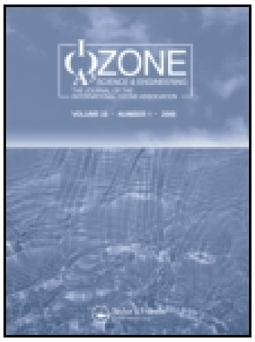

ISSN: 0191-9512 (Print) 1547-6545 (Online) Journal homepage: https://www.tandfonline.com/loi/bose20

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To cite this article: Paul R. Puckorius (1993) Ozone Use In Cooling Tower Systems – Current Guidelines – Where It Works, , 15:1, 81-93, DOI: 10.1080/01919519308552190

To link to this article: https://doi.org/10.1080/01919519308552190

OZONE SCIENCE & ENGINEERING
Vol. 15, pp. 81–93
Printed in the U.S.A.

0191-9512/93 $3.00 + .00
International Ozone Association

Ozone Use In Cooling Tower Systems - Current Guidelines - Where It Works

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Received for Review : 20 September 1991
Accepted for Publication : 31 August 1992

Abstract

This paper was prepared to provide guidelines for effective ozone use in cooling tower systems based on known scientific actions of ozone and practical cooling system operation. It does not attempt to explain the unknown or unpredictable actions attributed to ozone. Guidelines for ozone use in cooling tower systems usually can be predictable, depending upon the specific industry or site conditions found. Ozone is not a panacea as a stand-alone treatment in most cases, but can be under the right conditions. Applicability of ozone depends upon specific criteria that must be evaluated prior to its consideration or use. If ozone is to be tested, then it is critical to have adequate monitoring tools in place to evaluate its performance, rapidly, before system damage may occur. Ozone has a place today in cooling tower system protection, and likely a greater consideration and use when a better understanding of its mechanisms of action is developed.

Introduction

Ozone applications in cooling tower systems are relatively new, initially used in the late 1970s (1,2). Increased use and interest has only occurred in the late 1980s (3,4), primarily as a biocontrol agent but later as a stand-alone treatment replacing scale, corrosion, and biocontrol chemical treatments. Many of these claims were unsubstantiated or greatly exaggerated (5,6); however, some appeared to show success though they often defy scientific explanations (7-9). This paper was prepared to provide guidelines for effective ozone use in cooling tower systems based on known scientific actions of ozone and practical cooling system operation. It is not an attempt to explain the unknown or unpredictable actions attributed to ozone.

Cooling Tower Systems *Versus* Various Industries

Cooling tower systems, though basically the same (Figure 1), vary extensively in design, operation and contaminants for different industries. These variations are critical in predicting the performance and cost effectiveness of ozone use in cooling tower systems. There are a number of specific criteria that should be considered in predicting ozone effectiveness; some of these are:

a) ozone demand from organic and/or inorganic reducing agents from makeup water, air contamination, and/or process contamination;
b) excess time per cycle - the time to circulate water through the entire cooling system;
c) heat exchangers, particularly when water is on the shell side;
d) corrosion of heat exchanger tubing - mild steel is critical, and
e) water temperatures that can quickly deactivate ozone.

Other criteria are system-specific and a number of these factors create an unfavorable condition for ozone consideration and effectiveness (see Table I).

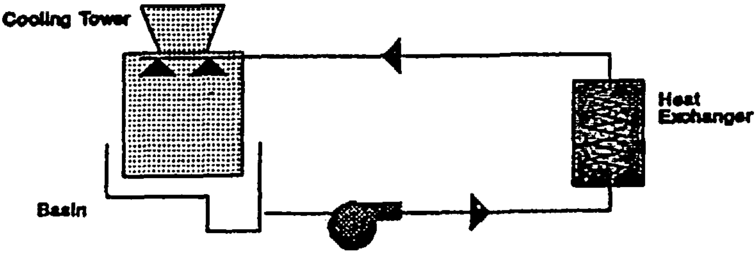

Figure 1. Basic Cooling Tower System.

