ELECTROLYTIC MEMBRANE DIALYSIS FOR TREATING WASTEWATER STREAMS – TASK 1.7

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ELECTROLYTIC MEMBRANE DIALYSIS FOR
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INTRODUCTION

Wastewater stream discharge, which is of increasing environmental concern, is addressed in the Code of Federal Regulations, which sets forth the legal details of the National Pollutant Discharge Elimination System to address this problem (1). A technology that will clean up relatively small quantities of water contaminated with ionic matter and separate dissolved species is needed. Dealing with this type of aqueous solution, particularly in the nuclear industry, requires that corrosive ions such as chloride be separated from radioactive species such as uranium prior to final radioactive waste disposition.

Differential dialysis (DD) and reverse osmosis (RO) are two physical separation technologies that have been advanced as means for purifying water. RO concentrates impurities by excluding them (on the basis of particle charge and size) from passing through a porous membrane. Typical RO membranes have pore sizes of 5×10^{-4} μm and use pressure to selectively push water through the membrane while rejecting the dissolved and undissolved nonaqueous material (salts and organic matter). Although it is a giant step toward cleaning the water, the process is objectionable if it is necessary to selectively remove components from the concentrate to allow its safe disposal. Replacing the RO membranes with nanofiltration (NF) membranes with pore sizes of 1×10^{-3} to 3×10^{-3} μm is a partial solution, allowing membrane passage of selected dissolved and/or undissolved nonaqueous material. Some NF membranes are so selective as to allow separation of monovalent ions from divalent ions, but they reject impurities on both a size and electrical charge basis. Thus because of rejection of some charged species by the membrane and because the water cleanup is less effective than RO, the RO technology with NF membranes is not a complete technology.

DD also uses membrane technology to selectively remove nonaqueous material from water on the basis of particle size by allowing it to diffuse through the membrane. The effectiveness of this technology is explained by pore models which show that the rate of diffusion in water is greater than that in the pores of the membrane where friction resistance on the solute from water is greater inside the pore than outside the membrane. Dialysis membranes are designed to have more tortuous pores, making the path longer thereby making the membrane more permeable to low molecular weight species (2). NF membranes are useful for this method. However, the method has serious drawbacks, including diffusion kinetics, adsorption of dissolved or suspended material to the membrane, electrokinetic charge on the membrane that inhibits free ion movement, and osmosis (O) resulting in substantial countercurrent flow. Diffusion kinetics is probably the greatest barrier to the success of this method. The concentration of diffusate particles (N) crossing the membrane is dependent on the membrane area (A), the diffusate concentration gradient ($C_o - C_i$), and time (t).

$$N \propto A (C_o - C_i)t$$

It follows that the rate decreases as the concentration gradient decreases and as the membrane blinds. It becomes apparent that this method for selective removal of diffusate material is not satisfactory.

Direct-current electrodes placed on opposite sides of the membrane can significantly enhance the transport of charged particles of sufficiently small size through the membrane. With the anode immersed in the diffusate (permeate) and the cathode in the retentate, anions, if sufficiently small, will migrate across the membrane toward the anode, thus separating them from their original solution. Reversing the electrode charges will encourage cation flow across the membrane. The Energy & Environmental Research Center has teamed with the U.S. Department of Energy to separate selected ions by electrolytic dialysis.

As with all membrane technologies, membrane efficiency decreases with use because of pore plugging or blinding (4). In water cleanup, the problem is typically addressed by chemical cleaning or backwashing the membrane periodically or a combination (3). Because of the limited scope of this project, membrane cleaning was not investigated.

OBJECTIVES

This project will determine whether electrolytic dialysis has promise in the separation of charged particles in an aqueous solution. The ability to selectively move ions from one aqueous solution to another through a semipermeable membrane will be studied as a function of emf, amperage, and particle electrical charge. The ions selected for the study are Cl^- and SO_4^{2-}. These ions are of particular interest because of their electrical conduction properties in aqueous solution resulting with their association with the corrosive action of metals. The studies will be performed with commercial membranes on solutions prepared in the laboratory from reagent salts. pH adjustments will be made with dilute reagent acid and base.

