

## ***Practical Guidelines For Safe Operation Of Cooling Tower Water Ozonation Systems***

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### ***Abstract***

Guidelines for the successful use of ozone as a stand-alone cooling tower water treatment method are discussed. Included are recommendations for system sizing, proper ozone residuals, mixing and distribution of the ozonated water, and potential problems and solutions. These include excessive or insufficient cycles of concentration, chemical contamination, low flow rates, high heat exchanger temperatures, and extended system turnover times. Also discussed are recommended maximum system downtimes, preferred types of towers and heat exchangers to treat with ozone, use of filtration systems, and elastomer compatibility with ozone. System monitoring and maintenance procedures are discussed along with ozonation safety considerations. With this information, two recently reported ozonation system failures are analyzed and the causes of failure are discussed.

### ***Introduction***

Over the course of the past decade, the use of ozone as the sole method of treating recirculating cooling tower water has gained many proponents. There are currently at least several hundred such systems operating in the United States and their successes and failures have been published widely (1-14). The successful applications have been characterized by low corrosion rates, very low biological counts, and scale-free achievement of relatively high cycles of concentration (zero blowdown in some cases). In most instances of reported problems, a number of operational shortcomings subsequently were found which were contributing factors. These included a failure to achieve a sufficient ozone residual due to inadequate system sizing, unreliable or unmaintained equipment (13), chemical contamination, and inadequate mixing or distribution of the ozone into the recirculating water. In those cases, this has resulted

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in excessive biological growth, corrosion, or scaling depending on the particular application and prevailing water conditions. In some other instances, scaling has been reported due to high heat exchanger skin temperatures(12,14), low velocity flow in heat exchangers (12), chemical contamination and lack of monitoring and equipment maintenance (13), or operation at excessive cycles of concentration (15).

Unfortunately, there has not been a satisfactory effort to present comprehensive, field oriented, practical guidelines and information that can be used by plant personnel to understand their own ozonated cooling tower water treatment operations. This paper attempts to fill that void and reports the authors' recommended general guidelines for sizing and system design. It also discusses operational problems users of cooling water ozonation systems may experience. It is not intended that this document be viewed as a comprehensive system design manual. To avoid potentially serious system design and hardware selection shortcomings which can jeopardize the success of a cooling tower ozone application, it is recommended strongly that specific system design and layout be performed only by suppliers with extensive actual real world experience in ozone mixing, degassing, and tower distribution design.

### *Background*

Between 1987 and 1992, the authors were involved in over 150 cooling tower ozonation systems which were installed primarily in California; generally under performance-guaranteed turnkey water service agreements. The systems ranged from as small as 2 lb/day of ozone to as large as 125 lbs/day of ozone. These quantities were applied to cooling towers ranging in size from 150 tons cooling centrifugal chillers, to 20,000 gpm towers operating in conjunction with surface condensers. These systems were utilized in the semiconductor, computer/peripheral, defense and medical electronics, aerospace, gas separation and transmission, cogeneration, chemical, pharmaceutical, food processing, and beverage manufacturing industries as well as in academic, hospital, and commercial HVAC environments.

Each of the ozonation systems was comprised of an ozone generator producing a specified quantity of ozone at 1-2% concentration (by weight) in the gas stream (air - see Figure 1). The ozone was injected at the approximate rate of 4-5 mg/L into the cooling tower through a sidestream recirculation loop according to U.S. Patent 4,172,786 (1).

Each of the sites selected was monitored twice daily by remote telemetry (Oxidation-Reduction Potential, Conductivity, Injection Loop Pressure, and 12 digital signals) to ensure continuous functional operation (see Figure 2).

Natural makeup water quality in these systems ranged from very low total dissolved solids (TDS) surface runoff water to high hardness, high silica well waters. Additionally, a number of the towers used reverse osmosis reject water, reclaimed deionized rinse and other waste waters, or zeolite-softened makeup water. The functional performance and economic benefits of many of these installations have been reported elsewhere (9-12).

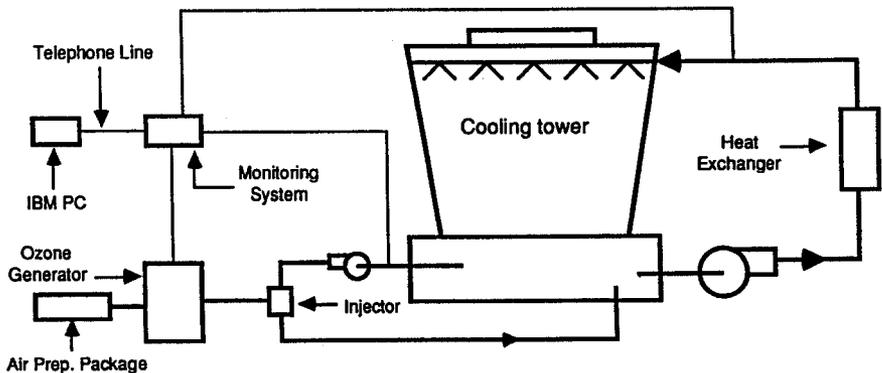


Figure 1. Cooling tower ozonation system.

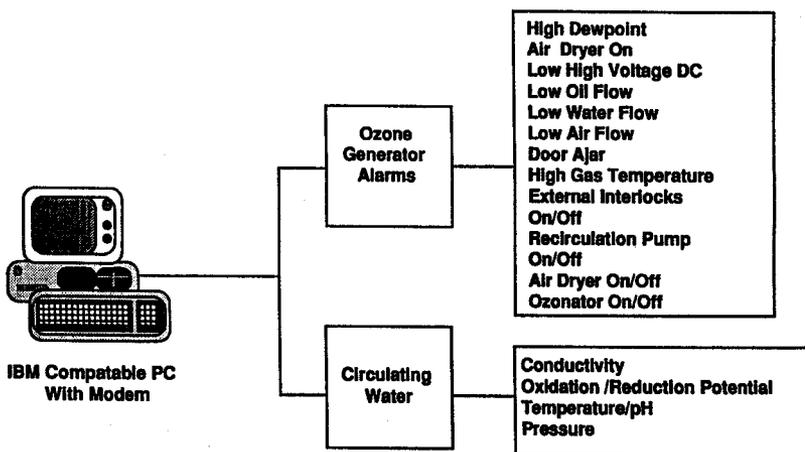


Figure 2. Cooling tower monitoring system.

The guidelines, problems, and limitations discussed in this paper all have been determined by the authors in the course of the design, installation, monitoring, and process troubleshooting of these ozonated cooling systems. The information is presented on the general premise that ozone can be used as a stand-alone treatment in most cooling water applications without any additional chemical treatment. Conditions are discussed under which this may not be feasible and, therefore, alternative treatment methodologies are discussed.

Many of the guidelines and limitations discussed are exemplified with specific field-obtained information. This information was obtained using accepted industry practices. The site-specific information presented here is not intended to be viewed as complete case studies. Rather, the data should be viewed in the context that it illustrates or clarifies certain recommendations or precautions discussed in the paper.

### *Expected/Target Performance Levels*

Prior to discussion of guidelines, it is useful to discuss the functional performance levels achievable by cooling water ozonation under proper conditions by reviewing historically reported results.

#### **BIOLOGICAL COUNTS**

Ozone long has been known for its excellent biocidal activity, and this is reflected by the very low levels of biological growth in ozonated cooling towers. Ozone attacks bio-organisms by directly oxidizing the coating of the wall in cell membranes and causes almost instantaneous cell death.

Provided that the dissolved ozone residuals are maintained uniformly above the desired minima, biological levels in the circulating water will be routinely less than 1,000 cfu/mL (6) and can even get below 100 cfu/mL (10). Heat exchanger and basin surfaces and fully wetted tower fill surfaces will be almost entirely slime- and algae-free, and turbidity of the water will approach 1-2 NTU. Occasionally, a small amount of algae growth may be seen on south-facing fill during hotter summer months in cross flow towers. This is particularly likely on those areas of the fill that are not fully wetted. Typically, this growth can be easily washed off with pressurized water. If the algae bloom is not serious, the end users may choose to wait until it is removed by the natural flushing action of ozonated water during the cooler winter months. Detectable slime in heat exchangers in properly ozonated cooling systems is nonexistent.

#### **CORROSION RATES**

During the past decade, ozone as a sole treatment in recirculation cooling water systems has been demonstrated to be very effective in controlling corrosion. Typically, corrosion rates of less than 2-3 mpy (mils/year) for mild steel and 0.2-0.3 mpy for copper can be expected in industrial application (10,12). HVAC applications typically are often less than those seen in industrial applications. In some softened water systems, corrosion rates less than 0.1 mpy for mild steel and less than 0.01 mpy for yellow metal are consistently achievable (10).

Some commonly accepted mechanisms of corrosion control in conventional chemical treatment programs also can be applied to the understanding of corrosion control in ozonated systems. Possible mechanisms are the following (20):

- o The destruction and prevention of microbiological growth and under-deposit corrosion;
- o The presence of alkaline pH conditions, long known to reduce corrosion;
- o Anodic passivation of the metal surfaces in a manner similar to chromates, molybdates, etc.;

- o Anodic and/or cathodic protection through adsorption of a silica layer on the metal surface.

### ***SCALING AND CYCLES OF CONCENTRATION***

The most controversial aspect of cooling towers is the ability to operate under scale-free conditions at higher cycles of concentration. Although there have been numerous documented cases of ozonation systems operating for extended periods with zero intentional blowdown (2,3,4,6,12), the underlying physical-chemical mechanisms are not well understood. It has been shown, however, that the conventional indices used to predict calcium carbonate precipitation in conventionally treated cooling tower waters are not accurate predictors of scaling potential in ozonated systems (16). A recent practical approach predicts the upper limits of operating conductivity in ozonated systems and is discussed elsewhere in this paper (16).

#### ***Recommended General Guidelines***

The following are recommended guidelines or considerations found useful by the authors across the wide variety of applications studied.