TABLE I. CRITERIA DETRIMENTAL TO ECONOMICAL OZONE USE

1. **Ozone Consumers** o Makeup water organics/iron/manganese/ammonia*/bioorganisms o Atmospheric organics/ammonia*/sulfides/sulfur dioxide o Process/organics/ammonia*/sulfides
2. **Retention Time - Time/Cycle = Capacity/Recirculating Rate** o Over ten (10) minutes
3. **Large Water Use** o Over 1 million gallons per day
4. **Temperature** o Over 110°F
* only above pH 9

OZONE DEMAND

Many organic and inorganic materials such as lignins, tannins, unsaturates, ferrous or manganous ions, sulfides, and sulfur dioxide are ozone demanding; even ammonia at high pH (above ca 9.0). The organics can be natural organics found in makeup water, due to process contaminants from the system and atmospheric gases. These materials can create excess ozone demand when continuously added to cooling water, even at fairly low concentrations such as a few mg/L or more. This may prevent economical ozone application.

Circulation time per cycle (the capacity of the system in gallons divided by the recirculation rate in gallons per minute) (T/C = volume/recirculation), when over 10 minutes, will exceed the known ozone life expectancy (9a) (ozone can be consumed within 5 minutes). Ozone life expectancy is dependent upon time and pH, as well as on the presence of ozone-consuming materials (9). Systems with a time per cycle less than 10 minutes are candidates for ozone. Those over 10 minutes are not likely candidates with ozone alone, or will require several ozone feed locations, or rely on other chemical additives such as the simultaneous use of bromides. Even then, they may not effectively control biomass.

Another criterion exists when numerous heat exchangers, particularly with shell side water, are present in the cooling system. These exchangers are "traps" of biomass, organics, etc. and can consume the ozone due to deposit "hide-out". This prevents development of ozone residuals going further into the system, causing these areas to be untreated.

Elevated water temperature is a major criterion that will rapidly destroy ozone. Usually (bulk) water at 110°F is considered high for ozone use (some believe 104°F or more is bad). It is not unusual to have (bulk) water temperatures over 130°F in some cooling water exchangers.

Still another criterion is that the cooling tower can air-strip ozone (this is also true for other oxidants) from the cooling water due to its low solubility. This can allow development of biomass and even the presence of *Legionella* bacteria in the cooling tower fill. As soon as the hot cooling water sprays into the upper sections of the cooling tower, no ozone will be present to keep the cooling tower internals clean. This is particularly true when evaporative film fill is used, but also can occur with the commonly used splash fill. A summary of this criterion is given in Table II.

COOLING TOWER SYSTEMS IN VARIOUS INDUSTRIES

Let's look at cooling tower systems in various industries and see how they differ from each major industry:

A. **HVAC or Air Conditioning Systems (see Figure 2)** are perhaps the best suited for successful ozone use. They seldom have major atmospheric or makeup water contamination that consumes ozone. They do not have any organic process inleakage. The time per cycle usually is less than 10 minutes, due to a small system capacity to recirculation rate ratio. Temperatures seldom exceed 100°F.

TABLE II. CRITERIA TO CONSIDER FOR OZONE USE

1. **Biocides Replacement Potential**
   - o Non-oxidizing -- good potential
   - o Oxidizing -- poor potential
2. **Heat Exchanger Tube Metallurgy**
   - o Mild steel -- critical
   - o Copper alloy -- concern
   - o Stainless steel -- no problem
3. **Heat Exchanger Design**
   - o Water shell side -- difficult to keep clean
   - o Water tube side -- easy to keep clean

