COOLING WATER SYSTEMS, PROBLEMS, OZONATION TREATMENT, AND OZONE DEMAND DETERMINATION

Authored by

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ABSTRACT

Current technology and research concerning the ozonation applications for cooling water treatment are reviewed. The subjects covered in this publication include: (a) cooling systems and problems; (b) corrosion causes, detection, treatment and control; (c) scaling, fouling, deposition treatment and control; (d) microbiological contamination, cooling water treatment, microbiological growth control; (e) ozonation for cooling water treatment including fresh water coolant and sea water coolant; (f) potential cooling water production using ozonation; (g) parameters for ozonation applications, such as residence time, temperature, cycles of concentration, dosage, etc.; (h) testing methods for ozone residual and ozone demand. Special emphasis is directed toward the use of ozonation as a cooling water treatment option and the recommended methods for determination of ozone demand and chlorine demand. Summation includes recommendations for areas of research and calls for further research by the researchers around the world.

KEYWORDS: Cooling Systems, Ozone, Ozonation, Pretreatment, Blowdown, Corrosion Control, Scale Deposition, Microbiological Growth Prevention, Cycles of Concentration, Ozone Demand Determination, Chlorine Demand Determination, Call for Research.
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<table>
<thead>
<tr>
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<th>Definition</th>
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<tbody>
<tr>
<td>AlPO₄</td>
<td>Aluminum phosphate</td>
</tr>
<tr>
<td>AOP</td>
<td>Advanced oxidation processes</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society of Testing of Materials</td>
</tr>
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<td>BAC</td>
<td>Biologically activated carbon</td>
</tr>
<tr>
<td>BOD</td>
<td>Biochemical Oxygen demand</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>Calcium carbonate</td>
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<td>CCM</td>
<td>Mixture chlorine concentration, mg/L</td>
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<tr>
<td>CCR</td>
<td>Chlorine reagent concentration, mg/L</td>
</tr>
<tr>
<td>CDS</td>
<td>Sample's chlorine demand, mg/L</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Chlorine</td>
</tr>
<tr>
<td>COC</td>
<td>Cycles of concentration</td>
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<tr>
<td>COM</td>
<td>Mixture ozone concentration, mg/L</td>
</tr>
<tr>
<td>COR</td>
<td>Ozone reagent concentration, mg/L</td>
</tr>
<tr>
<td>DAOFF</td>
<td>Dissolved air-ozone flotation and filtration</td>
</tr>
<tr>
<td>DBP</td>
<td>Disinfection by-products</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved oxygen</td>
</tr>
<tr>
<td>FePO₄</td>
<td>Ferric phosphate</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular activated</td>
</tr>
<tr>
<td>LIWT</td>
<td>Lenox Institute of Water Technology</td>
</tr>
<tr>
<td>O&amp;M</td>
<td>Operation and management</td>
</tr>
<tr>
<td>O₃</td>
<td>Ozone</td>
</tr>
<tr>
<td>OD-free</td>
<td>Ozone demand free</td>
</tr>
<tr>
<td>ODS</td>
<td>Sample's ozone demand, mg/L</td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solids</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UNIDO</td>
<td>United Nations Industrial Development Organization</td>
</tr>
<tr>
<td>USEPA</td>
<td>US Environmental Protection Agency</td>
</tr>
<tr>
<td>VCR</td>
<td>Chlorine reagent volume, mL</td>
</tr>
<tr>
<td>VM</td>
<td>Mixture volume, mL</td>
</tr>
<tr>
<td>VOR</td>
<td>Ozone reagent volume, mL</td>
</tr>
<tr>
<td>VS</td>
<td>Sample volume, mL</td>
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</table>
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COOLING WATER SYSTEMS, PROBLEMS, OZONATION TREATMENT, AND OZONE DEMAND DETERMINATION

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1. INTRODUCTION

1.1 Cooling Systems

Most of the industrial water supply is used as cooling water. Although "direct air" cooling is feasible for some applications, present technology still employs water as its major coolant. [1-30]

There are three basic types of water cooling systems. While every cooling method is different the design of the system may be one of three: (a) open recirculating cooling system; (b) closed recirculating cooling system; and (c) once-through cooling system. [1, 2, 8]

The open recirculating cooling system (Figure 1) is the most common. Water continuously circulates through a series of heat exchangers and is pumped into a cooling tower where the excess heat of the water is released through evaporation. The same water is recycled through the system continuously with occasional blowdown and makeup to maintain a certain water quality. [2]
The closed recirculating cooling system (Figure 2) uses the same water over and over. The heat is released through another series of heat exchangers and no blowdown or makeup occurs. [2]

In once-through cooling systems (Figure 3) there is a large volume of water used and passed through from influent to effluent only once. Because of the large volume of water the effluent has only a slightly higher temperature. The composition of the cooling water is fairly stable. [2]

Figure 1. Open Recirculating Cooling System [2]
Figure 2. Closed Recirculating Cooling System [2]

Figure 3. Once Through Cooling System [2]
1.2 Problems

The open recirculating cooling system (Figure 1) is the only system which involves a cooling tower and traditionally there have been recurring problems with the treatment of the water. Inadequate treatment of the recirculating water is responsible for three major problems: (a) corrosion of the system, (b) deposition involving scaling and fouling, and (c) microbiological contamination.

The practiced treatment for these problems has been chemical, using a variety of agents and biocides. However, this practice results in chemical residues and hazardous by-products in the water. [4, 8]. It is also not completely efficient to remove bacteria and viruses from the cooling systems. [5]

In recent years the use of ozone (O₃) has been considered as a viable alternative to chemical treatment. [31-50]. Overall test studies have shown that O₃ may actually surpass the chemical treatment approach in terms of effectiveness and cost.

