
Redox Technology as a Control Method for The Management of Oxidizing Biocides

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BACKGROUND

The dynamic nature of industrial cooling water applications provides a particularly difficult challenge for the control of microbiological activity.

To meet this challenge, oxidant-based micro biocides are a popular, cost-effective product of choice.

The maintenance of proper levels of oxidant is a prerequisite for good control. Unfortunately, there are a wide number of influences at work in cooling systems, which result in an ever-changing oxidant demand that must be satisfied to maintain system cleanliness. When this demand is not satisfied, microbiological activity flourishes. This results in reduced heat transfer rates, which in turn leads to a costly myriad of complications. (Figure 1)

Figure 1
Poor Microbiological Control Can Lead To These Problems

Higher Operating Costs

- Higher energy costs for pumps, cooling tower fans
- Reduced throughput of manufactured product
- Lowered product quality
- Higher maintenance
- Equipment damage
- Potential for unscheduled outage

Higher Treatment Costs

- Increased feed of scale/corrosion/deposit inhibitors
- Increased oxidant feed to kill microbio
- Increased feed for dispersants to prevent further system fouling
- Blowdown to clear out system reduces concentration necessitating higher feed levels of inhibitors to reach residuals

Reduction of Heat Transfer Rates

Bio growth leads to delignification and loss of tower fill and cooling capacity.

Algae fouls tower reducing cooling capacities and evaporative cooling.

Bacteria promotes slime formation leading to deposits in heat exchange equipment.

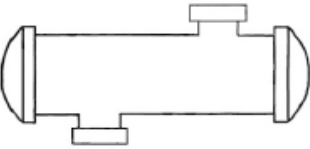
Biomass collection insulates heat exchange surfaces reducing ability to collect temperature.

Unchecked increase in scaling insulates heat exchange surfaces.

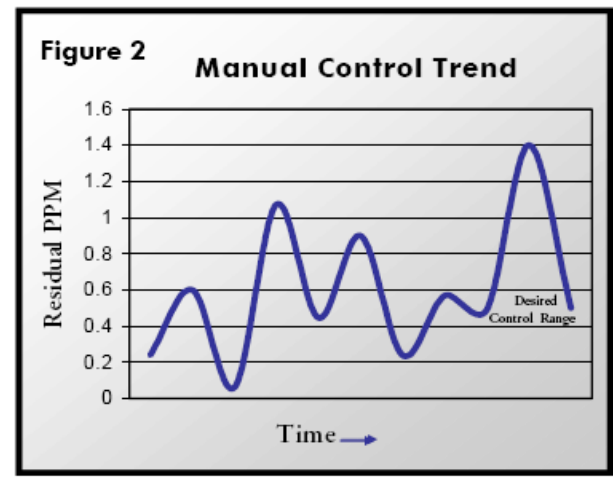
Oxidant overfeed promotes tower delignification and reduced cooling capability.

Microbio fouling leads to deposit corrosion; corrosion products amplify problem.

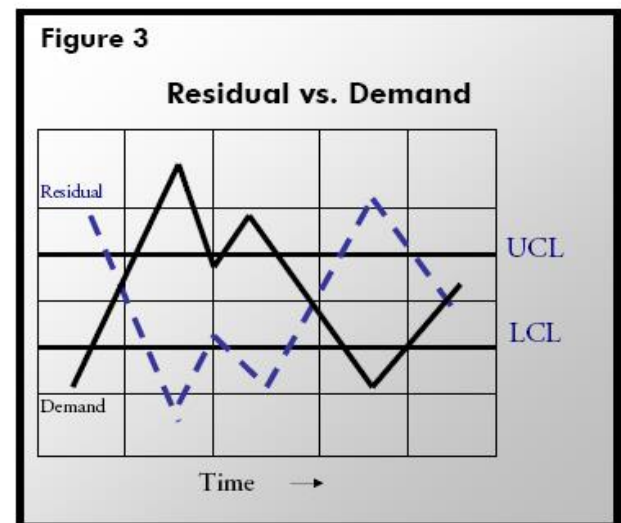
Process variables increase oxidant demand. If not met, microbiological fouling reigns.



