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**Evaluation of Aqueous Na^+/Cs^+
Separation by Electrodialysis**

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Summary

In support of the Hanford Site cleanup, electrodialysis is being investigated as a method to separate aqueous sodium (Na^+) and cesium (Cs^+) ions. The approach has many advantages over existing separation technologies; in particular, electrodialysis creates little secondary waste while producing usable acid and base streams.

The fundamentals of electrodialysis are presented in this report to provide a foundation for interpreting experimental data. A flat-plate laboratory-scale apparatus was used to determine the feasibility of separating Na^+/Cs^+ mixtures by electrodialysis. The results showed that Cs^+ is preferentially separated over Na^+ by a factor of 2 to 3 using a Nafion® 417 cationic membrane. The separation is relatively insensitive to solution ionic strength and flow-rate variations. The current efficiency of the separation ranges from 0.60 to 0.65 depending on the applied voltage.

The laboratory-scale system was characterized by dimensional analysis, which demonstrated that the process could be scaled up to a size attractive for the volume of waste at the Hanford Site. Preliminary experiments on a bench-scale system were also conducted. The initial results showed that the current-voltage response of the laboratory- and the bench-scale unit is identical.

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1.0 Introduction

The U.S. Department of Energy's Hanford Site in Richland, Washington, has 177 underground storage tanks containing approximately 61 million gallons of high-level radioactive waste. The current cleanup strategy is to retrieve the waste and separate the components into high-level waste and low-level waste. Many of these tanks contain high concentrations of sodium (Na^+) and relatively low concentrations of radioactive ions such as cesium ($^{137}\text{Cs}^+$). Limits have been set on allowable concentrations of radioactive ions in the final waste form to ensure that the tank waste and the final waste form are compatible, form a stable product, and meet regulatory standards (Straalsund et al. 1992; Swanson 1993). Therefore, it is necessary to preferentially remove and concentrate certain radioactive ions from the tank waste stream prior to final disposal.

The separation of Cs^+ ions from highly concentrated Na^+ solutions is exceptionally difficult for two reasons: 1) in aqueous solutions, Na^+ ions are hydrated with 4-5 water molecules, which increases the effective diameter of the solvated ion to approximately that of Cs^+ ion, and 2) the ions are of equal charge. These similarities create numerous problems when traditional separations methods, such as ion exchange, solvent extraction, and precipitation, are applied. Separation of Na^+ and Cs^+ by ion exchange is strongly influenced by the similar size and charge of the ions. Na^+ and Cs^+ compete equally for ion exchange sites and reduce the selectivity of the exchange material. The low capacity of the exchanger creates the need to use high volumes of exchange material and eluants. Although recent advancements in the silicotitanate material appear promising, most other ion exchange materials do not perform as effectively or are toxic. Solvent extraction requires high volumes of diluant organics to provide adequate separation of Cs^+ . Unfortunately, the organics used are typically toxic and pose regulating and permitting problems. Separation of Cs^+ by precipitation is a relatively inefficient process because many other ions coprecipitate with Cs^+ . This method is not selective and post treatment of the precipitate is required. Finally, all of these techniques suffer from inherently generating secondary waste during operation.

The problems associated with the traditional separation methods have prompted Pacific Northwest Laboratory (PNL)^(a) to investigate electrodialysis and other potential technologies for Na^+/Cs^+ separation. Electrodialysis combines an applied electric field and charge selective membranes to facilitate ion separation. The primary advantage to this method is that little secondary waste is produced during separation. Instead, acid and base streams are generated that can be used elsewhere in the overall tank waste remediation scheme. In addition, the process is continuous and robust enough to treat a wide variety of waste streams. Electrodialysis is already used extensively in industry. The practical and theoretical understanding of the transport processes is well documented; however, the technology is just now emerging as a method for radioactive waste treatment. This report provides an overview of the electrodialysis technology and discusses experiments conducted at PNL to separate aqueous Na^+ and Cs^+ .

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2.0 Electrodialysis Technology

Electrodialysis has been widely used both in industry and research laboratories to separate charged species. The driving force for ion separation is provided by an electric field that is applied across two electrodes: an anode and a cathode. The anode is positively charged and attracts anions, while the cathode is negatively charged and attracts cations. Membranes are inserted between the electrodes to selectively allow either positive or negative ions to pass. Membranes that allow transport of positive ions are called cationic, and those that transport negative ions are called anionic. Recently, membrane technology has advanced to produce stable, efficient membranes that do not degrade over extended use. This development has allowed electrodialysis to become a viable and attractive process for nuclear waste separations. Also, electrodialysis is most cost effective when ions are at low concentrations, which is often the case in nuclear waste applications.

2.1 Brief History of Electrodialysis

The basis for electrodialysis is founded on the work of Ostwald (1890) at the turn of the century. He used semipermeable membranes with limited ionic selectivity to treat electrolyte solutions. Ostwald suspected there was a "membrane potential" at the interface between the membrane and the solution which created the observed concentration difference. Later, Donnan (1911) explained this phenomenon by describing the selectivity of a cationic membrane. Donnan explained, for a cationic membrane, a negatively charged ion is repelled or excluded from the internal structure of the membrane because of the fixed negative charges within the polymer membrane matrix. This exclusion is strictly based on the ion charge and is commonly termed *Donnan Exclusion*. A thermodynamic treatment of this phenomenon was presented by Donnan and Guggenheim (1932), and they determined that the concentration of the anions in the pore of a cationic membrane was proportional to the square of the anion concentration of the external solution. Additional studies were conducted by Morse and Pierce (1903) and various German (1889, 1900) and British (1896) researchers. Later investigations of electrodialysis included Michaelis and Fujita (1925), Manegold and Kalauch (1939), and Meyer and Straus (1940). A "fixed-charge" theoretical treatment of ion-selective membranes was developed by Teorell (1935) and Meyer and Sievers (1936). These works provided a theoretical basis to develop synthetic ion-selective membranes during the early 1940s.

The first "three-compartment cell" was introduced by Pauli (1922). Pauli's cell performed a relatively inefficient desalination or "salt splitting" process as compared to today's standards, but the cell configuration is still commonly used. A simplified schematic diagram of the concept is shown in Figure 2.1. The figure depicts cationic and anionic membranes sandwiched between two electrodes, creating three internal compartments. The solution flowing in the compartment on the anode side is termed the anolyte, while the solution on the cathode side is termed the catholyte. A salt solution is fed to the center compartment, and the charged ions are isolated or "split" as a potential is applied across the electrodes. Anions are transported toward the anode and cations toward the cathode.

