

Application of Ozone in Cooling Water Systems

Reprint R-567

By R. J. Strittmatter, B Yang and D. A. Johnson, Nalco Chemical Company

ABSTRACT

The first comprehensive study — bench-top laboratory investigations, pilot scale testing, and critical monitoring and evaluation of field applications — addressing the effects of ozone as a stand-alone cooling water treatment program is presented. The study also represents the first critical comparison of ozone-treated systems with non-treated systems. Excellent corrosion control can be attained in ozone-treated cooling water systems. However, the corrosion rates are completely dominated by the water chemistry of the system and have no dependence on the presence of ozone at typical use levels. Good control of fouling can also be attained. However, as was the case with corrosion control, deposition on the heat exchange surfaces is not determined by the presence of ozone, but by several factors that traditionally influence fouling in a system. The strong biocidal properties of ozone resulted in excellent microbiological control in all PCT investigations, and in both case studies. Excellent agreement was observed among all stages of testing.

INTRODUCTION

The use of ozone in cooling tower treatment has received a great deal of attention in recent years. There are a number of factors which give this concept a great deal of appeal to cooling tower users. They include:

Minimal on-site chemical inventory — With the advent of SARA Title III and other legislation, the storage and handling of chemicals in general, and biocidal agents in particular, is more regulated and difficult. Since ozone is generated as it is used, these concerns are minimized.

Little or no toxicant discharge — The Clean Water Act and state and local regulation are placing increased pressure on cooling tower discharge into receiving streams. The high toxicity of ozone in water solution makes it an effective biocide. However, its rapid decomposition minimizes any downstream toxicity concerns. The by-products of ozonation of cooling tower water have not yet been subjected to the same scrutiny as have the by-products of halogen application, and are consequently not as stringently regulated.

The potential of water conservation — Numerous case histories of the use of ozone in “zero discharge” cooling tower

applications have been published. In water-short parts of the world, this carries an obvious appeal.

Balancing these significant benefits are some equally significant concerns:

The incompatibility of ozone with other inhibitors — Ozone is one of the strongest oxidizing agents known. Although little specific information has been published on the compatibility of ozone with industry standard corrosion and deposit control agents, the general feeling of the industry is that they are incompatible.

The impact of ozone on system materials of construction — Because of its oxidizing capacity, ozone has the potential to attack metals, wood, and elastomers used in cooling tower construction.

The lack of mechanistic understanding of claimed properties of ozone — It has been suggested in the literature that ozone itself can function as the sole treatment of a cooling tower, in which case it must provide corrosion and scale control. Case histories which have been presented are generally inadequately documented and do not have enough experimental control to conclusively assign these properties to the application of ozone. Many of the explanations which have been presented are hypothetical and/or not consistent with the principles of objective science. For example, it has been asserted that it is not possible to realistically study the properties of ozone in the laboratory. If this is true, then it logically follows that ozone behaves in some extra-natural manner in cooling towers.

The lack of general application guidelines — In general, the application of ozone has been on a case-by-case, quasi-experimental basis. To date, no body of information which allows a potential user to unequivocally evaluate the suitability of ozone to a particular situation has been made available to the public.

The purpose of this paper is to present some of the findings of an extensive research project which has been aimed at answering some of the above questions, with particular emphasis on understanding the mechanistic properties of ozone. These studies include intercorrelated laboratory and field investigations. The laboratory investigations provide the critical aspect of

good control of important variables, such as the presence or absence of ozone. In addition to their obvious importance, the field investigations also provide an important measuring stick for appraising the applicability of the laboratory results. Some specific areas which are addressed are:

- The relative effects of ozone and water chemistry on corrosion of mild steel. Mechanistic analysis of what is and is not occurring.
- The effect of ozone on the corrosion of copper and brasses.
- Studies of the effectiveness of ozone in preventing scalant precipitation and modifying crystal structures.
- Pilot cooling tower studies of the influence of ozone on scaling and corrosion under both blowdown-limited and zero-blowdown conditions.
- Field case histories of the application of ozone to cooling towers under both blowdown-limited and zero-blowdown conditions.

In order to conclusively define the properties associated with ozone, whenever possible, performance results obtained under identical conditions with and without ozone will be considered.

EXPERIMENTAL PROCEDURES

LABORATORY CORROSION STUDIES

In order to independently study the effect of ozone on corrosion of metals and the interactions of this effect with other parameters, a laboratory apparatus was constructed. It consisted of the following elements:

- A standard 0.75-liter laboratory electrochemical corrosion cell consisting of 0.5" cylindrical working electrodes of the appropriate metal alloy, graphite rod or platinum wire counter electrodes, and a Fisher saturated calomel reference electrode with a Luggin probe. In some experiments, the working electrode was rotated by a Pine rotator to simulate fluid dynamic effects.
- A Princeton Applied Research (PAR) model 273 potentiostat, controlled by a personal computer using the PAR 342C software system.
- A PCI model GL-1 corona discharge ozone generator rated at 1.0 lb/day (0.4 kg/day) of ozone production. Standard laboratory compressed air was first passed through an air preparation system (also provided by PCI) which removed entrained oil and moisture. The ozone/air mixture output by this unit was bubbled into the test cell. Ozone residuals were measured using a colorimetric test kit (Hach Chemical). Ozone residuals were controlled by modulating the output of the ozone generator and/or by bleeding off part of the ozone stream into a waste collector.

Corrosion rates were determined from either the polarization resistance method or from Tafel extrapolations. In either case, the PAR software was used for curve fitting and data analysis. Appropriate Tafel constants for each system were used to calculate corrosion rates from the linear polarization data.

Table 1 — Makeup water for pilot cooling tower tests

Ion	ppm	Unit
Ca	58	CaCO ₃
Mg	43	CaCO ₃
"M"	74	CaCO ₃
SiO ₂	13	ion
SO ₄	48	ion
Cl	99	ion
Na	84	ion

PILOT COOLING TOWER TESTS

The pilot cooling tower (PCT) apparatus contains all the features of a standard industrial cooling tower and related heat exchanger system, and has been described previously.^{1,2} It is designed to simulate the processes in an open recirculating cooling tower system as closely as possible. All PCT tests were grouped in sets of two and run concurrently under identical conditions with the exception that one was treated with ozone and the other was either treated with bromine or had no treatment. All heat exchange tubes were either stainless steel or titanium. Unheated mild steel surfaces were also investigated. The conditions investigated were typical of HVAC or light industrial cooling water systems.

The makeup water conditions are given in Table 1. Some tests were started at one cycle of concentration and maintained at 8 cycles of concentration; some tests were started at one cycle of concentration and run under zero-blowdown conditions (final cycles = 20 to 30), and some tests were started at high cycles (20 to 30) and run under zero-blowdown conditions. The recirculating and makeup water were analyzed daily for calcium, magnesium, "M" alkalinity, "P" alkalinity, silica, conductivity, and pH; chloride, sodium, sulfate, and nitrate were analyzed periodically.

In addition to the water chemistry analyses, total aerobic bacteria counts were analyzed three times per week. Each test was equipped with a Bridger Scientific DATS™ fouling monitor, an on-line mild steel Rohrback Corratel®[®], and mild steel corrosion coupons.

The ozone-treated tests were run on a PCT situated in a hood, along with an OREC model #SP-AR 0.5 lb/day (0.2 kg/day) ozonator. The feed gas to the ozonator is house compressed air, which is dried and filtered prior to ozonation. The ozone is injected by means of a Venturi eductor into a sidestream loop of water drawn from the basin. The ozonated stream is then returned to the basin. Normal ozone dosage was based on two separate criterion: tests were run with a targeted ozone concentration of 0.05 to 0.10 ppm ozone immediately before the heat exchange tubes, and tests were run with a targeted total aerobic bacteria count of 10³ CFU/ml or less. Ozone concentration was usually analyzed by the Indigo method, but the DPD method was used for quick and approximate measurements.

