Waste Water Treatment with Catalytic Chlorine Dioxide on RO Membranes in an Ethanol Plant

CLO2IX®

The Issue: A primary focus of water treatment today is facilities that turn corn into ethanol, which can be used as a renewable alternative fuel source, reducing greenhouse gas emissions. As with many industrial facilities, many ethanol facilities use city recycled waste water for cooling tower and process water instead of tap or well water. This approach is environmentally-friendly, but the water must go through additional purification steps before it can be used in the facilities.

Anderson Chemical Company treats one such facility. Under Anderson supervision, the additional treatment required before the water could be used began with clarification and primary oxidation and disinfection. The recycled waste water was piped to this facility by the city and held in large settling ponds until it was ready to be used. As needed, the water traveled from the settling ponds to large tanks (clarifiers) which stirred the water to remove any solids. At this point, sodium hypochlorite was added to oxidize organic compounds and disinfect bacteria in the water. From the clarifiers, the water was chlorinated further and sent to ultrafiltration (UF) prefilters and then UF membranes. As part of the facility's operation, the UF membranes were automatically backwashed to keep them clean. The final step in the treatment process was for the water to be further purified by reverse osmosis (RO) membranes. These RO membranes, however, could not tolerate residual chlorine from the UF membranes, so sodium bisulfite, which neutralizes the residual chlorine, was added before the RO membranes. This step rendered the sodium hypochlorite ineffective. Once the water had passed through the RO membranes, it was ready to be used as process water and in the cooling towers. Periodically, in addition to continuous chemical treatment, both the UF and RO membranes had to be cleaned in place (CIP) for them to maintain their proper flux rates.

Over the first five years of Anderson supervision, the region suffered a drought which caused the ponds to turn over more frequently, resulting in record-setting water turbidity levels. Typical readings for the area were 40-50 NTU, but the levels have risen to 180-210 NTU. Turbidity is made up of a combination of colloidal sediment and bacteria. The resulting increase in turbidity began to overwhelm the water treatment system, causing the time between UF backwash and membrane cleanings to become shorter. More sodium hypochlorite was added, the pump pressures on the UF and RO membranes were increased, and the UF and RO membranes were cleaned more frequently in an attempt to overcome the turbidity. UF and RO membrane life decreased due to the increased number of cleaning cycles. Costs increased rapidly, and the possibility of downtime became a concern, because any upset or downtime in the supply of water to the facility could potentially mean the loss of millions of dollars in lost product for the plant.

The system was designed to produce approximately 350 GPM of purified water. The transmembrane pressure (TMP)

Case Study
Anderson Chemical Company
Founded 1911
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Fig 1: New RO Membrane Performance