Figure 2.1 also shows the generation of hydrogen ions (H^+) at the anode and hydroxyl ions (OH^-) at the cathode. This occurs if the applied potential is sufficiently large enough to reduce water at the cathode and oxidize water at the anode. The reactions are shown below:

Figure 2.1. Simplified Schematic of Electrodialytic Separation of Sodium and Nitrate Ions

These reactions are very important because the free H^+ and OH^- ions can combine with co-ions transported from the center compartment to generate useful acid or base streams. Therefore, the overall electrodialytic process can desalinate a highly concentrated salt feed into a alkaline stream (catholyte), an acidic stream (anolyte), and a low concentration salt effluent.

2.2 Ion Exchange Membranes

Ion exchange membranes consist of a film of polymer resin or matrix with fixed moieties of positive or negative charge. As mentioned above, if the moiety is negative the membrane will reject negative ions (cationic), and if the moiety is positive the membrane rejects positive ions (anionic). The membranes are produced by synthesizing a polymer “backbone” or support and then reacting the polymer with an acid or base to permanently “fix” a charged site within the polymer matrix. Table 2.1 lists some of the common functional groups used as fixed charges on a membrane backbone. Synthetic forms of membranes were introduced in the 1940s and initially were based on phenol-formaldehyde backbone polymer. Later, other methods evolved (Strathman 1991), including a styrene polymerized with divinylbenzene backbone that was subsequently sulfonated or aminated to yield a cationic or anion membrane, respectively. One of today’s most popular membranes,

Table 2.1. Fixed Charge Moieties Used for Cationic and Anionic Ion Exchange Membranes

<u>Cationic Moieties</u>	<u>Anionic Moieties</u>
SO_3^-	NH_3^+
COO^-	RNH_2^+
PO_2^-	R_3N^+
RSO_2^-	R_2N^+
HPO_2^-	R_3P^+
SeO_3^-	R_2S^+

Nafion®, is produced by polymerizing a vinyl ether copolymer with tetrafluoroethylene. The appendix provides a list of manufacturers and properties of commercially available ion exchange membranes for electro dialysis.

The microstructure of an ion exchange membrane is illustrated by the simplified cross section of a cationic membrane shown in Figure 2.2. The shaded portions represent the polymer backbone, and the fixed charged sites are sulfonate groups. The negative fixed charges attract positive ions, such as Na^+ , which migrate and diffuse through the porous membrane toward the cathode.

Figure 2.2. Cross Section of a Cationic Electrodialysis Membrane with Sulfonate Fixed Charges

The physical and chemical properties of ion exchange membranes can be tailored for a particular application. The backbone polymer matrix defines the mechanical strength, and the fixed charges define the ion selectivity and electrical resistance. These properties can then be optimized by varying the degree of hydrophobic or hydrophilic character, distribution of the fixed-charge density, degree of crosslinking, and other parameters. A brief list of desirable membrane properties is given in Table 2.2.

Table 2.2. Important Properties of Ion Exchange Membranes Used for Electrodialysis

- High Ionic Selectivity
- Low Electrical Resistance
- Low Back Migration of Ions
- Good Mechanical Strength and Durability
- Chemical and Thermal Stability
- Rapid Recovery From Operational Upsets
- Inexpensive

In practice, varying membrane properties has opposing effects, and, therefore, compromises must be made. For example, a high degree of crosslinking will provide good mechanical strength and durability. This is necessary to prevent the membrane from fluttering under cell compression and usually increases the membranes chemical stability. However, high crosslinking also decreases the electrical conductivity of the membrane, and, therefore, higher voltages must applied to maintain a constant current flow.

2.3 Mass Transport

The transport phenomena relevant to understanding electrodialysis flow cells are presented here. These phenomena include a definition of mechanisms of transport, a limiting current, and relation of measured variables to dimensionless parameters.

2.3.1 Mechanisms of Transport

For an electrochemical system, an overall mass balance on a particular ionic species is described as: the accumulation of ionic species, i , is equal to change in the flux of i plus a generation or depletion term due to reaction. Mathematically, this is expressed by:

$$\frac{dC_i}{dt} = - \nabla \cdot N_i + R_i \quad (3)$$

where C_i is the concentration, N_i is the flux density, R_i is a reaction term, and t is time. The definition of a flux density includes three modes of ion transport: migration, diffusion, and convection. For a dilute solution, the flux density of an ionic species is given below:

$$N_i = -z_i u_i F C_i \nabla \Phi - D_i \nabla C_i + C_i v \quad (4)$$

where z_i is the valence state, u_i is the ionic mobility, F is Faraday's constant, Φ is the applied potential, D_i is the diffusivity, and v is the fluid velocity vector. The contributions of the terms in Equation (4) are from migration, diffusion, and convection, respectively. These mechanisms are briefly described below.

Transport by convection typically occurs from an external input of mechanical energy such as stirring or agitation. This mechanism is normally the predominant mode of ion transport for an electrochemical cell. In electroanalysis, convection is promoted by mesh screens within flow distributors. The screens create a tortuous path for fluid flow and force the fluid to travel at high velocities. Therefore, the inertia forces of the fluid dominate the viscous forces and uniform mixing is achieved.

Ionic migration is driven by the applied electric field and is purely electrostatic. The process does not distinguish between a supporting electrolyte and a specific electroactive species. Therefore, the charge can be carried by the supporting electrolyte or the electroactive species. In solutions with large excess supporting electrolyte, migration does not contribute significantly to ionic transport because little charge is transported by the electroactive species. However, in dilute solutions or depleted regions this mechanism can dominate mass transport. It should be noted that the ionic mobility and the diffusion coefficient are related at infinite dilution by the Nernst-Einstein relation:

$$D_i = RTu_i \quad (5)$$

where R is the universal gas constant and T is the solution temperature.

