ORP Provides Versatile Water Treatment

Shane Filer
Analytical Specialist
Honeywell Analytical
Fort Washington, PA 19034

Mark Janick
Chemical Engineer
Baltimore Gas and Electric
Baltimore, MD 21226

Abstract

There are relatively few measurements in power plant water which can be considered new, and even those measurements are typically very limited in focus. However, one newer measurement which has been found to be useful in multiple applications within a power plant is Oxidation/Reduction Potential (ORP). ORP measurement has been successful in controlling the addition of oxidants for the minimization of microbiological growth in both cooling water and makeup water. Likewise, ORP measurement can be used at later stages in cooling water effluent and makeup water to ensure proper breakdown of the oxidant by addition of a reducing agent. Another application which has seen extensive usefulness for ORP measurement is within the water/steam cycle. ORP has been successfully used to relate the water's corrosivity with respect to the system metallurgy. Proper measurement of ORP can be used to optimize the cycle chemistry in order to minimize system corrosion.

Oxidation / Reduction Potential

Chemical reactions which involve the transfer of electrons between reactants are known as oxidation-reduction, or redox, reactions. A species with lesser affinity for electrons in solution will lose electrons, increasing its electrical charge. This half-reaction is termed the oxidation, because the initial reactions which were studied early on involved oxygen as the oxidizing agent. The species will become more positive in the oxidation reaction. A species with greater affinity for electrons in solution will accept electrons, reducing its electrical charge. This half-reaction is termed the reduction, since the species becomes less positive. Equations 1 and 2 summarize the half reactions taking place.

$$X^m + pe^- \Rightarrow X^{m-p} \qquad \text{(reduction -- gain of electrons)} \qquad (1)$$
$$Y^n \Rightarrow Y^{n+q} + qe^- \qquad \text{(oxidation -- loss of electrons)} \qquad (2)$$
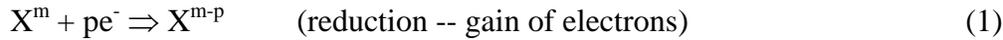
The X^m represents the species which is reduced to X^{m-p} by gaining p electrons. The Y^n represents the species which is oxidized to Y^{n+q} by losing q electrons. The species which gains electrons is reduced, and acts as an oxidizing agent. The species which loses electrons is oxidized, and acts as a reducing agent.

In order for the whole oxidation-reduction reaction to occur, the two half-reactions must occur simultaneously. If the example above is simplified by assuming that both oxidation and reduction reactions involve a single electron, Equation 3 can be written.

$$X^m + Y^n \Leftrightarrow X^{m-1} + Y^{n+1} \qquad \text{(standard redox equation)} \qquad (3)$$
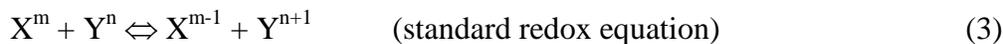
If a solution is strongly oxidizing, it has a deficiency of electrons available and thus will attempt to acquire electrons. Likewise, if a solution is strongly reducing, it has electrons available and will attempt to give up electrons. The tendency for a solution to donate or accept electrons can be sensed as an electrical potential on an inert electrode.

The ORP measurement utilizes an inert metal (typically platinum) measuring electrode which develops 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), although a saturated calomel electrode has been used on occasion. Millivolt values will be reported with respect to one or the other, depending upon which one was used, and care must be taken not to interchange the two, as millivolt differentials will exist. In an oxidizing environment, such as that caused by the presence of an oxidizing microbiocide, a higher ORP will exist, while a lower ORP will exist in a more reducing environment.

Microbiological Control in Makeup Water and Cooling Water

Water is one of the most vital ingredients in any steam-based power or cogeneration plants. However, natural water is a breeding ground for many types of microorganisms, such as algae, fungi, or bacteria, as well as many types of macroorganisms, such as zebra mussels, Asiatic clams, or barnacles. These organisms create quite a difficulty for plants, since they require purification of the water to ensure process efficiency and/or applicability of the water. The two most common processes in a power plant which require such microbiological control are the makeup water system and the cooling tower water. Both require a constant or periodic intake of water from some source, be it a lake, river, ocean, well or city supply. Historically, these micro- and macroorganisms have been controlled by adding an oxidizing biocide, such as chlorine, bromine, or ozone to effectively limit the microbial activity. Oxidizing biocides are toxic to the organism growth by removing electrons from it, thus irreversibly oxidizing protein groups such that normal enzyme activity is lost, which results in the death of the cell.[1]

