

Progress Report #5
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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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In the last two months, we have been working on several different tasks in our work plan, including **Tasks 1c, 1d (beginning), 2a, 2b (beginning), 3a, 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.

Anti-scalant degradation by peroxone (the combination of hydrogen peroxide and ozone) is difficult to measure directly, since analytical techniques for direct measurement of the anti-scalant are unknown. Although we have made progress on developing a direct measurement technique, we have not yet been completely successful. As a result, we use indirect methods of analysis—either measuring the total organic carbon (TOC) or, for phosphonate-based anti-scalants, the phosphate released into the water. The latter is more successful because the TOC measure cannot differentiate by-products from the partial oxidation of the anti-scalant (and these by-products might have none of the original anti-scalant properties remaining) from the raw anti-scalant. A few recent results from one of the anti-scalants we are studying are described here.

A synthetic brackish groundwater was prepared for analysis and concentrated five times to model the concentrate of an RO system with 80% recovery. Antiscalant (DQ 2066) was added to each 500-mL sample to obtain concentrations of 25 mg DQ 2066/L. This concentration was chosen as a result of the manufacturer recommended doses of approximately 2 to 20 mg/L (which, with five times concentration, would result in 10 to 100 mg/L in concentrate). For a given dose of ozone, hydrogen peroxide was varied to obtain $[H_2O_2]/[O_3]$ ratios of 0.2, 0.6 and 1.0. These ratios were selected because they agreed with values reported in the literature and because they provided a good range of data in our previous experiments. In these experiments, liquid hydrogen peroxide is added to the sample directly, and gaseous ozone is generated electrolytically and bubbled into the enclosed reactor (gas washing bottle) through a diffuser (glass frit). Two gas washing bottles are run in series, with the second gas washing bottle containing potassium iodide to monitor the amount of ozone unreacted in the first gas washing bottle containing the sample. The concentration of O_3 measured in the second bottle was then subtracted from our anticipated ozone application rate to obtain an actual ozone applied value.

Using the Ascorbic Acid Method from *Standard Methods for the Examination of Water and Wastewater 19th Edition*, the amount of dissolved orthophosphate was measured for each sample. Because the antiscalant contains phosphorous, oxidation of the compound releases orthophosphate into the solution. This result is then interpreted to provide a measurement of the amount of antiscalant degraded during experimentation.

Table 1. Antiscalant Degradation in Peroxone Experiments

O ₃ Applied (mg/L)	[H ₂ O ₂]/[O ₃] Ratio (mol/mol)	P Conc (μmol/L)	Antiscalant Degraded (%)
6	0.2	9.7	28.3
	0.6	11.9	34.5
	1	14.5	42.2
12	0.2	11.4	33.3
	0.6	13.2	38.3
	1	20.3	59.0
24	0.2	22.4	65.3
	0.6	23.1	67.1
	1	23.4	68.0

Note: Initial concentration of antiscalant was 25 mg/L (equivalent to 34.4 μmol/L), and there are 5 mol P/mol antiscalant

From the data collected above, two trends were observed. First, as the applied ozone increased, the degradation of the antiscalant increased. Second, for a given ozone applied value, increases in the [H₂O₂]/[O₃] ratio resulted in greater antiscalant degradation. This trend was less significant at higher ozone applied values. This result suggests that oxidation is less dependent on peroxide concentrations at sufficiently high ozone applications. Nevertheless, it is simpler to provide hydrogen peroxide than ozone.

The presence of aqueous phosphate was followed through the 3-stage process of peroxone treatment, precipitation, and subsequent solid/liquid separation. The results are shown in Figure 1 for ozonation times of 1 – 30 minutes. Little orthophosphate was present in all initial solutions tested, but phosphate is produced during the peroxone process by the degradation of the anti-scalant. Phosphate production increases with ozonation time, leveling off at longer ozonation times (or total dose of ozone). Nevertheless, all of the phosphate produced during ozonation was subsequently precipitated within the 30 minutes precipitation step, presumably as a calcium phosphate solid.

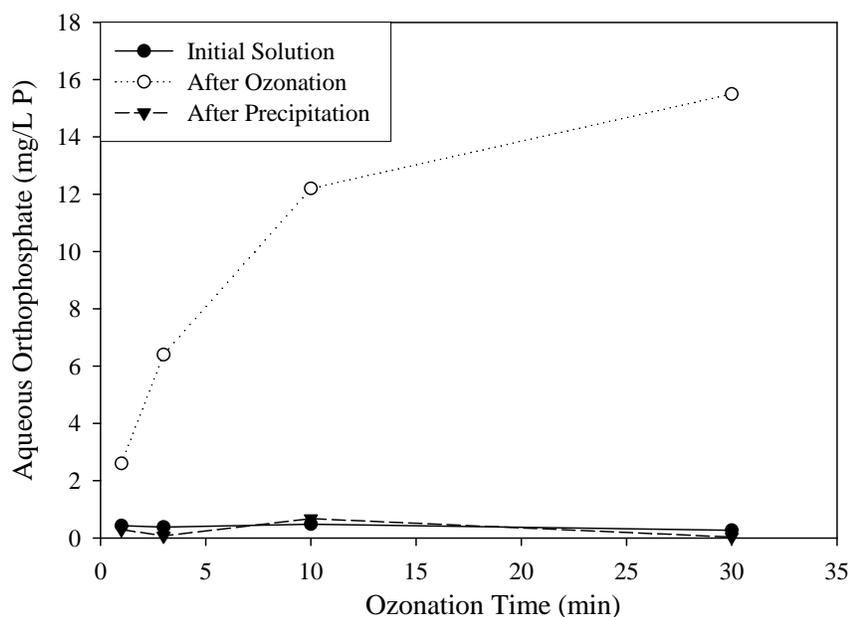


Figure 1. The production and precipitation of orthophosphate during the combined process of ozonation, precipitation, and filtration.

