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Pacific Northwest National Laboratory

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Preconceptual Design of a Salt Splitting Process Using Ceramic Membranes

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Prepared for the U.S. Department of Energy
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Salt Lake City, Utah

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Pacific Northwest National Laboratory
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Summary

Inorganic ceramic membranes for salt splitting of radioactively contaminated sodium salt solutions are being developed for treating U.S. Department of Energy tank wastes. The process consists of electrochemical separation of sodium ions from the salt solution using sodium (Na) Super Ion Conductors (NaSICON) membranes. The primary NaSICON compositions being investigated are based on rare-earth ions (RE-NaSICON). Potential applications include 1) caustic recycling for sludge leaching, regenerating ion exchange resins, inhibiting corrosion in carbon-steel tanks, or retrieving tank wastes, 2) reducing the volume of low-level wastes volume to be disposed of, 3) adjusting pH and reducing competing cations to enhance cesium ion exchange processes, 4) reducing sodium in high-level-waste sludges, and 5) removing sodium from acidic wastes to facilitate calcining. These applications encompass wastes stored at the Hanford, Savannah River, and Idaho National Engineering Laboratory sites.

The overall project objective is to supply a salt splitting process unit that impacts the waste treatment and disposal flowsheets and meets user requirements. The potential flowsheet impacts include improving the efficiency of the waste pretreatment processes, reducing volume, and increasing the quality of the final waste disposal forms. Meeting user requirements implies developing the technology to the point where it is available as standard equipment with predictable and reliable performance.

This report presents two preconceptual designs for a full-scale salt splitting process based on the RE-NaSICON membranes to distinguish critical items for testing and to provide a vision that site users can evaluate. Critical test items include 1) those associated with the manufacturing process, 2) implementation of the ceramic membranes into an electrochemical cell, and 3) process applications. Since ceramic membranes have not been widely implemented in electrochemical cell designs, this preconceptual design effort is focused on the electrochemical cells. Limited attention is given to designing the balance of the plant (lag storage, offgas treatment, etc.) except where these issues appear critical to implementing the process (for example, mitigating potentially flammable gas mixtures that could be generated as a result of the electrolysis of water).

A phased approach to the implementation of this technology is being used. In Phase I applications, limited amounts of sodium would be separated for onsite recycle. These applications present limited but significant technical challenges in which only alkaline waste solutions (i.e., pH>12) need to be processed after radionuclide decontamination (low radiation). These solutions contain low quantities of suspended solids. Phase II applications present an expanded set of technical challenges that includes processing acidic solutions, processing solutions before radionuclide decontamination (high radiation); processing slurries containing a high concentration of solids, and separating a large fraction of the sodium while producing a nonradioactive caustic product.

It is recommended that a flat-plate concept using 12.7-cm (5-in.) disks be pursued as the reference design for Phase I applications.. The disks are incorporated into a scaffolding designed to fit into commercially available plate-and-frame electrochemical cells. This initial design is attractive because disk-shaped membranes are more readily fabricated than tubes, and the flat geometry can be readily incorporated into standard commercially available electrochemical cells. Sealing the ceramic disks in the scaffolds is the critical design issue associated with the flat-plate design. Unit test cells are being fabricated that incorporate RE-NaSICON disks in scaffolds. These scaffolds will be incorporated into commercially available cells for testing over a range of conditions during a 1000-h test.

It is recommended that a cylindrical cell design based on RE-NaSICON tubes (5.1 cm OD, 61 cm in length) be pursued for Phase II applications. The design appears to be more robust and appropriate for a wider range of applications involving high radiation fields and high amounts of solids (slurries). Maintenance in a radioactive environment is expected to be much easier because the number of parts is kept to a minumum, thus reducing the time and effort required for manipulating contaminated parts remotely or with protective equipment. This design also may provide superior sealing properties for separating the electrolytic gases and producing pure caustic. While small RE-NaSICON tubes are currently fabricated for sensors, scale-up of the ceramic fabrication process would be a significant effort in addition to a custom-designed electrochemical cell based on the cylindrical geometry.

Glossary

DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
EPDM	ethylene-propylene-diene monomer
HDPE	high-density polyethylene
HLW	high-level waste
INEL	Idaho National Engineering Laboratory
LFL	lower flammability limit
MT	megaton
MW	megawatt
NaSICON	sodium super-ionic conductor
NPZ	nickel-plated zirconium
PEEK	polyether-ether keytone
PNNL	Pacific Northwest National Laboratory
PUREX	plutonium uranium extraction
RE	rare earth
SRS	Savannah River Site
TOE	total operating efficiency

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1.0 Introduction

1.1 Project Background

Producing nuclear materials within the U.S. Department Of Energy (DOE) complex generated acidic waste streams that were made highly alkaline by adding sodium hydroxide for storage in carbon-steel tanks. Many of the wastes are therefore dominated by sodium, which can hinder separations processes such as cesium ion exchange. The sodium also contributes to large disposal volumes and can decrease the durability of glass, a leading candidate for a final waste form. In addition to the large amounts of sodium already in the wastes, many existing disposal strategies call for adding more sodium to the wastes as they are prepared for conversion into the final waste forms.

1.2 Process Description

Pacific Northwest National Laboratory (PNNL), and Ceramatec Inc. are developing an electrochemical salt splitting process based on inorganic ceramic membranes (as shown in Figure 1.1). This process shows promise as a means to mitigate the impact of sodium. In this process, the waste is added to the anode compartment, and an electrical potential is applied to the cell. This drives sodium ions through the membrane, but the membrane rejects most other cations (e.g., K^+,Cs^+). The charge balance in the anode compartment is maintained by generating H^+ from the electrolysis of water. The charge balance in the cathode is maintained by generating OH^-, either from the electrolysis of water or from oxygen and water using an oxygen cathode. The normal gaseous products of the electrolysis of water are oxygen at the anode and hydrogen at the cathode. Potentially flammable gas mixtures can be prevented by providing adequate volumes of a sweep gas, using an alternative reductant, or destroying the hydrogen as it is generated. As H^+ is generated in the anode compartment, the pH drops. Producing OH^- in the cathode compartment results in a rise in pH as the sodium hydroxide product is recovered.

The ceramic membranes are from a family of materials known in the electrical battery industry as sodium (Na), super- ionic conductors (NaSICONs). The NaSICON ceramics are unique in that they possess channels within the crystal structure for fast sodium ion conduction. Silica tetrahedra "rings" and sodium and heavy metal ions form the structure around these channels, which are filled with highly mobile sodium ions. The primary NaSICON compositions that have been investigated are based on rare earth (RE) ions (i.e., $Na_5RESi_4O_{12}$).

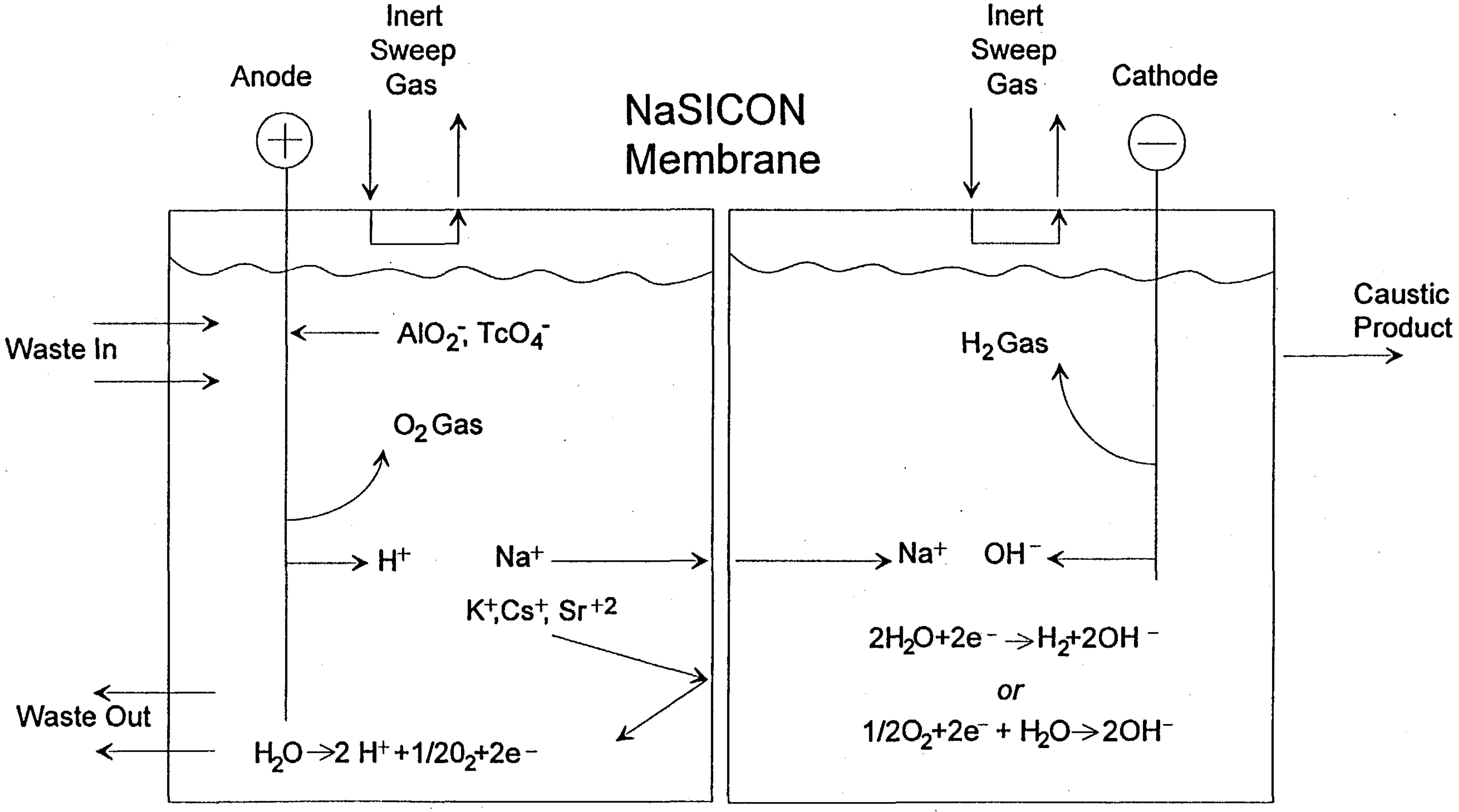

Figure 1.1 Schematic of an Electrochemical Process Using the NaSICON Membrane

1.3 Report Objective and Scope

This report presents two preconceptual designs for a full-scale salt splitting process based on the RE-NaSICON ceramic membranes to distinguish critical items for testing and to provide a vision that site users can evaluate. Critical test items include those associated with the manufacturing process, implementation of the ceramic membranes into an electrochemical cell, and process applications. Potential applications considered in this report include treating the tank wastes at Hanford, the Savannah River Site (SRS), and the Idaho National Engineering Laboratory (INEL).

Since ceramic membranes have not been widely implemented in electrochemical cell designs, this preconceptual design effort is focused on the electrochemical cells. Limited attention is given to designing the balance of the plant (lag storage, offgas treatment, etc.) except where these issues appear critical to implementing the process (for example, mitigating potentially flammable gas mixtures that could be generated as a result of the electrolysis of water).

1.4 Project Objective, Strategy, and Approach

The overall project objective is to supply a salt splitting process unit that impacts the waste treatment and disposal flowsheets and meets user requirements. The potential flowsheet impacts include improving the efficiency of the waste-pretreatment processes, reducing volume, and increasing the quality of the final waste disposal forms. Meeting user requirements implies developing the technology to the point where it is available as standard equipment with predictable and reliable performance.

A phased approach to the implementation of this technology is being used. In Phase I applications, limited amounts of sodium would be separated for onsite recycle. These applications present limited but significant technical challenges in which only alkaline waste solutions (i.e., pH>12) need to be processed after radionuclide decontamination (low radiation). These solutions contain low quantities of suspended solids. Phase II applications present an expanded set of technical challenges that includes processing acidic solutions, processing solutions before radionuclide decontamination (high radiation); processing slurries containing a high concentration of solids, and separating a large fraction of the sodium while producing a nonradioactive caustic product.

A large number of electrochemical cell designs have been developed for a host of applications, and extensive use of this body of knowledge has been made. Industries that are especially relevant to this project include 1) the chlor-alkali industry where caustic is produced in a divided electrochemcial cell, 2) the nuclear industry where heavy water and tritium-containing water are electrolyzed, and 3) multiple industries using chromium where divided flow-through concentric cylindrical cells may be used in electrodialysis for combined Cr(III) oxidation and cation removal. This is used to treat liquors containing dissolved chromium.

2.0 Design Requirements

2.1 Applications and Design Basis

A number of applications at Hanford, INEL, and SRS have been considered in developing the design requirements for the salt splitting process (Table 2.1). To perform these functions, it is possible that the system may be operated in three modes corresponding to the solutions in the anode compartment: 1) alkaline ($pH>12$) in which no aluminum hydroxide {$Al(OH)_3$} will precipitate, 2) neutral ($3<pH<12$), in which significant amounts of aluminum hydroxide will precipitate, and 3) acidic ($pH<3$) in which no aluminum hydroxide will precipitate. In all three operational modes, alkaline waste will be added to the anode compartment. The primary focus of the preconceptual design will be on the Phase I application, which is the recovery of caustic for recycle within the DOE complex with the cell operating in Mode 1 (anolyte $pH > 12$).

The average compositions of various tank waste feeds to the electrochemical cells are shown in Table 2.2. These average compositions have been developed from site flowsheets. The inventories for Hanford are from Orme (1995). The composition of the caustic recycle stream is based on inventories from stream 233, which is a low-level-waste vitrification feed (after ^{137}Cs is removed). The composition of the pH adjustment stream is based on stream 205, which is a cesium ion exchange feed. The composition of the two streams is very similar with the exception of cesium, which is assumed to be removed by ion exchange using a regenerable resin. The processing rates of the Hanford streams are based on a total processing time of 14 years with a total operating efficiency of 60%. The composition of the SRS waste stream is based on stream # 407 (decontaminated supernate) from Appendix G, Table 19-2 (SRS 1984). This is the stream composition after cesium has been removed by in-tank precipitation with tetraphenyl boron. The composition of the INEL waste stream is a projection of newly generated waste and is based on SBW 2008 flowsheets(a). The processing rates given in gallons per minute (gpm) for SRS and INEL are based on the annual processing rate and a total operating efficiency (TOE) of 60%.

(a) Personal communication with R.D. Boardman, based on SBW 2008 flowsheets (1995).

