Field Evaluation of Ozone for Control of Corrosion and Scale in a Zero Blowdown Application

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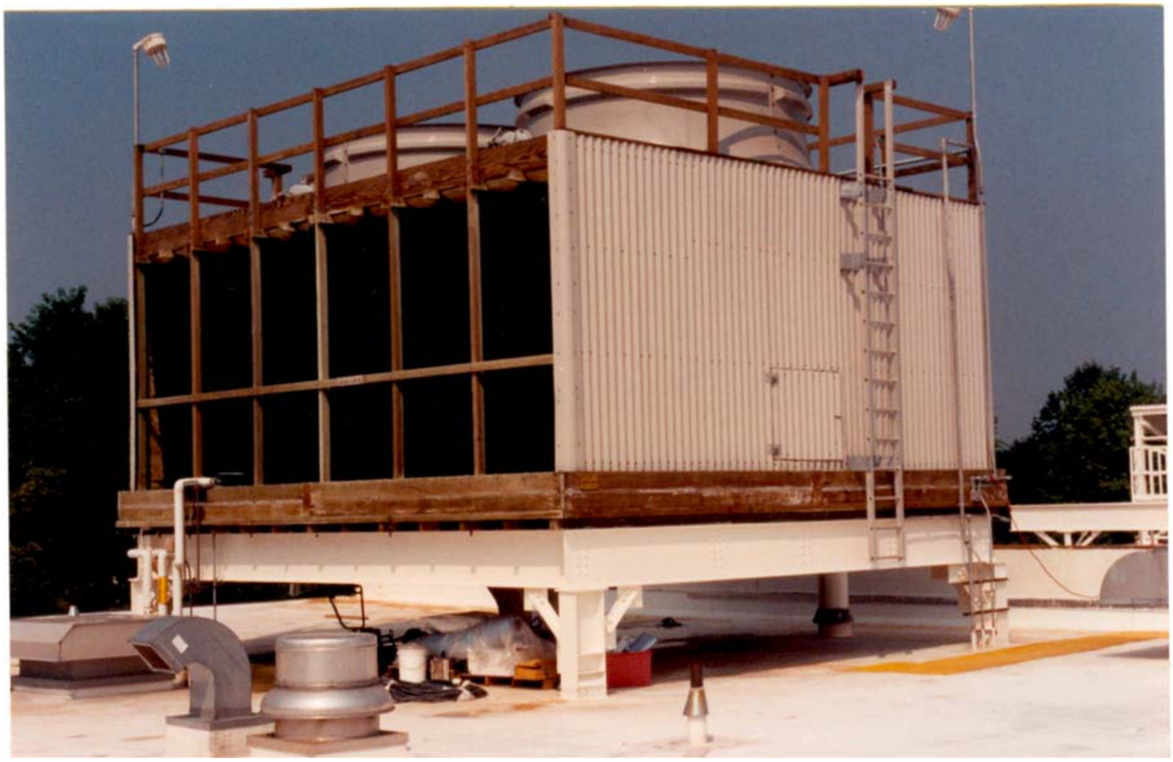
Introduction

Elimination of intentional evaporative cooling system blowdown, commonly referred to as zero blowdown, is being attempted more often due to environmental requirements, increased costs for makeup water and sewerage disposal, and a desire to minimize chemical usage and cost. Ozone treatment of cooling water has been reported by several sources to give acceptable results for control of corrosion and scale in zero blowdown cooling systems. These reports typically note the cooling system was operated with no blowdown and that control of both corrosion and scale was acceptable. Mass balance data has been presented with the explanation that hardness is removed as a non-scale forming precipitate which settles in the cooling system basin. Remaining information is then centered on the economic benefits of the conversion from a chemical treatment program to ozone treatment. Additional data concerning actual corrosion rates, scale formation, and water chemistry are lacking, or at best minimal.