### ***OZONE RESIDUALS***

The most critical parameter of importance in cooling tower ozonation systems is the maintenance of sufficient dissolved ozone residuals throughout the system. The difficulty in achieving sufficient, consistently uniform dissolved ozone residuals is due to the very short half-life of ozone in cooling water (generally measured in minutes), and high reactivity with some organic/inorganic contaminants.

The concept of a minimum ozone residual requirement is consistent with the authors' understanding that ozone exhibits a typical dose:response relationship with respect to its biocidal activity, scale control and corrosion inhibition. A sufficient minimal concentration of ozone must be maintained in the system at certain points throughout the cooling system to have the desired effect. Because ozone has such a short half-life in water, it is the natural rapid decomposition of ozone in the sidestream injection loop and in the cooling tower basin, and not either the reaction with oxidizable contaminants nor dilution by blowdown that primarily determines the residuals throughout the system. This is an important consideration in system sizing and design, as discussed later.

All ozone residuals recommended here are obtained using the indigo trisulfonate method. This is the only acceptable method currently available due to possible interferences in the cooling water which will affect other test methods. A number of other available dissolved ozone residual test methods will yield widely different test results (12).

As previously reported (12), the DPD method has been shown to provide results which range from 25% to 67% higher than those from the indigo trisulfonate method in one side by side comparison test. The iodometric titration method was shown to

provide results which were up to 400% higher than those from the indigo trisulfonate method in the same tests. Both the DPD test method and the iodometric titration test method are known to be sensitive to many oxidants other than ozone, and they would be expected to show higher residual values than the relatively specific indigo trisulfonate method.

All early researchers in cooling tower ozonation used the less accurate DPD, iodometric titration, or ortho-tolidine methods. When comparing residuals with past reported results, practitioners in the field should note carefully which methods of measurement were employed by the past investigators, as the results will vary depending on the method employed. Measurements made more than several years ago probably employed the iodometric titration methods, and therefore indicated ozone concentrations several times higher than actual, as measured by the indigo trisulfonate method.

Following are the authors' recommended range of minimum and maximum ozone residual concentrations (in mg/L) that should be maintained throughout the cooling tower recirculation system in order to provide the desired functional benefits:

#### RECOMMENDED RESIDUAL OZONE CONCENTRATIONS AT VARIOUS POINTS IN COOLING TOWER

Position in Tower	Minimum O <sub>3</sub> Residual	Maximum O <sub>3</sub> Residual
At Discharge From Injection/Mixing Recirculation Sidestream	0.5	1.5
At all Points Throughout the Tower Basin	0.025	0.25
At Tower Pump Basin or Pump Suction	0.075	0.15
At Heat Exchanger Inlet	0.04	0.08
At Tower Return Distribution Pans or Nozzles	0.010	0.04

#### SIZING

It is believed by the authors that proper ozonation system sizing for cooling towers using potable water as makeup is primarily a function of total volume of water in the cooling tower and distribution piping. The authors believe that it is the dilutive effect of large volumes of water in the basin of the cooling tower and in the plumbing of the cooling system that is primarily responsible for the lower residuals seen throughout the cooling system.

It is believed that the evaporation rate or fan utilization are minor considerations, except in those infrequent cases where gross contaminants are introduced into the tower via makeup water, process water contamination, or air scrubbing (as discussed later). The authors are further of the opinion that recirculation rate plays a role in system sizing only insofar as it determines the residuals of ozone once the ozonated

## PRACTICAL GUIDELINES FOR OZONE COOLING TOWERS 511

water is circulated throughout the system. The effect of recirculation rate in system sizing is minimal, because about 80% of the ozone injected in a mixing sidestream loop is decomposed by the time it is distributed and diluted in the tower and reaches the primary cooling pumps. Only about 20% of the total injected ozone is thereafter destroyed in the site's primary cooling circuit (12,14). This indicates that the recirculation rate is a minor consideration in system sizing and that obtaining a satisfactory residual at the cooling systems pump suction is much more critical.

Once the proper ozone residuals are achieved within the fairly broad allowable range, these residuals generally remain within the acceptable ranges at constant ozone generator output, even under varying recirculation rates. Correct ozonation application eliminates the ongoing necessity of multiple daily titration of numerous different chemicals and adjustments of their various feed pump rates due to changes in their tower water concentrations because of changes in the evaporation and blowdown rates. This generally results in more stable functional performance in ozonated cooling systems.

Using the above general concepts and through extensive trial and error analysis, the authors recommend the application of approximately 300-350 mg of ozone to each gallon of water in the entire cooling system (including piping, heat exchangers, and the cooling tower itself), per day. This calculation is simplified considerably by multiplying the volume of water in the system (in gallons) by the factor of 0.0007 to yield the recommended applied dosage in pounds of ozone per day. Thus, a cooling system with a total system volumetric capacity of 20,000 gallons would require a 14 pound per day ozonation system.

Again, it must be emphasized that this sizing is for cooling towers using potable quality makeup water without an excessive organic component (i.e., TOC less than 8 mg/L) and in the absence of any external or internal organic contamination (e.g., through leaking process heat exchangers). Undersizing of the ozonation system simply will result in insufficient ozone residuals throughout the system with various problems, as discussed later.

When calculating the volume of water in the recirculation system, special effort must be taken to measure accurately the depth of water throughout the basin, as variable basin depths often are found. Similarly, measurements of all pipe lengths and diameters must be made to estimate the amount of water in the cooling recirculation loop. The authors also have found that a useful approximation is to add 1 gallon of water for every ton of cooling capacity to the total calculated basin and estimated piping volumes to account for the water in the system heat exchangers and in the tower fill during operation.

### **MIXING**

For a cooling tower ozonation system to be effective, however, the applied ozone dosage also must be mixed efficiently and distributed into the cooling tower water. Many different mixing strategies have been attempted by practitioners to maximize mass transfer efficiency of the ozone into the water and to ensure that sufficient residuals remain upon distribution of the ozonated sidestream into the tower.

The most satisfactory solution has been the use of direct in-line injection through eductors (or bubblers in larger systems) into the sidestream recirculation loop immediately after the discharge of the sidestream recirculation pump. The authors have found that a sidestream recirculation flow rate of 20 gal/min per pound/day of injected ozone is sufficient to provide the correct ratios necessary to yield the desired residuals on distribution into the tower basin. The water-gas mixture then is circulated through appropriately sized lengths of piping to ensure that true bubble:froth mixing is achieved. Generally, mass transfer efficiencies of 85% or greater are achievable with the proper mixing system design. Efficient bubble:froth mixing for the correct time period is absolutely necessary to provide sufficient mass transfer to provide the desired ozone residuals upon injection into the tower basin, yet not allow the ozone to degrade to less than desired residual concentrations.

Special attention must be paid to the injection design to ensure mineral-laden water droplets do not enter the air injection passageways. The very dry air passing over the droplets will quickly evaporate the water, leaving behind a mineral residue. This can lead to premature clogging of the injector resulting in high gas pressure shutoff of the ozone generator.

### ***DEGASSING***

With tower fans operating, a properly designed ozonation mixing system would not outgas sufficient ozone to be detectable in the tower exhaust and degassing, and destruction of undissolved ozone from the ozonated sidestream is not necessary. However, in many applications, the ozonated sidestream recirculating water should be degassed and excess ozone destroyed prior to distribution into the tower basin to remove undissolved ozone and prevent ozone accumulation in the air surrounding the tower, particularly if in confined areas and/or when fans are off. Proper ozone destruction allows undissolved degassed ozone to pass through a catalytic ozone-destruction bed where it is converted into harmless oxygen.

### ***DISTRIBUTION***

The proper distribution of the ozonated water from the sidestream injection loop into the cooling tower basin is necessary to: 1 ) maintain biological control in the basin, and 2) provide sufficient ozone residual at the primary cooling pumps to enable a proper dissolved ozone residual to be maintained throughout the circulating system.

Due to the vagaries of the flow patterns which exist in the basin an initial plumbing layout may not provide sufficiently uniform residuals in the basin or sufficient residuals at the cooling pump suctions. Careful observation of the pattern of biological growth in the basin or measurement of the pump suction residuals will provide valuable information and indications of appropriate corrective measures. For instance, insufficient pump suction residuals often can be corrected by directing a larger percentage of the distribution discharge points to the general vicinity of the pump suction. Similarly, evidence of excessive algae growth in discrete areas of the basin can be alleviated by redirecting more flow from the existing distribution system outlets to the affected area.

Assuming that the applied dosages are otherwise sufficient to give the recommended ozone residuals, excessive biological growth due to poor ozone distribution in the basin more often is seen in shallow factory-built towers than in larger site-built towers with deep basins. This is because it is much more difficult to uniformly direct the sidestream of ozonated water into the basin to a specified location because of the high linear velocities of the tower water seen in shallow tower basins. Conversely, insufficient pump suction residuals more often are seen in deep basin, site-built towers because of the dilution effect of the large basin and the generally larger turnover time.

### *Potential Problems And Solutions*

#### ***INSUFFICIENT OZONE RESIDUAL***

Many cooling towers planned for conversion to ozonation have had insufficient biological protection in the past and contain a substantial amount of biomass on internal surfaces. To achieve desired results of ozonation promptly, the cooling tower and basin should be cleaned thoroughly immediately prior to startup. Generally, remaining organic material then will be oxidized within several days. With heavy preexisting biofouling and when the tower cannot be precleaned for operational reasons, the ozonation cleanup may require weeks to months for completion. During this cleaning phase, the water often becomes turbid and foams as the biomass sloughs from tower surfaces. As the organic matter is consumed, the pockets of foam gradually subside and the water often becomes very clear (less than 2-5 NTU). Continued higher turbidity and the presence of foam beyond the initial cleanup phase indicates insufficient ozone residuals and may be indicative of a contamination or sizing problem.

Insufficient ozone concentrations in cooling water also may be caused by decreased ozone generator output due to operational failure, inefficient mixing, ongoing process contamination, inadequate distribution of the ozonated sidestream into the basin, or simple undersizing. Care must be taken to eliminate each of these possible causes to isolate the problem if acceptable ozone residuals are not obtained.