Table 2.1 Applications

Application	Sites	Na Source	Comments
Phase I Applications			
Caustic Recycle	Hanford	Tank Waste Supernatant and Sludge Wash Solutions	pH range >12
	SRS	Tank Waste Supernatant and Sludge Wash Solutions	pH range >12
Phase II Applications			
Caustic Recycle	Hanford	Tank Waste Supernatant and Sludge Wash Solutions	pH range = $0 < pH < 14.5$
	SRS	Tank Waste Supernatant and Sludge Wash Solutions	pH range = $0 < pH < 14.5$
	INEL	Sodium Bearing Waste	pH range = $-0.3 < pH < 14.5$
Feed Adjustment for Ion Exchange	Hanford	Tank Waste Supernatant and Sludge Wash Solutions	pH range = $0 < pH < 14.5$ high gamma radiation fields from ^{137}Cs
Sodium Reduction in high-level waste (HLW) Sludge	Hanford, SRS	Leached Sludge	Large concentrations of sludge solids

Table 2.2 Average Composition of Aqueous Tank Waste

	Phase I		Phase II	
	Hanford Caustic Recycle Stream 233 (Orme 1995)	SRS stream 407 decontaminated supernate	Hanford pH adjustment for cesium ion exchange Stream, 205, (Orme 1995)	INEL SBW 2008 Flowsheets
Total Volume, L	6.78E+08	–	6.74E+08	–
Processing Rate	154 L/min (40.6 gpm) @TOE=60%	1.78E+07 L/yr (4.7E+06 gal/yr) or 56.47 L/min (14.9 gpm) @TOE=60%	154 L/min (40.6 gpm)	3.8E+06 L/yr (1E+06 gal/yr) or 12.13 L/min (3.2 gpm) @ TOE=60%
Sodium, megaton (MT)	7.8E+04	–	7.75E+04	–
Cations, M				
Al^{3+}	≈0	≈0	≈0	0.639
Ba^{2+}	8.5E-06	1E-04	8.6E-06	6.1E-05
Bi^{3+}	8.3E-05	ND	8.4E-05	ND
Ca^{2+}	6.1E-04	1.9E-05	6.1E-04	5.3E-02
Cd^{2+}	1.0E-04	≈0	1.0E-04	2.8E-03
Ce^{2+}	2.5E-05	≈0	2.5E-05	ND
Cr^{3+}	≈0	≈0	≈0	3.7E-03
Cs^{+}	4.6E-07	6.85E-10	2.1E-05	1.1E-05
Fe^{2+}	3.1E-08	≈0	3.2E-08	ND
Fe^{3+}	9.1E-04	≈0	9.1E-04	2.2E-02
H^{+}	≈0	≈0	≈0	1.57
Hg^{2+}	4.3E-07	2.24E-07	4.3E-07	1.1E-03
K^{+}	2.7E-02	≈0	2.7E-02	2.0E-01
La^{3+}	2.52E-06	≈0	2.52E-06	ND
Mn^{2+}	1.3E-09	≈0	1.3E-09	1.22E-02
Mn^{4+}	2.9E-04	≈0	2.9E-04	ND
Na^{+}	5.00	4.3	5.00	1.89
Ni^{2+}	ND	≈0	ND	1.6E-03
Ni^{3+}	2.1E-04	≈0	2.1E-04	ND
Pb^{2+}	ND	≈0	ND	1.4E-03

	Phase I		Phase II	
Pb^{4+}	6.8E-05	≈0	6.9E-05	ND
Rb^{+}	4.1E-09	≈0	4.2E-09	ND
Si^{4+}	8.4E-04	3.8E-03	8.4E-04	ND
Sr^{2+}	6.4E-06	7.5E-11	6.4E-06	5.1E-06
UO_2^{2+}	6.6E-04	4E-07	6.6E-04	ND
ZrO^{2+}	ND	ND	ND	2.9E-03
Anions, M				
$Al(OH)_4^-$	1.9E-01	0.31	1.9E-01	≈0
BO_3^{3-}	ND	ND	ND	1.8E-02
Cl^-	2.8E-02	2.19E-02	2.8E-02	2.9E-02
CO_3^{2-}	6.6E-02	1.64E-01	7.7E-02	≈0
$Cr(OH)_4^-$	8.3E-03	3.29E-03	8.4E-03	≈0
F^-	8.9E-02	1.49E-02	8.9E-02	6.9E-02
NO_2^-	3.1E-01	0.598	3.1E-01	ND
NO_3^-	2.52	1.95	2.54	5.51
OH^-	1.75	1.34	1.72	≈0
PO_4^{3-}	7.1E-02	8.55E-03	7.1E-02	1.4E-02
SO_4^{2-}	3.1E-02	0.14	3.1E-02	5.0E-02
TOC,gmole C/L	1.3E-01	0.11	1.3E-01	-
Radionuclides				
^{90}Sr, Ci/m^3	2.8	ND	2.8	ND
^{99}Tc (TcO_4^-), Ci/m^3 (M)	3.4E-2 (2.02E-05)	ND	3.4E-2 (2.02E-05)	ND
^{137}Cs, Ci/m^3	1.0	ND	47	ND
^{241}Am, Ci/m^3	1.2E-02	ND	1.2E-02	ND
^{239}Pu, Ci/m^3	2.4E-03	ND	2.4E-03	ND
^{241}Pu, Ci/m^3	7.1E-03	ND	7.1E-03	ND

ND = No Data

2.2 Flowsheets: Material and Energy Balances - Phase I

Two flowsheets are presented in the section dealing with Phase I applications at Hanford and SRS.

2.2.1 Hanford Site

Figure 2.1 shows a number of overall process parameters for caustic recycle at the Hanford Site after removing ^{137}Cs. It is assumed that the waste currently in the Hanford single and double shell tanks will be diluted to a sodium salt concentration of 5 M during retrieval and transport. The processing rate is based on the estimated site inventory and waste pretreatment requirements (Orme 1995) and a 14-year processing period. The flowsheet assumes that all of the available caustic (defined as the caustic above the amount required to maintain a pH of 12) is separated from the waste. The concentration of the caustic product is assumed to be 3 M and is consistent with planned applications. The amount of cooling required is based on the assumption that the electrochemical cells will operate at 5 V and that 3 of the 5 V will have to be removed as heat. The other 2 V will be consumed by cell reactions. The current requirements are estimated assuming a sodium transport efficiency of 95% (defined as sodium ions transported per electron transferred). The hydrogen generation rate is determined by assuming that electrolysis of water is the only cathode reaction. The volume of sweep gas is based on limiting the hydrogen concentration to 1% (25% of the lower flammability limit [LFL]). The estimated generation rate of oxygen at the anode is much smaller because it is assumed that a number of other oxidations occur preferentially to the electrolysis of water. These reactions include the oxidation of nitrite to nitrate, the oxidation of organics to carbonate, and miscellaneous metal species to higher oxidation states. The required membrane area is based on an assumed current density of 750 A/m^2. Approximately 30% of the sodium can be recovered from the waste as caustic for recycle.

2.2.2 Savannah River Site

Figure 2.2 shows a number of overall process parameters for caustic recycle at SRS after radionuclide decontamination. The assumed feed characteristics are given in Table 2.2. The flowsheet assumes that all of the available caustic (defined as the caustic above the amount required to maintain a pH of 12) is separated from the waste. The concentration of the caustic product is assumed to be 3 M. The amount of cooling required is based on the assumption that the electrochemical cells will operate at 5 V and that 3 of the 5 V will have to be removed as heat. The other 2 V will be consumed by cell reactions. The current requirements are estimated assuming a sodium transport efficiency of 95% (defined as sodium ions transported per electron transferred). The hydrogen generation rate is determined by assuming that electrolysis of water is the only cathode reaction. The volume of sweep gas is based on limiting the hydrogen concentration to 1% (25% of the LFL). The estimated generation rate of oxygen at the anode is much smaller because it is assumed that a number of other oxidations occur preferentially to the electrolysis of water. These reactions include the oxidation of nitrite to nitrate and miscellaneous metal species to higher oxidation states. The required membrane area is based on an assumed current density of 750 A/m^2.

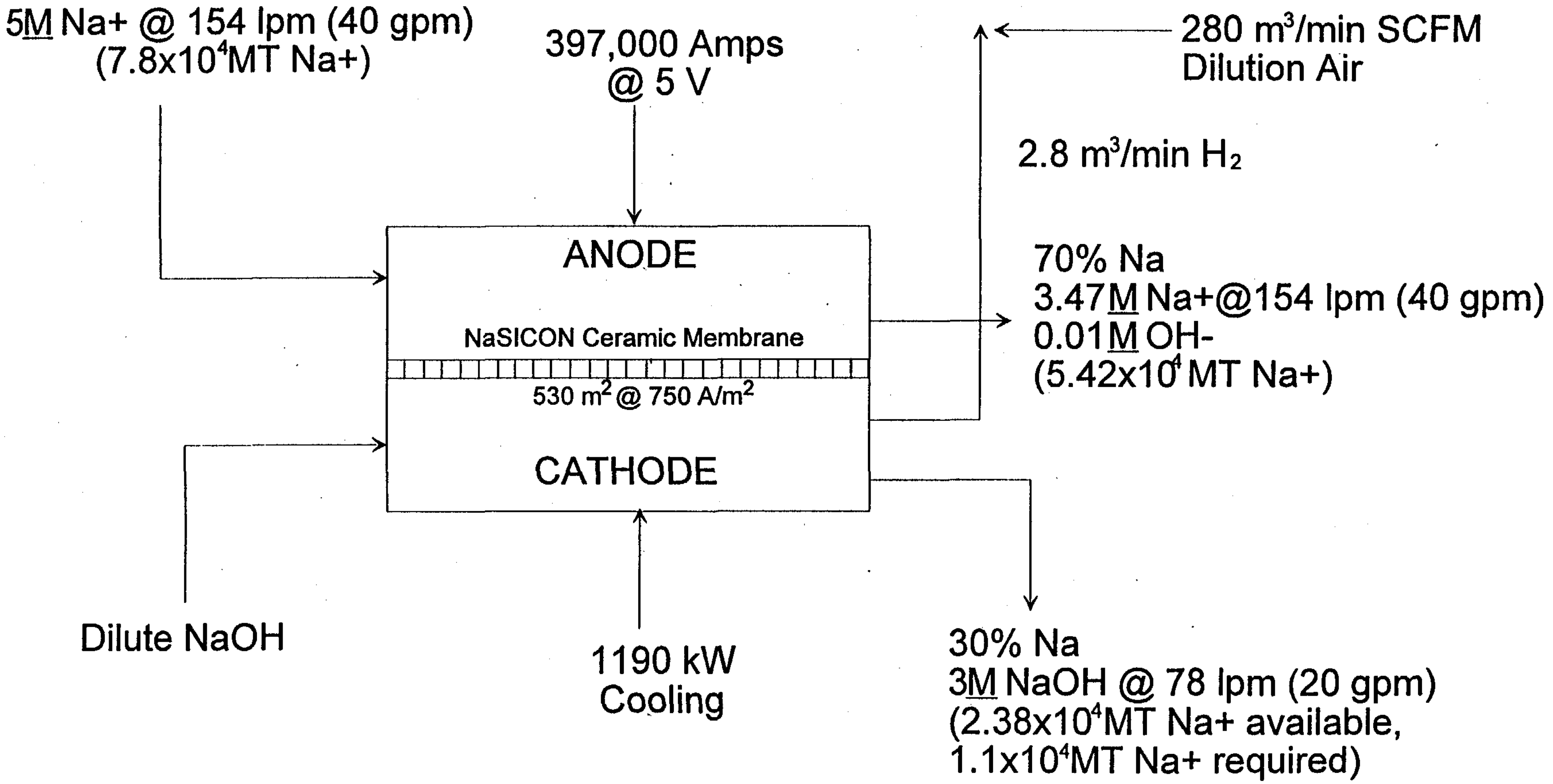

Figure 2.1 Caustic Recycle at Hanford - Phase I

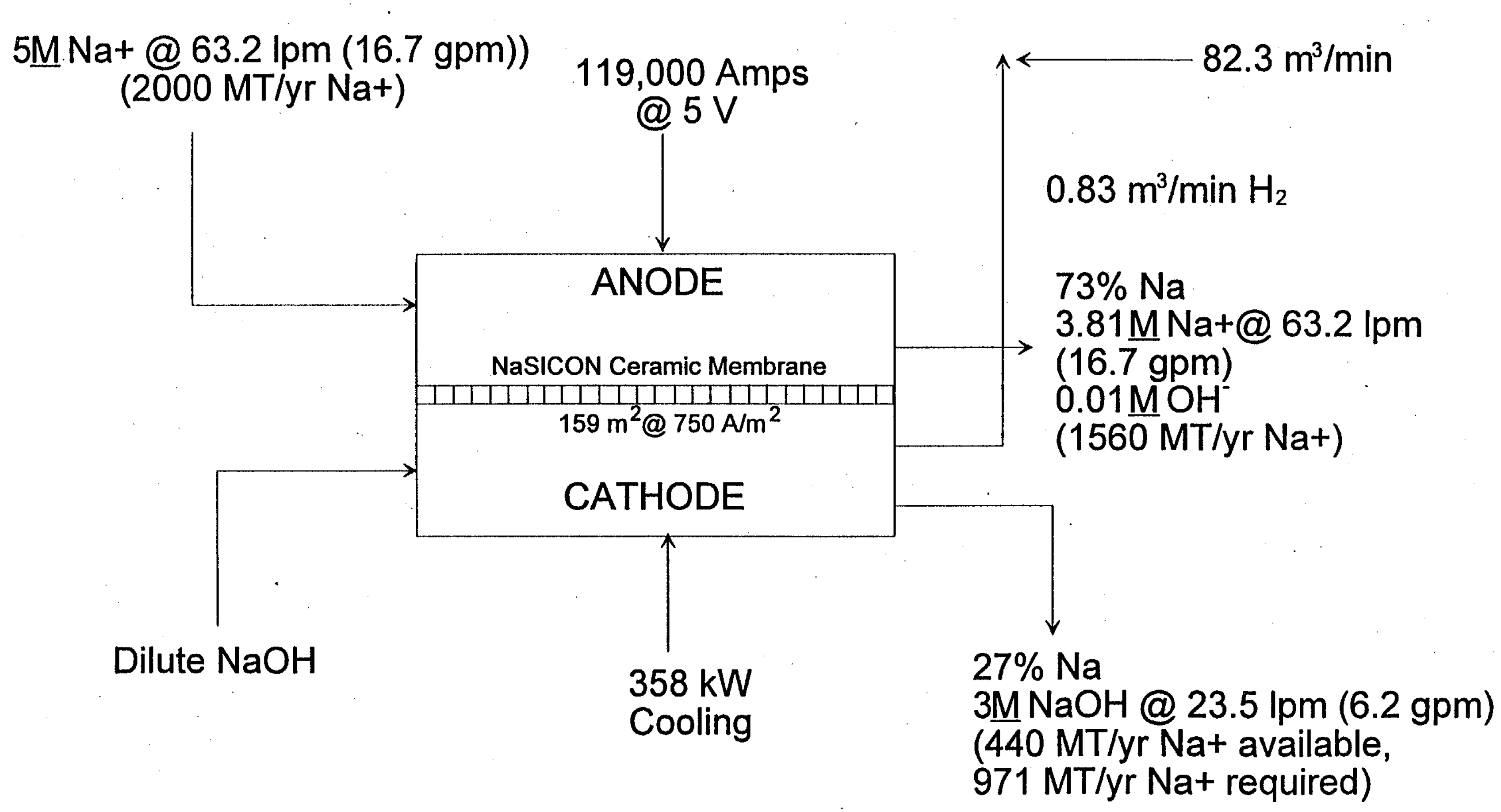

Figure 2.2 Caustic Recycle at SRS - Phase I

2.3 Electrochemical Cell and System Design Requirements

This section contains a discussion of the design requirements considered during the development of the preconceptual design. The requirements are presented in two sections representing Phase I and Phase II of the implementation strategy.

