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Economic Feasibility of Electrochemical Caustic Recycling at the Hanford Site

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March 2009



Pacific Northwest
NATIONAL LABORATORY

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Richland, Washington 99352

Summary

This report contains a review of potential cost benefits of NaSICON Ceramic membranes for the separation of sodium from Hanford tank waste. The primary application is for caustic recycle to the Waste Treatment and Immobilization Plant (WTP) pretreatment leaching operation. The report includes a description of the waste, the benefits and costs for a caustic-recycle facility, and Monte Carlo results obtained from a model of these costs and benefits. The use of existing cost information has been limited to publicly available sources. This study is intended to be an initial evaluation of the economic feasibility of a caustic recycle facility based on NaSICON technology.

The current pretreatment flowsheet indicates that approximately 6,500 metric tons (MT) of Na will be added to the tank waste, primarily for removing Al from the high-level waste (HLW) sludge (Kirkbride et al. 2007). An assessment (Alexander et al. 2004) of the pretreatment flowsheet, equilibrium chemistry, and laboratory results indicates that the quantity of Na required for sludge leaching will increase by 6,000 to 12,000 MT in order to dissolve sufficient Al from the tank-waste sludge material to maintain the number of HLW canisters produced at 9,400 canisters as defined in the Office of River Protection (ORP) System Plan (Certa 2003). This additional Na will significantly increase the volume of LAW glass and extend the processing time of the Waste Treatment and Immobilization Plant (WTP). Future estimates on sodium requirements for caustic leaching are expected to significantly exceed the 12,000-MT value and approach 40,000-MT of total sodium addition for leaching (Gilbert, 2007).

The cost benefit for caustic recycling is assumed to consist of four major contributions: 1) the cost savings realized by not producing additional immobilized low-activity waste (ILAW) glass, 2) caustic recycle capital investment, 3) caustic recycle operating and maintenance costs, and 4) research and technology costs needed to deploy the technology. In estimating costs for each of these components, several parameters are used as inputs. Due to uncertainty in assuming a singular value for each of these parameters, a range of possible values is assumed. A Monte Carlo simulation is then performed where the range of these parameters is exercised, and the resulting range of cost benefits is determined.

The major conclusions from the Monte Carlo model results discussed in this report are summarized below:

- A feasible region for minimal plant economics (e.g; 10% total return on investment) corresponds to approximately 10,000 MT sodium recycled. Total return on investments in the range of 30-60% can be achieved when 50,000 MT of sodium are recycled.
- Literature data for the growth rate of Gibbsite particles indicates that particles forming in the 1- to 10-micron range over the average vessel residence time of 1 week corresponds to a saturation ratio less than eight. The operation of the downstream WTP processes under these conditions and with particles of this size must be demonstrated in a separate experimental program.
- Recycling 10,000 MT of sodium results in a cost savings in ILAW glass of \$0.7B to \$1.0B. If 30,000 MT of sodium is recycled, \$2.5B to \$3.1B would likely be realized.
- Recycling 10,000 MT of sodium results in an estimated range of total capital cost for the caustic-recycle facility to be \$175M to \$325M. If 30,000 MT of sodium is recycled, \$200M to \$350M would likely be realized.

- Recycling 10,000 MT of sodium results in a total production cost for the caustic-recycle facility to be in the range of \$13M/yr to \$21M/yr. If 30,000 MT of sodium is recycled, \$21M/yr to \$30M/yr would likely be realized.
- If 10,000 MT of sodium is recycled, a specific production cost is estimated to be in the range of \$25/kg to \$45/kg. If 30,000 MT of sodium is recycled, \$15/kg to \$22/kg would likely be realized.
- The specific sales cost is invariant with the amount of sodium recycled. A specific sales cost is estimated to be in the range of \$84/kg to \$104/kg. The specific sales cost is a factor of 3.8 to 6.9 greater than the expected specific production cost range.
- An improved cost benefit analysis for caustic recycle facilities should focus on improving the basis for the following questions (listed in priority): How much sodium will be added for caustic leaching?
 - What level of supersaturation can be tolerated?
 - What is the cost savings from preventing additional ILAW glass production?
 - What are the total capital costs for the caustic-recycle facility?
 - What are the operating and maintenance costs for the caustic-recycle facility?

Acknowledgements

This analysis relied strongly on the elicitation of information and informed judgment from knowledgeable Department of Energy, Bechtel National Inc., Ceramatec Inc., and Pacific Northwest National Laboratory staff. Although this list is incomplete, the authors would like to acknowledge the following for their participation: Billie Mauss (DOE), Shekar Bologopal (Ceramatec Inc.), Anthony Nickens (Ceramatec Inc.).

Acronyms and Abbreviations

ACE	U.S. Army Corps of Engineers
DOE	Department of Energy
HLW	high-level waste
ILAW	immobilized low-activity waste
LAW	low-activity waste
LLW	low-level waste
MT	metric ton
O&M	operations and maintenance
ORP	Department of Energy-Office of River Protection
PNNL	Pacific Northwest National Laboratory
ROI	total return on investment
R&T	research and technology
TWRS	Tank Waste Remediation System
WTP	Waste Treatment and Immobilization Plant

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1.0 Introduction

Sodium is one of the most common components of the Hanford tank wastes and is a major contributor to the waste-oxide loading in the low-activity waste (LAW) glass. In addition to the large amounts of sodium already in the wastes, the current waste-treatment approach calls for adding additional sodium (primarily as NaOH) while pretreating the tank wastes, which would help control corrosion in the tank farms and also potentially increase the volume of LAW glass. Since the tank wastes already contain significant amounts of sodium, there is a potential benefit for a caustic-recycle process that would separate sodium hydroxide for recycle at the Hanford site. This would reduce the volume of LAW glass and minimize the need to purchase new NaOH.

The current pretreatment flowsheet indicates that approximately 6500 metric tons (MT) of Na will be added to the tank waste, primarily for removing Al from the high-level waste (HLW) sludge (Kirkbride et al. 2007). An assessment (Alexander et al. 2004) of the pretreatment flowsheet, equilibrium chemistry, and laboratory results indicates that the quantity of Na required for sludge leaching will increase by 6000 to 12,000 MT in order to dissolve sufficient Al from the tank-waste sludge material to maintain the number of HLW canisters produced at 9,400 canisters as defined in the Office of River Protection (ORP) System Plan (Certa 2003). This additional Na will significantly increase the volume of LAW glass and extend the processing time of the Waste Treatment and Immobilization Plant (WTP). Future estimates on sodium requirements for caustic leaching are expected to significantly exceed the 12,000-MT value and approach 40,000-MT of total sodium addition for leaching (Gilbert, 2007).

Electrochemical salt-splitting technologies for caustic recycle were investigated in the 1990s for application to the treatment of tank wastes at the Hanford, Savannah River, and Idaho National Engineering Laboratory 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 (i.e., Nafion) and ceramic-based, sodium-selective membranes (NaSICON) 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 membranes were found to have a lower current efficiency than the ceramic membranes, and they transported radioactive cesium at a higher rate than the sodium, resulting in a contaminated caustic product.

The likely increase in caustic demand for pretreating the tank wastes has resulted in renewed interest in caustic-recycle methods. Ceramatec Inc. has continued to develop the NaSICON membranes for caustic recycle. As part of this development effort, Ceramatec has engaged staff at Pacific Northwest National Laboratory (PNNL) to assist with applying this technology for caustic recycling at Hanford. This report addresses the economics involved in the deployment of such a facility at Hanford.

2.0 Scope and Objectives

This report contains a review of potential cost benefits of NaSICON Ceramic membranes for the separation of sodium from Hanford tank waste. The primary application is for caustic recycle to the WTP pretreatment leaching operation. The report includes a description of the waste, identification of the benefits and costs for a caustic recycle facility, and Monte Carlo results obtained from a model of these costs and benefits. The use of existing cost information has been limited to publicly available sources. This study is intended to be an initial evaluation of the economic feasibility of a caustic-recycle facility based on NaSICON technology.

3.0 Methods

The cost benefit for caustic recycling is assumed to consist of four major contributions: 1) the cost savings realized by not producing additional immobilized low-activity waste (ILAW) glass, 2) caustic-recycle capital investment, 3) caustic-recycle operating and maintenance costs, and 4) research and technology (R&T) costs needed to deploy the technology. In estimating costs for each of these components, several parameters are used as inputs. Due to uncertainty in assuming a singular value for each of these parameters, a range of possible values is assumed. A Monte Carlo simulation is then performed where the range of these parameters is exercised, and the resulting range of cost benefits is determined. The structure of the Monte Carlo simulation is shown graphically in Figure 3.1. The remainder of Section 3 is dedicated to discussing the range of parameters used in each of these structure elements.

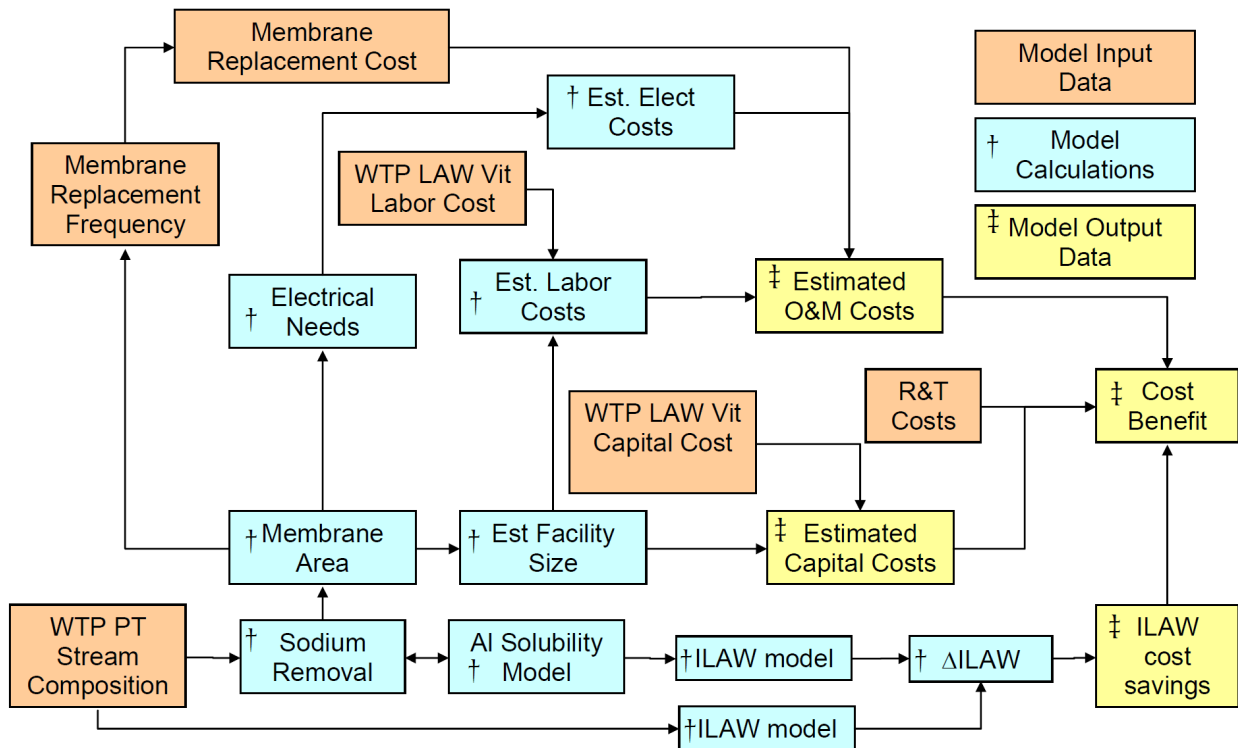


Figure 3.1. Illustration of WTP Process Integration

3.1 WTP Pretreatment Stream Composition

Kirkbride and coworkers (2007) provide process stream data for the Hanford tank waste as it is treated through the current baseline process. For the WTP caustic leaching unit operation, an estimated 6,700 MT of Na as fresh NaOH addition is required. The resulting pretreated LAW stream after cesium ion exchange and final LAW evaporation steps is shown in Table 3.1.