The concentration gradient established between the membrane or electrode and the bulk solution controls the contribution of diffusion to ion transport. Figure 2.3 shows concentration gradients on both the anode and cathode side of a cationic membrane. The laminar boundary layer region, δ , defines a region where the majority of the concentration and potential changes occur. This is commonly referred to as the Nernst-diffusion layer. Although the gradient is drawn with a linear slope, in practice, there is curvature to this profile. Ion transport is dominated by diffusion within the Nernst layer, but outside the layer convection controls transport. As will be described below, the stagnant Nernst region is where mass transport is limited in most electrochemical systems.

2.3.2 Limiting Current

As the potential is increased in an electrochemical process, the concentration of the electroactive species is depleted at the reacting surface. This depletion can occur both at membrane and at electrode surfaces (Figure 2.3). When depletion occurs, it limits the transport of charge carrying species and thus limits the system operating current. If the interfacial concentration of the reacting species is reduced to zero, the corresponding current is termed the "limiting current." It is very important to

Figure 2.3. Concentration Gradients on Anode and Cathode Side of a Cationic Membrane at Steady State

quantify this parameter for practical applications of electrochemistry. If the current of the system is driven above the limiting value, other, typically unwanted, side reactions such as water electrolysis will occur. Under these conditions, a decrease in the current efficiency of the desired reaction will result in an increase in operating costs.

Figure 2.4 shows a typical current versus voltage curve for an electrodialysis process depicting three characteristic regions (Helfferich 1959; Spiegler 1971; Forgacs et al. 1972). In Region I, the current increases almost linearly with the applied potential. This response is due to ohmic behavior of the solution and is controlled by a mixture of electron and mass transfer. As the potential increases, the current begins to approach a constant value or plateau shown as Region II in Figure 2.4. Here, a fully developed boundary layer is established at the membrane interface and the current is limited by the mass transport of current carrying ions within the diffuse layer. Finally, at higher potentials, side reactions are forced in Region III. Many investigators have attempted to determine which reactions are most probable in this region, but currently there is no uniform consensus (Rosenberg and Tirrell 1957; Gregor and Peterson 1964; Block and Kitchener 1966; Brady and Turner 1978; Makai and Turner 1978; Rubinstein and Shtilman 1979; Rubinstein and Segel 1979; Rubinstein 1981; Bassignana and Reiss 1983). The secondary reactions typically postulated are either the oxidation or reduction of water, while others have attributed the increased current to breakdown to electroneutrality (Taky et al. 1992a,b). The following discussion will focus on Region II where the current is under mass transfer control.

Figure 2.4. Characteristic Current Versus Voltage Curve for an Electrodialysis Process

Within the boundary or Nernst-diffusion layer, the contributions of convection are negligible and ionic transport is dominated by diffusion and migration. Therefore, Equation (4) can be simplified and is shown below in one dimension for Cartesian coordinates:

$$N_i = - z_i u_i F C_i \frac{d\Phi}{dx} - D_i \frac{dC_i}{dx} \quad (6)$$

By applying the Nernst-Einstein relation, Equation (6) is expressed as:

$$N_i = - D_i \left[\left(\frac{z_i F C_i}{RT} \right) \frac{d\Phi}{dx} + \frac{dC_i}{dx} \right] \quad (7)$$

Equation (7) describes the mass transport within the diffuse layer in the most general case, where migration effects are significant. However, for most practical applications, solution ionic strengths are large and migration transport can be neglected.

The current in an electrolytic cell is caused by the movement or flux of ions in solution. The ionic flux is related to the cell current, I , by:

$$I = F \sum z_i N_i \quad (8)$$

For high ionic strength solutions, the flux resulting from diffusion is substituted into Equation (8) to yield:

$$-I = zAFD \frac{dC}{dx} \quad (9)$$

where A is the active electrode area. The limiting current occurs when the interfacial concentration drops to zero and is given by:

$$-I_L = zAFD \frac{C_b}{\delta} \quad (10)$$

where C_b is the bulk solution concentration. Although this a simple treatment, Equation (10) shows the influence of controllable parameters such as electrode area, thickness of the diffuse layer, and bulk concentration of the electroactive species. At steady state, the limiting current can also be written in terms of the mass transfer coefficient, k_m :

$$-I_L = zAFk_m C_b \quad (11)$$

When Equations (10) and (11) are compared, it is clear that $k_m = D/\delta$.

2.3.3 Dimensionless Parameters

The relative thickness of the diffuse layer is a function of the fluid physical properties and the fluid velocity. A typical boundary layer thickness is approximately 10^{-2} cm and is more specifically characterized by the ratio of fluid viscous forces to inertia forces. This is represented by a dimensionless variable called the Reynolds number, Re , and given by:

$$Re = \frac{l v}{\nu} \quad (12)$$

where l is a characteristic length and ν is the kinematic viscosity. The boundary layer thickness is inversely proportional to the Re (Schlichting 1979). Therefore, operating the fluid at a high Re decreases the diffuse layer thickness and correspondingly increases the mass transfer coefficient. In practice, a high Re is obtained by operating at large flow rate or inserting turbulent promoters which force the fluid to mix vigorously.

In industry, there is a wide variety of electrochemical cell geometries, electrodes, and flow patterns. Normally, the flow fields are too complex to warrant exact numerical solutions for the velocity profiles by fluid mechanics. Instead, expressions are sought that use space-averaged quantities while permitting insight into the mass transfer characteristics. A very useful method incorporating this logic is dimensional analysis.

Dimensional analysis provides correlations that express the mass transport characteristics in terms of the fluid flow conditions and the electrolyte properties. This approach also facilitates analogies between heat and momentum transfer. In the most general case, a correlation describing mass transport by convective-diffusion is given below:

$$Sh = aRe^bSc^cGr^d \quad (13)$$

where

$$Sh = \frac{k_m l}{D} \quad (14)$$

$$Sc = \frac{\nu}{D} \quad (15)$$

$$Gr = \frac{l^3 g \rho}{\mu^2} \Delta \rho \quad (16)$$

ρ is the fluid density; μ is the fluid viscosity; g is the gravitational constant; and a , b , c , and d are empirical constants. Equation (13) includes contributions from both forced and free convection. The dimensionless groups defined in Equations (14-16) are termed the Sherwood number, Sh ; the Schmidt number, Sc ; and the Grashof number, Gr . The Sherwood number is a measure of the rate of mass transport and is related to the limiting current by the mass transfer coefficient. The Schmidt number compares the rate of transport by convection to that by diffusion. The Grashof number represents the ratio of buoyancy forces to viscous forces in a free-convection flow system.

