Silica Reduction in Cooling Tower Blow-down Reuse Using Low Cost Ceramic Ultrafiltration Membranes

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Abstract
In an effort to conserve water, a major power plant in the southwest USA built a cooling tower water blowdown (CTBD) treatment system consisting of electrocoagulation (EC), ultrafiltration (UF), and reverse osmosis (RO). Although the system reached the water quality treatment goals adequately, the UF membranes only lasted 3 years and the EC was abandoned due to costs and maintenance issues. Without EC in service at present the silica is not being removed. This resulted in RO system recovery decline and shortened RO membrane life. Nanostone Water Inc. began a pilot plant trial with its segmented ceramic monolith membrane using magnesium chloride and sodium hydroxide as pre-treatment as an alternative to EC + Polymeric UF. In the pilot testing silica was removed by an average of 80%. The ceramic membrane flux held stably at 100-130 GFD (170-220 LMH) without the need of high rates of crossflow, and with conventional flux maintenance using backwashes and chemically enhanced backwashes. This treatment process was shown to be stable over several weeks of continuous operation, and the membranes were thereafter fully recovered by conventional chemical clean-in-place. This presentation will describe the pilot testing results used and the conceptual design and operating cost estimates of the full-scale upgrade of the CTBD treatment plant, which benefits from the numerous advantages of the novel ceramic membrane used in the process.

Keywords
Blow-down, Ceramic, Cooling, Silica, Ultrafiltration

INTRODUCTION
Industrial companies require clean water for cooling, boiler makeup, and a variety of manufacturing processes. One of the biggest industrial users is cooling water for thermoelectric power generation. With continued water scarcity issues in various parts of the world, industrial companies are increasingly making the effort to reduce water footprint to mitigate risk. It is more common now for a power station to reuse treated municipal effluent water as makeup for cooling towers when access to the waste effluent is feasible. When reusing waste water from an outside source is not practical, many companies are now looking for ways to reduce and reuse water from internal sources. When considering areas to reuse water, cooling tower blow down (CTBD) often emerges as a target application given the large volumes of water used.

POWER PLANT CTBD REUSE CASE STUDY
In an effort to conserve water, a major power plant in the southwest USA built a CTBD water reuse treatment system consisting of: electrocoagulation (EC), ultrafiltration (UF), and reverse osmosis (RO). The makeup water to the cooling towers is a blend of primarily treated municipal effluent and some well water. The system is designed to treat up to 180 m³/hr (800 GPM) of CTBD water. In this case, the CTBD water contained total silica levels ranging from 80 to 120 mg/L which would limit the RO recovery rate if not substantially reduced. Several technical papers suggest that EC is an effective method to remove silica from CTBD streams and other water streams using both iron and alumina electrodes (Villegas, Zhaohui Liao). The sludge production from the EC process is generally less than chemical precipitation. In this case EC was assumed to be less maintenance intensive than a conventional chemical precipitation and clarification system. The downstream UF membrane selected was a polymeric submerged membrane plant designed to reduce turbidity from the EC process before feeding the RO system. Backwash water from the UF membrane is sent to an evaporation pond. The RO permeate water produced is returned to the cooling tower feed stream and the RO reject water is sent to the evaporation pond. The system as originally designed was expected to be highly automated and provide less operation intensity as compared to a conventional chemical.
Although the EC system reached the goal of silica reduction, the operation of the system overall proved to be more complex than expected. The EC plate replacement frequency was much higher than planned, and the process of exchanging the EC plates was very labor intensive. The annual operating cost impact of the EC system plate exchange exceeded $700,000 USD per year. The UF membranes downstream of the EC system also suffered from iron fouling and required chemical clean in place (CIP) every three (3) days during peak loads. The cleaning process required up to 8 hours of down time. During the cleaning cycles, all CTBD water was sent to the evaporation ponds directly. After only three (3) years of operation, the UF membranes required replacement at a cost of $900,000 USD. A detailed cost of operations analysis was conducted and is outlined below. All water costs, power, labor, chemicals, EC plate replacement, UF membrane replacement, and RO membrane replacement costs are considered. Cost inputs assume a theoretical 80% utilization factor and project an annual operating cost of just under $3M/yr for a 180 m3/hr (800 GPM) system.

