

EXHIBIT B
DEMONSTRATION BRACKISH GROUNDWATER DESALINATION PROJECT
SCOPE OF WORK

Detailed Scope and Schedule This research is designed to test two different possible process schemes to improve recovery in RO desalination of brackish groundwater, and thereby reduce the problems of waste disposal and management. Both schemes would take the concentrate from a conventional RO system and put it through side-stream treatment that would concentrate the waste and allow much of the liquid to be recovered. The research design progresses from batch laboratory experiments to continuous flow laboratory experiments and finally to small pilot-scale continuous flow tests at the two field sites belonging to the utility partners in this research. The first example is shown in Figure 2, and is relevant to Tasks 1, 2, and 4 described subsequently. A conventional RO system is the first three membrane stages shown on the upper left of the figure, except that the concentrate stream from the last is normally the disposal stream. In the proposed system, that stream would then be treated to deactivate the anti-scalants in one step, allow or encourage precipitation in a second step, and perform a solid/liquid separation (e.g., ultrafiltration or perhaps just sedimentation) in a final step. The resulting liquid stream would then be sent to an additional RO unit to improve the recovery of the overall system dramatically. Our research design emulates each of these additional steps, with primary experimental emphasis on the first two--deactivation of the anti-scalants and subsequent precipitation of solids, because the solid/liquid separation step is well understood.

Task 1. Laboratory Studies on Anti-Scalant Degradation. Two common types of anti-scalants are used in drinking water RO applications: phosphonates and synthetic organic polymers (acrylic acid, or acrylic acid blended with phosphonates). We will work on the anti-scalants that are being used or investigated at the two cooperating utility sites noted above. The use of phosphonates is likely because they are more common in drinking water applications. The defining characteristic of phosphonates is a phosphorus-carbon (P-C) bond, but the anti-scalants also have at least one fully-substituted amino group (nitrogen bonded to three carbons). Several commercial products are available, with their differences designed to target specific potential scaling compounds (e.g., calcium carbonate, calcium sulfate, several metal silicates, and strontium salts). The P-C bonds of phosphonates are more difficult to degrade (either chemically or biologically) than the phosphorus-nitrogen (P-N) bonds of traditional phosphate anti-scalants. No prior research on the chemical oxidation of these compounds has been identified, but preliminary results in our laboratory are promising that it can be done. Others (Hayes, 2000; Krzysko-Lupicka, 1997) have indicated that phosphonates are biodegradable, including by some salt-loving bacteria.

These anti-scalants will be tested for successful degradation in an advanced oxidation process (AOP) using ozone (O₃) and hydrogen peroxide (H₂O₂) to treat an aqueous solution of appropriate salts and anti-scalants. The O₃/H₂O₂ combination (often called "peroxone") has been shown to be one of the most successful AOPs in general molecular degradation, including recalcitrant contaminants found in wastewater and drinking water (Ito, 1998; Ledakowicz, 2001; Fahmi, 2003). It has also been shown that both the P-C and C-N bonds of representative anti-scalant molecules are susceptible to oxidative attack by a hydroxyl radical (the active molecule produced by the O₃/H₂O₂ system and in all AOPs) (Frost, 1987; Shadyro, 2003).

The batch experiments will be performed with a setup like that shown in Figure 3; the "kill flasks" are required to ensure that unreacted ozone gas is not released into the laboratory air. These flasks will be filled with 20 g/L KI solution to react with and destroy the ozone. After performing batch experiments to determine conditions that successfully degrade the anti-scalants, laboratory-scale continuous flow experiments will be designed and performed as a stepping stone to the ultimate field testing in later parts of this research. The continuous flow experiments will have flow in and out of the vessel labeled "Reaction Solution," and a separate supply of hydrogen peroxide solution will be added simultaneously.