Most electrochemical applications operate under well-mixed conditions in which forced convection dominates. Under these circumstances, the Gr number is negligible and Equation (13) simplifies to:

$$Sh = aRe^bSc^c \quad (17)$$

Equation (17) has been applied to many different electrode geometries. Table 2.3 lists some of the empirical constants for various electrode configurations (Walsh 1993). As seen from Table 2.3, the Re exponent increases as the flow conditions change from laminar to turbulent. In addition, the value of the Sc exponent is typically 1/3, which compares well with known hydrodynamic theory.

2.4 Applications

In most industrial applications, electrodialysis is performed in a "stack" configuration. The process is operated continuously with streams flowing either cocurrent or countercurrent. The cell is assembled by alternately stacking cationic and anionic membranes between two parallel flat-plate electrodes. Spacers and flow distributors are placed on either side of the membranes to direct flow

Table 2.3. Averaged-Mass Transport Correlations for Various Electrode Geometries

<u>Electrode Configuration</u>	<u>Flow Conditions</u>	<u>Correlation</u>
Rotating Disk Electrode	$102 < Re < 10^5$	$Sh = 0.62 Re^{0.5} Sc^{0.33}$
	$Re > 10^6$	$Sh = 0.011 Re^{0.87} Sc^{0.33}$
Rotating Cylinder Electrode	$100 < Re < 10^5$	$Sh = 0.079 Re^{0.7} Sc^{0.36}$
Annular Flow	$Re < 2000$	$Sh \approx 1.61 Re^{0.33} Sc^{0.33}$
	$Re > 2000$	$Sh = 0.023 Re^{0.8} Sc^{0.33}$
Parallel Plate, Horizontal	$Re < 2300$	$Sh = 1.85 Re^{0.33} Sc^{0.33}$
Channel Flow	$Re > 2300$	$Sh = 0.023 Re^{0.8} Sc^{0.33}$

uniformly across the membrane and to promote turbulence for mass and heat transfer enhancement. This design is commonly referred to as a “plate-and-frame” system. The flat geometry provides easy assembly and cleaning, and a relatively uniform current distribution across the electrode surface. Figure 2.5 shows a process diagram of the stack configuration. Some of the common electrode materials used in industry are listed in Table 2.4.

Figure 2.5. Flow Diagram of a Cocurrent Electrodialysis Process

Table 2.4. Anode and Cathode Materials Typically Used in Commercial Electrodialysis Units

<u>Anode Materials</u>	<u>Cathode Materials</u>
Pt, Pt/Ti, Ir/Ti, Pt-Ir/Ti(Pt/Nb,Pt/Ta)	Hg, Pb, Ni
PbO ₂ on Ti, Nb, or Carbon	Steels and Stainless Steels
Ni (alkaline media)	TiO _x
Pb (acid-sulfate media)	Graphite
Dimensionally Stable Anodes (DSA): Ru-Ti Oxide on Ti for Cl ₂ , IrO ₂ on Ti for O ₂	Low H ₂ Overpotential Materials on Steel: Ni, Ni/Al, Ni/Zn
Magnetite: Fe _{3-x} O ₄	Hastelloys: Ni-Mo-Fe, Ni-Mo-Cr
Conducting Ceramics: Ti ₄ O ₇	

Recent improvements in the performance of ion exchange membranes have allowed electrodialysis to be an attractive alternative for many industries. Applications of electrodialysis include brackish water desalination, wastewater treatment, production of table salt, production of chlorine and caustic soda (chlor-alkali industry), recovery of electrolytes, production of ultrapure water, demineralization of food products, electrochemical synthesis, nuclear waste treatment (Sugimoto 1978; Rauzen et al. 1978; Moskvina et al. 1980; Gurskii and Moskvina 1987; Abdul-Fattah 1987), and others. Production-scale units typically operate with 100 to 500 cationic-anionic membrane pairs per stack. The exposed electrode area ranges from 1 to 70 m². It should be noted that large-scale production electrodialysis units are economically competitive with other membrane separation techniques such as reverse osmosis, pervaporation, dialysis, and ultrafiltration.

Electrodialysis offers many advantages as a separation technology. The key feature of electrodialysis, setting it apart from other methods, is that no or little secondary wastes are generated upon separation. This advantage is especially important for hazardous waste treatment where handling secondary waste can control the economics of remediation. Also, the operating conditions of electrodialytic processes are attractive. Typical conditions include low temperature (< 70°C), continuous flows, and accommodation of large pH variations (pH = 0-14). In addition, the process is inherently modular, allowing simple scale-up procedures and precise control of the separation. Another cost-savings advantage is that during ion separation, acidic and alkaline streams are produced for use elsewhere in the process or for resale as commodities.

Along with the many attractive aspects of electrodialysis, some potential disadvantages need to be considered: membrane fouling and precipitation of salts as ions are transported across compartments of varying pH. In addition, the separation technique is limited to charged species or species

that are complexed with a charged ligand. Possible operating hazards, that are easily dealt with in practice, are the production of hydrogen gas at the cathode and the relatively large currents passed during operation. Under certain conditions hydrogen gas evolution can reach explosive limits; however, in practice off-gas streams are routinely diluted to safe levels with standard air blowers. Also, the high currents do not represent a problem because of the low cell voltages used per module or stack (< 100 V) and the use of safe designs which minimize possible exposure.

2.5 Economic Considerations

A simplified approach to evaluate the economics associated with an electrodialytic process is outlined in detail by Pletcher and Walsh (1990). Their method is summarized below and considers the total production costs of the cell alone, C_{Total} , to be function of three cost components:

$$C_{Total} = C_E + C_{Equip} + C_{Mix} \quad (18)$$

where C_E is the cost to drive the electrolytic process, C_{Equip} is the cost to purchase the electrolytic reactor or capital equipment, and C_{Mix} is the cost to mix or stir the electrolyte. All of these terms are a function of the operating current density and, thus, the importance of the limiting current is apparent. The ideal operating conditions will minimize the cell current density while maximizing the current efficiency.