To avoid these problems, the cooling system manager attempt to maintain control with residual monitoring. This conventional residual monitoring is often performed manually, intermittently and requires some degree of wet testing. While a host of result-influencing interferences affect the inability of these methods to recognize and respond to changes in the work balance of the oxidant being used. Because of this and the logistics normally employed, the administration of oxidant based programs routinely results in overfeed/underfeed scenarios. (Figure 2)



As demand changes, the rate of oxidant consumption by the system changes. This is responsible for shifts (peaks and valleys) in the residual oxidant value. The relationship between residual and demand is inverse. (Figure 3)



OXIDANT DEMAND

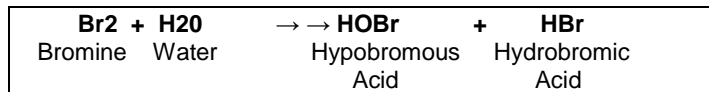
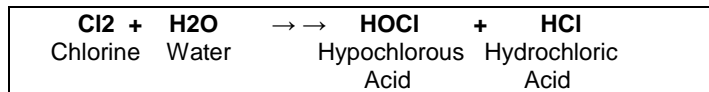
Unfortunately demand is never constant. Of all the influences affecting a cooling system, oxidant demand changes the most frequently and dramatically.

Many things affect demand:

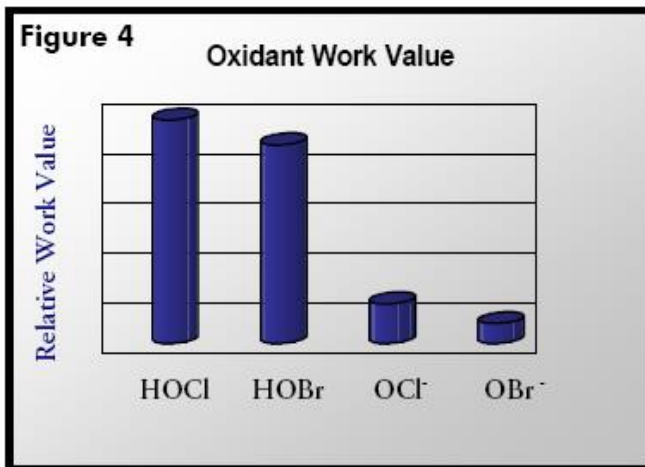
pH	wind direction	iron
temperature	manganese	climate
alkalinity	tower location	debris
process leaks	oxygen levels	proteins
make-up source	airborne organics	nitrites
organic carbon	make-up volume	sunlight
amino acids	lubricants	ammonia
other inhibitors	cycles / concentration	
nitrogen compounds		

In addition, routine pH shifts (even in a pH-controlled system) affect the work value of the oxidant. This is particularly true in the case of widely used chlorine and bromine-based micro biocides.

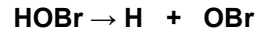
When these oxidants are added to a cooling system the following reaction occurs:



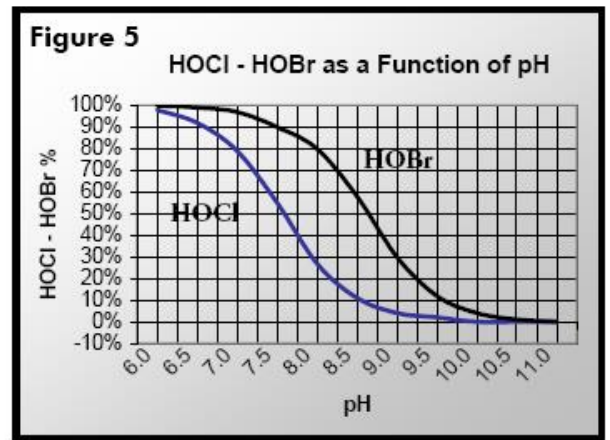
It is well known that the hypochlorous (HOCl / HOBr) forms of these oxidants are the active oxidizers responsible for microbiological control. They have 60-120x the work value of the hypochalite forms (OCl⁻ / OBr⁻). (Figure 4)



These active hypohalous forms undergo a breakdown or dissociation in the presence of H ions (pH) into the far less effective hypochalite form.



This is a reversible reaction which is driven by pH. The degree of this ionization to equilibrium is shown in Figure 5.

