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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 2a, 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 also note that Site 2 in our original proposal will not be available for this study, as the decision has been made to not develop desalination facilities at that site. On the other hand, the laboratory work for tasks 1, 2, and 3 have proven to be considerably more complex than originally thought, and thus we will soon be asking for a re-budgeting to move some funds from Tasks 3, 4, and 5 that had been devoted to Site 2 to the earlier tasks.

Continuous Flow Experimentation for Precipitation and Solid/Liquid Separation

In recent work, many of the goals of batch experimentation have been accomplished. Over recent weeks, we have been transitioning to the use of continuous flow experimentation. This represents a movement towards more realistic and practical applications of the more theoretical work accomplished to date.

In approaching the design of a continuous flow setup, we considered how to effectively translate results from the previous research into an appropriate design. As discussed in the last report, the use of hydrogen peroxide, when combined with ozone, resulted in diminishing antiscalant degradation in comparison to ozone alone and is thus not being utilized any further. Next, in developing the optimal use of ozone, we were limited by the maximum dose of dissolved ozone we could generate and deliver. In attempting to achieve a dissolved ozone concentration which would result in an acceptable 90/10 feed water/ozone dilution ratio, we concluded that the necessary concentration (>100 mg O_3/L in the stock solution) was unattainable in the laboratory. Upon further considerations, at a higher precipitation pH (>10), which is commonly utilized in softening practice, the effect of the antiscalant would be completely overcome simply by the resulting supersaturation conditions. Due to this elevated saturation index, the degree of precipitation is independent of the use of ozone to degrade antiscalant. Consequently, ozone application would not significantly benefit the process. With this new knowledge, we began a somewhat simplified approach to the design of a bench-scale (2 L reactor volume) continuous flow apparatus. The design consisted of 4 CFSTR slow mix reactors in series followed by a conical settling tank. For initial experimentation, sodium

hydroxide was utilized to raise solution pH and saturation index to reach a point of maximum calcium carbonate removal. Within recent days, successful runs have achieved desirable conditions that match our expectations. Eventually, lime and sodium carbonate will need to replace sodium hydroxide because of economic considerations for application in the field. After these initial experiments, we are now pursuing the use of a larger scale (12 L reactor volume) apparatus for eventual field studies on precipitation and sedimentation. Laboratory testing of this apparatus requires the production of large quantities of synthetic RO concentrate (at some significant expense) so we are limiting the number of experiments in this mode.

Electrodialysis Research

Because the electrodialyzer stack is bounded with cation exchange membranes, the anode rinse solution (anolyte) loses cations to the bounding concentrate cell, and the cathode rinse solution (catholyte) gains cations from the bounding diluate cell. Hence, it is most appropriate to formulate an electrode rinse solution that has the same initial concentration of cations as the concentrate and diluate solutions, so that the electrode rinse solution maintains an intermediate concentration of cations relative to the concentrate and diluate solutions during the experiment. As explained in the previous report, it is also necessary to create an electrode rinse solution lacking chloride (to avoid oxidizing chloride to chlorine gas at the anode). Replacing chloride with sulfate or carbonate is not plausible because of precipitation of alkaline earth salts, so the electrode rinse solution was formulated with nitrate as the replacement for chloride. At infinite dilution, the equivalent conductance of nitrate is approximately ten percent less than that of chloride (Bard and Faulkner, 2001, Electrochemical Methods).

A differential-element, batch-recycle electrodialysis experiment was performed using a 10 cell-pair CMV/AMV stack on the synthetic North Cameron RO concentrate waste (detailed in the previous report) and electrode rinse, each with 5 mg/L of Dequest 2066 DTPMP antiscalant (diethylene triamine pentamethylene phosphonic acid, molecular weight 573.2 g/mol). (A sample of the antiscalant currently used in the RO treatment of the North Cameron groundwater is being shipped from American Engineering Services in Tampa, FL.) Operating conditions were an applied voltage of one volt per cell-pair, a diluate flow rate of 1000 mL/min, and a concentrate flow rate approximately equal to the diluate flow rate but adjusted for zero trans-membrane pressure. The principal objective of this experiment was to demonstrate and critique the analytical methodologies of ion chromatography (IC) and inductively coupled plasma – atomic emission spectroscopy (ICP-AES).