1.3 Objectives

The purpose of this review is to determine the present state-of-the-art approaches to cooling water treatment with special emphasis on ozonation, while the objective is to determine areas where further research is necessary. This will be accomplished by
examining the problems of cooling water and the conclusions drawn thus far concerning ozonation as a remedy. The various parameters of ozone application will also be reviewed to determine the extent of information available. Development of new method for ozone demand measurement is another research objective. Lastly recommendations for further research in the area of cooling water ozonation and ozone analytical measurement.

1.4. Cooling Systems Terminologies

There has been a special partnership of the United Nations Industrial Development Organization (UNIDO) and the US Environmental Protection Agency (USEPA) for transferring the US new and well-established technologies to the developing countries and disseminating the useful technical information to the entire world. Wang and Wang’s recent publication, entitled, "Cooling Tower And Boiler Water Treatment Terminologies" is one of many technology transfer documents prepared by the Lenox Institute of Water Technology (LIWT). It introduces the UNIDO, USEPA, LIWT, and the cooling tower and boiler water treatment terminologies. The terminology subjects cover the following areas: the types of cooling tower and boiler, water treatment systems, evaporation, make-up water, blowdown, drift, leakage, cycle of concentrations, ton of refrigeration, water quality parameters, water quality standards, operational problems, scale, biofilm, fouling, corrosion, inhibitors, chemical treatment, non-chemical physical water treatment, physicochemical treatment, green
innovations, operation and management (O&M), O&M optimization, water recycle, and water reuse considerations.

1.5. Summary

Current technology and research concerning the ozonation applications for cooling water treatment are reviewed. The subjects covered in this publication include: (a) cooling systems and problems; (b) corrosion causes, detection, treatment and control; (c) scaling, fouling, deposition treatment and control; (d) microbiological contamination, cooling water treatment, microbiological growth control; (e) ozonation for cooling water treatment including fresh water coolant and sea water coolant; (f) potential cooling water production using ozonation; (g) parameters for ozonation applications, such as residence time, temperature, cycles of concentration, dosage, etc.; (h) testing methods for ozone residual and ozone demand. Special emphasis is directed toward the use of ozonation as a cooling water treatment option and the recommended methods for ozone demand determination and chlorine demand determination. Summation includes recommendations for areas of research and calls for further research by the researchers around the world.
2. CURRENT TECHNOLOGY FOR PROBLEM CORRECTION

2.1 Causes of Corrosion

The causes of corrosion in once through cooling system and open recirculating cooling systems are the same, however, the problems are intensified in the latter primarily due to the continuous replacement of oxygen in the cooling tower setup. [3] Corrosion is basically the reversion of a metal to its natural state. Major factors influencing the rate of corrosion include the pH, total dissolved solids (TDS), dissolved oxygen (DO) content, flow rates, temperature and chemical agents in the water.

2.2 Corrosion Detection and Treatment

Corrosion rate is determined by hydrogen detection, corrosion probes, meters and coupons. [1, 5] Current treatment for corrosion involves chemical addition to influence the electrical conductivity of the water and hence the corrosion rate. Some typical additives include chromate, silicates, polyphosphate, zinc and organic materials. the use of two or more inhibitors is common. [6, 8, 45-47]

The use of plastic pre-packaged factory assembled cooling tower units has been an alternative to corrosion control due to the fact that the plastic is corrosion resistant. [5] This is an option to be considered according to the needs of the individual company.
2.3. Ozonation in Corrosion Control

In a Japanese study it was found that the effect of dissolved ozone on metals increased the corrosion rates for low alloy steels, copper and brass at various water flow rates. [7]. A series of Russian tests confirmed these results for steel and recommended specific grades of stainless steel to be used in equipment for ozonizing water.

Ozonation does have a corrosive effect on metals due to its raising the dissolved oxygen (DO) content of cooling water. However, the use of ozone instead of chemical treatments produces a corrosion rate up to 50% less than that observed under chemical treatment [9-12]

Ozonation in conjunction with the addition of a polyphosphate inhibitor (in a German cooling tower) [13] was shown to decrease corrosion and pitting in the heat exchangers.

The amount of corrosion regardless of the treatment will vary with temperature, metal type, velocity of water flow, and pH. [3, 6]

2.4. Causes of Deposition, Scaling, Fouling

Corrosion and deposition are closely linked, both being somewhat dependent on the physical makeup of the water.

Suspended or dissolved solids in the cooling water are the primary causes of severe scaling and fouling of the cooling equipment. [5, 8] The principle scale causing substance in cooling water is calcium carbonate (CaCO$_3$) which when it reaches its solubility limit results in precipitation of scale on tubing surfaces. [5]. Scale is mostly inorganic and can be calcium phosphate,
magnesium salts and silica as well as CaCO$_3$. [2]

Fouling is an accumulation of solids other than scale [1] e.g. dirt, corrosion products, organics, microbial masses, aluminum phosphate (AlPO$_4$) and iron phosphate (FePO$_4$).