Specific objectives of the project include testing a selected membrane currently available for electrolytic dialysis, membrane resistance to extreme pH conditions, the effectiveness of separating a mixture of two ions selected on the basis of size, the efficiency of the membranes in separating chloride (Cl^{1-}) from sulfate (SO_4^{2-}), and separation efficiency as a function of electromotive force (emf).

EXPERIMENTAL

Electrolysis involving membranes were investigated for separating chlorides and sulfates from wastewaters containing heavy metals. The electrode used for measuring chloride concentration in the initial tests was calibrated over the range 1–10,000 ppm Cl.

The test equipment consisted of a tubular plexiglass vessel divided in half by a commercial NF polyethylene flexible membrane with a cylindrical carbon electrode extending from the top to within an inch of the bottom on each side of the membrane. The copper-coated carbon electrode

(anode) on one side was connected by a red lead (+) to a commercial variable DC power source, and the similar electrode (cathode) on the other side was connected by a black lead (−) to the variable DC power source. Electrical data were collected and stored by computer.

Nine hundred (900) milliliters of simulant (104 grams $CuSO_4 \cdot 5H_2O$ and 60 grams $CuCl_2 \cdot 2H_2O$) was poured into the cathode chamber of the two-chambered vessel, and 900 mL of 0.2 M NaOH was poured into the anode chamber. Each emf was applied across the membrane for a 2-hour duration. Two series of emf's, including 0.25, 0.50, 1.0 V and 1.0, 2.0, and 3.0 V, were applied during separate tests. Aliquots from the simulant side and the permeate side were taken at the beginning of the tests and after each 2-hour segment. Each aliquot was submitted for sulfate and chloride analysis.

The most noticeable physical change during the test was that the tests performed at voltages above 1 volt displayed a darkening of the NaOH in the anode chamber: the higher the voltage, the darker the discoloration.

During the test, applied voltage and subsequent resistance were recorded by a Fluke multi-channel voltmeter.

RESULTS AND DISCUSSION

Preliminary tests performed using membranes provided by Osmonics selected for their potential resistance to high pH have shown promise. Baseline tests involving simple dialysis (emf = 0) indicated only slight change in the rate of chloride transfer across the membrane as a result of increasing the basicity from pH 7 to pH 14. Electrolytic dialysis is a means of selectively removing ions by size and by charge from a contaminated solution such as low-level nuclear waste. Although technically a filtration technique, the membrane separation under the influence of a DC electrical field improves on filtration by making use of the membrane to hold back ions of one charge while ions of the opposite charge are encouraged to pass the membrane under the influence of an electrical field. The effect of the applied electrical field is to influence the distribution of the ions by altering the neutrality rule in a manner that will allow the desired anions to assemble in a chosen region (around the anode and across the membrane from the waste simulant) of the chemical system. In simplest form, the neutrality rule says that under electrolysis conditions, all parts of a solution will be essentially electrically neutral. The work required to separate a mole of univalent positive and negative ions is on the order of 10^{19} calories, so that mechanically separating the ions is unknown. Instead, providing a positively charged electrode results in a coulombic attraction for the anion and the resulting transference, providing sufficient electric current results in an equivalent amount of ions to be transferred across the membrane to the anode, which must be balanced by similar equivalents of ions within the chamber going to the cathode. Therefore, when a solution containing an electrolyte is placed in a chamber having an electrode of (−) charge, the movement of positive ions across the membrane is retarded by the electrical field while the negative ions' mobilities are toward the electrode on the other side of the membrane. Initial tests involved a determination of the effect of electrical potential on movement of Cl^- across a membrane. The pCl was monitored with an ion- specific electrode. However, the

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range of the ion selective meter was insufficient to analyze over the range of chloride ion in the test solutions. In addition, a SO_4-selective electrode was not available. Therefore, the use of specific ion electrodes to track pCl and pSO_4 was abandoned.