Subsequent to the initial operating experience, the end user elected to make a significant change in operation of the reuse system and take the EC system out of service completely. This was an improvement in operating cost by removing the expense of EC plate replacement and reducing the CIP frequency on the polymeric UF membranes from every 3 days to every 30 days. However, eliminating the EC allowed significantly higher levels of dissolved silica to pass through the UF membrane and enter the RO feed stream. To compensate, the RO recovery rate was reduced from a design of 75% down to 50% in an effort to control silica scale in the RO membrane. This results in an additional 82 million gallons of source water consumed annually. The RO CIP frequency also significant increased from every 45 days to every 14 days to compensate for higher levels of silica in the feed water. The increased CIP frequency also reduced RO membrane life from 3 years to 1 year.
Although operating expenses were reduced, the amount of CTBD recovered was substantially lower than the design specification. The power plant operators were able to make adjustments by sending more water to the evaporation pond and to an irrigation off take to compensate. Long term, the system performance is not considered practical and other alternatives were explored.

CERAMIC PILOT SYSTEM

The end user selected Nanostone Water to conduct a pilot study using a patent pending ceramic UF membrane, applied with a chemical precipitation process to reduce silica from the CTBD stream. The ceramic membrane (CM) tested is manufactured using an innovative process, where individual ceramic segments are potted together forming the monolith structure. This production method significantly reduces the production costs as compared to other ceramic membranes. The CM monolith structure is housed in a fiberglass reinforced plastic (FRP) vessel rated for 150 PSI (10 BAR) with 20m2 (215 ft2) of active surface area with a nominal particle retention rate of 30nm (0.03 micron).

The pilot system was deployed in a 40-foot containerized system with two independent process trains. Each train is designed to operate with either a smaller test membrane with 3m2 (32ft2) housed in a 100mm (4-inch) diameter PVC vessel or with the full scale CM module. The pilot system design allows a single small test module to process flows as little as 400 L/hr (1.8 GPM) to as much as 16 m³/hr (70 GPM) with two trains of the full scale module in operation. The goals of the pilot study were as follows:

1. Operate in direct feed coagulation / precipitation without conventional lime softener.
2. Determine chemistry needed to reduce silica from up to 120mg/L to < 25mg/L.
3. Reduce turbidity to < 0.1 NTU for RO feed.
4. Optimize design and prove stability of new technology.

Given the end user’s negative experience with their attempt to utilize EC technology, a thorough, long term pilot plan was developed to evaluate the ceramic membrane technology.

RESULTS

The first phase of the pilot study applied a direct feed of coagulant to work through process operating parameters for stable operation using the small test CM module. During this phase, the silica values were measured in and out of the system to acquire base line performance. The coagulant used for the first 60 hours of testing was alum (aluminum sulfate, Al₂(SO₄)₃·14.5H₂O) at a dosage of 9 mg/L as Al³⁺. The performance was stable. This was not expected to provide any significant silica reduction and results confirmed < 5% reduction rate, but the operation of the CM module proved to be stable. Due to the potential for fouling on the downstream RO with alum, the coagulant was changed to ferric chloride (FeCl₃). Jar testing performed showed a FeCl₃ dosage of approximately 35 mg/L as Fe⁺³ was required to get a floc to form without elevated pH. The various cooling tower treatment chemicals typically used include antiscalants and bio dispersants, which are believed to be the cause of requiring the high dosage rate of FeCl₃. In the figure below, the net driving pressure (NDP) of the CM UF membrane is plotted over time. During this phase of the pilot test, a variety of operating conditions were established including a filtration flux of 170 L/hr per m² of membrane (LMH) or 100 Gallons per day per ft² of membrane (GFD) in the first 200 hours of operation to 220 LMH or 130 GFD after
200 hours. A mild crossflow recirculation scheme was used for the first 300 hours of data at just 50% of filtration flow and dead end filtration mode was used after 300 hours.