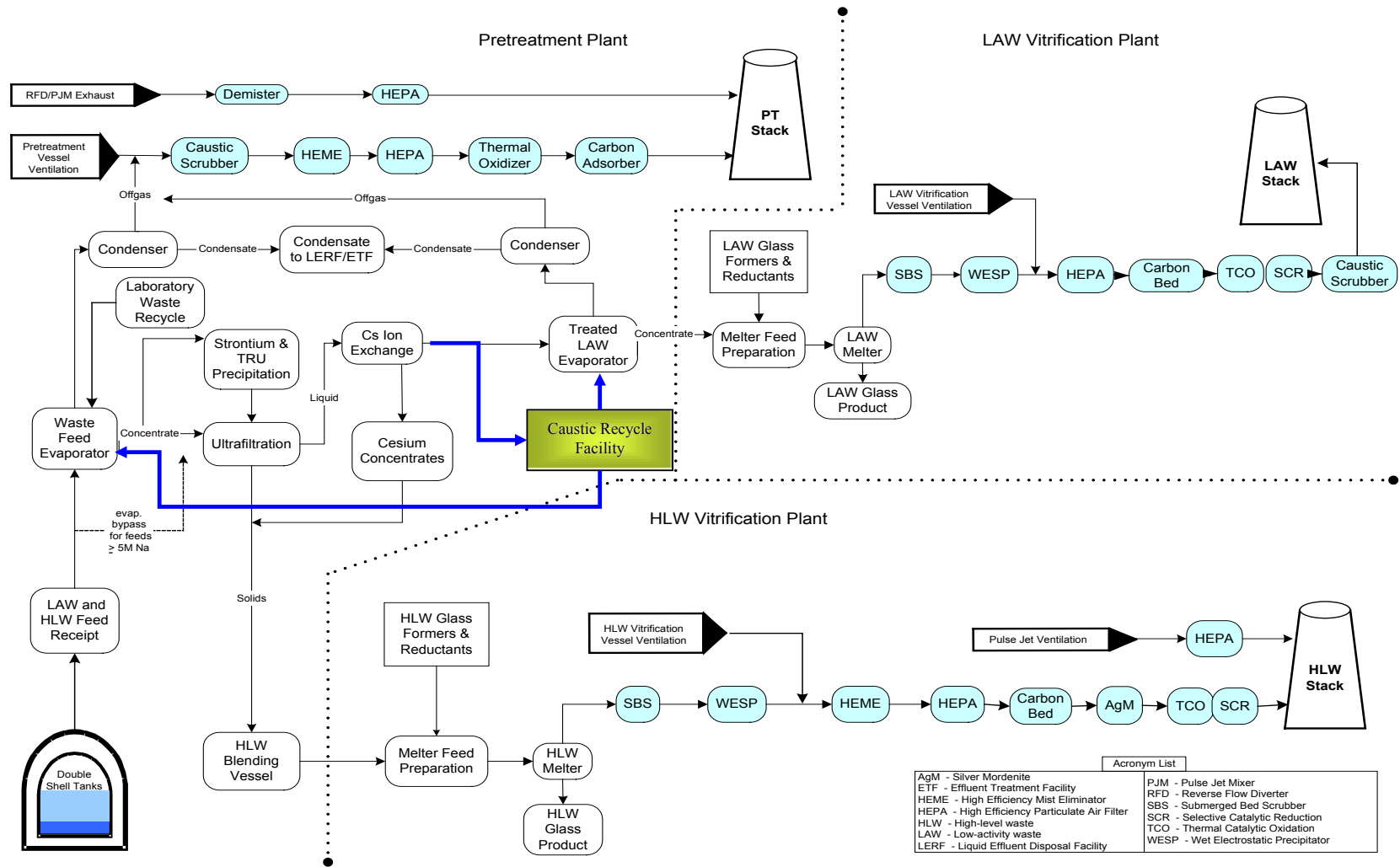
Table 3.1. Composition of WTP Stream Significant to Caustic Recycle; Adapted From Kirkbride and Coworkers (2007)

Species	Caustic-Leach Addition (MT)	Pretreated LAW (MT)	Est. Pretreated LAW Before Final Evaporation (MT)
Na ⁺	6,735	36,265	43,000
OH ⁻	4,982	3,288	8,270
Al(OH) ₄ ⁻	-	10,283	10,283
SO ₄ ⁻	-	4,006	4,006
Others	-	78,522	78,522
Water	15,060	138,890	432,243
Total	26,777	271,254	576,324
wt% Dissolved Solids	43.8%	48.8%	25.0%

The electrochemical caustic-recycle process operates more efficiently under moderately concentrated conditions. Therefore, the feed to the caustic-recycle facility would likely be taken directly as the cesium ion exchange effluent. An estimated composition of this stream can be calculated by adding water to produce a liquid phase density of approximately 1.2 g/mL. This corresponds to a dissolved-solids content of approximately 25.0% as shown in Table 3.1. The sodium-lean pretreated LAW would then be sent to the treated LAW evaporator for a final concentration step before LAW vitrification. The recycled sodium hydroxide would be used for future leaching operations. Figure 3.2 shows a potential WTP process integration scheme.

Many variables will affect the operation of the caustic-leaching unit. These variables include whether the aluminum is speciated as gibbsite or behomite, whether the aluminum is present in a pure phase or co-precipitated, the particle-size distribution of the aluminum species, the particle shape of the aluminum species, the reactor operating temperature, the reactor mixing conditions, the aluminate concentration in the reactor, the hydroxide concentration in the reactor, etc. In addition to these kinetic-based arguments, the solubility of aluminum species under caustic conditions in concentrated salt solutions is complex. Consequently, the total sodium required for caustic leaching and keeping the aluminum in solution should be considered an estimated value. As the caustic-leaching operation develops, a better estimate of the sodium required for caustic leaching will emerge.

For this reason, the concentrated sodium hydroxide added for caustic leaching will be considered an independent variable in this report. This is reflected by the variable feed composition shown in Table 3.2. The total quantity of sodium required for caustic leaching is shown as the variable X. The estimated composition of the caustic-recycle feed stream can then be calculated as shown in the table.



Acronym List	
AgM - Silver Mordenite	PJM - Pulse Jet Mixer
ETF - Effluent Treatment Facility	RFD - Reverse Flow Diverter
HEME - High Efficiency Mist Eliminator	SBS - Submerged Bed Scrubber
HEPA - High Efficiency Particulate Air Filter	SCR - Selective Catalytic Reduction
HLW - High-level waste	TCO - Thermal Catalytic Oxidation
LAW - Low-activity waste	WESP - Wet Electrostatic Precipitator
LERF - Liquid Effluent Disposal Facility	

Figure 3.2. Illustration of Possible WTP Process Integration Scheme

Table 3.2. Composition of WTP Streams Significant to Caustic Recycle With Variable Sodium Addition for Caustic Leaching; Adapted From Kirkbride and Coworkers (2007)

Species	Caustic-Leach Addition (MT)	Pretreated LAW (MT)	Est. Pretreated LAW Before Final Evaporation (MT)
Na ⁺	X	36,265	36,265 + X
OH ⁻	0.74 X	3,288	3,288 + 0.74 X
Al(OH) ₄ ⁻	-	10,283	10,283
SO ₄ ⁻	-	4,006	4,006
Others	-	78,522	78,522
Water	2.24 X	138,890	535,982 + 7.46X
Total	3.98 X	271,254	668,346 + 9.2 X
Wt% Dissolved Solids	43.8%	48.8%	25.0%

3.2 Sodium Removal

Sodium is recovered via the electrochemical process with a Ceramatec NaSICON membrane as shown in Figure 3.3. Anode, cathode, and overall reactions from this process are shown in the equations below. In this process, sodium ions are selectively transported across a ceramic membrane driven by an applied electrical potential.

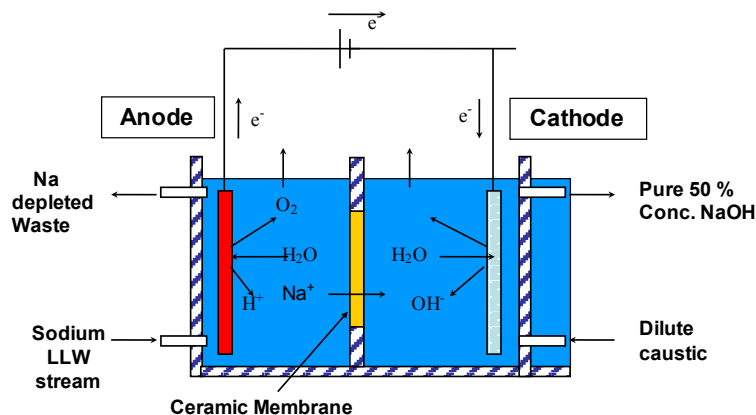


Figure 3.3. Schematic of a Two Compartment Electrochemical Process Using the NaSICON Membrane

For every mole of sodium entering the cathode cell, a mole of water is consumed, and a mole of hydroxide ions and half mole of diatomic hydrogen are produced. For every mole of sodium transported

from the pretreated LAW across the membrane, the anode reaction results in the consumption of a mole of hydroxide ions and the production of half a mole of water and a quarter mole of diatomic oxygen. Consequently, the pH of the pretreated LAW stream drops significantly as the reaction proceeds.