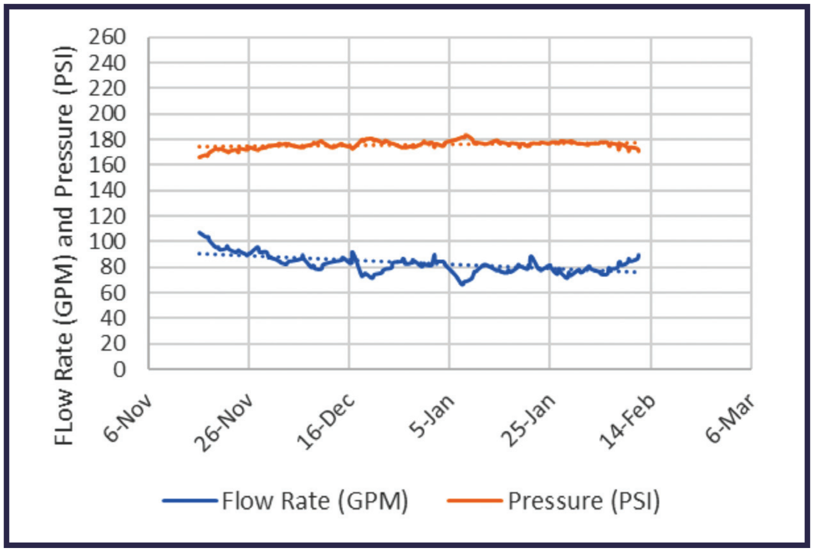
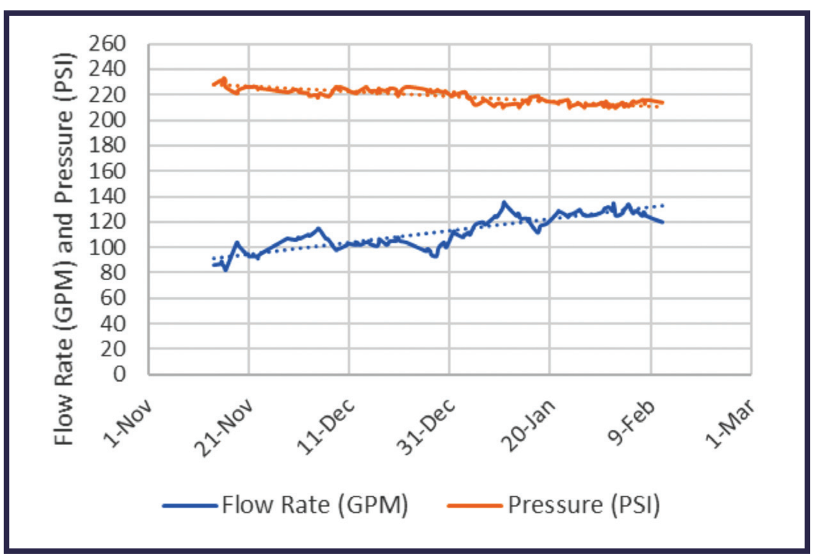


Fig 2: Year Old RO Membrane with CLO2IX® Chlorine Dioxide



triggers for membrane cleaning were 3 PSI for the UF membranes and 55 PSI for the RO membranes. When applying the TMP requirements for cleaning, it was found that the UF membranes were being cleaned every 3 days, and the RO membranes were being cleaned every 10 days on average. In addition, the UF membranes were being backwashed approximately every 4,500 gallons of processed water.

Further, it was observed that when the UF prefilters were removed from their housings, they were slimy, indicating the presence of a biofilm, even with the additional sodium hypochlorite. This observation was key. It was then known that biofilm existed in the system downstream of the two sodium hypochlorite injection points. The increased turbidity was not the only problem. The problem was twofold. First, biofilm was causing increased TMP throughout the system resulting in shorter cleaning cycles. This happens in all membrane systems but especially in RO membrane systems, because the residual sodium hypochlorite introduced into a typical treatment train to reduce microbiological fouling must be removed before it reaches the RO membranes, because the RO membranes are much more susceptible to oxidation from the sodium hypochlorite. When the sodium hypochlorite is removed before the RO system, biofilm is the result. In this case, however, the biofilm was not the only problem. The colloidal matter, sediment and bacteria in the incoming water, was sticking in the biofilm forming a layer of slimy dirt and bacteria on the UF and RO membranes. The addition of colloidal matter to the biofilm made the TMP increase much more rapidly than it would have if only the biofilm had been present or if only the colloidal matter had been present. Figure 1 is a graphical representation of the system operation after the sodium hypochlorite levels were increased and the RO membranes were replaced. As is shown on the graph, even with increased sodium hypochlorite dosage and new RO membranes, the increased pump pressure could not overcome the decrease in RO flow rate. During this time, the facility was spending $24,000/month on chemicals and membranes, membrane cleanings, and water costs had increased dramatically.

