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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 1d, 2c, 2d, 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.

Synthetic formulation of the North Cameron RO concentrate

A water composition analysis of groundwater that supplies the North Cameron reverse osmosis (RO) facility was performed by Ana-Lab Corp. (Kilgore, TX) in mid 2007. The mass- and mole-concentrations of the predominant ion composition of the raw groundwater results are summarized in Table 1; sodium and chloride ions contribute 56% of the salt mass and 49% of the ionic strength. A synthetic water was formulated to simulate the concentrate waste from the North Cameron RO facility (with recovery ratio, $r = 75\%$ and removal ratio, $R = 100\%$); taken together, these conditions suggest that RO concentrate would have a concentration of every constituent that is four times the concentration in the raw water. The predominant ion concentrations for that synthetic formula are also shown in Table 1. Because of an ion imbalance of -0.5 meq/L in the raw water composition analysis, it was necessary to increase the measured sodium concentration by five percent; all other constituents were supplied in proportion to the raw water analysis. This water is being used in this research until the operation of the North Cameron plant is restored; recall from the previous report that hurricane damage forced the plant to be shut down for repairs for some months.

Table 1. Groundwater and synthetic RO concentrate composition from North Cameron, Texas

Constituent	z	MW	C_{raw}	C_{raw}	$C_{simulated}$	$C_{simulated}$	$|\Delta C|/C_{conc}$
	[-]	[g/mol]	[mg/L]	[mM]	[mg/L]	[mM]	[%]
SiO_2	+0	60.08	12.4	0.206	49.6	0.826	0.0%
$B(OH)_3$	+0	61.83	61.2	0.990	244.8	3.959	0.0%
Na	+1	22.99	931	40.496	3921.6	170.581	5.3%
Ca	+2	40.08	153	3.818	612.0	15.270	0.0%
Mg	+2	24.31	81.4	3.349	325.6	13.396	0.0%
K	+1	39.10	15.6	0.399	62.4	1.596	0.0%
Sr	+2	87.62	7.42	0.085	29.7	0.339	0.0%
Mn	+2	54.94	0.045	0.001	0.0	0.000	-
Ba	+2	137.33	0.015	0.000	0.0	0.000	-
Cl	-1	35.45	1110	31.309	4439.7	125.228	0.0%
SO_4	-2	96.06	991	10.316	3964.0	41.265	0.0%
Br	-1	79.90	4.88	0.061	19.5	0.244	0.0%
HCO_3	-1	61.02	338	5.546	1353.7	22.186	0.0%

Electrodialysis Research

Initial electrodialysis experimentation with North Cameron synthetic RO concentrate waste has begun, and several challenges have been identified. First, it is necessary to create an electrodialysis electrode rinse synthetic formula that simulates the cation concentrations exactly, yet replaces the chloride ions with nitrate to avoid destroying the ion exchange membranes (as was observed in the first experiment using the North Cameron synthetic as diluate, concentrate, *and* electrode rinse solutions). The problem is the chloride can be oxidized to chlorine gas at the anode, and the high concentrations of chlorine gas in the electrode rinse cannot be tolerated   Second, it might become necessary to acquire conductivity probes that are not adversely affected by the antiscalant complexation chemistry; the first experiments suggested some interference in measurement of the electrodialysis concentrate presumably caused by the antiscalant. Third, it is necessary to develop ion chromatography (IC) and inductively-coupled plasma atomic emission spectrometry (ICP-AES) methods for characterizing the time-dependent anion and cation constituency (respectively) of the experimental solutions. These items, particularly the latter, will consume most of the time devoted to this portion of the research over the next several weeks.

Anti-scalant Efffectiveness

The anti-scalants chosen earlier in the research have been tested on the synthetic Texas water described above. The first test was for their effectiveness as anti-scalants; the results shown in Figure 2 indicate that these chemicals are indeed highly effective in preventing precipitation. With no antiscalant present, nearly 20% of the calcium in the concentrate precipitated at pH 8.3 as might be expected; these conditions led to a saturation index of greater than 25, or a ratio of the ion product to the equilibrium constant of more than 600. Anti-scalant doses above 1 mg/L for either chemical led to very little calcium being precipitated.
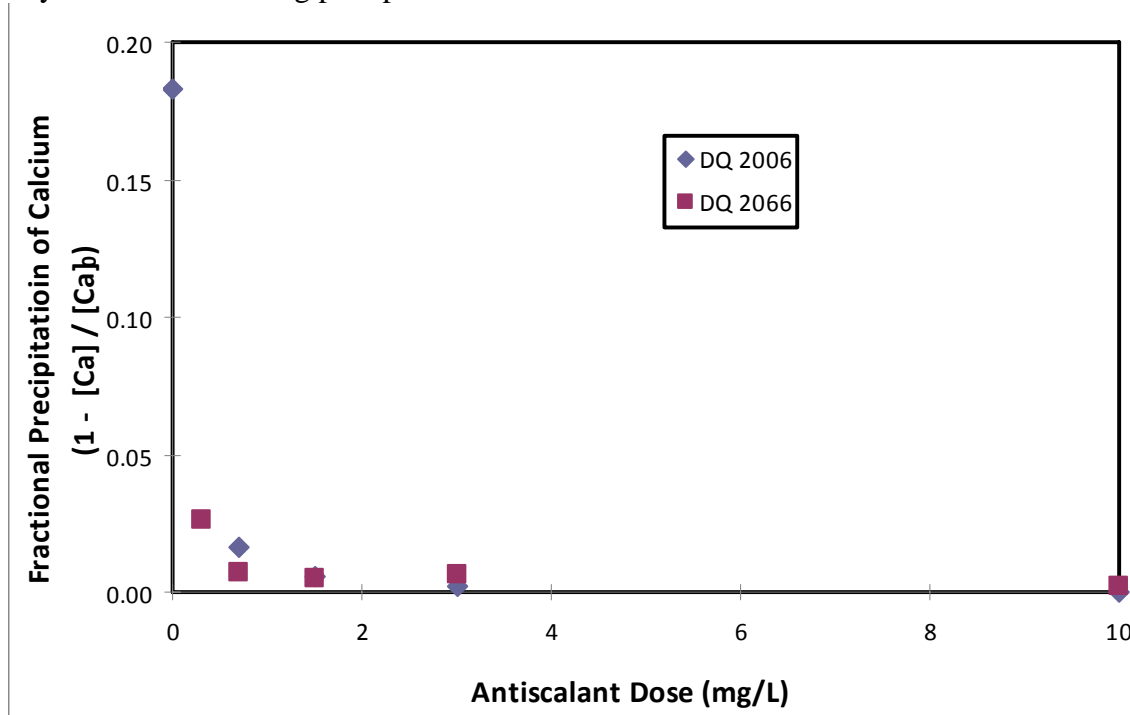