The results of initial tests to determine the removal of chloride and sulfate by electrodialysis at several emf's is shown in Figure 1. Removal of Cl and SO_4 ions from copper(II) salt solution using a membrane under the influence of applied electrical field responded to increased emf and resulted in as much as 24% decrease in anion content over 2 hours at an emf of 3 V. Since resistance of the electrolytic solution changes only slightly during these tests, current flow should increase as voltage increases. Increased current flow is directly related to increased ion flow with the result measured in terms of ion removal in these tests, as shown by Figure 1. As the process proceeded, a brown "scum" formed at the surface of the liquid simulant and as the "scum" migrated to the membrane, it formed a coating on the surface of the membrane, reducing the membrane porosity and slowing the permeation of the ions. At an emf of 4 V, the transport of the ions over the membrane dropped precipitously.

Rapid formation of the brown "scum" in the waste simulant chamber of the cell caused rapid membrane blinding. No analysis of the scum was carried out, but it was presumably copper oxide. Additional tests showed that removal was a function of emf (Figures 2 and 3) and of current flow (Figure 4). Although the permeation of the anions increases with emf, when the emf was greater than 2 V, blinding of the membrane became a problem. The rate of both Cl and SO_4 removal from the simulant decreased between 2 and 3 V and dropped precipitously at 4 V. As
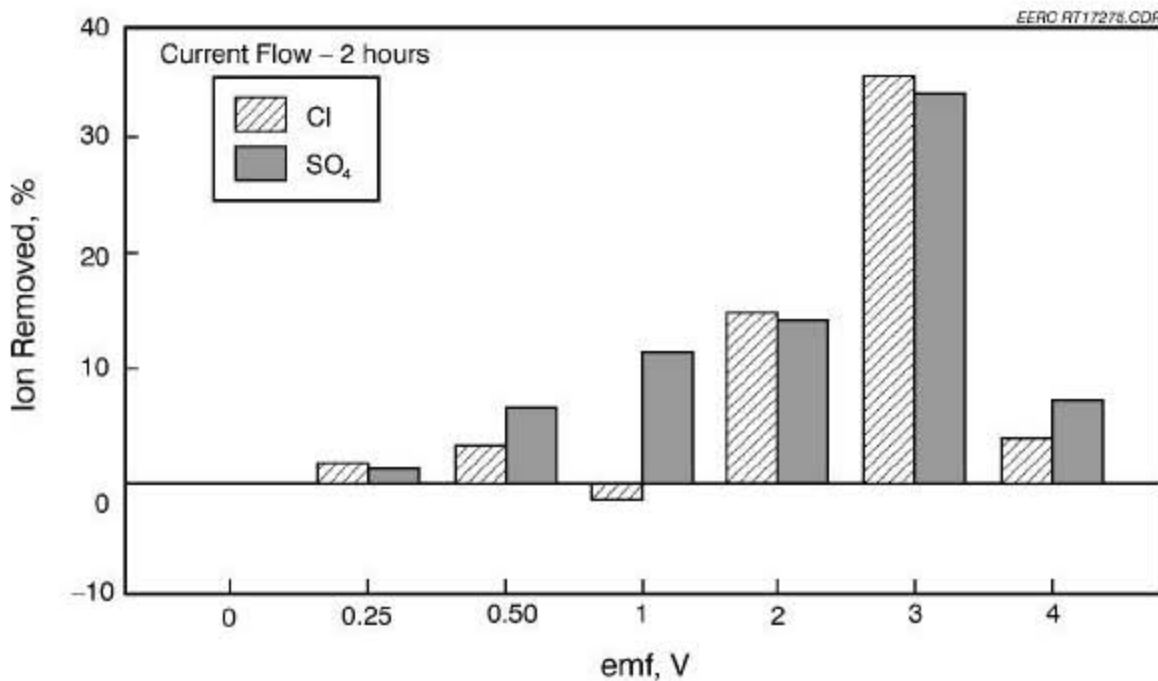

