Zero Liquid Discharge Desalination [Project #4163]

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OBJECTIVES:
The overall goal of this research was to investigate methods that reduce the cost for zero liquid discharge (ZLD) desalination of brackish water. Specific project objectives were as follows:

- Evaluate and compare treatment technologies for ZLD desalination.
- Evaluate the effect of high concentrations of natural organic matter (NOM) on ZLD treatment requirements and costs.
- Evaluate the effect of total dissolved solids (TDS) concentration on ZLD costs.
- Evaluate the viability of ZLD desalination as a treatment approach for removal of a single contaminant.

BACKGROUND:
Recovery in membrane separation processes, such as reverse osmosis (RO), electrodialysis (ED), and electrodialysis reversal (EDR) is limited by the membrane fouling potential of inorganic and organic precipitates. Inorganic fouling, also referred to as scaling, occurs when sparingly soluble salts precipitate and deposit on the membrane surface. Common salts of concern for brackish water desalination are calcium carbonate (CaCO₃), calcium sulfate (CaSO₄), and silica (SiO₂). Similarly, organic fouling is caused by the precipitation of organic compounds onto the membrane, and the fouling potential of organic compounds is increased in the presence of calcium.

One approach to reducing the costs for ZLD is to treat RO concentrate to reduce its membrane fouling potential, and then desalinate the treated concentrate in a second membrane application. The hypothesis is treatment costs will be reduced by a concurrent increase in the percentage of water recovered with membrane processes and decrease in reliance on thermal technologies. Treatment processes that can be used to reduce the membrane fouling potential of concentrate include softening, fluidized bed crystallization, activated alumina, coagulation with metal salts, and ion exchange. The most highly developed options for the second membrane desalination step are RO and electrodialysis.

A new electrodialysis technology, referred to as electrodialysis metathesis (EDM), was integral to the ZLD approach investigated in this project. Electrodialysis has been used for decades in the drinking water industry to produce potable water and in the chemical and food industries to recover valuable salts or brine products.
In electrodialysis, water is desalinated by the transport of ions through ion exchange membranes under the driving force of an electric potential between a cathode and an anode. Cations are pulled from the feed water toward the cathode and anions are pulled toward the anode. Cations pass through cation selective membranes into the concentrate compartment and are held there by repulsion from the anion selective membrane. Anions similarly pass through anion exchange membranes and are held in the concentrate compartment by cation exchange membranes. The result is alternating compartments of desalinated product water and a by-product concentrate containing all of the removed ions.

EDM differs from conventional electrodialysis by an innovative arrangement of ion exchange membranes and use of NaCl solution. These innovations cause EDM concentrate to be separated into two streams of highly soluble salts. One stream contains sodium and anions and the other chloride with cations. Separation of concentrate into two streams with highly soluble salts allows desalination at high rates of recovery that would lead to membrane fouling with RO or conventional electrodialysis. This characteristic makes EDM an attractive process for the second desalination step in ZLD.

APPROACH:
The investigative approach comprised the following steps:

- Preliminary analyses to evaluate water quality and establish treatment goals
- Preliminary testing to compare treatment options and select a ZLD approach for pilot-scale testing
- Pilot-scale testing with the selected treatment approach
- Evaluation of results to estimate full-scale treatment costs

Five water sources were evaluated with bench- and pilot-scale testing. The test results were used to conduct desktop studies on two additional sources. Diverse water types were evaluated to maximize the applicability of this work. Raw water TDS concentrations in the sources ranged from 270 to 28,000 mg/L, and total organic carbon (TOC) concentrations ranged from 2 to 20 mg/L. The geographical focus of this study was Florida where natural organic matter (NOM) is found in many brackish water sources.

RESULTS/CONCLUSIONS:
Three ZLD options were identified in the preliminary analyses and evaluated in preliminary testing. The first two options included combinations of ion exchange, softening, and coagulation processes for concentrate treatment followed by secondary desalination with RO. The third option comprised only of EDM for secondary desalination, except for two sources for which ion exchange preceded EDM for TOC removal. Based on minimization of cost, waste by-products, and energy consumption, the option with EDM was selected for further evaluation at pilot-scale.