Failure to achieve the desired dissolved ozone residuals will result in excessive scaling, biological growth, or localized corrosion, depending on where the insufficient residual occurs in the cooling system, on the particular physical characteristics of the tower, and on the prevailing mineral ratios in the recirculating tower water. Failure to achieve the desired residuals at the discharge of the ozone injection sidestream loop (greater than 0.5 mg/L) results in insufficient residuals throughout the remainder of the system. Insufficient ozone in the tower basin will allow surface biological growth. Excessive ozone concentrations in the tower basin (greater than 0.25 mg/L) may lead to increased corrosion of basin metal pans. The degree of corrosion is directly related to the water chemistry of the recirculating water. As discussed later, this impact is minimized or eliminated in highly cycled waters with sufficient alkalinity or silica.

At very high levels of basin water dissolved ozone, some outgassing of ozone from the water also may be detectable. Usually this will occur only when ozone is being injected into a tower which has recirculation pumps and/or fans turned off.

Outgassing due to excessive dissolved concentrations of ozone in the basin water is minimal compared to the degree of outgassing which can be experienced due to inadequate mixing or off-gassing from the ozonation injection loop prior to distribution in the tower basin.

Failure to achieve and maintain sufficient dissolved ozone residuals at the cooling pumps suction (greater than 0.075 mg/L) generally will result in inadequate residuals in the heat exchangers of the cooling system (less than 0.05 mg/L) and at the tower return (less than 0.01 mg/L). This can lead to fouling conditions in heat exchangers if high cycles of concentration are being maintained. Insufficient ozone residuals in heat exchangers under relatively low cycles of concentration often are accompanied by excessive corrosion rates of mild steel. Insufficient residuals at the heat exchangers or tower return will result in slime growth. If insufficient residuals at the tower return are accompanied by high cycles of concentration, then scaling in the tower fill also will occur.

Excessive residuals of ozone at the primary cooling pump suction (greater than 0.25 mg/L) could result in premature pump seal failure if the seal is not Viton; especially if seals already have been exposed to other strong oxidizing biocides or low pH conditions. The observed effects of ozone on elastomers throughout a cooling system is discussed more thoroughly elsewhere in this paper. The authors have not experienced effects of excess ozone at other points in the cooling circuit, because it is almost impossible to obtain an ozone residual greater than 0.25 mg/L at a heat exchanger or greater than 0.1 mg/L at the tower return.

It is generally less disadvantageous to have too much ozone in a cooling system rather than too little. Selection of ozone generator capacity by end users should err on the side of a larger size ozone generator if available ozone generators do not exactly satisfy their sizing requirements. This is because the impact of excessive ozone residuals are quite minor compared to the detrimental effects of inadequate ozone residuals. Further, nearly all commercial quality ozone generators have turndown capabilities which allows users to decrease ozone production if excessive ozone residuals do develop in the operation of the ozonation system.

Ozone generally does not exhibit an all-or-nothing response. Even ozone residuals which are less than the desired minimum concentrations will provide some measure of positive functional benefits. The authors have observed systems in which the ozone residuals throughout the system were only 50% to 60% of the desired minimum levels, yet results achieved by ozonation were still a substantial improvement over those with previous multichemical treatment programs in terms of biological control, scale prevention, and corrosion inhibition.

### ***EXCESSIVE CYCLES OF CONCENTRATION***

The cycles of concentration under scale-free conditions potentially achievable when ozone is being used in cooling towers has been the subject of much speculation. Past users have reported both scale-free operation at very high cycles of operation (1-6, 8-13), and the occurrence of significant scale formation in other highly cycled systems (15). Conventional water treatment indices which are used to predict the presence or

## PRACTICAL GUIDELINES FOR OZONE COOLING TOWERS 515

absence of calcium carbonate precipitation (e.g., the Langelier Saturation Index) have been reported to be unreliable in predicting scaling potential in ozonated cooling towers (1,4,6).

Use of these indices could not predict consistently at what cycles of concentration scaling would begin to occur in an ozonated cooling system. In many cases, cooling towers were operated safely under scale-free conditions at cycles of concentration far in excess of what was predicted by a conventional index. Further, although these systems showed no evidence of fouling or scaling, the water chemistry in these instances showed clear evidence of ongoing removal of dissolved calcium carbonate and other scale-forming minerals from the circulating water. This indicates that minerals are precipitating continuously in ozonated cooling water, yet do not do so in an adhering manner. It is probable that the historically reported limited usefulness of the conventional indices in predicting scaling tendencies in ozonated towers is due to the fact that they simply predict calcium carbonate solubility. This may be of limited usefulness in predicting at what levels adhering scale forms in an otherwise precipitating aqueous environment.

In response to these shortcomings, a new index, called the Practical Ozone Scaling Index (POSI), was developed by the authors to predict maximum, scale-free operating cycles of concentration in ozonated tower water. This index is discussed in a companion paper (16) to this paper. Using this index, the cycles of concentration (based on conductivity) that generally can be achieved in the absence of scaling can be calculated as follows:

Maximum conductivity (Cond(Tower) =

$$10^{(1/\log [(Ca \times Mg)/(Na + Cl)]/\log(Alk/10))} \times \text{Cond}(\mu)$$

where:

Ca	= Calcium Hardness in the makeup water expressed as CaCO <sub>3</sub>
Mg	= Magnesium Hardness in the makeup water expressed as CaCO <sub>3</sub>
Alk	= Total Alkalinity in the makeup water expressed as CaCO <sub>3</sub>
Cl	= Chlorides in the makeup water expressed as Cl <sup>-</sup>
Na	= Sodium in the makeup water expressed as Na <sup>+</sup>
Cond(Tower)	= Tower Water Conductivity
Cond(MU)	= Makeup Water Conductivity.

By example, in one application the makeup and circulating ozonated tower water were analyzed as listed in the table on the next page.

The maximum conductivity predicted by the POSI thus would equal:

$$10^{(1/\log[(30 \times 10)/(7 + 10)]/109(39/10))} \times 130 = 2964 \text{ micromhos or } 22.8 \text{ cycles.}$$

The Langelier Saturation Index for the recirculating water is 2.24; predicting precipitation of calcium carbonate and scaling tendencies. The ozonated cooling system was in fact observed to operate scale-free as predicted by the POSI.

Parameter	Makeup Water	Cooling Water	Cycles
pH	8.4	9.0	NA
Conductivity	130	2310	17.8
Calcium Hardness	30	245	8.2
Magnesium Hardness	10	320	32
Sodium	10	240	24
Chloride	7	400	57
Total Alkalinity	39	380	9.7
Temperature	55°F	85°F	NA

The maximum tower water conductivity so calculated is the upper conductivity range at which the cooling system can operate without scaling tendencies. It is believed by the authors to be conservative. Practical guidelines for increasing the cooling water conductivity above this predicted maximum level are discussed by the authors in more detail elsewhere (16). It is important to note also that scale which does develop once the upper safe operating conductivity is exceeded is initially minimal and may go almost unnoticed by most plant operators. As the circulating tower water conductivity increases more and more above the recommended level, however, the tendency for scale to deposit becomes more and more pronounced.

The true cycles of concentration that will be achieved in ozonated cooling waters must be based on the most soluble species (generally chlorides, sodium, and sulfate). The cycles of concentration of these ions always will be substantially greater than the cycles of concentration based only on comparable makeup/tower conductivity. In a study by the authors the cycles of concentration based on chlorides averaged almost exactly twice the cycles of concentration based on conductivity; and cycles of concentration based on sodium were about 1.7 times as high (16). From a practical view point, defining limits of concentration in terms of conductivity is very simple. However, the use of conductivity to estimate maximum achievable cycles of concentration will seriously underestimate the true cycles by an average of about 50%. This is very significant when calculating expected blowdown water consumption. It can introduce significant errors when evaluating comparative economics with conventional multichemical water treatment programs. The relationship of higher cycles of concentration of the more soluble species compared to conductivity (and even more so compared to the relatively insoluble species such as hardness, alkalinity, and silica) confirms the work reported earlier (1,4,5,6,12) and is indicative of precipitating water chemistry.

Excessive phosphate in the makeup water or introduction through contamination may lead to formation of calcium phosphate seed crystals due to high pH in the ozonated recirculating water. This reduces the solubility of many other mineral constituents of the tower water including calcium carbonate, chlorides, and silicates and will cause scaling at lower cycles than otherwise would occur (19). Phosphate occasionally is

added to water supplies as a corrosion inhibitor. If care is not exercised, relatively high and varying concentrations of phosphate may result. If makeup water total phosphate is in excess of 1.0 mg/L, then the otherwise recommended upper conductivity of the tower water should be reduced by dividing the normal recommended cycles by the concentration of the total makeup water phosphate (in mg/L).

### ***INSUFFICIENT CYCLES OF CONCENTRATION***

Just as excessive cycles of concentration can promote scaling in ozonated cooling systems, insufficient cycles of concentration will result in corrosion rates greater than those otherwise achievable. Low concentrations in the circulating water may indicate uncontrolled leaks in a cooling system, or excessive bleedoff.

In the authors' opinion, ozonated cooling water must be cycled up to the extent that the theoretical silica concentration of the tower water is in excess of 150 mg/L and/or the theoretical total alkalinity of the tower water (calculated based on makeup alkalinity without precipitation losses) is in excess of 450 mg/L. That is, if the silica and alkalinity concentration in the makeup water are 20 mg/L and 60 mg/L, respectively, the true minimum cycles that must be achieved in the cooling tower based on chlorides is 7.5 ( $7.5 \times 20$  mg/L silica = 150 mg/L and  $7.5 \times 60$  mg/L alkalinity = 450 mg/L).

There currently have been no reported additives that improve corrosion rates in ozonated towers with insufficient cycles or low pH due to acid feed. As discussed below, it is imperative that organic and inorganic phosphates not be added due to the precipitation that will result. Triazoles have been shown to be rapidly oxidized by ozone and have limited effectiveness in reducing yellow metal corrosion in ozonated towers.