Due to scale-down factors, ozonator-produced NO_x artificially reduced the "M" alkalinity of the recirculating water in the PCT tests to a much greater extent than found in

Table 2 — Makeup water for laboratory corrosion test #1

Ion	Makeup (typical)	Tower (authentic)	Unit
Na	40–100 ppm	5100 ppm	ion
Ca	60–70	490	CaCO ₃
Mg	50–70	1900	CaCO ₃
K	3–5	120	ion
SiO ₂	10–14	120	ion
“M”	70–80	40	CaCO ₃

typical field applications. Therefore, unless otherwise noted, the ozone-treated tests incorporated a dilute NaOH feed to neutralize the NO_x. The caustic feed was based on the pH and “M” alkalinity of the concurrent non-treated test.

One test set was equipped with a chemostat which supplied a continuous feed of bacteria and nutrient to the tower basin. The nutrient was a mixture of distilled water, tryptic soy broth, and dextrose; and the bacteria culture consisted of a typical cross-section of bacteria found in open recirculating cooling tower systems. The basin was also slugged with the nutrient mixture at the start of the tests and once during the tests.

CASE HISTORY MONITORING

A complete analysis of tower and makeup water samples was performed weekly, and the following species were closely monitored: sodium, calcium, magnesium, potassium, “M” alkalinity, silica, chloride, sulfate, nitrate, phosphorus, and conductivity. Total aerobic bacteria levels were also monitored. A Bridger Scientific DATS fouling monitor and two Rohrback Corraters continuously collected fouling and corrosion data, respectively. Corrosion coupons were also used for corrosion measurements. The fouling monitor, Corraters, and corrosion coupons were all located in the return line. Each system was visually inspected, including inspection of the heat exchangers.

LABORATORY CORROSION STUDIES

In order to gain independent information about the relative corrosion effects of ozone and other factors such as water chemistry, as well as to obtain information about operative corrosion mechanisms, a series of laboratory corrosion tests were conducted. Three test sequences are reported here:

1. A study of the relative effects of ozone on carbon steel using authentic ozone-treated water samples
2. A study of the relative effects of ozone and water chemistry factors on carbon steel using laboratory-prepared synthetic water
3. A series of tests on copper alloys comparing the relative effects of ozone with other oxidizers, using a single water chemistry

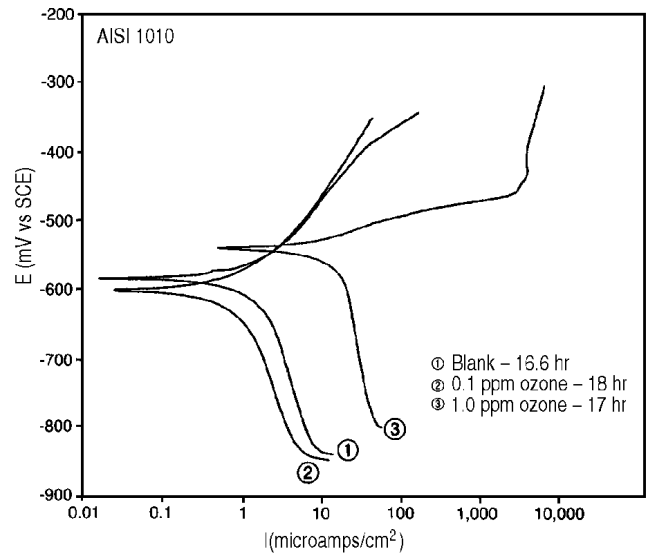


Figure 1 — Tafel scans of carbon steel in authentic ozone-treated water. Temperature = 100°F, rotation speed = 500 rpm, pH = 8.7 to 8.9, air saturated.

CORROSION OF CARBON STEEL IN AUTHENTIC OZONE-TREATED WATER

In the first comparison, a sample of authentic ozone-treated water from a medium-sized tower system was obtained. This tower was using ozone as the sole treatment and was operating in a “zero blowdown” mode. The composition of the makeup and tower water is shown in Table 2.

Examination of the water compositions shows that the “cycles” of nonprecipitating species such as sodium and potassium are much higher than those of calcium, alkalinity, and silica, indicating that considerable precipitation had occurred in the tower and that the water was still supersaturated with calcium carbonate (RSI <4.5).

Corrosion experiments using carbon steel working electrodes were conducted as described previously, using the water as received in the absence of ozone, in the presence of 0.1 ppm of ozone, and in the presence of 1.0 ppm of ozone. The results of a series of linear polarization measurements taken over time are shown in Table 3. At the conclusion of each of these experiments, a Tafel scan was taken; the results of which are shown in Figure 1.

A number of conclusions may be drawn from this comparison. Comparing the linear polarization corrosion rates (Table 3) obtained at comparable time periods (16.5 hours) shows that low and comparable corrosion rates were observed in the absence of ozone and in the presence of 0.1 ppm of ozone (1.1 mpy vs. 0.9 mpy, 0.028 mm/y vs. 0.023 mm/y). These rates were in good agreement with coupon data obtained from the operating tower. Another notable factor is the high and increasing carbon steel corrosion observed in the presence of 1.0 ppm of ozone. However, the lower pH of the system in this experiment may be the overriding factor in the higher corrosion rate result.

Table 3 — Corrosion rates of mild steel in an authentic ozone-treated tower water

Condition	Immersion time	Corrosion rate mpy(mm/y)	pH	Ecorr mV/SCE
Aerated	0.5 hr	5.73 (0.146)	8.85	-527
Aerated	16.5 hr	1.07 (0.027)	9.13	-594
0.1 ppm O ₃	16.5 hr	0.85 (0.022)	8.80	-604
0.1 ppm O ₃	19.0 hr	0.92 (0.023)		-606
0.1 ppm O ₃	21.3 hr	0.78 (0.020)	8.70	-613
0.1 ppm O ₃	23.5 hr	0.71 (0.018)	8.79	-616
1 ppm O ₃	16.5 hr	4.51 (0.115)	7.23	-555

Table 4 — Corrosion rates of AISI 1010 synthetic water, 100 F, 500 rpm

Ca (ppm)	HCO ₃ (ppm)	SiO ₂ (ppm)	Condition	Steady state corr. rate mpy(mm/y)
490	402	0	Aerated	2.2 (0.056)
490	402	120	Aerated	1.4 (0.036)
490	402	120	0.2 ppm O ₃	1.4 (0.036)
400	303	120	Aerated	3.2 (0.081)
400	303	120	0.1 ppm O ₃	2.7 (0.069)
303	215	120	Aerated	20 (0.5)
303	215	120	0.1 ppm O ₃	4.2 (0.11)
303	215	120	1 atm O ₂	4.3 (0.11)
303	215	120	1 ppm O ₃	7.2 (0.18)
200	112	120	Aerated	7.0 (0.18)
200	112	120	0.1 ppm O ₃	14 (0.36)

Examination of the open circuit potentials (Table 3) and the Tafel scans (Figure 1) indicates that the corrosion inhibition is attributable to the formation of a cathodically induced oxygen barrier film. The low open circuit potentials (less than -600 mV vs. SCE) and the general shape of the anodic branch of the Tafel plots are strong evidence that anodic passivation contributes little to corrosion control in this system, either in the presence or absence of ozone. Based on this data, the observed low corrosion rates are entirely a result of the water chemistry, with ozone playing no role. This conclusion is in contrast to previously published hypotheses³.

