COOLING TOWER BLOWDOWN PILOT STUDY

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Zero Discharge Strategy – Boiler Makeup from Cooling Tower Blowdown

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Keywords: reverse osmosis, zero liquid discharge, silica, cooling tower blow down.

Abstract: a pilot study is conducted to demonstrate the feasibility of treating cooling tower blow down containing high silica concentrations for reuse as boiler water make-up. Cooling tower blow down is treated over a period of several months with silica concentrations coming into the treatment process at 120 to 170 mg/L . The RO reject silica concentration was between 1062mg/L and 1567 mg/L without scaling of the RO membranes. Silica rejection was greater than 99.9%. The pilot study proved the reliability and economic viability of the patented process termed High Efficiency Reverse Osmosis™ .

Background

A number of new power plants and other major chemical/petroleum processing facilities are being required to achieve Zero Liquid Discharge (ZLD). A Zero Liquid Discharge system is required to accept wastewater streams such as Cooling Tower Blow Down (CTBD), Scrubber Blow Down (SBD), Ash Sluicing Blow Down (ASBD), etc, as feed. The CTBD is typically the largest and sometimes the only component. This paper covers the treatment of CTBD only and all subsequent discussions are based on the performance of ZLD systems where CTBD is the only feed. However, the general principles apply equally well to SBD, ASBD, and blends of two or more of the components.

It is imperative to reduce the volume of CTBD in order to achieve ZLD. Cooling Tower Blow Down is quite frequently “silica limited”, meaning that the CTBD treatment options are limited by the maximum levels of silica achievable in the treatment process. The overall objective is to minimize the volume of waste (blow down) from the CTBD treatment system. To accomplish minimization of the waste volume the capability of the selected CTBD treatment process to deal with very high silica levels can be critical.

Consider a case where the CTBD contains 150 ppm (mg/l) of dissolved silica. This is often considered the highest “safe” level that can be maintained in a Cooling Tower System. Since silica solubility in ambient or near ambient conditions is also approximately 150 ppm, the CTBD can be considered to be at, or very close to silica saturation. Higher concentrations of silica will result in precipitation in the piping or on the heat exchanger surfaces. Any method to reduce the volume of blow down to minimize wastewater (and water make-up) must consider the issue of silica concentration.

Traditional methods for treating CTBD for achieving ZLD have included such processes as mechanical evaporation, crystallization, spray drying, solar evaporation ponds, or combinations of these technologies. The High Efficiency Reverse Osmosis (HERO™) process was tested successfully and demonstrated the commercial feasibility of utilizing a membrane based process for achieving and maintaining very high levels of silica in the RO reject. While conventional RO systems are limited to maximum silica levels of 125-150 ppm in the reject, the HERO™ system demonstrated the ability to maintain 1600 ppm of Silica in the reject**.** This suggests that the CTBD volume can be reduced by a factor of ten (10) times using a relatively inexpensive membrane based process. The reject from the HERO™ system, which is approximately 10% of the original CTBD volume, can then be treated further with much smaller, expensive, “last resort” approaches such as crystallization, drying, or a solar evaporation pond, etc. In addition to offering significantly lower capital costs, the HERO™ technology also offers lower operating costs compared to traditional approaches.