Phase I

- The electrochemical cells and supporting process equipment shall
  - be sized to provide the processing rates specified for Phase I in Table 2.2 for each site. The cells shall operate at a nominal current density of 750 A/m^2 of the membrane.
  - produce 3 $\underline{M}$ caustic at production rates necessary to meet the needs of each site. The selectivity of the process shall be such that less than 1% of the aluminum in the feed will be transported to the product. The required radioactivity level will depend on the use of the recycled caustic and will probably be site dependent. It is desirable to produce caustic that contains a minimum of radioactivity to minimize safety and environmental concerns.
  - maximize the selectivity for sodium relative to other components
  - maintain the concentration of potentially flammable gases below 25% of the LFL. For hydrogen in air, the LFL is defined as 4% hydrogen.
  - accommodate disassembly, repair, and maintenance in a remote (i.e., shielded and not hands-on) environment. While Phase I applications are not expected to be very radioactive and may allow contact maintenance, the system will probably have to be designed for remote operation in case a process upset severely contaminates the unit. The system may be very radioactive for Phase II applications.
  - be designed to minimize maintenance requirements by using corrosion-resistant materials and minimizing moving parts
  - be designed to be as compact as possible within the constraints of the other requirements (much of the capital cost of a radioactive facility is due to hot cell space requirements defined by the equipment and processes they contain)
  - be designed to minimize the total mass and the mass of individual components for maintenance purposes
  - where significant voltages exist (i.e., > 15 V), the system should be insulated to eliminate electrical shock hazard
  - maintain the cell temperature between 30°C and 50°C at all expected operating conditions (this temperature range is a compromise between the cell conductivity, which goes up as temperature increases, and the corrosion rate of cell components, which increase with temperature)
  - be designed to accommodate easy decontamination and decommissioning
  - be designed to accommodate on-line automated process control.

- The materials of construction shall be
    - resistant to corrosion while in contact with tank waste compositions with pH values that range from 12 to 14.5 ($0.01\ \underline{M} < [OH^-] < 5\ \underline{M}$)
    - resistant to radiation to 10^6 Rads (this value is a conservative quantity [i.e., high] based on an assessment of the likely dose that cell components would receive over the 14-year processing time; it is assumed that most of the ^{137}Cs would be removed before the caustic recovery process)
    - non-hazardous materials within the constraints of the other requirements (hazardous materials, such as lead electrodes for cell fabrication, will be minimized to avoid the generation of hazardous and mixed wastes).

Phase II

- The electrochemical cells and supporting process equipment shall
    - meet all Phase I requirements
    - meet increased processing rates (processing rates are likely to be greater for Phase II applications as the volume of recoverable caustic increases, but treatment time is expected to remain constant)
    - provide caustic of sufficient purity that it may be released for unrestricted use (offsite release criteria will have to be developed for this to become possible [IT Corporation 1995])
    - handle solids that will originate from the precipitation of aluminum hydroxide and other sludge components and allow the processing of HLW slurries
    - operate continuously at 2000 A/m^2, based on the membrane area available for sodium conduction.
- The materials of construction shall
    - meet all Phase I requirements
    - be resistant to corrosion while in contact with tank waste compositions with pH values that range from -0.3 to 14.5 (i.e., $2\ \underline{M}\ H^+$ to $5\ \underline{M}\ OH^-$).
    - be resistant to radiation to 10^9 Rads (this value is based on a 14-year-lifetime processing feed that still contains ^{137}Cs; practically, this means minimizing and probably eliminating organic materials from the design).

3.0 Preconceptual Design Based on Flat Plates

Two preconceptual designs for a full-scale salt splitting process based on ceramic membranes are presented in this report. The reference design, which is most appropriate for Phase I applications, is based on a flat-plate geometry using ceramic disks. An alternative design, based on ceramic tubes (see Section 4), is more robust and appropriate for all applications.

The flat-plate geometry was chosen as the reference design for two reasons. First, the fabrication of flat ceramic membrane shapes is more advanced than the fabrication of tubes. Second, the parallel-plate geometry is widely used in industry and is well accepted; therefore, several commercial cells are available.

3.1 Overview of Flat-Plate Design

The flat-plate cell design uses the ElectroProd Cell, which is an industrial-sized plate-and-frame electrochemical cell from ElectroCell AB (Figure 3.1). These cells use electrodes with a surface area of 0.4 m^2 with up to 40 electrode pairs per cell stack. To utilize the NaSICON membranes in these cells, 25 ceramic disks (12.7 cm [5 in.] diameter) will be mounted inside a single plastic scaffolding. These scaffolds will be sandwiched between pairs of electrodes. Only the scaffolding will be custom-built. All other necessary parts, including the frame, gaskets, spacers, turbulence promoters, and electrodes, are standard cell items. To prevent leakage between the anode and cathode compartments, ethylene-propylene-diene monomer (EPDM) O-rings will be used to seal the ceramic disks in the scaffolds. Platinized titania will be used for the anode and nickel for the cathode. The electrodes will be connected in a monopolar configuration. The waste will be processed in a batch recycle mode in which a pump will recirculate batches of waste supernate through the anode compartment and back into the feed tank until specified conditions are reached. Similarly, caustic product will be recirculated through the cathode compartment. The recirculation tanks will also allow for gas-liquid separation. The temperature will be maintained between 30°C and 50°C using heat exchangers.

3.2 Selection of Flat-Plate Cell Configuration

Several electrochemical cell configurations could potentially use flat plates: plate-and-frame, tank cell, natural gas lift recycle, and dynamic systems. These will be discussed below.

Most industrial flow cells are constructed in a plate-and-frame arrangement and mounted in a filterpress. The electrodes, electrolyte chambers, and separators are constructed individually and mounted with suitable gasketing materials between each component. The electrodes are generally separated by only a few millimeters. Using this configuration, the anode and cathode are the same size. Thus the potential distribution and current density are reasonably uniform.

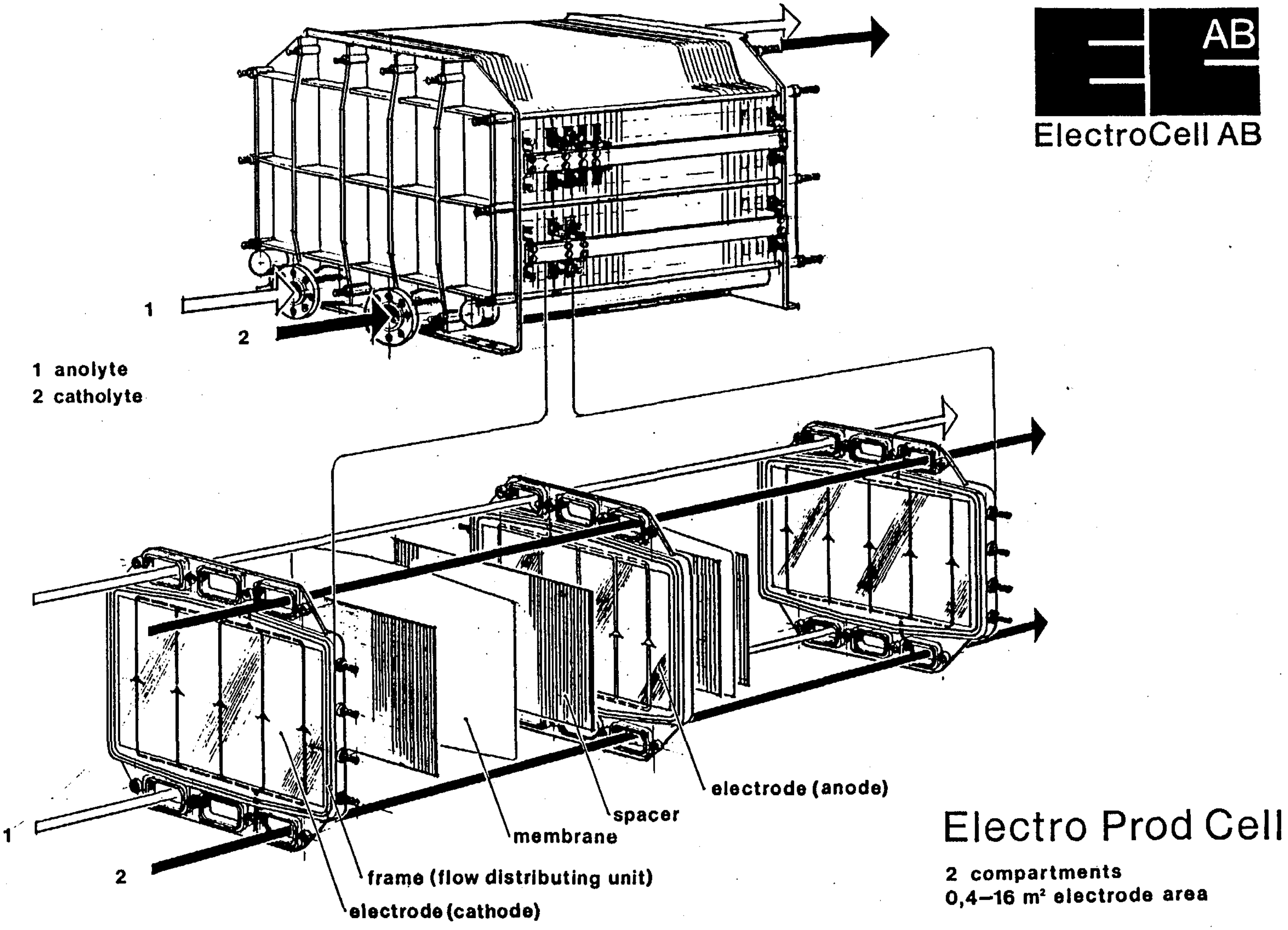

Figure 3.1 The Electro Prod Cell from ElectroCell AB (Taby, Sweden)

The tank cell configuration is simple in construction and inexpensive to manufacture. It is used in the electroplating, electrowinning, and battery industry (Walsh 1993). In this configuration, electrically charged plates are generally placed in a single electrolyte solution. Because of the potential for high bypass currents, the electrodes are connected in a monopolar configuration. Such systems are not generally meant for sealed compartments as required for this design. If the anode and cathode must be sealed using flat-plate ceramics, this option loses its simplicity and provides little advantage over the plate-and-frame arrangement.

Dynamic systems, such as a rotating disk (pump cell), increase the rate of mass transfer to the electrodes. While these cells are well established as laboratory tools, they are viewed as an unproductive complexity for this design. The rate-limiting step is the sodium conduction through the membrane, so improvements in mass transfer between the electrodes and membrane would provide little benefit. Moving electrodes would only add potential maintenance problems. The natural gas lift cell provides recirculation in the cells without pumping (Borrione and Ottaviani 1992). It also provides a means to recover the hydrogen and oxygen. It is based on the principle that the two-phase mixture (liquid with gas bubbles) is less dense than the liquid alone. The liquid in the electrochemical cell will flow upward because of gas generation; liquid in a column of equal height outside the cell will flow downward. Gas separators are on top of the electrochemical cell. The gas is removed, and the bulk of the liquid is recirculated. The liquid level is controlled by a weir. The flow rate increases with current density. This design is attractive for radioactive applications because the pumps (high maintenance items) can be eliminated. The plate-and-frame configuration is considered as the best option for the ceramic flat plates because of its wide industrial acceptance and commercial availability. It is the workhorse of the chlor-alkali industry as well as being a common and simple bench-scale design tool. Plate-and-frame cells provide a relatively large surface area in a small footprint. In these systems, scale-up can be achieved by increasing electrode size or simply adding more electrodes.

While flat-plate systems possess numerous advantages, one significant concern remains. The cells rely on gaskets and O-rings to prevent solution leakage between compartments and out of the cell. Since a system has hundreds of compartments, sealing becomes a critical issue. This design attempts to address these concerns.

3.3 Commercially Available Cell Selected

The commercially available ElectroProd Cell produced by ElectroCell AB (Taby, Sweden) was used for this design because it is a production-size unit. ElectroCell also produces a laboratory-scale system (the Electro MP cell) cell with an electrode area of 100 cm^2 that is available onsite for feasibility testing. By using a commercially available cell, most of the critical parts and systems have been previously designed and tested. For example, the cell provides a system of flow to the individual cells and the distribution of flow inside the cells (both significant engineering concerns).

The ElectroProd Cell has an electrode area of 0.4 m^2 with as many as 40 electrode pairs per stack (see Figure 3.1). In a two-compartment system, this is a maximum electrode area of 16 m^2. The maximum recommended current density is 4000 A/m^2 of membrane area, although this application is based on 750 A/m^2. A module can have flow rates between 10 and 600 liters per minute (L/min). Since these cells are used in the chlor-alkali industry, commercial materials exist that will be chemically compatible with the waste composition (See Section 3.5, "Materials of Construction"). The cell stacks will be operated in a batch-recycle mode. The supernatant (anolyte) and caustic solutions (catholyte) will be recirculated between their respective holding tanks and the cells to facilitate removal of electrolytic gases and improve mass transfer rates.

Based on caustic recycle at the Hanford Site discussed in Section 2.2, if the system were operated at a current density of 750 A/m^2 with a feed flow rate of 154 L/min (40.6 gpm) and current efficiency of 95%, a 530 m^2 membrane area would be required to process the supernatant. The design basis NaSICON disk size is 12.7 cm (5 in.) diameter. To achieve the required area for processing at this rate, 46,300 disks would be required. To accommodate these disks, scaffolds containing 25 disks will replace the standard organic membranes commonly found in the ElectroProd cell (See Figure 3.2). Each stack in turn can hold 40 scaffolds. Therefore, 46 cell stacks would be required to provide the necessary surface area.

3.3.1 Design of the Scaffolding

Since a commercially available plate-and-frame cell was selected and has been previously developed and operated, most components do not need to be discussed here. The primary concerns with this configuration are the scaffolding and ceramic plates and the method of holding these plates in place during operation without leakage.The design basis size for the NaSICON plate is 12.7 cm (5 in.). The reason for this limit is twofold. First, the ceramic membranes are fragile. Even small differential pressures between the anode and cathode could fracture larger membranes. By making the plates small, the force on any given plate is reduced. Second, the 12.7-cm plates are within the industrial base for standard uniaxial pressing. Larger plates would require extremely large presses, and it would be difficult to ensure the homogeneity (density gradients and cracking) of the plates.

