HERO PROCESS VOLUME REDUCTION OF COOLING TOWER BLOWDOWN AS PRECONCENTRATOR FOR ZLD APPLICATION

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Summary: Silica concentration frequently limits the cycles of concentration in cooling tower circulating water. This is particularly true in western and southwestern areas of the USA and Mexico where the raw feedwater has high silica. This paper describes a high efficiency reverse osmosis system, discusses technical and commercial considerations involved in the selection of the process, and presents preliminary operating data from the first full-scale application of the process for zero liquid discharge at a power plant.

INTRODUCTION

High Efficiency Reverse Osmosis (HERO™) is an innovative membrane process for high silica and difficult to treat water and wastewater. The process has excellent potential for treatment of cooling tower blowdown whereas conventional reverse osmosis (RO) is generally considered to be ineffective or unreliable. In some instances, HERO may be used to replace or supplement an evaporation process as a cost-effective method of achieving zero liquid discharge (ZLD).

The HERO process patent was issued in July 1999. The first uses of the technology, dating back to the mid-1990s, were in the semiconductor industry for treatment of water with high silica content and for the production of ultrapure water. Since then, many new applications have been identified and the number and type of installations have expanded rapidly. Two primary applications in the power industry are 1) treatment of gray water for use as cycle makeup, and 2) treatment of wastewater, including cooling tower blowdown, for reuse or as a preconcentrator in a ZLD system.

Until recently, alternative treatment methods considered for ZLD applications consisted of combinations of thermal and membrane processes, sometimes coupled with evaporation ponds. These processes included RO, electrodialysis reversal, vapor compression evaporators (brine concentrators), crystallizers, and spray dryers. This paper describes the HERO process, discusses technological and commercial considerations that may influence a decision to use the process for wastewater treatment, and presents preliminary operating results from the first full-scale installation in conjunction with a power plant ZLD system.

PROCESS DESCRIPTION

A simplified schematic of the HERO process is shown in Figure 1. The process is essentially the same for all applications and has been described in detail in previous technical papers.[(1),(2),(4),(5)] The description that follows is specific to a power plant wastewater source consisting principally of cooling tower blowdown.

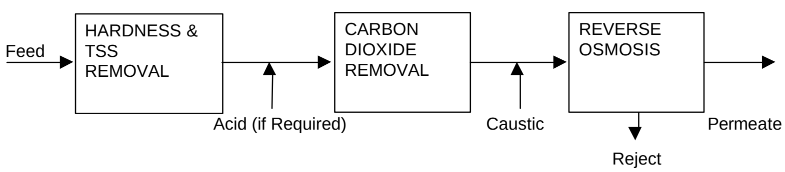

Figure 1. HERO Process Schematic

The basic process consists of three steps:

- Hardness and suspended solids removal.
- Carbon dioxide removal.
- RO treatment at elevated pH.

Pretreatment steps that make up the HERO process are customized depending on the water chemistry and site specific design criteria. The preferred hardness removal method for a large power plant with high TDS cooling tower blowdown consists of a conventional lime-soda ash softening system followed by filtration and weak acid cation (WAC) ion exchange. Lime-soda ash softening in a conventional solids contact clarifier, or in a dense solids process, is usually an economical method of removing the bulk of the hardness (calcium and magnesium) and other scale forming cations such as iron, barium, and strontium. The effluent from the clarifier is filtered with dual media gravity or pressure filters for reduction of suspended solids.

Secondary softening is accomplished by weak acid cation (WAC) ion exchange. WAC ion exchange, when operated in the hydrogen cycle, will efficiently remove hardness associated with alkalinity. Alkali addition may be needed for adjustment of the hardness-to-alkalinity ratio in the feedwater. Hydrogen ions released in the cation exchange reaction react with the carbonate alkalinity to form carbonic acid for subsequent removal in the degasifier. The WAC ion exchanger has a very low leakage characteristic that is important to avoid potential scaling of the RO membranes.

The second step in the process is alkalinity removal. A forced draft degasifier is typically used for this step. The acidic nature of the WAC ion exchange step results in the carbonate alkalinity being converted to free carbon dioxide that can be easily removed. Supplemental acid feed can be used if necessary to convert all carbonate alkalinity to carbon dioxide. The degasification step reduces the amount of caustic required to elevate pH in the subsequent step.

