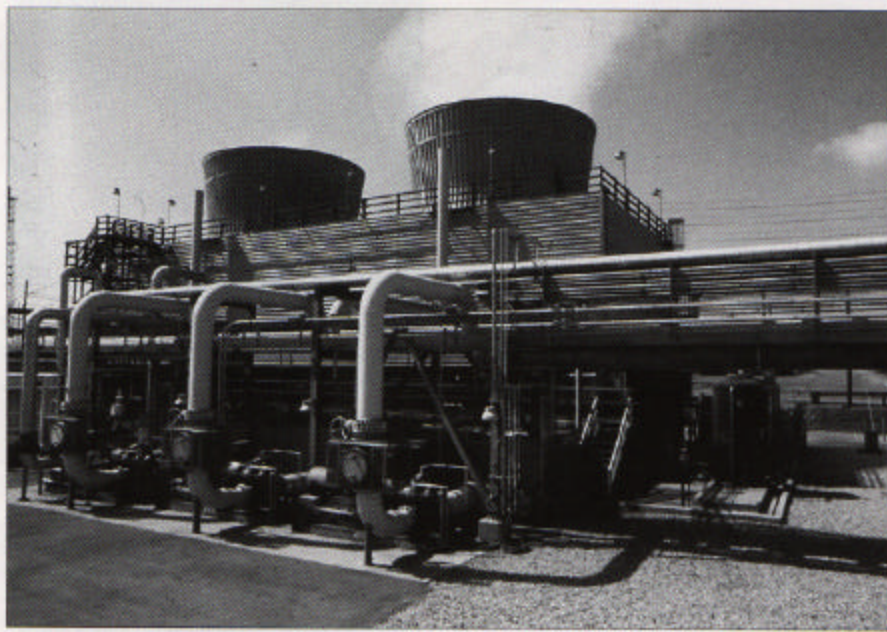


Automatic Control of Oxidizing Biocides in Cooling Water



An on-line system monitors the changing oxidant demand in the cooling water system and automatically feeds the required amount of oxidizing biocide to achieve and maintain system cleanliness.

Conventional methods of control proved ineffective for maintaining proper oxidizing biocide levels in one of the cooling towers serving a large Southern California refinery. By adopting redox control to match halogen feed rates to the system's changing demand, oxidizing biocide levels are now consistently maintained within the specification range, minimizing the tower's susceptibility to corrosion and biofouling.

The cooling water system primarily serves one of the refinery's hydrogen gas generating units, but is periodically manifolded to simultaneously serve a hydrotreater. The cross-flow system has an inlet and outlet temperature design of 107°F and 80°F, respectively, and is operated at between six and eight cycles of concentration, depending upon the silica content in the makeup water. The plant alternates between using its own well water and metropolitan water for its cooling tower operations.

Biological control for the system is accomplished through a sodium hypochlorite (NaOCl) program.

Maintaining the oxidizing biocide level in the 2-year-old system in the specification range of 0.3 ppm and 0.6 ppm total halogen presented significant problems for plant operators. Operators would measure total halogen levels on a scheduled basis and adjust the NaOCl feed pump stroke based on the test results.

Total halogen levels fluctuated widely using this conventional approach, often swinging back and forth from less than 0.1 ppm to in excess of 1.0 ppm. High NaOCl residual accelerated corrosion of both mild steel and copper alloy. The mild steel corrosion rate registered as high as 2.6 mils per year (mpy). This was believed due to copper plating on carbon steel surfaces. Admiralty corrosion rates approaching 0.8 mpy were not uncommon. Periods of inadequate biological control

prompted algae growth and the biofouling of heat exchangers, reducing heat transfer rates.

Residual-Based Dosing Inaccurate

One of the inefficiencies operators found with establishing halogen dose based on wet tests was that periodic residual measurement did not provide an accurate indication of the ever-changing oxidant demand in the system. As with virtually all cooling water systems, the system's oxidant demand is affected by numerous factors including routine shifts in pH, temperature and alkalinity. In addition, the system water receives boiler blowdown, which further impacts the oxidant demand in the Demand system. These constant changes in demand

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could not be accurately determined, or predicted, through intermittent residual measurement.