Biocide Control

It is necessary both to measure the total number of organisms present in the system and to identify the types of organisms in order to ensure proper biological control. Visual techniques alone may be adequate to determine if a problem is occurring with a large macroorganism. However, these techniques will never be enough to determine if a problem is occurring with microbiological growth, since by the time that organisms are visible, the situation is already critical. Performing standard plate counts for bacteria and fungi is an example of testing that can be done to ensure that organism growth is below a minimum number. Various other tests can be done to gauge the type of organism growth that is present in the water. Typical microbiological control programs are designed to reduce 99% or better of the organisms in the water by determining the concentration of oxidant required for a given point in time to both kill any existing microorganisms and also prevent any further growth from occurring. Typically, a residual of the oxidant of choice, based upon the determined concentration requirement, is maintained in order to ensure that any excursions of organic growth are immediately arrested.[2]

However, control by means of this residual method has many shortcomings. The concentration units which residual levels are reported in do not provide an adequate representation of the quantity of organics which will be oxidized. This is because an amount of oxidant will always oxidize the same amount of microorganisms, regardless of the concentration level.[3] Another shortcoming is that the oxidizing ability of 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 the oxidant to do its job while the residual measurement shows nothing.[2-4] Another problem with the residual measurement is that some oxidants can exist in many forms in the water, and residual cannot take into account any changes of the amounts of the various forms (all with varying oxidizing power) within the water.[3,4] Last of all, residual control has little ability to respond to changes in demand, which can occur due to fluctuating organic levels and nitrogen compound levels, as well as any effects of flow, heat, light, or exposure to air. In fact, when the demand increases, the oxidant strength will diminish, although this effect may not be noted by residual measurements.[3,5] As a result of these many shortcomings, control of oxidant addition by residual control will typically result in endless overfeed and underfeed of the oxidant.

This overfeed/underfeed situation will cause two major 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 setpoint 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 which 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.

Research shows that a microorganism's ability to survive in water is mainly influenced by the oxidation/reduction potential (ORP) of the water.[1,3,4,6] This is because the action of an oxidizing microbiocide is to remove electrons from an organism, effectively destroying certain processes which keep the organism alive. Since this transfer of electrons is an oxidation-reduction reaction, ORP gives an indirect measurement of the potential to prevent microbiological growth in the water. ORP has been successfully used to perform accurate control of oxidant addition.[3,4,7,8] 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.

One of the most common questions asked regarding the ORP measurement when used for biocide control is "Can ORP be used to measure residual oxidant (chlorine, bromine, etc.)?" This approach acknowledges that there *is* indeed a problem with the residual control, but obviously lacks a fundamental understanding of exactly *what* the problem is. The hope is simply that ORP will do a better job of measuring the residual oxidant, and can thus take the place of the residual meter. The reasons that ORP is a significant improvement over traditional residual control are missed entirely.

Whereas residual measurements simply respond to the concentration of excess oxidant which exists, ORP responds to the oxidant's toxicity to the organisms.[1,3,4] 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. The dosage required may change significantly from day to day or season to season due to the four reasons listed earlier. However, it is usually observed that control by ORP will significantly reduce the cost of chemicals for a given application while minimizing organism growth. Any costs associated with maintenance for the ORP measurement are small compared to the cost-savings associated with the improved biocide control.

Cooling Water
A power plant cools down the steam exiting the low pressure turbine by passing the steam across a series of tubes filled with cool water known as a condenser (Figure 1). The transfer of heat from the steam to the cool water is a vital part of the efficiency of the plant, since the cooling of the steam forces condensation back to water. This increases the pressure differential between the inlet to the high pressure turbine and the outlet of the low pressure turbine, allowing the steam to do more work. This condensing process must be maintained at an optimal level in order to maximize the megawatt output. However, many factors can work against the component life and efficiency of the condenser, especially microbial growth.