The cost to power the electrolytic process is given as direct function of the operating cell potential. This is shown below:

$$C_E = W_1 q E_{cell} \quad (19)$$

where W_1 is the cost of electricity in dollars per kilowatt-hour, q is the total charge required for the separation, and E_{cell} is the applied cell potential. The equipment cost associated with the cell is linearly proportional to the electrode area, A , required:

$$C_{Equip} = W_2 A \quad (20)$$

where W_2 is the cost per electrode area, and this cost is assumed not to change with current density. Finally, the electrolyte mixing costs are specific to the type of process geometry. In most cases, this value can be estimated by:

$$C_{Mix} = W_1 P t \quad (21)$$

where P is the power required to mix or pump the electrolyte, and t is elapsed time.

The total production cost is the combination of Equations (18-21) and is shown below:

$$C_{Total} = W_1 q E_{cell} + W_2 A + W_1 P t \quad (22)$$

Electrodialytic processes are commonly operated under constant current conditions, and, therefore, it is useful to express the total cost as a function of current density, i . For galvanostat conditions, $q = i t$, and $E_{\text{cell}} = i R_T$ where R_T is the overall cell resistance. The total cost as a function of current density is given by:

$$C_{\text{Total}} = W_1 q i R_T + \frac{W_2 A q}{i t} + \frac{W_1 P q}{i} \quad (23)$$

The minimum total cost is obtained by differentiating Equation (23) and setting the quantity equal to zero:

$$\frac{dC_{\text{Total}}}{di} = W_1 q R_T - \frac{(W_2 A q / t) + W_1 P q}{i^2} = 0 \quad (24)$$

Equation (24) can be rearranged to provide the optimum operating current density, i_{min} , as shown below:

$$i_{\text{min}} = \left[\frac{(W_2 A / t) + W_1 q}{W_1 R_T} \right]^{1/2} \quad (25)$$

In general, the minimum current density is a function of electrode area, cost factors W_1 and W_2 , and overall cell resistance. The cost components and minimum current density are shown graphically in Figure 2.6.

Figure 2.6. Cost as a Function of Current Density for a Typical Electrodialytic Process

3.0 Electrodialysis Experiments for Na⁺/Cs⁺ Separation

The experiments for this study were conducted on both a laboratory and a bench scale. The laboratory study was used to screen the feasibility of Na⁺/Cs⁺ separation using electrodialysis, and the bench-scale study provided data for process scale-up. Results are given for both parts of the experimental work.

3.1 Equipment

This section describes the equipment used for the electrodialysis experiments, as well as the solution preparation and analysis.

3.1.1 Laboratory-Scale Equipment

The laboratory experimental apparatus consisted of an electrodialysis cell, a central pumping unit, flow meters, and a potentiostat. Figure 3.1 shows a schematic of the experimental system. An ElectroCell AB Micro Flow Cell (Electrosynthesis Co., Inc., Lancaster, NY) was used to perform electrodialysis experiments. The micro-flow cell was operated in a three-compartment configuration with parallel flat-plate electrodes. The electrode materials were a nickel cathode and a dimensionally stable anode designed for O₂ evolution in low pH solutions. A spacer with a mesh flow distributor was inserted into each compartment to provide a uniform and reproducible flow field for all experiments. A Nafion® 417 cationic membrane was used for the Na⁺/Cs⁺ separation, and an RAI Raipore R-1030 anionic membrane was used to prevent the migration of protons to the catholyte compartment. Inert Kynar® gaskets were used to provide leak-tight seals around the membranes, spacers, and electrodes.

Figure 3.1. Block Diagram of the Experimental Apparatus Used to Separate Mixtures of Na⁺ and Cs⁺

Each electrode or membrane had an exposed area of 10 cm², resulting in approximately 1.5 cm³ for the volume of each compartment. The system was operated in a one-pass mode without recycling. The anolyte, catholyte, and feed solutions were pumped from their reservoirs to their respective cell compartments with a MasterFlex® Model 7567 pump unit (Cole Palmer, Niles, IL). The unit was capable of driving three peristaltic pump heads simultaneously on a single drive shaft. The system tubing material was primarily PFA Teflon® with the exception of a small portion within the pump heads, which was Tygon® R-3603. Gilmont (Barrington, IL) direct reading flow meters of glass and PTFE Teflon® were installed on the inlets and outlets of the cell, and minor flow adjustments were made with micrometer valves on the downstream side. This ensured that all three compartments had equal pressure drops, thereby decreasing the possibility of cross-flow between compartments.

The electrical driving force for the ion separation was provided by a PAR Model 175 Universal Programmer in conjunction with either a PAR Model 173 or Model 371 Potentiostat/Galvanostat (EG&G, Princeton, NJ). The Model 173 was used for Na⁺/Cs⁺ concentration ratios of 1 and 10, while the Model 371 was necessary for the ratio of 100 because of the large currents generated. All experiments were run in a traditional linear or cyclic voltammetric procedure. The Model 175 was used to vary the potential from approximately 2 to 9 volts at scan rates ranging from 1 mV/s to 5 mV/s. The voltage and current data were collected by a Macintosh IIfx computer through an analog-to-digital board (National Instruments, NB-MIO-16H, Austin, TX). The data acquisition board was 12-bit, corresponding to a resolution of 2.44 mV. The computer acquisition rate was approximately 1.5 seconds and was controlled using LabVIEW2 software (National Instruments, NB-MIO-16H, Austin, TX).

For the laboratory-scale unit, all three compartments were pumped with 18 MΩcm water to balance the flows and check for leaky seals. The reservoirs were then switched to the appropriate solutions and pumping resumed. Samples from each of the effluent streams (anolyte, catholyte, and feed) were separately collected from mid-stream. The total volume collected was typically 10 mL and varied slightly, depending on the operating flow rate.

3.1.2 Bench-Scale Equipment

The bench-scale apparatus was a commercially available unit purchased from Tokuyama Soda Co., Ltd (Model TS-1-10) with an electrode area of 100 cm². Although the unit had the capability of operating from 1 to 10 cell pairs, only a standard three compartment with one cell pair was used. The cell geometry was a flat-plate and frame configuration with an anode, cathode, charge-selective membranes, gaskets, and spacers. The anode and cathode were platinumized titanium, which provides excellent chemical resistance against the aggressive acidic and alkaline streams. The cationic membrane was a Neosepta CMX, and the anionic membrane was a Neosepta AMX, both were standard grade. Mesh spacers were used to provide a channel for fluid flow and promote turbulence within the electrodialytic cell compartments.