Another deficiency found with residual measurement was its inability

to recognize and respond to changes in the work value of the oxidant. In nearly all halogen applications, both organic and inorganic chloramines are formed along with dissociated and undissociated hypochlorous acid (undissociated hypochlorous acid has 60-to-100 times the oxidative power of its dissociated form). The resultant mix of chlorine species is primarily a function of PH, the organic types, and the ammonia content of the water. For example, hypochlorous dissociates according to the pH of the water. The same free chlorine residual will be twice as effective at a pH of 7.2 than at 7.8. But conventional residual measurement, such as that being used to establish halogen dosage at the refinery's cooling water system, cannot distinguish, or account for, these fluctuations in biocidal efficacy.

Due to the lack of correlation between total halogen residual and actual oxidant work value and the oxidant demand in the system, the cooling water system at the refinery was subjected to never ending overfeed/underfeed situations. The system would swing back

and forth between having too much oxidizing biocide, which accelerated corrosion, to having too little oxidant, which resulted in poor microbiological control and periodic fouling.

Redox: Measuring Oxidant Demand

Because precise levels of an oxidizing biocide must be maintained for the cooling tower's microbiological control program to be effective, it was determined an alternative approach to NaOCl control was essential. Following a comprehensive pilot test, the plant gained accurate biocidal control of the cooling water system by adopting an on-line controller that constantly monitors the redox in the system and automatically controls NaOCl feed rates to meet the changing oxidant demand.

Redox (also referred to as ORP, Oxidative Reduction Potential) is a direct measure of the rate of oxidation. The transfer of electrons is the common and

initiating event in any oxidative reaction. Immediately prior to the electron transfer there exists a potential for the transfer. Halogen forms that are toxic to microorganisms are miss-

An on-line controller monitors the ORP in the system and automatically adjusts feed rates to meet oxidant demand.

ing one or more electrons and they satisfy their need for electrons by stealing them from organics or other donors through an electrical attraction. This electrical attraction, or potential, is redox and is measurable in millivolts.

Redox, recorded in millivoltage, is a direct indicator to the oxidative strength

of the treated system. The higher the concentration of oxidizing biocide, the higher the voltage. Conversely, the higher the concentration of organics, the lower the voltage. A Redoxsensing unit can measure this voltage, providing a direct measurement of the work value of the oxidant present in water.

Adopting Redox Control

Working with representatives of Stranco, Inc., Bradley, Ill., the refinery installed a High Resolution Redox™ (HRR) control system to control NaOCl feed. The controller monitors the oxidant demand in the cooling water system (by measuring the redox potential) and automatically feeds the required amount of oxidant to achieve and maintain system cleanliness.

The controller senses the current demand for NaOCl via a redox electrode in a continuous sample flow. NaOCl is regulated using the HRR controller's time based proportional mode to control the NaOCl pump. A dial on the controller allows the operators to set the desired redox setpoint.

Using redox control, the precise amount of oxidant is continuously fed to meet the real-time demand of the cooling tower. Accurate control of the oxidant level is now maintained, resulting in improved biological control and reduced potential for fouling and corrosion problems. Corrosion rates in the system are currently at 0.5 mpy admiralty, compared to 0.8 mpy prior to adopting Redox control. Mild steel corrosion has also dropped to a more reasonable 2.0 mpy rate.

Although NaOCl had previously been fed to maintain upper and lower



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control limits of 0.6 ppm and 0.3 ppm total halogen, respectively, tests with automatic demand-based control showed a 0.25 ppm residual to be as effective in minimizing biological fouling. Halogens feed rates have been subsequently reduced by about 50 percent, from approximately 60 gpd under manual control to about an average 30 gpd with automatic feed.

Using HRR measurement and control for monitoring the oxidant demand and automatically treating the system with the oxidant dose required to achieve and maintain system cleanliness has proved effective in optimizing the microbiological control program for the refinery's cooling water system. The cooling water system will soon be under a HRR-controlled sodium bromide/ sodium hypochlorite program to determine if corrosion levels can be reduced even further. The plant's expectation is to provide a mild steel corrosion rate approaching 1.0 mpy and an admiralty rate well below 0.3 mpy. In addition, based upon the improved performance at this tower, the plant has installed HRR controllers to automatically feed oxidizing biocides at two other cooling towers serving the refinery.