Two NaSICON plate shapes were considered for study: the round disk and the square plate. The round disk has 21.5% less area (a disadvantage—more unused surface area in the electrochemical cell) than the square flat plate, but it has a 21.5% decrease in circumference length (an advantage—less sealed length). The round disks have one real advantage: they will not have uneven mechanical stress concentrations on their corners as are found in square plates, thus reducing the possibility of breakage while providing a more uniform sealing pressure around the edges.One scaffold will consist of two 6.3-mm (1/4-in.) plastic sheets. The sheets will be machined to allow the NaSICON disks to be firmly held between the sheets while exposing 12 cm (4 3/4 in.) to the anolyte and catholyte solutions (See Figure 3.3). The disks will be arrayed on the scaffolds as closely as possible while still allowing space to attach the two scaffolds together. To seal around each disk, O-rings will be used on both sides of the ceramic. The two plastic sheets will be attached, and each O-ring will be compressed with six 5-mm-diameter x 7-mm-long (3/16-in. x 7/16-in.) plastic screws. These screws will penetrate one of the scaffold sheets and screw into the second scaffold sheet 5 mm (3/16 in.), but will not penetrate completely through it, ensuring that no leakage occurs through the screw holes. With the scaffolding, flow distributors, and ceramic membrane, the electrode gap will be approximately 25 mm. This is considerably larger than most other electrochemical cells (1 to 4 mm for the ElectroProd) that typically used thin organic-based membranes. However, the ceramic membrane (2.7 mm) itself is roughly 10 times thicker than a typical Nafion membrane (250 microns). In spite of the large gap, because of the high conductivity of the anolyte and catholyte, most of the voltage drop in the cell will be across the ceramic membrane. Therefore, this gap should not be a significant problem.

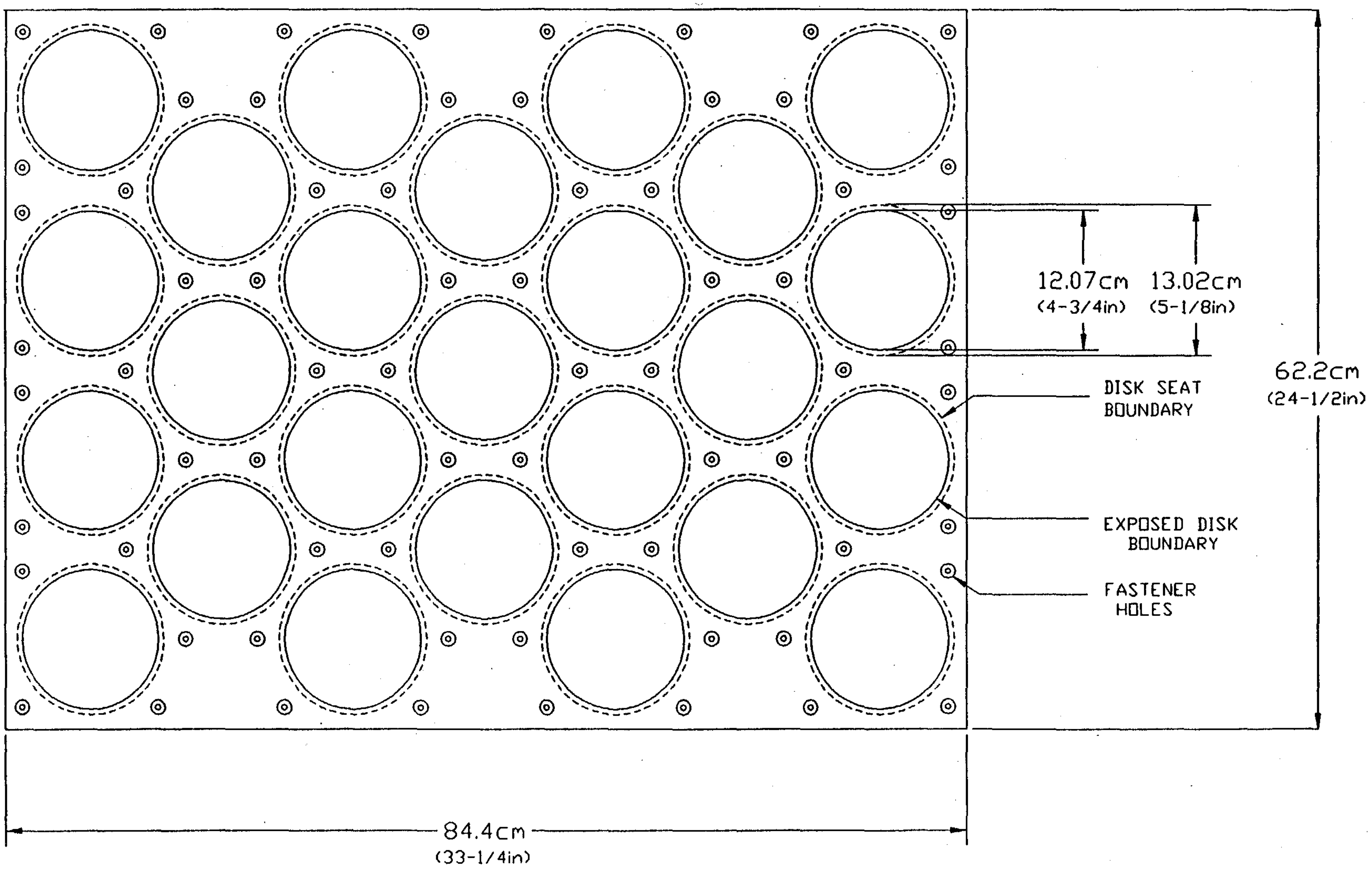

Figure 3.2 Design of the Scaffolding to Implement 12.7-cm (5-in.) NaSICON Disks into the Electro Prod Cell. The ceramic disks are sandwiched between two of the above plastic scaffoldings.

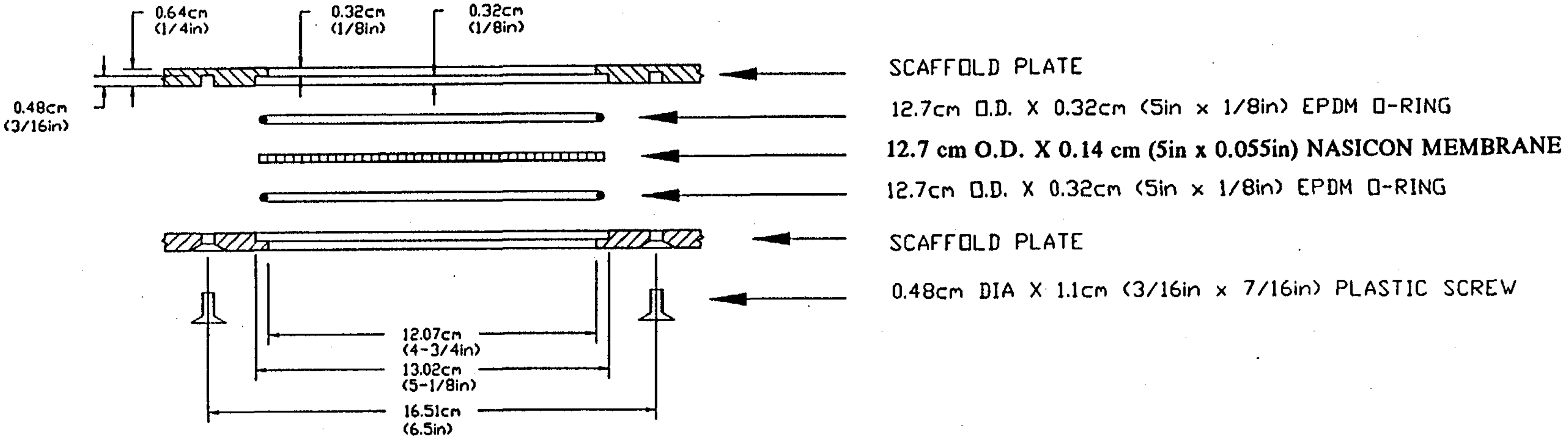

Figure 3.3 Exploded View of the Scaffolding Assembly

3.3.2 Electrodes and Electrical Connections

Electrodes must have adequate mechanical strength, be resistant to corrosion, have a high electrical conductivity, and achieve a high reaction rate at a low overpotential (Walsh 1993). The simplest electrode is a single metal, homogeneous plate. To improve the surface characteristics while still providing the electrical and mechanical properties of the electrode, very thin surface coatings are often used. Platinized titanium is one such example. To increase the electrode surface area, porous or mesh electrodes may be used. These types of electrodes are desirable if the process is limited by a reaction at the electrode surface. For our particular application, the rate-limiting step is associated with the NaSICON disk where sodium ions are being transported across the membrane. Therefore, porous electrodes will not be used to increase reaction rates. Furthermore, porous electrodes have disadvantages of high pressure drop and plugging, which may be a concern in processing waste supernates. A porous electrode may be considered for the cathode if a gas-diffusion electrode is used (see Section 5.3).

The cell will be constructed in the monopolar design in which each cell's anode and cathode will be connected to the appropriate polarity of the power supply. The monopolar design was chosen because of its increased simplicity of construction and operation (Ross 1990). The cell configuration is shown in Figure 3.4. As a monopolar cell, the cathodes are surrounded on both sides by catholyte solutions. Similarly, the anodes have anolyte solutions on both sides. Therefore, different coatings are not required on each side of the electrodes as in the bipolar design. In the monopolar design of the Electroprod cell, the electrical connectors attach to the side of the cell (See Figure 3.1).

In the chlor-alkali industry, busbars are generally constructed from copper or aluminum because of their exceptional conductivity. In most cases, aluminum is preferred. To prevent their corrosion, these metals are coated with epoxy and nickel plated at contact surfaces (Walsh 1993). Quick-release contacts and flexible cables to the cell have been used to facilitate maintenance. These will be used in the radioactive environment. One possible option being considered is a plutonium uranium extraction (PUREX) connector (a crane-remotable connection generally used for piping) to connect and disconnect the busbars.

3.4 Balance of Process

The balance of the process discussed below includes tankage, cooling system, power requirements, and gas separations. Table 3.1 shows operating characteristics and parameters for the system. Figure 3.5 provides a flow diagram of the process. Both the waste (anolyte) and the recycled caustic (catholyte) will operate as in a batch-recycle mode. Batches of waste will be transferred to a tank and then recirculated through the electrochemical cells until specific criteria are met (probably pH). The spent solution will be transferred out of the tank and a new batch received. Table 3.1 provides the "Dimensions" of the system, which include only the electrochemical cells themselves, each with approximately 40 scaffolds. The footprint, on the other hand, includes space for required tankage (18,950 L [5000 gal] supernate tank and 7580 L [2000 gal] catholyte tank), pumps, piping, electrochemical cells, power connections, etc. It is assumed that the electrochemical cells would be separated by 1 m on all sides and that the associated equipment would require 30 m^2 for a total area of 280 m^2.

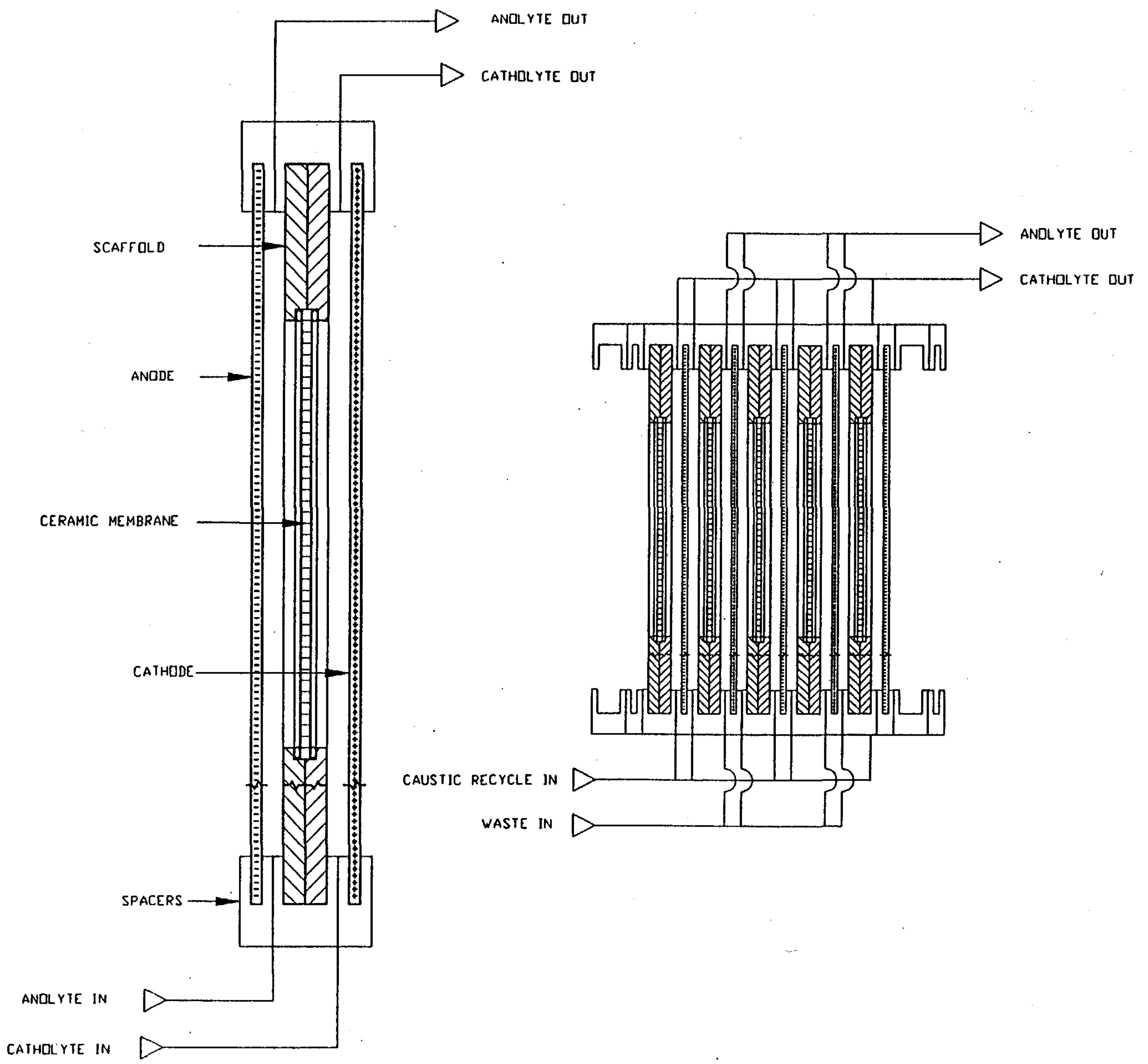

Figure 3.4 Cell Configuration Using Flat Plates Based on a Scaffolding and Monopolar Design