Figure 1. Chloride and sulfate ion removal from waste stimulant using a membrane.
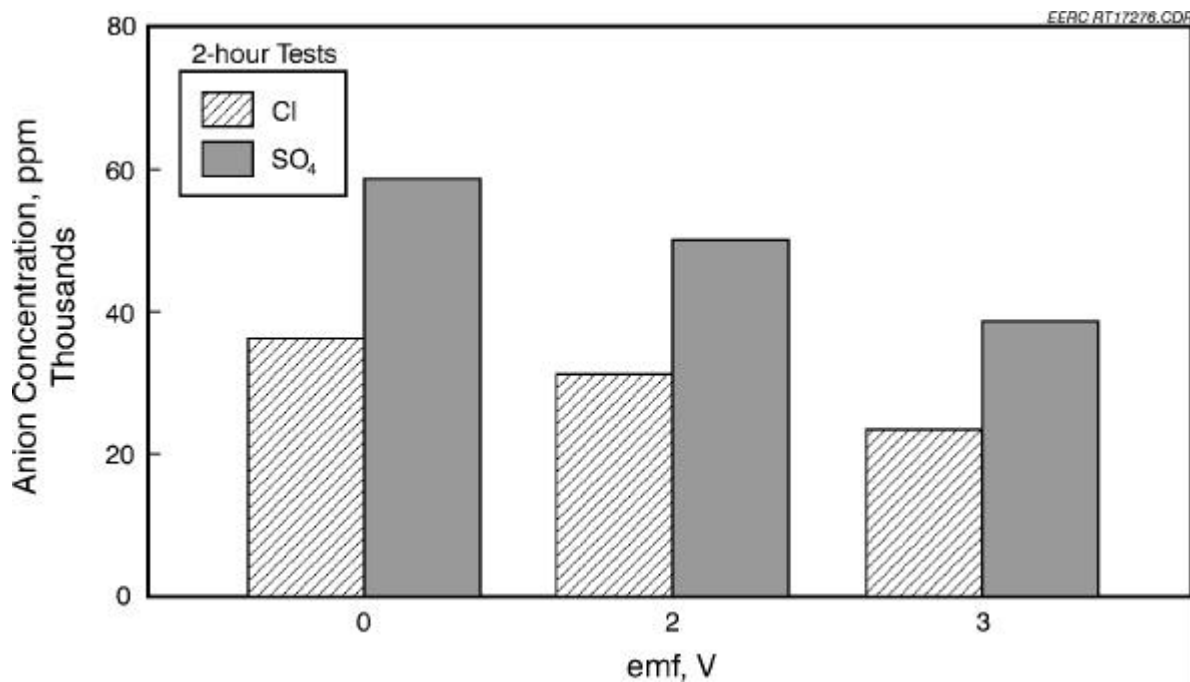
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Figure 2. Comparison of ion removal from a waste simulant through a membrane using applied emf.
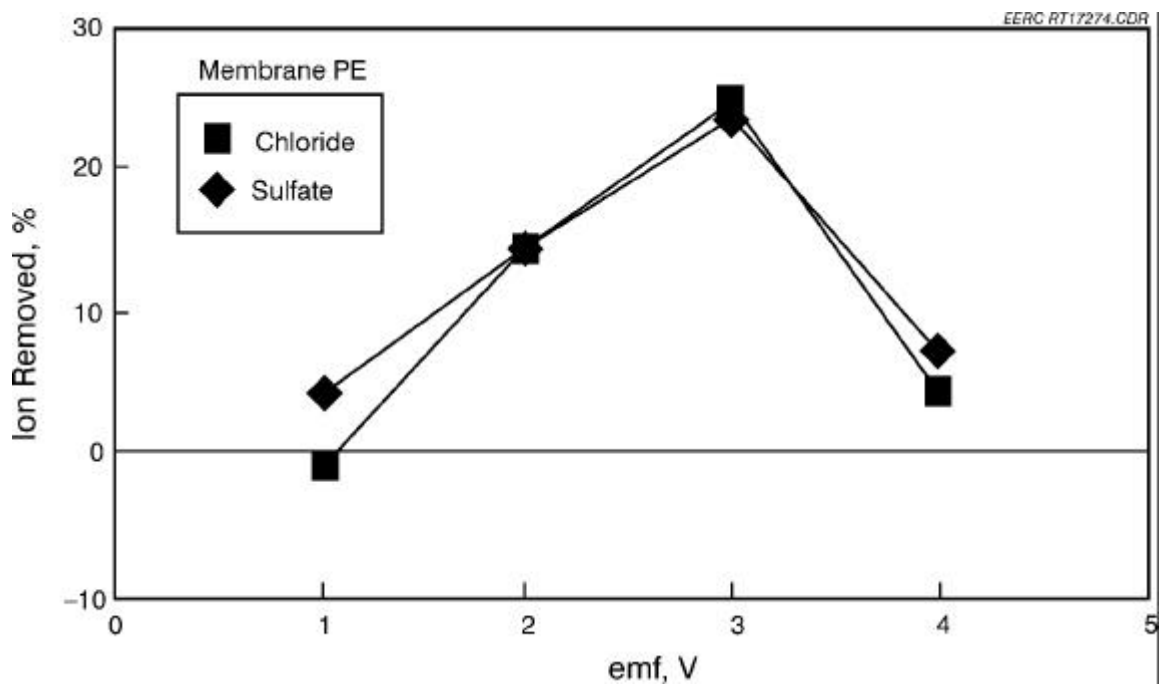