The electrodialysis treatment performance on the North Cameron synthetic waste demonstrated similar trends to the sodium chloride solutions previously tested; the chemical composition of the North Cameron synthetic RO concentrate was given in our previous report. The diluate conductivity (an indicator of salinity) decreased at a near-constant rate at the beginning of the experiment, but the removal rate slowed as the diluate conductivity diminished, as shown in Figure 1. The removal rate is proportional to the electrical current density because the ions carry the electrical current as they are removed, as shown in Figure 2. The results in these two figures make it clear that electrodialysis is an effective treatment for RO concentrate and also suggest that the current density should not be driven below approximately 50 amps/m^2, as little additional removal occurs beyond that point.
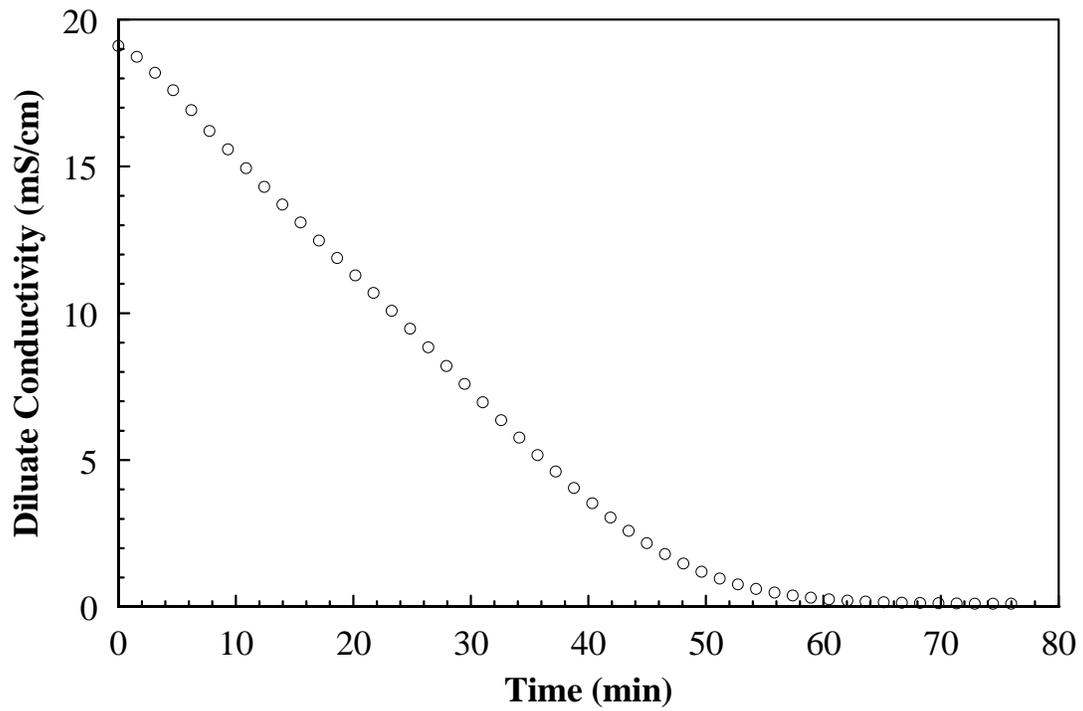
Figure 1. Electrodialysis desalination of North Cameron RO concentrate waste
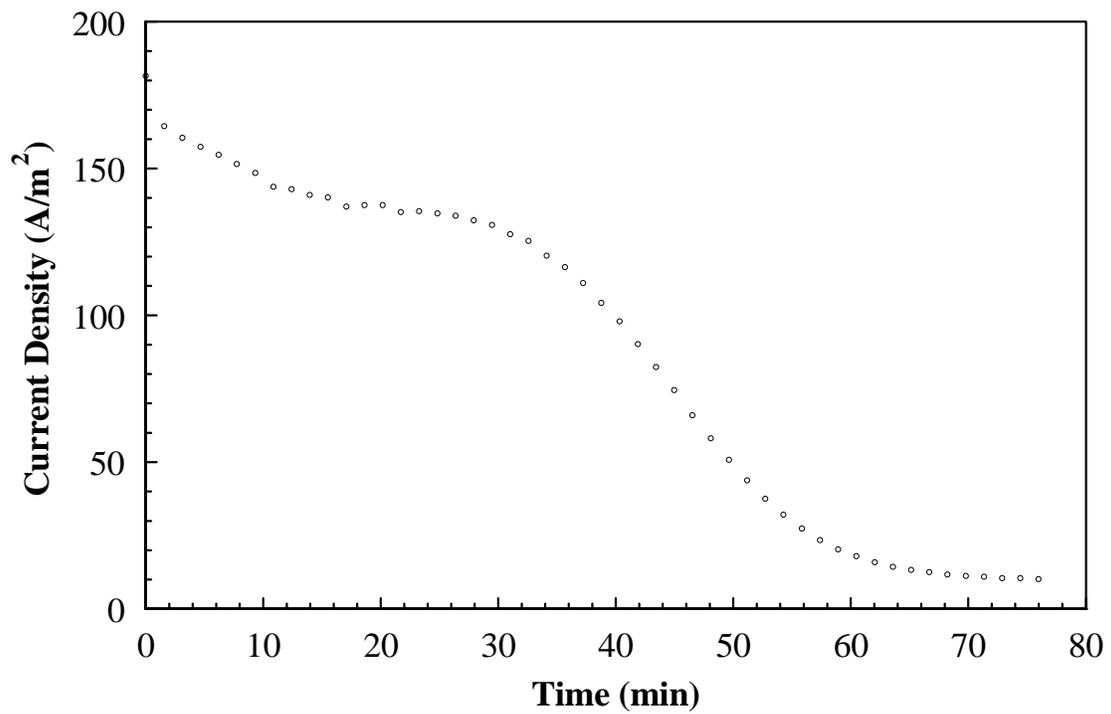
Figure 2. Electrical behavior