The drop in pretreated LAW pH can be significant enough to precipitate dissolved species in the LAW. This study limits the amount of sodium transported across the membrane to an amount that will not result in aluminate saturation to a series of assumed temperatures. The solubility model used for this sodium-transport constraint is discussed in Section 3.3.

3.3 Aluminum Solubility Model

One limitation of any caustic-recovery stream will be to avoid fouling the caustic recovery cell from the precipitation of aluminum. Therefore, to understand how much caustic can be removed from a process stream, it is necessary to understand the equilibrium conditions between Al and hydroxide.

Misra (1970) developed an empirical model for the quantity of sodium required to dissolve gibbsite from simulant data:

$$\ln[Al(OH)_4^-] = 5.71 - \frac{2486.70}{T} + \frac{33.71[NaOH]}{T} + \ln[NaOH] \quad (3.3.1)$$

where T = temperature in Kelvin
 $[Al(OH)_4^-]$ = concentration in solution
 $[NaOH]$ = concentration added.

Figure 3.4 provides a summary for the Al solubility for a 2, 4, 6, 8 and 10 -M hydroxide solution as a function of temperature. Note that this equation was developed for pure sodium hydroxide solutions. Other anions will cause some increase in the solubility of aluminum. However, for the sake of conservatively estimating how much caustic can be recovered, we will use the solubility of aluminum based only on the hydroxide concentration of the process streams.

As seen in Figure 3.4, the solubility of gibbsite increases dramatically as the temperature is increased. Note that the baseline process for dissolving aluminum requires cooling of the solution to 25°C. Therefore, to verify that the Al remains in solution, it will be necessary to keep the Al:NaOH ratio at approximately 0.1 or less.

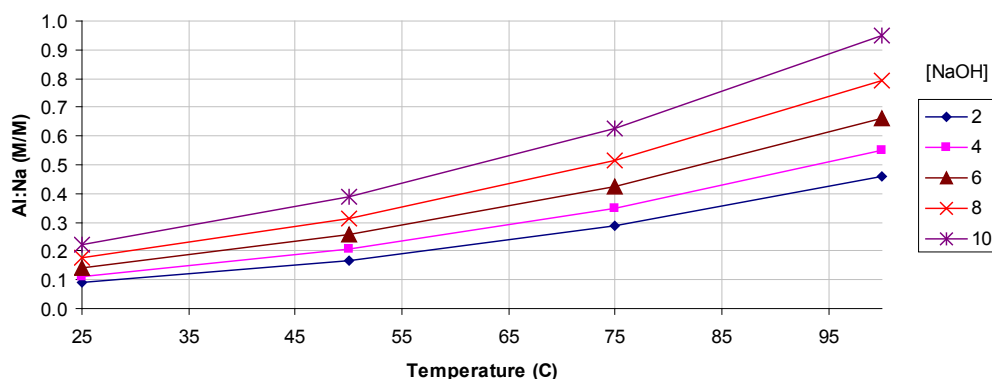


Figure 3.4. Gibbsite Solubility – Molarity of Al in Solution for Given Initial Solution NaOH Molarity

With the solubility equation established, a term called the saturation ratio can be defined. The saturation ratio is the ratio of the actual solution of aluminate concentration to the concentration at the solubility limit. This is shown in Equation 3.3.2. When the saturation ratio is less than one, the solution is under-saturated, and it is over saturated when the saturation ratio exceeds one.

$$SR = \frac{[Al(OH)_4^-]_{actual}}{[Al(OH)_4^-]_{saturation}} \quad (3.3.2)$$

where SR = saturation ratio of the solution
 $[Al(OH)_4^-]_{actual}$ = actual concentration of $[Al(OH)_4^-]$ in solution (mol l-1)
 $[Al(OH)_4^-]_{saturation}$ = concentration of $[Al(OH)_4^-]$ in solution at saturation from Equation 3.3.1 (mol l-1).

Through Equations 3.3.1 and 3.3.2, the saturation ratio under a number of conditions can be determined. For waste caustic-leaching operations, the aluminate solution is heated to 60° to 100°C during leaching. The leaching reaction slows as the solubility limit is reached. The solution is then cooled to 25°C for further downstream processing. Figure 3.5 shows the saturation ratios for caustic-leach solutions that are heated and reach saturation at elevated temperature and then cooled to 25°C for further processing. For example, an aluminate solution that is just saturated at 50°C will have a saturation ratio of 1.8 at 25°C. A heated leachate solution that is saturated at 100°C will have a saturation ratio from 4 to 5 (depending on sodium hydroxide concentration) when cooled to 25°C.

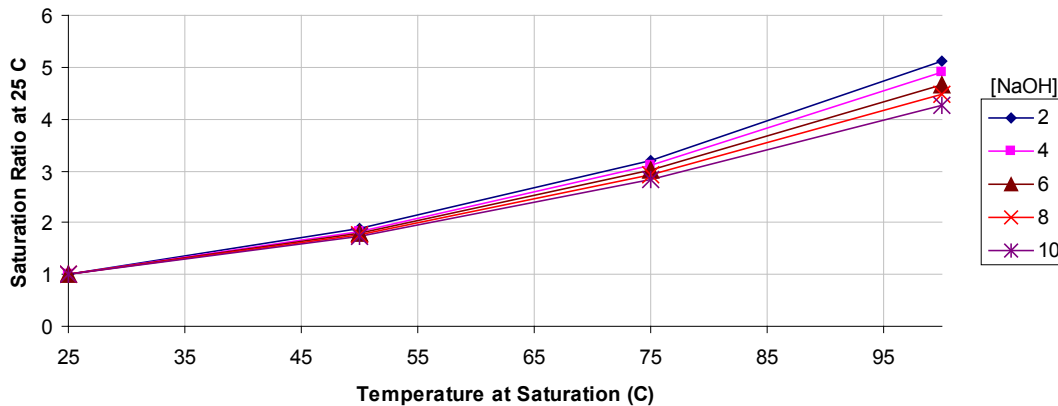


Figure 3.5. Saturation Ratio at 25°C of Just Saturated Solutions at Elevated Temperatures

The saturation ratio has been shown to govern the precipitation rate of over-saturated aluminate solution. Li and coworkers (2005) generated the data shown in Figure 3.6. These data show that the crystal growth rate for these solutions varies exponentially with the saturation ratio. In general, the measured precipitation rates were slow, being under 1 nm/min at a saturation ratio of 8 and trending toward 0 at a saturation ratio of 1.

A power-law fit of the data shown in Figure 3.6 was used to predict the time needed to precipitate Gibbsite particles of various diameters. The residence time of the TCP-01 vessel in the WTP pretreatment plant is on the order of 1 week. Preventing large, process-impacting particles (greater than

10 microns) from forming in this vessel corresponds to a maximum particle-size range of 1- to 10-microns forming over the average vessel residence time of one week. This region is shown in Figure 3.7 and indicates a target saturation ratio range of 1.5 to 8 for process compatibility. The operation of the downstream WTP processes under these conditions must be demonstrated in a separate experimental program.

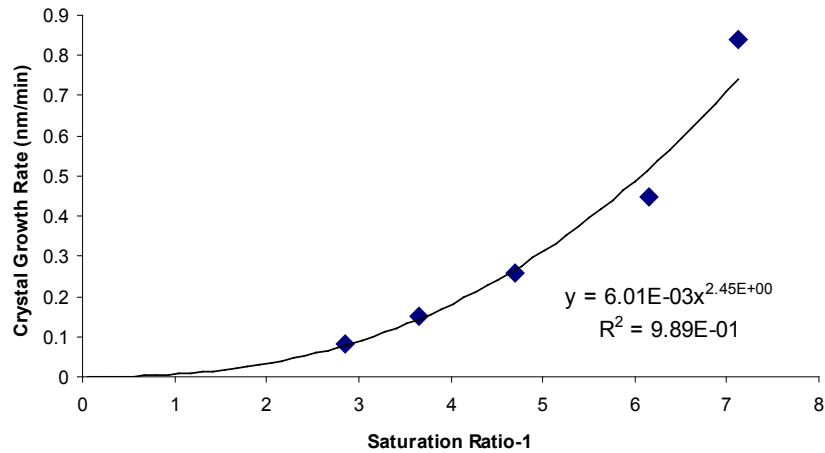


Figure 3.6. Experimentally Measured Crystal Growth Rates of Saturated Sodium Aluminate Solutions at 22°C

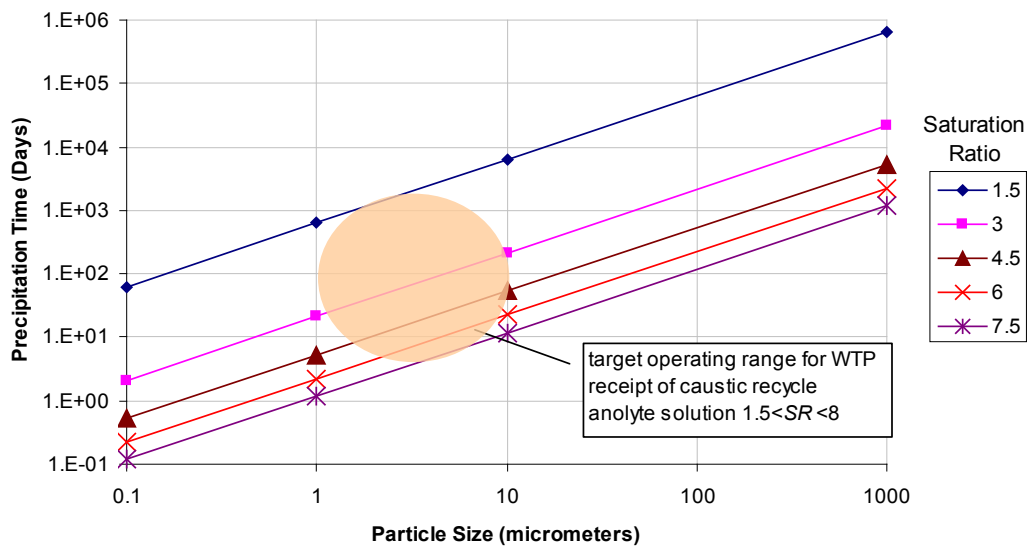


Figure 3.7. Predicted Time Needed to Precipitate Gibbsite Particles of Various Sizes Under Different Saturation Ratio Conditions

3.4 ILAW Glass Model

Hamel and coworkers (2006) have recently presented a revised U.S. Department of Energy (DOE) glass model. The oxide loading in the ILAW glass has a maximum Na₂O loading of 23% by mass. The maximum SO₃ loading in this model corresponds to 1.2% by mass.