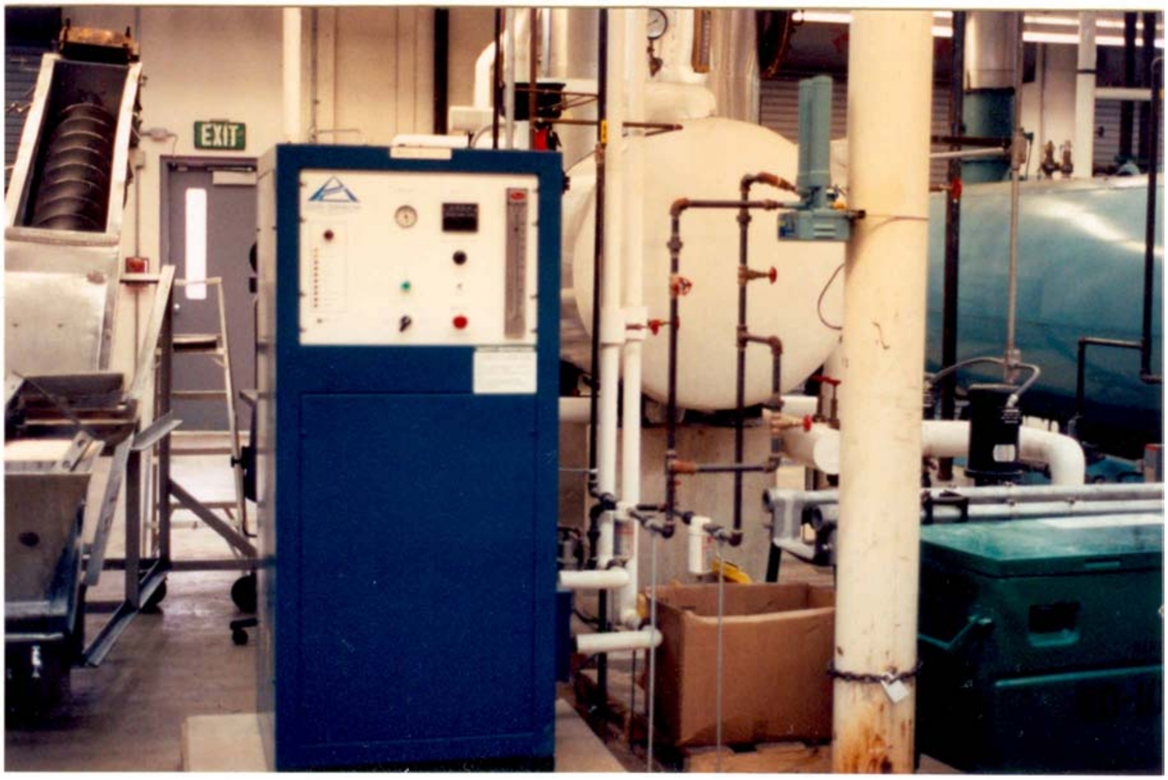
While ozone is acknowledged to be an excellent biocide, the reported ability to also control corrosion and scale under the severe conditions imposed by zero blowdown operation has been greeted with skepticism within the water treatment industry. Despite there being no reasonable scientific theory to explain the reported results, several firms are actively promoting use of ozone treatment for obtaining zero blowdown operation of cooling systems. We, Industrial Chemical Corporation and ProChemTech, were given an opportunity to evaluate a new zero blowdown cooling system using only ozone treatment for a period of eight months following start-up. The following is a summary report of the study and results obtained.

System/Experimental

An industrial plant located in Baltimore, Maryland, was to be expanded during 1991 by installation of a new cooling system. Corporate staff, being aware of the environmental and economic benefits of zero discharge and the reported use of ozone to achieve it, determined that this technology should be used in the new system. During installation of the new system, we were contacted by plant engineering staff and ask if there was any interest in monitoring the performance of the ozone technology. The opportunity presented was accepted with Industrial Chemical Corporation providing field sampling, and ProChemTech undertaking the analytical work.