EFFECTS OF OZONE vs. WATER CHEMISTRY ON CARBON STEEL CORROSION

The first test sequence provided indications that the precipitation of mineral species was playing a dominant role in corrosion control in ozone-treated systems. A second series of experiments were performed using the same methodology but with synthetic test solutions. In this series, the concentrations of scale-producing solutes (calcium, alkalinity, and silica) were varied and comparisons were made of carbon steel corrosion rates in the presence and absence of low levels of ozone.

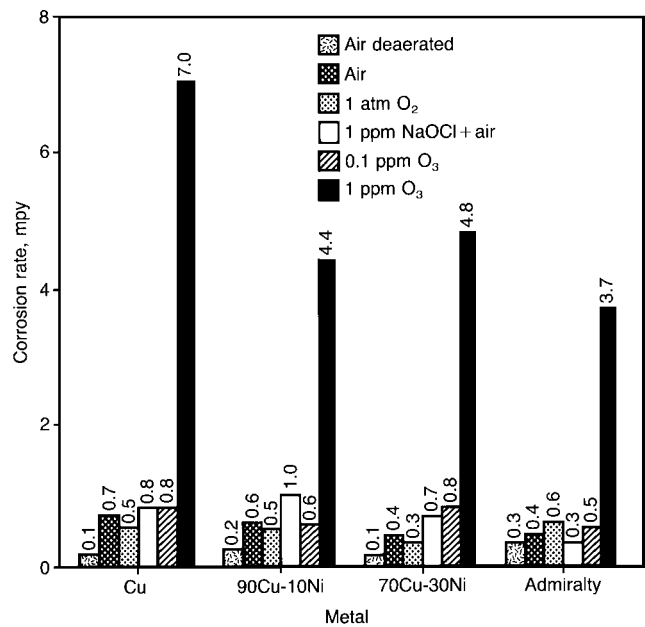


Figure 2 — Corrosion rates of copper and its alloys in synthetic Lake Michigan Water.

The results are shown in Table 4. Examination of the data shows that, under the conditions of the field tower discussed in the previous section (490 ppm Ca, 402 ppm “M”), silica does not play a significant role in determining the corrosion rate. Clearly, the saturation level of calcium carbonate is the most important factor.

With regard to the effect of ozone, the data can be divided up into three zones:

1. Under conditions of elevated alkalinity (>300 mg/l CaCO₃), ozone at typical use levels does not play any role in determining the carbon steel corrosion rate. Under these conditions, industry-acceptable corrosion rates are observed (<3.0 mpy, <0.076 mm/y).
2. Under conditions of marginal alkalinity (200 to 300 mg/l CaCO₃), 0.1 ppm of ozone appears to result in improved carbon steel corrosion rates. However, the corrosion rates observed under these conditions with or without ozone are greater than is normally considered acceptable by the water treatment industry (>4.0mpy, >0.10 mm/y).
3. At low alkalinity (<200 mg/l CaCO₃), low levels of ozone gave a slight acceleration of corrosion. Corrosion rates under these conditions are significantly greater than industry-standard corrosion rates (>6.0 mpy, >0.15 mm/y).

COMPARISON OF OZONE WITH OTHER OXIDIZERS ON CORROSION OF COPPER ALLOYS

The third sequence was performed to determine the behavior of common copper alloys in the presence of ozone and other oxidizers under a specific water chemistry. Static specimens of copper, admiralty brass, 70/30 cupronickel, and 90/10 cupronickel were exposed to synthetic Lake

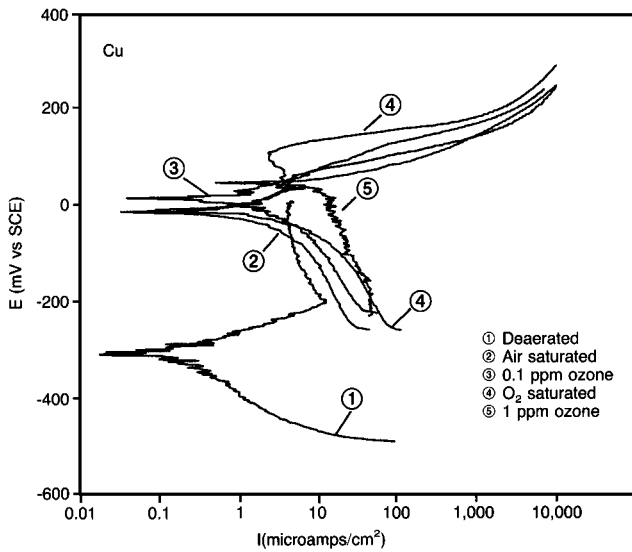


Figure 3 — Tafel plots for copper in medium hardness water. Temperature = 100°F, scan rate = 0.5 mV/sec, static electrode, synthetic Lake Michigan water.

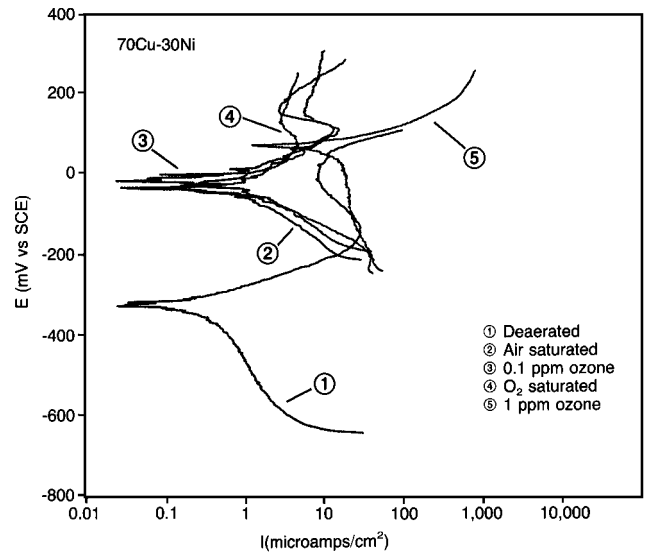


Figure 5 — Tafel plots for 70/30 cupronickel in medium hardness water. Temperature = 100°F, scan rate = 0.5 mV/sec, static electrode, synthetic Lake Michigan water.

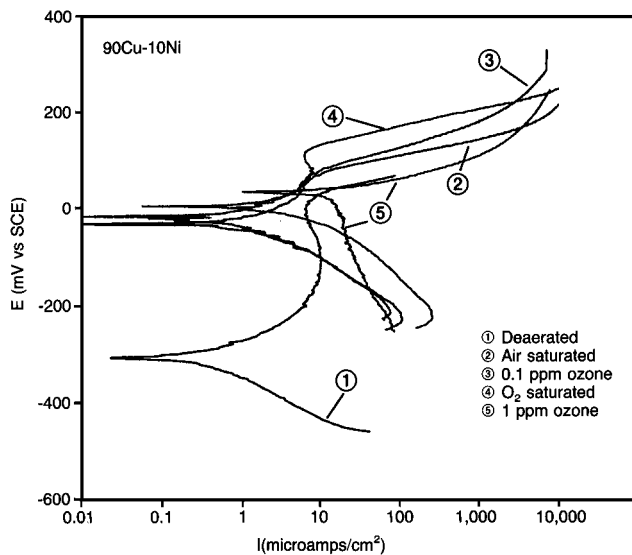


Figure 4 — Tafel plots for 90/10 cupronickel in medium hardness water. Temperature = 100°F, scan rate = 0.5 mV/sec, static electrode, synthetic Lake Michigan water.