Both micro- and macroorganisms 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.[2] The effects of the organisms are widely varied. Many cooling systems utilize 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 the condenser and buildup in a cooling tower basin. These organisms include barnacles, clams, jellyfish, and mussels. 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 of algae are known to cause silica fouling. Dead algae will collect in the water, increasing the suspended solids which can cause fouling, providing bacterial food which will enhance bacterial growth, as well as absorbing microbiocides which can minimize the effectiveness of microbiological control. Fungi growth 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 which 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.[2]

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 which can clog heat exchangers. Some aerobic bacteria types 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 which cause plugging, pitting corrosion and reduced heat transfer. Certain types of bacteria can destroy nitrite corrosion inhibitors. Other bacteria types can form ammonia, which can attack copper-based construction materials. Safety issues can also arise from bacteria forms known as pneumonia, including the Legionella pneumophilia, which can cause Legionnaires disease.[2]

Control of microbiological growth in a cooling water system is commonly done with chlorine addition, 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). ORP control can be done with a feedback loop with the sensor placed either before or after the heat exchanger, although a location after may be better to ensure that any drop in oxidant levels within the heat exchanger is compensated for. 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.[1,3,4,8,9]

Dechlorination (or a similar removal of another type of oxidizing biocide from the water) for environmental protection is typically 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. 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.[1,3,4,8,9] Not all oxidants require this procedure, since some, such as ozone, will break down quickly on their own.

Makeup Water

All power plants require a constant or periodic intake of water to make up for losses in the steam production process. For example, a power plant's water system is constantly losing some of its water due to sampling systems, steam losses, and blowdown. The needed 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 should be treated to remove and prevent biological growth. City water supply almost always has been treated already with a biocide of some sort, so additional treatment may or may not be necessary.

A typical makeup water system (Figure 2) will perform biocide treatment to the raw water upon entrance to the makeup system.[10] 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. Traditional control maintains a large residual as long as possible in order to discourage further growth. This process is called hyperchlorination. Unfortunately, the amount of oxidant feed necessary can shift often due to changes in flow, raw water organism content, or even varying oxidant levels already present if the raw water is from a municipality.

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 membranes 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 that this may be done – activated carbon beds or chemical injection with sulfur dioxide (SO_2) or sodium bisulfite ($NaHSO_3$).[2,9,10]

Activated carbon beds can actually serve two purposes within a makeup water system – to dechlorinate the water and to adsorb any organics which remain in the water. The efficiency of the carbon beds in removing the chlorine is dependent upon a number of things, including the 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. Maintaining 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 system are employing chemical injection to dechlorinate, and using special anion-exchange resins for organic removal.[2,10]

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 reverse osmosis systems and/or damage to ion exchange resins. However, overfeed of the reducing agent can result in unneeded chemical costs and increased anion-exchange resin regeneration.[10]

Oxidation-reduction potential can successfully be used for two reasons in makeup water – oxidant addition and removal. 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 the oxidant addition and +200 mV or lower for the oxidant removal.[1,3,4,8,9] Control points should be determined by lab analysis for microbiological activity and level of oxidant present.

Water Chemistry Optimization in the Steam / Water Cycle

The ultimate purpose of the water chemistry treatment chosen for a given plant is to prevent corrosion from occurring, which can lower the efficiency of the plant and cause large capital expenditures. The corrosion reactions which can occur on the system metal are oxidation/reduction-based, and thus ORP can be used at various points within the water/steam cycle to establish a baseline for determining the potential for corrosion in the system. Figure 3 shows some of the common points where ORP can be measured in a fossil-based plant. Sampling points in a nuclear power plant would be similar. ORP testing at various plants has shown the potential to vary most with changes in dissolved oxygen and oxygen scavenger, since both affect the oxidizing or reducing environment of the system. Tests done at boiling water reactors (BWR) nuclear plants employing hydrogen water chemistry have shown a direct relation between hydrogen and the corrosion potential as well.