The quantity of ILAW glass produced under the variable sodium loadings in this report is calculated as shown in Equation 3.4.1.

$$M_{ILAW,CR} = \max \left\{ \frac{\frac{1}{2} \left(\frac{62 \text{ g/mol}}{23 \text{ g/mol}} \right) (36,265 \text{ MT} + X - Y)}{0.23}, \frac{\frac{1}{2} \left(\frac{80 \text{ g/mol}}{96 \text{ g/mol}} \right) (4,006 \text{ MT})}{0.012} \right\} \quad (3.4.1)$$

3.5 Delta ILAW

The baseline amount of ILAW produced is calculated using the same glass model shown in Equation 3.4.1.

$$M_{ILAW} = \max \left\{ \frac{\frac{1}{2} \left(\frac{62 \text{ g/mol}}{23 \text{ g/mol}} \right) (36,265 \text{ MT} + X)}{0.23}, \frac{\frac{1}{2} \left(\frac{80 \text{ g/mol}}{96 \text{ g/mol}} \right) (4,006 \text{ MT})}{0.012} \right\} \quad (3.5.1)$$

When X is zero in Equation 3.5.1, the mass of ILAW produced is 212,512 MT for the sodium-limited case and 139,100 MT for the sulfate-limiting case. To be sulfate limiting, a total of 23,700 MT of sodium being vitrified as LAW is required. This equates to the sodium addition for leaching, X, being equal to 0 and sodium recycled, Y, being 12,500 MT.

The change in ILAW mass due to caustic recycling is calculated from Equation 3.5.2.

$$\Delta M_{ILAW} = M_{ILAW} - M_{ILAW,CR} \quad (3.5.2)$$

In the sodium-limiting case, Equation 3.5.2 can be reduced to the following:

$$\Delta M_{ILAW} = -5.86 \cdot Y \quad (3.5.3)$$

This indicates that there is nearly a factor of six reduction in the mass of ILAW produced for recovering a unit mass of sodium.

3.6 ILAW Cost Savings

DOE/ORP-2007-03 provides an economic assessment of Hanford waste-treatment options. One of the options, case 2, provides operating cost estimates for a second LAW vitrification facility. These costs are estimated at \$114M/yr for a facility with a 1220 MT Na/yr throughput capacity. As shown in Table 3.3, this translates to a cost of \$93,400/ MT Na. After converting this value to a MT of glass basis, a Monte Carlo distribution assumption for ILAW cost savings is shown in Table 3.4.

Table 3.3. Estimation of ILAW Immobilization Costs; adapted from Curtis (1995) in 2008 Dollars Assuming 3% Annual Rate of Inflation

Case 2 Supplemental LAW Vitfriciation Operating Costs	Case 2 Supplemental LAW Vitfriciation Capacity	Case 2 Supplemental LAW Vitfriciation Operating Costs
\$M/yr	MT Na/yr	\$/MT Na
\$114	1220	\$93,400

Table 3.4. Monte Carlo Distribution Assumptions for ILAW Cost Savings

Description	Distribution Type	Low	Median	High
ILAW Cost Savings (\$/MT ILAW), ΔC_{ILAW}	Triangular	\$ 12,800/MT ILAW	\$15,900/MT ILAW	\$19,100/MT ILAW

3.7 Estimated Membrane-Area Requirements

The flux of sodium across the membrane can be determined from Equation 3.7.1.

$$j_{Na} = \frac{\varepsilon w_{Na} I'}{F} \quad (3.7.1)$$

where j_{Na} = mass flux of sodium across the membrane ($\text{kg day}^{-1} \text{m}^{-2}$)

ε = sodium transport efficiency

w_{Na} = molecular weight of sodium (g mol^{-1})

I' = current flux across the membrane (A m^{-2})

F = Faraday constant ($96485 \text{ A s mol}^{-1}$).

For the Monte Carlo simulation, the sodium transport efficiency is assumed to vary from 95% to 100% with a median value of 99%. This is consistent with previous experimental results for the Ceramatec membrane technology and is shown in Table 3.5.

Table 3.5. Monte Carlo Distribution Assumptions for Sodium Transport Efficiency

Description	Distribution Type	Low	Median	High
ε	Triangular	0.95	0.99	1.00

The membrane area needed is then determined by Equation 3.7.2

$$A_{Na} = \frac{R_{Na}Q}{j_{Na}} \quad (3.7.2)$$

where A_{Na} = total membrane area required (m²)
 R_{Na} = quantity of sodium to be recovered per unit volume of feed (kg L⁻¹)
 Q = maximum flow rate to be input to the caustic-recovery facility (L min⁻¹).

3.8 Estimated Facility Size

A preliminary layout for a caustic-recycle facility was created as part of this project. The facility consists of an electrochemical cell area approximately 60 feet by 35 feet. Twenty electrochemical cell modules were contained in this area, producing a ratio of 100 ft² per module. The remainder of the facility consists of feed and product tanks, piping, and pumps. Since the same volume of feed is expected to be processed through the facility regardless of the amount of caustic recovered, this area was assumed to remain constant regardless of the number of electrochemical modules required. The total facility footprint was approximately 70 feet by 120 feet. Subtracting out the area for the electrochemical modules produces 6,420 ft².

Each module contains 40 scaffolds, and each scaffold contains 48 disk membranes. Each disk membrane has a surface area of 45.6 cm². This design results in 8.8 m² of membrane area per module. The total facility size based on the required membrane area is shown in Equation 3.8.1.

$$A_{CR} = \left(100 \frac{\text{ft}^2}{\text{module}}\right) \cdot \left(8.8 \frac{\text{modules}}{\text{m}^2}\right) A_{Na} + 6420 \text{ ft}^2 \quad (3.8.1)$$

where A_{CR} = area of the caustic recycle facility (ft²)
 A_{Na} = total membrane area required (m²).

3.9 LAW Vitrification Facility Costs

DOE/ORP-2007-03 estimates the cost for the LAW vitrification facility to be \$1.152B according to the U.S. Army Corps of Engineers (ACE 2006). These costs include the following:

- Direct costs
 - Equipment, installation, instrumentation, piping, electrical, insulation, painting, etc.
 - Buildings, process and auxiliary
- Indirect costs
 - Engineering and supervision
 - Construction expense and contractor fee
 - Contingency.

The LAW building is a mixed-use occupancy building with a gross floor area of approximately 260,000 ft² (excluding approximately 42,300 ft² of below-grade process area), with an approximate footprint of 162 ft wide by 300 ft long. The LAW building consists of the following areas: Main Process Areas, Receiving and Storage Areas, Annex Building, and LAW Switchgear Building. The total cost per square foot for the LAW vitrification facility is then \$4,430/ft².

3.10 Estimated Capital Costs

Capital costs were estimated from Equation 3.10.1.

$$C_{CR} = C_{LAW} \cdot \left(\frac{A_{CR}}{A_{LAW}} \right)^{n_{CR}} \quad (3.10.1)$$

- where
- A_{CR} = area of the caustic recycle facility (ft²)
 - A_{LAW} = area of the LAW vitrification facility (260,000 ft²)
 - n_{CR} = scaling factor exponent (–)
 - C_{CR} = estimated capital costs of the caustic recycle facility (\$)
 - C_{LAW} = capital costs of the LAW vitrification facility (\$).

For the Monte Carlo simulations used in this cost-benefit analysis, the range of values presented in Table 3.6 is used. The total facility costs were based upon the discussion in Section 3.9. The low value of $1/3$ for the scaling-factor exponent was selected because it was used as a basis for estimating vitrification costs in a report by the National Research Council (1996). The median value of $1/2$ was selected based on the use of this value to scale nuclear power plants (DOE 1985). The high value of $2/3$ was selected based on the use of a scaling factor of 0.7 for Hanford treatment and immobilization facilities in the Curtis thesis (1995).

Table 3.6. Monte Carlo Distribution Assumptions for Capital Costs of Caustic Recycle Facility

Description	Distribution Type	Low	Median	High
C_{LAW}	Triangular	\$922,000,000	\$1,152,000,000	\$1,382,000,000
n_{CR}	Triangular	$1/3$	$1/2$	$2/3$

3.11 LAW Vitrification Labor Costs

As discussed in Section 3.6, approximately 1,100 Hanford vitrification FTEs were assumed to be required in the Curtis thesis (1995) and the National Research Council (1996). This number is consistent with staffing levels at the Defense Waste Processing Facility at the Savannah River Site. Assuming a third of these FTEs will be dedicated to LAW vitrification produces about 350 FTEs. For the Monte-Carlo simulations, the number of LAW vitrification employees was allowed to vary between the values shown in Table 3.7.

Table 3.7. Monte Carlo Distribution Assumptions for LAW Vitrification Labor Costs

Description	Distribution Type	Low	Median	High
Number of LAW vitrification FTEs	Triangular	350	700	1100

The labor rate for Hanford process operators was estimated with burdening at \$52/hr (DE-RP06-07RL14728). Assuming 1800 man-hours to a man-year, the total labor cost is estimated at \$65,500,000/operating year.

3.12 Estimated Labor Costs

Labor costs were estimated from Equation 3.12.1,

$$L_{CR} = L_{LAW} \cdot \left(\frac{A_{CR}}{A_{LAW}} \right)^{n_L} \quad (3.12.1)$$

- where
- A_{CR} = area of the caustic recycle facility (ft²)
 - A_{LAW} = area of the LAW vitrification facility (260,000 ft²)
 - n_L = scaling-factor exponent for labor (--)
 - L_{CR} = estimated labor costs of the caustic-recycle facility (\$)
 - L_{LAW} = labor costs of the LAW vitrification facility (\$).

For the Monte Carlo simulations used in this cost-benefit analysis, the scaling-factor exponent for labor was allowed to vary as presented in Table 3.8. The median value of the labor scaling-factor exponent was selected at 0.8. This value is consistent with the labor cost exponent supplied by Curtis (1995) for the nuclear power industry and Perry and Green (1997) for the chemical industry.

Table 3.8. Monte Carlo Distribution Assumptions for Estimated Labor Costs

Description	Distribution Type	Low	Median	High
n_L	Triangular	0.7	0.8	0.9

3.13 Estimated Electrical Needs

Electrical needs are determined by Equation 3.13.1,

$$E_{Na} = \frac{FV_{Na}}{\varepsilon W_{Na}} \quad (3.13.1)$$

where E_{Na} = energy required to transport a unit mass of sodium across the membrane (kW hr kg⁻¹)
 V_{Na} = electrical potential across the membrane (V)
 ε = sodium-transport efficiency
 W_{Na} = molecular weight of sodium (g mol⁻¹)
 F = Faraday constant (96,485 A s mol⁻¹).