The High Efficiency Reverse Osmosis Process

High Efficiency Reverse Osmosis is a patented process developed by Mr. Deb Mukhopadhyay. The overall process is depicted in Figure 1. Specifics of the process vary with the application and water quality. The HERO^{TM} process is applicable to such opportunities as industrial waste minimization and recycling, improved ultra-pure water quality and capacity, and as demonstrated in this pilot study the process works well for the minimization of cooling tower blow down particularly where the process is silica limited. For recovering cooling tower blow down that is silica limited the HERO^{TM} process works on the basic principal that silica solubility increases with increasing pH, reference Amjad et.al and others. An alkalie (NaOH) is added upstream of the RO and a PID loop control is used to maintain a specific pH in this single stage pH control process. The specific process for this cooling tower blow down minimization is depicted in Figure 2. To keep metals from precipitating onto the RO membranes (as the pH is elevated) the higher valence cations are efficiently removed with a weak acid cation exchange bed prior to the RO, refer to Figure 2. Depending upon the hardness to alkalinity ratio some alkalinity may need to be added upstream of the WAC bed, refer to Figure 1. To permit efficient elevation of the pH with caustic the bicarbonate alkalinity is removed with an atmospheric deaerator – an inexpensive process. Since this was a pilot test several additional steps are included that are not necessary in the full scale system. For example a UV unit was used on the front end of the process to test the capability of medium pressure UV to remove bromine biocide rather than the typical less efficient addition of sodium bisulfite. The UV unit was found to be effective. As a precaution a sodium zeolite resin bottle is also used just ahead of the RO to ensure that there is no higher valence cation leakage from the WAC bed due to channeling effects or poor regeneration.

Pilot Test Details

Primary Objectives

The primary objective of the pilot test was to establish the HERO™ system as an effective and reliable way to reduce CTBD. To accomplish this it was vital to demonstrate the capability of the HERO™ system to achieve high levels of silica in the concentrate stream. The results of this report focus on:

1. System Recovery
2. Silica Rejection
3. Silica Level in the Concentrate Stream
4. Axial Differential Pressure (to demonstrate stability of the system)

The test began on February 23, 1999 and continued until March 30, 1999. The system operated during the day and was turned off at night. As though familiar with the operation of an RO can attest the on/off duty cycle is generally much tougher on the RO membranes and this duty cycle is generally more likely to cause membrane scaling or performance problems.

Test Site

The pilot test was performed at a semiconductor industry plant located in the northwestern portion of the United States. The site draws its water from various wells onsite. Feed to the pilot unit is blow down from the cold side of an open recirculating cooling tower. Table one outlines the water analysis of the cooling tower makeup as well as the cooling tower blow down (which was the feed to the pilot system). The study was operated at a stable temperature.

Constituent (ppm as ions)	Tower Blowdown (feed to system)	Tower Make – Up
PH	8.9	6.5
Conductivity (Us/cm)	540	150
P–Alkalinity	18	0
M-Alkalinity	180	53
Calcium	153	40
Magnesium	92	24
Total Hardness	245	64
Iron	0.3	1.2
Silica	150	40
Chloride	18	4
Sulfate	18	4
Nitrate	14	3

Table 1 – Water Qualities

Pilot System and Sample Points

Figure 2 is a process flow diagram of the pilot system. The flow rate (feed) into the system throughout the test ranged from 6 – 8.5 gpm.

The weak acid cation vessel (WAC) is a rental unit that is regenerated off-site. The bottle has 20 ft^3 of resin. This was oversized relative to the system requirements in order to avoid excessive down time for off site regenerations. A recirculation stream was continuously run through the WAC to avoid channeling.

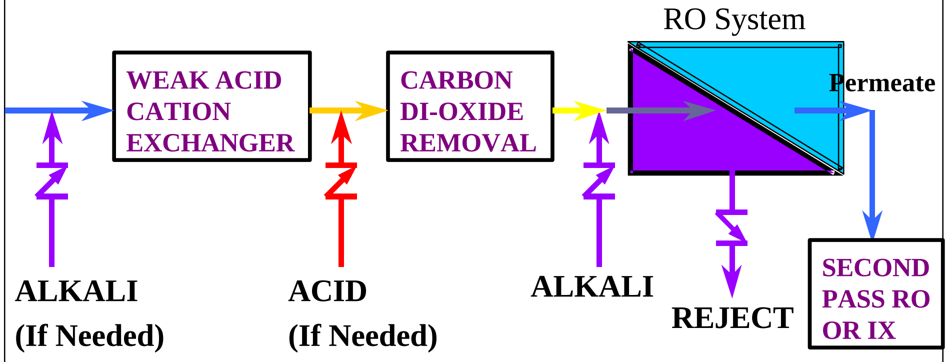
A one-micron cartridge filter was placed downstream of the WAC to catch any resin leakage. The water was then passed through a 500-gallon dearation tank. The dearation was accomplished by introducing water through spray nozzles into the feed tank.