### ***EXCESSIVE COOLING SIDE HEAT EXCHANGER SKIN TEMPERATURES***

High temperature limitations of ozone treatment also have been observed and reported elsewhere. Based on scalometer studies in which the effects of flow rates through throttled heat exchangers were observed, one published report (14) showed that ozone exhibited localized decreased effectiveness as a scale inhibitor when encountering skin temperatures on the cooling water side in excess of 135°F.

The authors' own experiences also confirm the existence of high temperature limitations in cooling tower ozonation. At an air separation plant, some scaling was observed in one high temperature tube-in-shell heat exchanger with cooling-side shell skin temperatures estimated to be about 170°F. In this particular 12-foot exchanger, some scaling was observed only on the first 24 inches of the hot end of the exchanger. The remainder of the heat exchanger remained scale free (12). Additional field observations by the authors have confirmed that upper limits exist for cooling side skin temperatures at about 135°F-140°F, above which localized scaling will occur.

As a practical estimate, this limit generally will not be exceeded until process side gas temperatures exceed 320°F or process side liquid temperatures exceed 250°F. This occurs in most air compressor aftercoolers, as well as in a number of petrochemical and refining applications. As expected, high temperature scaling is exacerbated by higher cycles of concentration in the ozonated cooling water.

Remediation of high temperature problems is accomplished most easily by cooling the high temperature heat exchangers with low conductivity closed loop water.

### ***NONTURBULENT COOLING WATER FLOW OVER HEAT TRANSFER SURFACES***

Low flow-through heat exchangers is a generic problem also experienced in many conventional cooling water systems. Practitioners of cooling tower ozonation are advised to take special precautions to avoid applications in which less than turbulent flow results over heat exchanger surfaces. Low flow of highly cycled ozonated water through heat exchangers can result in a hard sludge or localized deposition in the heat transfer tubes (12).

From the perspective of a cooling tower ozonation system, low flow problems may occur in applications in which the Reynolds Number is less than 10,000 - 15,000. By comparison, the typical 1-inch pipe corrosion rack with the recommended minimum flow of 8 gal/min yields a Reynolds Number of about 26,000.

Low flows may occur in throttled or partially bypassed heat exchangers such as lube oil coolers and chillers. Shell side cooling in tube and shell heat exchangers also may present low flow conditions. Remediation of the problem requires increasing flow through the heat exchanger which may require some piping modifications or staging of heat exchanger use to prevent process over-cooling.

### ***CHEMICAL CONTAMINATION***

Chemical contamination of an ozonated cooling system can have a variety of deleterious effects on an ozonated cooling tower depending on the contamination nature and the prevailing water chemistry.

#### ***Phosphate/Borate Contamination***

By far, the most serious contamination that may occur in an ozonated cooling tower is the sudden introduction of a high concentration (greater than 3-4 mg/L) of phosphate or borate into highly cycled tower water. One common mode is inadvertent addition of phosphate or borate by a chemical service technician. Cross contamination by phosphate, phosphonate, or borate-treated cooling tower, closed loop, or process water has been seen in numerous applications (see Figures 3-5). Contamination of reclaimed water used as makeup due to excessive use of a phosphate polymer as an antiscalant in the process also has occurred (see Figure 6). Severe deposition has been seen in newly ozonated towers in which either phosphate-

based cleaning solution (from new construction cleaning) or chemical treatment formulations (in previously chemically treated towers) were not completely flushed out from all dead legs in the system prior to ozonation.

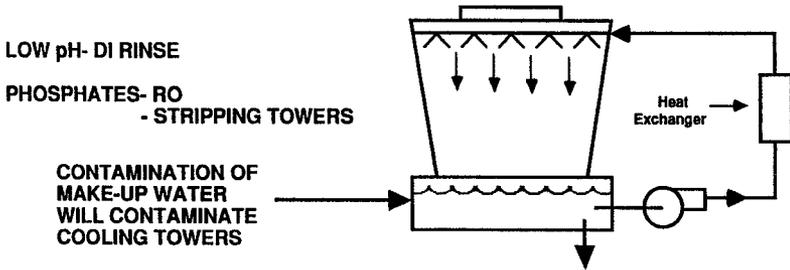


Figure 3. Contamination of reclaimed industrial makeup water.

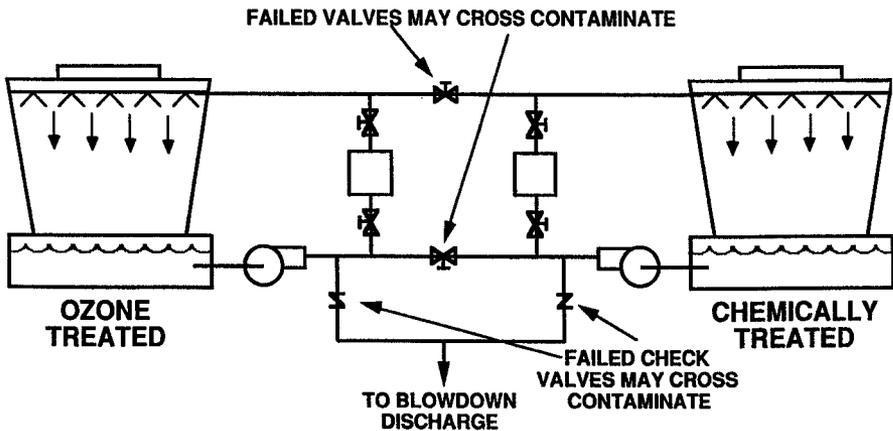


Figure 4. Cross-contamination through leaking valves isolating a chemically treated cooling tower.

Small amounts of calcium phosphate precipitation would not amount to sufficient scale to be deleterious, given the large surface areas in towers, exchangers, and cooling water distribution systems. However, as discussed above, the presence of phosphate crystals can cause the sudden, immediate coprecipitation of a variety of other species from the mineral saturated water (19). The coprecipitation occurs because the phosphate precipitates act as seed crystals upon which further crystal growth occurs.

This phenomenon also has been shown to occur in the laboratory environment using highly cycled tower water into which small amounts of chemical formulations containing phosphates or borates are added. Under numerous such conditions, substantial precipitation can be shown to develop.

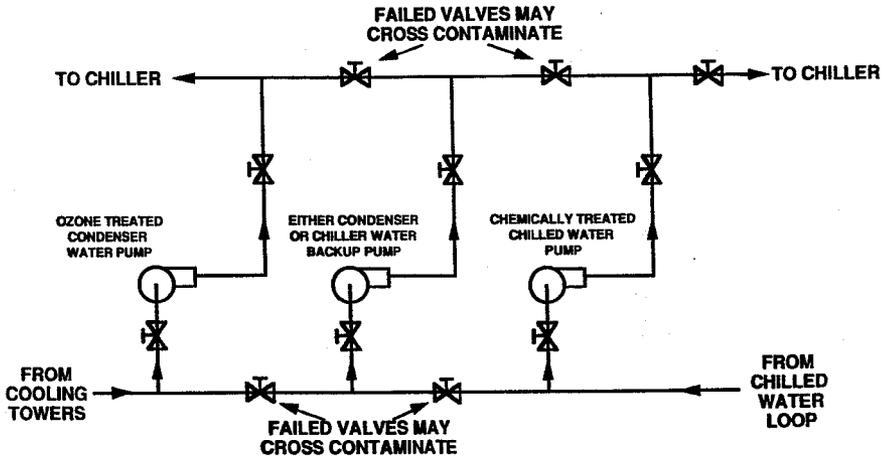


Figure 5. Cross-contamination from a closed loop system through leaking valves isolating a dual purpose backup system.

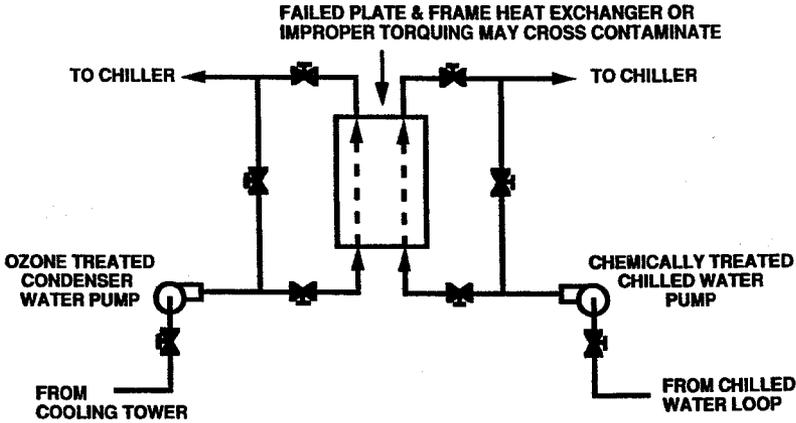


Figure 6. Contamination from a leaking plate and frame heat exchanger providing free winter cooling.

To offer assistance to new end users in correctly identifying phosphate/borate-based precipitation, the authors offer the following field-derived observations:

1. Upon contamination, the circulating water will quickly become visibly milky and feel slippery to the touch. Swirls of milky precipitate can even be seen in what was previously crystal clear water. A viscous white substance then will begin to adhere to tower structures. Some evidence indicates this may be initial silicate precipitation.