For the Monte Carlo simulation, the electrical potential is assumed to vary between 2 to 5V with a median value of 3.5V. This is consistent with previous experimental results for the Ceramatec membrane technology and is shown in Table 3.9.

Table 3.9. Monte Carlo Distribution Assumptions for Electrochemical Cell Potential

Description	Distribution Type	Low	Median	High
V_{Na}	Triangular	2 V	3.5 V	5 V

3.14 Estimated Electrical Costs

Electrical costs are determined by Equation 3.14.1,

$$C_E = c_E E_{Na} Y \quad (3.14.1)$$

where C_E = total electrical cost for the caustic-recycle facility (\$)
 c_E = electrical price rate for the caustic-recycle facility (\$ kW⁻¹ hr⁻¹)
 E_{Na} = energy required to transport a unit mass of sodium across the membrane (kW hr kg⁻¹)
 Y = total amount of sodium transported across the membranes in the caustic-recycle facility (kg)

For the Monte Carlo simulation, the electrical price rate is assumed to vary between \$0.05/kW hr to \$0.15/kW hr with a median value of \$0.10/kW hr. This is shown in Table 3.10.

Table 3.10. Monte Carlo Distribution Assumptions for Electricity Prices

Description	Distribution Type	Low	Median	High
c_E	Triangular	\$0.05/kW hr	\$0.10/kW hr	\$0.15/kW hr

3.15 Membrane-Replacement Frequency

For the Monte Carlo simulation, the membrane-replacement frequency is assumed to vary between 0.5 to 2 replacement cycles per year with a median value of 1. Historically, the Ceramatec membranes have been successfully demonstrated with operating durations up to 3,000 hrs. At 60% caustic-recycle facility availability, this corresponds to a replacement frequency of under twice per year. A reasonable reliably goal would be to develop the membrane technology to the point that replacement is needed at a frequency of once per year. The distribution description is shown in Table 3.11.

Table 3.11. Monte Carlo Distribution Assumptions for Membrane Replacement Frequency

Description	Distribution Type	Low	Median	High
Membrane replacement frequency, f_M	Triangular	0.5 yr ⁻¹	1 yr ⁻¹	2 yr ⁻¹

3.16 Membrane Replacement Costs

Each Ceramatec module is assumed to cost \$140,000 including the module housing, electrodes, scaffolds, and ceramic membranes. Each module contains 8.8 m² of membrane area. This equates to a membrane cost of \$16,000/m². Due to ALARA and labor concerns, refurbishing electrochemical cell modules with replacement membranes is assumed to be impractical. Therefore, a replacement strategy of disposing of the spent-cell modules and replacing with new modules is assumed. Based on this strategy, membrane replacement costs can be determined by Equation 3.16.1. The cells would be refurbished if the cost is lower.

$$C_M = c_M f_M A_{Na} \quad (3.16.1)$$

where C_M = total cost for the electrochemical cell modules (\$ yr-1)

c_M = cost per unit of membrane area includes cost of housing, electrodes, scaffolds, and ceramic membranes (\$ m-2)

f_M = replacement frequency of the modules (yr-1)

A_{Na} = total membrane area required (m2).

For the Monte Carlo simulation, the membrane replacement costs are assumed to vary between \$12,000/m² to \$20,000/m² with a median value of \$16,000/m². Table 3.12 shows the distribution description.

Table 3.12. Monte Carlo Distribution Assumptions for Membrane Replacement Costs

Description	Distribution Type	Low	Median	High
c_M	Triangular	\$12,000/m ²	\$16,000/m ²	\$20,000/m ²

3.17 Estimated Research and Technology Costs

For the Monte Carlo simulation, the membrane research and technology costs are assumed to vary from \$10,000,000 to \$30,000,000 with a median value of \$20,000,000. The distribution description is shown in Table 3.13.

Table 3.13. Monte Carlo Distribution Assumptions for Research and Technology Costs

Description	Distribution Type	Low	Median	High
Membrane R&T costs, C_{RT}	Triangular	\$10,000,000	\$20,000,000	\$30,000,000

3.18 Estimated Total Capital Investment

The elements that compose the total capital investment are described in Peters and Timmerhaus (1991). They present a breakdown of these elements typical of the chemical industry by a percentage of more-easily-estimated values. Table 3.14 shows this breakdown and the basis for each calculation. The high value in the range of percentages given by Peters and Timmerhaus (1991) was assumed in this report. The Peters and Timmerhaus (1991) high value of 20% for purchased equipment was changed to 19.4%. This forces the fixed capital-investment value to be consistent with the calculated direct and indirect costs. Table 3.14 allows one to estimate the cost of each sub-category from the calculation in Section 3.10.

Table 3.14. Basis to Eliminate Total Capital Investment

Category	Calculation Basis
Research and Technology	C_{RT} from Section 3.17
I. Direct Costs	Summation of costs shown below
A. Equipment, installation, instrumentation, piping, electrical, insulation, painting	
1. Purchased Equipment	19.4% of C_{CR} from section 3.10
2. Installation	35% of purchased equipment
3. Instrumentation and controls	20% of purchased equipment
4. Piping	30% of purchased equipment
5. Electrical	30% of purchased equipment
B. Buildings, process and auxiliary	50% of purchased equipment
C. Service facilities and yard improvements	60% of purchased equipment
D. Land	6% of purchased equipment
II. Indirect Costs	Summation of costs shown below
A. Engineering and Supervision	20% of direct costs
B. Construction expense and contractor's fee	20% of direct costs
C. Contingency	10% of fixed capital investment

Table 3.14. (contd)

Category	Calculation Basis
III. Fixed Capital Investment	C_{CR} from section 3.10 + R&T costs should equal R&T + Direct Costs + Indirect Costs
IV. Working Capital	10% of total capital investment
V. Total Capital Investment	Fixed Capital Investment + Working Capital

3.19 Estimated Operating and Maintenance Costs

In addition to the estimate for total capital investment, Peters and Timmerhaus (1991) present a similar breakdown for the elements of operating and maintenance costs. Table 3.15 shows this breakdown and the basis for each calculation.

Table 3.15. Basis to Estimate Operating and Maintenance Costs

Category	Calculation Basis
I. Manufacturing Costs	Summation of costs shown below
A. Direct Production Costs	
1. Raw Materials	n/a
2. Operating Labor	L_{CR} from Section 3.12
3. Direct supervisory and clerical labor	15% of operating labor
4. Utilities	C_E from Section 3.14
5. Maintenance	10% of fixed capital investment
6. Operating Supplies	15% of maintenance
7. Laboratory Charges	15% of operating labor
8. Patents and Royalties	n/a
B. Fixed Charges	Summation of costs shown below
1. Depreciation	10% of equipment
2. Local Taxes	n/a
3. Insurance	1% of fixed capital investment
4. Rent	10% of value of the rental property
C. Plant-overhead costs	60% of operating, supervisory, and maintenance
II. General Expenses	Summation of costs shown below
A. Administrative Costs	15% of operating, supervisory, and maintenance
B. Distribution and selling costs	n/a
C. Research and development costs	n/a
D. Financing	n/a
III. Total Production Cost	Manufacturing Costs + General Expenses
IV. Gross-earning cost	Gross annual sales – Total Production Costs
V. Gross annual sales	Total LAW Cost Savings, $\Delta C_{ILAW} \Delta M_{ILAW}$

3.20 Estimated Cost Benefit

From the data calculated from Table 3.14 and Table 3.15, several cost-benefit values can be calculated. These values are shown in Table 3.16 and include specific sales and production costs, turn-over ratio, and total return on investment (ROI). ROI was the primary calculation objective in this report.

Table 3.16. Cost Benefit Terms and Basis for Calculation

Category	Calculation Basis
Specific Sale Cost/kg	Gross annual sales/Sodium Recycled $\Delta C_{ILAW} \Delta M_{ILAW} / Y$
Specific Production Cost/kg	Total Production Costs/Sodium Recycled
Turn-over ratio	Gross annual sales/Total Capital Investment
Return on Investment	Gross earning cost/Total Capital Investment

4.0 Results

The results discussed in this section include the ROI, the cost savings, the capital costs, the operations and maintenance (O&M) costs, and the sale and production costs. There is also a sensitivity analysis on the Monte Carlo results. All of the results in this section are based on constant value of money in 2008 dollars. A discounted cash flow analysis could be applied to this model and would lead to significantly lower return on investment and cost benefit values. This is due to the cost savings from this project occurring decades in the future while the start-up costs for building and deploying the technology occur decades sooner.

4.1 Return on Investment

Monte Carlo simulations were performed using the model described in Section 3. A decision matrix was established where the amount of sodium added for leaching purposes was varied between 10,000 to 50,000 MT in 10,000-MT increments. The amount of sodium recovered was varied to correspond with an aluminate saturation temperature between 25°C and 100°C in 15°C increments. This results in 30 scenarios to map out the feasible operating region for a caustic recycle facility.

In each scenario, 1,000 realizations were performed. The probability distribution for ROI was calculated in for each of these scenarios. A plot showing the range of these distributions against the amount of sodium recycled is shown in Figure 4.1. The 10% line represents the set of points where 10% of the realizations are below a particular ROI at a given amount of sodium recycled. Likewise, the 50% and 90% lines represent the points where 50% and 90% of the realizations are below a particular ROI. Interestingly, the breakeven point for each of these cases is about 5000 MT sodium recycled. A threshold region for minimal plant economic feasibility is assumed to be between 3 to 12% ROI centered on about 7.5%. This corresponds to approximately 10,000 MT sodium recycled for each case.