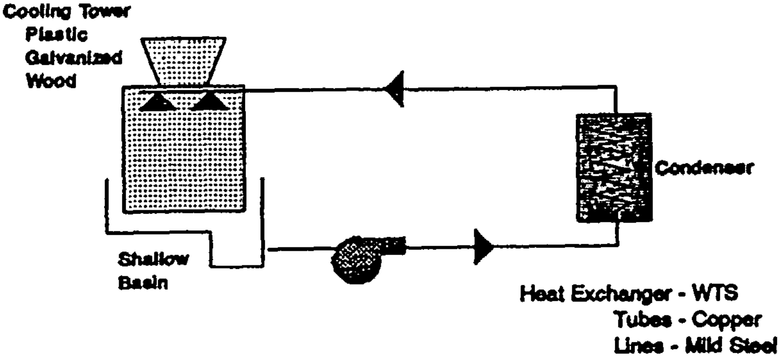

Figure 2. Typical HVAC system.

HVAC systems usually have one or, at the most, several heat exchangers (condensers) and they all have tube-side water cooling, which is easiest to keep clean. The materials of construction are mild steel piping that can tolerate 5 mpy (mils per year) corrosion rates, and heat exchanger tubing of copper or copper alloy that can tolerate 0.5 and even 1.0 mpy. The most common makeup source is clean, chlorinated or chloraminated city water. They are relatively small water users compared to utility or industrial plants, and often use nonoxidizing biocides. These systems are relatively easy to treat for biomass. Ozone, due to the system characteristics and operation, could be effective, but not always cost effective.

B. Oil Refineries And Chemical Plants generally are poor candidates for ozone use. Perhaps the greatest obstacle to economic ozone use in these systems is the high ozone demand created by organics and inorganics entering these systems. This ozone demand can originate from the makeup water, which is usually partially treated water, atmospheric gases/vapors drawn into the water by the cooling tower, and process contaminants originating from the heat exchangers. The time per cycle is often 20 minutes or more and water temperatures often exceed 130°F. These materials quickly consume ozone.

As shown in Figure 3, these cooling tower systems have many heat exchangers. Many use mild steel tubes that require very good corrosion protection with rates of 0.5 mpy or less and no pitting corrosion. This is attainable with standard chemical treatment programs and is essential when using ozone. Some exchangers have tubes of copper alloy (Admiralty and copper nickel), and/or stainless steel (304 and 316) where corrosion rates less than 0.2 mpy with no pitting are required. The many heat exchangers (tens or even hundreds) in each system have cooling water on both the tube side and shell side. Many of these factors are detrimental to effective ozone use.

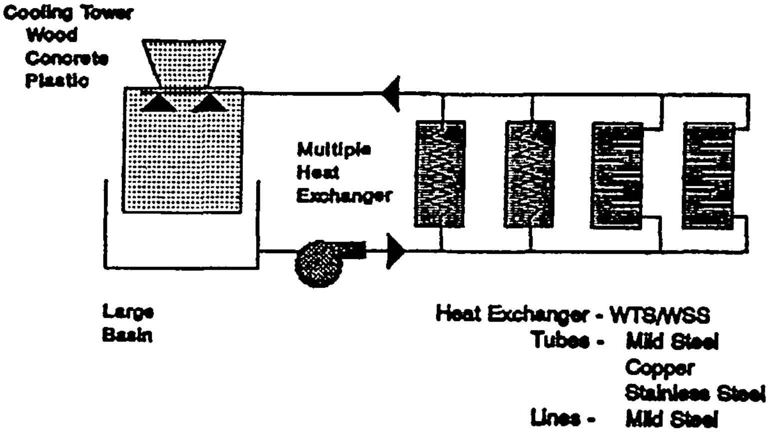

Figure 3. Typical refinery/chemical plant system.

C. Utility Fossil Stations (Figure 4) also are poor candidates for effective ozone use, but for different reasons. They often have moderate to high organic loading due to use of untreated or marginally treated makeup water. However, they do not have process contamination and only minimal atmospheric ozone-consuming contaminants. They generally have a very long time per cycle, often in excess of 30 minutes. This is due to their large capacity (12 million gallons) and circulation rates of 400,000 gpm. The water temperatures frequently exceed 120°F. These criteria can result in very high ozone use in these plants.