Small samples (100 µL) were collected from the diluate reservoir just prior to initiation of the experiment and at times 30, 40, 50, and 60 minutes during the experiment (which bracket the significant change in electrical current density). Samples were drawn from the concentrate and electrode rinse reservoirs 30 seconds before and 30 seconds after the diluate sample, respectively; the small difference in time for the three sets of samples is considered insignificant.

The experimental samples were diluted to 15 mL (1/150 dilution) for chemical composition analysis. Five of the 15 mL from each dilution were retained for anion analysis by ion chromatography (IC), and the remaining 10 mL dilutions were each acidified with 100 µL of concentrated nitric acid for cation analysis by inductively coupled plasma, atomic emission spectroscopy (ICP-AES). Standard concentration curves were developed for chloride, bromide, nitrate, and sulfate with a Metrohm IC system, and standard curves were developed for boron, carbon, calcium, potassium, magnesium, sodium, and strontium with Spectro ICP system. Results from the IC analysis are shown in Figure 3, and ICP results are shown in Figures 4 and 5.

With the exception of boron, the electrodialysis treatment is effective at separating electrolytes with removal ratios greater than 99 percent in a single stage (though it is often impractical to operate full-scale systems this way). As ions are removed from the diluate, solvating water molecules "bound" to ions are transported through the ion exchange membranes (a process known as electroosmosis). By the end of this experiment, the initial one-liter concentrate and diluate reservoir volumes had lost and gained nearly ten percent of their initial volume, respectively. Subsequent experiments will be performed to characterize the ion-specific removal as a function of operational parameters.