The third and final treatment step is the RO. This equipment is made up of standard components that are readily available from suppliers and includes inlet cartridge filters. Caustic is fed to the inlet of the RO to elevate the operating pH. Silica is highly soluble at elevated pH and therefore does not limit the recovery of the RO unit. Unlike conventional RO that is limited to about 150 mg/l SiO_2 in the reject, an RO operating in the HERO mode can concentrate silica to 2000 mg/l and greater. This characteristic makes the HERO process exceptionally well suited for treatment of cooling tower blowdown. The elevated pH has the additional advantages of eliminating biofouling potential, emulsifying any oil that may exist in the wastewater supply, and enhancing the rejection of organic constituents.[3]

The overall result is that the reliability and availability of the RO is greatly improved over the conventional mode of operation. Membrane cleaning operations are greatly reduced or eliminated, even in difficult to treat wastewater.

PROCESS SELECTION

Design of the Griffith Energy Project near Kingman, Arizona, was initiated in 1999. The plant is a 500 MW gas fired combined cycle unit. The makeup water source is a high silica well water. Permitting considerations dictated that the plant be designed for ZLD. Alternative technologies were investigated to determine the most cost effective ZLD design. Following extensive evaluation, the HERO process, in conjunction with a brine disposal pond, was selected as the least cost alternative.

The selection of the HERO process represented the first full-scale application of the technology for preconcentration of cooling tower blowdown. Considerations that led to the selection included the following:

- The HERO process was the lowest cost technology evaluated.[5]
- A pilot scale installation had previously demonstrated treatment of high silica cooling tower blowdown.[1]
- The process was verified to be in successful operation treating high silica water supplies at several industrial high purity water treatment installations.
- Although the process was relatively new, it was made up of individual treatment steps that were being used successfully in various industrial applications.
- The disadvantages of conventional RO treatment were overcome by desirable features including non-scaling operation, resistance to biofouling, and reduced plugging tendency.
- Compatibility with anticipated cycling operation (frequent starts and stops) of the plant.
- Capability to achieve 90 percent or greater RO recovery.
- Shorter delivery time compared to evaporative processes.

- Lower electrical energy usage and lower operating cost than evaporative processes.

RO membrane life was recognized as a concern, but the risk was mitigated by the vendor's warranty and the significant life cycle cost savings potential.

DESIGN BASIS

Plant design was initiated before the well field was developed. Therefore, water analyses from test wells were assumed to be representative and were used to develop design basis water analyses. The circulating water chemical analysis was calculated from a comprehensive plant water mass balance study and an assumed 12 cycles of concentration in the cooling tower. Design wastewater treatment system capacity is approximately 300 gpm.

The design water analysis for the well water and the feed stream to the ZLD treatment system is shown below.

Constituent	**Well Water**	**Circulating Water**
Calcium, mg/l as $CaCO_3$	50	840
Magnesium, mg/l as $CaCO_3$	55	120
Sodium, mg/l as $CaCO_3$	128	1,536
Potassium, mg/l as $CaCO_3$	7	84
M. Alkalinity, mg/l as $CaCO_3$	160	200
Sulfate, mg/l as $CaCO_3$	30	360
Chloride, mg/l as $CaCO_3$	68	1,920
Nitrate, mg/l as $CaCO_3$	3	36
Silica, mg/l as SiO_2	43	120
pH	7.8	7.84
TDS, mg/l	417	3,255

LIME-SODA ASH SOFTENING

The wastewater treatment system at the Griffith Energy facility has been in operation for several months. The actual water analysis encountered is somewhat different from the assumed design analysis because the well water varied from the design analysis and continuous full load plant operation was not possible during the startup and commissioning phase of the project. The characteristics of the water are as indicated below.

Softening with soda ash alone was attempted initially. Difficulty was experienced with establishing a sludge inventory in the softener. Several factors are believed to have contributed to this condition.

- The plant experienced frequent starts and stops during startup operations. As a result, the circulating water scale inhibitor dosage could not be accurately controlled. Excess polymer in the water tends to interfere with good solids separation.
- The ratio of magnesium to total hardness in the water supply was higher than anticipated. Magnesium hydroxide precipitate is more difficult to settle than calcium carbonate.
- Operation of the solids contact clarifier was not optimized with respect to coagulant and polyelectrolyte dosages.

Lime slurry feed was initiated to supplement soda ash feed to the reaction zone of the solids contact clarifier. An immediate improvement in operation was observed. The improvement is attributed to an increase in the relative amount of calcium carbonate precipitate.