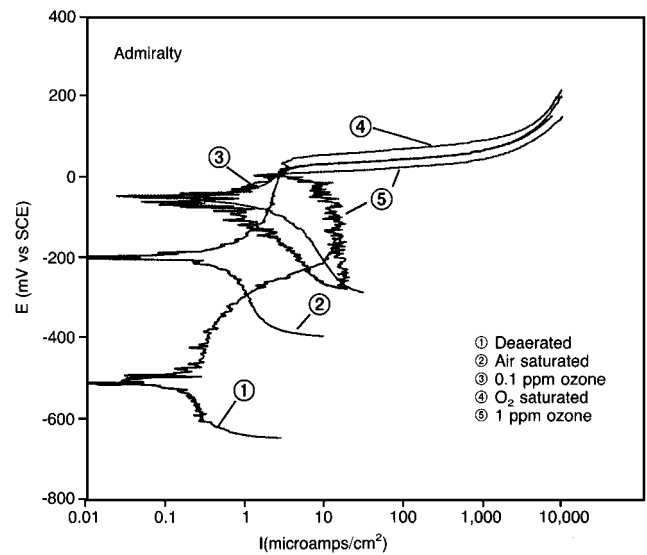


Figure 6 — Tafel plots for admiralty brass in medium hardness water. Temperature = 100°F, scan rate = 0.5 mV/sec, static electrode, synthetic Lake Michigan water.

Michigan water in the presence of various oxidizing environments (deaerated, aerated, 1 atmosphere oxygen, NaOCl aerated, 0.1 ppm ozone, and 1 ppm ozone). Linear polarization measurements of corrosion rates vs. time were done with Tafel scans at the end of each experiment. The data are summarized in Figures 2 through 6.

A number of conclusions are apparent from the data. In contrast to previously published reports,⁴ ozone gave slight to pronounced increases in the corrosion rates of all the alloys versus normal levels of oxygenation (air column, Figure 2). High (1 ppm) levels of ozone were extremely aggressive to all the metals tested. Typical use levels of ozone (0.1 ppm) either gave no effect (copper, 90Cu/10 Ni,

admiralty) or was slightly aggressive (70 Cu/30 Ni). Sodium hypochlorite addition also typically gave slight increases in corrosion to the yellow metals.

Lu and Duquette⁴ noted the elevation of the open circuit (corrosion) potential of 70 Cu/30 Ni upon exposure to ozone. The effect was not noted in our study. The only factor observed to make significant changes in open circuit potential was the dissolved oxygen level.

What was observed was an inhibition of the formation of anodic passive regions upon the addition of ozone, particularly in the case of the cupronickels (Figure 4 and Figure 5). It is this effect, rather than significant changes in open

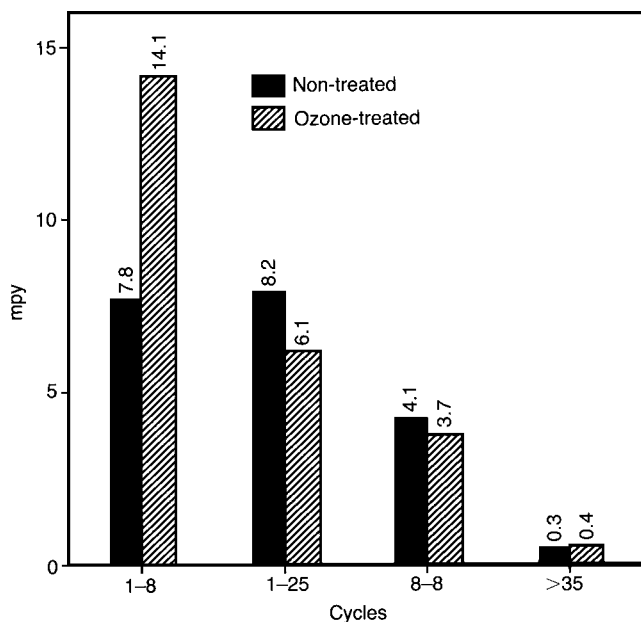


Figure 7 — A comparison of ozone-treated and non-treated mild steel PCT tube corrosion rates as a function of tower water saturation level.

circuit potential, which seems to be the determining factor in the effect of ozone on yellow metal corrosion. The most obvious explanation of this phenomenon is that ozone is attacking or inhibiting the formation of a protective cuprous oxide layer on the metal surface.

PILOT COOLING TOWER INVESTIGATIONS

The laboratory corrosion investigations provide an easily controlled environment, allowing determination of the unconfounded effects of ozone on corrosion. However, in a dynamic cooling water environment, several interdependent factors couple to determine the performance results. Therefore, it is important to compare the results obtained at the bench top with results obtained under open recirculating cooling water system conditions. PCT investigations include all of the important factors, while allowing the critical ability to systematically control variables.

The PCT results are divided into three major sections:

1. The effects of ozone on corrosion
2. The effects of ozone on scale formation
3. Biocidal effects of ozone

THE EFFECTS OF OZONE ON CORROSION

As was the case in the laboratory studies, the corrosion rate of mild steel is dominated by the saturation level of the water, and not by the presence or absence of ozone in the system. This point is clearly illustrated by comparing the average coupon corrosion rates of ozone-treated and non-treated tests based on saturation level (cycles of concentration) during the exposure period:

Cycles	Ozone-treated mpy (mm/yr)	Non-treated mpy (mm/yr)
1-8	10.9 (0.277)	10.0 (0.254)
>20	3.1 (0.079)	1.8 (0.046)

The low-cycle corrosion rates for the ozone-treated tests and the non-treated tests are essentially equal, and are more than three times the acceptable value. A slight difference exists between the high-cycle corrosion rates, but this is likely due to lower pH in the ozone-treated tests (run with no NO_x neutralization). More importantly, a dramatic decrease in corrosion rate occurs in both the ozone-treated and non-treated tests as the saturation level of the water is increased.

The mild steel tube corrosion rates corroborate the coupon data. Ordering the mild steel tubes first by the initial cycles of concentration to which they were exposed, and second by the final cycles of concentration to which they were exposed, clearly illustrates the relationship between saturation level of recirculating water and corrosion rate (Figure 7). The low-cycle tests have the highest corrosion rates, while the high-cycle tests have extremely low corrosion rates. The difference between the corrosion rates in the non-treated and ozone-treated tests for the first set of tests is large; however, both values are well above accepted industry standards. As the cycles increase, and the corrosion rates become more acceptable, the difference between the ozone-treated and non-treated tests becomes insignificant.

THE EFFECTS OF OZONE ON SCALE FORMATION

Scale formation in the PCT tests was determined by several factors that traditionally influence deposition on heat exchange surfaces, including water chemistry, nucleation sites, system dynamics, and skin temperature, but was not directly influenced by the presence of ozone in the system. (Scale formation was indirectly influenced due to the biocidal effects of ozone, which will be addressed in the next section.) The deposit rates on the heat exchange tubes exhibited clear and dramatic responses to changes in the test variables, ranging from excellent deposit control to 35 times the acceptable value, but the observed trends in the deposit rates were identical in the ozone-treated tests and the non-ozone-treated tests.

Water Chemistry

Conventional chemical treatment programs prevent scaling and deposition by dispersion of mineral scale or by completely inhibiting precipitation of mineral scale. Therefore, the most common and most convenient method for monitoring and evaluating system performance in terms of scale formation is water chemistry analyses. If 100% transport is maintained in the system, i.e., all ions are accounted for in the water analysis, then the heat transfer surface remains free of mineral scale.