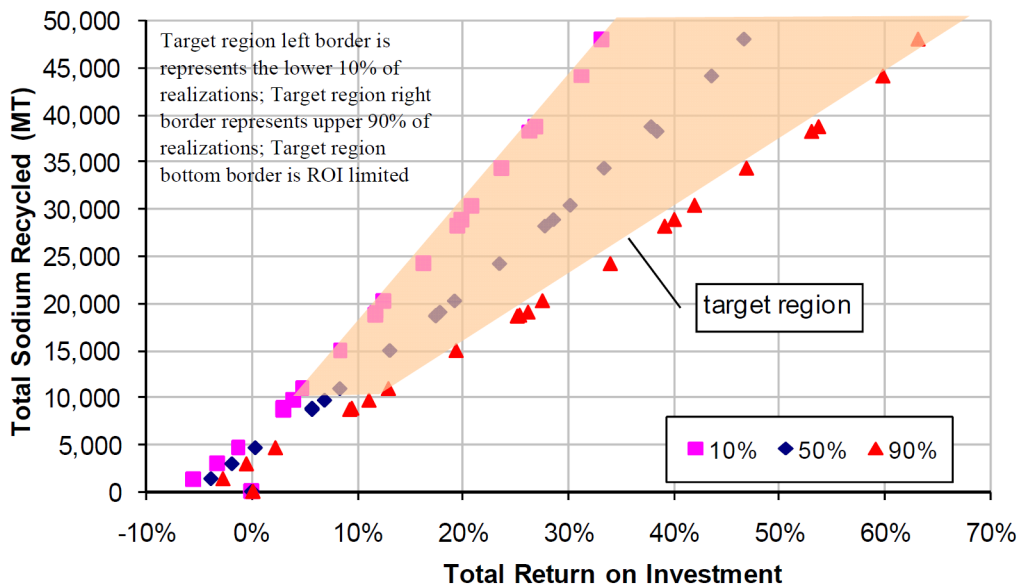


Figure 4.1. ROI for Various Amounts of Caustic Recycled

Figure 4.2 is a plot showing the 30 decision matrix scenarios and the total amount of sodium recovered under each condition. This figure shows that to reach the aluminate saturation level at 25°C, approximately 40,000 to 50,000 MT of sodium will need to be added during caustic-leaching operations. The pretreated LAW would then be processed through the cesium ion exchange process under supersaturated or under-saturated conditions. The pretreated LAW with cesium removed would then be used as a feed to the caustic-recycle facility. Recovering any sodium from this point will supersaturate the solution at 25°C. The x-axis shows the saturation temperature of the pretreated LAW after sodium has been recovered. For instance, if 30,000 MT of sodium is added for leaching and 20,000 MT of the sodium is recovered in the caustic-recycle facility, the solution would be saturated with aluminate at 70°C and be supersaturated at 25°C.

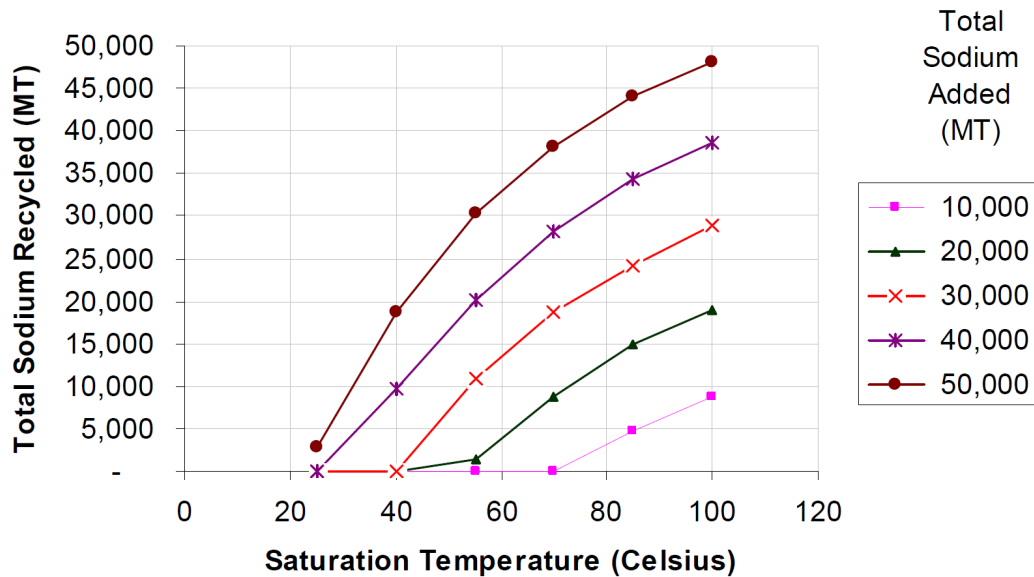


Figure 4.2. Total Sodium Recycled with Various Amounts of Sodium Added for Leaching and Aluminate Saturation Temperatires for the Sodium-Recycled Product

The degree of supersaturation at each aluminate saturation temperature can be quantified with the saturation ratio (see Equations 3.3.1 and 3.3.2). Figure 4.3 is a plot showing the saturation ratio as a function of aluminate saturation temperature. This plot shows the non-linear nature of the relationship and how the saturation ratio varies between 1 and 5.2 over an aluminate-saturation temperature range of 25 to 100°C.

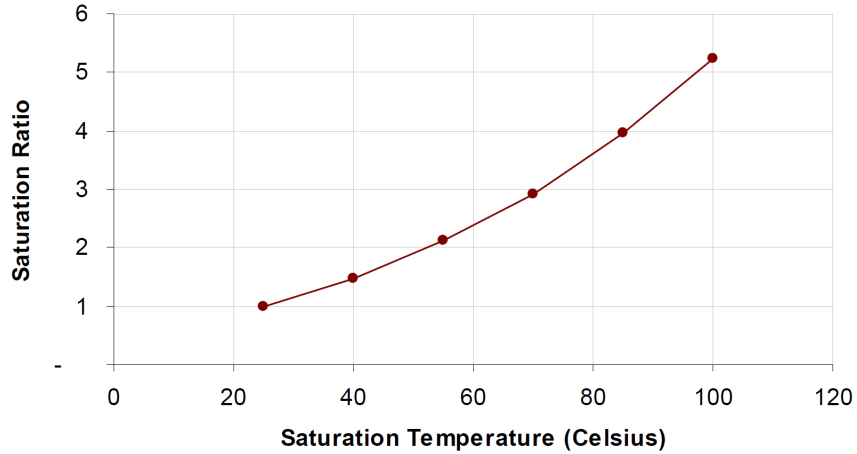


Figure 4.3. Sodium Aluminate Saturation Ratio as a Function of Saturation Temperature

A plot similar to Figure 4.2 that shows the aluminate saturation ratio on the x-axis rather than the aluminate saturation temperature is shown in Figure 4.4. Recycling 10,000 to 45,000 MT of sodium would require 15,000 to 50,000 MT of sodium addition and results in saturation ratios between 1.5 and 5.

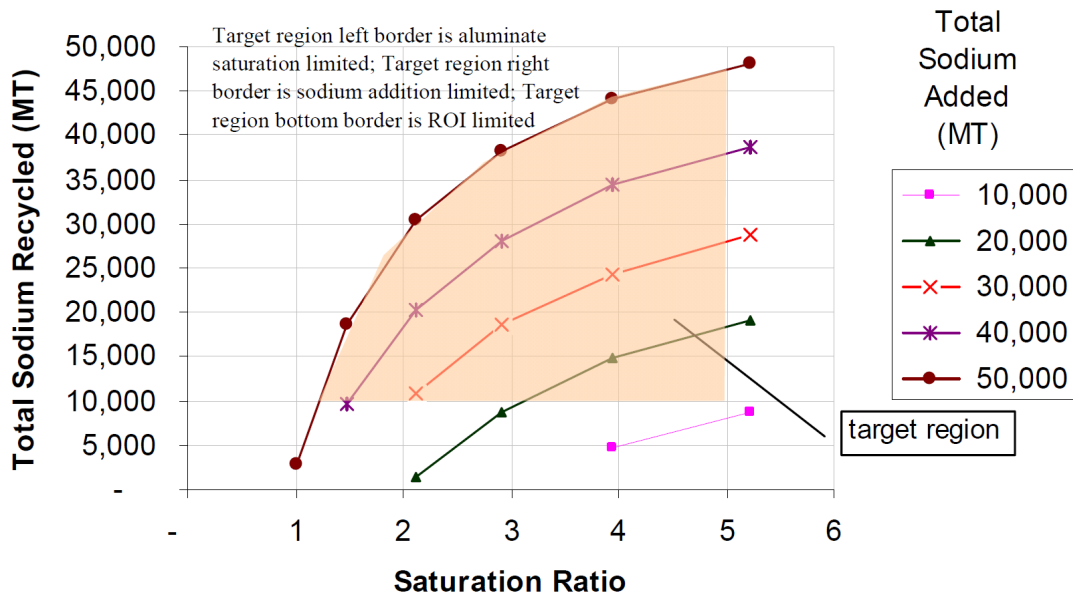


Figure 4.4. Total Sodium Recycled with Various Amounts of Sodium Added for Leaching and Aluminate Saturation Temperatures for the Sodium-Recycled Product

The ROI as a function of saturation ratio is shown in Figure 4.5. The top, middle, and bottom plots represent the data set where 90%, 50%, and 10% of the realizations had ROI values below those provided, respectively. These data show that a minimum of 10,000 MT of sodium needs to be added to achieve a reasonable ROI. In this case, the resulting LAW sodium-recycled product will have a saturation ratio of approximately five. If 40,000 MT of sodium is added for caustic leaching, a reasonable ROI is achieved at a saturation-ratio range of 1.5 to 3.