D. Utility Nuclear Power Stations also are poor candidates for ozone for many of the same reasons as the fossil fuel stations. Yet, this depends upon the cooling water system design (Figure 5). If the design utilizes a separate condenser cooling system, the criteria are similar to those of a fossil plant; however, if the service water and condenser water are combined, ozone use is not practical and likely to be ineffective. This is due to the redundant safety-related service water equipment which has a lack of water flow during normal operation but remains filled with water. The lack of flow prevents ozone from entering and effectively treating the system.

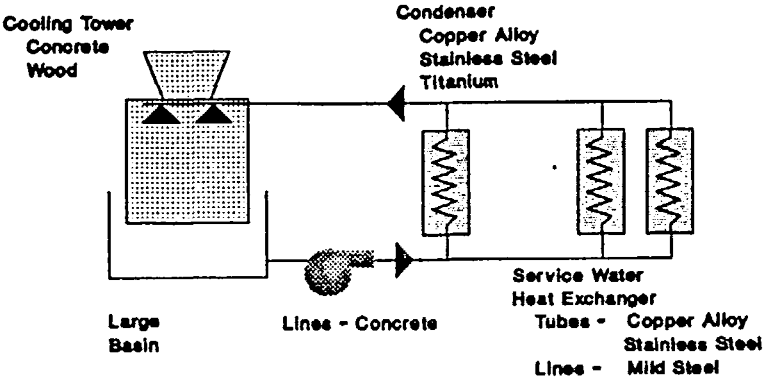

Figure 4. Typical utility fossil fueled plant.

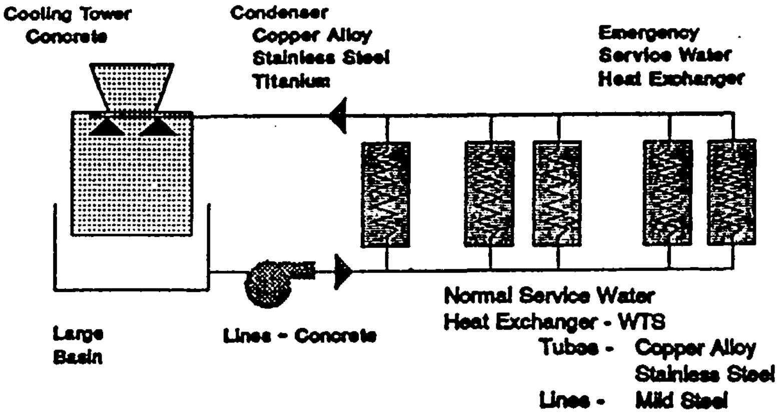

Figure 5. Typical utility nuclear plant.

E. Steel Mills (Figure 6) also are very poor candidates for ozone use because of much the same criteria as those of oil refineries and chemical plants. They generally utilize poor quality makeup water, and encounter considerable atmospheric and process contamination, such as dirt, dust, iron oxide, and sulfurous gases; thus, have excess ozone demand. These cooling tower systems generally are very complex with jacketed cooling (water on shell side), multiple heat exchangers, and long time per cycle due to large system volumes with relatively low circulating rates. Water temperatures commonly exceed 120°F. All of these criteria are negative to the effective use of ozone.

F. Light Manufacturing Industry Cooling Systems often are similar to the HVAC cooling systems and thus may be good candidates for ozone. However, the criteria outlined for oil refineries and/or chemical plants can be found in some of these facilities. If there is excess ozone demand or rapid ozone loss, these criteria would reduce the potential for successful ozone use. A summary of ozone use versus industries is given in Table III.

