Membrane replacement	m <sup>2</sup>	800	11.5	9,200	25	230,000	Unit cost per Electrosynthesis Co.; one-year lifetime assumed; labor is included in process maintenance on next line.
Process maintenance @ 5% of capital facility/year	\$/year	1,989,400	1	1,989,400	25	49,735,000	5% unit cost from WSRC-OS-97-00008
Low-level solid waste	m <sup>3</sup>	5,000	4	20,000	25	500,000	Raytheon/BNFL trade study and PNNL disposal costs
Evaporator operating costs	gal	1.50	1.74E+6	2,610,000	25	65,250,000	Saltstone Feed Evaporator Study; volume is distillate volume not feed.
Transportation of caustic	m <sup>3</sup>	211	297	62,667	24	1,504,008	Assume all caustic is trucked as 50 wt % solution as there is no caustic return line.
<b>Totals</b>				<b>5,795,237</b>		<b>144,818,258</b>	

**Table B-10. Incremental operating costs for caustic recycle at the Savannah River Site—Case 2**

Item	Unit	Unit cost (\$)	Quantity per year	O&M cost (\$/year)	# of yrs	Total cost (1998\$)	Basis/comments
Operating years including one-year start-up	year				25		High-Level Waste System Plan, Rev. 8
Operating hours	hour		5,256		25		60% TOE. Note that 70% is assumed in WSRC-OS-97-00008.
Number of shifts			5				Four shifts were assumed in WSRC-OS-97-00008. Increased to five to ensure complete coverage due to vacations and other leave
Additional personnel—operators	each		10				2/shift assumed in WSRC-OS-97-00008
Additional personnel—supervisors	each		5				1/shift assumed in WSRC-OS-97-00008
Direct labor (fully burdened)—operators	man-year	60,000	10	600,000	25	15,000,000	WSRC-OS-97-00008
Direct labor (fully burdened)—supervisors	man-year	75,000	5	375,000	25	9,375,000	WSRC-OS-97-00008
Electric power	MWh	57	6,285	358,245	25	8,956,125	Unit cost from WSRC-OS-97-00008
Support utilities—HVAC, lighting, potable water, sewer	1 lot	60,000	51	60,000	25	1,500,000	Quantity and unit cost from WSRC-OS-97-00008. Probably overestimate cost as the nitrate destruction plant in WSRC-OS-97-00008 is much larger (10 electrochemical cells vs 1).
Membrane replacement	m <sup>2</sup>	800	44.8	35,840	25	896,000	Unit cost per Electrosynthesis Co.; one-year lifetime assumed.
Process maintenance @ 5% of capital facility/year	\$/year	2,603,200	1	2,603,200	25	65,080,000	5% unit cost from WSRC-OS-97-00008
Low-level solid waste	m <sup>3</sup>	5,000	4	20,000	25	500,000	Raytheon/BNFL trade study and PNNL disposal costs
Evaporator operating costs	gal	1.50	2.47E+6	3,705,000	25	92,625,000	Saltstone Feed Evaporator Study; volume is distillate volume not feed.
Transportation of caustic	m <sup>3</sup>	211	494	104,234	24	2,501,616	Assume all caustic is trucked as 50 wt % solution as there is no caustic return line.
<b>Totals</b>				<b>7,861,519</b>		<b>196,433,741</b>	

## Savannah River Site—Cost Savings of Caustic Recycle

The caustic recycle process provides cost savings by:

- reducing the volume of saltstone produced and
- reducing the amount of caustic that must be procured.

The variable cost of producing saltstone has been estimated at \$4.88/gal (\$1.29/L). The potential cost savings for Case 1 is therefore estimated to be \$186 million, as shown in Table B-11. The potential cost savings for Case 2 is similarly estimated to be \$281 million. The costs for LLW immobilization and disposal shown in Table B-11 are only those dependent on the total amount of LLW produced. It was assumed that the LLW production rate would be constant but that the length of processing time would be reduced for cases 1 and 2. This assumption implied the LLW immobilization and disposal capital costs would not change. It was also assumed that caustic sells for an average of \$300/MT. Therefore, cost savings due to avoiding procurement of caustic are estimated at \$2.0 million for the 6,500 MT of NaOH that is required. These savings are identical for both cases since the caustic requirement is constant.

**Table B-11. Cost savings basis for Savannah River Site**

Item	Baseline	Case 1	Case 2
LLW immobilization and disposal volume, m <sup>3</sup>	769,000	478,000	356,000
LLW immobilization and disposal cost, 1998\$ million	992	616	458
Caustic recycle and evaporation capital, \$ million	N/A	39.8	52.1
Caustic recycle and evaporation operating, \$ million	N/A	144.8	196.4
Caustic recycle and evaporation D&D, \$ million	N/A	8.9	11.7
Subtotal—Caustic recycle and evaporation, \$ million	N/A	193.5	260.2
Caustic cost, \$ million	2	0	0
Total cost, \$ million	994	810	718
<b>Caustic recycle savings, \$ million</b>	<b>0</b>	<b>184</b>	<b>276</b>

For the baseline, a sodium concentration of 4.6 mole/L is used, which corresponds to the estimated retrieved waste volume. This assumption implies that supernatant treatment for radionuclide removal does not substantially change the composition or the volume. For cases 1 and 2, evaporation of the saltstone feed is necessary to realize a reduction in the volume of saltstone. A sodium concentration of 6.8 mole/L is used as the end point for evaporation, which is the approximate point at which salts start to precipitate. The saltstone volume is based on 1.77 times the saltstone feed volume and accounts for the addition of the saltstone forming materials. Table B-11 shows potential costs savings that can be realized through the addition of caustic recycle technology in the tank waste remediation process.

## APPENDIX C

### ACRONYMS AND ABBREVIATIONS

Al	Aluminum
BNFL	British Nuclear Fuels Limited
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
Cs	Cesium
D&D	decontamination and decommissioning
DOE	Department of Energy
dpm/g	disintegrations per minute per gram
Dy-NaSICON	dysprosium sodium super ion conductor
EIS	environmental impact statement
ESP	Efficient Separations and Processing Crosscutting Program
FY	fiscal year
H <sup>+</sup>	hydrogen ion
HLW	high-level waste
INEEL	Idaho National Engineering and Environmental Laboratory
K	Potassium
LLW	low-level waste
mA/cm <sup>2</sup>	milliamperes per square centimeter
MT	metric ton
Na	Sodium
NaOH	sodium hydroxide
NAS	NaSICON
NaSICON	sodium super ion conductor
Nd-NASICON	neodymium sodium super ion conductor
Ni	Nickel
OH <sup>-</sup>	hydroxide ion
OST	Office of Science and Technology
PNNL	Pacific Northwest National Laboratory
Pt/Ti	platinized titanium
RCRA	Resource Conservation and Recovery Act
RE	rare earth
RPP	River Protection Project
Sr	Strontium
SRS	Savannah River Site
SRTC	Savannah River Technology Center
Tc	Technetium
TFA	Tanks Focus Area
TOE	total operating efficiency
TRU	Transuranic
TWRS	Tank Waste Remediation System
WIT	Waste Integration Team