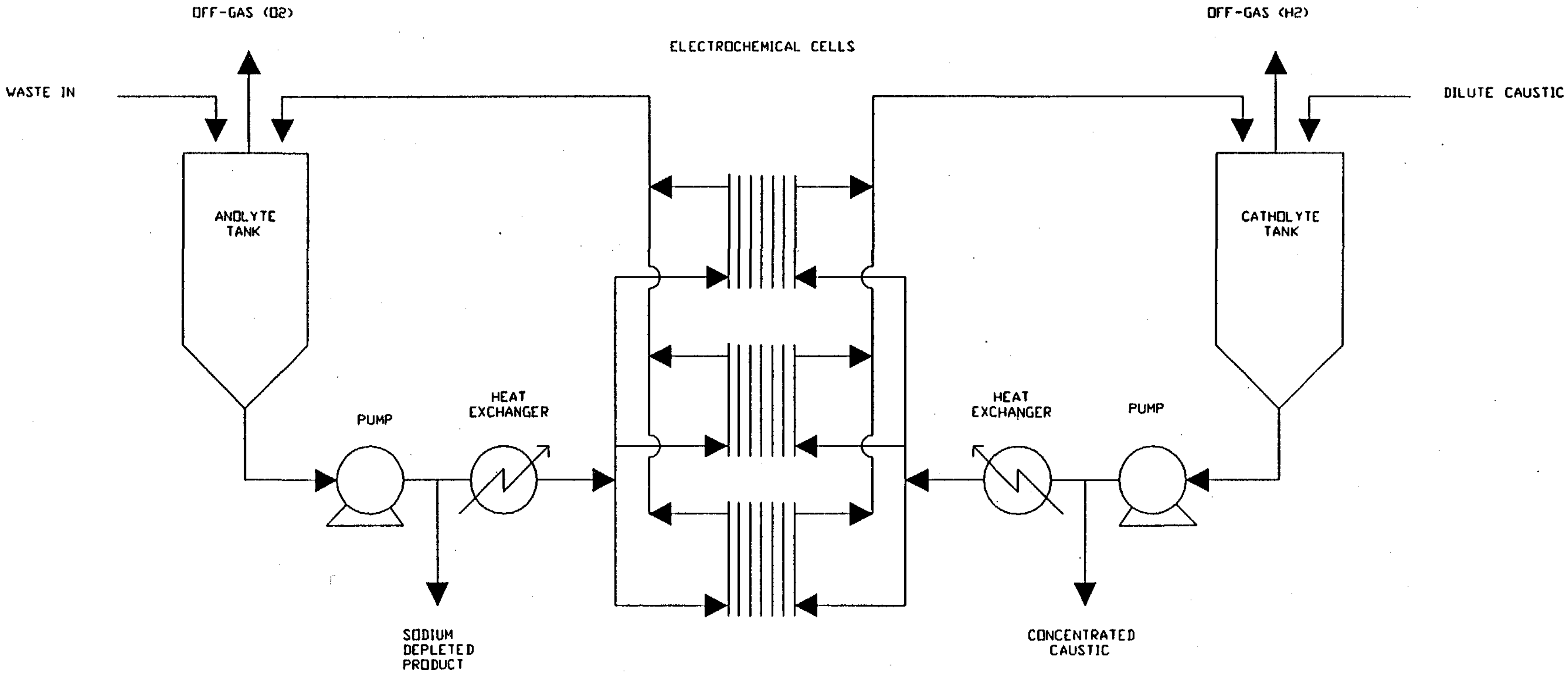

Figure 3.5 Process Flow Diagram Based on a Semi-Batch Configuration

Table 3.1 Operating Characteristics and Parameters: Caustic Recycle at Hanford, Flat Plate

Characteristic	Scaffold	Cell Stack	Total
Number of 12.7-cm (5-in.) Ceramic Disks	25	1000	46,300
Number Required	1850	46	NA
Amperage (A)	215	8630	397,000
Power Requirements (kW)	1.1	43	1980
Cooling Requirements (kW)	0.65	26	1190
Minimum Cooling Flow Rate (L/min)	0.93	37	1700
Hydrogen Generation Rate (L/min)	1.5	60	2760
Dimensions (H, L, W) (m)	0.85 x 0.62 x 0.025	1.03 x 1.52 x 1.16	NA
Footprint (L, W) (m)	NA	NA	280

3.4.1 Cooling System

Each cell will be operated at 5 V. Approximately 2 V will be used for electrochemical water-splitting, and the remaining 3 V will result in resistive heating. Overall, the cells will produce 1.2 megawatts (MWs) of heat, which must be dissipated. Although the ElectroProd cell has the capability of internal cooling, for simplicity and to reduce the size of the stacks, the cooling will occur in a separate heat exchanger in the recycle loop, and the solution will be allowed to heat while in the cells. Since the optimum processing temperature is between 30°C and 50°C, the maximum temperature rise in the cells will be limited to no greater than 10°C. To achieve this limited temperature rise inside the electrochemical cell, the flow rate in the cells must be greater than 0.93 L/min per scaffold or 37 L/min per stack (the sum of the catholyte and anolyte flow rates). This flow rate that allows the solution to heat up by 10°C while in the cell is less than the specification flow rate for the ElectroProd Cell, suggesting that this approach is feasible.

3.4.2 Gas Separation

During operation, hydrogen will be generated in the cathode, and oxygen will be generated in the anode. The cells run upflow to ensure that the gases are swept out of the cell. These gases will then be separated from their respective solutions in the recirculation tanks. The tanks should be located near the cell stacks and routed such that gas pockets could not form in the piping. Methods of mitigating the hydrogen-generation concern is discussed in Section 5.0.

3.4.3 Power Requirements

Since the cells will be operated in the monopolar arrangement, AC voltage will be rectified from 440 VAC or higher to 5 VDC. The current requirement for the entire system will be 397,000 amps. Each scaffold system will require 1.1 kW, and a cell stack will require 43 kW of power. Power requirements to the facility will be greater because of inefficiencies associated with the rectifier.

3.5 Materials of Construction

All materials in the electrochemical cell must be stable over a temperature range of 20 to 60 °C and provide chemical resistance to the composition in the tank supernate. Based on conservative calculations, the materials will experience 10^6 Rad accumulated dose over the lifetime of the equipment (15 years). The requirements for specific materials in the plate-and-frame cell are shown in Table 3.2.

3.5.1 Gasket/O-Ring Material

Table 3.3 shows some of the options investigated for the O-rings. All of these materials are elastomers. Although elastomers seal best, they compression-set when exposed to prolonged radiation. Therefore, the O-rings may be the type of component that limits the lifetime of the plate-and-frame cell in high-radiation environments. Of the elastomers, EPDM has the highest radiation and chemical resistance and meets the 10^6 Rad requirement for Phase I applications. It is commercially available and readily formable. The ElectroCell AB company uses EPDM as one of its standard gasketing materials. For sealing the scaffold, 12.7-cm-diameter EPDM O-rings can be purchased off-the-shelf.

3.5.2 Scaffolding and Spacer Materials

The scaffolding material must be 1) electrically insulating, 2) chemically and radiochemically stable, and 3) flexturally strong and have a low coefficient of thermal expansion. Since all the materials included in Table 3.4 are electrically insulating and exceed the 10^6 Rad accumulated dose required during Phase I, only flexural strength and thermal expansion need to be compared. High flexural strength and low coefficient of thermal expansion do vary with these materials, but all can be improved by using glass-fiber filling. Based on the data provided in Table 3.4, polyether-ether ketone (PEEK) is best suited for the scaffolding.. However, its high cost may make it economically unattractive. Polypropylene and high-density polyethylene (HDPE), especially with glass fill, may also be acceptable. Although ceramics have been considered in the table, their lower toughness makes them less desirable.

The spacers can be constructed from similar material as the scaffolding. The spacers, however, do not require the high flexural strength and low thermal expansion that is needed for the scaffolding. Polypropylene, HDPE, and PEEK are all acceptable materials for the spacers.

3.5.3 Anode Material

The anode is subjected to a very corrosive environment. To address this concern, the chlor-alkali industry uses RuO_2 on titania because it has an average lifetime of over 10 years(a). In their case, they need a

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(a) Personal conversation with D. Mazur, March 1996.

material that is selective to chlorine over oxygen. For salt splitting radioactive waste, oxygen generation is the preferred reaction pathway rather than chlorine. Platinum has the lowest oxygen overpotential of any material (Pletcher and Walsh 1982) and, similar to RuO_2, has very high corrosion resistance. Therefore, it would be considered a better material than other anodes such as stainless steel, nickel, and nickel oxides.

3.5.4 Cathode Material

Since the cathode is exposed to a less corrosive environment than the anode, several materials could be acceptable for the cathode. Options include platinized titania, stainless steel, nickel, and nickel composites. All materials may be equally suitable from a corrosion standpoint. To clean the electrode surface without corroding it, platinized titania could be used to allow the electrode polarity to be reversed. Stainless steel has the advantage of low cost, but nickel has a high electrical conductivity, approximately 10 times higher than titanium and stainless steel. Since the system will be monopolar, an even current distribution is required. For this reason, nickel is preferred. Furthermore, the chlor-alkali industry commonly uses nickel as its cathode (Pletcher and Walsh 1982). Nickel composites should also be considered to improve the overpotential. The Ni-Mo-Co composite has been shown to improve hydrogen evolution over nickel alone (Simpraga et al. 1995).

Table 3.2 Material Requirements for the Components of the Plate-and-Frame Configuration

Cell Component	Temperature Range (°C)	Chemical Resistance	Radiation Resistance	Mechanical Requirements	Sealing Requirements	Other Requirements
Cathode	20-80°C	5 $\underline{M}$ NaOH	10^6 Rad	Suitable for Plate-and-Frame Configuration	None	Low H_2 over-potential
Anode	20-80°C	Tank Supernate:0-4 $\underline{M}$ NaOH, 0-3 $\underline{M}$ $NaNO_3$, 0-0.6 $\underline{M}$ sulfates, 0-0.5 $\underline{M}$ chlorides, carbonates, phophates; localized H^+ concentrations	10^6 Rad	Suitable for Plate-and-Frame Configuration	None	Low O_2 over-potential
Ceramic Membrane	20-60°C	Tank Supernate	10^6 Rad	$\Delta P < 15$ psi, High compressive strength	Critical	Na Selectivity
Scaffolding	20-60°C	Tank Supernate	10^6 Rad	Low Thermal Expansion, High Flexural Strength	Holds disks securely against O-ring to prevent leakage	Provides space for liquid flow, electrical insulator
Spacer/Flow Distributor	20-60°C	Tank Supernate	10^6 Rad	Dimensional Stability	None	Electrical insulator
Cell Frame	20-60°C	Air, Possibly Tank Supernate	10^6 Rad	Metal	None	None
Gaskets/O-Rings	20-60°C	Tank Supernate	10^6 Rad	Flexible after rad dose and chemical attack	Must provide seal	None

Table 3.3 Gasket/O-Ring Material Options

Material	Radiation Resistance (Bruce and Davis 1981)	Chemical Resistance in 5 M NaOH (Harrington 1992) (Max Temp)
EPDM	10^6 Rad	98°C
Nitrile Rubber	10^6 Rad	38°C
Neoprene	8×10^5 Rad	70°C
Natural Rubber	2×10^6 Rad	22°C
Silicone	5×10^5 Rad	48°C

Table 3.4 Scaffolding Material Options

Material	Radiation Resistance (Bruce and Davis 1981)	Chemical Resistance (Harrington 1992)	Thermal Expansion (/°C) (Juran 1989)	Flexural Modulus (psi) (Juran 1989)
Polypropylene	3×10^6	Max Temp = 82°C in 5M NaOH	81×10^{-6}	170×10^3
			21×10^{-6} (w/ glass)	310×10^3 (w/ glass)
HDPE	10^7	Max Temp = 60°C in 5 M NaOH	70×10^{-6}	125×10^3
			48×10^{-6} (w/ glass)	700×10^3 (w/glass)
Polyimide	10^7	Attacked by dilute alkali	13×10^{-6}	450×10^3
PEEK	10^9 (Manufacter)	No attack and little to no adsorption in 10-50% NaOH (Manufacter)	40×10^{-6}	560×10^3
			12×10^{-6} (w/ glass)	1260×10^3 (w/ glass)
Alumina	Radiation Resistant	Resistant to NaOH	9×10^{-6}	60×10^3
Zirconia	Radiation Resistant	Resistant to NaOH	11×10^{-6}	20×10^3

4.0 Preconceptual Design Based on Ceramic Tubes

The preconceptual design of a salt splitting process based on ceramic membrane tubes is presented in this section. This design provides a robust unit that can function well in any of the proposed applications. Therefore, provisions are incorporated that 1) eliminate organic materials, 2) ensure that potentially flammable gases are segregated from the outside air and the oxygen in the anode compartment, 3) provide a method of sealing that prevents contamination of the caustic, and 4) allow the processing of slurries.

4.1 Overview

The overall cell design based on ceramic tubes is shown in Figures 4.1 and 4.2. The design incorporates a flowthrough concentric cylindrical geometry with the membrane and cathode inserted into a cylindrical perforated anode. A number of cathode assemblies are provided in a common anolyte tank. The cathodes and ceramic tubes are configured as an integral unit that can be readily exchanged for a new one in the event of failure. A pump is used to recirculate the catholyte solution (caustic product) from the catholyte tank through the cathode assemblies and back to the catholyte tank. The catholyte return stream will be a 2-phase flow situation consisting of the caustic product and the electrolytic gases. The waste feed is contained in the anolyte tank with agitation provided by air sparging and electrolytic gases. Alternatively, a separate anolyte tank could also be used with recirculation provided by pumping. A separate catholyte tank is required because of the relatively small volume of the cathode compartment and the need to remove electrolytic gases. Electrolytic gases from the anode and cathode compartment are collected separately for treatment. The temperature is controlled by heat exchangers in the anolyte and catholyte tanks.