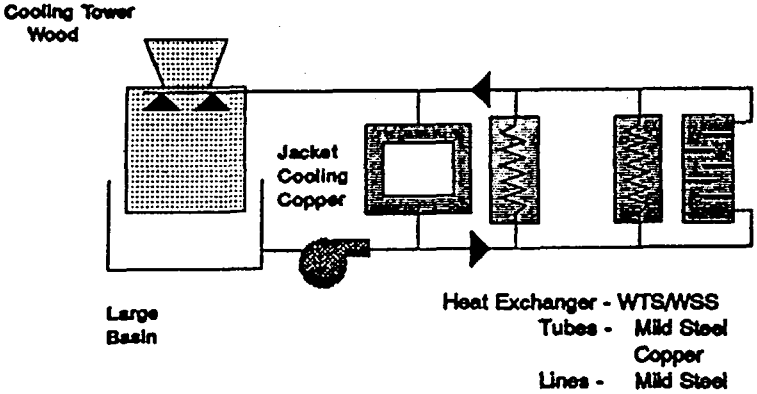

Figure 6. Typical steel plant.

TABLE III. APPLICABILITY OF OZONE *versus* INDUSTRY

Industry	Ozone Applicability
HVAC	Good
Oil Refineries	Very Poor
Chemical Plants	Very Poor
Utilities - Fossil	Poor
Utilities - Nuclear	Very Poor
Steel Mills	Poor
Light Manufacturing	Good

Predictive *Versus* Non-Predictive Ozone Performance

Cooling water system treatment must include five specific parameters for successful equipment protection. These are:

- Proper initial conditioning
- Scale control
- Fouling control
- Corrosion control
- Microbiological control

If treatment for any one of these areas is not effective, the entire program can fail, resulting in equipment damage - even system failure (9b).

Ozone has properties that are well-known, and thus its effectiveness is predictable based on these known properties. Yet, there are reported results of ozone application that are claimed by some, yet have no proven guidelines for prediction of effectiveness. We wish to address how ozone can be used with confidence and indicate where ozone use should be approached cautiously. One predictable ozone action is for biological control - that is, as long as ozone can reach the biomass found in the entire cooling tower system.

Ozone is the second strongest oxidant known, second to fluorine, thus it will oxidize or "burn-up" biomass and oxidize many organics and inorganics which it contacts. Unfortunately, when ozone is injected into water, it is both short-lived and easily volatilized. It rapidly reacts and thus is consumed, so none may be available for biocontrol thereafter. If volatilized, it is lost from the water and again unavailable for biocontrol. Cooling towers are efficient water/air mixers and gas strippers. They will remove gases such as ozone, chlorine, chlorine dioxide, as well as bromine. Thus, when the cooling tower is treated with ozone, it can often be heavily contaminated with biomass which may contain *Legionella* bacteria and other undesirable microorganisms, yet the heat exchangers may be biofree.

Ozone demand includes most organics and easily oxidizable inorganics that can enter the cooling system from three sources in addition to system materials and organic treatment additives. All can contribute to ozone consumption (10,11) - they are:

Cooling Tower Contaminants/Sources/Ozone Consumers

- **Makeup water** - organics/bio-organisms/ammonia/iron/manganese/sulfides/nitrites

- **Atmospheric** - organics/ammonia/sulfides/sulfur dioxide/bioorganisms

- **System** - oils/organics/iron/copper/galvanizing/plastics/filter media/wood and wood preservatives

Ozone effectiveness can be predicted, but it is not effective when chemical oxygen demand (COD) levels are above 20 mg/L, and when COD is continuously entering the cooling system. Ozone, being an extremely rapid reactant, can control biomass in some heat exchangers, but not necessarily throughout a complex system incorporating many exchangers, and holding a considerable volume of water. Ozone may not be effective when system volume divided by recirculation rate exceeds 10 minutes.

Another predictable ozone property is temperature degradation. It is known that ozone is destroyed more rapidly as the water temperature increases. A temperature of 130°F provides rapid destruction (12). Thus, temperatures of 110°F or greater are considered to be excessive and may result in too rapid ozone destruction for it to be effective.

