- 93% Sulfuric Acid
  = 5 % reduction = -1 truck/yr
- Net chemical reduction
  ~ 18 trucks/yr + 7 totes/yr
  - ~ 83,000 fewer gallons of chemical/yr

This is a major benefit to any plant that wishes to reduce operator time associated with off-loading trucks and improve safety by minimizing the risks associated with chemical handling. This also benefits ZLD plants by reducing the TDS loading going to the ZLD process (crystallizers/evaporators). This translated to lower chlorides and sulfates in the cooling water as shown in Figure 6.

In a separate study by Worley Parsons, commissioned by another Combined Cycle Gas Turbine (CCGT) grey water/ZLD plant in California, they concluded that a switch from bleach to ClO_2 would result in a 20% reduction of TDS in their cooling tower blowdown, which reduces the solids loading going to the ZLD process.

Significant improvement in yellow-metal corrosion rates While not important to this plant because they don't have any copper metallurgy in their system, this would be an important benefit for those plants that do. Figure 7 shows the dramatic reduction in copper corrosion rates during the ClO_2 trial compared to when bleach was fed both before and after the trial. As expected, mild steel corrosion rates were unaffected.

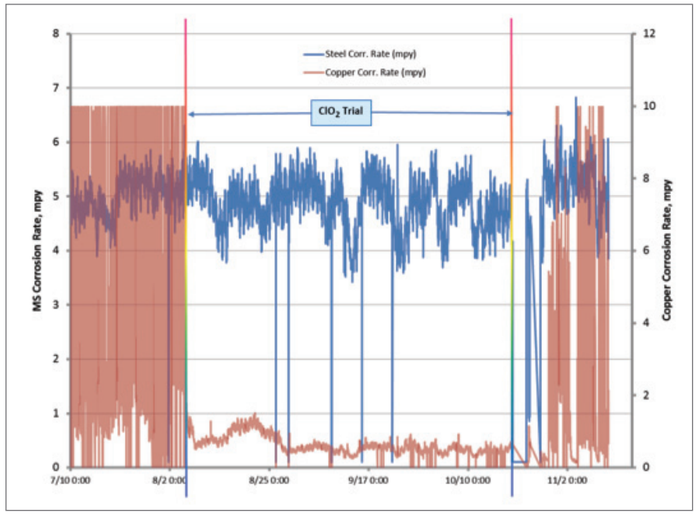

Figure 7 – *Cooling water corrosion rates for copper and mild steel*

THM	Measured byproduct (ppb) during Bleach Feed	Measured byproduct (ppb) during ClO_2 Feed
Bromodichloromethane	3.2	<0.5
Bromoform	0.7	<0.5
Chloroform	16.3	<0.5
Dibromochloromethane	2.0	<0.5

Byproduct	Percent reduction with ClO_2 treatment compared to bleach
AOX	47.4%
TOX	50%

Halogen byproducts

Below are the results of the analysis of the effluent water that was treated with ClO_2 during the trial compared to treatment with bleach before the trial. Measurements of byproducts were measured after two weeks of treatment at 0.2-0.4 ppm ClO_2 residual.

SUMMARY

The PURATE – Chlorine Dioxide program met all the plant's performance objectives, including their goal of reducing total cost of their existing biocide and oxidant treatment. The success of the trial was best summarized by the plant's Operations Manager who said *"Even if there is no cost reduction, the operational benefits are very positive for us."*

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Southern power plant sees significant safety and operational benefits from PURATE™ chlorine dioxide trial

NALCO Water
An Ecolab Company

CASE STUDY – POWER
CH-1851

BACKGROUND

A 750 MW gas fired combined cycle power plant in Texas wanted to test chlorine dioxide as a biocide to replace their biocide and oxidant treatment program using both bleach (sodium hypochlorite) and sodium permanganate. This power plant had been using bleach as a biocide for their raw make-up water upstream of their clarifier, again at their CWST (clarified water storage tank) and in their cooling tower. In addition to the bleach, the plant uses sodium permanganate to help oxidize and remove manganese in the clarifier during summer months when incoming manganese levels in their lake water source spiked above 0.5 ppm.

