

Oxidation Reduction Potential Measurement for Microbiological Control in Makeup Water and Cooling Water



Background

Water is a vital part of many industrial processes, from the manufacturing process for semiconductors to the creation of steam for generating electricity to the production of drugs in the pharmaceuticals industry. However, natural water is a breeding ground for many types of microorganisms, such as algae, fungi, or bacteria, as well as many types of macro organisms, such as zebra mussels, Asiatic clams, or barnacles. To avoid the significant difficulties these organisms present, many industries must purify water to ensure process efficiency and applicability of the water. The two most common processes in industrial plants requiring such microbiological control are the makeup water system and cooling tower water. Both require a constant or periodic intake of water from some source - a lake, river, ocean, well, or city supply.

The Problem

Historically, micro- and macro organisms in water have been controlled by adding an oxidizing biocide such as chlorine, bromine, or ozone to effectively limit microbial activity.

Laboratory screening procedures are coupled with maintaining a residual level of the biocide to ensure the maximum "kill" rate. This method has typically resulted in a periodic underfeed, leading to organism growth, or overfeed, adding unneeded expense and potential component damage. In contrast, the measurement of oxidation reduction potential (ORP) has proven more effective in consistently controlling biocide addition while effectively destroying the organisms, maximizing cost savings and component life.

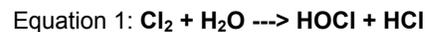
Oxidizing Microbiocides

The most common way of limiting or preventing the presence of microbiological organisms in a water system is to feed a chemical that is toxic to the organisms, such as an oxidizing microbiocide, into the water. These oxidants (disinfectants) include chlorine, bromine, sodium hypochlorite, chlorine dioxide, ozone, and potassium permanganate. Oxidizing microbiocides inhibit

microorganism growth by removing electrons from the cell, irreversibly oxidizing protein groups. The effect is to interfere with normal enzyme activity, resulting in the death of the cell. A wide variety of oxidants are available to accommodate the various factors that affect individual cooling water or makeup water systems, such as pH and temperature of the water, contaminant level and type, safety concerns, economics, and discharge restrictions of the plant.

Chlorine

The most commonly used disinfectant for microbiological control is chlorine. It is known to be excellent for controlling algae and spore growth, as well as many strains of bacteria. When chlorine gas comes into contact with water, it hydrolyzes and forms hypochlorous and hydrochloric acids.



In addition to the above reaction, hypochlorous acid will ionize according to the following reversible reaction:



The effectiveness of chlorine as a biocide (known as the biocidal efficacy) is determined by the amount of hypochlorous acid, not the hypochlorite ion. Hypochlorous acid is a very strong oxidizing agent. It inhibits a cell's protein production and respiration processes, effectively destroying the cell. However, the pH of the water directly affects ionization of the hypochlorous acid. At a pH of approximately 6.0, only 5% of the hypochlorous acid ionizes to form the hypochlorite ion, while a pH of 7.0 yields ionization of around 25%. At pH 8.0, about 75% of the ionization occurs. The effectiveness of chlorine as an oxidizing agent is limited to pH levels below 8.0 pH. A pH range of 6.5 to 8.0 is considered the practical range for the use of chlorine as an oxidizing microbiocide, since lower pH levels can cause corrosion of piping, while higher pH levels render the chlorine ineffective.

Although chlorine is widely used as an oxidizing agent, it has many inherent environmental, health, and safety concerns associated with it. The major disadvantage of chlorine use is the formation of chlorinated organics in the water, which can have a negative effect on the environment and process components. Another disadvantage of chlorine is potential safety problems associated with chlorine gas. In addition, chlorine tends to react with ammonia or nitrogen when they are present in the water, forming chloramines, which are believed to be harmful to the environment. Formation of chloramines requires the addition of excess chlorine to effectively disinfect the water, since chloramines reduce the effectiveness of the hypochlorous acid, thus wasting the chlorine. Chlorine addition also effectively lowers the pH of the water as hydrochloric and hypochlorous acids form, making pH control more difficult. As a result of the many problems associated with chlorine, many other oxidants are seeing more widespread use.

Bromine

Bromine behaves very similarly to chlorine; the addition of bromine to water forms hypobromous acid and the hypobromite ion.

