Monitoring Cooling Water for Potential Reuse – Part I

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Introduction

The challenge to meet the expanding demands of the world's population for water is staggering. Water demand increased worldwide by ten times between 1900 and 2000. The world currently is facing water shortages in Africa, the Middle East, and parts of North America, Asia and Europe. Clearly, many developing countries containing over half of the world's population are currently experiencing water shortages from minor to extreme in nature. The use of water for cooling systems varies greatly by industry. In some industries, such as the electric power generation industry, the cooling needs are very high. In the chemical, petrochemical and refining industries the use of cooling water is essential for the operation of the key processes in those plants. In some areas, due to limitations in water supplies or intermittent drought conditions, water for industrial use is often limited or severely restricted. Many states encourage industries to find ways to reduce water consumption. Therefore, these plants investigate ways to reduce use of water resources. In the plant, the biggest consumers of water are the cooling systems. Because of that fact, they become an obvious place for water savings. However, cooling systems function not only to cool, but also receive contaminants. Due to their very function, they concentrate the chemical constituents and make the blow down desirable to use, but difficult to use without additional treatment. Furthermore, additional chemical testing and online monitoring can aid in making the water usable.

Contents in Reuse Water To Be Concerned About

Discharges or blow down from cooling water systems eventually end up as wastewater unless the plant has a zero discharge program or water reuse program. In the U.S., once the water is discharged into a receiving steam or other body of water, it is subject to the National Public Discharge Elimination System (NPDES) permit program. These permits limit the types and amounts of pollutants that may be discharged. The constituents that are limited vary based on individual state restrictions and the restrictions of the receiving body of water. These permits may be further affected by the Total Maximum Daily Limit (TMDL) that restricts the addition of pollutants to all bodies of water in the U.S. The U.S. Environmental Protection Agency (EPA) or the state issues these permits, if the state has gained primacy from the EPA. The presence of these permits and their restrictions dictate the nature of treatment before discharge. They also affect the decision of whether to discharge or to instead, reuse the water.

The list of potential contaminants in cooling water could be enormous because of the various organic and inorganic chemicals that could leak into a cooling water system. However, the list can be simplified as follows:

- Organic compounds – caused by leakage from process. Online analyzers or laboratory tests for COD, BOD, or TOC can track these compounds.
- pH/alkalinity and Conductivity – pH and alkalinity are key indicators of the overall nature of the water. Conductivity is another general indicator of the water quality.
- Turbidity/Suspended solids – matter that is particulate in nature. Suspended solids sensors can be used for online analysis.
- Dissolved chemicals – ionized chemicals that can be detected by discrete testing and/or specific chemical tests or ion specific electrodes. This subject will not be covered in detail for this article. Examples would be hardness, sulfate, silica, chlorine, etc.
- Microbiological content – cooling water would normally be routinely monitored for microbiological content. High microbial counts could lead to concerns in receiving locations. This subject will also not be covered in detail in this article.

In addition to specific chemical constituents, certain parameters can be measured and are generally part of the NPDES permits. Those constituents include pH, alkalinity, total suspended solids or turbidity (TSS), total dissolved solids (TDS) or conductivity, BOD (Biochemical Oxygen Demand), or COD (Chemical Oxygen Demand) and others. Specific chemical treatments could require additional testing based on the state or local permit requirements. Examples include molybdenum, iron, copper, and others.

When considering a water reuse program, the same limitations in water quality would be considered. The reuse water would be directed to one of the existing water systems in the plant. These could include return back to the cooling water system, to boiler water systems, to fire water systems, or back to other process water systems. Treatment of these waters would be necessary in most cases. The nature of the treatment would depend upon the source.