Ozone alone clearly does not prevent nor promote precipitation of mineral scales. No difference in the precipitation of CaCO₃ is observed between ozone-treated systems and

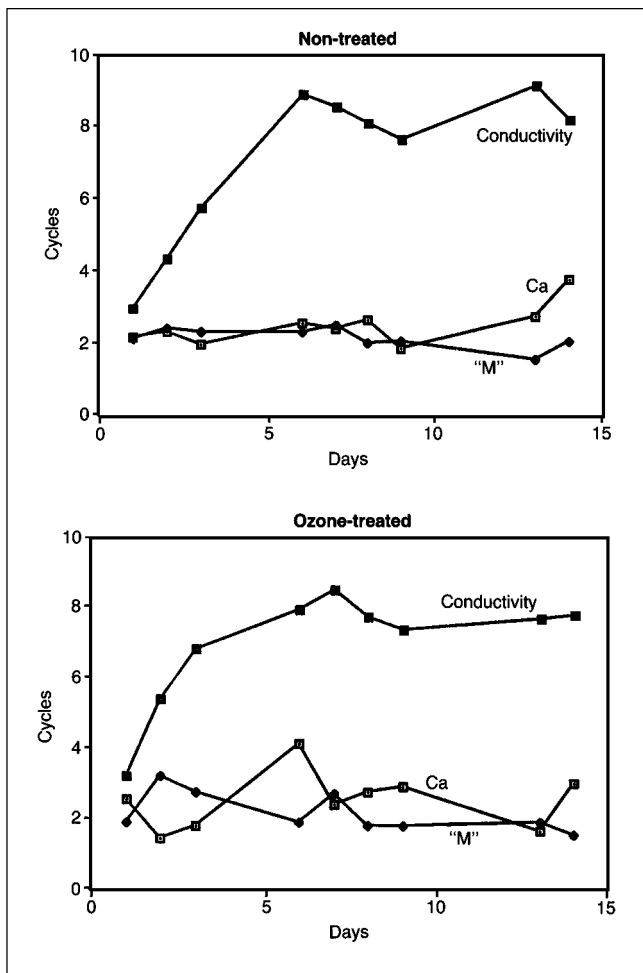


Figure 8 — Calcium, “M” alkalinity, and conductivity cycles of concentration for equivalent non-treated and ozone-treated tests.

non-treated systems, as demonstrated by a representative plot of calcium, “M” alkalinity, and conductivity cycles of concentration for equivalent non-treated and ozone-treated tests (Figure 8). The agreement between the concentration ranges of Ca and “M” for the two tests is remarkable:

	Ozone-treated	Non-treated
Actual Ca	99–233 ppm	107–210 ppm
Theoretical Ca	450 ppm	450 ppm
% Transport	22–52	24–47
Actual “M”	114–166 ppm	114–170 ppm
Theoretical “M”	570 ppm	570 ppm
% Transport	20–29	20–30

The results presented here are in close agreement with previous observations reported in the literature.⁵

Crystal Growth and Formation of “Sandy” CaCO₃

One theory for the prevention of scale in ozone-treated systems is that ozone changes the crystal morphology of the precipitated CaCO₃, rendering it less adherent to heat ex-

change surfaces and causing it to settle in the basin.⁶ A common assertion is the appearance of a CaCO₃ “sand” in the basin of ozone-treated systems.

Off-white “sandy” deposits have been found in the basin of some of the PCT tests; however, the deposits were found in both the ozone-treated tests and the non-treated tests. The chemical composition of a typical deposit was 54% calcium, 45% carbonate, and 1% silicon, in accord with that expected from the water analyses. The formation of a basin deposit under certain conditions, both with and without ozone, indicates that this phenomenon is due to system dynamics and not related to ozone.

To directly analyze the effects of ozone on the crystal morphology of CaCO₃, a scanning electron microscope (SEM) study was performed on CaCO₃ crystals formed in both a synthetic water (low organic levels) and a natural water (typical organic levels). No modification of the crystal morphology occurs in the ozone-treated tests relative to the non-treated tests, as demonstrated by magnification at 2000X of the CaCO₃ crystals from natural water tests (Figure 9). Similar results were observed in analogous investigations on actual PCT tube deposits, which were formed on heat exchange surfaces under recirculating water conditions.

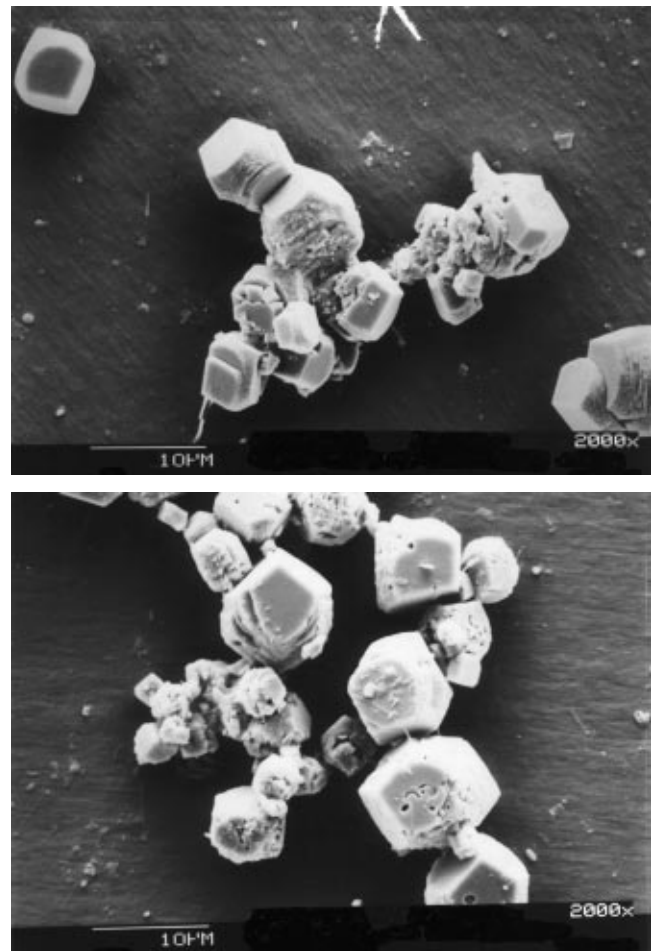


Figure 9 — SEM photographs of CaCO₃ crystals formed in a natural water, (top) non-treated and (bottom) ozone-treated.

Nucleation

A key requirement for crystallization from solution of a material directly on site of scale formation is nucleation.⁷ Heterogeneous nucleation, the deposition of solute on a pre-existing substrate, requires less energy than homogeneous nucleation, deposition which does not require the presence of a foreign substance. Cooling water systems inherently contain numerous nucleating sites such as the walls of pipes and the tower fill. Also, foreign substances such as dust, gas bubbles, and microorganisms, and factors such as vibration and agitation cause nucleation.⁸ Therefore, heterogeneous nucleation is the predominant scale deposition mechanism in cooling water systems.

Under severely precipitating conditions, as is the case in the systems in question, nucleation has a profound influence on the location of scale formation. At the PCT scale, the presence, quantity, and location of nucleation sites can be manipulated to simulate different conditions. For example, the surface of the heat exchange tubes can be varied, and/or the presence of nucleation sites on the tower fill and in the basin can be varied.