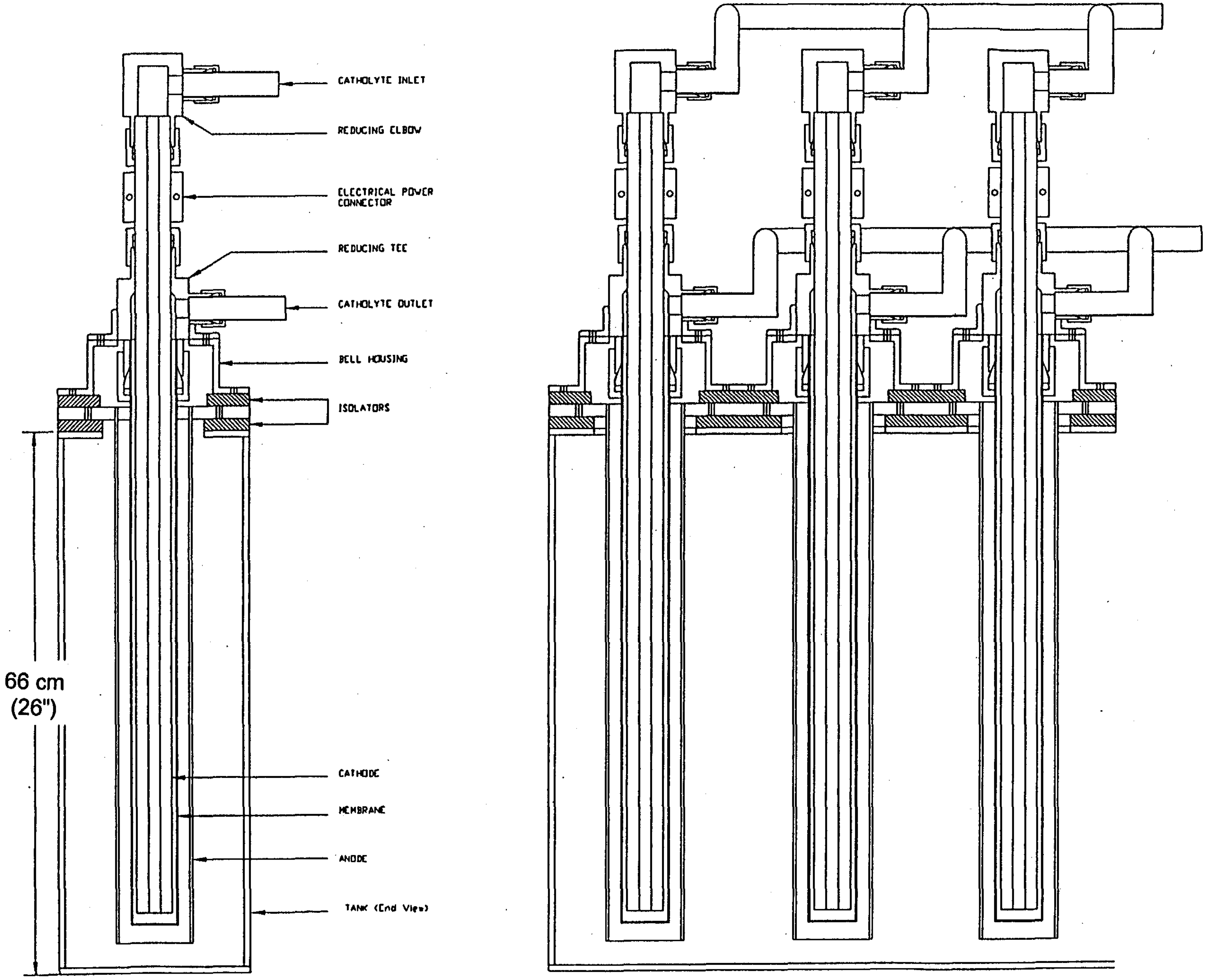

Figure 4.1 Electrochemical Cell Design Based on RE-NaSICON Tubes

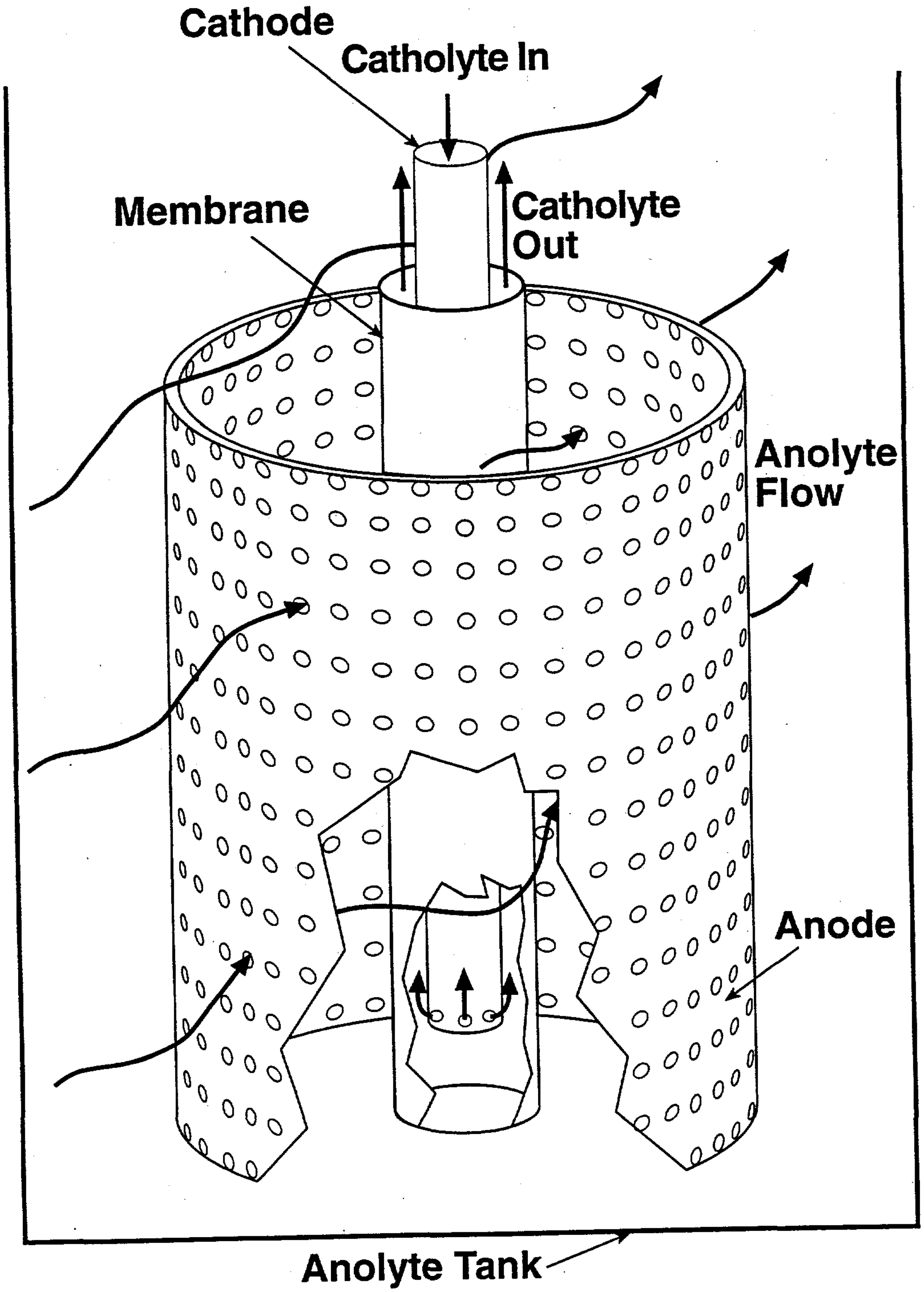

Figure 4.2 Electrochemical Cell Design Based on RE-NaSICON Tubes

4.2 Cathode Assembly

It is envisioned that the cathode assembly would be provided as an integral unit that could be readily exchanged for a new one in the event of failure (Figures 4.3 and 4.4). The cathode fits inside of the ceramic tube, and both the cathode and the tube are suspended from the cathode cap assembly. Commercially available swagelock fittings are used for much of the cathode cap and catholyte connections to minimize the design and fabrication of specialized parts. The cathode and associated materials will consist of caustic-resistant materials such as nickel or stainless steel. The vapor space at the top of the cathode is kept to a minimum to minimize the volume of flammable gases that could potentially collect.

A pump is used to supply the recirculating catholyte solution to the top of the cathode where it flows down the interior of the cathode and back up through the 6.35-mm (0.25-in.) gap between the cathode and the ceramic membrane. The solution flow is from the bottom to the top to facilitate disengagement of the electrolytic gases. The catholyte return stream is a 2-phase flow of electrolytic gases and caustic product.

A pressure greater than the surroundings will be maintained in the cathode compartment because the potential impact of leaks is minimized. If caustic product leaks from the cathode to the anode, a small loss in efficiency would result. If feed were to leak from the anode compartment into the product, a large volume of product would be contaminated. If flammable gases were to leak from the cathode loop, it is likely that they would be widely dispersed in the much larger air volume surrounding the cells, preventing the formation of a flammable gas mixture. A lower pressure in the cathode compartment would allow a small air leak to produce a flammable gas in a confined space.

Seals are provided around the ceramic membrane and around the cathode using a crushable feral. Sealing pressure is applied by tightening the threaded pieces. The feral would be made of an inorganic material such as boron nitride or a soft metal such as nickel.

The design minimizes the stresses that would be applied to the membrane by isolating the membrane from any loads. This is accomplished by suspending the cathode from the swagelock fittings and the cathode cap while suspending the ceramic membrane separately. The only stresses applied to the membrane are from the radial stresses caused by the feral and the longitudinal forces, which are due to the mass of the membrane. Flexure forces could be applied by impacts during assembly.

The details of the ceramic tube are shown in Figure 4.5. The 5.08-cm (2-in.) ceramic tube has a glassy glaze or a metal coating applied by standard ceramic/metal joining technology over the top 5 cm to provide additional structural strength and a good sealing surface for the standard feral. The remaining length of 56 cm (22 in.) is assumed to be available for sodium conduction.