Ongoing Research
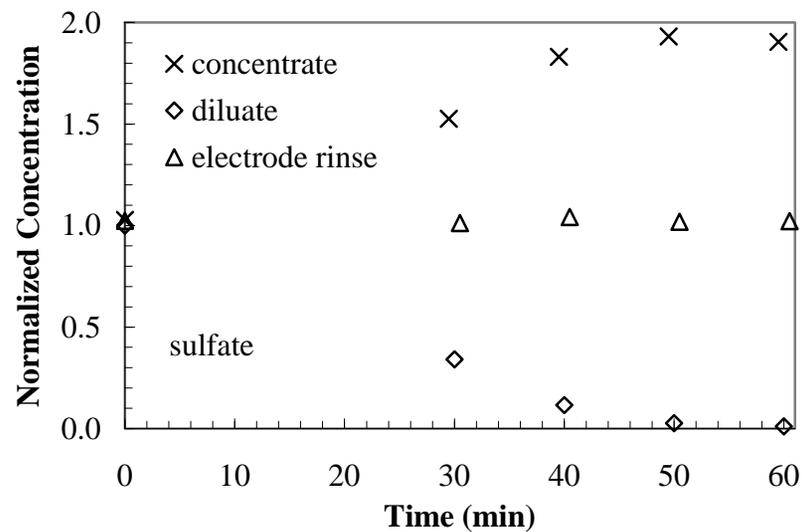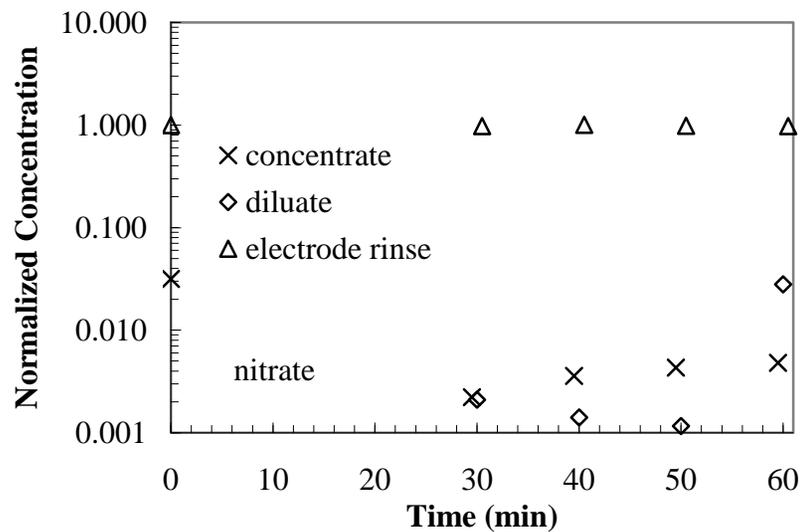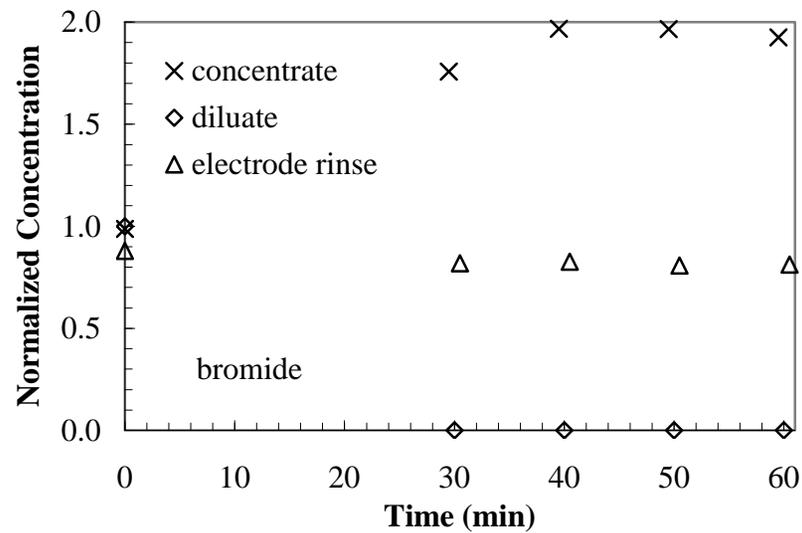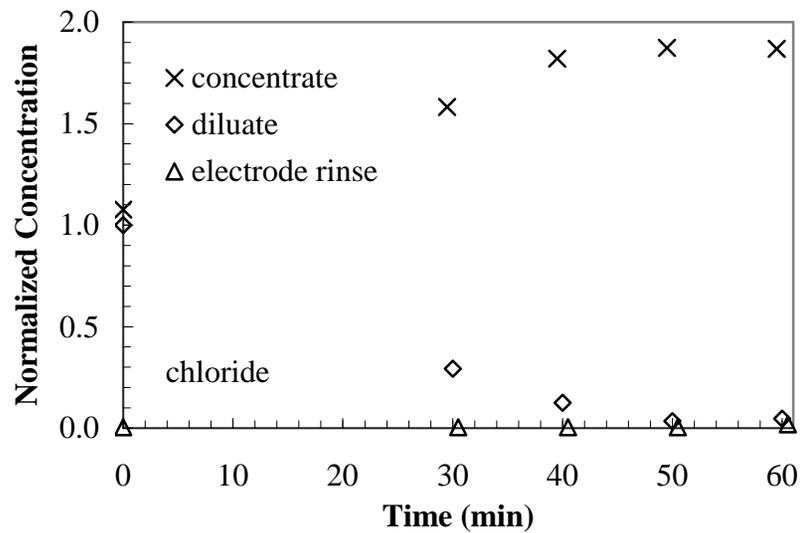
The research is progressing well on all aspects.