The increased sodium hypochlorite levels and increased pump rates ultimately failed to solve the problem. The only solution was to attack the biofilm straight on, and the best way to attack biofilm is with the best biofilm cleaner, chlorine dioxide. Unfortunately, not all chlorine dioxide would work in this application. In order to attack the biofilm within the RO membranes, the chlorine dioxide had to be free of chlorine and ozone, which limited the options. Fortunately, Anderson was familiar with CLO_2IX® generators and knew that the Catalytic Chlorine Dioxide produced by them was safe and effective for the entire water treatment system.

The Solution:

Anderson worked with Dripping Wet Water, Inc. to find the best CLO_2IX® generator for this application. The first parameter they considered was the elimination of downtime on an ongoing basis. The second parameter considered was the desired Catalytic Chlorine Dioxide residual at various points in the system train. The third parameter considered was at which points in the train would be best to dose the Catalytic Chlorine Dioxide. And the final parameter considered was how to clean up the system so that the ongoing treatment protocol would be effective.

To eliminate downtime during regular operation, Anderson decided to install two smaller generators since having two generators onsite would ensure that Catalytic Chlorine Dioxide would continue to be available if one of the generators were down for maintenance. Anderson also determined that a residual Catalytic Chlorine Dioxide level of 0.1 mg/l in the permeate and reject of the RO system would ensure that the biofilm had been removed, and the system was clean. In order to achieve the 0.1 mg/l Catalytic Chlorine Dioxide level in the permeate and reject of the RO system, it was decided to continue to dose at the same points in the treatment train as the prior sodium hypochlorite treatment: before the clarifiers and before the UF prefilters. And finally, it was decided to clean the system slowly, which meant that a low dose of Catalytic Chlorine Dioxide would be added sequentially at the chosen dosing points, beginning with the point ahead of the clarifiers and dosing until a residual was found after the clarifiers and continuing down the train until the desired 0.1 mg/l residual was found in the RO permeate and reject. RO membrane cleanings would also continue so that as the biofilm was attacked and loosened from the membrane surface, the colloidal layer stuck to it could be removed without contaminating the other parts of the water treatment system.

The initial cleaning phase took approximately two months. At first, the RO membrane cleaning showed little improvement in either flow rate or pressure. Remember, the system was very dirty, and the choice was to clean it slowly. By the third cleaning, brown liquid began to come out of the RO membranes, and by the fifth cleaning, the membranes and system were clean.

After a few months of treatment with the Catalytic Chlorine Dioxide generators, the desired 0.1 mg/l chlorine dioxide residual was consistently maintained in the RO permeate and reject. The UF membranes were cleaned every 4 days instead of every 3, and the RO membranes were cleaned approximately every 60 days instead of every 10 days. In addition, the throughput before backwash on the UF membranes had increased from 4,500 gallons to 7,000 gallons on average. Figure 2 is a graphical representation of the system operation after the water treatment system had been cleaned and a steady state was achieved with Catalytic Chlorine Dioxide. The membranes were a year old, but they were maintaining the same percent rejection as new RO membranes. As is shown on the graph, the pump pressure is trending down as the flow rate is trending up, demonstrating the continuous biofilm cleaning performed by the Catalytic Chlorine Dioxide. A financial analysis of the new treatment protocol was also performed. Under the new protocol using Catalytic Chlorine Dioxide, the ethanol plant was saving $30,000/month, or $360,000/year, on chemicals, membranes, membrane cleanings, and water.

Conclusion:

The success achieved using Catalytic Chlorine Dioxide surpassed Anderson's and the ethanol plant's expectations. Although they were limited by where they could obtain generators that produced chlorine dioxide free of ozone and chlorine, the CLO_2IX® generators proved themselves to be a cost-saving alternative to traditional water treatment methods as well as providing significant operational improvement.

As water becomes more costly and less available, more water will be recycled, and more companies will face the problems of this ethanol plant. Water treatment protocols will need to evolve to meet the changing feed water conditions. Fortunately, Catalytic Chlorine Dioxide is a solution available now that can be implemented immediately to meet the demands of the problems faced both today and tomorrow.