Dissolved Oxygen

Dissolved oxygen plays an important part of the corrosion process on metal surfaces in power plants. Oxygen is an oxidizing substance, so it will directly affect the ORP levels in the system water, causing a more positive potential. Control points of the oxygen concentration vary among different water chemistry treatments, but can typically be summed up in two methods. The first method attempts to remove as much oxygen as possible (typically down to 5 ppb or lower) through some form of mechanical (deaerator) and/or chemical (oxygen scavenger) means. Expected levels of ORP with this method range from as low as -400 mV to as high as 100 mV. The lower potentials will exist when oxygen scavenger is used in addition to mechanical deaeration, while the higher potentials will exist when only mechanical deaeration is used.. The second method maintains a higher level of oxygen (typically 50 to 150 ppb). This method will usually yield potentials between 100 mV to 200 mV, depending upon the level of oxygen maintained in the water. The type of method chosen will determine the expected potentials.[11-15]

Oxygen Scavenger

Oxygen scavengers, such as hydrazine or carbohydrazide, have traditionally been used for chemical removal of oxygen from the system. However, as the understanding of the importance of the system ORP has increased, the role of chemicals such as hydrazine is shifting from that of "oxygen scavenger" to that of "reducing agent." These reducing agents can be useful (or harmful, depending on the system metallurgy) for corrosion prevention since the presence of most "oxygen scavengers" will create a more reducing environment in the system. The results of testing performed at a number of power plants, both nuclear and fossil based, show a more negative ORP with increasing oxygen scavenger concentrations. The addition of these reducing agents will typically yield potentials well below 0 mV, typically as low as -300 mV or more. [11-15]

Hydrogen Water Chemistry

In BWR nuclear plants, hydrogen is often added to the feedwater to avoid stress corrosion cracking of stainless steel piping. It has been shown that the intergranular stress corrosion cracking (IGSCC) of sensitized stainless steel can be minimized by maintaining the system potential below the critical potential, typically -230 mV in high purity water.[16,17] Hydrogen addition to the feedwater decreases the amount of oxidizing species in the reactor water by recombination in the downcomer, and thus reduces the production of oxidizing species from the radiolysis of water in the core.[17] The addition of hydrogen to the feedwater creates a more reducing potential (more negative) due to decrease of oxidizing species which results from the increased hydrogen concentration. The potential of BWR water with "normal" hydrogen water chemistry has been observed to be typically in the range of +50 to +200 mV.[16,17] Only at increased dosages of hydrogen will the potential be seen to drop down to well below the -230 mV range.[16,17]

Location

Typical power plant water has different properties, such as pH, oxygen / oxygen scavenger concentrations, or temperature, depending upon the location in the system. Because of these varying characteristics of the water, as well as different metallurgy used throughout the system, the ORP response (as well as the optimum ORP) can change significantly from one point to another. A change in chemistry in one portion of the system may cause no change in the ORP at one point and drastically alter the readings at another point. This has been observed at many plants. Although the majority of the ORP measurements have been made in the feedwater or economizer, other points in the process are also important to monitor for better characterization of the overall system response to varying changes, such as load increases, leaks, or chemical excursions.

ORP And Corrosion

ORP has a strong relation to corrosion within a system, since the reactions associated with corrosion are oxidation/reduction based. Any oxidants or reductants present in the system are directly linked to corrosion production in a system. Optimal concentration limits of oxidants and reductants vary depending upon the type of metallurgy and the type of water chemistry treatment being done at a plant. Figure 4 shows an example of the optimal control ranges for ORP at the feedwater sampling point in both nuclear and fossil plants for various water chemistry treatments.

All-Ferrous Metallurgy

The trend in past years at most plants has been to remove as much of the dissolved oxygen as possible, which almost always requires addition of an oxygen scavenger such as hydrazine. This can have a detrimental effect in all-ferrous plants, since removing oxygen by oxygen scavenger will lead to a strongly reducing environment (-300 mV or lower), which has actually been seen to increase the erosion/corrosion of iron-based materials as well as increasing the transported feedwater corrosion products.[11-13] It has been observed that high levels of flow-accelerated corrosion (FAC) occur in all-ferrous plants when the ORP is less than -300 mV due to either an oxygen level of less than 1 ppb or oxygen scavenger level of greater than 20 ppb, or both.[13]

The primary oxidation reaction on steel surfaces is the oxidation and dissolution of iron:

$$Fe \Rightarrow Fe^{2+} + 2e^- \tag{4}$$

The two primary reduction reactions on steel surfaces are the reduction of hydrogen (Equation 5) and the reduction of oxygen (Equation 6):

$$2H^+ + 2e^- \Rightarrow H_2 \tag{5}$$
$$O_2 + 2H_2O + 4e^- \Rightarrow 4OH^- \tag{6}$$