Typical performance of the lime–soda ash softener is shown below. Data presented for the outlet are prior to filtration and acid injection for stability control.

Constituent	**Softener Inlet**	**Softener Outlet**
Calcium, mg/l as $CaCO_3$	398	---
Magnesium, mg/l as $CaCO_3$	132	---
Total Hardness, mg/l as $CaCO_3$	530	101
M. Alk., mg/l as $CaCO_3$	54	116
Silica, mg/l as SiO_2	110	~50
Turbidity, Ntu	---	~7

Silica reduction in the softener is a function of magnesium removal and water temperature. Preliminary operating data indicate that reduction will be in the range of 1 mg/l SiO_2 for every 2 to 3 mg/l of magnesium hardness removal at approximately 90 F operating temperature.

WEAK ACID CATION EXCHANGE

System design includes two weak acid cation exchangers arranged for alternating series operation. The intent of this design was to always assure very low hardness in the water going to the RO by operating the two WACs in series. Initial operation indicates that series operation of the WACs is unnecessary because hardness leakage from the WAC exchangers is consistently less than 0.1 mg/l throughout the service run. Typical performance of a single WAC exchanger is shown below.

Constituent	WAC Inlet	WAC Outlet
Total Hardness, mg/l as $CaCO_3$	120	<0.1
Alkalinity, mg/l as $CaCO_3$	200	Near "0"
Silica, mg/l as SiO_2	50	50
pH	9.7	~4.2

Regeneration of the WAC exchangers is performed with 0.7 percent sulfuric acid solution. The quantity of water produced per regeneration has exceeded design projections.

RO OPERATION

Three 50 percent capacity lines of RO are provided for redundancy. Each RO is a two-stage, single pass, 3 X 1 array designed to operate at an average flux rate of approximately 20 gpm/sf/d. Typical performance of the units operating in the HERO mode is presented below.

Parameter	RO Inlet	RO Reject	RO Permeate
Hardness, mg/l as $CaCO_3$	<0.1	0.86	N. R.
SiO_2, mg/l as SiO_2	~50	~325	0.18
Conductivity, uS/cm	---	---	~160
Flow, gpm	147	N. R.	134
pH	10.3	10.4	N/A

The data available to date are representative of initial system operation. Important performance observations include the following:

- The recovery from the RO is typically 90 percent or greater.
- WAC effluent hardness below 0.1 mg/l is sufficiently low to prevent membrane scaling.
- Silica rejection exceeds 99.5 percent.
- Membranes have not experienced biofouling or plugging and have not been taken off line for cleaning after approximately three months of intermittent operation.

System reliability is reported to be excellent to date. One instance of scaling of the RO membranes resulted from inadvertent "on-line regeneration" of a WAC exchanger when acid was overfed at the clarifier outlet. The membrane was cleaned on-line using a preplanned procedure involving temporarily shutting off caustic feed to the RO, stopping the degasifier blower, and reducing the recovery rate. The unit was returned to normal operation within approximately one hour when the differential pressure returned to normal.

CONCLUSIONS

Initial operation of the High Efficiency Reverse Osmosis system at the Griffith Energy facility has demonstrated the capability of the process to reduce the volume of cooling tower blowdown by 90 percent or greater. No major deficiencies were disclosed that would preclude consideration of the process for future application for treatment of cooling tower blowdown. Observations that warrant consideration in the design of future installations include the following:

- Pretreatment ahead of the RO is critical to the design and successful operation of the HERO process. In particular, the lime softening and filter operation warrants careful design and operation. Solids contact clarifiers are sensitive to changes in water temperature, rate of flow, and overfeed of circulating water inhibitors. A highly automated system design and knowledgeable operations personnel are recommended.
- Weak acid cation exchangers provide satisfactory hardness removal coupled with high removal efficiency. Series operation is unnecessary to achieve the very low hardness required to prevent scaling of membranes. However, a standby WAC exchanger is needed to allow continuous operation during regeneration outages.
- The system has operated intermittently for several months without being taken off line for cleaning. However, off-line cleaning capability is recommended for emergencies and possible long-term membrane plugging.

Performance to date of this first full-scale application of the HERO process for treatment of cooling tower blowdown demonstrates the potential for expanded use of membranes for wastewater treatment applications. The process effectively extends the recovery limits and dramatically improves system reliability compared to conventional RO. Recoveries on the order of 90 percent offer opportunities for economical volume reduction for treatment and reuse and ZLD applications. Further experience and development is needed to establish the limitations of the technology.

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