The importance of mineral scale nucleation sites away from the heat exchange tubes was clearly demonstrated by the PCT tests. Tests run with “clean” (nucleation sites absent) heat exchange tubes and “dirty” (nucleation sites present) tower fill and basin, resulted in all tubes being free of deposition after 14 days of operation, despite CaCO_3 precipitation commencing on day five. Similar tests run with completely “clean” systems (nucleation sites absent from heat exchange tubes, tower fill, and basin), resulted in unacceptable deposit rates for at least four of the eight tubes, some tubes having deposit rates greater than ten times the acceptable value. These nucleation site effects caused similar results in both the ozone-treated and the non-treated systems, and serve to demonstrate that scale formation can be highly system dependent.

Ozone vs. Bromine

In order to investigate the direct effects of ozone on scale information, all difficult-to-control variables which may influence deposit rates and fouling need to be removed from the experiment. This entails excluding any easily corroded metallurgy (e.g., mild steel), and ensuring that both the ozone-treated system and the control is free of microbiological contamination, i.e., the control is treated with an effective biocide.

Comparison of a representative bromine-treated test with an identical ozone-treated test, both of which incorporated only stainless steel heat exchangers, clearly demonstrates the similarity in scale control between the two treatments. Under a variety of heat fluxes and skin temperatures, the eight-tube averaged, stainless steel deposit rates were nearly identical, with the bromine-treated test averaging $86.0 \text{ mg/cm}^2/\text{yr}$ and the ozone-treated test averaging $82.6 \text{ mg/cm}^2/\text{yr}$, both being greater than eight times the acceptable value (criterion for successful control is $<10 \text{ mg/cm}^2/\text{yr}$)². In addition, the distribution of deposit rates relative to skin tem-

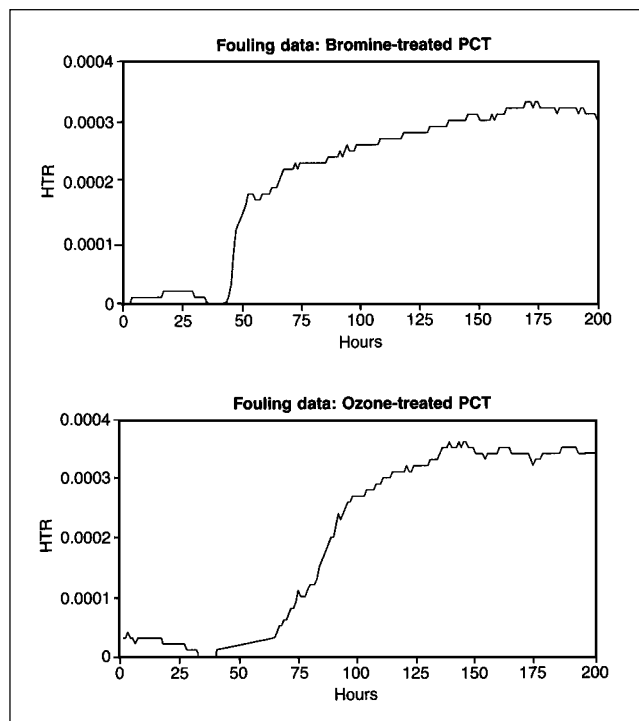


Figure 10 — Comparison of fouling monitor data for a chlorine/bromine-treated PCT test and an ozone-treated PCT test run under identical conditions.

perature and heat flux was extremely similar between the two tests, in spite of its two order of magnitude range.

Real-time monitoring of fouling in the systems strongly supports the weight measurement results (Figure 10). Both the ozone- and bromine-treated tests show a dramatic increase in fouling after a comparable amount of elapsed time, followed by a leveling of fouling at a nearly equivalent point. The sharp increase in fouling observed correlates well with the water chemistry analyses — calcium and “M” alkalinity were no longer in balance with the more soluble ions after three days in the bromine-treated test, and after four days in the ozone-treated test. The slight time difference between initialization of fouling is readily accounted for by the slightly lower “M” alkalinity in the ozone-treated tests at any given time, caused by the necessary lag-time for proper NO_x neutralization.

BIOCIDAL EFFECTS OF OZONE

Excellent microbiological control was observed in all ozone-treated tests, as measured by total aerobic bacteria counts. As expected, a significant difference in microbiological activity was observed between the ozone-treated and non-treated tests (Figure 11). The ozone-treated tests had total aerobic bacteria counts of 10^3 CFU/ml or less, while the non-treated tests had counts of 10^4 to 10^6 CFU/ml. The difference in bacteria counts is clearly due to the presence of ozone and not to some other system parameter, as exhibited by an increase in aerobic bacteria to the non-treated test levels upon discontinuation of the ozone feed.

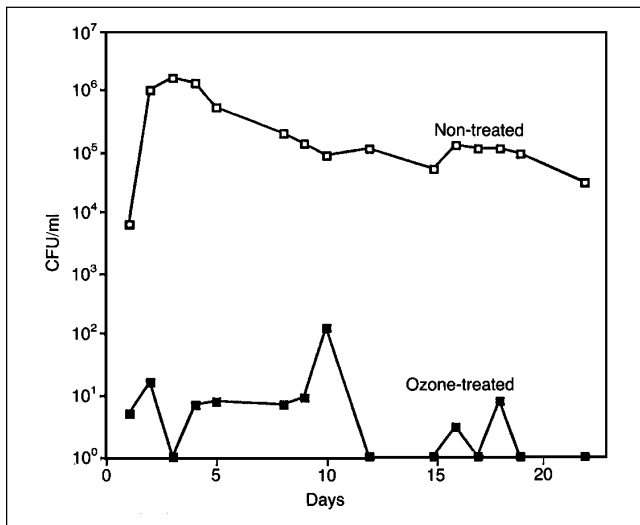


Figure 11 — A representative plot of total aerobic bacteria counts from a non-treated and an ozone-treated PCT test.

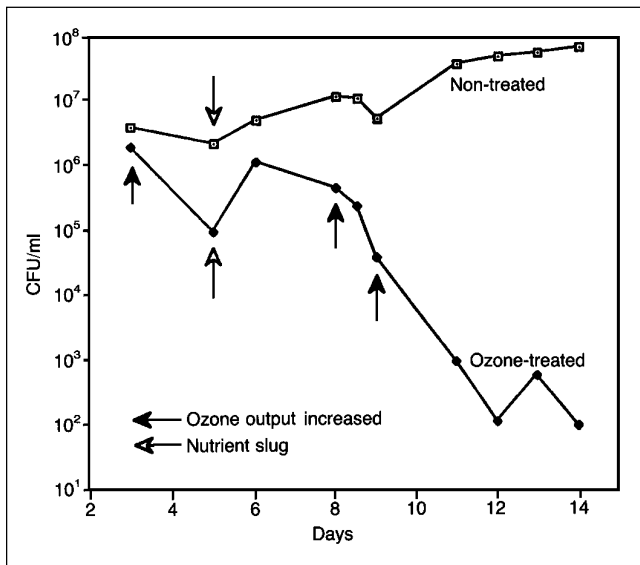


Figure 12 — Total aerobic bacteria levels for a non-treated and an ozone-treated PCT test incorporating a nutrient and bacterial feed.