The reduction of hydrogen is seen to be favored at more reducing potentials while the reduction of oxygen is favored at higher (more oxidizing) potentials.[18] The optimal ORP control point appears to be somewhat dependent upon the pH of the plant water.[16,19] It has been shown that providing a less reducing environment in all-ferrous plants at the recommended pH levels (typically 8-10 pH depending upon the specific water chemistry treatment) will minimize corrosion product generation.[11-13,16] This can be done by lowering oxygen scavenger levels or eliminating the oxygen scavenger levels and adding oxygen. This process converts the magnetite (Fe_3O_4) to ferric oxide hydrate (FeOOH), which has a much lower solubility.[13]

At one plant, the ORP increased from -340 mV to +100 mV when the level of hydrazine was reduced from 40 ppb to zero. The total iron decreased from 14 ppb to about 5 ppb.[12] At another plant, which has an all-ferrous system, hydrazine feed was discontinued to reduce iron transport. The ORP was observed to increase from -125 mV to -50 mV when the hydrazine dosage was dropped from 20 ppb to 0 ppb. The feedwater pH of 9.2 to 9.6 remained the same during the test period. Iron transport through the feedwater cycle did decrease from an average of about 3 ppb to less than 1 ppb within an 8 month time period following the change in treatment.[14]

Some plants with all-ferrous metallurgy have begun switching to an Oxygenated Treatment (OT) in which a small concentration of dissolved oxygen, typically 50-150 ppb, is maintained in order to minimize corrosion. Conversion to OT will correspond to an oxidizing environment typically on the order of +100 mV or more.[11,12] This has been shown to eliminate flow accelerated corrosion by forming a protective oxide layer on the material surface.[13]

One plant experienced an increase of 500 mV during the transition from reducing to oxidizing operating conditions, during which the corrosion rates dropped to two to three times lower than those experienced during reducing conditions.[19] This highly oxidizing environment is expected since no oxygen scavenger is present and higher concentrations of dissolved oxygen are present, both of which raise the ORP. All-ferrous plants switching to OT and thus more positive ORP levels have experienced significant drops in corrosion products.

Mixed Metallurgy
Systems with mixed metallurgy have been found to have minimal corrosion occurring when a more reducing (more negative) potential is present.[11,20] While understanding of copper alloy corrosion is not yet adequate, a relationship with ORP has been established. Cuprous oxides (Cu_2O) and cupric oxides (CuO) can form on copper base alloys. Formation of cuprous oxide provides a protective barrier adjacent to the metal surface. Cupric oxide can form by oxidation of the cuprous ions. Cuprous oxide formation is thus preferred at lower reducing potentials, while a more oxidizing environment will support the growth of the cupric oxide. Reducing regimes are thus preferred in mixed metallurgy environments. Even when dissolved oxygen levels are kept below the 7 ppb limits typical of mechanical deaeration, an oxygen scavenger such as hydrazine, which lowers the reducing potential, should be maintained, or serious copper deposition problems can occur.[13]

This effect was observed at one plant which has a copper nickel condenser and all-ferrous feedwater heaters.[14] Hydrazine injection had been terminated in an attempt to reduce the potential for erosion/corrosion and iron transport through the boiler cycle. A slow loss in turbine efficiency was observed after the change. It was theorized that oxygen in the boiler water converted copper in boiler deposits allowing it to volatize and deposit on the first stages on the HP turbine. Hydrazine injection was then re-established with a goal on maintaining a more reducing environment in the feedwater and boiler water.