The research plan for this proposed system for enhanced recovery in RO systems includes separate phases for the oxidation/degradation and for the subsequent precipitation and solid/liquid separation. In an associated study that we are doing for the American Water Works Association Research Foundation (AwwaRF), the primary emphasis is on the deactivation/degradation of the anti-scalants. In this proposed work for the TWDB, that research will be supplemented, but a greater emphasis will be placed on the precipitation that must be performed to demonstrate that the anti-scalants have truly been inactivated, and on the solid/liquid separation step. These research steps, first in batch and subsequently in lab- and field-scale continuous flow pilot tests, will ensure that we have properly tested the technical feasibility of the treatment train. The independent variables to be investigated within the deactivation part of the research will include the ratio of peroxide to ozone, pH, buffering system, ion composition to emulate real Texas waters, and the concentration of anti-scalants.

Each of these variables will be chosen at levels that allow us to see the effects of the variable and yet be in a range that is likely to be useful in practice; for example the ozone and peroxide doses will be based on previous reported research. The synthetic waters will be based on a database of groundwater quality maintained by the TWDB, and actual concentrate from the two utility partners associated with this research will be used as appropriate in a final test of the feasibility of the approach. The end product of this research should be a well-documented protocol for determining the conditions for any water to be subjected to this type of treatment.

Task 2. Laboratory Studies on Precipitation and Solid/Liquid Separation. To test the effectiveness of the anti-scalant degradation, a precipitation step will be performed to emulate the full-scale system. In the laboratory phase of this research, these studies will be performed in batch and continuous flow experiments. In the final phase of the proposed research, we will perform pilot scale tests in the field, at both of the sites (if available) where a brackish groundwater demonstration is already planned or underway (i.e., San Angelo or North Cameron). The conditions for precipitation (e.g., pH changes and possible addition of chemicals to facilitate precipitation) will be determined with the guidance of a chemical equilibrium modeling program (Mineql or Minteq) that can predict the types and amount of precipitation expected to form in these systems if equilibrium is attained. Experiments will then be performed to test the extent of precipitation that is achieved in reasonable times. The extent of precipitation for each set of experimental conditions will be determined using aqueous measurements of major cations and anions in solution as well as quantification of the mass of precipitate phase and characterization of the composition of the solid phase. Determination of the aqueous concentrations of metals and anions will be determined using inductively coupled plasma (ICP) spectroscopy and ion chromatography, respectively. Solid phase characterization will include x-ray diffraction, x-ray photoelectron spectroscopy and scanning electron microscopy with x-ray microanalysis. While it

is expected that many pure solid phases such as calcium sulfate dihydrate (gypsum), calcium silicate and calcium carbonate will precipitate in these systems, it is also likely that mixed solid phases or solid solution phases will control the solution phase concentration of ions.

The results from these tests will confirm if precipitation of solids can achieve a water quality (perhaps after another pH change) that is acceptable for further re-application to a final RO membrane. In previous research, we have shown that pretreatment to remove silica by precipitation can improve the performance (recovery) of RO systems, but further work on that problem will also be incorporated into the proposed work if appropriate for the local groundwater sources. In recent research, we have investigated homogeneous and heterogeneous precipitation of calcium carbonate and the impact of solid solution formation on metal ion removal from water. The techniques developed in that work are directly applicable to the proposed project.

The final step will be solid/liquid separation. The most common separation after precipitation is sedimentation but the more likely candidate here is ultrafiltration because it will yield a higher fraction of the water to be fed to the additional RO membrane on the far right of Figure 2. The benefit of this system can be seen in the following example. If each RO stage achieved 40% recovery of its influent, the current three-stage system would achieve a recovery of 78.4%. If the intermediate treatment shown in the bottom part of Figure 2 resulted in a loss of 4.6% of the water and a two-stage RO could follow, the recovery would rise to 89.3%. Stated more dramatically, the amount of concentrate to be disposed of would be reduced in *half*; from 21.6% of the influent to 10.7% (counting both waste streams in the new system). Again, continuous flow experiments will be performed at both the benchscale in the laboratory and in a small field pilot-scale unit. To test this hypothesis, ultrafiltration experiments will be conducted over the range of conditions employed in the previous stage of treatment. Again, continuous flow experiments will be performed at both the bench-scale in the laboratory and in a small field pilot-scale unit. The ultrafiltration experiments will be conducted in a laboratory scale unit manufactured by Millipore.