The new cooling system uses the above pictured Marley Company duel cell, induced draft crossflow cooling tower of approximately 1000 tons capacity for evaporative heat rejection. System materials of construction include treated wood, fiberglass, polyvinyl chloride, and galvanized steel in the cooling tower; black iron piping; and yellow metal alloys in the air compressor and chiller served by the system. A steam heated coil constructed of galvanized steel pipe is installed in the cooling tower basin, which serves as the system cold well, for freeze protection.



Ozone treatment of the cooling system is supplied by the pictured PCI Ozone and Control Systems Model G 7 ozonator, which is rated 0 to 7 lbs/day of ozone. The unit operates as a side stream device, generated ozone is injected into cooling water passing through the unit. Cost of this unit is reported by the manufacturer to be in the $20,000 range. We did note that several gpm of one pass city water was being used to cool the ozonator as cooling system water was reported to be to warm for such use.

Ozonated water is piped from the ozone generator and discharged directly into the cooling tower basin as shown. A definite ozone odor was present around the cooling tower at all outputs exceeding one lb/day, with plant personnel reporting that the ozone being released into the air during higher outputs was intolerable near the cooling tower.

Makeup water supplied to the cooling system from January to May, 1992, was softened by passage through a sodium cycle cation exchange water softener. From May, 1992, to the end of the study period, unsoftened city water with hardness values around 90 mg/l was used as makeup. The cooling system was operated in zero blowdown mode for the entire study period with the only exception being several complete system drains for cleaning of the cooling tower basin.

Due to the initial use of softened water for makeup in the cooling system, a unique opportunity was presented for an evaluation of ozone control of corrosion without any effect from cycling of water hardness. A four position crossflow corrosion coupon rack with a flow control was installed in the system for use of standard metal strip corrosion test coupons as supplied by Metal Samples, Inc. Sampling and chemical analysis of the city, makeup, and cooling waters was also undertaken in order to ascertain the water chemistry of the cooling system.

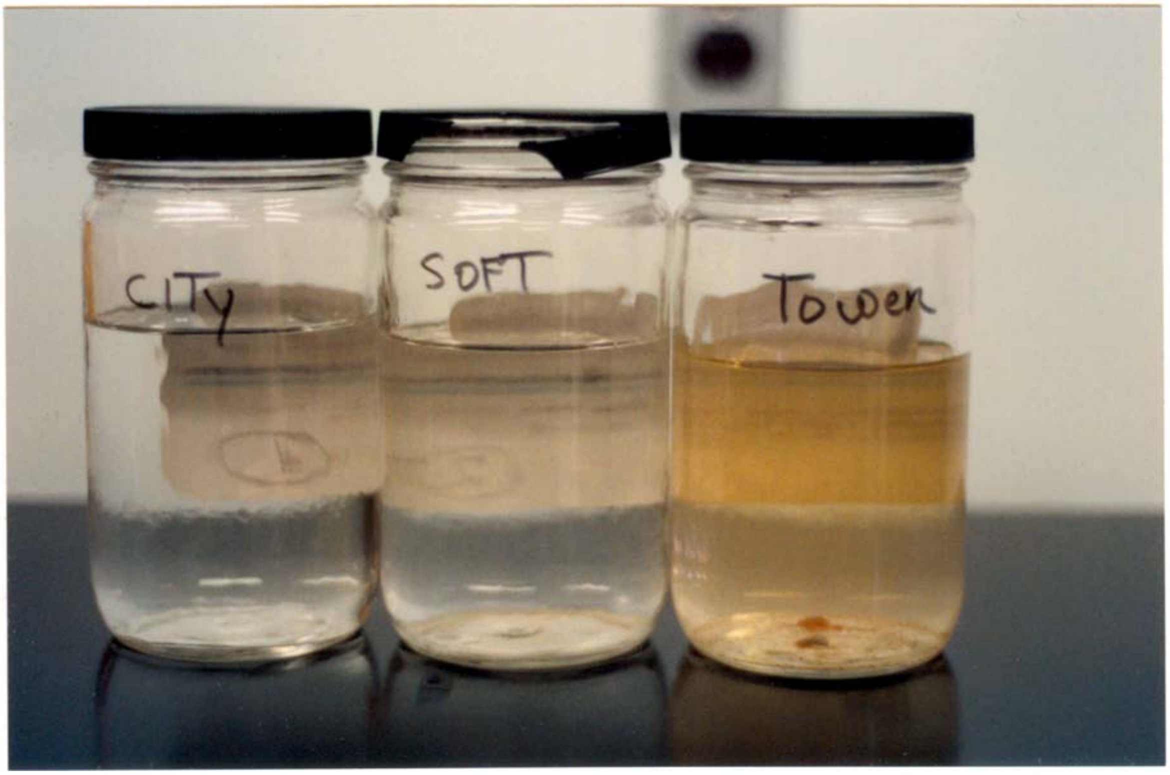
Following our finding of excessive corrosion rates in the cooling system, the ozone system supplier recommended a switch from softened to hard water makeup. The conversion was accomplished on May 6, 1992; which now presented us with an opportunity to evaluate the ability of the ozone treatment to control scale.