**Figure 4:** Phase 1 Pilot Test Results with Direct Coagulant Feed at Various Operating Conditions

The hydraulic cleaning method used throughout the majority of phase one testing was a fast step change high pressure and high flow backwash method with a vessel partially filled with UF permeate water and compressed air charged to approximately 5 BAR (70 PSI). This backwash method can also be accomplished with a backwash pump that ramps up to pressure against a closed valve before being released to the permeate side of the membrane. Various durations of filtration and backwash times were studied throughout the test period. The established operating conditions were 50 min filtration cycles, a 1 second high pressure backwash, and a 46 second feed water flush at normal filtration flow. The estimated recovery of the plant in this design is 97%. In the final 24 hours of phase 1 testing, the hydraulic cleaning method was changed to using a standard pump for backwashing. In this test, the filtration cycles were the same 50 minute duration followed by a backwash flow rate set for approximately 4 times the filtration rate for a 4 second duration. The cycle concluded with a 46 second feed flush at the same flow as filtration flow to achieve the same recovery rate of 97%. This test also showed a stable operation for the 24 hour period.

At approximately 150 hours of operation, the coagulant feed was lost for a period of time estimated at several hours before being restored. After the event, the NDP slowly climbed from a level of 0.3 BAR (4 PSI) to 1.4 BAR (20 PSI). At approximately 180 hours (7 days), a routine chemical clean in place (CIP) using sodium hypochlorite at 300 mg/L with NaOH to raise the pH to 12 followed by a hydrochloric acid CIP to pH 2 was applied. In both cycles the temperature was elevated to 40 C (104 F). The CIP cycle reduced the NDP near to the starting point. Another CIP was performed after an additional 180 hours (7 days) returning the NDP to the same levels observed at the beginning of the pilot testing. Representative water quality results during the first phase of testing are shown in the table below:

**Table 1.** Phase 1 Pilot Test Water Quality Results with Direct Coagulant Feed

<table>
<thead>
<tr>
<th>Total Silica Feed</th>
<th>Total Silica UF Permeate</th>
<th>NTU Raw Feed</th>
<th>NTU UF Feed After Coagulation</th>
<th>NTU UF Perm</th>
</tr>
</thead>
<tbody>
<tr>
<td>80-120mg/L</td>
<td>70-110 mg/L</td>
<td>1.31</td>
<td>50 NTU</td>
<td>0.03-0.07</td>
</tr>
</tbody>
</table>

The first phase of the pilot test concluded with a demonstration of the full scale CM module to verify the process design developed with the small test modules correlated to the results of the full scale module. The flux of the small test modules ranged between 170-220 LMH (100-130GFD). A flux of 200 LMH (118GFD) was selected to test the full scale module. The test conditions for the full scale module were 50 minute filtration cycles, 1 second high pressure backwash, and 46 second feed flush. The FeCl3 dosage rate was the same as with the small test modules. Results from the full scale module are plotted in the figure below. The NDP in this profile showed stable results similar to the small test module. At the 72 hour mark, the backwash sequence was changed to incorporate a
standard pump for backwashing at lower pressure. In this test, the filtration cycles were kept at the 50 minute duration followed by a backwash flow rate set at 4 times the filtration rate for a 4 second duration. The cycle concluded with a 46 second feed flush at the filtration flow to achieve the same recovery rate of 97%. This test also showed a stable operation for a 48 hour period.

**Figure 5:** Phase 1 Pilot Test Results with Direct Coagulant Feed With Full Scale CM Module

With the CM UF membrane demonstrating stable operation on a challenging CTBD water with direct coagulation feed, the focus shifted to establishing the chemistry required to meet the silica goals of < 25 mg/L in the UF permeate water. Jar testing experiments showed that ferric and alum without elevated pH did little to reduce the silica content. Elevating the pH to approximately 11 with the FeCl3 showed improved results but failed to reach the silica reduction goal established by the end user. Magnesium chloride (MgCl2) with elevated pH to 11 showed the best results with an 80% reduction in silica which met the quality goal of < 25 mg/L silica.