## PRACTICAL GUIDELINES FOR OZONE COOLING TOWERS 521

2. Well-defined elongated crystals will be observed to form a soft floc over the initial viscous depositions. The precipitation begins very rapidly (within minutes), once sufficient level of contamination occurs, and continues until a new lower mineral concentration stabilizes and further precipitation stops. The rate of precipitation is a function of the TDS of the cooling water and the degree of contamination.
3. Deposition generally begins at the point of the cooling water return to the tower; either in the distribution pans or in the upper fill in towers with nozzles. It is then washed down into the tower basin. In one extreme case, over 1.5 inches of deposition was seen to occur on the upper distribution pans of one large tower within a one-half hour period following massive contamination. Fortunately, due to turbulent flows through heat exchangers, deposition in tubes is minor compared to the amounts of deposits seen throughout a contaminated system. If the flow of water is over condenser or cooler tubes or heat exchanger bundles, significant adherence of the scale to the external surfaces of the tubes can be expected due to the non-turbulent nature of the flow there.
4. Deposits initially are quite soft and can be removed with a high pressure hose if cleaned within several days. If allowed to "air cure", these deposits become very hard and even resistant to acid cleaning.
5. Scale formed in this manner will appear rapidly, accumulate in thick layers in low flow areas throughout the system and show a complex mixture of many different minerals. This compares to the slow growing, thin sheets of scale on tower fill, heat exchanger surfaces, and return distribution pans caused by high TDS or low ozone residual excursions in the cooling water. Scale formed during high TDS excursions generally is entirely calcium carbonate with minor amounts of silica.
6. In cases of repeated contamination, the scale will appear to be growing in layers; like rings in a tree trunk. The scale formation inside the ozonated sidestream loop can become so thick that it begins to break off in sheets from the piping inside diameter. These migrate and fuse as chips at downstream pipe elbows and restrictions.
7. To ascertain whether observed scaling in ozonated towers is caused by phosphate or borate contamination, it is impractical to analyze for phosphates or borates in the precipitate. Rather, sudden physical appearance of elongated crystals fusing over time to form masses of mineral scale, and the complex mixture of the scale are indicative of precipitation induced by contamination. If contamination from a chemically-treated closed loop has occurred, elevated levels of some unaffected minerals or metals from the contaminating water source may still be present (e.g., molybdates and nitrates from nitrite).
8. Should a user experience sudden, voluminous precipitation due to contamination, it is imperative that cleaning activities commence immediately to remove as much floc in as short a period of time as possible while the precipitate remains soft. Maximum blowdown should be used for several days, accompanied by tower fill spraydowns, basin vacuuming, and strainer and sensor cleaning.

Further efforts must be made to locate and isolate the source of the contamination through the use of "double block and bleed" or other appropriate replumbing strategies. If such replumbing is impractical, additional efforts then should be focused on replacing the phosphonates, or borates in the contamination source with different chemical formulations.

The authors are of the opinion that contamination-induced precipitation in ozonated cooling towers is the most formidable obstacle facing new users of ozone.

### ***Organic Contamination***

Organic contamination of an ozonated cooling system will result in the consumption of free ozone by the organic contaminant. This can result in insufficient ozone residuals through the cooling system.

Elimination of process leaks or makeup water pretreatment to lower organic contamination are the preferred methods to eliminate the problem. Two additional remedial courses of action can be taken. This first is to oversize the ozonation system, to add excess ozone to overcome the organic load. The authors recommend that excess ozone be provided in a 0.5:1 ratio of applied ozone to organic load in excess of 8 mg/L of TOC in the makeup water. The second course of action is to increase ozone output of existing ozone equipment. This can be accomplished by adding an oxygen separator to the system to provide an oxygen-enriched feed gas to the ozone generator. This will increase ozone output by 2-3 fold.

### ***Acid Contamination***

Generally acids will contaminate an ozonation system only if present in reclaimed makeup water. The presence of acids will have the same effect as intentionally feeding acid for pH adjustment. Corrosion rates will increase depending on the level of acid contamination. Neutralization of the acid in the tower and/or makeup water must be performed to eliminate acid contamination.

### ***Ammonia Contamination***

Ammonia contamination from leaking condenser tubes, process, or air contamination represent a unique type of contamination. Normally, ozone will oxidize ammonia into nitrate only at pH above 9. However, the authors have observed several ammonia-contaminated systems in which increases in nitrates have occurred coextensive with pH depression. In one such contamination, system pH dropped to 5.0 with a subsequent dramatic increase in corrosion rates (13). It was discovered that nitrates in the circulating water reached a level equal to 7,000 cycles of concentration compared with 15 cycles measured on chlorides.

Based on known aqueous ozone chemistry, formation of nitric and nitrous acids can occur only from nitrate and nitrite ions, respectively, at low pH; oxidation of ammonia even at pH > 9 is slow and will not drop the pH in and of itself. Oxidation

of ammonia by ozone in the gas phase is relatively rapid, however. It is possible that nitrate production could occur by transfer of dissolved ammonia into the gas phase in the bubble of ozone-containing gas, froth-mixing circuit, and subsequently redissolved as nitrate in the water. Regardless of reaction pathway uncertainties, the source of the ammonia leak must be eliminated to resolve this problem.

### ***EXTENDED SYSTEM TURNOVER TIME***

Extended cooling system turnover time in an ozonated cooling circuit is an example of a low ozone residual problem. That is, the length of time taken by the cooling water to travel from the pump suction to a heat exchanger and return to the tower is so long that insufficient ozone residuals remain in the water to achieve the desired functional results. The authors have found that applications with a total system turnover time (total system volumetric capacity divided by the recirculation rate) of greater than 10 minutes will present problems if the basin and pump suction residuals are in the lower end of the ranges previously specified. If the cooling water distribution system turnover time (total piping volumetric capacity divided by the recirculation rate) is greater than 5 minutes, special precautions also must be considered.

To minimize this problem, replumbing of the ozonated water distribution system in the tower basin must be effected to deliver more of the ozonated discharge to the general area of the cooling water pump suctions to increase dissolved ozone residuals at the pump suctions. This may even require residuals of greater than 0.15 mg/L at the pump suctions.

The proper distribution design in different towers under various operating conditions is one aspect of cooling water ozonation that has not been reduced to a quantifiable set of practices and rules. The guidance of experienced practitioners should be sought by new users of cooling tower ozonation.

One extended turnover problem involves usage of wall mounted, water-cooled air conditioning units often seen in computer rooms, clean manufacturing rooms, and HVAC or process cooling applications. Cooling water for these units is taken as a spur line from a convenient cooling water supply line; directed to the heat sources, and delivered back to a return line in a parallel "ladder" arrangement (see Figure 7).

These spur lines often have a throttling valve or piping reduction at the far end of the line designed to create a pressure differential between the spur supply and return lines. This allows flow of water across the condenser/coil in the air conditioning units when the diaphragm valves open. When there is no or little load on the air conditioning units, most of the diaphragm valves will be closed. This results in very low flows through the spur line loop. Only when there is heat load and the diaphragm valves fully reopen does full flow resume.

This can cause both low flow deposition in the spur supply and return line. It also will create insufficient ozone residuals at the heat exchangers because water in the supply line may sit stagnant for hours with a resultant loss of ozone residual.

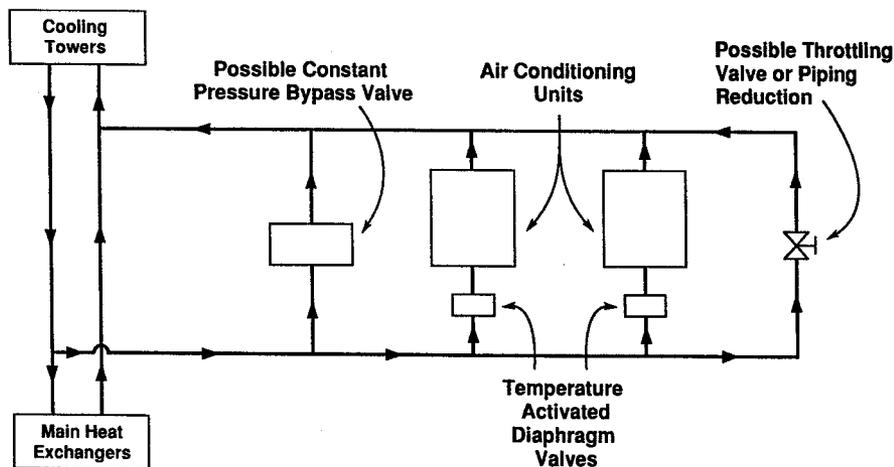


Figure 7. Potential low residuals at heat exchangers due to extended turnover times in cooling water piping spur lines.

Similar problems may develop if a constant pressure bypass valve is installed. When the diaphragm valves are closed the bypass valve opens and allows water to short circuit in the "ladder" to maintain constant pump discharge pressure. Under low load conditions, stagnant water (with respect to ozone residual) develops in the spur lines downstream from the constant pressure by pass, and low residual ozonated water is delivered to the air conditioning units.

The solution to this problem is to remove constant pressure bypass valves and/or plumbing restrictions and ensure that a throttling valve is installed at the far end of the spur line. This valve should be closed only enough to provide the absolute minimum pressure differential between the spur feed and return lines. Often only 2-3 psi is required.

### *Other Guidelines*

#### **ALLOWABLE SYSTEM DOWNTIME**

Because ozone has a very short half-life in cooling water (on the order of minutes or less), and quickly degrades into simple diatomic oxygen, a failure or breakdown of the ozonation system will result in little or no detectable ozone residuals throughout the system within a short period of time. The allowable response time by which corrective action must be taken thus would be expected to be relatively short in an ozonated system compared to a conventional chemical treatment program involving much more environmentally persistent compounds. Depending on the conditions involved, however (i.e., water chemistry, cooling load, etc.), there is a reasonable period of time available to users of cooling water ozonation systems to repair equipment or otherwise resume ozonation before serious deleterious effects occur.

The first effects of extended system downtime are the appearance of biological growth on south facing fill and on basin bottoms exposed to sunlight (typically seen more often in cross flow, induced draft towers). Even if an ozonation system shutdown occurred during very hot weather, however, the appearance of biological growth generally will not be apparent until at least several days after system failure. During colder winter months, the authors have observed some systems that remained biologically acceptable even one month after ozonation system failure. The relatively lengthy periods of time between an equipment breakdown and the appearance of excessive biological growth is due to the very clean and sanitized condition of properly ozonated towers prior to the loss of ozone residual. Also, because ozonated towers generally have such low TOC levels (below 4-8 mg/L), there is not a readily available food source for newly developing biological populations, which further minimizes biological growth seen upon equipment failure or other loss of ozone residual in the tower. Due to the cleaning effect of turbulent water flow through heat exchanger tubes, fouling in exchangers generally develops even more slowly than in tower basins or on tower fill when ozone residuals drop to less than acceptable levels.