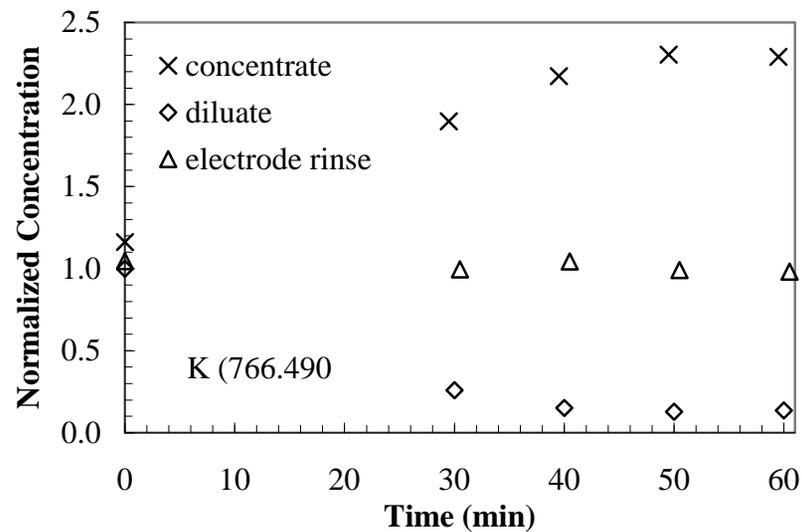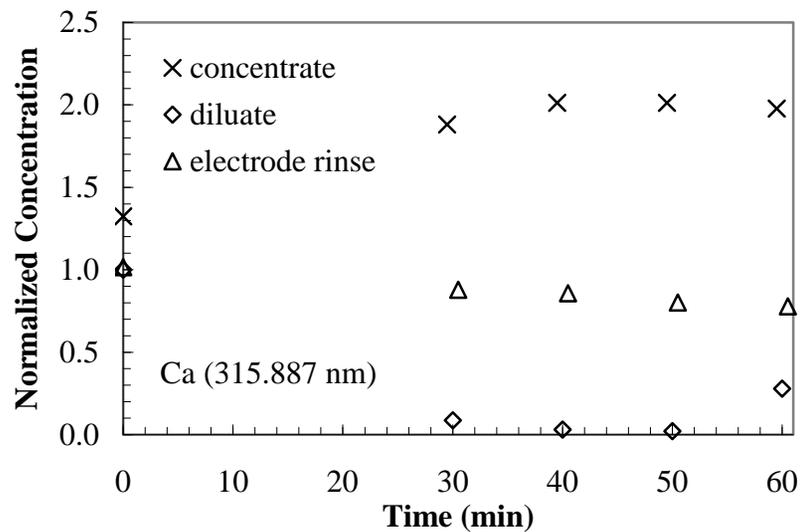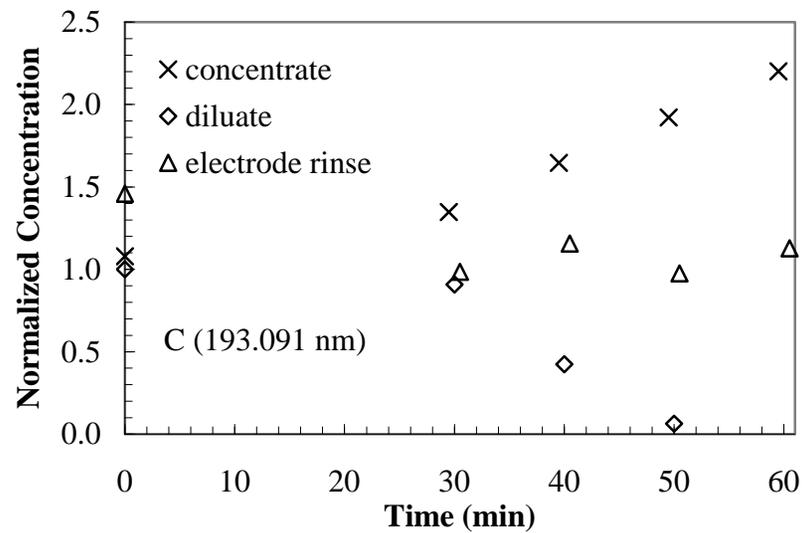**Figure 3.