Testing, Surveillance and Monitoring

Cooling Tower Control

The purpose of a cooling tower is to cool down industrial processes and/or provide cooled water for HVAC control. Hot process water is cooled and then directed through the process, where it absorbs heat and is then sent back to the tower to be re-cooled. Large amounts of water are required as evaporation occurs during the cooling cycle. Since water is very valuable, primary concerns are efficiencies in the design of cooling towers and in chemical treatment of the cooling water. Hot water entering the cooling tower is sprayed through cooler air to speed evaporation. For efficient cooling, it is very important to maintain a large surface area for exposing the water to the air for an extended period of time. These heat transfer surfaces must be protected from corrosion and scale. After the water is cooled, it is collected in a sump and pumped back through the process piping. Proper control of a number of parameters will keep the tower operating efficiently and prevent damage to vital parts from scale, corrosion, and biological growth. As air flows through the tower, airborne contaminants are picked up by the water/air interface. These contaminants would be carried through the system if they were not taken care of prior to distribution. pH is one of many parameters that controls the water chemistry of the tower. Maintaining a pH level between 6.0 and 8.0 is fairly common. Blow down from the cooling tower is concentrated from three times up to ten or more times. This concentrated stream goes to the waste treatment plant, if it exists, for additional treatment and discharge. This stream is subject to study for reuse instead of discharge.

Organic contaminants

The presence of any organic chemical in the reuse stream makes the water unusable for any reuse purpose without further treatment. Acceptable organic levels are essentially near zero. Laboratory tests for organics include the oil and grease test, plus tests for BOD, COD, and TOC. The oil and grease test is used less than the others. A description of the testing and online instruments for COD, BOD, and TOC are listed below:

Chemical Oxygen Demand (COD)

The Chemical Oxygen Demand (COD) test uses a strong chemical oxidant in an acid solution and heat to oxidize organic carbon to CO_2 and H_2O. By definition, chemical oxygen demand is "a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant."[1] Oxygen demand is determined by measuring the amount of oxidant consumed using titrimetric or photometric methods. Toxic substances do not adversely affect the test, and test data is available in 1-1/2 to 3 hours, providing water quality assessment and process control. COD test results can also be used to estimate the BOD results on a given sample. An empirical relationship exists between BOD, COD and TOC. However, the specific relationship must be established for each sample. Once correlation has been established, the test is useful for monitoring and control.

Biochemical Oxygen Demand (BOD)

Biochemical Oxygen Demand (BOD) is the amount of oxygen, expressed in mg/L or parts per million (ppm), that bacteria take from water when they oxidize organic matter. The carbohydrates (cellulose, starch, sugars), proteins, petroleum hydrocarbons and other materials that comprise organic matter enter the water from natural sources and from pollution. They may be dissolved, like sugar, or suspended as particulate matter, like solids in sewage. Organic matter can be oxidized (combined with oxygen) by burning, by being digested in the bodies of animals and human beings, or by biochemical action of bacteria. Because organic matter always contains carbon and hydrogen, oxidation produces carbon dioxide (the oxygen combining with the carbon) and water (the oxygen combining with the hydrogen). Bacteria in water live and multiply when organic matter is available for food and oxygen is available for oxidation. About one-third of the food bacteria consume becomes the solid organic cell material of the microorganisms. The other two-thirds is oxidized to carbon dioxide and water by the biochemical action of the bacteria on the oxygen dissolved in the water. To determine BOD, the amount of oxygen the bacteria use is calculated by comparing the amount remaining at the end of five days with the amount known to be present at the beginning. At room temperature, the amount of oxygen dissolved in water is 8 mg/L. At freezing, it increases to 14.6 mg/L; it also increases at high barometric pressures (low altitudes). At the boiling point, the solubility of oxygen is zero. During the five-day period of a BOD test, the bacteria oxidize mainly the soluble organic matter present in the water. Very little oxidation of the solid (insoluble) matter occurs in that short time.

By comparing the BOD of the incoming water stream and the BOD of the effluent water leaving the plant, the efficiency and effectiveness of sewage treatment can be judged.