The liquid stream from the solid/liquid separation step will be carefully monitored for a wide variety of inorganic species and for total organic carbon (TOC). The monitoring will determine whether this stream must be put through the final RO system shown in Figure 2, or whether it can be used directly and blended with RO product water from the conventional system. Conventional RO systems yield product water that cannot be directly sent to a public distribution system since it contains essentially no alkalinity; as a result, supplementary metal cations and carbonate are usually added prior to distribution. The liquid stream from our solid/liquid separation might provide sufficient metal cations to reduce or eliminate the need for other additions, and also eliminate the need for the final RO shown in Figure 2. These possibilities will be investigated from the data obtained in our experiments.

Task 3. Laboratory Studies of Electrodialysis as Side-Stream Treatment. The second possible intermediate treatment scheme, illustrated in Figure 4, will use electrodialysis (ED) to improve recovery; as before, the experiments will use as the input waste concentrate (real or synthetically made to emulate the real concentrate) from the two partnering utilities. Electrodialysis utilizes ion exchange membranes to create a waste concentrate containing a very high fraction of the original ions and a product (diluate) very low in ionic strength. ED is a proven technology that, prior to the recent invention of thin composite RO membranes, was a leading desalination technology. ED achieves approximately a 50% recovery in each stage, but

even a two-stage system would allow 75% of the current RO waste stream to be recycled to the additional RO units. As with the other process scheme, it is conceivable that the use of ED would eliminate the need for further RO treatment; that is, the ED diluate, while not as pure a product as that obtained from RO, could be mixed with the product streams from the earlier RO units to provide water that meets all drinking water standards. If that is proven possible, it would avoid the double pressurization required in the first proposed system. ED is less susceptible to some of the scaling problems that plague RO systems because of the ion separation that occurs in the unit and the lack of a mechanical pressure driving materials toward the membrane.

The initial laboratory experimental work on the ED system would emulate that performed by Moon *et al.* (2004). There, a bench-scale ED unit was used in a batch mode to gradually create a cleaner water in one reservoir and a dirtier water in another as the ion separation took place. We expect to obtain a small pilot continuous flow system for the later laboratory experiments and the field studies.

Although not shown in Figure 4, it appears likely that the anti-scalant deactivation step to be investigated in Task 1 will be required before electro dialysis. Some of our experiments will be designed to test for this necessity. This combination would be particularly beneficial if the anti-scalants produced uncharged species (complexes) that would not be removed in ED, and the deactivation step released those ions.

Task 4. Pilot Field Study of Oxidation/Precipitation/Separation/Final RO. The laboratory studies in the proposed research are all geared to developing a small-scale continuous flow treatment train that can be field tested at one or both of the utility desalination sites to be involved in this research. We expect to do a field test of sufficient duration to demonstrate the feasibility of the proposed treatment train to convert existing RO concentrate into a sufficiently clean water to enter a final reverse osmosis unit. All three of the treatment units (oxidation, precipitation, and solid/liquid separation) will be operated in series, using concentrate that is obtained as a slip stream from the operating plants at North Cameron and San Angelo. (Note, we are aware that it is possible that the timing of the San Angelo pilot tests already funded by TWDB and the (smaller) pilot tests proposed herein, will not coincide. If that occurs, we will do more extensive laboratory work on that water and more extensive field studies at the other site.)

We expect the field studies in each location to take several (4 to 8) weeks. Our experience is that the setup is generally the most time-consuming, but the cooperation of our utility partners and the use of their facilities should minimize the time for setup. Tests will be performed until steady state conditions are reached under a variety of loading conditions, using different levels of the independent variables for each process as appropriate based on our earlier laboratory studies. For example, we plan to perform experiments with different concentration of ozone and peroxide, different detention times (flow rates) in our system, and different flux rates for membrane (ultrafilter) solid/liquid separation. Field measurements of pH, turbidity (to assess experimental conditions), anti-scalant concentration (to assess anti-scalant degradation) and selected metals and alkalinity (to assess precipitation) will be made on-site to guide the pilot operation. These measurements will be made using a pH meter, conductivity meter, turbidimeter, chromatographs, and spectrophotometers currently available in our laboratory that can be dedicated to the field during the pilot testing. Duplicate aqueous samples from each process and precipitates will be taken, preserved, and brought to Austin for more rigorous analysis.