Figure 3.2 shows a schematic diagram of the bench-scale apparatus. The system consists of the Tokuyama Soda cell, feed tanks, a power supply, and four centrifugal pumps with associated flowmeters. The power supply was a Model 730 "Boss" Electrochemical Process Control Unit (Electrosynthesis Co., Inc., Lancaster, NY). The Boss-Unit operates from 240 V AC and provides an output voltage of 60 V and a current of 50 A. The Boss-Unit also controls four 0.07-hp fluid pumps

Figure 3.2. Block Diagram of the Large-Scale Electrodialysis System Showing All Streams Recycling

used to circulate the anolyte, catholyte, and feed streams. The cell current, voltage, and solution flow rates are continuously monitored by the Boss-Unit. For personnel safety, control limits can be set and if these values are exceeded during operation, the Boss-Unit will immediately shut down all power to the system.

A small modification was made to accommodate experiments that did not recycle the three-compartment streams. For these "once-through" experiments, 10-L carboy tanks were installed to increase storage capacity. The flow rates used for all experiments ranged from 0.42 L/min to 0.48 L/min. As with the laboratory-scale cell, all three-compartment flows were started before a potential was applied across the electrodes to identify any leaking seals or unbalance flows.

3.1.3 Solution Preparation and Analysis

Different solutions were used for the laboratory- and bench-scale experiments. For the laboratory-scale experiments, the reagents used were sodium nitrate (ACS, Aldrich, Milwaukee, WI), cesium nitrate (99.999%, Aldrich, Milwaukee, WI), potassium hydroxide (AR, Mallinkrodt, Paris, KY), and nitric acid (AR, Mallinkrodt, Paris, KY). These reagents were used as received. All solutions were prepared with 18.2 MΩcm water (Milli-Q UV Plus, Millipore Corp., Bedford, WA). For the bench-scale apparatus, the reagents used were nitric acid (61-71%, J.T. Baker, Phillipsburg, NJ), sodium nitrate (technical grade, Noah Technology Co., San Antonio, TX), and potassium hydroxide (technical grade, Noah Technology Co., San Antonio, TX).

An Instrumentation Laboratory 451 AA/AE Spectrophotometer was used to determine the sodium and cesium concentrations in each effluent stream. Atomic emission was used to measure the sodium concentration, while atomic absorption was used to quantify cesium. The error in each measurement was estimated to be 4% and was completely dominated by the instrument error.

3.2 Results and Discussion

The electro dialysis system was characterized by a dimensional analysis (discussed below) to show the extent of scale-up capabilities. The mass transfer characteristics were shown to behave similarly to other parallel flat-plate configuration systems. The empirical expression presented here demonstrates that large-scale equivalent ion separation by electro dialysis is readily achievable. Preliminary experiments with the bench-scale unit indicate it behaves similarly to the laboratory-scale apparatus.

3.2.1 Laboratory-Scale Experiments

The results of the laboratory study are depicted by the figures and equations below. Figure 3.3 shows a representative cyclic voltammogram for an electro dialysis experiment with an aqueous feed solution of 10 mM NaNO_3 and 10 mM CsNO_3 . The anolyte and catholyte consisted of 56-mM solutions of HNO_3 and KOH , respectively. Each solution was pumped at a rate of 5 mL/min, and the voltage was ramped at 1 mV/s. Little hysteresis was observed in the reverse scan, and increasing the scan rate by as much as a factor of 5 had no noticeable effect. The voltammogram exhibits the characteristic S-shape observed for mass transfer limited systems.

The curve contains three distinct regions in which different mechanisms control the current (see Section 2.4). In the first region, the behavior is approximately ohmic, corresponding to the existence of a quasi-equilibrium state at the interface between the membrane and the solution. This is followed by a second region where a "transport-limited" current plateau is observed. In this situation, the current is limited by the rate of mass transfer across the stagnant boundary layer adjacent to the

Figure 3.3. Cyclic Voltammogram for an Electro dialysis Experiment Involving an Aqueous Feed Solution of 10 mM NaNO_3 and 10 mM CsNO_3 at a Flow Rate of 5 mL/min

membrane surface, with the concentrations of the species that carry charge through the membrane approaching zero at the membrane surface. The final region is characterized by a rapid current increase with increasing voltage and a corresponding increase in signal noise. The cause of this behavior has been the subject of several studies (Rosenberg and Tirrell 1957; Gregor and Peterson 1964; Block and Kitchener 1966; Brady and Turner 1978; Makai and Turner 1978). These initial reports postulated that the current increase is due to the oxidation and reduction of water at the membranes. However, more recent results (Rubinstein and Shtilman 1979; Rubinstein and Segel 1979; Rubinstein 1981; and Bassignana and Reiss 1983) indicate that the phenomenon may be caused by a breakdown in electroneutrality adjacent to the membrane surface, or perhaps a combination of the two effects (Taky et al. 1992a,b).

Increasing the flow rate to 10, 25, and 50 mL/min resulted in the behavior shown in Figure 3.4. As the fluid velocity increased, the transport-limited current increased from 18 mA to 24, 36, and 50 mA, approximately with the square root of the velocity. Such behavior is expected. In the transport-limited current region, the rate of mass transfer across the boundary layer will vary linearly with the boundary layer thickness (Helfferich 1962), which, in turn, varies with the square root of the fluid velocity (Blasius 1908).

From Figures 3.3 and 3.4 it is clear that a limiting current can easily be measured. This value can then be used in a dimensional analysis to provide a correlation between mass transport

Figure 3.4. Current Versus Voltage Response for Flow Rates of 5, 10, 25, and 50 mL/min

characteristics and fluid flow conditions. The desired relationship is given by Equation (17). In this case, the mass transfer coefficient in Equation (14) is obtained from the measurement of the mass transfer limiting current by:

$$k_m = \frac{i_{lim}}{zFAC_b} \quad (26)$$

A log-log plot of the Sh number versus the Re number will provide the constants a and b in Equation (17). As mentioned above, the Sc exponent is usually assigned a value of $1/3$, based on known hydrodynamic theory.