The development of scale and corrosion problems due to the sudden loss of ozone residuals more often develops subsequent to the appearance of biological growth. Although the development of new biological growth can contribute to both scale formation and/or excessive corrosion rates, it is the prevailing makeup and tower water chemistry that determines which of these problems subsequently will develop following a loss of ozone residuals. If the makeup water is relatively high in hardness and alkalinity and the tower is highly cycled, scaling will result. This can be minimized by rapid blowdown to reduce operating cycles upon loss of ozone residual. Conversely, if the makeup water is comparatively low in alkalinity and silica and the tower water circulating at comparatively low cycles of concentration, then corrosion will be the predominant secondary problem that develops.

If cooling systems are operated intermittently due to production scheduling or occupancy factors in comfort cooling towers, the authors have successfully applied ozone in such applications by ensuring that the ozonation system and the primary cooling pumps are restarted for a period of not less than six times the system turnover time every 48 hours. Thus, a cooling system with a turnover time of 5 minutes should be operated for 30 minutes once every other day if not otherwise ozonated during normal operations.

### ***PREFERRED TYPES OF COOLING TOWERS AND HEAT EXCHANGERS***

There are distinct differences in the functional performance of ozonated cooling systems based on the physical characteristics of the cooling towers and heat exchangers in the cooling circuit. Tube side cooling is preferable to shell side cooling in ozonated cooling systems in terms of fouling or scaling. It is recommended that cooling system operators determine the velocities through all heat exchangers (but particularly those with shell side cooling) prior to ozonation to ensure sufficient flow to heat exchanger surfaces. Users with insufficient shell side cooling in tube-in-shell heat exchangers should increase flow through those heat exchangers to the maximum flow rate allowed by the process cooling.

Evaporative coolers, evaporative condensers, and splash type tube bundle heat exchangers are subject to greater scaling and fouling tendencies than are cooling system users employing tube side cooling, especially when water spray or distribution pattern over tubes does not result in fully wetted surfaces. Given a tendency towards greater scaling on these types of externally wetted tubes, the authors recommend extensive efforts to increase water flow and to distribute the cooling water more uniformly over the tube surfaces. Proper use of sand filters also is recommended in these applications to reduce levels of suspended solids in the circulating water and minimize fouling tendencies.

Although linear velocities in plate and frame heat exchangers are low compared to those of tube side cooling heat exchangers, the design characteristics of plate/frame units result in turbulent water flow through the tortuous pathways in these heat exchangers. As a result, they do not exhibit the same fouling tendencies as shell side or splash type tube cooling.

Some researchers have noted that any initial appearances of scale in ozonated cooling systems occurs in the tower fill (14), particularly if thin film or similar non-splash type fill is used. This is consistent with the authors' observation. As a result, accumulations of scale particles may tend to build in tightly packed fill without sufficient water flow to flush the materials down into the basin. In such towers it is especially important to hold the conductivity below the point at which scaling begins to occur and, if possible, to maintain maximum design flows through the tower fill.

The authors have noted increased tendencies towards deposition formed on the walls of forced draft towers compared with induced draft towers operating under otherwise identical conditions. Such deposition tendencies are believed to be due to impingement are localized in the cooling tower, and do not extend throughout the cooling system. This type of deposition is observed more often in highly cycled waters with poor make-up water quality. As with shell side and splash type tube bundle cooling, tendencies toward deposition are minimized with the proper use of sidestream filtration.

### ***ELASTOMERS AND COMPARABLE MATERIALS OF CONSTRUCTION***

Because ozone is such a powerful oxidizing agent, consideration of the potential effect of ozone on various nonmetallic materials of construction is warranted. The authors believe that no more consideration need be given to these materials of construction in an ozonated system (with a few exceptions) than similarly would be devoted to materials selection if acid, chlorine, or other aggressive chemicals were employed in chemical treatment programs. Only materials known to be resistant to oxidation should be selected.

In the experiences of the authors, the construction material that must be completely avoided when using ozone is natural rubber, which will be oxidized very rapidly. Except for diaphragms or stressed, extremely aged, or oxidized elastomers, the authors do not recommend replacing seals or gaskets prior to commencement of ozonation. When natural rubber seals, diaphragm seals, or very degraded seals already are present in a system, these elastomers should be replaced with Viton. Viton has shown

good durability and resistance to oxidation in ozonated environments. The authors have observed Buna-N and EPDM pump seals lasting well in excess of five years without failure under ozonation. However, ozone does accelerate degradation of these types of pump seals if they have been previously exposed to low pH or high chlorine conditions, are already well-oxidized, or are in a worn condition prior to ozonation. When pump seal failures are experienced, replacement with Viton seals is recommended.

With wood-in-tower basins or fill, previous work has shown that ozonation removes infiltrating biological growth that is a main cause of wood failure in towers (6). That study did not show fiber destruction or delignification.

PVC is not recommended for use with ozone in the gas phase due to the corrosive nature of gaseous ozone. Some also have recommended against its use in contact or mixing devices (22). The authors have used schedule 80 PVC pipe exclusively in the sidestream ozone injection/mixing loop and have observed systems in operation for over five years without deleterious effects of the continuous mixing of high concentration ozone gas in a turbulent water flow. In fact, virtually every cooling tower ozonation system in use in the United States uses PVC pipe exclusively in the mixing circuit. Given this endurance in highly concentrated ozonated environments, it is highly unlikely that PVC degradation would occur elsewhere in ozonated cooling systems (e.g., PVC fill) which is consistent with the author's empirical experiences.

If basin or other metal coatings are desired for repair purposes in ozonated towers, vinyl ester resins have been seen to be more resistant to ozone oxidation than epoxy resins. Further, epoxy resins have shown greater oxidation resistance than most polyester resins. In fact, most polyester applications observed by the authors have shown limited resistance to high concentrated ozone environments such as seen in tower basin coatings. Polyester materials otherwise exposed to very low levels of ozone in tower drift or in ambient air appear unaffected. The authors also have found that simple RTV silicone provides excellent oxidation resistance, is easily applied, and is very useful for repairing tower leaks above the water line such as between tower panel flanges.

### ***FILTRATION SYSTEMS***

Use of filtration systems is recommended in any cooling tower water treatment program for removal of suspended solids from the circulating water. While the authors have found benefit in sand type media filters, they have not found significant benefit nor removal of suspended solids from ozonated cooling water by use of centrifugal type separators. As to sand filters, users of ozonated and conventionally treated cooling water must consider the tendency of such filter media to become scaled when filtering highly cycled waters with high hardness levels. The authors recommend that such filters be backwashed at least twice per day with large volumes of fresh makeup water (not tower water) to avoid media scaling. Numerous sand filters have run trouble-free for years under these operating conditions. In several cases, however, proper backwashing was discontinued for as little as a week and serious filter scaling occurred.

The authors have determined empirically that anthracite or common, washed garden-grade sands show much lower tendencies toward scaling than the uniform, processed media offered by most industrial filter media suppliers.

In many newly ozonated systems that have experienced high corrosion rates under multichemical treatment in the past, it is common to observe sloughing of corrosion byproducts with subsequent distribution in the recirculating cooling water. The byproducts often are in the form of small, coin-size, blackened iron oxide chips which are loosened by ozonation removed from pipe and heat exchanger end caps. In the first several weeks of ozonation, these byproducts often collect in system strainers and filters where they are easily removed from the system. Occasionally, one or more of the byproduct chips may migrate to the heat exchangers and become lodged in the tubes. This constriction has the effect of reducing the flow rate through the particular affected tube with resultant low flow depositions. As a result, the first heat exchanger inspection following commencement of ozonation may show several random tubes that appear fouled while all other tubes are design clean.

Simple rodding of the affected tubes will clear the obstruction and buildup behind it, and future inspections should not exhibit this fouling phenomenon because all of the corrosion byproducts generally are removed within several weeks.

#### *System Monitoring/Equipment Maintenance*

More so than with any other type of water treatment program, ozonated cooling systems must have a regular monitoring and equipment maintenance program to ensure that the system operates continuously in a proper manner. As historically reported (11), a number of ozone system failures have been reported that were primarily due to equipment failure that was not repaired in a timely manner. This can lead to functional degradation of system performance. If not correctly diagnosed, the failures then would be attributed improperly to technological deficiencies rather than to equipment breakdown.

Due to the short half-life of ozone, it is imperative that cooling water ozonation systems users monitor the process and equipment on a periodic basis. It is recommended that monitoring be conducted at least twice per day, 365 days a year. The recommended analog and digital inputs for monitoring are shown in Figure 2. This monitoring regime should be supplemented with periodic measurement of ozone residuals throughout the basin and careful monitoring of makeup water and tower water quality to ensure satisfactory performance.

Both cooling towers treated with ozone and the ozonation equipment itself must be maintained regularly and cleaned to ensure optimal system performance. The recommended procedures for ozonated tower maintenance are similar to those recommended when conventional chemical treatment programs are used. These include periodic (quarterly or twice annually) vacuuming of debris such as airborne dust or makeup water introduced foulants from the tower basin.

Ozonation as described by the authors has not resulted in formulation of a sandy form of calcium carbonate in basins, except when the makeup water is high in phosphates or other contamination has induced excessive precipitation.

One area of cooling towers in which deposits may be noticed during normal operations is the outermost edges of cross-flow fill and on non fully wetted surfaces on the bottom of counter flow fill. This is not an indication of an overall scaling condition in ozonated systems. The outermost portions of cross-flow tower fill are an area of greatest evaporation. Such evaporation (as pure H<sub>2</sub>O) will leave deposits on the fill edge appearing as small, well defined crystals. They are easily removed by periodically spraying the fill with a hose to wash any accumulations into the basin.

In some factory-built cross-flow towers, the fill of the cooling tower may extend all the way to the bottom of the tower basin. This design does not lend itself to proper cleaning of the tower basin and tower fill, and allows substantial accumulation of sludge and precipitable material beneath the fill. This problem, common also to conventionally treated towers, can be solved by removal of the lower 2-3 inches of the fill with a hot wire wand. This allows more complete basin distribution of the sidestream return to the towers and simplifies basin cleanings.

Also, due to ozone's short half-life, surface areas of the tower that are exposed to sunlight but only partially or intermittently wetted, may experience some algal growth. The noncontinuous water or mist provides sufficient moisture to sustain growth, but contains insufficient ozone residual for disinfection. Any such patches of biological growth which may develop in the tower are cosmetic only and can be easily sprayed off during periodic housekeeping functions.