Finally, the feed to the reverse osmosis unit was passed through a sodium zeolite softener bottle and a one-micron cartridge filter. The softener acted as a safety feature for the pilot in case of any hardness leakage in the WAC.

The reverse osmosis unit was arranged in a 1:1:1 array. The first vessel consisted of three 4-inch elements and the following two vessels consisted of three 2.5-inch elements each. The primary sample points are shown on Figure 3 with additional sub points on the RO skid. Data for the following performance monitors were taken:

- Feed pH
- Concentrate pH
- Inlet Flow
- Concentrate Flow
- Product Flow
- 1st Stage Pressure
- 2nd Stage Pressure
- 3rd Stage Pressure
- Inlet Pressure
- Outlet Pressure
- Concentrate Pressure

Flow Diagram for HERO System



WEAK ACID CATION EXCHANGER

CARBON DI-OXIDE REMOVAL

RO System

Permeate

SECOND PASS RO OR IX

ALKALI
(If Needed)

ACID
(If Needed)

ALKALI

REJECT

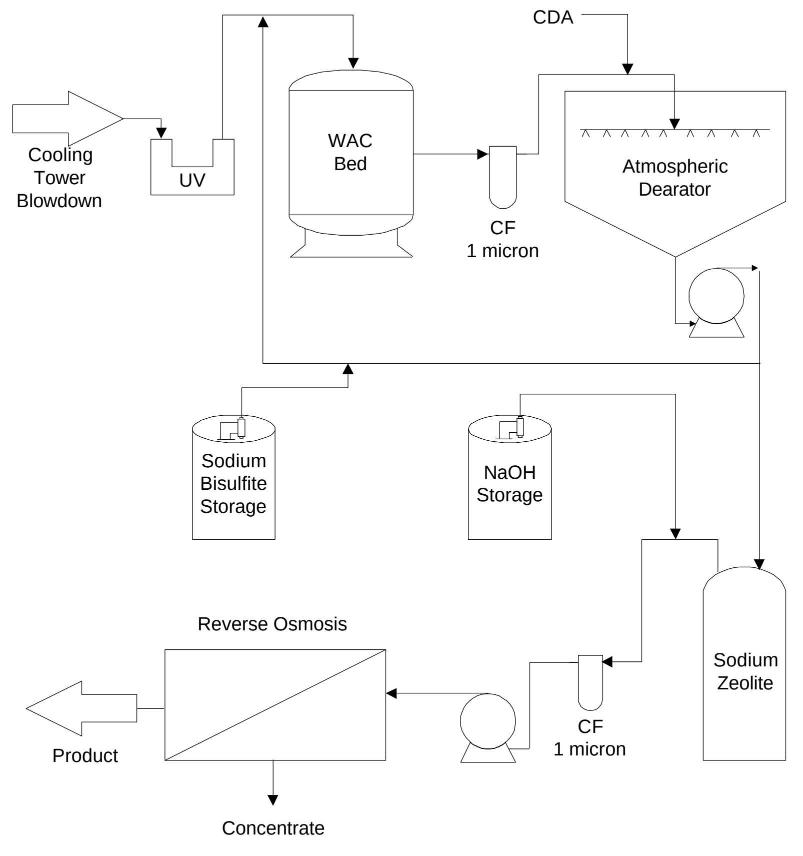


Figure 2: Cooling Tower Pilot

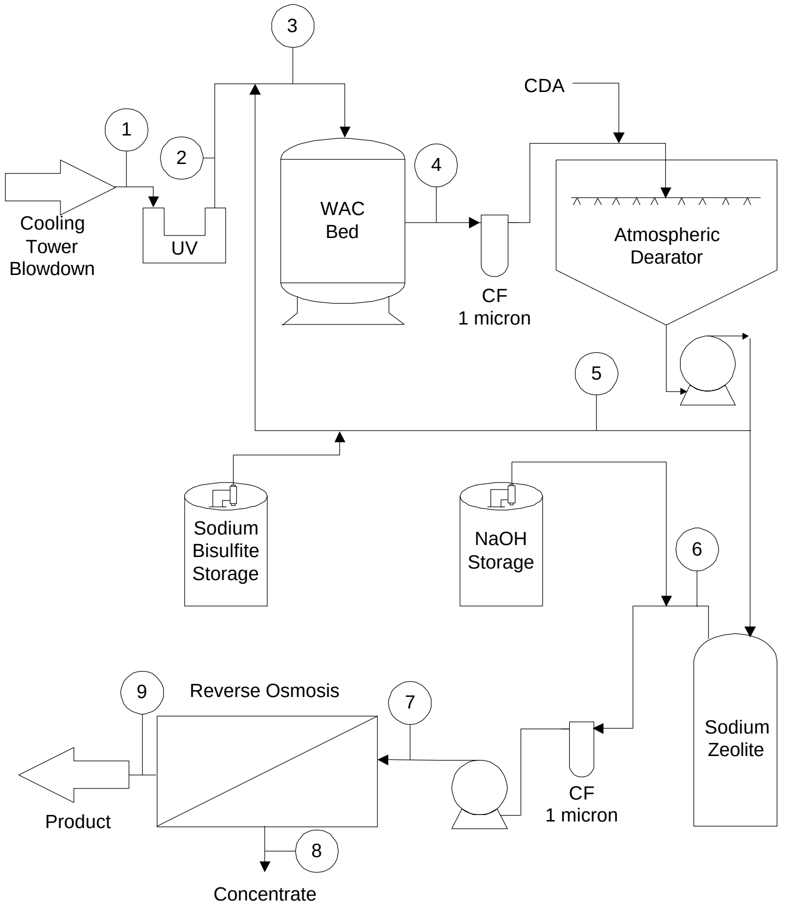


Figure 3: Sample Points

Results of Pilot Study

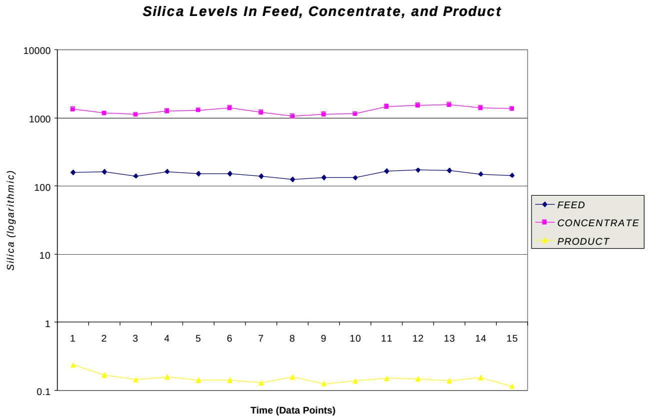
The results of the pilot study indicate that the HERO™ process will be a viable and economical solution for the reduction / recycle of cooling tower blow down. The results that lead to this indication are system recovery rate, the silica concentration maintained in the concentrate stream, and the stability of axial differential pressure.

System Recovery

For most of the test period, the system recovery was approximately 89%**.** Near the end of the test, recovery was increased to 91%**.** Thus, for a blow down of 100 gallons-per-minute (144,000 gallons-per-day) all but 9 gpm (1300 gpd) are recovered. This small remaining blow down stream can then be more economically treated by evaporation, crystallization etc.