Plant engineering agreed to maintain steam flow to the heating coil throughout this period. This permitted easy evaluation of scale formation on a heat exchanger within the cooling system that was exposed to the maximum concentration of ozone. As before, corrosion coupon studies were undertaken along with sampling of makeup and cooling system waters. A substantial amount of scale was also obtained from the heating coil on July 7, 1992, and chemically analyzed.

Results

The first set of water samples was obtained on January 6, 1992, shortly after system startup. Chemical analysis of these samples using Standard Methods procedures by Analytical Services, Inc., a certified drinking water laboratory, gave the following results:

Parameter	City	Makeup	Tower
pH su	7.30	7.45	8.65
total alkalinity mg/l	52	54	274
conductivity mmhos	253	254	1258
calcium mg/l	21.2	0.23	1.39
magnesium mg/l	5.4	0.035	0.145
iron mg/l	0.04	0.05	13.6
copper mg/l	0.23	0.03	3.90
zinc mg/l	ND	ND	0.524
silicon mg/l	1.9	1.8	8.0
chloride mg/l	35	38	157
sulfate mg/l	7	15	91
nitrate mg/l	1.3	1.2	0.82
phosphate mg/l	0.55	0.50	0.55
dissolved solids mg/l	108	108	712
total hardness mg/l	75	0.72	4.07
cycles on chlorides			4.5
saturation index, 100 F	-0.82		-0.01



As shown in the preceding photo, the cooling water sample was reddish in color with some red floc present, likely due to the substantial amount of iron in the water. The analysis data clearly indicates that substantial corrosion was taking place within the cooling system prior to the sampling.

A set of corrosion coupons was installed on January 21, 1992, and removed for analysis 31 days later on February 21, 1992. The following results were obtained using standard NACE evaluation procedures.

Coupon Material	Corrosion Rate
1010 mild steel	12.69 mil/yr
1010 mild steel	12.17 mil/yr
CDA 110 copper	0.21 mil/yr
CDA 260 brass	0.69 mil/yr

The conclusion reached from the water analysis results that the ozone treated system was corroding at an excessive rate is confirmed by the above corrosion coupon results. As a basis for comparison, chemically treated cooling systems using softened makeup water and operated at high cycles typically obtain corrosion rates below 1 mil/yr on identical 1010 mild steel corrosion coupons.

As shown by the following closeup of a portion of one of the above steel corrosion coupons, corrosion and resultant deposition of corrosion products was substantial.

CLOSE UP PHOTO OF CORROSION COUPON, OZONE/SOFT WATER

A second set of water samples was obtained on February 25, 1992, and analyzed as before with the following results obtained.