** IC results for anion concentrations (Cl^-, Br^-, NO_3^-, and SO_4^{2-})
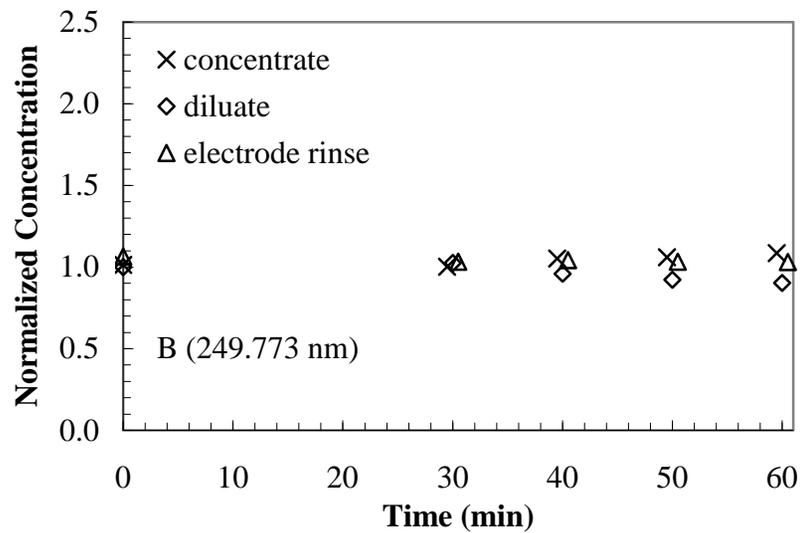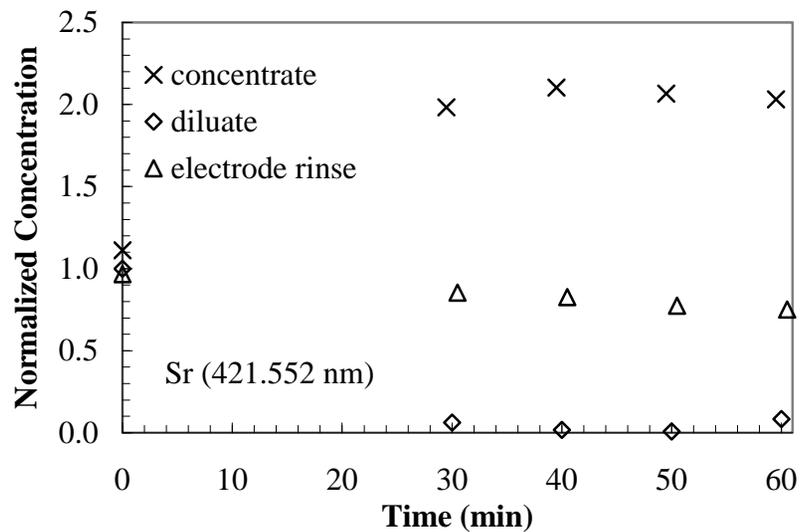