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Improving Recovery: A Concentrate Management Strategy for Inland Desalination

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To the University of Texas at Austin

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Introduction

In the last two months, we have been working on several different tasks in our work plan, including **Tasks 1c, 1d, 2b, 2c, 2e, and 3b**. In this report, we focus on a few of the results that demonstrate the progress of the research and the promise that it holds as a strategy for concentrate management in the desalination of brackish groundwater.

We have also received the news that the North Cameron Plant has been repaired and is back on-line, and we are making preparations to visit the plant and obtain water for experimentation. As reported earlier, the plant was seriously damaged by hurricanes last fall and was out of service for an extended period.

Electrodialyis Research

A mathematical model is being developed to simulate the results of single-pass electrodialysis operation, and subsequent modeling will utilize this single-pass model to simulate the batch-recycle experimentation. The single-pass model is a one-dimensional, theoretical and empirical treatment that captures the principal electrochemical transport phenomena within the electrodialyzer: (1) convection of ions along the flowpath, (2) electromigration of ions, (3) electro-osmosis of water, and (4) osmosis of water.

The electrodialyzer is treated as an electrolytic cell, and the model calculates the current density, i, through a discrete element along the flow path according to the expression:

$$i = \frac{\Delta\phi_{res}}{R}$$

where $\Delta\phi_{res}$ is the electric voltage drop by resistance through the electrodialyzer, and R is the electrical resistance of the stack. The effective resistive voltage drop at a point along the flow path is less than the voltage applied to the electrodes, $\Delta\phi_{app}$, because of thermodynamic and kinetic losses:

$$\Delta\phi_{res} = \Delta\phi_{app} - \left(\Delta\phi_{equ} + \eta + \Delta\phi_{lj} + \Delta\phi_{diff}\right)$$

where $\Delta\phi_{equ}$ is the voltage drop from gas equilibrium at the electrodes, η is the overpotential of the gas production, $\Delta\phi_{lj}$ is the voltage drop from liquid-junction potentials, $\Delta\phi_{lj}$ is the voltage drop from liquid-junction potentials, and $\Delta\phi_{diff}$ is the voltage drop from diffusion potentials. Analytical expressions for these parameters are derived from fundamental electrochemical texts (Bard and Faulkner 2001; Newman and Thomas-Alyea 2004).

The resistance of the stack at a point along the flowpath, R, is modeled as:

$$R = R_{anolyte} + R_{CEM} + R_{C,BL-C} + R_{C,bulk} + R_{C,BL-A} + R_{AEM} + R_{D,BL-A} + R_{D,bulk} + R_{D,BL-C} + R_{catholyte}$$

where $R_{anolyte}$ is the resistance of the anode rinse (anolyte), R_{CEM} is the resistance of the cation exchange membranes (CEMs), $R_{C,BL-C}$ is the resistance of the concentrate diffusion boundary layers (DBLs) adjacent to CEMs, $R_{C,bulk}$ is the resistance of the concentrate bulk solutions, $R_{C,BL-A}$ is the resistance of the concentrate DBLs adjacent to anion exchange membranes (AEMs), $R_{D,BL-A}$ is the resistance of the diluate DBLs adjacent to the AEMs, $R_{D,bulk}$ is the resistance of the diluate bulk solutions, $R_{D,BL-C}$ is the resistance of the diluate DBLs adjacent to CEMs, and $R_{catholyte}$ is the resistance of the cathode rinse (catholyte) solution. The resistances of AEMs and CEMs are taken from published analyses (Strathmann 2004; Tanaka 2007), and the resistances of the solutions are functions of chemical composition (Landolt and Börnstein 1960).

Preliminary results from the single-pass model show mathematical similarity to the batch-recycle results. The mathematical model was tuned to simulate the single-pass performance of the laboratory scale electrodialyzer used in this research, except with variable flow path distance. The treatment of a 0.1 mol/L sodium chloride solution with varying voltage is shown in Figure 1 and demonstrates the initial linearity, transition, and final plateau of salt separation observed in the batch-recycle experimentation. The model also captures the variation in the relative rates of removal corresponding to the variation of voltage. Plots of current density and water transport (not shown) also demonstrate similarity to the batch-recycle experimentation.