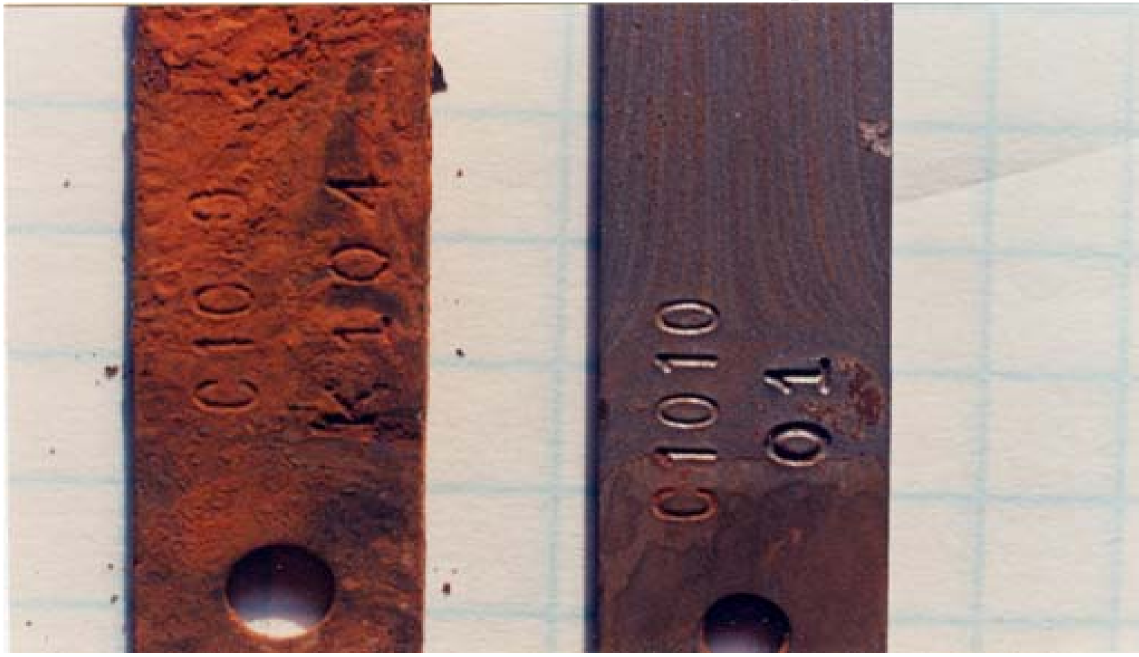
Parameter	City	Makeup	Tower
pH su	7.10	6.89	8.60
total alkalinity mg/l	50	46	204
conductivity mmhos	270	268	1270
calcium mg/l	24.5	0.24	1. 30
magnesium mg/l	5.6	0.023	0.115
iron mg/l	0.08	0.16	13.1
copper mg/l	ND	ND	2.20
zinc mg/l	0.007	0.020	0.373
silicon mg/l	1.5	1.8	14.5
chloride mg/l	23	22	121
sulfate mg/l	36	30	149
nitrate mg/l	1.5	1.6	8.87
phosphate mg/l	0.45	0.45	0.48
dissolved solids mg/l	128	128	636
total hardness mg/l	84	0.69	3.72
cycles on chlorides			5.3
saturation index, 100 F	-0.98		-0.22

The results from the second set of water samples are very similar to those obtained from the first set, showing elevated levels of iron, copper, and zinc; indicating high rates of corrosion within the cooling tower system.

The above second set of corrosion coupons were installed on April 7, 1992, and removed 30 days later on May 6, 1992. Analysis of these corrosion coupons gave the following results.