Figure 1. Effectiveness of Anti-Scalants in Preventing Precipitation of Calcium Carbonate in Synthetic North Cameron Water. (pH 8.3; S = 25.3).

The results in Figure 1 were obtained in a protocol, newly-developed in this research, that could be expanded as a standard method for utilities to determine anti-scalant needs. As can be seen from these results, only a very low dose is necessary to prevent precipitation in this water. In most cases, utilities depend on recommendations from chemical suppliers to set the dose to be used in their RO plants. Clearly, it is in the chemical supplier's interest to quote a very conservative (high) estimate of the required dose, both for the increased sale and the reduction of risk. These results suggest that a dose of 1 mg/L of either anti-scalant would be sufficient, and a quite conservative value would be 5 mg/L. Although data on anti-scalant doses have not been widely reported, it does appear that utilities are using much greater values, such as 25 mg/L, for similar waters. One recommendation that is likely to come out of this research, after further development, is that utilities do their own batch testing to set the anti-scalant dose.

Anti-scalant Degradation.

One of the same anti-scalants that was used in the previously reported results (DQ 2066) was subjected to the ozone treatment with various doses of hydrogen peroxide. This was done to determine the most effective peroxide to ozone ratio for anti-scalant inactivation. As before, anti-scalant degradation is indicated by the release of phosphate from the molecule. Typical results are shown in Figure 2, and indicate that the peroxide was not only ineffective in improving the degradation, but actually reduced the amount of degradation achieved. Most of our previous results have indicated that peroxide reduced the degradation at low doses but improved it at higher doses, but that is not the case in the (synthetic) North Cameron water, for reasons that are unclear at this time. On the basis of these results, it appears that, at least for this anti-scalant, the peroxide treatment is unnecessary.
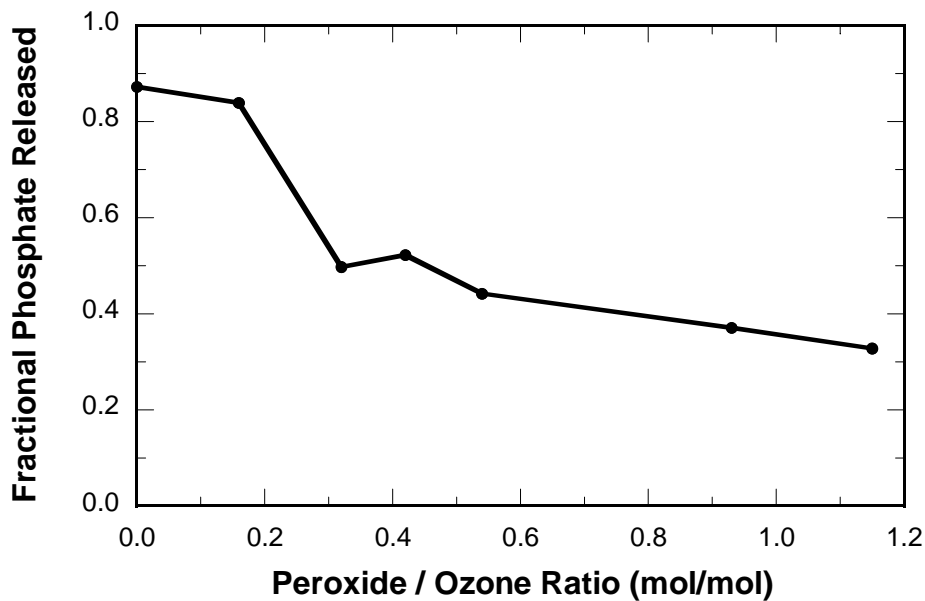

Figure 2. Antiscalant Degradation in Synthetic North Cameron Water. (Anticalant DQ 2006 at 5 mg/L; pH 7.8; ozone reacted = 25 mg/L).

Ongoing Research

The research is progressing well on all aspects. We expect to see many aspects of the research coalescing into a more unified picture in the coming weeks.