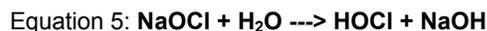


Hypobromous acid is also a very strong oxidizing agent and acts to disrupt the protein production and respiration processes of a cell. There are many benefits to bromine over chlorine. However, it, however. The ionization of hypobromous acid does not occur until much higher pH levels than those needed for the ionization of hypochlorous acid. A pH of 8.0, which would yield about 75% ionization of hypochlorous acid, yields ionization of only slightly less than 20% of the hypobromous acid. A pH level of 9.0 must be reached before the ionization of hypobromous reaches 75%. Bromine addition is thus more useful in systems that maintain higher pH levels. Similarly to chlorine, bromine will react with ammonia and nitrogen to form bromamines. However, bromamines are considerably more powerful disinfectants than the associated chloramines, so additional bromine is not necessary to compensate, as with chlorine. The corrosive effect on process components are lessened as well with bromine, since hypobromous acid is not as powerful as hypochlorous acid. The environmental issues associated with chlorine are also minimized with bromine. For these reasons, bromine use has seen a significant increase as plants seek to minimize the problems

associated with chlorine while maintaining the oxidizing power needed to prevent organism growth.

Sodium Hypochlorite

A similar oxidant to chlorine is sodium hypochlorite (NaOCl). This salt reacts with water to form hypochlorous acid, which is the same oxidizing agent that chlorine produces in water.



Sodium hypochlorite is considered safer to handle and ship than chlorine, and thus may be preferred for these reasons. However, it is slow to decompose and has adverse reactions with ammonia and organics. pH control can be more difficult because of the formation of sodium hydroxide, a strong base. In applications like cooling towers, where higher pH levels are typically desired, sodium hypochlorite may be preferred over chlorine addition, which will lower the pH levels.

Chlorine Dioxide

Another oxidant that is seeing widespread use in place of chlorine is chlorine dioxide (ClO₂). Chlorine dioxide does not hydrolyze in water and thus its activity in water is not closely related to pH levels. Another benefit is that chlorine dioxide reacts relatively quickly and is not reactive with ammonia, thus demonstrating a better kill rate than chlorine. In addition, it does not produce chlorinated organics, as chlorine and sodium hypochlorite do, making chlorine dioxide the oxidant of choice in more and more cooling tower and makeup water applications where high pH, ammonium-nitrogen contamination, and/or high levels of organic contamination are present. The only disadvantage to chlorine dioxide is that it must be produced on site.

Ozone

Ozone (O₃) is an unstable, gaseous form of oxygen produced by conditions of high energy. It is considered to be the most powerful oxidizing agent that is commonly used. Whereas oxidants such as chlorine or bromine attack the protein and respiration systems of a cell, ozone basically disintegrates the cell wall. It breaks down to form oxygen and water, which are not harmful to the environment. However, it is only partially soluble in water, and its solubility decreases at higher temperatures. As water temperature exceeds 25° C, the solubility of ozone decreases progressively to the point that ozone cannot be effectively used at temperatures around 65° C. In addition, ozone reacts so quickly with organics that high levels of ozone must be produced in systems with heavy organic loads, which can

compromise microorganism control. Because of its instability, ozone must be made on site.

ORP and Microbiocide Control

To ensure proper microbial control, it is necessary to measure the total number of microorganisms present in the system in addition to identifying the types of organisms. Visual techniques alone are never enough to determine whether a problem is occurring, since by the time organisms are visible, the situation has become critical. Standard plate counts for bacteria and fungi is an example of a test that can be done to ensure that organism growth is minimized. Various other tests can be helpful in gauging the type of organism growth present in the water. Typical microbiological control programs are designed to eliminate 99% or more of the organisms in the water, as well as prevent any future growth from occurring. Traditional microbiocide control has come from maintaining a residual of the oxidant of choice in order to ensure that any excursions of organic growth are immediately arrested.