Silica Concentration

Silica feed to the RO ranged from approximately 120 ppm to 170 ppm. Silica concentration in the reject stream ranged from approximately 1100 ppm to 1600 ppm. The HERO™ system continuously exceeded 99.9% silica rejection. Figure 4 illustrates the silica levels of the feed, reject, and permeate streams on a logarithmic scale.



Silica Levels In Feed, Concentrate, and Product

Figure 4 – Silica Concentration Level Comparison in Different Streams

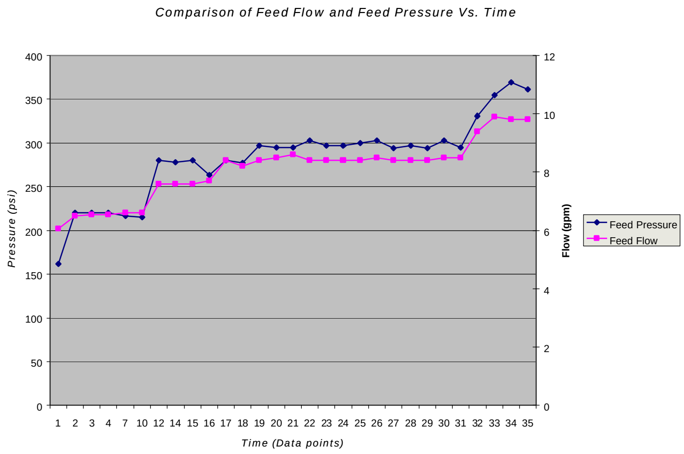


Figure 5 – Comparison of Feed Flow and Feed Pressure vs. Time

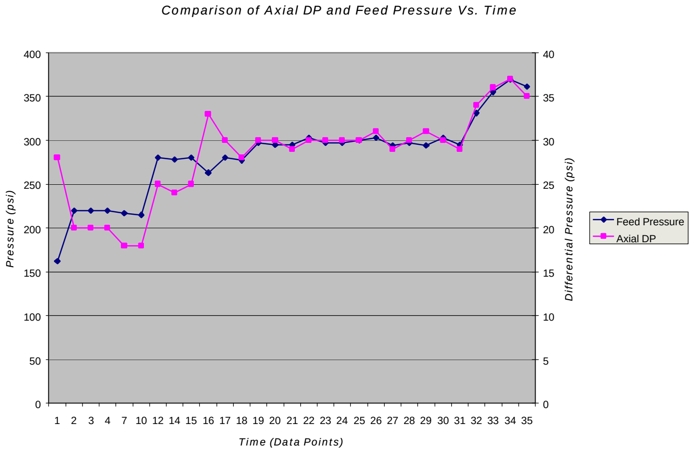


Figure 6 – Comparison of Axial DP and Feed Pressure vs. Time

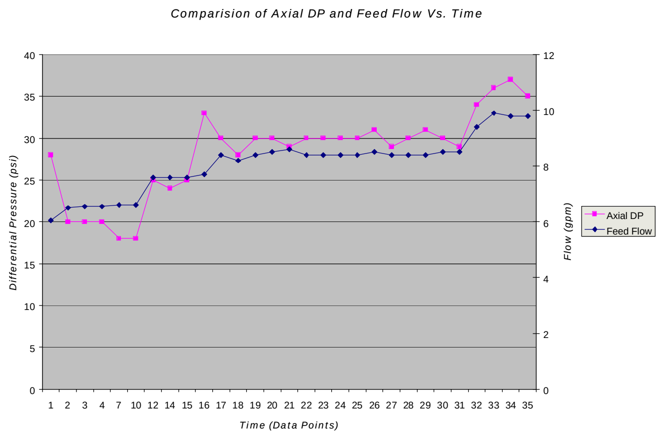


Figure 7 – Comparison of Axial DP and Feed Flow vs. Time

System Stability

Pressure of the feed, concentrate, and product streams were continuously monitored throughout the pilot study. The axial differential pressure (difference between the feed and reject stream pressures) was stable the entire study. The axial DP started out at approximately 20 psi, and remained stable until the flux was increased and the DP moved to a stable 30 psi.