BIOCONTROL

Ozone is a known biocontrol agent. It has shown very effective performance on all types of microorganisms, including *Legionella pneumophila* (13), yet it must be able to contact the bioorganisms to be effective. Two areas of a cooling system that are most vulnerable are 1) **cooling tower**, where we have identified the cooling tower problem (air stripping of the ozone) and, 2) **heat exchangers**, particularly those with water on the shell side that are most prone to deposit "hide-out". The inability to control deposits with shell side cooling is not specific to ozone. It is also a concern with any biocide, but particularly with oxidants such as chlorine, bromine, chloride dioxide and ozone. Deposits are not penetrated for effective biocontrol due to surface oxidant consumers. Certainly continuous high levels of oxidant, if present, will eventually clean up the exchangers. However, this may not be possible with a limited chemical delivery system with limits on oxidant discharge and impact on corrosion.

Thus, ozone use as a biocide is limited in cooling tower systems due to its rapid reaction rate, temperature limitations, and air-stripping. However, there are some cases where bromide salts (14,15) are being used with ozone, much the same as they are with chlorine compounds. The ozone oxidizes the bromide salts to hypobromous acid and hypobromite ions which are effective biocontrol chemicals, much more persistent than ozone. Ozone is consumed, but a much more predictable biocontrol results.

SCALE CONTROL

Scale control by ozone is claimed by some to be very effective. Some reports (5) indicate good results; however, there is no effective prediction method presented for specific water qualities and there have been numerous failures. When analyzed, the data are confusing and suspect. Some of these cases originally reported good scale control, yet after a short period, severe scale development caused ozone discontinuation. Perhaps the most commonly referred to current success story, JPL (Jet Propulsion Laboratories) in Pasadena, California, has in fact not used ozone for the last ten (10) years due to severe scale buildup in their cooling tower (16).

There is a variety of hypotheses as to possible scale control mechanisms, but all have deficiencies. No predictive methods have been presented that have been effective. It is important to note that there are a number of non-ozone use case histories (17) reporting scale control obtained in a similar manner claimed to occur with ozone. These mechanisms also are not predictable. Perhaps of greatest concern to cooling system operations, is that if interruption in ozone occurs when a severe scaling water condition exists, severe scaling will occur rapidly. This could shut down cooling tower operation before the failed ozonation system has been returned to service. Ozone use as a scale inhibitor is not yet predictable.

FOULING CONTROL

Ozone has no known effect on control of foulants such as suspended solids, iron, mud and silt.

CORROSION CONTROL

Corrosion control is another non-predictable effect of ozone. It is well known that ozone levels of 0.2 mg/L or more deteriorate many materials (8). These include mild steel, copper alloys, galvanized steel, cooling tower wood, and PVC pipe, as well as PVC cooling tower fill. Ozone levels below 0.2 mg/L may have some benefit in establishment of protective metal oxides, but there is no predictive method for ozone use in corrosion inhibition. Ozone use at these low levels, however, can protect various metals which are dependent upon surface oxide protective film integrity, such as stainless and titanium (Table IV lists acceptable metal corrosion rates for all chemical treatments including ozone).

TABLE IV. ACCEPTABLE CORROSION RATES (MPY)

Heat Exchanger Tubes	MS	0.5 MPY or less
Heat Exchanger Tubes	CU	0.2 MPY or less
Heat Exchanger Tubes	SS	0.2 MPY or less
Lines	MS	3-5 MPY
All cases -- no pitting		
MPY = mils per year; MS = mild steel; CU = copper alloy; SS = stainless steel		

Yet, some corrosion control has been obtained in cooling tower systems when using ozone. This has occurred, not due to ozone *per se*, but due to the action of ozone on some system materials. Some examples reported (8) are; 1) that high levels of nitrates were found when air (not completely dried) is used for ozone production, resulting in over 200 mg/L nitrate in the cooling tower water, 2) chromate wood preservatives were oxidized and leached from the cooling tower wood, and over 5 mg/L hexavalent chromate in the cooling tower water due to high cycles, and 3) several mg/L of zinc salts were found in the cooling tower water due to corrosion of galvanized cooling tower components. These chemicals generated by ozone reduced corrosion of mild steel and copper (with chromate).