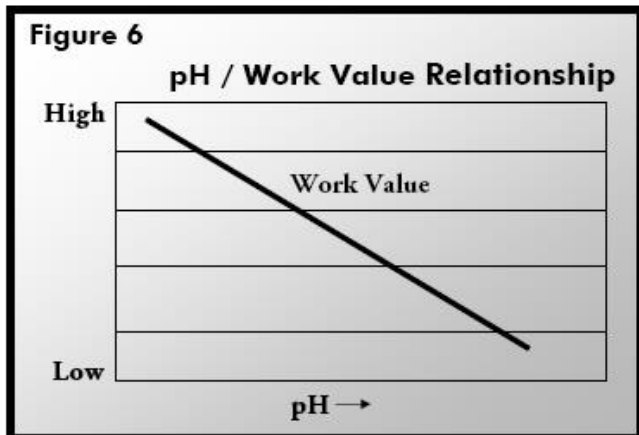


To further illustrate this dissociation :

pH	% HOCl	% OCl ⁻	% HOBr	% OBr ⁻
6.5	92	8	99	1
7.0	79	21	97	3
7.5	55	45	90	10
8.0	27	73	80	20
8.5	11	89	58	42
9.0	4	96	30	70

Hypobromous exists in a higher percentage than hypochlorous at higher pH values. (This has given rise to its popularity in alkaline systems; however it is far more costly than chlorine, so this trade-off must be evaluated in each system.)

This pH / hypohalous relationship is the heart of the work value issue.



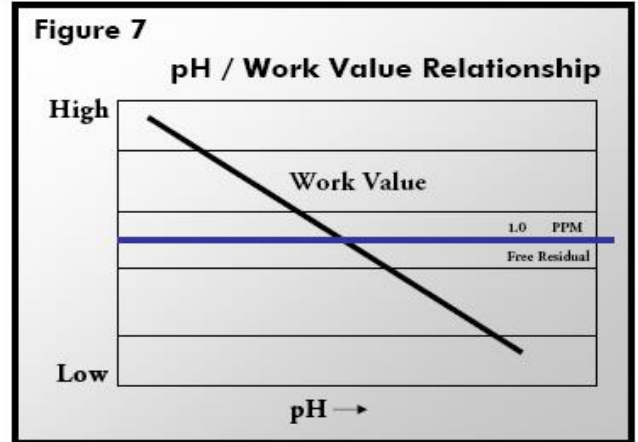
An increase in pH decreases the work value of both chlorine and bromine based biocides. Routine shifts in pH of 0.5 pH units are common in well-controlled systems. At an operating pH of 8.0, a shift of 0.5 pH decreases HOCl work value by 59% and HOBr work value by 27%. Conversely, a drop in pH from 8.0 to 7.5 increases the work value of HOCl by 103% and the work value of HOBr by 12%.

This fluctuation in work value is not distinguishable with conventional residual tests. All commonly used test kits and “automated test kits” see free oxidant as a single value, which is the sum of the hypochlorous AND hypochlorite species of oxidant. They cannot discern the degree of dissociation occurring in the system. The oxidant programs administered and controlled in this fashion do not account for work value fluctuations. The impact of this deficiency can be dramatic.

If the work value of 1.0 ppm free chlorine residual at a pH of 8.0 will keep the system free of bio-fouling, it follows that an increase in pH and corresponding decrease in work value will result in fouling. Yet, under this exact scenario, our test kit will show 1.0 ppm free Cl₂ residual and no change in feed rate will be initiated! The test kit sees HOCl and OCl as having the same work value!

Following this scenario, a decrease in pH will increase the work value (oxidizing power) beyond the targeted range. This will result in overkill to a degree which may promote corrosion, destroy other organic inhibitors present and lead to further deposition in the system. Our test kit will still see 1.0 ppm free residual and no change in feed rate will be initiated.

(Figure 7)



Without automated response to demand control, which accounts for the ever-changing work values, the system is subjected to a series of never ending overfeed/underfeed situations. No other aspect of a comprehensive water treatment program is subject to this degree of performances fluctuation.

The cooling system manager is faced with the challenge of precisely controlling the oxidant program in the face of changing demand variables and thus changing oxidant requirements. To complicate matters, the work values of the oxidant change routinely.