As the flow rate of the system was increased, the pressure increased, as did the DP. The correlation between these can be seen in Figures 5, 6, and 7. The differential pressure demonstrated stability throughout the study, and only increased proportionally when the system flux was increased.

Total Organic Carbon removal

In some water recycle systems cooling tower blow down or other wastewaters may be considered for recycle back to applications where removal of organics is necessary. The HERO process was found to have excellent capability for the removal of organics, refer to Figure 8. Incoming organic carbon levels 12 mg/L were reduced to 200 to 350 ug/L in the RO product water for a 97% to 98% removal efficiency. TOC removal is an important issue for cooling *towers in general due to biogrowth, but has particular importance to some industrial plants that reclaim municipal wastewater and mix it with industrial wastewaters to provide a source for make-up water to the cooling towers.*

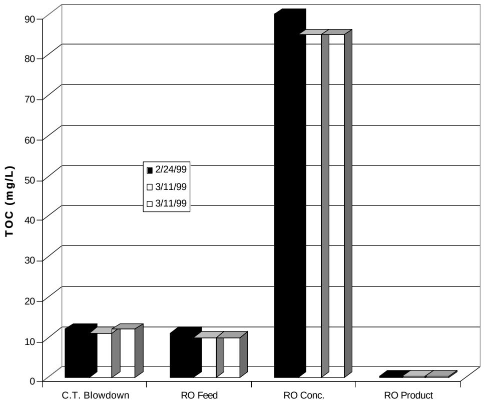


Figure 8 – TOC Reduction in HERO Process

Bromine Biocide Removal

Bromine Biocide is used in cooling towers to inhibit biogrowth. Oxidizers like bromine, chlorine, hydrogen peroxide and ozone will have a detrimental effect on ion exchange resins and thin film composite RO membranes in the water minimization system. A reducing agent, typically sodium bisulfite, is used at a two times stoichiometric concentration to eliminate the residual oxidizer ahead of the IX or RO in water and wastewater applications. A medium pressure UV unit was found to be an efficient process for the removal of bromine in the cooling tower blow down in the range of 0.1 to 0.5 mg/L and spike concentrations to 3 mg/L are treatable. Figure 9 illustrates the bromine removal efficiency over the range of concentrations observed in the cooling tower blow down at the test site.

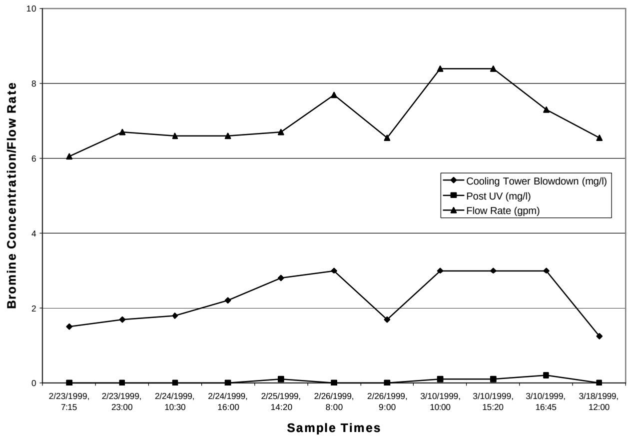

Bromine Concentration/Flow Rate
10
8
6
4
2
0
Cooling Tower Blowdown (mg/l)
Post UV (mg/l)
Flow Rate (gpm)
2/23/1999, 7:15
2/23/1999, 23:00
2/24/1999, 10:30
2/24/1999, 16:00
2/25/1999, 14:20
2/26/1999, 8:00
2/26/1999, 9:00
3/10/1999, 10:00
3/10/1999, 15:20
3/10/1999, 16:45
3/18/1999, 12:00
Sample Times

Figure 9 – Bromine Reduction in the Medium Pressure UV

Conclusions

The results of the pilot study exceeded expectations. The system's effectiveness, reliability and stability in recovering CTBD for recycle was demonstrated.