**Table 2. Phase 1 Pilot Test Water Quality Results with Direct Coagulant Feed**

<table>
<thead>
<tr>
<th>Coagulant Used</th>
<th>Best Dosage</th>
<th>pH</th>
<th>Silica Before / After</th>
<th>% Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum or Ferric Chloride</td>
<td>9 mg/L as Al+++</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferric Chloride + NaOH</td>
<td>35 mg/L as Fe+++</td>
<td>6.5</td>
<td>100/95</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>Magnesium Chloride + NaOH</td>
<td>35 mg/L as Fe+++</td>
<td>9-11</td>
<td>80-90/40-50</td>
<td>35-55%</td>
</tr>
</tbody>
</table>

With the elevated pH, a contact time of approximately 20 minutes is required for the CaCO3 to complete its reaction and stabilize. In order to reach this 20 minutes of contact time, the CM pilot was equipped with extra lengths of hose and a 55 gallon barrel shown in the figure below. The MgCl2 and NaOH injection point was at the suction of the membrane feed pump where it then travelled through the hose, the 55 gallon barrel, and then back to the inlet of the CM test module. The system started operation with direct feed of the precipitation chemicals, through the contacting vessels, and back into the CM test module without removal of sludge. The operating parameters for the CM test module were set at dead end filtration at a flux of 170 LMH (100 GFD), 20 minute filtration cycles, high pressure backwash for 5 second duration, followed by a feed flush at 100% of service flow for 46 seconds giving an estimated recovery rate of 92%. The performance of the CM module was stable through the test. The turbidity of the feed water after chemical precipitation was significantly higher as compared to the FeCl3 only operation and the NDP had a faster increase over time as expected. The system was set in operation continuously for 38 hours where a CIP cycle was performed returning the pressure to the starting original point. A second CIP conducted at 80 hours also returned the NDP to starting point. The system was then operated with an acid chemically enhanced backwash (CEB) every 24 which produced a more stable operation. The CEB process is a shortened cleaning cycle...
where HCl, was injected during a backwash cycle to reduce the pH and clean the membrane. The membrane then soaked for 15 minutes in the acidic solution and a second backwash flushed the chemical out of the system before returning to service.

Figure 6: Phase 2 Pilot Test Results with Direct Feed of Silica Precipitation Chemicals

The water quality measurements taken during this phase of the test showed excellent results in turbidity removal, silica reduction, and hardness reduction of approximately 50%. A total suspended solids (TSS) measurement performed on the UF feed water after chemical precipitation showed values in the range of 500 to 600 mg/L.

Table 3. Water Quality Results during Silica Precipitation Operation

<table>
<thead>
<tr>
<th>Turbidity Raw Water</th>
<th>Turbidity UF Feed (no settling)</th>
<th>Turbidity UF Permeate</th>
<th>Silt Density Index (15 min) UF Permeate</th>
<th>Hardness UF Feed</th>
<th>Hardness UF Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6 to 2.0 NTU</td>
<td>270–450 NTU</td>
<td>0.03 – 0.09 NTU</td>
<td>2.1</td>
<td>648 mg/L</td>
<td>335 mg/L</td>
</tr>
</tbody>
</table>

Figure 7: Silica Feed and UF Permeate Measurements During Operation With Chemical Precipitation Process.

As discussed earlier, one of the goals of the pilot was to operate the silica precipitation process without a settling step upstream of the ceramic membrane. The performance of the CM module was stable and measurements confirm the pilot trial was meeting the goals of turbidity and silica reduction. However, the operation of the pilot was difficult due to scale build up at the pump injection point. The operation the system had to be shut down several times so that the feed pump and hoses could be cleaned with acid. This same problem of scale build up in the feed pipe and pump would likely be present in a full size system and so the pilot plant was modified such that the chemicals injected into a mixing tank to provide sufficient residence time for a full reaction prior to being applied to the pilot membrane. With a mix tank providing at least 20 minutes of contact time, a sludge removal step was
added just after the mixing tank. A full scale system design will ultimately have the backwash water from the CM membrane returned to the beginning of the mix tank with sludge removal added subsequent to the mix tank. Since the CM membrane already demonstrated its ability to handle high levels of TSS (600mg/L) during the direct feed phase of the pilot, the confidence in the ability of the membrane to perform after the settling step was established.