Environmental restrictions and oxidant minimization rule out the old method of continuously overfeeding. New combinations of oxidants, higher production requirements, increasingly stringent quality control issues, tighter operating guidelines, delignification concerns and economies all point to the growing need for judicious use and control of oxidants.

This need can only be filled by technology, which recognizes changes in work values and responds to fluctuations in demand. This must be done continuously, on-line and automatically.

The automation of conventional wet test methods simply automates a technology, which suffers from the drawbacks highlighted earlier and thus does not fill the need described.

REDOX TECHNOLOGY

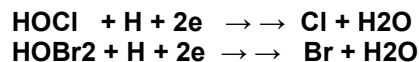
When chlorine or bromine-based micro biocides are added to a cooling system, their job is to oxidize unwanted organics.

This oxidation is a process of electron transfer. When an oxidant is fed in the presence of an organic, it “steals” electrons from the species that are killed. Nature insists that for every oxidation there is a reduction. (This is also an electron transfer to maintain balance. A reductant “gives” electrons to the reduced species.) It is this oxidation-reduction reaction that is the core of the only technology that can fill the needs described earlier.

We will refer to this technology as High Resolution Redox (also known as ORP or Oxidation-Reduction Potential).

When HOCl enters into a Redox reaction, two electrons are “stolen” from the oxidized species (typically a biospecies in a cooling tower) and are accepted by the HOCl. The result is an oxidized organic, chlorides and water.

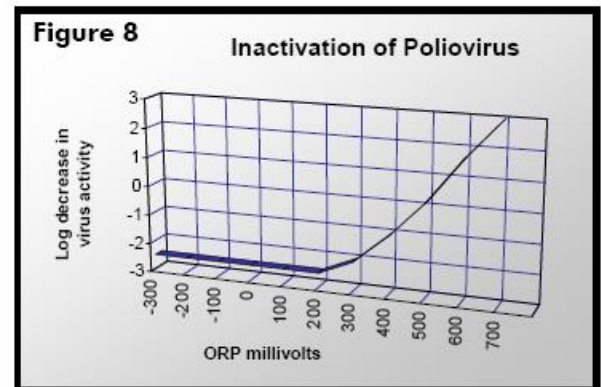
The HOCl side of the reaction is as follows:



A HOBr Redox reaction is almost identical except the result is bromides rather than chlorides. It is impossible to show the organic side of the reaction because it would depend on the organic species involved.

Some of the early research on the relationship between ORP and microbiological kill rate was conducted by Ebba Lund at the University of Gothenburg in Sweden in the late '50s and early '60s. Her research indicated a direct link between disinfection rate and the Oxidation Potential achieved by adding various oxidizers. The experiments study the inactivation of poliomyelitis virus as ORP varied. The results indicated that “the inactivation rate by chlorous (and other) compounds may be described solely in terms of their oxidative effect.”

Many studies on the kill rate by oxidants have let to similar conclusions. The correlation between HRR values and kill rate approaches 98%! A strong positive correlation. On the other hand, free residual correlation to kill is less than 60%! A weak negative correlation. The Redox correlation to kill gives the operator the unique capability of predictive performance.



This translates to an accuracy which allows its owners to know what microbio results they will achieve in advance. The guessing games overfeed to assure results, and biofouling are eliminated. This predictive performance makes HRR a much better tool for evaluating treatment efficacy than residual testing. It is also a practical way to pace oxidant feed to demand.

The predictive performance of Redox comes from the ability to accurately measure transfer (which results in the destruction of the microbiological population) and therefore measure the oxidant’s ability to perform.

Redox technology measures the degree of electron transfer and reliably determines the oxidant’s work value. This capability allows the system manager to respond properly to changes in oxidant demand which would affect results.

From a practical point of view, this response takes the form of accurate pacing of whatever oxidant is being used. Feed rates are adjusted to match demand. This eliminates the problems associated with the under and overfeed scenarios highlighted earlier.

A summary of the benefits of Redox control are shown below:

- ◆ Maintains optimized heat transfer rates
- ◆ Provides automatic response to system upsets
- ◆ Reduces system variability
- ◆ Eliminates damaging overfeed/underfeed of oxidizing biocides
- ◆ Improves system reliability at lower costs
- ◆ Enhances capability to achieve environmental compliance