SITUATION

This plant had varying degrees of success properly removing the manganese each summer and did not like having to handle the permanganate totes associated with this treatment. Microbial control in the cooling system was considered excellent while they were able to feed bleach continuously, but they struggled with the reliability and maintenance of feeding bleach to three different locations within their plant. The amount of time operators spent repairing these bleach feed systems and the permanganate feed system was considered a problem as these man-hours could be more effectively used elsewhere in the plant.

SOLUTION

When NALCO Water met with plant manage-ment to outline the capabilities of its PURATE technology to generate chlorine dioxide on-site, they quickly agreed to run a 90-day trial to quantify its benefits as both an effective biocide and oxidant.

While chlorine dioxide (ClO_2) has been used for over eight decades in many industrial and drinking water applications. However, it wasn't until the development of the unique PURATE process, that ClO_2 became a viable, cost-effective biocide option in recirculating cooling towers to replace bleach or chlorine gas.

The PURATE process generates chlorine dioxide gas on-site using two precursors, one of which is sulfuric acid, instead of the more commonly known three precursor technology (bleach, hydrochloric acid and sodium chlorate). Since most power plants use sulfuric acid to control pH and alkalinity in their cooling towers, this means ClO_2 can be generated by simply mixing the PURATE chemical product with the sulfuric acid through a PURATE SVP Pure generator. The PURATE technology produces chlorine dioxide at a greater than 95% efficiency, which is significantly greater than the three precursor approach and more cost-effective.

For this trial, the plant opted to use the 78% sulfuric acid out of totes, which is the required concentration to ensure maximum ClO_2 generation efficiency, instead of diluting down their existing 93% sulfuric acid used for pH control in their tower. The trial started on August 7, 2014, using an MSA-M8-DS PURATE generator, which was designed to feed chlorine dioxide to three different applications points in the plant; 1) Pretreatment – upstream of the clarifier, 2) CWS (clarified water storage) tank, and 3) Cooling tower – circulating pump intake. This unit is also capable of using the 93% H_2SO_4 through a dilution module to create the required 78% strength for the proper reaction.

Figure 1 – *PURATE SVP Pure chlorine dioxide generator (SVP-Pure ClO_2 Generator (MSA)).*

Trial Objectives

The plant and NALCO Water agreed on the following objectives for the trial to replace both bleach and sodium permanganate in the raw water pretreatment system and the cooling tower:

1. Improved microbial control in the pretreatment system (clarifier, clarified water storage tank, and filters) while maintaining microbial control in the cooling tower.
2. Better or equal manganese precipitation in the clarifier without sodium permanganate.
3. Reduced operator exposure to bleach and sodium permanganate.
4. Reduced sulfate and chloride levels in the tower through lower sulfuric acid and bleach usage, which lowers the potential for stainless steel cracking and TDS (total dissolved solids) load on ZLD (zero liquid discharge) system.
5. Improved control of biofilms and fewer deposits on heat exchange surfaces.

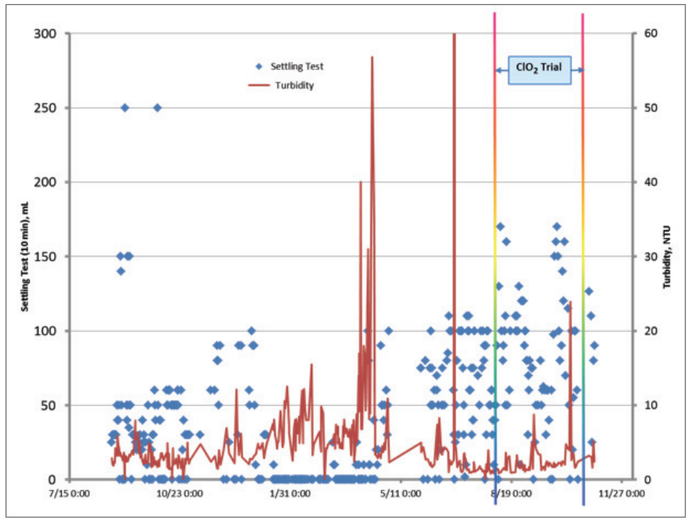

Figure 2 – *Clarifier settling and turbidity*

6. Reduced total cost of the microbial control program (biocides).
7. Reduced formation and discharge of chlorinated byproducts: THM and AOX.