Control by means of the residual method has many shortcomings. The concentration units used to report residual levels do not provide an adequate representation of the quantity of organics that will be oxidized. This is because an amount of oxidant will always oxidize the same number of microorganisms, regardless of the concentration level. Another shortcoming is that the oxidizing ability of the oxidant is often related to the pH of the water. The residual measurement cannot take into account the pH, and therefore fluctuations in the water pH will affect the ability of a measured amount of oxidant to do its job. Another problem with residual measurement is that some oxidants can exist in many forms in the water, and residual measurements cannot take into account any changes within the amounts of the various forms (all with varying oxidizing power) within the water. Last of all, residual control has little ability to respond to changes in demand, which can occur from fluctuating organic levels and nitrogen compound levels, as well as any effects of flow, heat, light, or exposure to air. In fact, when demand increases, oxidant strength will diminish, although this effect may not be noted by residual measurements. As a result, control of the addition of an oxidant by residual control will result in endless overfeed and underfeed of the oxidant.

This overfeed/underfeed situation will cause two problems to occur. An overfeed of oxidant will result in extreme excesses of chemical costs as well as potential damage to system components and metallurgy. An underfeed of oxidant will result in potentially irreversible damage and loss of efficiency due to

microorganism growth. Both problems should be avoided at all costs, yet the only way to improve residual control is to increase the periodic checks in plate counts and perform more adjustments to the setpoints of the residual control. This method can yield only slightly better results, but will waste time, money, and energy in performing the often daily checks that are required. In cases where the oxidizing agents must be removed from the water (typically known as "dechlorination" when chlorine is used), the same problems exist.

ORP can be used to perform accurate control of oxidant feed. The ORP value is a direct reading of the activity of the oxidizing and reducing agents in the water as they correspond to oxidation-reduction reactions. Research shows that a microorganism's ability to survive in water is mainly influenced by the ORP of the water. This is because the action of an oxidizing microbiocide is to remove electrons from an organism, effectively destroying certain processes that keep the organism alive. Since this transfer of electrons is an oxidation-reduction reaction, ORP gives a direct correlation of the ability of the water to prevent microbiological growth.

ORP measurement uses an inert metal (typically platinum) measuring electrode that detects a millivolt potential due to the transfer of electrons within the process. The polarity and strength of the millivolt potential created is dependent upon the levels of oxidizing and reducing agents in the water. The millivolt potential is established on the measuring electrode with respect to a reference electrode, which is similar to that used in pH measurements. The typical reference electrode is the silver/silver chloride (Ag/AgCl) electrode, although a saturated calomel electrode has been used on occasion. Millivolt values are reported with respect to one or the other, depending on which is used, and care must be taken not to interchange the two, as millivolt differentials will exist.

In an oxidizing environment, caused by the presence of an oxidizing microbiocide, a higher ORP will exist, while a lower ORP will exist in a reducing environment. It is important to note that the actual crossover point between water being oxidizing or reducing is dependent upon the reference electrode. This point is typically somewhere between +200 to +250 mV, depending upon whether the Ag/AgCl or the calomel electrode is used and, to a lesser extent, the temperature and oxygen content of the water.

Whereas residual measurements simply respond to the concentration of excess oxidant that exists, ORP responds directly to the oxidant's toxicity to the organisms. For each

individual site and application, an ORP value must be established based upon laboratory tests for organism growth. The control setpoint will typically be the optimal ORP value that, when maintained, will consistently prevent growth of microorganisms at the minimal dosage of oxidant required. Any costs associated with maintenance for the measurement are minimal compared with the cost-savings associated with the improved biocide control.

Cooling Water

Many industrial processes necessitate the removal of heat for critical plant processes, such as steam production. A common means of removing heat from a water or air stream is by passing the stream across a series of tubes filled with cool water known as a heat exchanger. The transfer of heat to the cool water is usually a vital part of the efficiency of a plant, and it must be maintained at an optimal level in order to maximize the process output. Many factors can work against component life and efficiency of the heat exchanger, especially microbial growth.

Microorganisms such as algae, fungi, or bacteria can enter a cooling water system through the incoming water or through the air itself if a cooling tower is present. In fact, a cooling water system can provide optimum conditions for growth, since temperature and pH ranges are usually ideal, and nutrients such as sunlight, organic matter, and inorganic salts are found in abundance.