Figure 3.5 shows such a plot using the following parameters: $C_b = 20$ mM, $\mu = 0.01$ g/cm·s, $\rho = 1$ g/cm³, $D = 1.70 \times 10^{-5}$ cm²/s [the molar average for sodium and cesium (Harned and Shropshire 1958a,b)], and $d_e = 0.375$ cm [the equivalent diameter of the laboratory-scale flow cell (Knudsen and Katz 1958)]. Figure 3.5 indicates a relationship of:

$$Sh = 1.0 Re^{0.44} Sc^{1/3} \quad (27)$$

Figure 3.5. Log-Log Plot of the Sherwood Number Versus the Reynolds Number

Walsh (1993) has tabulated numerous correlations for parallel flat-plate flow cells, and the fitted constants obtained here agree well with the expected values (also refer to Table 2.3 for typical constant values for a parallel flat-plate configuration). This dimensional analysis verifies that this technique can easily be scaled for field applications. The next step is to determine how well cesium can be separated from sodium.

The separation efficiency is a useful parameter for determining the feasibility of separating sodium and cesium ions by electrodialysis. The separation efficiency, α , is defined as the ratio of the fraction of cesium that passes through the cationic membrane to the fraction of sodium that passes through the cationic membrane. It is expressed as:

$$\alpha = \frac{[Cs^{+}_{Catholyte}] / [Cs^{+}_{Feed}]}{[Na^{+}_{Catholyte}] / [Na^{+}_{Feed}]} \quad (28)$$

where $[Cs^{+}_{Catholyte}]$ is the concentration of Cs^{+} in the catholyte effluent, $[Cs^{+}_{Feed}]$ is the concentration of Cs^{+} in the entering feed, $[Na^{+}_{Catholyte}]$ is the concentration of Na^{+} in the catholyte effluent, and $[Na^{+}_{Feed}]$ is the concentration of Na^{+} in the entering feed.

Figure 3.6 shows the separation efficiency plotted as a function of the current normalized to the transport-limited current. For each flow rate, a maximum α value of 2 to 3 occurs at currents below the transport-limited value, indicating the cationic membrane is preferentially allowing Cs^{+} to transport into the catholyte. At currents above the transport-limited value, α decays to a constant value ranging between 1.2 and 1.3.

Figure 3.6. Separation Efficiency as a Function of the Current Normalized to Its Transport-Limited Value for Flow Rates of 5, 10, 25, and 50 mL/min

This behavior is consistent with that observed by Rubinstein (1984) in an investigation of valency-induced counterion selectivity of ion exchange membranes. At currents below the transport-limited value, the membrane composition is near its quasi-equilibrium value and the system selectivity is predominantly membrane-determined. At higher currents, the higher flux of Cs^+ through the membrane leads to its depletion in the stagnant boundary layer and a corresponding shift in the equilibrium Cs^+ concentration in the membrane. The result is a decrease in the membrane selectivity. As the current increases further, both Cs^+ and Na^+ are strongly depleted from the boundary layer, and transport across the boundary layer becomes the limiting step of the process. Under these conditions, most membrane selectivity is lost and the separation efficiency is determined by the relative mobilities of Cs^+ and Na^+ . A comparison of the diffusivities of Cs^+ and Na^+ (Harned and Shropshire 1958a,b) shows good agreement between the experimental (1.2 to 1.3) and theoretical (1.27) values of α at currents above the transport-limited plateau.

The effect of increasing the sodium nitrate concentration relative to that of the cesium nitrate is shown in Figure 3.7, with the separation efficiency plotted versus the normalized current. It is observed that the separation efficiency decreases slightly as the sodium nitrate concentration increases. However, the α values fall within the same range as those in Figure 2.5. As with the previous data, the maximum separation efficiency occurs prior to the transport-limited current plateau.

Figure 3.7. Separation Efficiency as a Function of Current Normalized to Its Transport-Limited Value for Na^+/Cs^+ Concentration Ratios of 1, 10, and 100; a Cs^+ Concentration of 10 mM; and a Flow Rate of 10 mL/min

As mentioned earlier, numerous studies have focused on understanding the cause of the current increases beyond the transport-limited plateau. This question is addressed here by calculating the current efficiency, η , defined as the fraction of current passing through the membrane that is carried by the sodium and cesium ions:

$$\eta = \frac{I_{\text{Na}^+} + I_{\text{Cs}^+}}{I} \quad (29)$$

where

$$I_{\text{Na}^+} = QF[\text{Na}^+_{\text{Catholyte}}] \quad (30)$$

$$I_{\text{Cs}^+} = QF[\text{Cs}^+_{\text{Catholyte}}] \quad (31)$$

I is the total current passed, and Q is the volumetric flow rate. Figure 3.8 shows the current efficiency as a function of the normalized current for a flow rate of 10 mL/min, and Na^+ and Cs^+ concentrations of 10 mM. Similar behavior was observed for the other experiments.

If the rapid current increase beyond the limiting value was exclusively due to water splitting, the current efficiency of Na^+ and Cs^+ would decrease at currents above the transport-limited plateau. Throughout the range of currents covered, the current efficiency was relatively constant at 0.60 to 0.65. This implies the increased current resulted from a proportional increase in each of the ion fluxes across the membrane, rather than water splitting at the membrane. Another possible explanation for the increased current is the physical breakdown of the ion exchange membranes. However, the lack of hysteresis in the cyclic-voltammogram shown in Figure 3.3 suggests that this is not the case.

The one data point in Figure 3.8 that does not fall in the 0.60 to 0.65 range is the first at $I/I_L = 0.28$. It is believed that, at this low current, the contributions of the diffusive flux across the membrane and/or leakage around it are comparable to the migratory flux, resulting in an *apparent* efficiency of greater than unity. This is supported by the presence of Na^+ and Cs^+ in the anolyte stream at concentrations comparable to those necessary to cause the excess efficiency.

3.2.2 Bench-Scale Apparatus

The bench-scale unit was used primarily for sodium nitrate separation to form nitric acid and sodium hydroxide. This system was chosen as a model system to demonstrate the ability of salt splitting and to identify the limiting current for larger geometry. Figure 3.9 shows the current response as the voltage was ramped at a rate of 100 mV/min. The feed solution was 0.1 M sodium nitrate, the catholyte was 0.01 M potassium hydroxide, and the anolyte was 0.01 M nitric acid. From Figure 3.9, a limiting current plateau is clearly evident. The transport-limiting current for these conditions is approximately 70 mA. Duplicate experiments were run to demonstrate the reproducibility of the measurement. Above an applied voltage of 3 volts, it is believed the measured currents deviate because of slight differences in feed concentration and flow-rate variation.