Task 5. Pilot Field Study of Electrodialysis. The field study of electrodialysis will be conducted quite similarly to that for the oxidation/precipitation/separation studies. Again, the details of the experimental design will be determined from the results of the laboratory studies. For example, the laboratory studies might prove conclusively that the oxidative degradation step is or is not necessary before ED, and the field studies would be based on that conclusion. However, the research design would certainly include some variation in such operating conditions as the voltage applied and the type of membrane employed. As in the other field studies, the monitoring for specific contaminants would occur by bringing samples back to the UT-Austin laboratories, but gross parameters, including the conductivity, would be measured on the two site of our utility partners. All analytical equipment to be used would be supplied from UT-Austin, and carried into the field.

Detailed Schedule

| Task # | Description | Time (mo. from start) | Dates |
|----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|---------------------|
| 1 | Laboratory Studies on Oxidation of Anti-Scalant Compounds | 0-12 | 8/1/07 to 7/31/08 |
| 1a | Identify and obtain anti-scalants likely to be used at the chosen Texas sites | 0-2 | 8/1/07 to 9/30/07 |
| 1b | Demonstrate feasibility of oxidation of anti-scalants with H ₂ O ₂ and O ₃ | 0-4 | 8/1/07 to 11/30/07 |
| 1c | Study several conditions (<i>e.g.</i> , pH, ratio of H ₂ O ₂ and O ₃) of oxidation using synthetic waters (analogs of the chosen TX waters, as RO concentrate) in batch tests | 4-8 | 11/1/07 to 3/31/08 |
| 1d | Develop continuous flow system for oxidation and test a few conditions found successful in batch tests | 9-11 | 4/1/08 to 6/30/08 |
| 1e | Study limited number of (optimal) conditions using real waters transported to laboratory from TX sites in both batch and continuous flow tests | 10-12 | 5/1/08 to 7/31/08 |
| 2 | Laboratory Studies on Precipitation and Solid/Liquid Separation | 4-16 | 11/1/07 to 11/30/08 |
| 2a | Using water quality data from the TX sites, identify likely precipitates in RO concentrate and associated optimal precipitation conditions through equilibrium modeling | 4-6 | 11/1/07 to 1/31/08 |
| 2b | Batch tests of precipitation as f(pH) on synthetic TX waters (RO concentrate) with and without anti-scalant (and no preceding oxidation) | 6-9 | 1/1/08 to 4/30/08 |
| 2c | Batch tests of precipitation on same waters as in 2b with preceding oxidation identified in Task 1c | 10-12 | 5/1/08 to 7/31/08 |
| 2d | Batch tests of precipitation with and without preceding oxidation on real TX waters (RO concentrate) (Same waters as in Task 1e) | 12-14 | 7/1/08 to 9/30/08 |
| 2e | Develop continuous flow system for precipitation and solid/liquid separation studies | 10-14 | 5/1/08 to 9/30/08 |
| 2f | Continuous flow tests on precipitation and solid/liquid separation with and without preceding oxidation using real waters | 14-16 | 9/1/08 to 11/30/08 |

Detailed Schedule (Cont'd)