The effects of the microorganisms vary widely. Algae growth will result in oxygen production, which can accelerate the corrosion reaction. Some forms of algae are responsible for the accelerated deterioration of nitrite-based corrosion inhibitors. Other types are known to cause silica fouling. Dead algae will collect in the water, increasing the suspended solids, which can cause fouling, providing food that will enhance bacterial growth, as well as absorbing microbiocides, which can minimize the effectiveness of microbiological control. Fungi growing in a cooling tower can attack the wood, causing surface rot or internal wood decay, which ultimately can destroy a tower. Fungus growth can form bacteria-like slimes that can clog heat exchange tubes, lowering the efficiency of the heat exchanger, as well as causing site-specific corrosion whenever the slimes cling to pipe walls.

Minimizing bacteria growth is perhaps the most difficult microbiological control, since so many different species of bacteria can exist in cooling water systems. Problems associated with bacteria are perhaps the most widespread of all the

microbial concerns. Slimes can form that clog heat exchangers. Some aerobic bacteria form strong acids, which can lower the pH of the water in general, as well as locally dropping pH levels to as low as 1.0. Typically, anaerobic bacteria can grow underneath the aerobic bacteria, causing site corrosion. "Iron" bacteria can produce iron deposits that cause plugging, pitting corrosion, and reduced heat transfer. Certain types of bacteria can destroy nitrite corrosion inhibitors. Other bacteria can form ammonia, which can attack copper-based construction materials. Safety issues can also arise from bacteria forms known as pneumonia, including the *Legionella pneumophila*, which can cause Legionnaires' disease.

Many cooling systems use fresh water as the intake water, which can introduce numerous forms of macrofouling, such as clogging of filters or screens. Large aquatic organisms can enter the water supply, causing plugging in heat exchangers and buildup in a cooling tower basin. These organisms include barnacles, clams, jellyfish, and mussels.

Microbiological growth in a cooling water system is typically controlled by addition of chlorine, although sodium hypochlorite, bromine, chlorine dioxide, and ozone are becoming more common as their benefits are realized. Underfeed of the biocide will result in microbiological growth, while overfeed of the biocide can result in excess chemical costs and potential damage to the system metallurgy (corrosion) or the cooling tower (wood delignification). Oxidation-reduction potential can be used to correct the underfeed and overfeed problems by providing a measurement of the minimum amount of biocide addition necessary to prevent microbial growth.

ORP control can be implemented with a feedback loop, with the sensor placed either before or after the heat exchanger, although a location after may be better to ensure compensation for any drop in oxidant levels within the heat exchanger. Determination of the ORP control setpoint must be done for each individual site, since there will be many variations between sites, including organism type, water chemistry, temperature, and oxidant type. For the most part, control setpoints for oxidizing biocide addition will be within the +550 to +650 mV range.

Dechlorination (or a similar removal of another type of oxidizing biocide from the water) for environmental protection typically is done by addition of a reducing agent, such as sodium bisulfite or sulfur dioxide, in order to properly reduce the oxidant, such as chlorine or bromine. Since regular water with no oxidizing or reducing agents present (except oxygen, which is a mild oxidizer)