There are several physical factors determining the potential for scale in water. They are temperature, pH, amount of scale forming material and the influence of other dissolved materials such as calcium, sulfate, magnesium, and silica as well as the rate of heat transfer. [2, 3]

Fouling and scaling deposition is undesirable because it promotes corrosion and hinders the performance of the heat exchanging equipment. [1, 5, 8]

2.5 Treatment for Deposition Control

Scaling in the water is controlled by chemicals, oxygen and carbon dioxide which unfortunately have a positive influence on corrosion. [5]

Typically, organic phosphonates, polyacrylates and surface active reagents are used to remove deposits containing high iron and silica and prevent additional deposition. [2, 3, 8]

Deposition is controlled mechanically by tower basin cleaning, blowdown, and filtration. [17]

Present treatment for fouling and scale can be summarized as follows: (a) pretreatment of cooling water to remove scale forming minerals; (b) acidification to keep scale-forming minerals dissolved; and (c) mechanical adjustments to the system and the use of inhibiting chemicals. [2]
2.6 Ozonation in Deposition Control

Recent testing of ozone for treatment of cooling water from different sources indicates several common findings. Ozonation leads to no biofouling, algae growth or biological slime. Ozone removes scale. Inorganic materials are removed by precipitation using ozone as a flocculating agent. Total dissolved solids (TDS) are also reduced. [14]

Ozone, combined with flocculation, sedimentation and filtration assures the highest quality process water. [13].

2.7 Cause of Microbiological Contamination and Treatment Technology

A few years ago, the isolation of Legionella responsible for Legionnaires disease initiated concern for the reduction of bacterial and viral contaminants in cooling tower water. Apart from the now obvious health hazards, some bacteria, fungi, yeasts and algae are contributors to the overall fouling and corrosion problems already discussed. [2] Those cooling systems which have a source of oxygen, open recirculating and once through have problems with microbial contamination.

Traditional treatment of this problem has been the addition of chemical biocides, the most popular being chlorine. The advantage of chlorine is its excellent ability to kill microbes. However, there has been some concern recently over the health effects of chlorine's disinfection by-products (DBP). Also, chlorination doesn't penetrate as do the non-oxidizing biocides and bio-dispersants. Cooling towers offer a favorable warm environment for microorganism growth. Eventually some microorganisms develop a resistance to a particular biocide. This leads to the
frequent alternation of the chemical [14].

2.8 Ozonation for Control of Microbiological Growth

The most positive results for cooling water treatment with ozone come in the area of microbiological growth (Tables 1, 2). Tests have shown that ozone inhibits or actually eliminates this problem. [5, 8, 14, 15] It was the French who began using ozonation for bacterial disinfection and viral inactivation [20, 21, 22].

In a study done using ozone treatment for cooling water in an air conditioning system the conclusion was that ozone could potentially eliminate Legionnaires disease from a cooling tower system. Ozonation gave a lower total plate count (7,000 - 54,000 colonies/mL) than the average chemical treated cooling tower. [15] Section 4.1 further illustrates the effect of ozonation on reduction of total plate count.

2.9. Recent Advances in Cooling Water Control Technologies

Wang and Wang's memoir, entitled, "Cooling Tower And Boiler Water Treatment Technologies" [8] is another technology transfer documents which introduces the recent advances in cooling tower and boiler water treatment technologies. Their publication [8] covers the following areas: the types of cooling tower and boiler, water treatment systems, evaporation, make-up water, blowdown, drift, leakage, cycle of concentrations, ton of refrigeration, water quality parameters, water quality standards, operational problems, scale, biofilm, fouling, corrosion, inhibitors, chemical treatment, non-chemical physical water
treatment, physicochemical treatment, green innovations, operation and management (O&M),
O&M optimization, boiler blowdown, chiller management, water recycle, and water reuse
considerations.

TABLE 1

Ozone Treatment Of Plant Cooling Water [30]

(Average applied ozone dosage 0.4 mg/L)

<table>
<thead>
<tr>
<th>Season</th>
<th>Standard Plate Count Organisms/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer</td>
<td>400</td>
</tr>
<tr>
<td>Autumn</td>
<td>567</td>
</tr>
<tr>
<td>Winter</td>
<td>245</td>
</tr>
<tr>
<td>Spring</td>
<td>1546</td>
</tr>
</tbody>
</table>
TABLE 2

Ozone Treatment Of Cooling Water In A Solvent Plant [30]

(average applied ozone dosage = 0.4 mg/L)

<table>
<thead>
<tr>
<th>Season</th>
<th>Standard Plate Count Organisms/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter</td>
<td>2343</td>
</tr>
<tr>
<td>Spring</td>
<td>1983</td>
</tr>
</tbody>
</table>

21
Aqueonics Division of Arco Environmental, Inc., USA, studied the utilization of ozone as the single treatment for air conditioner cooling water. They concluded that ozone was effective as a disinfectant, and consistently reduced the concentration of total dissolved solids, alkalinity, hardness, calcium, and magnesium. [5]

U. S. Ozonair of South San Francisco, California, USA, has reported that a properly sized and designed ozonation system unconditionally guarantees sterilized water. Ozone destroys total bacteria, E. Coli and viruses. As little as 0.2 mg/L of dissolved ozone in water will not permit microbial life to reproduce. [15]

The apparent difference in the amount of biological growth has to do with the ratio of ozone to water. Arco used .007 mg/L while U.S. Ozonair used as much as .2 mg/L. [5, 15].

The effect of ozonation as a disinfectant is partially dependent on the amount of particulate matter in the water. An increasing amount of particles has a negative effect on the inactivation of bacterial and viral entities by ozone disinfection. [18].