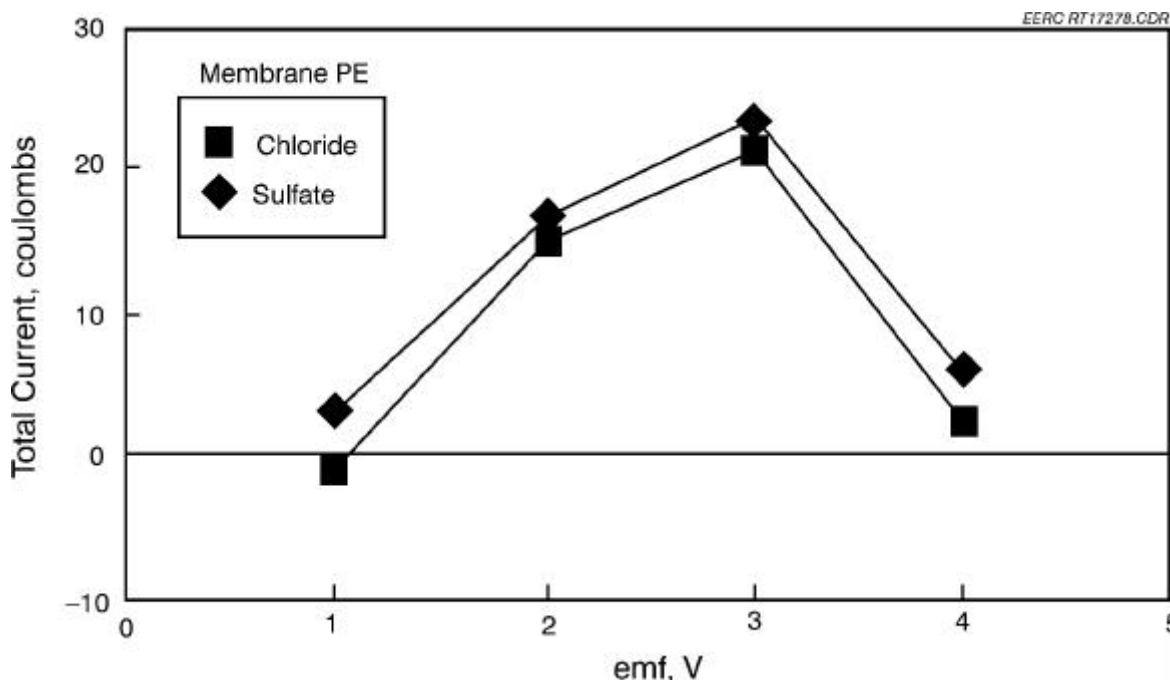Figure 3. Changes in ion concentrations at emf applied for 2 hours.

Figure 4. Coulombs used to remove chloride and sulfate ions in 2 hours at applied emf.

expected, the unflushed membrane blinded with elapsed time. The only effort to investigate membrane blinding was to reverse the membrane and, consequently, the direction of flow of the anions through it. Although a slight improvement in flow was realized by the reversed membrane, it did not return to the original permeability. Copper did not pass the membrane but was retained in the simulant. The membrane can be cleaned with dilute acid or reversed to counteract blinding.