Significance of BOD

Measurement of BOD is considered a basic means for determining the degree of water pollution. It is one of the most important measurements made in a wastewater treatment plant. By comparing the BOD of the incoming water stream and the BOD of the effluent water leaving the plant, the efficiency and effectiveness of sewage treatment can be judged. For example, if an incoming water stream has a BOD value of approximately 300 mg/L, and if the effluent from the sewage treatment plant has a BOD of about 30 mg/L, the plant has removed 90 percent of the BOD. If water of a high BOD value flows into a river, the bacteria in the river will oxidize the organic matter, consuming oxygen from the river faster than it redissolves from the air. If this happens, fish will die from lack of oxygen; a consequence known as a fish kill. The blow down stream from a cooling tower can have a high BOD level in some circumstances. This will particularly be true if organics from the process have leaked into the cooling water stream and/or if the microbiological treatment program in the cooling tower has failed or been overwhelmed by process contaminants. It is critical that the BOD level be known to determine the potential value of the water for reuse or to determine if further treatment to remove BOD is necessary.

Measuring BOD

Two methods are widely used for BOD measurement. One method, the dilution method, is a standard method of the American Public Health Association (APHA) and is approved by the U.S. Environmental Protection Agency (USEPA). The other method, the manometric method, has been used for over 75 years in many sewage plants and other installations throughout the world. The dilution method involves placing incremental portions of the sample into bottles and filling the bottles with dilution water. The dilution water contains a known amount of dissolved oxygen. The dilution water contains a portion of inorganic nutrients and a pH buffer. The bottles are completely filled, freed of air bubbles, sealed and allowed to stand for five days at a controlled temperature of 20 °C (68 °F) in the dark. During this period, bacteria oxidize the organic matter using the dissolved oxygen present in the water. At the end of the five-day period, the remaining dissolved oxygen is measured. The relationship of oxygen that was consumed during the five days and the volume of the sample increment are then used to calculate the BOD.

Measurement of BOD by the manometric method is easier because the oxygen consumed is measured directly rather than with chemical analysis. Because the sample is usually tested in its original state (not diluted), its behavior more closely parallels that of the waste in an actual sewage treatment plant. As the oxygen in the sample is used up, more oxygen will dissolve into the water from the above air space. The manometer measures the drop in air pressure in the bottle. This continuous indication of the amount of oxygen uptake by the sample is an important feature of the manometric method. The rate of oxygen uptake at any time is determined from a graph of the results, which also provides considerable insight into the nature of the sample.

Because BOD and COD tests directly measure the amount of oxygen required to stabilize a waste sample, results reflect the original oxidation state of the chemical pollutants.

Total Organic Carbon (TOC)

The Total Organic Carbon (TOC) test uses heat, ultraviolet light, and a strong chemical oxidant (or a combination of these three) to oxidize organic compounds to CO_2 and H_2O. Oxygen demand is measured indirectly by determining the amount of CO_2 produced using infrared spectroscopy, conductivity, or coulometry (an electrochemical technique). The CO_2 is measured and reported as TOC mg/L based on Standard Methods. Because BOD and COD tests directly measure the amount of oxygen required to stabilize a waste sample, results reflect the original oxidation state of the chemical pollutants. This is demonstrated using the following example, where two compounds with the same number of carbon atoms in different oxidation states are oxidized to CO_2 and H_2O.

Oxalic Acid: $C_2H_2O_4 + 1/2O_2 \rightarrow 2CO_2 + H_2O$

Ethanol: $C_2H_6O + 3O_2 \rightarrow 2CO_2 + 3H_2O$

While TOC results are identical for both compounds, the oxygen demand of ethanol is six times greater than oxalic acid, and will thus have a much greater effect on the dissolved oxygen content of receiving water. The key is to understand that TOC and BOD or COD are related but give different types of data. However, the value in using TOC versus BOD or COD is in the speed of the test results. This is particularly important when using online analyzers. This subject is discussed in more detail in Part II.

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