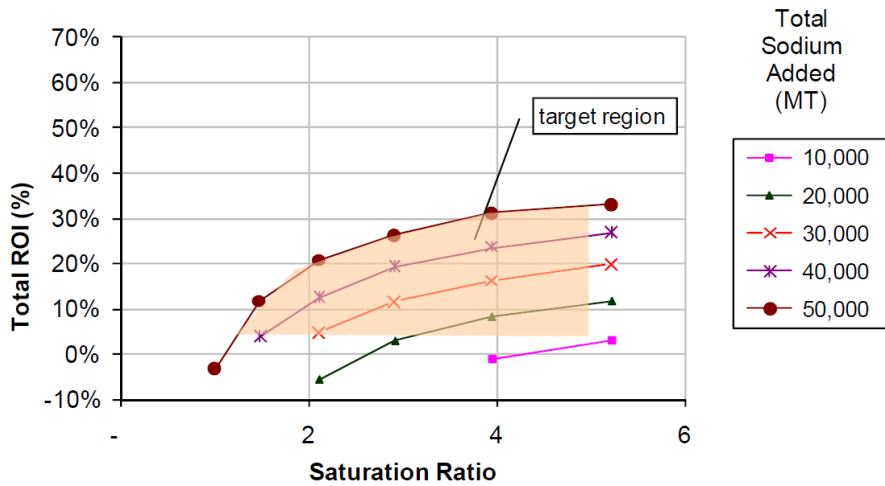
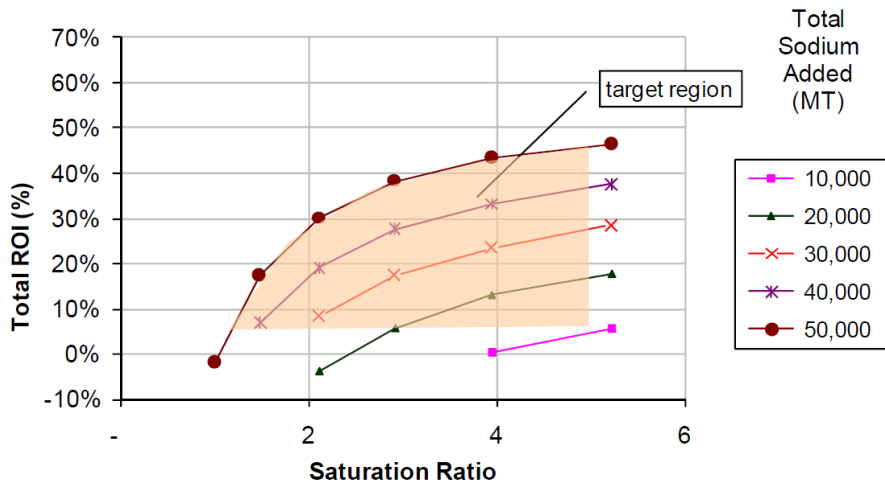
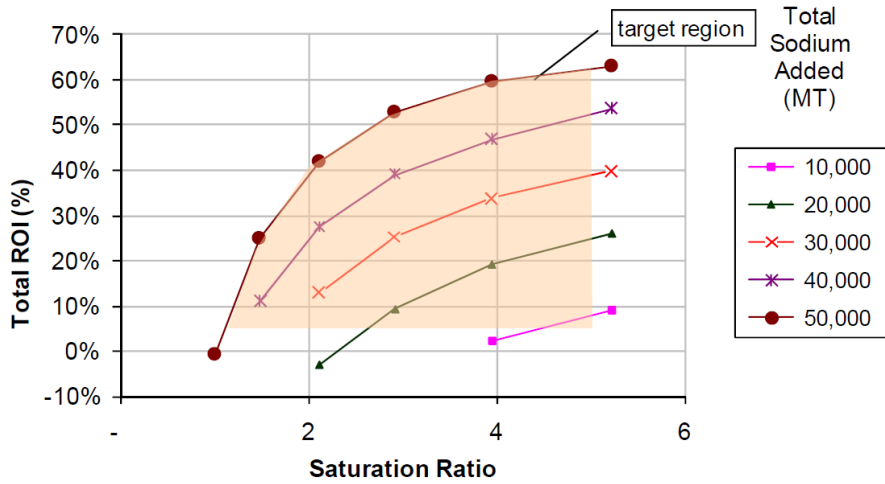


Figure 4.5. ROI as a Function of Aluminate Saturation Ratios with Various Amounts of Sodium Added for Caustic Leaching; top – 90%; middle – 50%; bottom 10% of Monte Carlo Realizations Below Each Curve

4.2 Cost Savings

The range of specific cost-savings values in this assessment was described in Section 3.6. Figure 4.6 shows the Monte Carlo output for net cost savings as a function of total sodium recycled. If 10,000 MT of sodium is recycled, a cost savings in ILAW glass of \$0.7B to \$1B would be realized. If 30,000 MT of sodium is recycled, \$2.5B to \$3.1B would likely be realized.

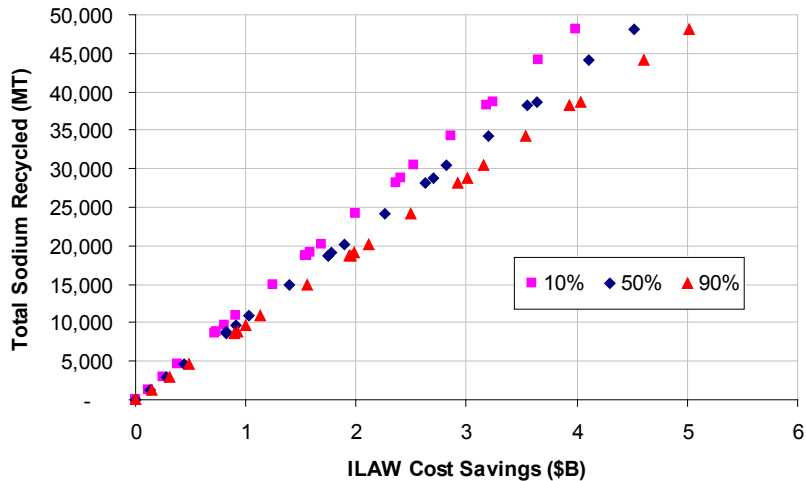


Figure 4.6. ILAW Net Cost Savings as a Function of Total Sodium Recycled

4.3 Capital Costs

The range of total parameters in capital investment calculations in this assessment was described in Section 3.10. Figure 4.7 shows the Monte Carlo output for total capital costs as a function of total sodium recycled. If 10,000 MT of sodium is recycled, a total capital cost for the caustic-recycle facility is estimated to be in the range of \$175M to \$325M. If 30,000 MT of sodium is recycled, \$200M to \$350M would likely be realized.

4.4 O&M Costs

The components of the total-production-cost calculation were described in Section 3.19. Figure 4.8 shows the Monte Carlo output for total production costs as a function of total sodium recycled. If 10,000 MT of sodium is recycled, a total production cost for the caustic-recycle facility is estimated to be in the range of \$13M/yr to \$21M/yr. If 30,000 MT of sodium is recycled, \$21M/yr to \$30M/yr would likely be realized.

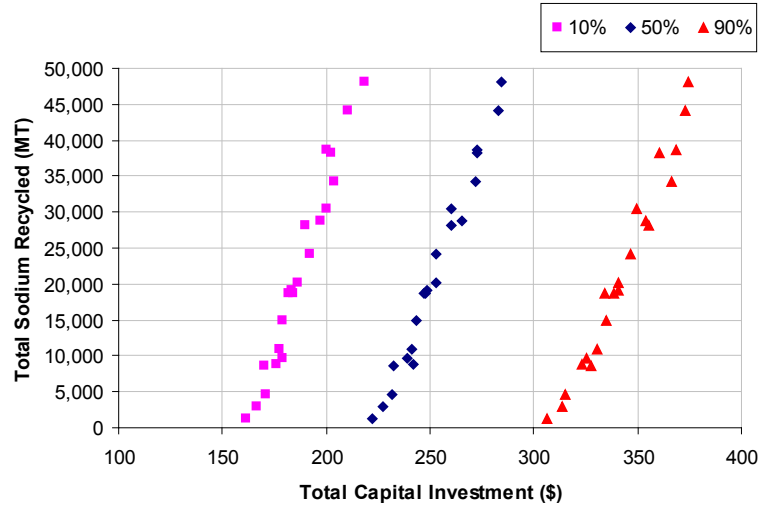


Figure 4.7. Total Capital Investment as a Function of Total Sodium Recycled

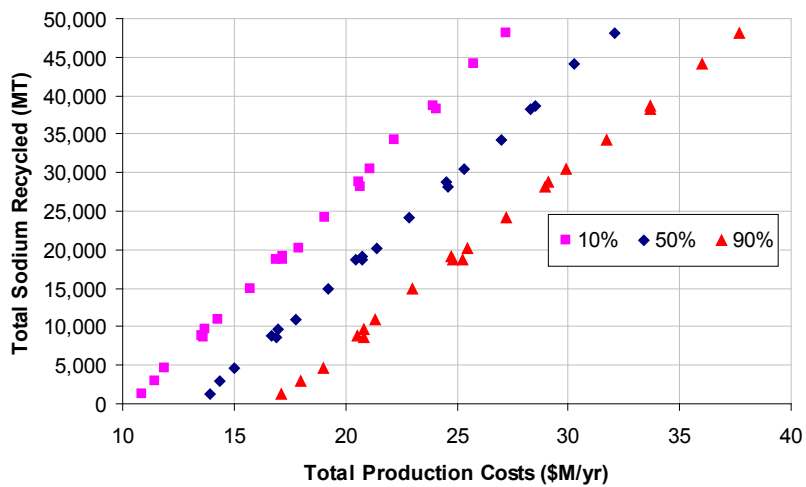


Figure 4.8. Total Production Costs as a Function of Total Sodium Recycled

4.5 Specific Sale and Production Costs

The components of the specific calculations for sale and production costs were described in Section 3.20. Figure 4.9 shows the Monte Carlo output for specific production costs as a function of total sodium recycled. If 10,000 MT of sodium is recycled, a specific production cost is estimated to be in the range of \$25/kg to \$45/kg. If 30,000 MT of sodium is recycled, \$15/kg to \$22/kg would likely be realized.

The Monte Carlo output for specific sales as a function of total sodium recycled is shown in Figure 4.10. In this model, the specific sales cost is invariant with the amount of sodium recycled. A specific sales cost is estimated to be in the range of \$84/kg to \$104/kg. The specific sales cost is a factor of 3.8 to 6.9 greater than the expected specific production cost range.

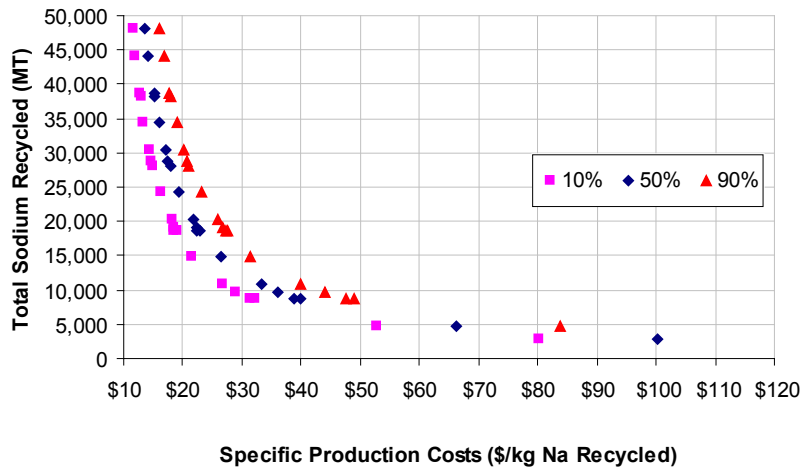


Figure 4.9. Specific Production Costs as a Function of Total Sodium Recycled

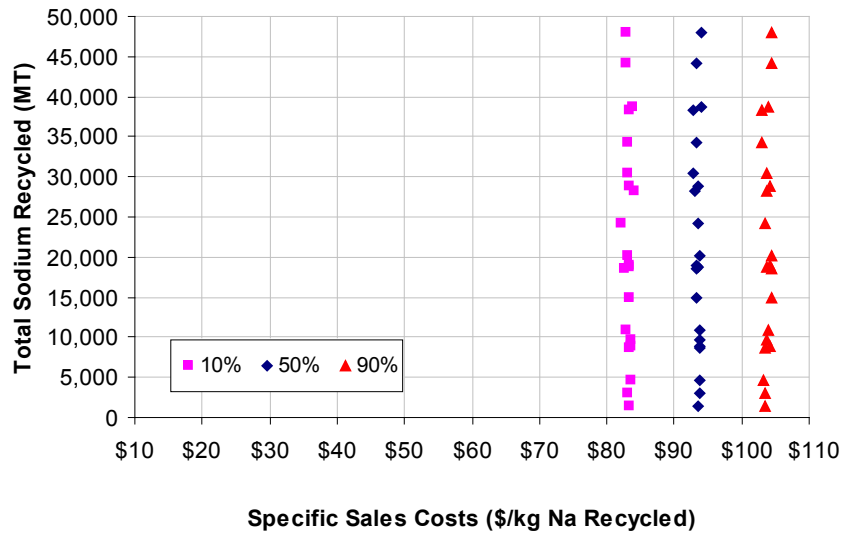


Figure 4.10. Specific Sales Costs as a Function of Total Sodium Recycled

4.6 Impact on Hanford Waste Processing

DOE/ORP-2007-03 states that 60,000 MT of sodium is processed as LAW in the baseline scenarios of that document. This corresponds to 12,000 MT of sodium being added to the 48,000 MT sodium inventory in the waste tanks. The “1A” case was limited by LAW throughput and yielded a 60 year