With respect to the electro dialysis, we are in the process of developing a mathematical model for (simplified) versions of this process, and it has been enlightening in directing the research design. Specifically, we are focusing on tradeoffs in (what would translate to) operating costs and capital costs. As explained in an earlier report, we can run the system in a single-pass mode or in a batch-recycle mode; the latter is generally more useful for understanding the effects of several variables, even though the former is a more direct emulation of how full-scale systems work.

The batch-recycle experimental procedure allows the investigation of electro dialysis system behavior that cannot be observed with the single-pass experimental setup. Several batch-recycle experiments were performed with five cell pairs (six cation exchange membranes and five anion exchange membranes) having an active cross sectional area of 64 cm². Each experiment began with one liter of 100 mN NaCl (5844 mg/L) in each of the three reservoirs (concentrate, diluate, and electrode rinse), and a constant electric potential of five volts was applied to the electro dialyzer electrodes. As a function of time, the following parameters were monitored at two-second periodicity (0.5 Hz): voltage and current (and, hence, electrical power and resistance) of the electro dialyzer; electrical conductivity, temperature, and pH of each of the three reservoir solutions; mass of the diluate reservoir; flow rate of each of the three recycling streams; and pressure head of the concentrate and diluate streams at the influent and effluent of the electro dialyzer.

The concentration of a NaCl solution as a function of its electrical conductivity (κ) is well-defined in the concentration range of one to 100 mN; with our laboratory equipment, the relationship was found to be as follows:

$$c_{NaCl} = 8.562 \kappa^{1.0307}$$

where, in this empirical equation, c_{NaCl} must be in units of mN (milli-Normal) and κ must be in units of mS/cm. The R^2 value of this equation is 0.99996, indicating an extremely good fit of the data; this equation was used to convert the recorded values of conductivity into NaCl concentration.

The concentration of the diluate reservoir as a function of elapsed experimental time is shown in Figure 2 for three experiments with different recycle (concentrate and diluate) flow rates. All these experiments were run at constant voltage (1 V/cell pair). In each experiment, the diluate concentration decreased monotonically with time, as expected; the concentrate concentrations (not shown) are the mirror image of these graphs since ions that leave the diluate enter the concentrate. Comparing different experiments, the data indicate that, as the recycle flow rate increased, the diluate reservoir concentration decreased more rapidly, despite the fact that detention time within the dialyzer during each pass of the solution is smaller at the higher flow rate. Nevertheless, the results are consistent with the mathematical model that we have developed; the model assumes that a non-convective boundary layer is adjacent to each membrane surface, and that the thickness of that boundary layer is inversely related to the flow rate (or Reynolds number) in the cell. The smaller boundary layer at the higher flow rate allows a greater electrical current to pass through the solution for the same electrical potential drop across the boundary layer. Since the current is carried by the moving (separating) ions, the greater current improves the rate of desalination in the electro dialyzer.

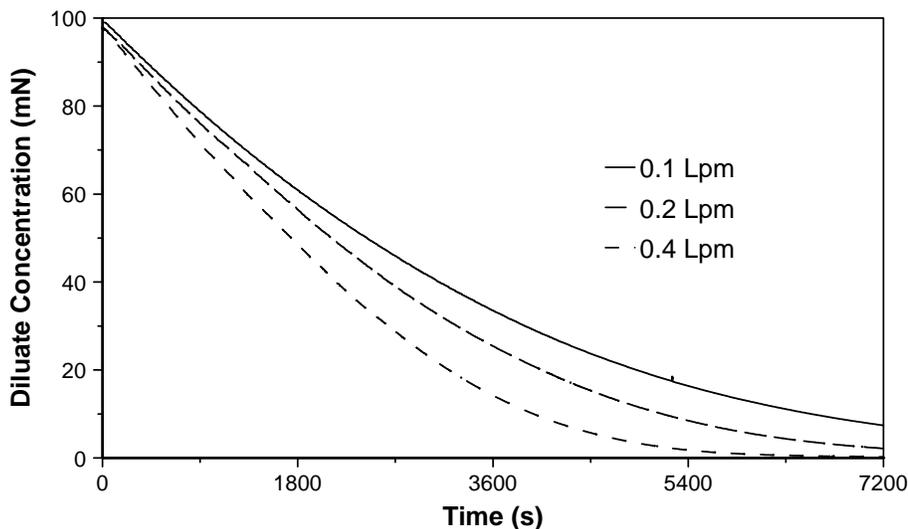


Figure 2. Desalination by Electrodialysis: Effect of Flow Rate in the Batch-Recycle System. (Initial Solution: 100 mN NaCl; applied potential = 1 V/cell pair; 5 cell pairs)

In the coming weeks, we expect to perform numerous experiments with increasingly complex water chemistry, while systematically varying the variables that have a strong influence on the kinetics of ion separation: applied electrical voltage, flow rates of the concentrate and diluate, and initial concentrations of various major constituents. Some results will be shown in the next report.