Coupon Material	Corrosion Rate
1010 mild steel	20.57 mil/yr
CDA 110 copper	0.25 mil/yr

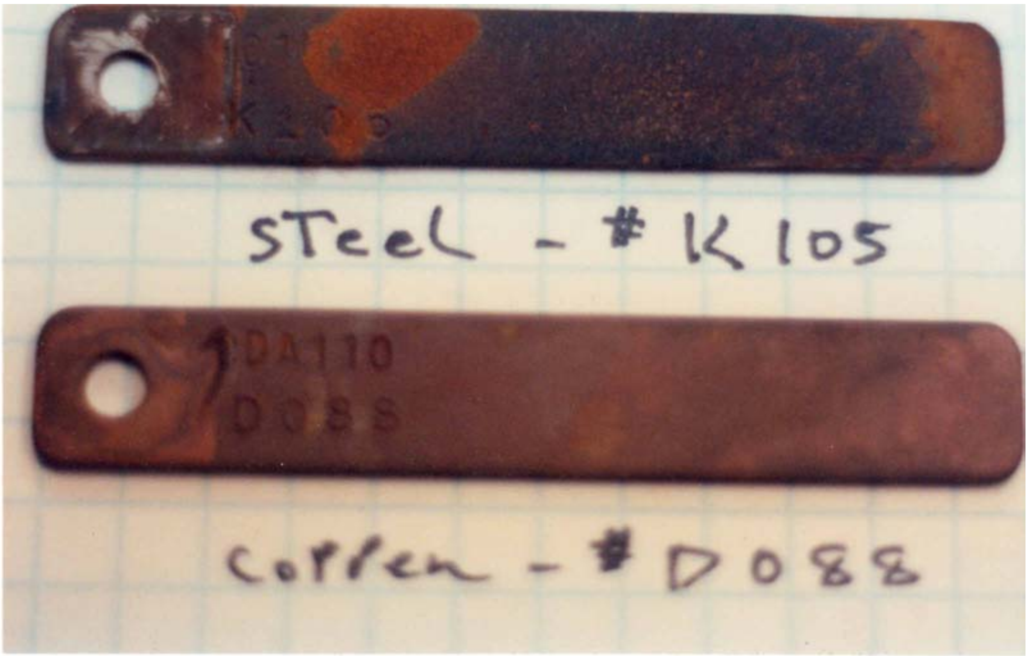
These results confirm the previous findings that the corrosion rates in the system were excessively high.



COUPONS FROM OZONE AND CHEMICALLY TREATED SYSTEMS

The previous photo compares a 1010 mild steel corrosion coupon exposed for 30 days in the ozone treated cooling system beside a similar coupon exposed for 60 days in a cooling tower system running high cycles with soft water makeup and a molybdate-silicate chemistry program. Corrosion rate on the ozone treated coupon is 20.57 mil/yr, while the chemically treated coupon showed a rate of 0.29 mil/yr.

Based on our findings, which had been reported to the plant engineer and transmitted to the ozone system supplier, the decision had been made to change the makeup to hard water. This was accomplished on May 6, 1992, immediately after removal of the second set of corrosion coupons.



The above third set of corrosion coupons was installed on May 7, 1992, and removed 30 days later on June 7, 1992. Analysis of these corrosion coupons gave the following results.

Coupon Material	Corrosion Rate
1010 mild steel	2.17 mil/yr
CDA 110 copper	0.15 mil/yr

As expected, these results show a substantial decrease in corrosion rate due to use of hard water in the cooling system and resultant operation under scale forming conditions.