Figure 3.8. Current Efficiency of Na^+ and Cs^+ as a Function of the Normalized Current for a Solution of 10 mM NaNO_3 and 10 mM CsNO_3 , and a Flow Rate of 10 mL/min

Figure 3.9. Current as a Function of Applied Potential Indicating the Mass Transport Limiting Current for the Bench-Scale Apparatus Operating at 0.42 L/min

Figure 3.10 shows the measured current as a function of voltage for various flow rates. Over a large voltage range, the current response is reproducible for the three flow rates examined. The current displays the expected linear behavior obtained by other investigators at high applied potentials (Walsh 1993). At these high voltages, side reactions dominate the current and are assumed to be a combination of water splitting and ionic transport. However, the partitioning between these two mechanisms is not discernible from these data. This issue is beyond the scope of this work but can be addressed in future studies.

Figure 3.10. Current Versus Applied Voltage for Flow Rates of 0.42, 0.37, and 0.17 L/min

4.0 Conclusions

Electrodialysis has been shown to be an effective method for the separation of monovalent cations, specifically, sodium and cesium ions in aqueous solution. The largest separation of Cs^+ and Na^+ occurred at currents below the transport-limited current plateau where the flux is limited by the rate of transport across the membrane, rather than across the stagnant boundary layer. At these currents, the flux of cesium across the membrane was two to three times greater than that of sodium. The magnitude of the separation efficiency remained essentially constant for $[\text{Na}^+]/[\text{Cs}^+]$ concentration ratios up to 100. This result suggests that the separation efficiency of the system is membrane-specific, allowing different separations to be performed by judicious choice of membranes pairs.

The current efficiency for sodium and cesium remained constant for currents up to eight times the limiting value. This information provides insight into the mechanisms that contribute to the rapid increase in current beyond the limiting current. For the system examined here, the increased current resulted from an increase in sodium and cesium flux across the cationic membrane and not exclusively from water splitting at the membrane.

For Hanford waste applications, the ability to separate equivalent ions is very attractive and opens the possibility of applying electrodialysis to a wide variety of systems with appropriate choice of operating conditions and ion-selective membranes. Electrodialysis has the ability to separate ions of opposite charge, ions of different valence state, and, as shown here, ions of equal valence state. This accommodates applications where selective ion separation is desired, such as tank waste pretreatment. Also, electrodialysis can easily be designed as the primary treatment or incorporated into an existing facility for secondary ion separation.

The approach is most cost effective at low concentrations where costs of other methods such as reverse osmosis and evaporation are high. The technique also creates minimal secondary waste which is abundant in other methods. However, before electrodialysis can be implemented for nuclear waste remediation, the radiological stability of the ion-selective membranes must be evaluated. This task was beyond the scope of the present work, but it is anticipated that exposure to low gamma radiation fields will not significantly degrade the polymer-based ion-selective membranes.

5.0 References

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Appendix

An Abbreviated List of Commercially Available Ion Exchange Membranes Used for Electrodialysis

Appendix

An Abbreviated List of Commercially Available Ion Exchange Membranes Used for Electrodialysis

Membrane	Type	Ion Exchange Capacity (meq/g)	Thickness (mm)	Resistance 0.5N NaCl 25°C (Ω -cm ²)	Perselectivity 1.0/0.5N KCl (%)
Asahi Chemical Industry Company Ltd., Chiyoda-ku, Tokyo, Japan					
K 101	Cation	1.4	0.24	2.1	91
A 111	Anion	1.2	0.21	2-3	45
Asahi Glass Company Ltd., Chiyoda-ku, Tokyo, Japan					
CMV	Cation	2.4	0.15	2.9	95
AMV	Anion	1.9	0.14	2-4.5	92
ASV	Anion	2.1	0.15	2.1	91
DMV	Cation	-	0.15	-	-
Flemion®	Cation	-	-	-	-
Ionac Chemical Company, Sybron Corporation, Birmingham, NJ 08011, U.S.A.					
MC 3470	Cation	1.5	0.6	6-10	68
MA 3475	Anion	1.4	0.6	5-13	70
MC 3142	Cation	1.1	0.8	5-10	-
MA 3148	Anion	0.8	0.8	12-70	85
Ionics Inc., Watertown, MA 02172, U.S.A.					
61AZL386	Cation	2.3	0.5	6	-
61AZL389	Cation	2.6	1.2	-	-
61CZL386	Cation	2.7	0.6	9	-
103QZL386	Anion	2.1	0.63	6	-
103PZL386	Anion	1.6	1.4	21	-
204PZL386	Anion	1.9	0.57	8	-
204SXZL386	Anion	2.2	0.5	7	-
204U386	Anion	2.8	0.57	4	-
Du Pont Company, Wilmington, DE 19898, U.S.A.					
N 117	Cation	0.9	0.2	1.5	-
N 901	Cation	1.1	0.4	3.8	96
Pall RAI Inc., Hauppauge, NY 11788, U.S.A.					
R-5010-L	Cation	1.5	0.24	2-4	85
R-5010-H	Cation	0.9	0.24	8-12	95
R-5030-L	Anion	1.0	0.24	4-7	83
R-5030-H	Anion	0.8	0.24	11-16	87
R-1010	Cation	1.2	0.1	0.2-0.4	86
R-1030	Anion	1.0	0.1	0.7-1.5	81
Rhone-Poulenc Chemie GmbH, Frankfurt, Germany					
CRP	Cation	2.6	0.6	6.3	65
ARP	Anion	1.8	0.5	6.9	79
Tokuyama Soda Company Ltd., Nishi-Shimbashi, Minato-ku, Tokyo 105, Japan					
CL-25T	Cation	2.0	0.18	2.9	81
ACH-45T	Anion	1.4	0.15	2.4	90
ACM	Anion	1.5	0.12	4-5	-

AMH	Anion	1.4	0.27	11-13	-
CMS	Cation	>2.0	0.15	1.5-2.5	-
ACS	Anion	>1.4	0.18	2-2.5	-
AFN	Anion	<3.5	0.15	0.4-1.5	-
AFX	Anion	1.5	0.14	1-1.5	-

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