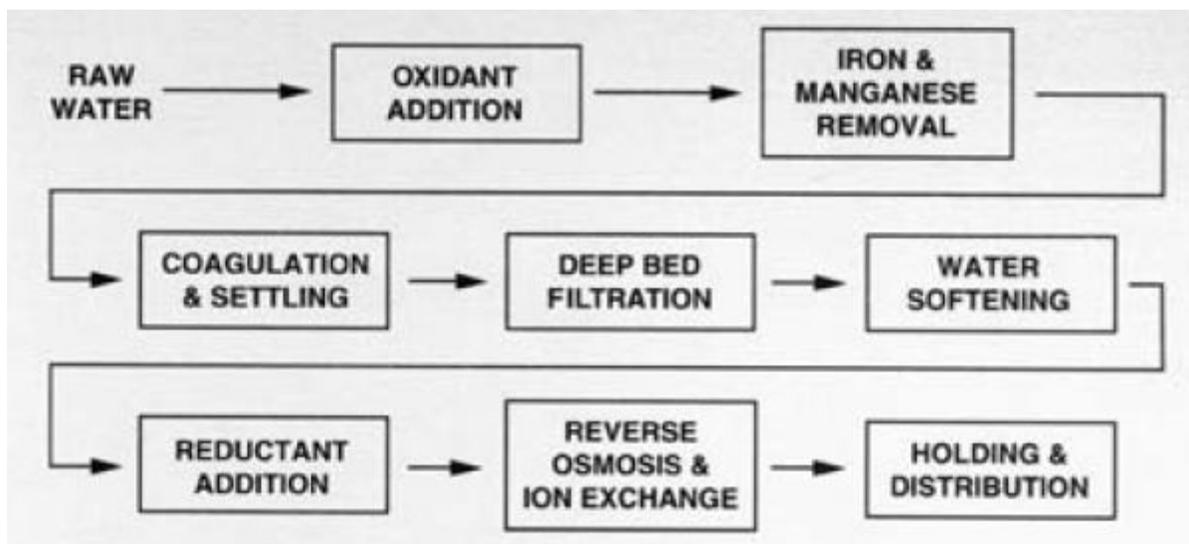
will result in a reading of approximately +200 mV with the Ag/AgCl electrode, an ORP of less than this value means that the environment is reducing. Research has shown that addition of enough sulfur dioxide or sodium bisulfite to provide an ORP value of just below +200 mV will result in the reduction of the oxidant. Not all oxidants require this procedure, since some, such as ozone, will break down quickly on their own.

Control of microbiological growth is not an option for the vast majority of cooling water systems. Inadequate control has resulted in shortened component life, loss of efficiency, and wasted chemical costs. Yet microbiological control remains one of the most misunderstood and thus neglected parts of a chemical treatment program for cooling water. Measurement of ORP offers major improvements over treatment programs using residual control of an oxidizing biocide, resulting in

improved life for heat exchangers and cooling towers, minimal usage of treatment chemicals for chlorinating and dechlorinating, and increased efficiency of plant processes that utilize the cooling water for heat exchange purposes.

Makeup Water

Many plants require a constant or periodic intake of water to make up for losses in their processes. For example, a power plant's water system is constantly losing some of its water to sampling systems, steam losses, and blowdown. The raw water may be obtained from a nearby river, lake, ocean, well, or even city supply. Because the incoming water often harbors numerous organisms, this water must be treated with a biocide to remove and prevent microbiological growth. The city water supply has almost always been treated already with a microbiocide of some sort, so additional treatment may or may not be necessary.



Typical Makeup Water System

The effect of biological growth on makeup water can be significant. A typical makeup water system (see Figure) will perform biocide treatment to the raw water upon entrance to the makeup system. The typical oxidant used is chlorine, although sodium hypochlorite is finding more widespread use in smaller systems. The chlorination is done as early as possible in order to immediately reduce the organic growth to acceptable limits. A large residual is typically maintained as long as possible in order to discourage any further growth. This process is called hyperchlorination. Unfortunately, the amount of oxidant feed necessary can shift often according to changes in flow, raw water organism content, or even varying oxidant levels already present if the raw water is from a municipality.

Another application in the system where oxidant addition has been seen to be useful is in the removal of iron and manganese,

which can form mineral deposits on pipe walls and process components, lowering the makeup water system's effectiveness. Aeration can be used to remove these mineral contaminants, since contact with oxygen can cause them to form insoluble compounds that can be removed by filtration, coagulation, or flocculation. However, the oxidative reaction that takes place using aeration is rather slow. An oxidant such as potassium permanganate or chlorine in conjunction with a filter bed of greensand (a zeolite containing manganese) can serve to speed up the oxidative process. Although this process requires constant addition of the oxidant and periodic bed regeneration, it is preferable to allowing a reduction in component efficiency due to iron or manganese deposits.

Unfortunately, the oxidants that can prevent so many problems early on in the makeup water process can actually be harmful

later on. The presence of a strong oxidizer such as chlorine can degrade ion-exchange resins, resulting in more frequent regenerations, which can be costly. In addition, reverse-osmosis systems are typically very susceptible to water treated with chlorine and quickly degrade upon exposure. For these reasons, the makeup water must be dechlorinated prior to any reverse-osmosis or ion-exchange units in the system. There are typically two ways to accomplish this—activated carbon beds or chemical injection with sulfur dioxide (SO₂) or sodium bisulfite (NaHSO₃).