In cooling systems where blowdown operation remains necessary, Nakayama et al, determined that while ozone-injected water remained free from algicidal fouling, the numbers of bacteria and planktonia in receiving waters were not affected. [19].
3. PRETREATMENT WITH OZONE

3.1 Ozone and BAC as a Pretreatment of Secondary Effluent for Use as Cooling Water

A study was undertaken by Jacobs Engineering Group Inc., USA, investigating the possibility for pretreatment of potential cooling water using both ozone and granular activated carbon (GAC). Table 3-5 summarize the results. [23]. Basically when ozone dosage increased, total organic carbon (TOC) levels decreased more than when only biologically activated carbon (BAC) technology was applied. Also the rate of carbon usage had an inverse relationship with ozone dosage. [24].

Preozonation of water to be treated with biologically activated carbon (BAC) enhanced the removal of organic micro-pollutants by BAC alone. [16, 17].

3.2 Ozone Treatment of Seawater Coolant

Marine Research Inc. examined the effectiveness of ozonation for reducing slime buildup in a cooling system. The results indicated that ozone treatment was less effective in reducing slime growth than chlorine. This is in contradiction to the literature which suggests ozone is a better biocide. The author suggests that discrepancies might be explained by the non-existence of ozone residual in seawater and that the measured oxidants are similar to those produced upon chlorination of sea water. [24] This is supported by R. S. Ingols in a paper dealing with
ozonation of sea water. [25] The same researchers found that ozone was more effective using a fresh water coolant. [26]

3.3 Ozone Pretreatment to Eliminate Tertiary Treatment for Potential Cooling Water

Merril and Parker [27] found that ozone controlled corrosion and biofouling. Scaling, however, was not prevented at economically justifiable level.

TABLE 3.
Effect Of Ozone On Toc Levels [23]

<table>
<thead>
<tr>
<th>Ozone (mg/L)</th>
<th>Initial TOC (mg/L)</th>
<th>Final TOC (mg/L)</th>
<th>TOC Redu. (mg/L)</th>
<th>TOC Redu. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>81.5</td>
<td>81.5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>26</td>
<td>81.5</td>
<td>77.0</td>
<td>4.5</td>
<td>5.5</td>
</tr>
<tr>
<td>60</td>
<td>81.5</td>
<td>73.0</td>
<td>8.5</td>
<td>10.4</td>
</tr>
<tr>
<td>159</td>
<td>81.5</td>
<td>60.0</td>
<td>21.5</td>
<td>26.4</td>
</tr>
</tbody>
</table>
### TABLE 4

Effect Of Ozonation-Biodegradation On Toc Levels [23]

<table>
<thead>
<tr>
<th>Ozone (mg/L)</th>
<th>Initial TOC (mg/L)</th>
<th>Final TOC (mg/L)</th>
<th>TOC Redu. (mg/L)</th>
<th>TOC Redu. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>—</td>
<td>81.5</td>
<td>74.0</td>
<td>7.5</td>
<td>9.2</td>
</tr>
<tr>
<td>26</td>
<td>77.0</td>
<td>71.0</td>
<td>6.0</td>
<td>7.8</td>
</tr>
<tr>
<td>60</td>
<td>73.0</td>
<td>65.0</td>
<td>8.0</td>
<td>11.0</td>
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<tr>
<td>159</td>
<td>60.0</td>
<td>44.0</td>
<td>16.0</td>
<td>26.7</td>
</tr>
</tbody>
</table>

### TABLE 5

Carbon Usage Rates [23]

<table>
<thead>
<tr>
<th>Ozone Dosage (mg/L)</th>
<th>Carbon Usage Rates (kg AC/m$^3$ Flow)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.06</td>
</tr>
<tr>
<td>26</td>
<td>0.04</td>
</tr>
<tr>
<td>60</td>
<td>0.03</td>
</tr>
<tr>
<td>159</td>
<td>0.02</td>
</tr>
</tbody>
</table>
3.4 Cooling Tower Water Treatment by Dissolved Air-Ozone Flotation and Filtration

Lenox Institute of Water Technology (LIWT) has conducted many basic and applied research in the area of cooling water treatment and ozonation [8, 32, 35, 38, 43-44, 48-59]. An ozone-assisted physical-chemical treatment process involving the use of chemical coagulation-precipitation, clarification (either sedimentation or flotation) and filtration for cooling tower raw make-up water treatment, side-stream recirculating water treatment, or blowdown water treatment was one of many LIWT projects using bench-scale laboratory tests, continuous pilot plant demonstration, and full-scale cooling tower operation. [48-58] Only the preliminary laboratory data [58] are introduced at this stage. The results show that 95 % of iron ions, 67.8 % of copper ions, 100 % of total coliform bacteria, and over 98 % of total hardness can be removed by the ozone-assisted dissolved air-ozone flotation and filtration (DAOFF) process system. The DAOFF system may be adopted for (a) production of cooling tower make-up water using raw reservoir/stream water or raw groundwater water as the source water; (b) treatment of cooling tower side-stream recirculation water for scale removal, new scale prevention, corrosion, bacteria disinfection, algae control and water purification; or (c) treatment of cooling tower blowdown water for final discharge to a deep well (without groundwater contamination), an ocean, or a receiving water (without thermal pollution nor excessive TDS). Ozone kills all bacteria slimes which commonly bind the scale on the metal surface, and keeps the hardness in suspension, so the suspended hardness will not form scale, and may be effectively removed by filtration.
4. PARAMETERS FOR OZONE APPLICATIONS

4.1 Residence Time

The various parameters for ozone application include: (a) residence time, (b) temperature limits, (c) cycles of concentration, (d) dosage, and (e) others.