With a mix tank and sludge removal step installed upstream of the pilot system, the membrane was again put into service. Initially, the performance was stable as expected. The operating parameters setup were 170 LMH (100 GFD) operating flux with essentially dead end filtration mode and a 20% concentrate bleed going back to the mix tank to aid in seeding the precipitation reaction. Filtration cycles were 20 minutes with a backwash scheme using a pump at 4-5 times the filtration flow for a 12 second duration followed by a feed flush of 46 seconds at 100% of filtration flow. As practiced earlier, the acid CEB cleaning steps were performed at 24 hour intervals. For the first 48 hours the system was performing well but a new challenge surfaced. During operation there were several sudden increases in NDP on the membrane suggesting high TSS loading. Investigations revealed that sludge was building up in the feed tanks of the pilot system downstream of the mix tank and sludge removal point. When the sludge level was high enough in the feed tank, large amounts were released into the pump suction and CM module causing heavy fouling. During this period between 200 and 400 hours of operation, several adjustments were attempted with the sludge blowdown system. To reverse the occurrence of extreme fouling, aggressive cleanings to pH 1 proved quite effective. This demonstrates that the ceramic membrane can completely recover from catastrophic fouling conditions that would likely render polymeric membranes ineffective. However, the system operation was not stable due to the sludge handling aspects of the pilot.

**Figure 8**: Picture of Ceramic Test Module after Sludge Breakthrough and after a CIP

A solution was found to minimize sludge build-up and the unpredictable breakthrough of large volumes of sludge into the system. At this point, the operation was stabilized with acid CEB’s performed every 24 hours. The backwash operation was again a standard pump running at 4 times the filtration flow with backwash frequencies at 20 minutes and backwash duration at 10 seconds. The feed flush at 100% of filtration flow for 46 seconds was also utilized.

**Figure 9**: Phase 2 Pilot Test Results with Mixing and Settling Silica Precipitation Chemicals after Adjustment of Sludge Handling
With the sludge breakthrough now solved, the system stability was much improved, but the pressure increase between CEB cycles was higher than desired. After close examination of the backwash flow profile, it appeared that the slower ramp up of a standard backwash pump was not as effective as a fast step change in pressure and flow for backwash. For a better comparison of the two methods, a fast step change backwash test condition was conducted but with lower pressures to effect a flow rate of 4 times filtration flow point. The pressure required to reach the 4 times filtration flow was only 0.8-1.0 BAR (12-15 PSI) as compared to previous fast step change backwashes with 5 BAR (72 PSI) used in previous high pressure backwash methods. The frequency and duration of backwash were kept the same as with the original method. The results were dramatically improved indicating a faster step change of backwash water pressure and flow was more effective than a slow increase in pressure and flow. The fast step change of backwash water can be delivered with a compressed air tank or by using a pump ramping up to pressure against a closed valve prior to activating the valve. The CEB cycle was kept at 24 hour period for consistency, however the data shows little pressure increase over the 24 hour period. Consequently, it is expected that the acid CEB frequency could be extended beyond 24 hours in a full scale system.