Two of the major properties to be considered in removing the anions from the simulant by this method were charge and size. In spite of Coulomb's law, i.e., $F \propto q_1 q_2$, Cl^- migration to the anode chamber was greater than SO_4^{2-}, implying that size must be the more important factor when moving these two ions through the membrane and to the electrode in accordance with the principles of conductance. Figure 5 shows that the process using this membrane is selective toward Cl^-. Although Cl^- has a negative charge, causing it to cross the membrane into the anodic chamber, the smaller charge which translates to a smaller coulombic force, its change in concentration is greater than the SO_4^{2-}, owing to its ability to navigate the tortuous membrane pores. The smaller charge may also have an advantage when inside the membrane in that it is less rigorously attracted to the membrane material, thus less likely to form a boundary layer which may retard the flow.
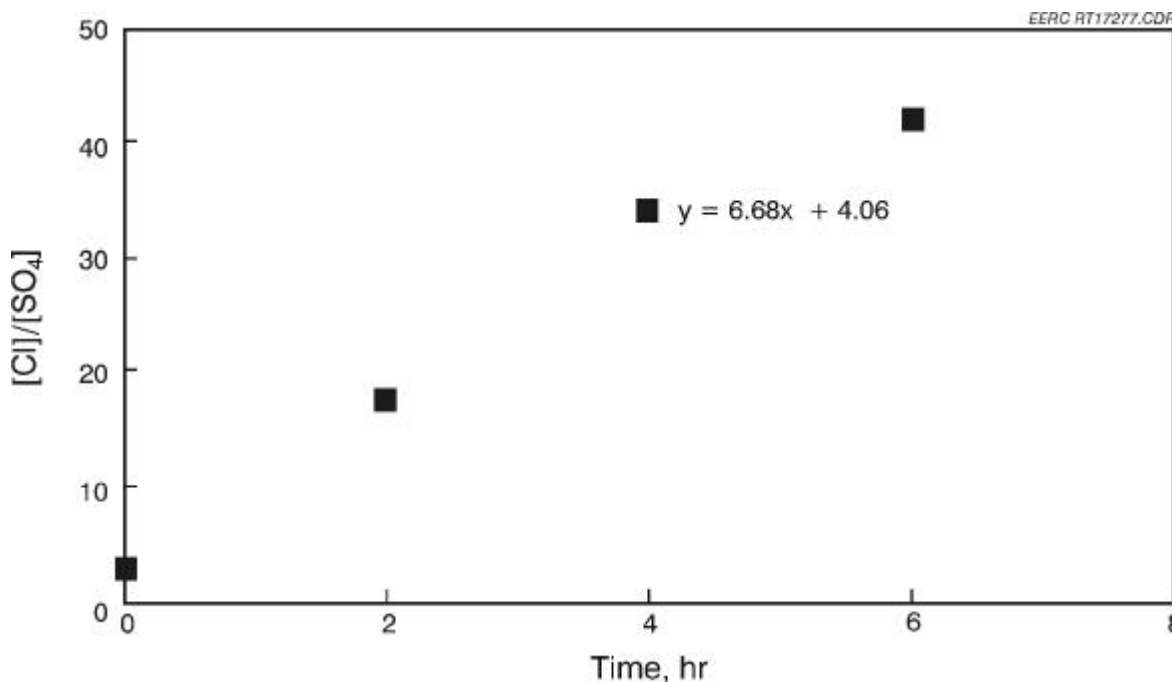
Figure 5. Selectivity of ion removal using membrane electrodialysis.

CONCLUSIONS

Electrolytic dialysis is significantly different from O and RO. In O, the cleaner water crosses the membrane to dilute the selected ions as they remain in the original contaminated water. In RO, the ions also remain in the original contaminated water, but because of pressure on the contaminated side, water, without selected ions, passes the membrane, thus concentrating the ions in the original wastewater. Under the influence of applied emf, chloride and sulfate ions move across the membrane, lowering the concentration of the selected ions in the wastewater. This study showed that selected ions do move across the membrane as expected. The rate at which they are separated is being determined from simulated contaminated water. As expected, blinding of the membrane as a function of time determines the lifetime of the membrane. A means of keeping the membrane open is under investigation. Not only is it possible to remove anions from a simulant by this method but also to remove them selectively.

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