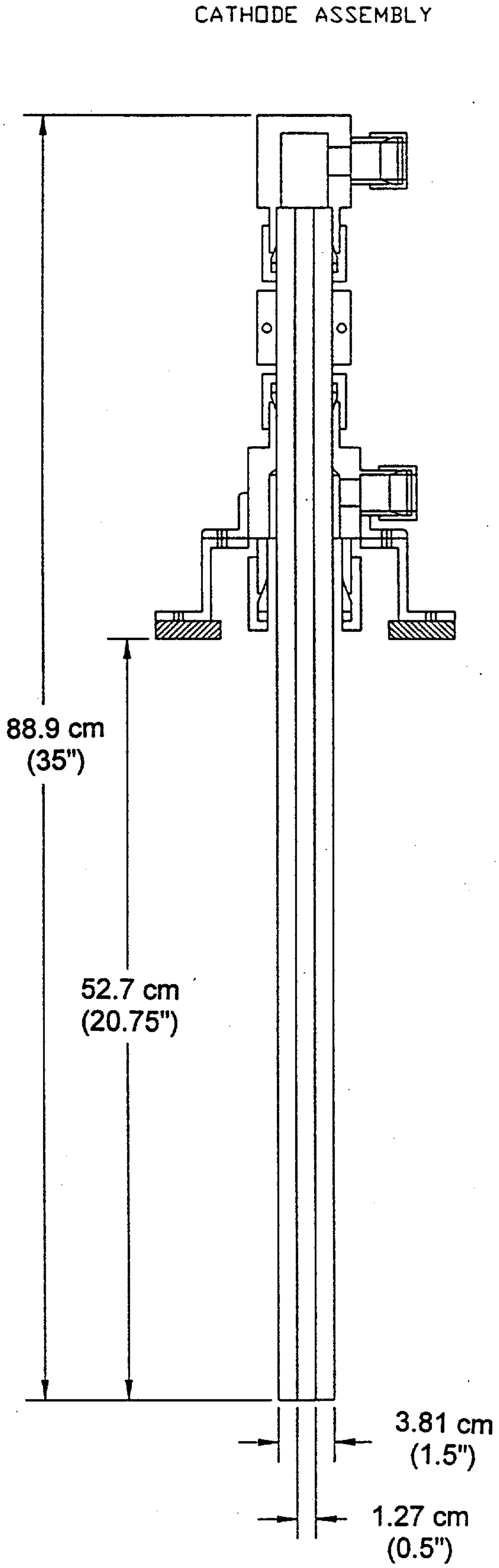

Figure 4.3 Cathode Assembly

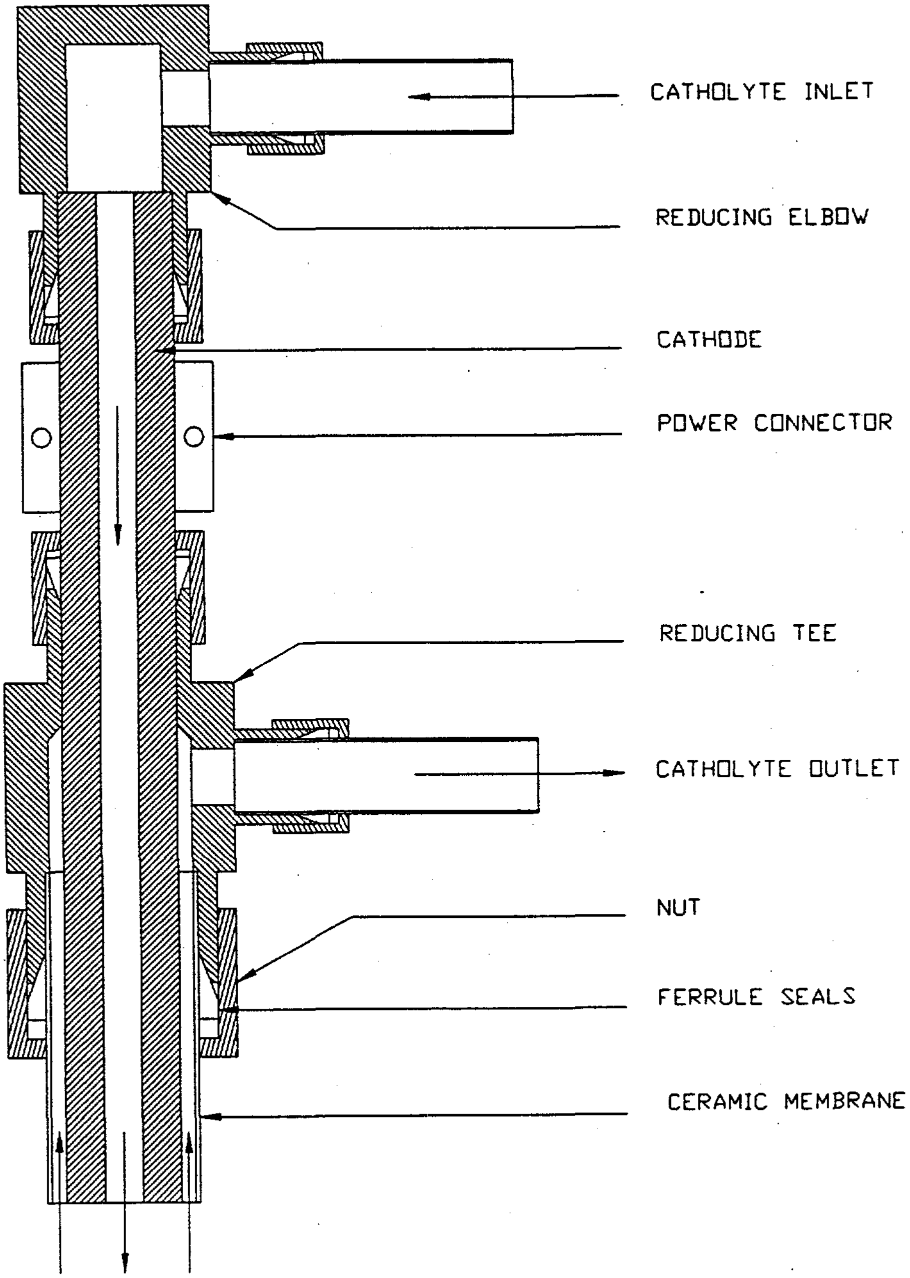

Figure 4.4 Expanded View of Cathode Top

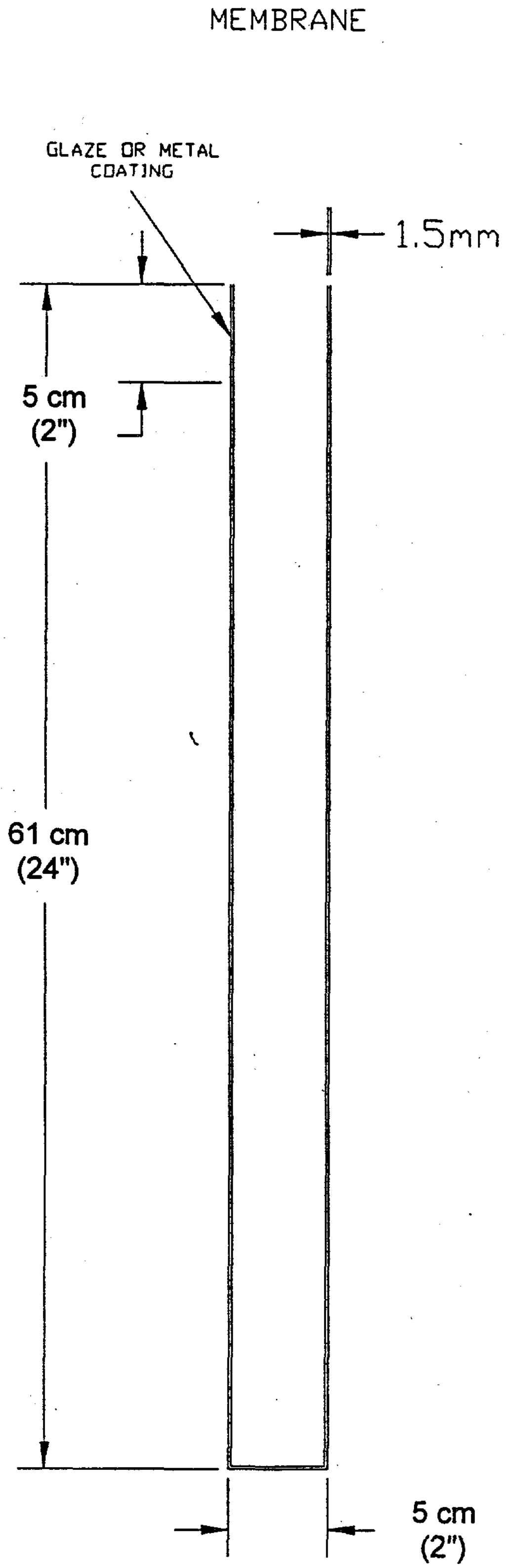

Figure 4.5 RE-NaSICON Membrane Dimensions

4.3 Anode and Anolyte Tank

As shown in the Figures 4.2 and 4.6, the anode consists of a perforated tube with a diameter of 7.62 cm (3 in.). It is connected to the power distribution busbar at the top. This arrangement also provides suspension for the anode. It is desirable to keep the anode off of the bottom of the tank to facilitate the removal of solids. Power connections are provided in two locations at opposite sides of the anode tube to provide structural integrity and to minimize the IR losses in the electrode. The gap between the anode and the outside of the ceramic tube is assumed to be 1.27 cm (0.5 in.) and is sufficiently large to allow gases and solids to pass easily around and through the anode. An air sparge provides a low-maintenance method for mixing the anolyte solution. The use of platinized titania or IrO_2 coated titania for the anode material provides good chemical stability with a reasonable cost and electrical conductivity. The anolyte tank is shown in Figure 4.7.

4.4 Operating Characteristics and Parameters

Some of the pertinent operating characteristics and parameters are shown in Table 4.1.

The total area per tube available for sodium conduction is assumed to be 880 cm^2 based on a tube diameter of 5 cm ($\approx$2 in.) and a conduction length of 56 cm. With a current density of 75 mA/cm^2, the total current per tube is 66 A. Assuming a cell potential of 5 volts, the power requirement is 330 W per tube.

Assuming that 3 of the 5 volts are due to IR losses, the heat removal requirement is 200 W/tube. If the temperature rise per tube is assumed to be 10°C, the required total (feed and product) recirculation rate is about 17 L/h. Experimentation or more advanced calculations would be required to optimize the recirculation flow rates.

Based on a total required membrane area of 530 m^2, it is estimated that 6010 cathode assemblies would be required for caustic recycle at Hanford. The total electrochemical cell footprint, including the catholyte tanks, is estimated to be 173 m^2 (1870 ft^2). This is based on the number of tubes and assuming that each cell requires a 10.16-cm x 20.32-cm (4-in. x 8-in.) area. This area is increased by an additional 40% to account for the catholyte tanks.

The hydrogen generation rate is estimated at 0.021 mole/min or 0.46 standard L/min per tube. The volume of air required to maintain the hydrogen level at less than 1% (25% of the LFL) is estimated to be 46 L/min (1.6 scfm) per tube.

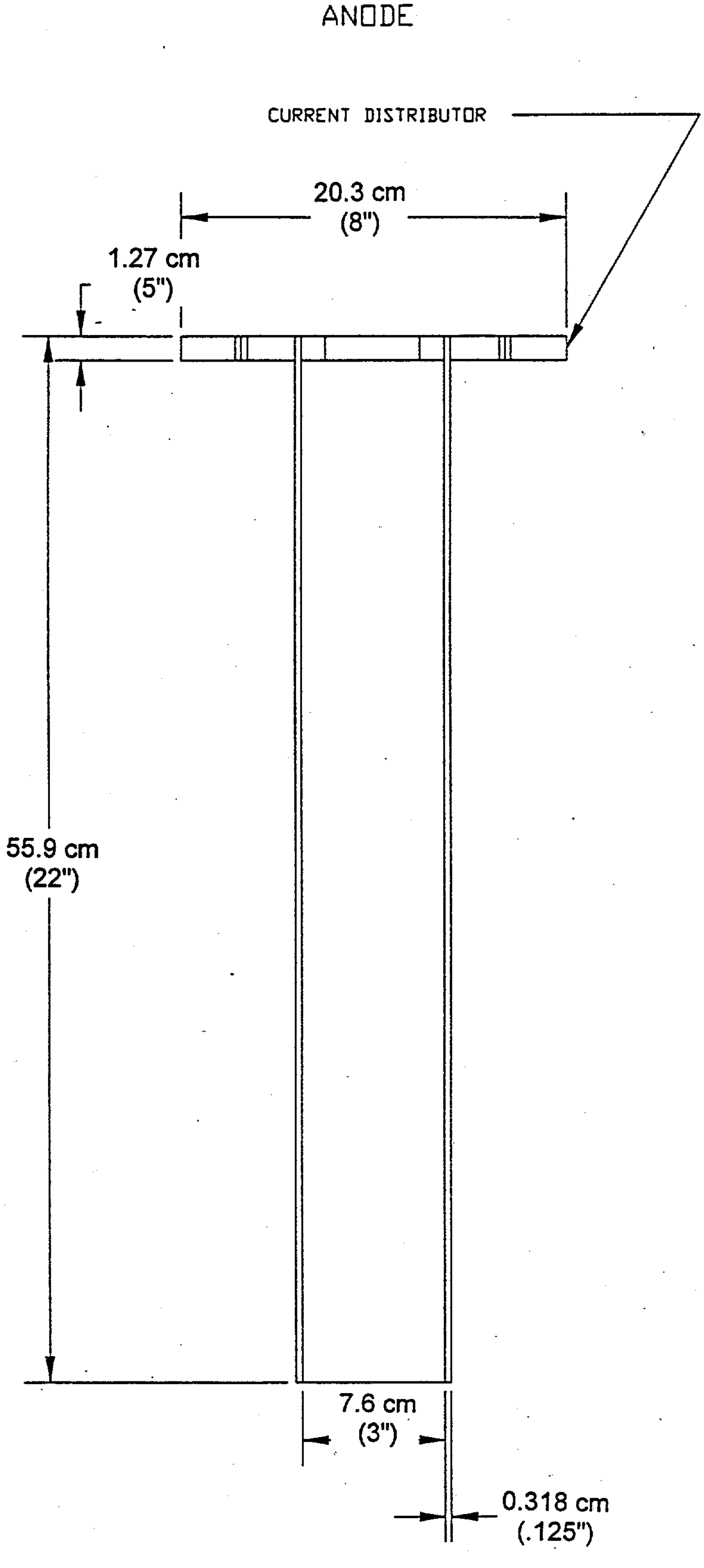

Figure 4.6 Anode Detail

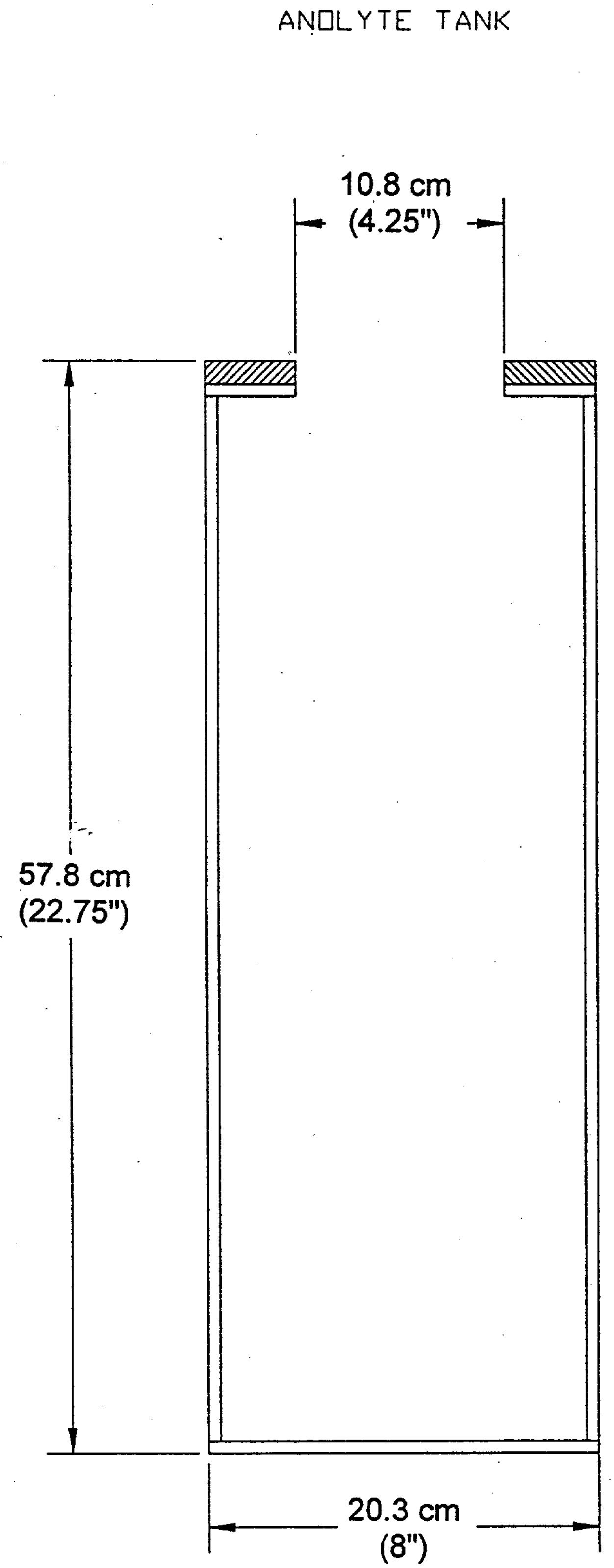

Figure 4.7 Anolyte Tank Detail

Table 4.1 Operating Characteristics and Parameters, Caustic Recycle at Hanford, Tubes

Membrane Dimensions	L = 61 cm (≈2 ft) D = 5 cm (≈2 in.)
Membrane Sodium Conduction Length	56 cm
Membrane Area	880 cm^2
Current per Tube	66 amps
Power per Tube @ 8 V	330 W
Heat Removal per Tube	200 W
Total Feed and Product Recirculation Rate for Heat Removal (10°C Delta T)	17 L/h
Total Number of Tubes for Caustic Recycle at Hanford	6010
Electrochemical Cell Footprint	173 m^2 (1870 ft^2)

4.5 Design Variations

Moving vs Nonmoving Electrodes

Moving electrodes are sometimes employed to improve the rate of mass transfer to the electrode surfaces, but these are viewed as an unproductive complexity for this design. The rate limiting step is the sodium conduction through the membrane, so improvements to the mass transfer to the electrodes would provide little benefit. Since moving electrodes would only add potential maintenance problems, but provide little benefit, they are not seriously considered in this design.

Electrical Connections - Monopolar vs Bipolar

The electrical connections to the cells in this design are, of necessity, monopolar. If the cells were connected in a bipolar arrangement, a number of concentric cells (and membranes) of different sizes would need to be designed and fabricated. Since this engineering and fabrication effort would be expensive, a monopolar connection is preferred.

Open End Ceramic Tubes

Using open tubes instead of closed-end tubes could be an alternative membrane configuration based on a cylindrical geometry. These tubes would be used with a cathode in the center of the ceramic tube and the anode on the outside of the tube. The tubes would be mounted vertically to prevent gases from collecting in the cell. Solutions would enter the bottom of the tubes and exit the top. While this alternative appears to be entirely feasible, it was not pursued because it appears to offer no advantages over the closed-end tubes and presents a greater sealing challenge.

5.0 Safety Considerations

During salt splitting, the following reaction occurs on the cathode to produce hydrogen gas:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH$$

Several approaches are considered below for mitigating potentially flammable gas mixtures as a result of the hydrogen gas generation. Methods to dilute hydrogen below its flammability limit are described in Sections 5.1 and 5.2, methods of preventing hydrogen formation are described in Sections 5.3 and 5.4, and methods of destroying the hydrogen after it is formed are described in Sections 5.5 through 5.8. Hydrogen getters are a means of collecting the hydrogen in a safe form and are described in Section 5.9.

5.1 Air Dilution

Hydrogen will be produced at a volumetric flow rate of 2800 L/min in the 2.0 MW system described in Section 2.2.1. Lewis and VonElbe (1987) show that the hydrogen LFL remains at > 4% vol in air, in pure oxygen, and in other diluent mixtures (N_2, CO_2). The operational safety limits for a nuclear facility for purging radiolytically generated hydrogen are < 1% vol in air[a]. Therefore, for this analysis, 1% hydrogen will be the design limit. To prevent the hydrogen from exceeding the 1% vol limit, a purge rate of > 280,000 L/min (280 m^3/min) is required. The hot cells typically operate with one air change approximately every 2 min (324 Building C-Cell). At this air change-out rate, the hydrogen problem would be mitigated even if the hydrogen were only purged to the equipment room (see footprint dimensions in Table 3.1). A 75-horsepower blower capable of exhausting 370,000 L/min of air would be sufficient. Therefore, an air purge could prevent hydrogen accumulation.

5.2 Inert Diluent

An inert gas could purge the hydrogen, thus minimizing the total gas-purge flow required in the cathode tank. The hydrogen could be removed with air from the cathode tank at a higher concentration and then be expelled from the facility as part of the offgas system. While the hydrogen is purged with the inert diluent, combustion cannot occur. However, once the purge gas/hydrogen mixture is expelled to the air of the offgas system, the hydrogen must be diluted sufficiently to prevent deflagration. In a nitrogen diluent, the LFL is less than 4% hydrogen and 5% oxygen (Lewis and VonElbe 1987). To ensure that these two limits are not exceeded, 52,500 L/min of nitrogen would be required to purge the cathode tank. This large quantity of nitrogen (66 kg N_2/min or 20,700 MT/yr) may make this approach economically unattractive.

(a) *Safety Analysis Report for 324 Building Waste Technology Engineering Laboratory,* PNL-7989, January 1992., Pacific Northwest Laboratory, Richland, Washington. This document was never approved by DOE, so it never became a part of the 324 Building Authorization Basis for facility operations.

5.3 Oxygen Cathode

It is possible to electrochemically prevent hydrogen formation: when oxygen reacts with the water at the cathode, caustic is still produced, but no hydrogen forms. This reaction is illustrated below.