It has also been observed at many plants that optimization of the hydrazine level in copper-based systems can be done with the ORP measurement in order to prevent copper attack by excessive hydrazine levels.[16] ORP monitoring has been used while chemically cleaning boilers to ensure the proper environment to dissolve iron oxide, insure passivation of clean surfaces, and prevent precipitation of copper. Monitoring has also been used in ammoniated EDTA cleanings to prevent corrosion following the iron removal stage.[14]

Conclusions

The measurement of oxidation/reduction potential is by no means new. However, it has only been within the last decade that a significant number of plants have begun to realize the benefits of the ORP measurement in the cooling water, makeup water, and steam/water cycle. The measurement of ORP has shown major improvements in cooling water biological control. Traditional treatment programs utilize residual control of an oxidizing biocide, but ORP control has resulted in improved life for condensers and cooling towers, minimal usage of treatment chemicals for chlorinating and dechlorinating, and increased efficiency of plant processes which utilize the cooling water for heat exchange purposes. The same principles apply for plant makeup water. Control of micro- and macroorganisms, both at the initial intake of raw water and throughout parts of the system, is important to maximize the 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 utilizing residual control of an oxidizing microbiocide, 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 which utilize the makeup water. The ORP measurement has also been seen to be useful in determining the response of the system metallurgy to the water chemistry. ORP has been observed to be affected most by the activity of oxidizing (oxygen) and reducing (oxygen scavenger, hydrogen) species in the water. The ORP of a system has been observed to be directly related to various types of corrosion, such as flow accelerated corrosion (FAC) in all-ferrous plants, intergranular stress corrosion cracking (IGSCC) in BWR nuclear plants, or cupric oxide formation in mixed metallurgy plants. The optimum ORP control point has been seen to vary somewhat from plant to plant, largely depending upon type of water treatment, concentration of oxidizing and reducing species, type of metallurgy, and location of the measurement. ORP has been observed to be equally or more sensitive to system transients as traditional measurements of hydrazine and oxygen concentration. It is expected that ORP will become a standard measurement at multiple points throughout a plant's water/steam cycle, and will be used along with measurements of pH, oxygen and oxygen scavenger concentration in order to optimize the water chemistry.