The literature contains several different suggestions for residence time depending on the specific cooling system tested and the amount of treatment necessary. [9, 14] There were no available standards for residence time as residence time is a function of the individual system. Table 6 shows reduction of total plate count as a function of time using ozone application.
TABLE 6.
Reduction of Total Plate Count As A Function Of Time Using Ozone Application [15]

<table>
<thead>
<tr>
<th>Total Plate Count (#/mL)</th>
<th>Residence Time (week)</th>
</tr>
</thead>
<tbody>
<tr>
<td>62000</td>
<td>0</td>
</tr>
<tr>
<td>630</td>
<td>1</td>
</tr>
<tr>
<td>420</td>
<td>2</td>
</tr>
</tbody>
</table>

4.2 Temperature

Temperature limits were also a function of the individual system and process. This may be a
determining factor in the efficiency of an ozonation system. Solubility of ozone is dependent on
temperature and pressure. [14] As temperature goes up ozone solubility decreases. Table 7
shows the effect of water temperature on ozone solubility under an unknown pressure. The
higher the pressure, the higher ozone solubility will be.
TABLE 7
Solubility of Ozone in Water as a Function of Water Temperature.

<table>
<thead>
<tr>
<th>Water Temperature (°C)</th>
<th>Ozone Solubility (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1100</td>
</tr>
<tr>
<td>10</td>
<td>800</td>
</tr>
<tr>
<td>20</td>
<td>575</td>
</tr>
<tr>
<td>30</td>
<td>400</td>
</tr>
<tr>
<td>40</td>
<td>300</td>
</tr>
<tr>
<td>50</td>
<td>200</td>
</tr>
<tr>
<td>60</td>
<td>90</td>
</tr>
</tbody>
</table>

Experiments were done by a utility company in New Jersey, USA, using varying temperature changes, ranges and differing ozone concentrations. Their recommendations include testing efficiency of ozone under differing application schedules.

4.3 Cycles of Concentration

Cycles of concentration (COC) is a technical term used to describe the mass flow relationship between the amount of system feed water and the amount of blowdown sent down the drain. It is sometimes referred to as cycle or concentration ratio. COC compares total dissolved solids (TDS)
in makeup water with concentrated TDS in the circulating water through evaporation. COC is determined by calculating the ratio of the concentration of TDS in the blowdown water compared to the TDS in make-up water. TDS enters the system in the make-up water and exits the system in the blowdown water. COC is also approximately equal to the ratio of volume of make-up to blowdown water, using the following equation, where makeup refers to the fresh water added to the system and blowdown refers to the water being drained from the system. \[ COC = \frac{\text{Makeup water, gallons/minute}}{\text{Blowdown water, gallons/minute}} \]. COC can also be estimated by dividing the conductivity of the water in the system by the makeup water conductivity. For example, chlorides are soluble in water, so the cycles of concentration are equal to the ratio of chlorides in circulating water to chlorides in makeup water. From this COC value, an operator can calculate the required water blowdown in order to replenish the loss in evaporation. A cooling tower operator wants to maximize COC which will minimize blowdown water quantity and reduce make-up water demand. However, this can only be done within the constraints of your make-up water and cooling tower water chemistry. TDS increases as COC increases, which can cause scale and corrosion problems unless carefully controlled. [8]

Concentration cycles in various ozonation studies range from 30 - 50. [15] which is very encouraging. The Jet Propulsion lab testing concluded that further study is recommended to determine the limits of temperature, ambient conditions and ozone concentration. [9]

4.4 Dosage
Again dosages used were varied and geared to suit the cooling system tested. Dosages ranged from .01 mg/L to 0.4 mg/L. 0.4 mg/L was used by Emery Industries as a continuous application. This successfully treated 4000 gpm (gallons per minute). [31]

4.5 Additional Parameters

Additional parameters affecting ozonation including pH, pressure, etc., can be found from another extensive report by Dr. Lawrence K. Wang in his US National Technical Information Service report. [35]

5. Testing Methods for Ozone Residual and Ozone Demand

5.1. Ozone Residual Determination

J. D. Johnson proposes and reviews several methods for ozone testing. [31]. R. G. Rice [4] suggests four viable alternatives: (a) potassium Iodide method (ASTM) [31]; (b) ultraviolet (UV) absorption method; (c) amperometric method and (d) amperometric membrane electrode method.

F. L. Evans III [33] suggests the Leuco crystal violet method as a more sensitive approach. Calibration curves are available for this method and the KI method. Evans [33] suggests that new methods capable of detecting sub-mg/L levels of ozone be developed.
Ozone determination in the laboratory is readily accomplished using either the old standard Iodometric Titration Method [59], or the new standard Indigo Colorimetric Method [60]. The new Indigo Colorimetric Method [60] is quantitative, more selective, and simpler in comparison with the old Iodometric Titration Method [59] which measures total oxidant, unless the substances subject to interferences are removed or masked. Therefore, the traditional Iodometric Titration Method has the advantage of measuring the total oxidant concentration by not eliminating the other oxidant's interferences in ozone analysis.

Ozone is very unstable, and there is no ozone standards commercially available. Ozone must be generated by an ozone generator on site using air and/or oxygen gas as the raw materials. The titration method can determine the ozone concentration at the end point by calculation based on the strength of the titrant. This is another advantage of the Iodometric Titration Method over an colorimetric method for ozone residual analysis. It is difficult for an environmental chemist to plot ozone calculation curves when ozone standard solutions are not available for colorimetric analysis.