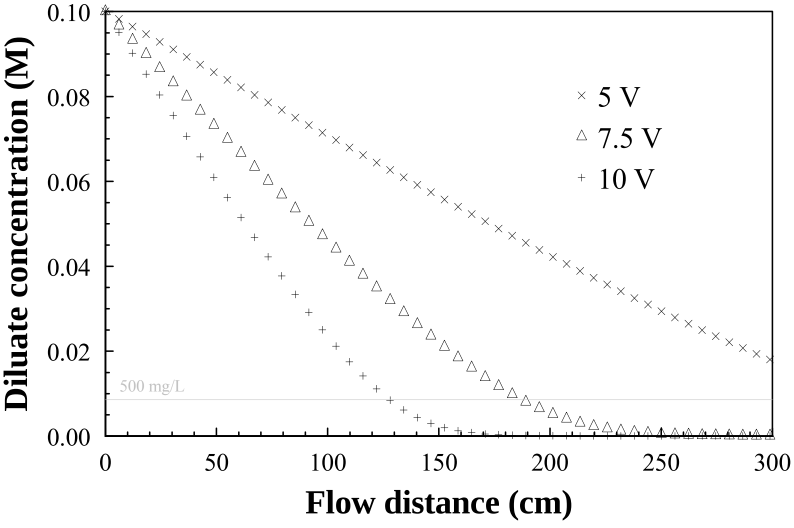

Figure 1 Mathematical model of single-pass electrodialyzer efficacy (10 cell-pair CMV/AMV, 800 mL/min concentrate and diluate flow rates)

After extending the single-pass model to multi-component salt solutions, the single-pass model will be incorporated in a mathematical model that simulates the hydraulic circulation of the batch-recycle experimentation in the laboratory.

Even so, these single-pass mathematical results are similar to the batch-recycle experimental results we have seen in the laboratory. For example, a comparison of the diluate conductivity is shown in 2 for similarly performed batch-recycle electrodialysis experiments: 10 cell-pair CMV/AMV stack; synthetic North Cameron RO concentrate waste; 10 V applied; 1000 mL/min flow rate; one with 5 mg/L of Dequest 2066 antiscalant and the other with 4 mg/L of Dequest 2006 antiscalant. (A sample of the antiscalant currently used in the RO treatment of the North Cameron groundwater has been acquired from American Engineering Services in Tampa, FL, which future ED experiments will utilize.) These brief experimental results indicate that the type and concentration of antiscalant impact the performance of the ED system. Subsequent experimentation will elucidate these effects.

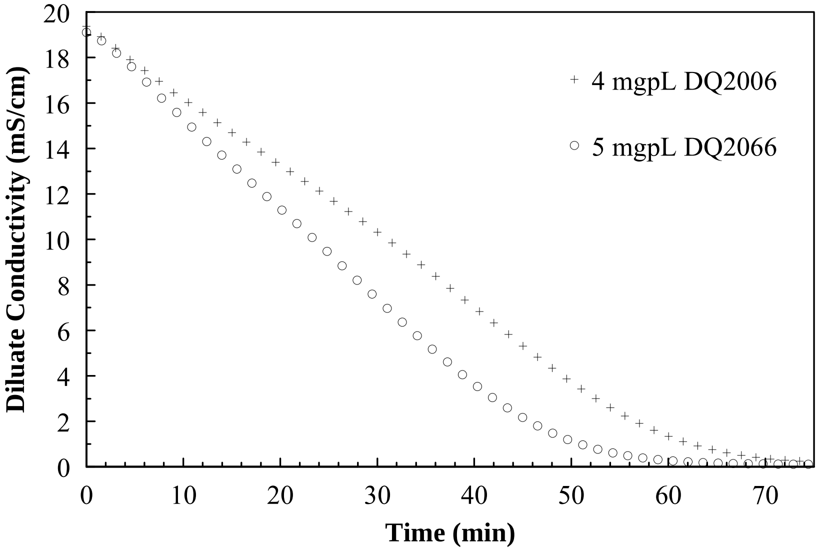

Figure 2 Experimental results of batch-recycle ED experimentation (10 cell-pair CMV/AMV, 1000 mL/min concentrate and diluate flow rates)

Anti-scalant Oxidation and Precipitation Experimentation

We have also continued to work with synthetic North Cameron water and with the anti-scalant they use at that plant for work on the oxidation of the anti-scalant with advanced oxidation experiments and subsequent precipitation. Example results for the oxidation work are shown in Figure 3, showing the effects of increasing peroxide to ozone ratio (at a fixed ozone dose) for the oxidation of the anti-scalant (measured in terms of phosphate release). The results in Figure 3 quite clearly demonstrate that, at the pH of these waters (pH=8.0), peroxide had a negative effect on the oxidation. On the basis of this (and other similar results), we have concluded that the oxidation should be done with ozone alone rather than a mixture of ozone and hydrogen peroxide.