EDM was pilot tested with concentrate samples from four of the water sources. The TDS range of the concentrate samples was 3000 to 16,000 mg/L, and the samples were supersaturated with salts that would foul RO or ED membrane systems if either were
used for further treatment. Water quality and EDM performance parameters were monitored to evaluate (1) the effectiveness of EDM in separating the concentrate into two streams of highly soluble salts, (2) the rate of product water recovery by EDM, and (3) energy requirements for desalination with EDM. Water quality analyses of the EDM concentrate streams showed the process was highly effective in separating the concentrate into two highly soluble streams. Recovery of RO concentrate during EDM pilot tests ranged between 99.8 and 99.9%, and the EDM operated without any sign of membrane fouling.

Pilot test results were scaled up to calculate EDM recovery, water quality, and energy requirements for full-scale application. Full-scale ZLD treatment costs were calculated for each of the seven water sources. The treatment process comprised of EDM followed by thermal desalination in a crystallizer. The ion exchange process, MIEX®, was included for TOC removal ahead of EDM for two of the sources.

Treatment costs were calculated per volume of RO concentrate recovered. Cost on the basis of total plant production can be calculated by dividing these costs by 5 for an RO plant operating at 80% recovery or by 4 for a RO recovery of 75%. Treatment costs included amortized equipment capital cost and O&M cost. Capital cost was amortized over 20 years at a 6% rate of return. O&M comprised of energy, chemicals, and membrane replacement. Similar treatment costs were calculated for conventional ZLD with thermal desalination to assess the potential for cost reduction with the EDM method.

The treatment costs for ZLD with EDM were highly dependent on TDS. Five of the sources evaluated had raw water TDS concentrations of 1400 mg/L or less. The ZLD treatment costs for these sources ranged from $2.42 to $4.35 per kgal. The two other sources had TDS concentrations of 5300 and 28,000 mg/L. Treatment cost for the 5300 mg/L TDS source was $15.90 per kgal, and the cost for the 28,000 mg/L TDS source was $42.43 per kgal. Compared with conventional ZLD, treatment costs for the five lower TDS sources were 22 to 37% of the ZLD cost with thermal desalination. Treatment cost for the 5300 mg/L TDS source was comparable to that of conventional ZLD, and the EDM method was 60% more expensive than ZLD with thermal desalination for the 28,000 mg/L TDS source. Consequently, this approach appears to be particularly advantageous for the higher quality brackish sources that utilities would first seek to use.

ZLD costs with the EDM method were reduced 30% for six of the sources by treating the EDM concentrate to develop beneficial products. This was not evaluated for the 28,000 mg/L TDS source because its treatment costs for the EDM option were prohibitive. The cost savings resulted primarily from recycle of the EDM concentrate to the process to replace NaCl consumed during electrodialysis. This reduced the flow treated by thermal desalination and reduced NaCl costs for EDM desalination. The salt products generated would be gypsum, calcium carbonate, and dolomite. Although these salts have commercial value, in this analysis the final salt products were treated as cost neutral, having neither commercial value nor disposal cost. In the two options that included MIEX for TOC removal, treatment to remove TOC increased the ZLD treatment cost by 28 to 36%.
APPLICATIONS/RECOMMENDATIONS:
As utilities face the challenges of increased use of alternative water sources and the need to remove emerging contaminants at very low concentrations, economical and sustainable management of RO concentrate will assume increasing importance. This research demonstrated a promising method of zero liquid discharge desalination using a new electrodialysis technology.

Although EDM is a new technology, it is nevertheless simply electrodialysis with an innovative arrangement of ion exchange membranes. Electrodialysis has been in use in large scale applications for more than 50 years, and its principles have been understood for more than 100 years. Consequently, there is little left to overcome in the learning curve for this technology, and it is likely that EDM will be available for full-scale implementation in the near future.

It is recommended that utilities faced with current or projected concentrate management challenges consider the ZLD approach evaluated in this research. The calculations in this report can be used as a model to evaluate ZLD with EDM and compare costs for this ZLD approach with other concentrate management options. If this preliminary evaluation looks promising, a utility is advised to conduct a pilot study with EDM to develop design and cost criteria specific to its water source.

RESEARCH PARTNERS:
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