The Lenox Institute of Water Technology (LIWT) has conceived the idea of combining the advantages of both the titration method (which is able to determine the strength of ozone based on the titrant's known strength) and the colorimetric/spectrophotometric method (which is able to determine the ozone concentration quickly), so the analysis will be accurate and quick. Wang and Wang's recent [51] publication introduces: (a) ozone residual determination by iodometric titration-assisted spectrophotometry; (b) total oxidant determination by iodometric titration-assisted spectrophotometry; (c) traditional ozone residual determination by iodometric titration method; (d) ozone residual determination by iodometric titration-assisted indigo colorimetric method. The new methods use identical chemical reagents required for ozone residue analysis.
by a historical standard iodometric titration method, but need no titration step once a set of ozone calibration curves is established for subsequent spectrophotometric analysis. The basic principle involves the liberation of iodine from a potassium iodide solution in the presence of ozone residue (and other oxidants if the interferences are purposely not eliminated). After an acidification step for fixation of the ozone content (or total oxidant content, if intended for total oxidant analysis) in solution the liberated iodine by ozone (and other oxidant, if included) produces a yellow color. The degree of color intensity is proportional to the original ozone concentration in water, and can be measured spectrophotometrically or colorimetrically. The range of ozone concentration measurable is from 0.03 to 6.0 mg/L. The new method has a precision of ± 1% for ozone concentrations of 3 mg/L or greater. For total oxidant determination, the oxidant interferences are not eliminated, and the results will be expressed as total oxidant as "mg/L of O$_3$". The total oxidant "as mg/L of O$_3$" can also be converted to "as mg/L of Cl$_2$" by mathematical calculation. The authors recommend that the traditional iodometric titration method be restored to be one of the Standard Methods for ozone residual analysis.

5.2. Ozone Demand Determination

5.2.1 Approximate Indirect Ozone Demand Determination Method

5.2.1.1 Chlorine Demand Determination

The procedure for chlorine demand determination can be outlined as follows:
1. Take a water sample containing organic matter and/or inorganic reducing agents for analysis of its chlorine demand (CD), and measure its sample volume, VS. Its chlorine demand CDS is unknown and to be determined.

2. Take a chlorine reagent, with known volume, VCR, and known concentration of chlorine reagent, CCR

3. Add the chlorine reagent into the water sample for chlorine residual determination in accordance with the Standard Methods [60]. If the resulting chlorine residual is measured to be zero, increase VCR and/or CCR, and repeat procedures 1 through 3, until there is chlorine residual showing up in the sample-reagent mixture. Record the chlorine residual as CCM (i.e. chlorine concentration of the mixture). Calculate the volume of mixture VM = VS + VCR. The following is a material balance equation (Equation 1) showing that the input chlorine minus chlorine demand equals the mixture' chlorine residual.

\[ VCR \times CCR - VS \times CDS = VM \times CCM \]  

Since chlorine reagent volume VCR (mL), chlorine reagent concentration CCR (mg/L), sample volume VS (mL), mixture volume VM (mL), and mixture chlorine concentration CCM (mg/L) are all known, the sample's chlorine demand CDS (mg/L) can then be calculated by Equation 1. Chlorine demand text must give sufficient contact time, and the contact time for chlorination reaction shall be specified in the test.

5.2.1.2 Approximate Ozone Demand Determination
The sample's chlorine demand (CDS) is not its ozone demand (ODS), but should be approximately equal to ODS because both are strong oxidizing agents. The sample's approximate ozone demand (ODS) can be calculated by Equation 2.

\[
\text{Approximate ODS} = \text{CDS} \times \left( \frac{O_3}{Cl_2} \right)
\]  

(2)

Accordingly

\[
\text{Approximate ODS} = \text{CDS} \times \left( \frac{3 \times 16}{2 \times 35.45} \right) = 0.677 \text{ CDS}
\]  

(2a)

The units of ODS and CDS are both mg/L.

5.2.2 Direct Ozone Demand Determination

Ozone is a very unstable gas, and it must be generated on-site with an ozone generator. Since ozone gas cannot be stored in a pressurized cylinder like chlorine gas, and there is no ozone reagent with known concentration available, like chlorine reagent, determining ozone demand is not an easy task. Section 5.2.1 has introduced an approximate ozone demand (OD) determination procedure. With an approximate OD value, it will be quicker when a direct ozone demand determination is intended. Nevertheless, having an approximate OD value is not required for the direct OD determination.

The procedure for direct ozone demand determination can be outlined as follows:

1. Take a water sample containing organic matter and/or inorganic reducing agents for analysis of its ozone demand (OD), and measure its sample volume, VS. Its ozone demand ODS is unknown and to be determined.
2. Prepare an ozone reagent by bubbling ozone gas (which is generated on-site by an ozone generator) into a BOD bottle containing ozone-demand-free distilled water and a magnetic mixing bar). Filling the BOD bottle up with the OD-free distilled water to the bottle up, and seal the bottle with a BOD bottle stopper tightly without gas space. Place the BOD bottle on a magnetic mixing device for mixing making sure the ozone concentration is uniform within the bottle. Quickly determine the ozone reagent's ozone residual of BOD bottle water in accordance the either the Standard Methods [60] or the Wangs' iodometric titration-assisted spectrophotometry [51]. Keep the BOD bottle being sealed immediately after water sampling. The latter's spectrophotometry [51] is a quick measurement once a calibration curve is established. At this stage, the concentration of ozone reagent COR (mg/L) is known.