Activated carbon beds can actually serve two purposes within a makeup water system—to dechlorinate the water and to adsorb any organics that remain in the water. The efficiency of the carbon beds in removing the chlorine depends upon a number of things, including pH, temperature, and organic load in the water. Unfortunately, carbon beds can become a nurturing environment for organic growth and therefore need to be sanitized often. The pH levels necessary for the carbon beds to effectively dechlorinate can often be harmful to components downstream. In addition, carbon fines can be released from the bed, causing problems downstream with other components. Because of the number of problems associated with carbon beds, many makeup water systems are employing chemical injection to dechlorinate and using special anion-exchange resins for removal of organics.

Dechlorination by means of chemical injection involves adding a reducing agent such as sulfur dioxide or a form of bisulfite, such as sodium bisulfite. The bisulfite (or sulfur dioxide) is oxidized and the chlorine reduced, thus removing the harmful effects of chlorine in the water. The bisulfite ions are converted to sulfate ions, which are removed in the anion exchanger. The chlorine ions are converted to chloride ions, which are also removed by the anion exchanger. Failure to completely dechlorinate can result in hydrolytic destruction of a polyamide reverse-osmosis unit or damage to ion-exchange resins. However, overfeed of the reducing agent can result in unneeded chemical costs and increased anion-exchange resin regeneration.

Oxidation-reduction potential can successfully be used for both oxidant addition and removal in makeup water. An ORP feedback loop can be placed into the system loop where oxidant addition is required (typically at the raw water inlet point). A second ORP feedback loop can be added just prior to the reverse-osmosis or ion-exchange systems in the makeup water system. Typical control points are site-specific, but typically reside within the +600 mV range or higher for oxidant addition and +200 mV or lower for oxidant removal. Control points should be determined by lab analysis for microbiological activity and level of oxidant present.

In order to provide quality water for many plants with minimal costs, the efficiency of makeup water components is vital. Control of micro- and macroorganisms, both at the initial intake of raw water and throughout parts of the system, is important to maximize component life. Inadequate control can result in increased regeneration or permanent destruction of vital components, loss of efficiency, and wasted chemical costs. Control by ORP has shown major improvements over treatment programs employing residual control of an oxidizing biocide, resulting in improved life for ion-exchange resins and reverse-osmosis systems, minimal usage of treatment chemicals for chlorinating and dechlorinating, and increased efficiency of plant processes that use the makeup water.

Honeywell's ORP Measurement and Control Solution

ORP Probes

Honeywell's ORP probes (7777 series) provide a platinum measuring electrode with a low-maintenance gel-filled reference electrode for long-term accuracy and reliable performance. The probes may be connected to a Honeywell 9782 analyzer or 7096 analyzer to achieve the desired control.

Features and benefits of the ORP probes:

- Rugged polypropylene construction
- Factory-sealed reference gel, designed to last the life of the electrode
- Required accuracy at an economical cost
- Proven in thousands of applications worldwide
- Fast, off-the-shelf delivery.

ORP Analyzers

Honeywell offers two analyzers, both with local display, dual-relay outputs for high or low alarms, and a 4-20 mA output.

The 9782 series ORP analyzer was designed to be the easiest analyzer to use while providing you with the widest selection of advanced features:

- Menu-driven displays
- Intuitive prompts and instructional messages
- Text descriptions for diagnostics and alarms
- Self-guided calibration procedures
- Multiple parameters on a single display

- Conveniently grouped key pad
- Dynamic function keys
- Auto-calibration and auto-clean.

Honeywell's 7096 ORP analyzer offers basic, economical pH/ORP measurement and control. The analyzer ensures accurate and reliable pH/ORP measurements, while the 1/4-DIN, NEMA 4 front-panel design makes the analyzer ideal for OEM applications where panel space is limited.

Additional features of the 7096 pH/ORP analyzer:

- Dual alarm relays
- User-programmable security lock
- Easy-to-read LCD display
- EEPROM backup
- Probe diagnostics.

More Information

For more information on ORP Measurement, visit www.honeywellprocess.com, or contact your Honeywell account manager.

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