Conclusions

Guidelines for ozone use in cooling tower systems usually can be predictable depending upon the specific industry or site conditions found. Ozone is not a "panacea" as a stand-alone treatment in most cases, but can be under the right conditions. Ozone applicability depends upon specific criteria that must be evaluated prior to its consideration or use. If it is to be "tried", then it is extremely critical to have adequate monitoring tools in place to evaluate its performance, rapidly, before system damage occurs (18). Ozone has a place today in cooling tower system protection, and likely a greater consideration and use when a better understanding of its mechanisms is developed.

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Key Words

Ozone; Cooling Tower Systems; HVAC Systems; Air Conditioning Systems; Oil Refineries; Chemical Plants; Fossil Fuel Utility Stations; Nuclear Utility Power Stations; Steel Mills; Light Manufacturing Industries; Biofouling Control; Scale Control; Corrosion Control;

Résumé

Cette contribution a pour but de formuler des recommendations basées à la fois sur les connaissances scientifiques et sur l'expérience pratique concernant 'utilisation efficace de l'ozone dans les tours de refroidissement. Il ne s'agit pas de tenter d'expliquer des effects inconnus ou imprévisibles quelquefois attribués à l'ozone. Des recommendations pour l'utilisation de l'ozone dans les tours de refroidissement peuvent généralement être formulées en fonction du type d'industrie et des conditions du site. Dans la majorité des cas, le traitement par l'ozone seul n'est pas une panacée, mais l'ozone peut être utilisé si on respecte les bonnes conditions d'application. Les possibilités d'application de l'ozone dépendent de critères spécifiques nécessitant une évaluation préliminaire avant on utilisation effective. Si le traitement par l'ozone est essayé, il est nécessaire de disposer de l'équipement adequat pour un contrôle rapide sur site. Afin d'en évaluer les performances avant toute déterioration éventuelle du système. L'ozone trouve aujourd'hui sa place dans la protection des tours de efroidissement et, on peut en attendre encore plus de développement grâce à une meilleure connaissance de ses mécanismes d'action.

Zusammenfassung

Der Artikel gibt Richtlinien für die effektive Anwendung von Ozon in Kühlturmsystemen, basierend auf bekannten Reaktionen von Ozon und den üblichen Fahrweisen von Kühlsystemen. Es wird nicht versucht, die unbekannten oder unvorhersehbaren Wirkungen, die Ozon zugeschrieben werden, zu erklären. Richtlinien für den Einsatz von Ozon in Kühlturmsystemen sind in der Regel voraussagbar und hängen von der bestimmten industriellen Nutzung und den spezifischen Randbedingungen ab. Ozon ist nicht in allen Fällen das alleinige Heilmittel, aber es kann es bei den richtigen Rahmenbedingungen sein. Der Einsatz von Ozon hängt von ganz spezifischen Kriterien ab, die vor dem Einsatz untersucht werden müssen.

Wenn der Einsatz von Ozon untersucht wird, dann müssen unbedingt geeignete Untersuchungen vorhanden sein, um die Wirkungsweise zu kontrollieren. Diese Kontrollen müssen schnell und an den geeigneten Stellen erfolgen, um Schäden zu verhindern. Ozon hat heutzutage seinen Platz beim Schutz von Kühlturmsystemen und wird zukünftig wohl noch an Bedeutung gewinnen, insbesondere wenn ein besseres Verstehen der Mechanismen und Wirkungsweisen erreicht wird.