One other cosmetic observation by the authors is the unexpected appearance of thin, glassy sheets of almost pure calcium carbonate on the upper exposed surfaces of the underwater PVC pipe of the basin distribution system. This deposition appears in almost all ozonated systems, even those operating at relatively low cycles of concentration and where there is absolutely no other indication of scaling elsewhere in the cooling circuit (including the PVC fill). There is an unexplained attraction between the underwater PVC pipe in the basin and the form of calcium carbonate found. Growth of this deposit is exceedingly slow and functionally has no impact on system operations.

### *Ozonation Safety Considerations*

Ozonation systems have enjoyed a long history of safe operation when compared to the use of other compressed, site-stored oxidizing gases (e.g., chlorine). Reasons, comparative toxicology, exposure threshold limit values, and recommended or required safety precautions of ozone use have been discussed previously (17). Even though there are lessened risks of significant overexposure when using ozonation systems for water treatment, the potential for excessive exposure, always exists when ozone is being generated and used in an industrial environment. In response, the Uniform Fire Code recently incorporated new safety design considerations for Ozone Systems (Appendix II-G, page 494) (18). Many aspects of the code changes employ standard safety precautions in widespread use with other compressed toxic gases.

These safety precautions have been employed routinely in the past by most vendors of large ozonation systems. These include external interlocks, exhaust treatment of ventilated cabinets, and secondary containment. The new requirements are discussed below.

For all non-residential ozone generators which have a maximum daily output capacity of greater than 0.5-lb per day, the proposed code changes specify that generators must be either in (1) unoccupied, ventilated rooms labeled with appropriate warnings and continuously monitored for ozone with an alarm system, or (2) approved cabinets with ventilation. Generators and ozone piping also must be labeled appropriately with specified warnings, and the generators must be anchored seismically per Uniform Building Code requirements.

Ventilation exhaust from a room or cabinet must provide at least six air changes per hour and be directed to a treatment system designed to reduce the discharge concentration of the exhausted gas to 5 ppm. This is 50% of the level determined to be immediately dangerous to life and health (IDLH). Air intake into the ozone generator must be at a velocity greater than 200 ft/min to ensure that fugitive emissions do not escape from the generator. A high ambient ozone concentration monitor interlock on the ozone generator may be used in lieu of exhaust treatment when ozone generators are in rooms.

Secondary containment of all valves, fittings, gages, and piping carrying ozone gas must be installed, except for welded stainless steel pipe. The secondary containment also must be vented to an appropriate exhaust treatment system.

All materials which come into contact with the ozone gas must be completely ozone-compatible to prevent ozone degradation leading to leaks. Acceptable materials include stainless steel, glass, Teflon, etc.

An external interlock also must be provided for the ozone generator to ensure shutdown of the generator in the event of an external system failure or process shutdown. The external interlock coverage must include: failure of the ventilation system, failure of the ambient ozone concentration monitor (if being used in a room), shutdown of the process being treated (generally indicated by a pump on/off condition, and high ORP interlock.

Also, emergency shut-off switches must be on the generator and within 10 feet of the primary exit if the generator is in a room.

#### *Use Of The Guidelines To Analyze Ozonation Application Failures*

Recently there have been a number of reported failures of ozonation systems (13,15). These case studies did not identify or explain the causes of the failures, however. This implies to readers of those reports that the technology of ozonation is inappropriate for end users in similar applications. In each of these cases, however, a number of operational shortcomings occurred which determined the outcome of the ozonation system performance. To illustrate how the guidelines discussed in this

paper may be employed to troubleshoot failed applications of ozonation technology, two unrelated applications were investigated and the causes of failure are discussed below:

***Gas Refining Facility***

The first case history reported the results of ozonation of cooling water at a CO<sub>2</sub> refining facility operating from January of 1990 through September of 1991 (13). The report indicated that overall corrosion rates were high (from 6 to 25 mpy) and that excessive scaling and biological growth occurred; particularly in the later months of operation. The report summarized the operational failures of the ozonation system by stating

"...under optimized feed and control conditions, evidence showed that corrosion rates were high and deposits occurred...".

Readers of this report would be inclined to believe that ozonation in similar applications is ill advised. Upon detailed examination of the reported operating data and analysis of other unreported details of the application, however, it is clear that neither "optimized feed" nor "control conditions" existed at the plant. Instead, evidence indicates the cooling water system was contaminated continuously by ammonia leaks in the refining process and that the ozonation equipment was producing far less ozone than the design minima due to operational neglect.

By analysis of the data reported in the paper, two water quality parameters showed extremely large variations compared to water quality parameters reported by investigators of other successful ozonated cooling systems. The first parameter noted as abnormal was the extreme variation and low ranges of pH in the circulating cooling water. The authors of the report noted that the pH of the ozonated water had dropped to between 6.0 and 6.5. Subsequent measurements made by other investigators showed the pH dropping to as low as 4.5 and accompanied by wide swings in the pH range (up to 2 pH units in a two-hour period). This was in marked contrast to reports of very stable and high pH (between 8.6 and 9.0) found in numerous other ozonated towers (1,2,4-6,12,14,16,20). It has been proposed that it is the presence of stable, highly alkaline conditions in ozonated cooling water that may be primarily responsible for the low corrosion rates typically seen in properly ozonated systems (20). The extremely low and variable pH reported in the cooling water indicated that major system upsets occurred. The resulting low pH adversely affected the corrosion rates found in the ozonated cooling system.

Further evidence of serious system upsets was indicated by the variable conductivity and nitrate levels of the recirculating water. For example, during one 10 week period, the conductivity of the circulating water ranged from 5.5 cycles of concentration (at 840 micromhos) to over 100 cycles of concentration (at 15,500 micromhos) based on an average makeup water conductivity of about 150 micromhos. During the same period, the nitrate cycles of concentration simultaneously ranged from 19.1 to almost 4,300 based on a makeup concentration of 1 mg/L of nitrate ion. At one later point, the nitrate levels reached a high of 17,500 mg/L while the conductivity reached up to 45,000 micromhos. The wide conductivity swings were due to the fact that the

conductivity controller on the tower was inoperative and the blowdown from the tower was manually controlled. Also, free makeup water was provided by the adjacent chemical plant that provided the feedstock  $\text{CO}_2$  to the plant. During periods of process water shortages at the adjacent chemical plant, deliveries of water to the gas refining plant would be greatly reduced and operators at the gas refining plant would turn off the blowdown in the cooling towers to conserve available water. This resulted in wide intraday and interday conductivity swings.

The very high nitrate levels were believed to be due to the oxidation of ammonia leaking into the system, as discussed earlier in this paper. Further, the nitrate levels were observed to increase dramatically and the pH of the tower water dropped precipitously whenever the plant went into a high pressure, full production operating mode. This strongly indicated that major leakage of ammonia into the circulating water occurred coextensive with full production operation. The cause of the depressed pH is unknown. On at least one occasion a large ammonia exchanger that had failed and was thought to be offline was found to have cooling water circulating through it. When the exchanger subsequently was valved off and opened for inspection, ammonia concentrations on the water side were so excessive that outgassing occurred, forcing evacuation of the area by plant personnel.

Efforts by the plant to further isolate and repair other sources of leaks were largely unsuccessful. Removal of the major source of ammonia leakage, however, resulted in much more stable tower water pH and greatly reduced mild steel corrosion rates; subsequently averaging just over 4 mpy from February through June of 1991 (as determined by an independent laboratory). During the identical period of time in an adjacent chemically treated tower, average mild steel corrosion rates over 8 mpy were determined, or about twice the level simultaneously achieved in the ozonated cooling water. Thus, on a comparative basis, the ozonated tower actually was providing better corrosion protection than the chemically treated tower. This information was not reported by the authors of the case history which otherwise indicated superior functional control in the chemically treated tower.

The increase in deposition on the tubes in the ozonated tower was an unrelated problem that occurred only during the later months of operation of the system as shown in the report. The depositions were immediately preceded by a precipitous drop in the oxidation reduction potential of the cooling water; generally indicating a lack of sufficient ozone residual. The problem went unheeded for several months even as the approach temperatures deteriorated rapidly. Upon later inspection, it was determined that the air dryer had failed and the dewpoint of the feed air to the ozone generator was insufficiently low to allow full ozone production. Also, the site had opted to use cooling tower water to cool the ozone generator electrodes instead of plant makeup water to conserve available water supplies. Use of cooling water is not recommended for ozone generator cooling because the very low velocities encountered tend to result in localized deposition in the ozone generator which reduces the operational efficiency. Exacerbating the problem was the fact that the plant personnel had not cleaned the cooling tower basin since the inception of ozonation and there was up to 2-3 inches of dirt and sludge accumulated in the basin. This sludge was circulated into the ozone generator with the cooling water and it resulted in fouling and complete blockage of a heat exchanger in the ozone generator designed to reduce operating temperatures. This further decreased ozone output. Also, the electrodes in

## PRACTICAL GUIDELINES FOR OZONE COOLING TOWERS 533

the ozone generator had not been cleaned since the inception of ozonation. Substantial electrode fouling occurred, further contributing to reduced ozone output.

Combined, these maintenance shortcomings reduced the ozone generator output by greater than 60% and resulted in insufficient residuals throughout the system. As discussed earlier, insufficient ozone residuals will result in excessive scaling and biological growth, just as insufficient chemical residuals in conventionally treated water will result in functional degradation .

Because ozonation equipment and processes are currently not well understood by many end users, plants without adequate maintenance resources should not employ ozonation without reliable local backup service capability.

### *Cogeneration Facility*

A second ozonation case study recently reported involved a 50 MW cogeneration facility. Much additional information was available but unreported in this case study. The facility in question did not have an outside source to receive cooling water blowdown and the discharge was instead directed to onsite percolation ponds. Because the percolation ponds did not percolate to the extent expected, numerous additional ponds were constructed to receive the blowdown water. The percolation ponds still could not accommodate the blowdown from the cooling tower at 4,000 micromhos conductivity which was the recommended blowdown setpoint and the upper limit at which the blowdown could be discharged under the site's NPDES permit.