3. Transfer a known volume of the ozone reagent (VOR) from the remaining BOD bottle into a known volume of water sample (VS) for ozone residual determination in accordance with the Standard Methods [60] or the Wangs' iodometric titration-assisted spectrophotometry [51]. If the resulting ozone residual is measured to be zero, increase VOR and/or COR, and repeat procedures 1 through 3, until there is ozone residual showing up in the mixture. Record the ozone residual as COM (i.e. ozone concentration of the mixture). Calculate the volume of mixture VM = VS + VOR. The following is a material balance equation (Equation 3) showing that the input ozone minus ozone demand equals the mixture' ozone residual.

\[
VOR \times COR - VS \times ODS = VM \times COM
\]

(3)
Since ozone reagent volume VOR (mL), ozone reagent concentration COR (mg/L), sample volume VS (mL), mixture volume VM (mL), and mixture ozone concentration COM (mg/L) are all known, the sample's ozone demand ODS (mg/L) can then be calculated by Equation 3. Since ozonation needs sufficient contact time, ozone demand text must give sufficient contact time, and the contact time for ozonation reaction shall be specified in the test.
6. SUMMARY AND CALL FOR FURTHER RESEARCH

After reviewing the literature several areas for study have been recommended.

First it is evident that further information is necessary to define limits for application such as residence time, dosage, cycles of concentration and temperature limits for the most efficient ozone application.

Secondly, the area of pretreatment of water for ozonation may be further investigated. Also the use of ozonation as part of a pretreatment regime in conjunction with other processes such as flotation, filtration, activated carbon treatment, ultraviolet (UV), advanced oxidation processes (AOP) [36], etc. should be investigated. All this is for the purpose of producing higher quality cooling water.

Thirdly, while various methods for the determination of ozone exist, this area should be examined to produce alternative methods or improve existing ones to facilitate on-site testing and eliminate various interferences. The sensitivity and dependability of residual ozone testing and ozone demand determination could possibly be made more efficient.

Finally for water quality control of any ozonation research, various analytical techniques in addition to ozone analysis, need to be developed.
Chlorine demand: The difference between the amount of chlorine applied to a treated water supply and the amount of free, combined, or total available chlorine remaining at the end of the contact period. The chlorine demand is determined by the amount of chlorine oxidizable material present in the water.

Closed circuit cooling tower: There is no direct contact between the air or cooling tower water and the cooling fluid or refrigerant. The system contains an external and an internal circuit. The internal circuit consists of tube bundles (closed coils) that are connected to a heat exchanger for the hot refrigerant, which is cooled and returned in a closed loop. The external circuit is used to cool the internal circuit by recirculating and evaporating water like an evaporative condenser. Air is drawn through the recirculating water cascading over the outside of the hot tubes.

Corrosion inhibitor: It is a substance that slows or prevents corrosion by formation of a protective film on the interior surface of pipes, tubes, or tanks.

Corrosion: Corrosion is an electrochemical or chemical process that leads to the destruction of the system metallurgy. Corrosion is enhanced by elevated dissolved mineral content in the water and the presence of oxygen, both of which are typical of most cooling tower systems. There are different types of corrosion encountered in cooling tower systems including pitting, galvanic, microbiologically influenced, and erosion corrosion, among others. Loss of system metallurgy, if pervasive enough, can result in failed heat exchangers, piping, or portions of the
cooling tower itself.

**Disinfection:** It is a process of destroying or inactivating pathogenic organisms (bacteria, viruses, fungi, protozoa, etc.) by physical and/or chemical means.

**Legionnaires’ disease, or Legionellosis:** It is a disease which can be caused by Legionella bacteria in cooling towers. Tighter regulations and control on cooling tower operators mean that effective control of Legionella is essential for cooling tower operations.

**Once-through cooling system:** In once-through cooling systems, there is a large volume of water used and passed through from influent to effluent only once. Because of the large volume of water the effluent has only a slightly higher temperature. The composition of the cooling water is fairly stable.

**Open circuit cooling tower systems:** In open circuit systems the recirculating water returns to the tower after gathering heat and is distributed across the tower where the water is in direct contact with the atmosphere as it recirculates across the tower structure. They are designed to maximize air and water contact to provide as much evaporation as possible. This is accomplished by maximizing the surface area of the water as it flows over and down through the tower structure.

**Ozone (O₃):** It is an unstable gas with three oxygen atoms, and has a pungent odor. Since ozone is very reactive, it must be produced on-site using ambient air or oxygen. It is a strong oxidizing agent. Ozone has been used for decades as a primary disinfectant for industrial and municipal water treatment. Ozone possesses one of the highest redox levels compared to other oxidizing biocides, making it suitable for neutralizing waterborne bacteria. A small amount of
ozone, such as, 0.1 ppm, with a contact time of 5 min will neutralize 99.9 percent of *Legionella* bacteria, especially in the presence of UV.

**Ozone demand:** The difference between the amount of ozone applied to a treated water supply and the amount of ozone residual at the end of the contact period. The ozone demand is determined by the amount of ozone oxidizable material present in the water.

**Ozone systems:** An ozone system is a process equipment (ozonator) that produces ozone as a disinfectant to kill or inhibit the growth of microorganisms, and as an oxidizing agent to destroy organic pollutants (such as BOD, COD, TOC) and certain inorganic pollutants (such as hydrogen sulfide). It is difficult to maintain an effective residual of ozone throughout a cooling water system because of ozone’s high reactivity and fast dissipation. Successful application of ozonation for biological control requires that sufficient ozone-generating capacity be provided to sustain a level of ozone residual that will control microbial contamination throughout the cooling-water system.

**Scale (or hard water scale):** It is a coating or precipitate deposited on metal, glass, or ceramic surfaces. Boiler water, heat exchanger water, cooling tower water, etc. that contain carbonates or bicarbonates of calcium or magnesium are likely to form scale when heated. Scale is mainly caused by supersaturation of a hardness compound in the hot bulk water. So it is a big problem for operation and management (O&M) of a cooling tower.