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|----------|-------------------------------------------------------------------------------------|-------|------------------------|
| 3 | Laboratory Studies on Electrodialysis of RO Concentrate | 7-19 | 2/1/08 to 2/29/08 |
| 3a | Set-up and preliminary testing of laboratory ED system | 7-10 | 2/1/8 to 5/31/08 |
| 3b | Semi-batch, semi-continuous testing of synthetic RO concentrates from both TX sites | 11-15 | 6/1/08 to 10/31/08 |
| 3c | Testing of real waters from TX site 1 | 16-17 | 11/1/08 to 12/31/08 |
| 3d | Testing of real waters from TX site 2 | 18-19 | 1/1/09 to 2/28/09 |
| 4 | Pilot Field Study of Oxidation/Precipitation/Separation/Final RO | 17-22 | 12/1/08 to 5/31/09 |
| 4a | Set up at Site 1 | 17-19 | 12/1/08 to 2/28/09 |
| 4b | Operating tests at Site 1 | 19-20 | 2/1/09 to 3/31/09 |
| 4c | Set up at Site 2 (if available) | 20-21 | 3/1/09 to 4/30/09 |
| 4d | Operating Tests at Site 2 (if available) | 21-22 | 4/1/09 to 5/31/09 |
| 5 | Pilot Field Study of Electrodialysis/Final RO | 19-25 | 2/1/09 to 8/31/09 |
| 5a | Set up at Site 1 | 19-20 | 2/1/09 to 3/31/09 |
| 5b | Operating tests at Site 1 | 20-22 | 3/1/09 to 5/31/09 |
| 5c | Set up at Site 2 (if available) | 22-23 | 5/1/09 to 6/30/09 |
| 5d | Operating Tests at Site 2 (if available) | 24-25 | 7/1/09 to 8/31/09 |
| 6 | Final Report Submission | 30 | 1/31/10 |
| 6a | Draft Report Writing | 25-28 | 8/1/09 to 11/30/09 |
| 6b | Finalization of Report | 29-30 | 12/1/09 to 1/31/10 |

**Schedule for TWDB Project
Improving Recovery: A Concentrate Management Strategy for Inland Desalination
University of Texas**

| 2007 | | | 2008 | | | | | | | | | | | | 2009 | | | | | 10 |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|-----|-----|--|--|----|
| Aug | Sept | Oct | Nov | Dec | Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | Jan | | | |
| Start | | | | | | | | | | | | | | | | | | | | |
| Task 1. Laboratory Studies on Oxidation of Anti-Scalant Compounds | | | | | | | | | | | | | | | | | | | | |
| Task 1a. Identify and obtain anti-scalants likely to be used at the chosen Texas sites | | | | | | | | | | | | | | | | | | | | |
| 2 mo. | | | | | | | | | | | | | | | | | | | | |
| Task 1b. Demonstrate feasibility of oxidation of anti-scalants with H ₂ O ₂ and O ₃ | | | | | | | | | | | | | | | | | | | | |
| 4 mo. | | | | | | | | | | | | | | | | | | | | |
| Task 1c. Study several conditions (e.g., pH, ratio of H ₂ O ₂ and O ₃) of oxidation using synthetic waters (analogs of the chosen TX waters, as RO concentrate) in batch tests | | | | | | | | | | | | | | | | | | | | |
| 5 mo. | | | | | | | | | | | | | | | | | | | | |
| Task 1d. Develop continuous flow system for oxidation and test a few conditions found successful in batch tests | | | | | | | | | | | | | | | | | | | | |
| 3 mo. | | | | | | | | | | | | | | | | | | | | |
| Task 1e. Study limited number of (optimal) conditions using real waters transported to laboratory from TX sites in both batch and continuous flow tests | | | | | | | | | | | | | | | | | | | | |
| 3 mo. | | | | | | | | | | | | | | | | | | | | |
| Task 2. Laboratory Studies on Precipitation and Solid/Liquid Separation | | | | | | | | | | | | | | | | | | | | |
| Task 2a. Using water quality data from the TX sites, identify likely precipitates in RO concentrate and associated optimal precipitation conditions through equilibrium modeling | | | | | | | | | | | | | | | | | | | | |
| 3 mo. | | | | | | | | | | | | | | | | | | | | |
| Task 2b. Batch tests of precipitation as f(pH) on synthetic TX waters (RO concentrate) with and without anti-scalant (and no preceding oxidation) | | | | | | | | | | | | | | | | | | | | |
| 4 mo. | | | | | | | | | | | | | | | | | | | | |