The effects of ozone on microbiologically-induced fouling were investigated by a set of tests incorporating an artificial nutrient and bacteria feed (as described in **Experimental Procedures**). The bacteria levels of the non-treated test increased throughout, approaching 10^8 CFU/ml by the end of the 14-day period (Figure 12). The levels during the first half of the ozone-treated test were high, but decreased to 10^2 CFU/ml as the ozone output was increased to meet the demand of the bacteria and nutrient being added to the system. The fouling of the heat transfer tubes exhibited a definite and immediate response to changes in the ozone feed system, as measured by fouling monitor data (Figure 13). Severe fouling immediately commenced upon initiation of the bacteria/nutrient feed mixture, indicating that

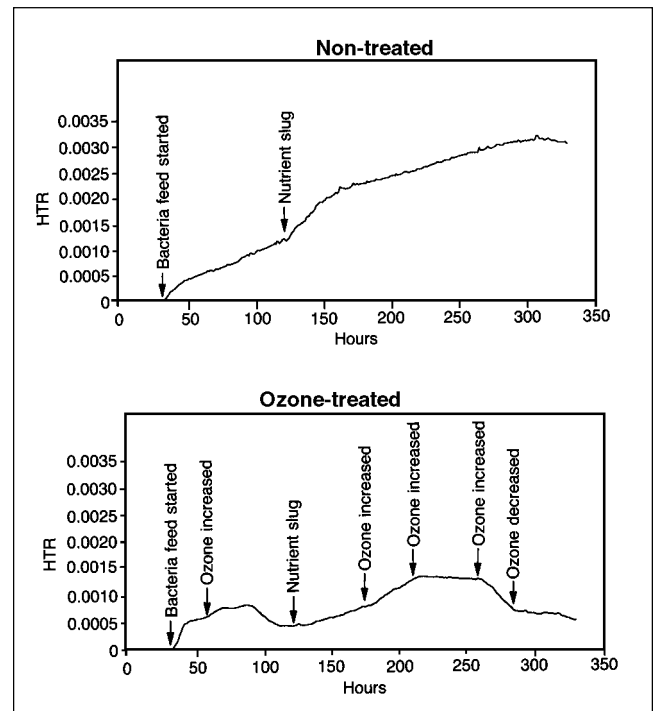


Figure 13 — Heat transfer resistance vs. time as measured by a Bridger fouling monitor for a non-treated and an ozone-treated PCT test incorporating a nutrient and bacterial feed.

the fouling is microbiologically induced. In the non-treated system the fouling increased throughout the test, increasing most rapidly after the addition of a nutrient slug. In the ozone-treated system, the fouling was decelerated, suppressed, or even reversed upon increase of the ozone output. The responses of the fouling monitor indicate that ozone may actually clean a fouled system if the foulant is microbiologically based. However, it should be noted that the quick response observed in this system was only achieved after maximizing the output of the ozonator, which is an usually large amount of ozone for the volume of water treated (0.2 kg/day for 50 l of water).

CASE HISTORIES

Excellent agreement was observed between the laboratory corrosion studies and the PCT investigations. However, these results can be deemed of little practical importance unless it is clearly shown that they correlate to results obtained in actual field applications. In this light, the results from two closely monitored case histories are presented here. As the variables are harder to control than at the PCT stage, the results have been divided into three major categories:

1. Water chemistry
2. Fouling control
3. Corrosion control

Table 5 — Makeup water, Site #1

Ion	ppm	Unit
Ca	66	CaCO ₃
Mg	43	CaCO ₃
“M”	109	CaCO ₃
SiO ₂	21	ion
SO ₄	43	ion
Cl	58	ion
Na	54	ion

CASE HISTORY #1

Case history #1 was conducted on a small comfort cooling system servicing a facility in southern California. The metallurgy of the heat exchanger is copper and the transmission lines are mild steel. Ozone was used as a stand-alone chemical treatment, and the results represent one-year operation. Ozone is injected by means of a Venturi eductor into a sidestream loop of water drawn off of the basin, and the ozonated stream is returned to the basin.

Water Chemistry

The composition of the makeup water for this facility is presented in Table 5. During the first four months of the study, the concentration of the tower water was slowly raised from 3 to 14 cycles (the tower cycles refer to the sodium cycles, which is representative of the other highly soluble ions). For the next eight months, the system was operated at approximately 5 to 10 cycles of concentration, with stress conditions as high as 20 cycles. CaCO₃ precipitated throughout this time period, as demonstrated by the Ca and “M” alkalinity cycles of concentration being consistently 3 to 4. Silica and/or magnesium silicate also precipitated, but to a much lesser extent.

Fouling Control

As was demonstrated in the PCT investigations, precipitation does not necessarily mean that scaling of the heat exchange surfaces is occurring. However, the online fouling monitor does provide real-time information regarding the formation of scale on the heat exchange surfaces. The fouling monitor in question was operated in a “worse-case scenario” manner, such that any potential for fouling of the system’s heat exchange surface would be detected by the fouling monitor, prior to scale forming in the system.

Under normal operation, fouling of the system was not a problem. However, a direct correlation between an increase in the cycles of concentration and a general increase in fouling, as measured by the fouling monitor, was realized. In addition to this correlation, sharp and dramatic increases in fouling were observed. These increases occurred over a short period of time, and coincided with an increase in bulk water temperature. The fouling decreased slowly over a period of days after the sharp rises (Figure 14). An explanation for this type of behavior is that the scale forms during the hottest skin temperature, but is not tenacious, being sloughed off by the water due to its high fluid velocity.

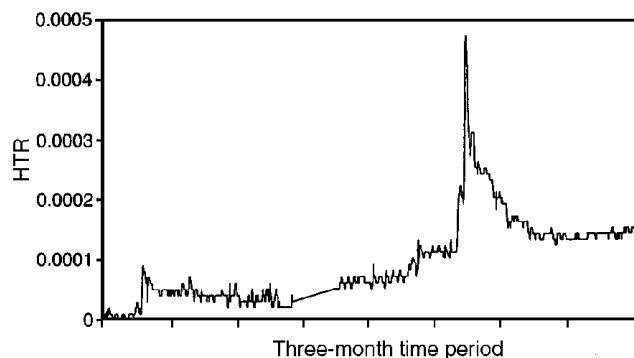


Figure 14 — Fouling monitor data for Site #1

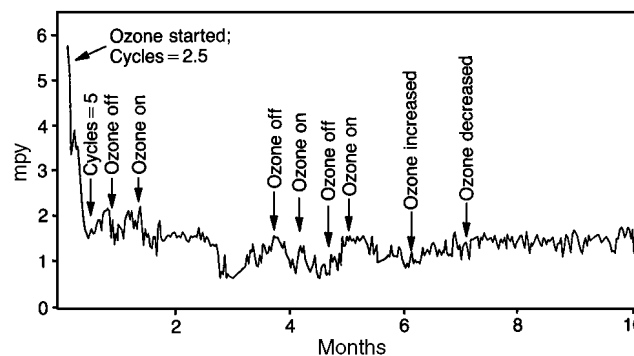


Figure 15 — Mild steel corrosion rates from Site #1. Note the periods of no ozone feed to the system.

Support for this explanation is found in the fact that an off-white-to-brown, flaky, solid material was observed in the basin. The chemical composition of the material is 43% Ca, 28% carbonate, and 18% Si, in close agreement with that expected from the water chemistry analyses. Visual inspection of the system indicated those large amounts of deposition formed on the tower fill and in the basin. However, no significant scaling was observed on the surface of the heat exchange tubes.

Corrosion Control

Good mild steel and copper corrosion control was achieved throughout the trial. Initially, a dramatic decrease in corrosion rate was observed, going from approximately 5 mpy (0.1 mm/y) to less than or equal to 1 mpy (0.02 mm/y) in the mild steel corrosion rate, and 0.2 mpy (0.005 mm/y) to less than 0.1 mpy (0.002 mm/y) in the copper corrosion rate. The Corratel-measured corrosion rates remained at approximately 1 mpy (0.02 mm/y) for mild steel and less than 0.1 mpy (0.002 mm/y) for copper for the duration of the trial. Excellent agreement was found between both mild steel and copper coupon data and the Corratel data, lending confidence to the results.