RESULTS

The plant agreed that the above objectives were met during the 90-day trial. There were two major benefits the plant valued the most:

1. ***Increased clarifier performance*** Within a few days of switching from bleach and permanganate to ClO_2, operators saw a noticeable improvement in effluent clarity, a removal of algae from the weirs and better sludge quality. Figure 2 shows higher "settling test" volume, which resulted in better solids capture and lower outlet turbidity during the time ClO_2 was being fed.

Figures 3 and 4 show the effect ClO_2 had on removing algae growth from the clarifier's weirs.

This improvement in clarifier performance is attributed to chlorine dioxide not having the negative impact that bleach has on the functionality of the chemicals to coagulate and flocculate the solids.

Manganese was successfully oxidized and removed in the clarifier during the chlorine dioxide trial once the proper dosage was found (Figure 5). This demonstrated that ClO_2 could replace both the bleach and sodium permanganate treatment for removing manganese in this process.

2. ***Dramatic reduction in chemical usage*** Projected out over a year, the use of PURATE/ClO_2 would reduce the total amount of chemical brought on site as follows:
   - Current Treatment
     - Bleach = 90,962 gal/yr ~ 20 trucks/yr
     - Permanganate ~ 7 totes/yr
   - Treatment with PURATE/ClO_2
     - PURATE ~ 128,577 lbs = 11,279 gal ~ 3 trucks/yr
   - Permanganate = 0 totes/yr

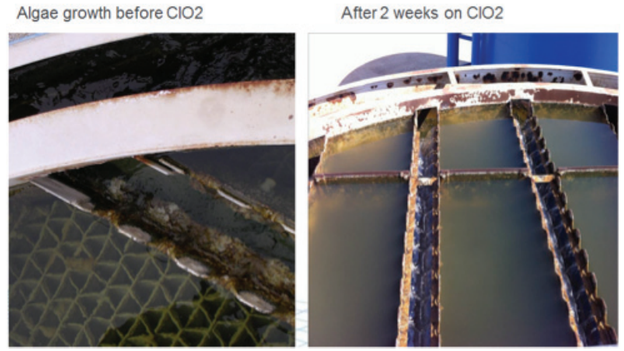

Figure 3 and 4 – *Clarifier weirs before and after switch to ClO_2*

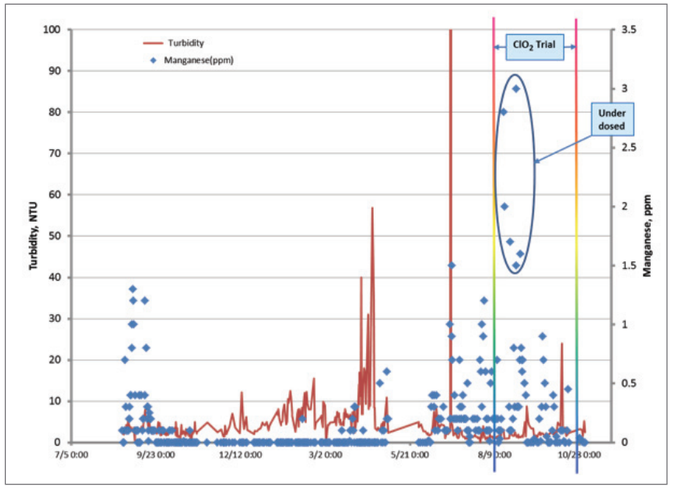

Figure 5 – *Clarifier turbidity and manganese effluent levels*

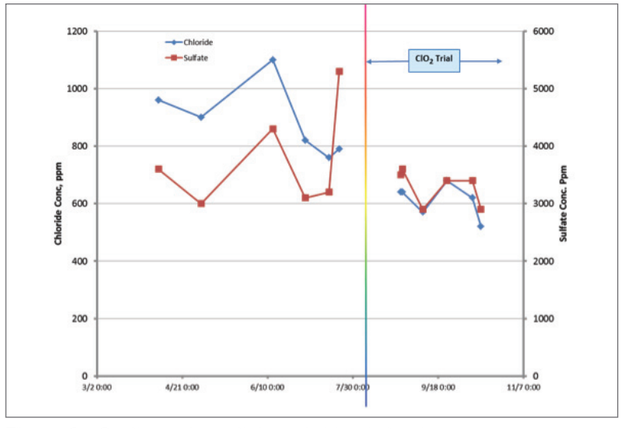

Figure 6 – *Cooling water sulfate and chloride levels*