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$$

By bubbling gases such as oxygen through a gas-diffusion electrode, they can react in an aqueous environment.

The oxygen-reduction reaction has been studied extensively in fuel cells. Oxygen cathodes have also been used successfully for metal-air batteries and have been studied on a trial basis in the chlor-alkali industry (Pletcher and Walsh 1982). However, these electrodes are far from perfect. Researchers are continuing to search for better gas-diffusion electrode materials to catalyze the oxygen-reduction reaction. The reduction of oxygen is a slow reaction and even platinum, the best of the metals, requires an overpotential of greater than 0.3 V for a reasonable current density. With other metals and some carbons, the overpotential may need to be as high as 1.5 V (Pletcher and Walsh 1982).

Approximately 2800 L/min of hydrogen are generated for the 2.0 MW application described in Section 2.2.1. If, instead, oxygen were used in a gas-diffusion electrode, a total of 1400 L/min would be required, and no hydrogen would be produced. This is 630 MT of oxygen/yr (TOE of 60%).

Radiation compatibility may also be a concern for these systems. The most successful (and commercially available) gas-diffusion electrodes are polytetrafluoroethylene-catalyst mixtures. The Teflon prevents the flow of catholyte into the cathode while providing a high surface area for oxygen reaction with the catalyst (Fuhrer et al. 1994). A porous sintered metal electrode would be a better, more radiation-resistant alternative.

5.4 Sacrificial Reductant

A sacrificial reductant is a material added to the catholyte that would be reduced at the cathode instead of allowing the electrolysis of water. Thus, the generation of hydrogen would be prevented. The ideal reductant would be a nonhazardous material that would add nothing to the catholyte and be converted to one of the product constituents or a nonhazardous gas. A metal such as Cu^{2+} would certainly work except that it would either contaminate the caustic or plate out on the cathode. Nitrate or another nitrogen-containing compound is a possibility, except that one of the goals of this process is to recover caustic by separating it from a high nitrate stream. Perhaps the most promising material that may be added is hydrogen peroxide (H_2O_2). This could be reduced via the following reaction in alkaline media (Bard et al. 1985):

$$HO_2^- + H_2O + 2e^- \longrightarrow 3OH^- \quad E_B{}^\circ = 0.867\ V$$

This reaction has a relatively high potential, and peroxide is one of the most powerful oxidizing agents known, so it would be readily reduced at the cathode. While this option appears theoretically promising, additional investigation into stability and reduction rates is required.

5.5 Hydrogen Depolarization Electrode

Using a gas-diffusion electrode, hydrogen can be collected from the cathode and destroyed. In these cells, the hydrogen produced at the cathode is returned to the anode and oxidized to protons at a gas-diffusion electrode. By oxidizing hydrogen rather than water, the cell voltage can be reduced by over 1 V while disposing of the hydrogen. Once again, a radiation-resistant gas-diffusion electrode would be required.

A hydrogen-diffusion electrode has been studied by Hobbs (1993) and Kalu et al. (1995) in radioactive waste simulants. In these tests, a hydrogen-diffusion electrode was used to reduce the energy requirement and prevent nitrite from oxidizing rather than to mitigate hydrogen. In 1993 testing, little was learned other than that a hydrogen-depolarization electrode is possible. Early in their test, the anode flooded and severely corroded, losing its ability to act as a gas-diffusion electrode. In the 1995 testing with an improved gas-diffusion anode, the reaction worked properly, and no concerns were expressed with the electrode itself. The cell voltage was 3 V with the hydrogen electrode as compared to 4.5 V with ordinary electrodes, indicating that substantial energy savings might be achieved.

5.6 Oxidation of Hydrogen in a Fuel Cell

Using a fuel cell, the hydrogen produced at the cathode of the electrochemical cell would be recombined with oxygen or air to produce water and electrical energy. A fuel cell converts the chemical energy of fuel directly into electrical energy in efficiencies much greater than thermal-power conversions (30 to 40%). Fuel cells have been known to operate at 73 to 90% efficiencies. Based on efficiencies for hydrogen fuel cells, approximately 10% of the 2.0 MW of power required could be recovered (at approximately 1 V) from this process. The hydrogen from the cathode should be relatively pure and contain only low concentrations of impurities. Since most fuel cells have difficulty with CO_2 poisoning using hydrocarbons, but have had good success with hydrogen, this fuel cell should be relatively simple to employ (Pletcher and Walsh 1982). Therefore, use of a fuel cell could mitigate the hydrogen flammability problem while recovering some of the energy that was lost in generating the hydrogen.

5.7 Catalytic Conversion

Recombiners catalytically promote the reaction of hydrogen and oxygen to form water. Recombiners use precious metals such as palladium dispersed on an inert substrate or possibly a water-sorbing substrate such as molecular sieves. The recombiners require both oxygen and hydrogen to be present; thus oxygen or air would have to be added to the offgas stream to have enough oxygen to consume the hydrogen. A problem is that the recombiner enhances reaction rates, and a significant concern exists about controlling the rates; i.e., the chances for explosion or deflagration are enhanced by the recombiner. Thus, if a recombiner were used, the gasses should be in such a condition that they are not an explosive mixture. The recombiner would need to be used after the offgas is diluted by 280 L/min air, the same amount of air required for the air-dilution option. Therefore, this option provides little advantage over dilution alone.

Such catalytic recombiners are feasible, however. Similar systems have been designed for processing air to remove tritium spills. Such systems are in place at tritium facilities in Sandia Livermore, Mound Laboratories, and Los Alamos at the Tritium Systems Test Assembly. However, such systems are costly, about $35/L/min, or a total of about $10M in 1980 dollars. Recombiners thus are not attractive.

Another option is using CuO or Hopcalite (a mixture of CuO and MnO_2). This material would be a solid that reacts with hydrogen to produce water at 300°C. After use, the CuO is reduced to Cu. The CuO can be regenerated by heating in air at approximately 600°C for approximately 6 h. Used in this way, the hydrogen is converted to water in a controlled way since the source of oxygen is the solid. Approximately 3.55 Kg of CuO (or Hopcalite) are required to convert 1 m^3 of hydrogen to water. A total of 4.8 metric tons would be required to convert 8 h worth of offgas. These materials are readily available from any chemical supplier.

5.8 Water/Gas Shift Reaction

Another possibility is using water/gas reactions. The classical reaction is

$$\text{C (Coke)} + H_2O \longrightarrow CO + H_2$$

Reverse reactions could remove hydrogen:

$$CO_2 + H_2 \longrightarrow CO + H_2OCO + H_2 \longrightarrow C + H_2OCO_2 + 2H_2 \longrightarrow C + 2H_2O$$

A review of equilibrium constants (*J. Phys. Chem.* Ref. Data, Vol 14, Suppl 1., 1985, "JANAF Tables") indicates that the purely gas-phase reaction is not favorable; however, those reactions that generate C (soot, probably) are highly favored, at least up to 600 or 700K. This suggests that at least 1400 L/min CO_2 could be added to the offgas stream to oxidize the hydrogen. About 45 Kg of carbon/soot would be produced per hour. This material would probably need to be removed. Since Hanford/Richland is in a U.S. Environmental Protection Agency (EPA) air quality zone, particle emissions may not be allowed. If the particles can be removed, and if the reaction kinetics are high enough, the water-gas reactions could be an attractive option.

5.9 Hydrogen Getters

Clemmer recently investigated getters for controlling hydrogen during dry storage of N-Reactor fuels (PNNL-11073, to be published). Getters are often metals that form hydrides, such as Zr. Getters could be used for hydrogen control to reversibly sorb hydrogen into a solid form for subsequent processing. One limitation of most metal getters is that they react and become passivated upon exposure to oxygen or water (also nitrogen). The passivated materials are coated with an oxide film that prevents gettering of hydrogen. Thus, commercially available getters such as SAES ST707 would quickly cease to getter hydrogen when exposed to the ~2 cfm oxygen plus water (saturated 60°C) in the offgas. A possible solution to this problem is to coat the getter with a selective coating that is highly permeable to hydrogen, yet unreactive and impermeable to oxygen. Such a material is nickel-plated zirconium (NPZ), developed at PNNL as a getter for tritium. This material is likely to perform well in the presence of the water and oxygen and at a temperature of 60°C. However, the capacity of a metal getter is limited. Further, to repeatedly cycle a metal-hydride getter and avoid embrittlement and cracking, the loading is limited to a hydrogen-to-metal ratio of about 0.3. Under this circumstance, each standard m^3 of hydrogen requires 27 Kg of NPZ. To sorb 8 h of hydrogen offgas, approximately 36 metric tons of NPZ would be required. Thus, getters are not an attractive option.

5.10 Assessment

Diluting the hydrogen with air to 25% of the LFL (1%) appears to be the most feasible method for preventing potentially flammable gas mixtures. The required volume of air is in line with the volumes routinely pulled through hot cells, the method is very reliable, and technology development is not required. Air dilution is the preferred option for mitigating hydrogen. Dilution with an inert gas is also a reasonable approach, but appears to offer no advantages over the use of air and requires also a supply of inert gas. For this reason, it will not be pursued further.

This study indicates that an oxygen cathode or a sacrificial reductant such as hydrogen peroxide could be used to prevent the generation of hydrogen. Although these options appear attractive, system complexity would be increased, and additional development work would be required. The oxygen cathode, while having been studied extensively, requires a radiation-resistant and reliable gas-diffusion electrode. Using hydrogen peroxide as a sacrificial reductant has not been studied, and its stability and reactivity would have to be evaluated.

The options that destroy hydrogen after it has formed that appear attractive include the hydrogen depolarization electrode, fuel cell, catalytic recombination, and water-gas shift reaction. All four cases will require handling of the flammable hydrogen gas, including collection and transport. Safety issues associated with this handling would have to be addressed. System complexity would also be increased. The hydrogen depolarization electrode and fuel cell provide energy savings while destroying the hydrogen gas produced. Either CuO or Hopcalite could be used, although several tons would be needed. The water/gas reactions that would add about 1400 L/min CO_2 to the offgas may be an attractive option, if the resulting carbon/soot can be managed.

The catalytic recombination of hydrogen and oxygen gas and hydrogen getters were not acceptable approaches and will not be considered further. The use of catalyts for recombination of the hydrogen with oxygen gas is not attractive because of the very high flow rates (equivalent to the air purge rate) and the cost (about $10M). The use of hydrogen getters is also not attractive because of the large amount of material required; about 36 metric tons would be needed every 8 h for the Hanford application.

6.0 Assessment and Recommendations

The advantages and disadvantages of each design are discussed below.

6.1 Flat-Plate Design

Advantages

Incorporating the ceramic membranes into a flat-plate configuration allows stacking into a plate-and-frame configuration, and the equipment footprint is minimized. Since the cost of a radioactive processing facility is generally driven by the required radioactive processing floor space, the flat-plate design may minimize facility costs.

Several well established electrochemical cell designs are commercially available and can be used to incorporate the scaffolds containing the ceramic membranes. This allows standard equipment, including a wide variety of electrode materials, to be used.

The fabrication capability to make small disks already exists. Scale up of the production of larger disks is proceeding and (3.9 cm [1.6 in.]) disks have been produced.

The ceramic fabrication rate of the disks is anticipated to be higher than tubes since a uniaxial pressing process will be used for production.

Disadvantages

A flat-plate geometry will not be as resistant to flexural loading (i.e, pressure differentials on either side of the membrane). To minimize this issue, disks are used instead of squares, and multiple 12.7-cm (5-in.) disks are used instead of a single large disk.

Obtaining a good seal becomes a critical issue since each cell stack will contain hundreds of seals. Uniform pressure is required on the O-rings to ensure sealing and prevent cracking of the ceramic. Sealing is important for maintaining product purity and for separating electrolytic gases.

Using organic polymers for the scaffolding and O-rings probably makes this design inappropriate for applications involving high radiation fields. It may be possible to eliminate or minimize organic materials, but this has not been pursued because it is not necessary for the low radiation applications envisioned for the flat-plate design.

This design will not handle waste solutions with large amounts of solids (i.e., 5 to 30 wt%). This is not viewed as a serious issue since most applications are likely to use filtered aqueous solutions.

Maintenance could be a significant issue in a radioactive environment due to the large number of bolts and screws that would have to be manipulated remotely or with special protective equipment.

6.2 Cylindrical Design (Tubes)

Advantages

The tube geometry is structurally superior (tubes are stronger) since cylinders are more resistant to flexural and bending forces because of the three-dimensional structure.

A cylindrical geometry has been used in Na/S batteries that use ceramic tubes (i.e., beta alumina) as separators. This provides a technology base for electrochemical cells based on a cylindrical geometry.

However, differences between the Na/S batteries and the salt splitting process inhibit the transfer of technology to the salt splitting design. The Na/S batteries are nonaqueous systems, and electrolytic gases are not generated during operation.

Issues associated with sealing are minimized. The number of seals is much smaller than with the flat plates, and it is easier to obtain a good seal on tubes. Leakage, if it occurred, would be from the cathode (product) to the anode (feed) compartments, so contamination of the product would not occur. The liquid level in the cathode will be higher than the anolyte level, and the pressure in the closed catholyte loop will be greater than in the open anode tank.

Providing a sealed cathode unit will make leak checking for quality assurance much easier.

An "organic free" design can be developed by using tubes because only inorganic materials are used. Inorganic materials are more resistant to radiation damage, so this design is more appropriate for applications involving high radiation fields.

Tubes facilitate an anolyte tank concept that can process slurries containing relatively large amounts of solids.

Disadvantages

Although small RE-NaSICON tubes are currently manufactured for sensors, a fabrication process for full-scale tubes must be developed. This development effort is estimated to require a full man-year of effort and approximately 9 months to provide initial tubes for testing.

Cylindrical geometries are not standard commercially available cells. Significant design and engineering issues would have to be addressed, including distributing and collecting the feed and product and removing the electrolytic gases.

6.3 Recommendations

It is recommended that the flat-plate concept be pursued as the reference design for Phase I applications because 1) disks are more readily fabricated than tubes, 2) the flat geometry can be readily incorporated into standard commercially available plate-and-frame electrochemical cells, and 3) the immediate applications may not require a robust design such as that based on tubes. This design appears to be most suitable for removing caustic from aqueous waste streams containing relatively low amounts of radioactivity (i.e., after removal of ^{137}Cs) and solids.

Sealing the ceramic disks in the scaffolds is the critical design issue associated with the flat-plate design. Unit test cells are being fabricated that incorporate RE-NaSICON disks in scaffolds. These scaffolds will be incorporated into commercially available cells for testing over a range of conditions during a 1000-h test.

It is recommended that the cylindrical cell design based on RE-NaSICON tubes be pursued for Phase II applications. The design based on tubes appears to be more robust and appropriate for a wider range of applications involving high radiation fields and high amounts of solids (slurries). This design also may provide superior sealing properties for separating the electrolytic gases and producing pure caustic. While small RE-NaSICON tubes are currently fabricated for sensors, scale-up of the ceramic fabrication process is a significant effort in addition to a custom-designed electrochemical cell based on the cylindrical geometry.

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