The trends in the corrosion rates correlate extremely well to the water chemistry of the system, but have no correlation with the presence of ozone in the system. Immediately prior to initialization of ozone treatment, the system was operating with no conventional chemical corrosion protection, thus the high mild steel corrosion rates. The initial dramatic decrease in corrosion rate coincided with both an

Table 6 — Makeup water, Site #2

Ion	ppm	Unit
Ca	75	CaCO ₃
Mg	73	CaCO ₃
“M”	76	CaCO ₃
SiO ₂	14	ion
SO ₄	60	ion
Cl	101	ion
Na	93	ion

increase in the cycles of concentration of the recirculating water and the initialization of ozone treatment. The tower was operating at approximately 2.5 cycles initially, and the concentration was steadily increased to approximately 5 cycles. For the remainder of the trial, the cycles of concentration of the tower water was greater than or equal to five. The ozone treatment was held constant during the initial decrease in corrosion, but then was discontinued for a ten-day period. Also, for the remainder of the trial, the ozone feed rate was varied several times, including two more discontinuations of ozone feed. Using the mild steel corrosion rate to demonstrate the point, Figure 15 clearly shows no response to the changes in the ozone treatment.

CASE HISTORY # 2

Case history #2 was conducted on a light industrial system in the western United States. Ozone was used as a stand-alone chemical treatment, and injection is similar to that of case history #1 and the PCT studies.

Water Chemistry

The composition of the makeup water for this facility is presented in Table 6. The system operated at 10 to 20 cycles of concentration for the first six weeks of ozone treatment (again, the tower cycles refer to the sodium cycles, which is representative of the other highly soluble ions). In contrast to case history #1, the concentration of the tower water was then rapidly raised from 10 to 20 cycles to nearly 70 cycles of concentration in a seven-week period by complete shut-off of the blowdown. The system operated at a concentration as high as 90 to 100 cycles. Calcium, “M” alkalinity, and silica were severely out of balance, with the concentration cycles of each being between 7 and 12 throughout the trial.

Fouling Control

An increase in fouling was observed corresponding to the rapid increase in concentration of the recirculating water. Removal and inspection of the fouling monitor heat exchange tube revealed an off-white deposit covering the entire region of applied heat. Inspection of the system revealed an almost identical, off-white, tenacious scale, which was uniform throughout the heat transfer equipment. The chemical composition of the deposit was 60% Si, 13% Mg, 9% Ca, and 8% carbonate, with minor components comprising the remaining 10%. Also, the tower fill was covered with scale. The chemical composition of the tower fill scale

was 49% Ca, 29% carbonate, and 16% Si, in accord with the water analyses. The zero blowdown operation continued for over one year during a water-short period. Due to overdesign of the system, the observed fouling did not affect operations until increases in ambient temperatures caused significant increases in bulk water temperatures.

The water analyses indicate that a tremendous amount of solids have precipitated from solution in this system. From the commencement of ozone treatment until the inspection was performed, calculations indicate that approximately 10,000 kg of CaCO₃ and 2,000 kg of SiO₂ precipitated from solution, representing approximately 5 m³ of solid material. The tower fill for this facility has nearly 500,000 ft² (50,000m²) of surface area. A uniform coverage of scale would result in a layer 0.1 mm thick. The observed scale was approximately 0.2 to 0.6 mm thick, easily accounting for the precipitated solids.

Corrosion Control

As was the case with site #1, the corrosion rates correlate extremely well with the saturation level of the water. A mild steel corrosion coupon, which was exposed while the recirculating water was at 10 to 20 cycles, had a corrosion rate of 1.5 mpy (0.038 mm/y). An admiralty coupon exposed during the same time period had a surprisingly high corrosion rate of 0.7 mpy (0.018 mm/y). Both mild steel and admiralty coupons, which were exposed while the system was operating at greater than 20 cycles of concentration, had corrosion rates of <0.1 mpy (<0.003 mm/y). However, upon drying, a white film covering the entire surface of the coupons became apparent. The film consisted primarily of silica.

SUMMARY AND CONCLUSIONS

The work presented here represents the first comprehensive study — bench-top laboratory investigations, pilot scale testing, and critical monitoring and evaluation of field applications — addressing the effects of ozone as a stand-alone cooling water treatment program. It also represents the first investigation to critically compare ozone-treated systems to non-treated systems. Excellent agreement was observed among all stages of testing, establishing not only the relevance, but the importance — due to control of variables not possible in the field — of investigating the properties of ozone in the laboratory. The use of established pilot testing provides a means of evaluating the suitability of ozone to a particular situation.

Several conclusions concerning the mechanistic aspect of ozone treatment have been clearly demonstrated:

1. Excellent corrosion control can be attained in ozone-treated cooling water systems. However, the corrosion rates are completely dominated by the water chemistry of the system and have no dependence on the presence of ozone at typical use levels. The laboratory corrosion rates agree nearly quantitatively with the pilot scale corrosion rates, both of which agree nearly quantitatively with corrosion rates obtained from field applications.

2. Ozone has no direct effect on the precipitation of mineral scale in a recirculating cooling water system, nor does it affect the crystal morphology of precipitating species. Again, nearly quantitative agreement is observed between water chemistry at the pilot scale and water chemistry in field applications. Also, as have been reported in ozone field applications elsewhere and observed in the present field studies, "sandy" deposits formed in the basin of some of the PCT tests, irrespective of the presence of ozone.
3. Good control of fouling can be attained in ozone-treated cooling water systems. However, as was the case with corrosion control, deposition on the heat exchange surfaces is not determined by the presence of ozone, but by several factors that traditionally influence fouling in a system.
4. The strong biocidal properties of ozone resulted in excellent microbiological control in all PCT investigations, and in both case histories studied. The unique combination of high toxicity during treatment with no toxicant discharge makes ozone an attractive biocide.

ACKNOWLEDGEMENTS

The authors would like to thank D.P. Pruss, M.V. Buncio, O.X. Fedyniak, T.A. Krol, A.M. Blondin, P.R. Young, T.L. Stuebner, and R.W. Cloud for assistance in collecting the data.

REFERENCES

1. (a) R. Nass and D.T. Reed, "Small-Scale Short-Term Methods of Evaluating Cooling Water Treatments... Are They Worthwhile?" International Water Conference, 1975. (b) K.E. Fulks and A.M. Yeoman, "Performance Evaluation of Non-Metal Cooling Water Treatments," CORROSION/83, paper no. 279, (Houston, TX: NACE, 1983).
2. E.B. Smyk, J.E. Hoots, K.P. Fivizzani and K.E. Fulks, "The Design and Application of Polymers in Cooling Water Programs," CORROSION/88, paper no. 14, (Houston, TX: NACE, 1988).
3. G. Wofford, C. Slezak and M. Bukey, *Industrial Water Treatment* 23, 2 (1991): p. 33, and references therein.
4. H.H. Lu and D.J. Duquette, *Corrosion* 46, (1990): p. 843.
5. D.A. Meier and J.D. Lammering, ASHRAE Transactions 93 (part 2) (1987).
6. J.M. Brooke and P.R. Puckorius, "Ozone for Cooling Tower Systems: Is It a Panacea?" CORROSION/91, paper no. 212, (Houston, TX: NACE, 1991). And references therein.
7. J.D. Cowan and D.J. Weintritt, *Water-Formed Scale Deposits*, Gulf Publishing, Houston, 1976, p. 204.
8. Ibid, p. 209.