**Scale and biofilm buildup:** Buildup of scale and biofilms on cooling tower surfaces will inhibit heat transfer and adversely affect cooling tower performance.
**Scale inhibitor (or scale prevention compound, or antiscalants):** It is a chemical additive, such as sodium polyphosphate, that prevents the buildup and formation of a scale.

**Scaling:** Scaling is the precipitation of inorganic dissolved solids that have become saturated in water. Scale formation reduces the heat exchange ability of the system because of the insulating properties of scale, making the entire system work harder to meet the cooling demand.

**Sterilization:** It is a process of destroying all forms of microorganisms on and in an object by physical and/or chemical means.

**Total coliform:** Bacteria of the family Enterobacteriaceae including all aerobic and facultative anaerobic, gram-negative, nonspore-forming, rod shaped bacteria that ferment lactose in 24-48 hours at 35 degree C. Coliform bacteria are commonly found in the intestinal tracts of warm-blooded animals, therefore, total coliform is used as an indicator of possible bacterial or fecal contamination. The number of Total Coliform includes both Fecal Coliform and Escherichia coli.
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APPENDIX

INTRODUCTION OF THE EDITORS OF ENVIRONMENTAL SCIENCE, TECHNOLOGY, ENGINEERING AND MATHEMATICS (STEM) SERIES

1. Editor Lawrence K. Wang

Editor Lawrence K. Wang has served the society as a professor, inventor, chief engineer, chief editor and public servant (UN, USEPA, New York State) for 50+ years, with experience in entire field of environmental science, technology, engineering and mathematics (STEM). He is a licensed NY-MA-NJ-PA-OH Professional Engineer, a certified NY-MA-RI Laboratory Director, a licensed MA-NY Water Operator, and an OSHA Instructor. He has special passion, and expertise in developing various innovative technologies, educational programs, licensing courses, international projects, academic publications, and humanitarian organizations, all for his dream goal of promoting world peace. He is a retired Acting President/Professor of the Lenox Institute of Water Technology, USA, a Senior Advisor of the United Nations Industrial
Development Organization (UNIDO), Vienna, Austria, and a former professor/visiting professor of Rensselaer Polytechnic Institute, Stevens Institute of Technology, University of Illinois, National Cheng-Kung University, Zhejiang University, and Tongji University. Dr. Wang is the author of 750+ papers and 50+ books, and is credited with 29 invention patents. He holds a BSCE degree from National Cheng-Kung University, Taiwan, ROC, a MSCE degree from the University of Missouri, a MS degree from the University of Rhode Island and a PhD degree from Rutgers University, USA. Currently he is the book series editor of CRC Press, Springer Nature Switzerland, Lenox Institute Press, World Scientific Singapore, and John Wiley. Dr. Wang has been a Delegate of the People to People International Foundation, a Diplomate of the American Academy of Environmental Engineers, a member of ASCE, AIChE, ASPE, WEF, AWWA, CIE and OCEESA, and a recipient of many US and international engineering and science awards.
2. Editor Mu-Hao Sung Wang

Editor Mu-Hao Sung Wang has been an engineer of the New York State Department of Environmental Conservation, an editor of CRC Press, Springer Nature Switzerland, and Lenox Institute Press, and a university professor of the Stevens Institute of Technology, National Cheng-Kung University, and the Lenox Institute of Water Technology. Totally she has been a government official, and an educator in the USA and Taiwan for over 50 years. Dr. Wang is a licensed Professional Engineer, and a Diplomate of the American Academy of Environmental Engineers (AAEE). Her publications have been in the areas of water quality, modeling, environmental sustainability, solid and hazardous waste management, NPDES, flotation technology, industrial waste treatment, and analytical methods. Dr. Wang is the author of over 50 publications and an inventor of 14 US and foreign patents. She holds a BSCE degree from National Cheng-Kung University, Taiwan, ROC, a MS degree from the University of Rhode Island, RI, USA, and a PhD degree from Rutgers University, NJ, USA. She is the Co-Series Editor of the Handbook of Environmental Engineering series (Springer Nature Switzerland), Coeditor of the Advances in Industrial and Hazardous Wastes Treatment series (CRC Press of
Taylor & Francis Group) and the Coeditor of the Environmental Science, Technology, Engineering and Mathematics series (Lenox Institute Press). She is a member of AWWA, NYWWA, NEWWA, WEF, NEWEA, CIE and OCEESA.
Dr. Yuriy I. Pankivskyi has 25 years of professional experience of scientific research and environmental education. He has expertise in strategic environmental assessment, environmental impact assessment, drinking water treatment, waste waters treatment, water and air pollution control, solid waste management. He works as environmental consulting engineer for industrial enterprises, state administrations of cities and towns of Western Ukraine, communities, private firms and institutions and as researcher, educator for state universities. He is the Associate Professor and Deputy Head of Department of Ecology of Ukrainian National University of Forestry. His research and publications have been in areas of water and air quality control, waste water treatment, environmental sustainability and education, analytical methods, investigations of multifunctional material for optoelectronics and environment testing. Dr. Pankivskyi is author of over 70 scientific publications. He earned his Specialist degree from Lviv State Ivan Franko University (Ukraine), ME degree from Lenox Institute of Water Technology (MA, USA), and his PhD degree from Lviv National Ivan Franko University (Ukraine). He is a member of National Ecological Center of Ukraine (Lviv Department).