Economic Viability

By operating with such high silica levels in the reject stream without fouling of the reverse osmosis membranes, the HERO™ system demonstrated the capability to achieve a high recovery of CTBD. With this high recovery rate 89% to 91%, the HERO ™ system greatly reduces (by a factor of 10) the amount of wastewater that is either discharged or goes to further treatment, and the associated amount of make-up water required - both having significant costs associated with them. Thus, the HERO™ process for the recycle/recovery of CTBD should have significant savings over alternative methods.

Reliability and Operational "Safety"

The HERO™ system also exhibited excellent reliability. There was no fouling of the RO membranes over time even though the cooling tower blow down stream is full of organics and bacteria. The stable Axial DP levels established that no biofouling occurred. The reason for no biofouling of the RO's is the high pH created by the feed of caustic directly ahead of the RO's. Consider that caustic is often the base chemical fed to RO's to clean them after biofouling.

Another interesting finding during the course of the study was the resilience of the HERO™ system. Besides the high silica levels achieved, the system performed very well in spite of many operational nuances that were caused by operator error or by an apparatus fault. For example, operator error led to many fluctuations of the pH dosing influent to the RO system. The recommended operating set point of the HERO™ process is pH=11. The system was run for close to one hour at a pH as high as 12 and at a pH as low as 6.6 without any system damage. The boundary layer on the RO membranes appears to be very stable. An elevated pH is maintained for a significant period of time beyond the point where the pH probe on the concentrate (which is controlling the caustic feed rate) is registering a very low pH=6.6 or very high pH=12. The conclusion from this observation is that in a HERO™ system, potential membrane scaling is less time dependent than would be anticipated. This indicates that there is a "safety" level in the process operation to ensure long term, effective and efficient usage of the RO system.

High Quality Product

The product/permeate from the HERO™ system is high enough in quality that it can be utilized as boiler feed make-ups with very little or no additional treatment. The cooling tower blow down quality and single pass RO product water quality from the pilot are shown in Table 2. Improved RO product water quality is readily accomplished beyond the levels indicated (if desired) by addition of a second pass to the RO or incorporation of a post WAC or SAC (strong acid cation) exchange bed downstream of the RO. McBride at Intel demonstrated the capability of a SAC downstream and brought the sodium level down to less than 7 parts-per-trillion (ppt). By comparison a SAC resin downstream of a classic RO process produced sodium levels of 431 ppt. In a separate demonstration on a well water source (at this pilot test site) a post WAC ion exchange bottle was placed on the HERO^{TM} pilot test single pass RO product and water quality improved by an order of magnitude as indicated in column three of Table 2.

The results of this pilot study indicate that operating a reverse osmosis process as a HERO™ system should have economical as well as operational benefits.

Constituent	CT Blowdown (ppb)	RO Product (ppb)	Post WAC (ppb)
Aluminum	8.0	1.1	<0.02
Barium	55	<0.2	<0.005
Calcium	102,000	0.59	<0.005
Iron	780	0.83	<0.10
Lithium	13	0.65	
Magnesium	38,000	<0.2	<0.02
Manganese	4.1	<0.2	<0.03
Potassium	18,720	33	<0.05
Sodium	41,000	12,700	5.4
Strontium	560	<0.2	<0.01
Fluoride	3,100	<5	<0.005
Chloride	31,000	122	1.9
Nitrite	<50	22	<0.05
Bromide	4,100	20	<0.05
Nitrate	65,000	1,440	<0.05
Sulfate	29,000	<5	0.22
Phosphate	430	<5	<0.05

Table 2 – HERO Pilot Water Quality Data

Acknowledgements

The authors wish to acknowledge the hard work and dedication of Matthew Brinkman in putting the pilot system and controls together.

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