**Figure 10:** Phase 2 Pilot Test Results with Mixing and Settling Silica Precipitation Chemicals Using Fast Step Change Backwash

![Graph showing backwash results](image)

In summary, the Nanostone ceramic UF pilot with silica precipitation process met the goals set by the end user:

1. Operate in direct feed coagulation / precipitation without a conventional lime softener.
   - Direct feed of the precipitation chemistry was successfully demonstrated but deemed not to be practical with the potential for scale formation at the injection point. A mixing tank and settling step upstream of the ceramic UF membrane proved more practical for the full scale operation.
2. Reduce silica from up to 120 mg/L in the feed to < 25 mg/L in the UF permeate.
   - Multiple tests proved this goal was achieved.
3. Reduce the turbidity in the feed water to < 0.1 NTU for RO feed.
   - In all turbidity samples take the UF permeate was always < 0.1 NTU.
   - The ceramic membrane proved it could operate in direct feed with 600 mg/L of TSS in the feed. With a setting and hydraulic cleaning system optimized the process achieved stable operation.
   - Even with extreme upsets of sludge feeding directly to the membrane, with aggressive chemical cleaning to pH 1 the ceramic membrane fully recovered.
PROPOSED FULL SCALE SYSTEM
With the successful demonstration of the ceramic UF technology employing the silica precipitation chemistry, a full scale conceptual design outline and operating cost analysis was developed to compare to the existing system. The proposed system design includes a reaction tank to provide 20 minutes of contact time to allow the chemical precipitation process to fully react. A rough settling step is included to remove sludge from the system providing a ceramic UF feed quality at TSS levels of ~ 100 mg/L. This design allows for a much smaller, less expensive, and more simplified settling step as compared to a conventional settling system designed to produce ~ 10 NTU turbidity. There will be a small amount of concentrate continually recycled to the front of the reaction tank to aid in seeding the chemical precipitation process. Backwash water from the ceramic UF will also be returned to the front of the reaction tank. With this design, there is a single point of sludge removal from the system at the base of the reaction tank. The ceramic UF backwash design will utilize a conventional pump but will have a valve in place such that the backwash pump can ramp up to a set pressure before the fast acting valve is opened. With this design the fast step change in backwash flow and pressure will provide a more effective hydraulic cleaning as compared to a pump slowly ramping up to speed as demonstrated in the pilot study.

Figure 11: Nanostone Water Proposed System Design with Silica Precipitation and Ceramic Ultrafiltration Membrane System

Based on the proposed design described above a cost of operation analysis was conducted to compare to the operating cost of the system originally installed. The total operating cost of the proposed system is projected to be $1.9M/yr, a savings of $1M/yr or approximately 34%. The cost of the silica precipitation chemicals in the analysis is roughly the same expense as the EC plate exchanges. However, the labor cost and system down time is significantly less. The main savings are derived from the retrofit in the UF system to ceramic membranes. A substantial savings of over $500,000 per year is realized by improving the 3 day CIP cycles of the polymeric UF membrane with a more efficient acid CEB for the ceramic UF membranes. Another significant savings relates to the longer life cycle of the ceramic membranes and eliminating costs involved with polymeric UF membrane replacement. The polymeric UF membranes were replaced at 3 years versus the expected life of 10 years for the ceramic UF. This represents a savings of over $250,000 per year. Additional savings resulting from lower power consumption are also expected. The polymeric UF membrane system currently used consumes an estimated $140,000 per year more in electricity primarily due to an aeration system which is not required with the ceramic UF membranes.
SUMMARY AND OUTLOOK
Treating CTBD water has historically been a difficult application for polymeric UF membranes. This case study using EC and polymeric UF exemplifies the challenge. However, given the robustness of the ceramic membrane demonstrated in this pilot study, successful operation employing direct coagulation and silica precipitation proved highly effective. With the more cost competitive segmented ceramic monolith design, treating CTBD is much more feasible. This same chemical precipitation process followed by a ceramic UF system can be applied generally to any “Phys/Chem” system such as lime softening. Using a ceramic membrane downstream of the process gives the operation much more freedom to operate without tightly controlling the turbidity of the effluent stream. And the inherent robustness of ceramics eliminates any concern of small precipitation particles or “pin floc” traveling downstream to the RO. This allows a significantly smaller footprint, a less costly settling system, lower chemical costs, elimination of frequent membrane replacement, and in general, a higher level of reliability and effectiveness.

REFERENCES