As for precipitation of calcium carbonate (and possibly other salts), we have done a variety of experimentation with and without prior oxidation of the anti-scalant. The results (not shown graphically) indicate that the anti-scalant does an excellent job of preventing precipitation at relatively low values of supersaturation; under those conditions, oxidation of the anti-scalant makes a substantial improvement in the amount of precipitate that can be formed. On the other hand, at high values of supersaturation, the anti-scalant makes only a marginal difference in the amount of precipitate formed, and therefore oxidation of that anti-scalant also has only a marginal benefit. Since a high degree of precipitation is desired, it appears that the better solution is to use a high pH to precipitate most of the calcium carbonate and, under those conditions, the oxidation step can be omitted.

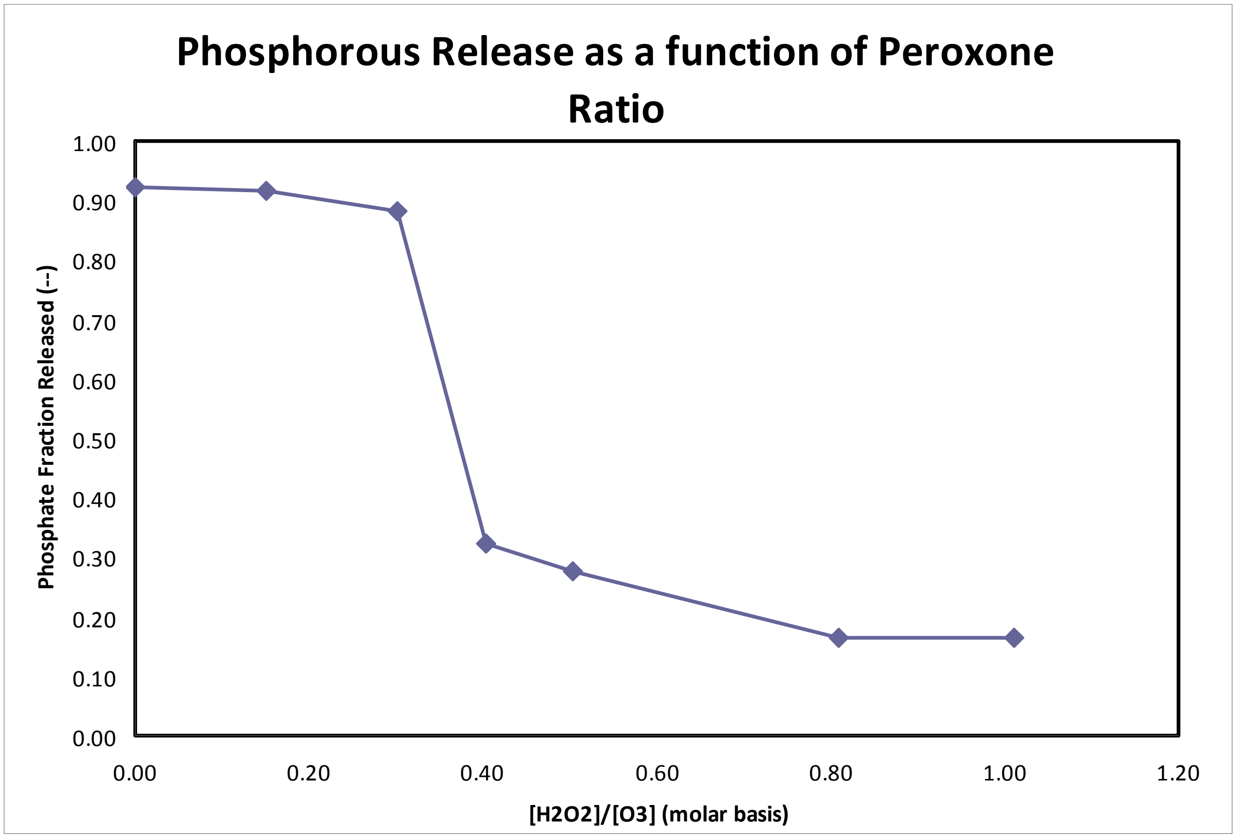

Figure 3. Antiscalant degradation using the North Cameron Plant's anti-scalant and synthetic North Cameron Water.

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