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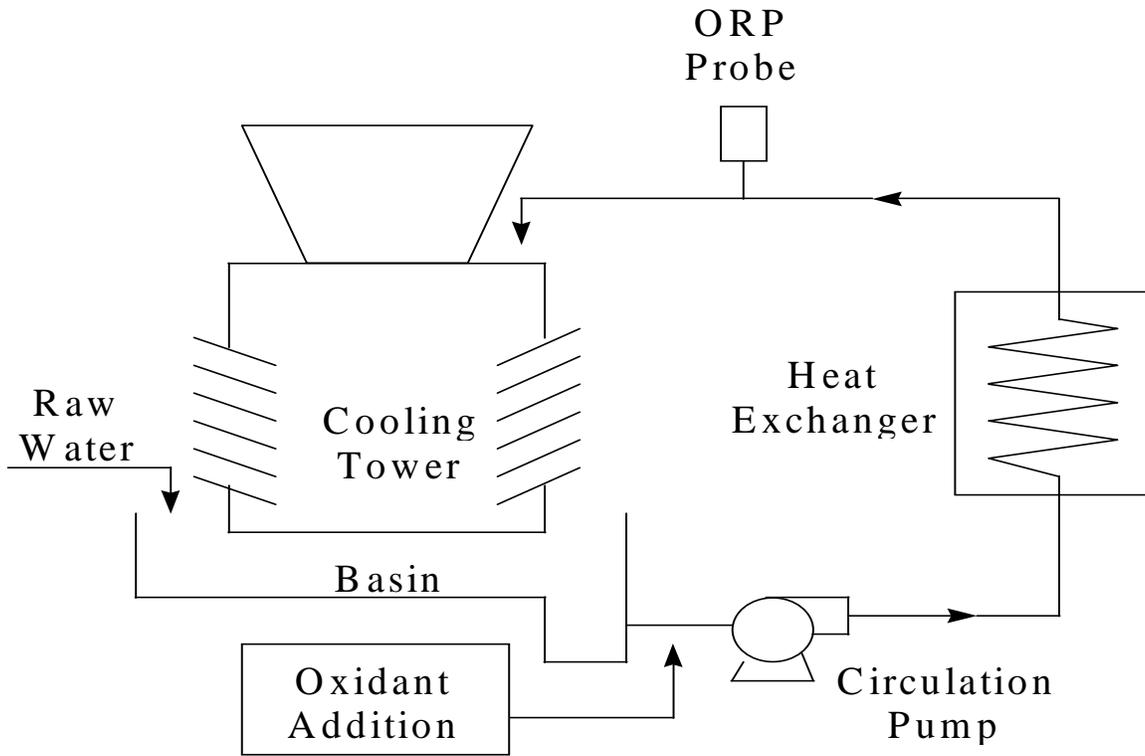
Figure 1: Cooling Tower Water System[21]
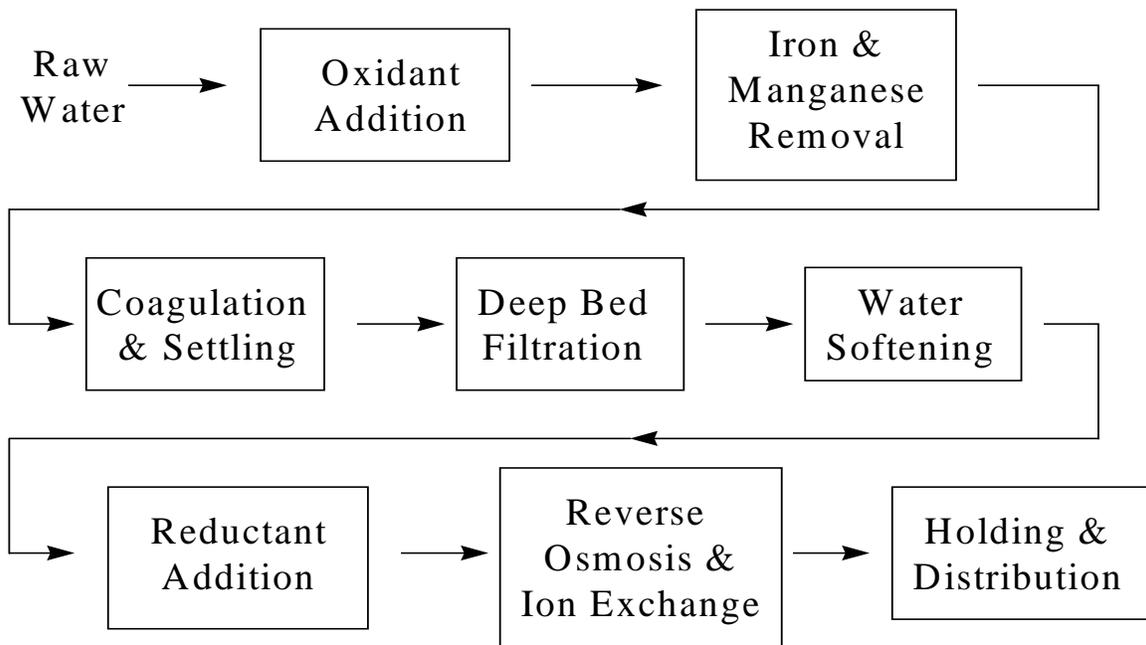
Figure 2: Typical Makeup Water System[21]
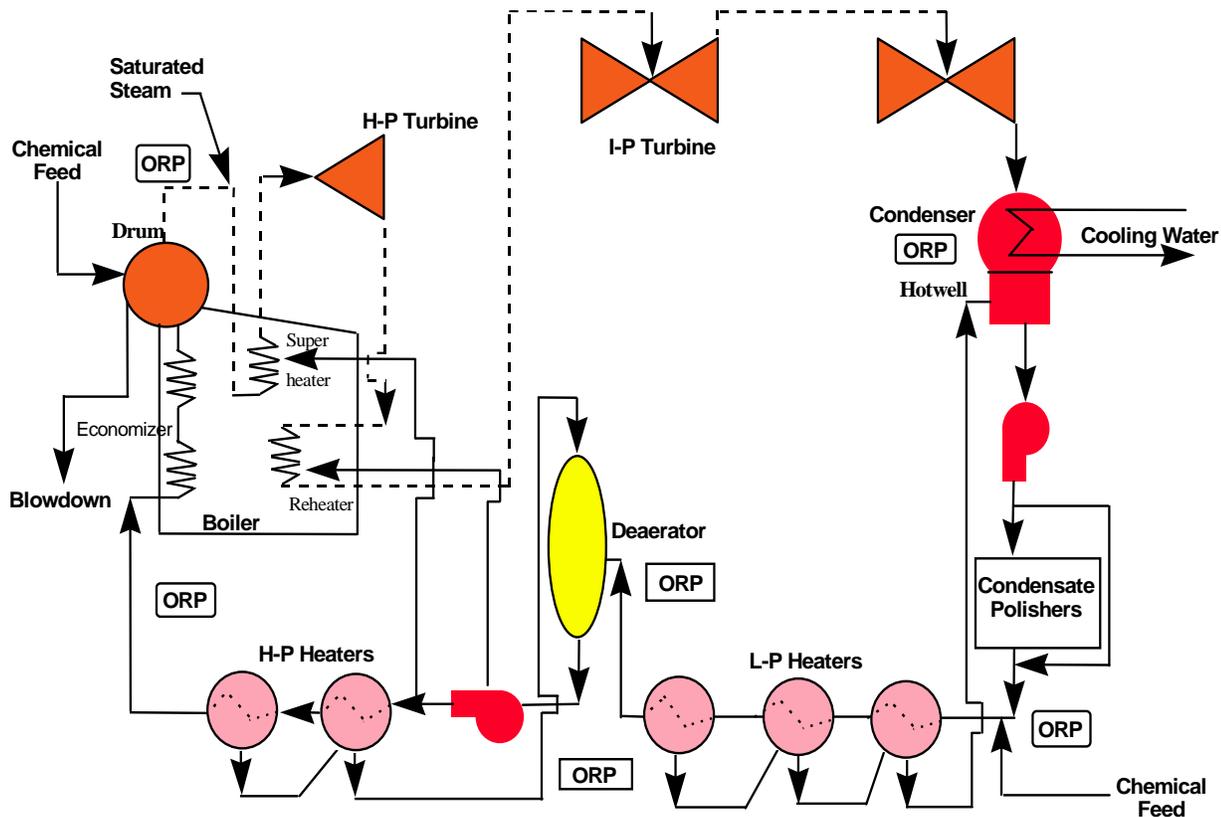
Figure 3: ORP Sampling Points in a Fossil-based Power Plant[15]
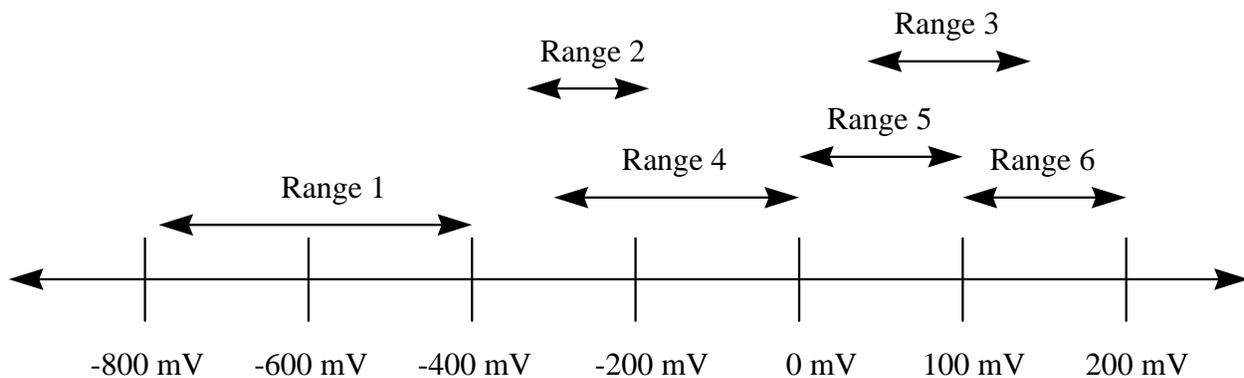
Range 1: Pressurized Water Reactor Nuclear Plant, Primary Side
Range 2: Boiling Water Reactor Nuclear Plant, High Hydrogen Addition
Range 3: Boiling Water Reactor Nuclear Plant, Normal Water Chemistry
Range 4: (a) Pressurize Water Reactor Nuclear Plant, Secondary Circuit
       (b) Mixed Metallurgy Fossil Fuel Plant, Oxygen Scavenger Addition
Range 5: All-Ferrous Fossil Fuel Plant, No Oxygen Scavenger Addition
Range 6: All-Ferrous Fossil Fuel Plant, Oxygen Addition

Figure 4: Typical Oxidation/Reduction Potentials[15]