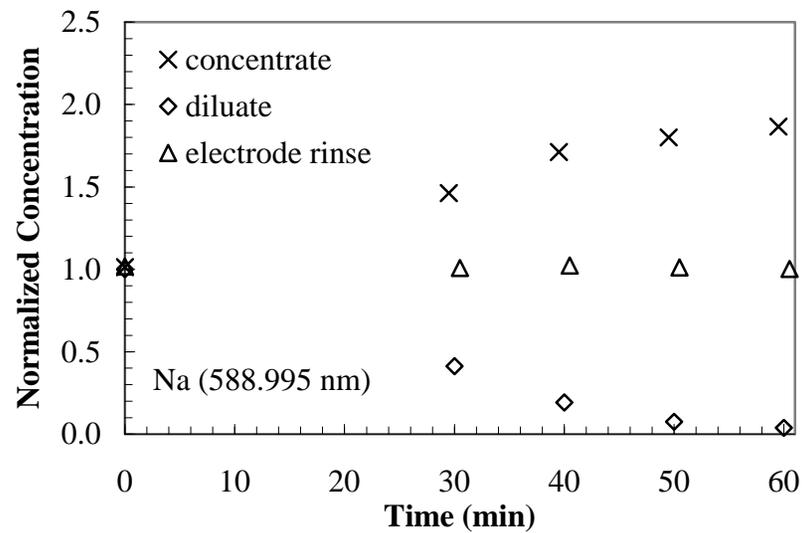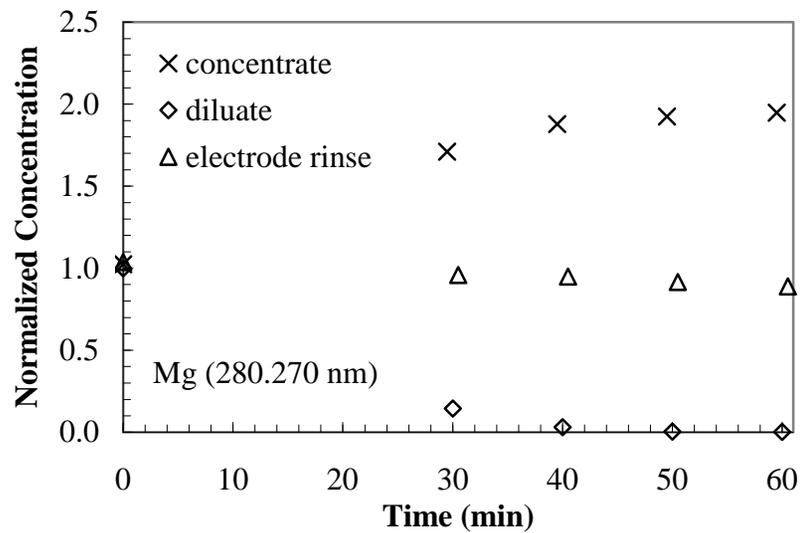
Figure 4. ICP results for B, C, Ca, and K

Figure 5. ICP results for Mg, Na, and Sr