campaign for both HLW and LAW. For the “1B” case study, additional DST are built to allow for a 27 year HLW campaign and 60 year LAW campaign. Case “1B” was selected for comparison to a case with caustic recycle implemented. The basis of this document is LAW cost savings where a 27 year pretreatment / caustic recycle campaign is assumed and is more consistent with the “1B” case. When 12,000 MT of sodium is added for leaching, DOE/ORP-2007-03 determines a \$49B lifetime cost. If additional sodium is added for leaching, LAW vitrification will extend beyond the 60 year campaign significantly inflating costs. If caustic recycle is implemented and the LAW vitrification feed is supersaturated, reduced costs can occur due to the reduced amount of LAW glass produced. Figure 4.11 shows that \$2.0B to \$2.5B in lifecycle costs savings can be achieved when 40,000 MT of sodium is added (90,000 MT sodium to LAW) with saturation ratios between 3 to 5.

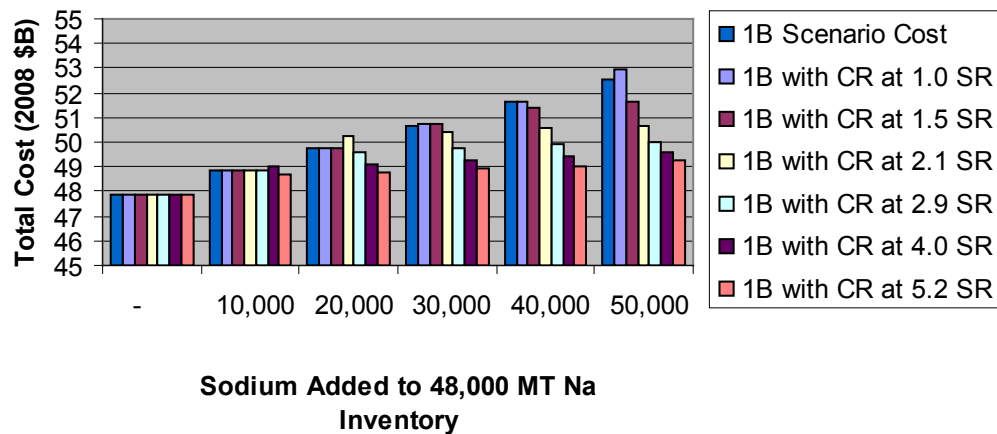


Figure 4.11. Comparison of DOE/ORP-2007-03 Case 1B with Caustic Recycle Implemented

4.7 Sensitivity Analysis

Figure 4.12 shows a sensitivity analysis on the Monte Carlo results in the form of a tornado chart. The figure indicates that the major questions to be answered to obtain a more accurate forecast on ROI are the following:

1. How much sodium will be added for caustic leaching?
2. What level of supersaturation can be tolerated?
3. What is the cost savings from preventing additional ILAW glass production?
4. What are the total capital costs for the caustic-recycle facility?
5. What are the operating and maintenance costs for the caustic-recycle facility?

An improved cost-benefit analysis for caustic-recycle facilities should focus on answering these questions, in that order.

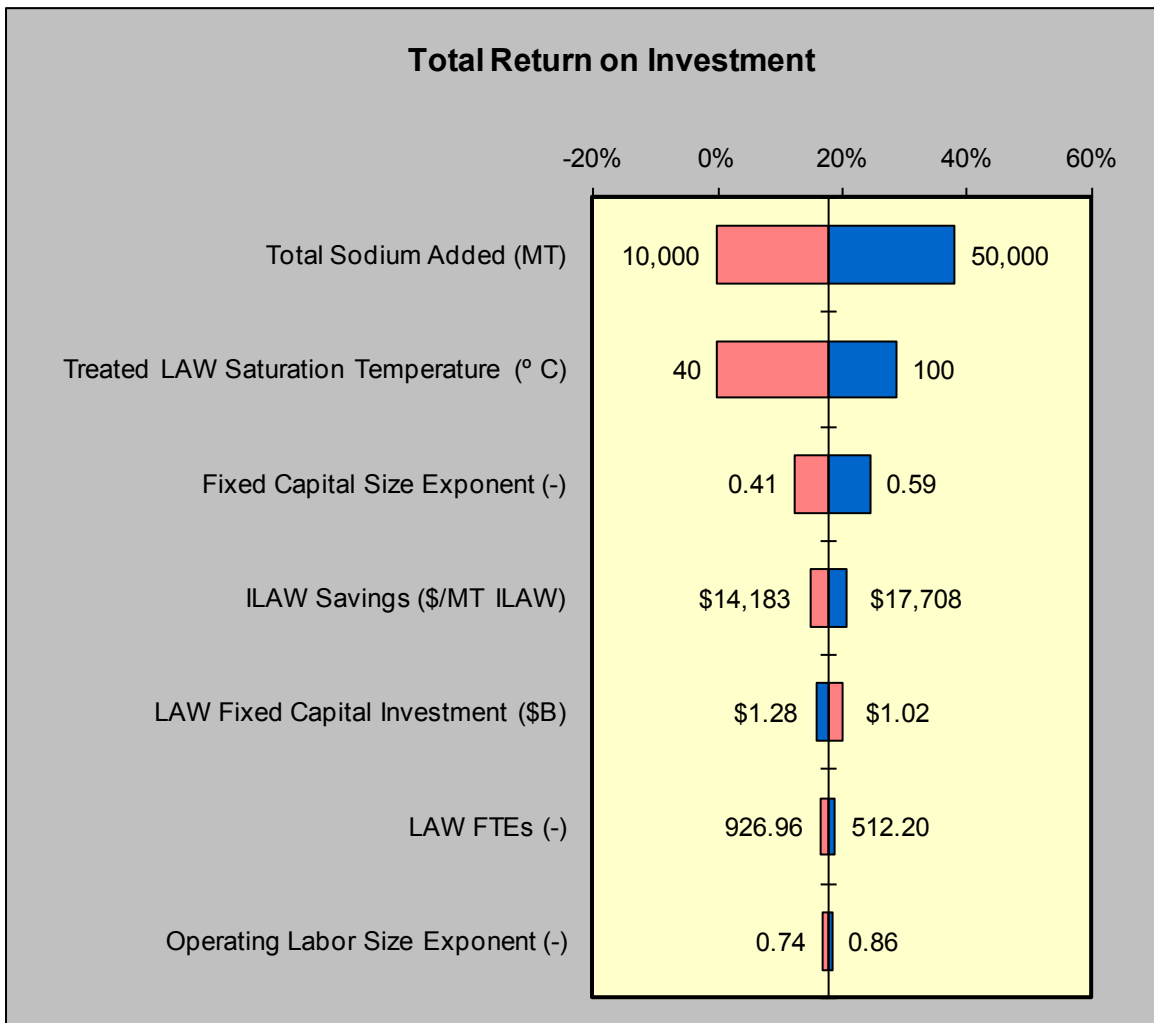


Figure 4.12. Tornado Chart Illustrating the Sensitivity of the Model Parameters on ROI

5.0 Conclusions

The major conclusions from the Monte Carlo model results discussed in this report are summarized below:

- A feasible region for minimal plant economics (e.g; 10% total return on investment) corresponds to approximately 10,000 MT sodium recycled. Total return on investments in the range of 30%-60% can be achieved when 50,000 MT of sodium are recycled.
- Literature data for the growth rate of Gibbsite particles indicates that particles forming in the 1- to 10-micron range over the average vessel residence time of 1 week corresponds to a saturation ratio less than eight. The operation of the downstream WTP processes under these conditions and with particles of this size must be demonstrated in a separate experimental program.
- Recycling 10,000 MT of sodium results in a cost savings in ILAW glass of \$0.7B to \$1.0B. If 30,000 MT of sodium is recycled, \$2.5B to \$3.1B would likely be realized.
- Recycling 10,000 MT of sodium results in an estimated range of total capital cost for the caustic-recycle facility to be \$175M to \$325M. If 30,000 MT of sodium is recycled, \$200M to \$350M would likely be realized.
- Recycling 10,000 MT of sodium results in a total production cost for the caustic-recycle facility to be in the range of \$13M/yr to \$21M/yr. If 30,000 MT of sodium is recycled, \$21M/yr to \$30M/yr would likely be realized.
- If 10,000 MT of sodium is recycled, a specific production cost is estimated to be in the range of \$25/kg to \$45/kg. If 30,000 MT of sodium is recycled, \$15/kg to \$22/kg would likely be realized.
- The specific sales cost is invariant with the amount of sodium recycled. A specific sales cost is estimated to be in the range of \$84/kg to \$104/kg. The specific sales cost is a factor of 3.8 to 6.9 greater than the expected specific production cost range.
- An improved cost benefit analysis for caustic recycle facilities should focus on improving the basis for the following questions (listed in priority): How much sodium will be added for caustic leaching?
 - What level of supersaturation can be tolerated?
 - What is the cost savings from preventing additional ILAW glass production?
 - What are the total capital costs for the caustic-recycle facility?
 - What are the operating and maintenance costs for the caustic-recycle facility?

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