As a result, the facility was forced to either operate the cooling tower at zero blowdown or pay for offsite transportation and discharge of blowdown water. The expense of the latter option was prohibitive and the site was forced to implement zero blowdown operation of the cooling system despite warnings of the risks involved.

The case study also incorrectly reported that "the tower fill was covered with scale". In fact, scale accumulations occurred only in the lower 4-6 inches of fill counterflow material and only after over a year of operation. The scale developed only when the site changed water supplies from a surface water source (indicated in the case study) to a well water source substantially higher in hardness and lower in salinity. While remaining at zero blowdown, hardness increased in the makeup water from less than 100 mg/L to over 400 mg/L. The makeup water chemistry reported in the case study was not the same makeup water used when the fill deposits began to occur. The deposits found in the fill had no appreciable impact on cooling tower performance.

Although the presence of a silica layer on surface condenser tubes was reported in the paper, it was not disclosed that the deposit was exceedingly thin and did not result in any appreciable loss of vacuum or heat transfer efficiency in the exchanger. Of interest, other researchers also have reported the presence of a similar silica deposition in other ozonated towers, and it has been proposed that this may be a corrosion protective mechanism common to many ozonation systems (20). The paper did not disclose that measurable condenser loss of vacuum occurred only after the makeup water source deteriorated and the plant remained at zero blowdown, as discussed

above. The same heat exchanger on which the deposit was noted had been exposed to live steam that inadvertently had been bypassed into the surface condensers on several occasions also contributed to the deposition seen. Also, the scalometer heat flux was in excess of the heat flux typically encountered at the plant.

References in the report that the water "was severely out of balance" due to mineral removal does not take into account the abundance of reported field data, indicating that calcium, alkalinity, and silica normally precipitate in an ozonated environment, even under scale-free conditions (16). The fact that precipitation occurred in the ozonated water thus was used incorrectly to justify a presumed scaling of the entire fill surface.

Due to a lack of adequate air supply capacity, the ozone generators also were not able to operate at full capacity. This resulted in less than design operating conditions with periodic long periods of insufficient ozone residuals less than the recommended minima discussed earlier in this paper. Nevertheless, the ozonation system provided substantial functional and economic benefits to the facility, and enabled operation to continue for well over a year in an otherwise uneconomical environment.

In summary, readers should view reports of system failure with caution and carefully review the completeness of the data presented. If complete data is made available, use of the guidelines presented herein should enable prospective users to determine the underlying cause of failure and prevent similar mistakes when undertaking their own ozonation applications.

### **Conclusions**

Ozonation of cooling water is a technology with tremendous potential to provide increased functional protection at overall reduced costs with significant environmental benefits. Limitations to the technology exist, however, which must not be ignored or overlooked by users.

For the most part, these limitations have been identified and quantified, and workable solutions can be implemented to minimize their impact, as discussed herein. However, the technology of cooling water ozonation is relatively new and not widely nor well understood. Therefore, practitioners should ensure that they have knowledgeable personnel with experience in the design, installation, operation, and troubleshooting of cooling tower ozonation applications to maximize the significant functional benefits and minimize potentially serious deleterious effects.

### **References**

1. FRENCH, K.R.; R.D. HOWE; M.G. HUMPHREY, "Ozone Inhibits Corrosion in Cooling Towers", *Technical Support Package for NASA, Contract No. NAS 7-100*, Jet Propulsion Laboratory, California Institute of Technology, 1980.
2. HUMPHREY, M.G.; K.R. FRENCH, "Cooling Tower Water Conditioning Study", in *Ozone Treatment of Water for Cooling Applications*, R.G. Rice, Editor (Stamford, CT: International Ozone Association, 1981), pp. 31-41.

3. DOUGLAS, B.W.; MADDAUS; D. O'MALLEY, "Water Conservation at Exel Microelectronics; Water Conservation at Intel Corporation; Water Conservation at Tandem Computers; Water Conservation at Xerox Palo Alto Research Center", in *Industrial Water Conservation in the San Jose Area*, prepared for the City of San Jose and the California Department of Water Resources by Brown and Caldwell Consulting Engineers, 1990.
4. MERRILL, D.; J. DRAGO, "Evaluation of Ozone Treatment in Air Conditioning Cooling Towers", Research Project 1260-4, prepared for the Electric Power Research Institute by Brown and Caldwell Consulting Engineers, 1979.
5. BALDWIN, L.V.; E.S. FEENEY; R. BLACKWELDER, "The Investigation and Application of Ozone for Cooling Water Treatment", NASA, presented at the 46th Annual Meeting of the International Water Conference, Pittsburgh, PA, 1985.
6. KINNEY, R., "Ozonation as Cooling Tower Water Treatment - A Pilot Study", IBM Technical Report 20.0430, 1983.
7. LEITZKE, O.; K. ROHLEDER; M. MURRAY, "Application of Ozone in the Treatment of Cooling Water", in *Ozone Treatment of Water for Cooling Applications*, R.G. Rice, Editor (Stamford, CT: International Ozone Association, 1981), pp. 31-41.
8. EDWARDS, H.B., "OZONE, An Alternative Method of Treating Cooling Tower Water", *J. Cooling Tower Institute*, 8(2):10-21 (1987).
9. PRYOR, A.; M. BUKAY, "Water Conservation Through Cooling Tower Ozonation", *Ultrapure Water*, 7(4):24-30 (1990).
10. PRYOR, A., "Economics and Performance of Cooling Tower Ozonation: Six Case Histories", paper No. IWC 90-15, 51st Annual Meeting of the International Water Conference, Pittsburgh, PA, Oct. 23, 1990.
11. PRYOR, A.; M. BUKAY, "Historical Perspective of Cooling Tower Ozonation", *Industrial Water Treatment*, Oct. 1990.
12. PRYOR, A., "Ozone Treatment of Cooling Water at a Gas Production Facility", *Corrosion* 91, paper 585, Houston, TX: NACE, 1991.
13. LAWSON, T.; A. FELTZIN, "Ozonation in a Carbon Dioxide Planing Cooling System", *Corrosion* 92, paper 393, Houston, TX: NACE, 1992.
14. COPPENGER, G.D. et al, "Ozone Treatment of Cooling Water: Results of a Full Scale Evaluation", *Cooling Tower Institute*, Technical Paper 89-07, Houston, TX, 1989.
15. STRITTMATTER, R.J., et al, "Application of Ozone in Cooling Water Systems" *Corrosion* 92, paper 347, Houston, TX: NACE, 1992.
16. PRYOR, A., "A New Practical Index for Predicting Safe Maximum Cycles of Concentration In Ozonated Cooling Towers", *Corrosion* 93, paper 482, Houston, TX: NACE, 1993.
17. PRYOR, A., "Ozone Toxicology, Exposure Threshold Limit Values, and Safety Precautions", *Ozone News* 18(6), 1990.
18. PRYOR, A.; T. BUFFUM, "New U.S. Uniform Fire Code Safety Design Considerations for Ozone Systems", *Ozone News* 29(3), 1992.
19. GILL, J.; VARSANIK, R., "Study of Cooling Water at High Cycles", Technical Paper No. TP-85-15, *Cooling Tower Institute*, 1985.
20. WOFFORD, G., et al., "Corrosion Control in Ozonated Cooling Water Systems" *Industrial Water Treatment*, January, 1991 .

21. RICE, R.G.; J.F. WILKES, "Fundamental Aspects of Ozone Chemistry in Recirculating Cooling Water Systems - Data Evaluation Needs", *Ozone: Science & Engineering*, 14(4):329-365, 1992.
22. DIMITRIOU, M.A., Editor, *Design Guidance Manual* (Stamford, CT: International Ozone Association, 1990).

### Key Words

Ozone; Cooling Tower Water Systems; Guidelines for Ozone Operation; Causes of Ozone Failures;

### Résumé

Ce document discute des recommandations générales pour un emploi efficace d'une méthode de traitement de l'eau des tours de refroidissement par ozone seulement. Sont incluses des recommandations pour le dimensionnement du système, la détermination des résiduels d'ozone appropriés, le mélange et la distribution de l'eau traitée, la liste des problèmes éventuels ainsi que leur solution. Ceci comprend le facteur de concentration (trop) bas ou trop élevé la pollution chimique, les vitesses de circulation trop faibles, les températures élevées dans les échangeurs de chaleur, et les systèmes à long temps de recirculation.

Sont aussi précisés les temps maximaux d'arrêt recommandés, les meilleurs modèles de tours de refroidissement et d'échangeurs de chaleur en cas d'utilisation de l'ozone les conditions d'emploi de filtres et la compatibilité des élastomères avec l'ozone. Les procédures de contrôle et de maintenance sont discutés en relation avec la sécurité d'emploi de l'ozone. Les informations ont permis d'analyser deux cas récents de dysfonctionnement et d'en examiner les causes.

### Zusammenfassung

Beschrieben werden Richtlinien für den erfolgreichen Einsatz von Ozon als alleinige Technik zur Kühlturmwasseraufbereitung. Es werden Empfehlungen gegeben für: Die Dimensionierung des Systems, für ausreichende Ozonrestkonzentrationen, für Mischung und Verteilung des ozonten Wassers und für andere mögliche Probleme. Diese beinhalten: Zu hohe bzw. zu niedrige Konzentrationszyklen, chemische Verunreinigungen, niedrige Durchflußraten, hohe Wärmetauschertemperaturen und überlange Umlaufzeiten. Ferner werden diskutiert: Maximale empfohlene Ausschaltzeiten, bevorzugte Kühlturmtypen und Wärmetauschersysteme für den Ozoneinsatz, der Einsatz von Filtersystemen und die Verträglichkeit von Kunststoffen mit Ozon. Die Überwachung und Wartung der Systeme werden besprochen im Zusammenhang mit Sicherheitsüberlegungen beim Ozoneinsatz.

In diesem Zusammenhang werden zwei kürzlich aufgetretene Fehlschläge in Ozonsystemen diskutiert und analysiert.