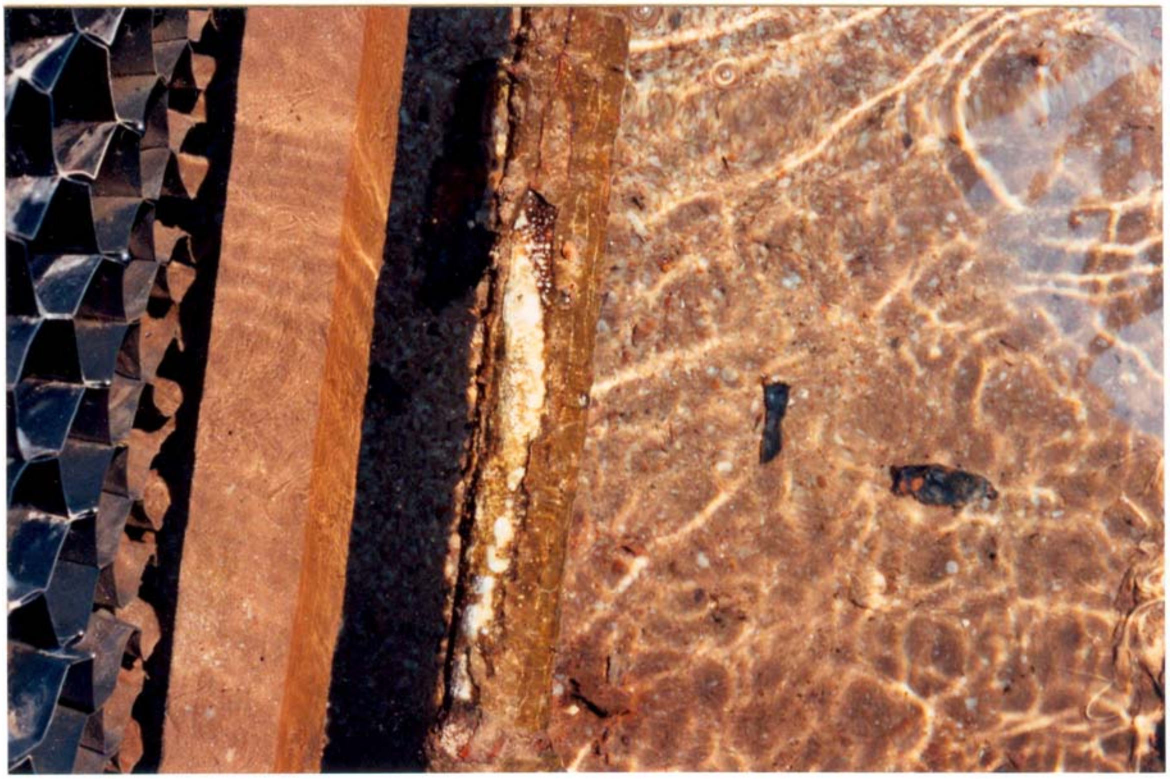
Substantial buildup of scale was noted on the heating coil in the cooling tower basin during this time period. A sample of scale was obtained on July 7, 1992, and analyzed with the following results obtained.

Parameter	Results as weight %
Loss on ignition	39.47
Calcium as CaO	14.0
Magnesium as MgO	4.1
Iron as Fe_2O_3	15.7
Copper as CuO	0.71
Aluminum as Al_2O_3	0.91
Silicon as SiO_2	17.1
Sulfate as SO_4	0.29
Phosphate as PO_4	0.028
Zinc as ZnO	0.056

Closure = 92.36%

These scale analysis results show that calcium, magnesium, iron, and silicon are present in scale formed from the ozone treated cooling water. Based on the previous corrosion rates, the iron component is believed to result from deposition of corrosion products, while the calcium, magnesium, and silicon are supplied from the makeup water.

As shown by the following photo, the scale is a hard material which adheres to the surface on which it forms. The evident spalling is believed to be due from thermal stress resultant from loss of heat transfer. Active scale formation is evident in those areas where the older scale has spalled off.



On July 12, 1992, a third set of water samples, the first following conversion to hard water makeup, were obtained. The following results were obtained on analysis of these samples.

Parameter	City/Makeup	Tower
pH su	7.50	8.45
total alkalinity mg/l	60	176
conductivity mmhos	270	7250
calcium mg/l	26	360
magnesium mg/l	6.6	190
iron mg/l	0.08	0.60
copper mg/l	0.06	0.25
zinc mg/l	0.010	0.035
silicon mg/l	2.1	22.1
chloride mg/l	26	1462
sulfate mg/l	19	727
nitrate mg/l	1.4	5.6
phosphate mg/l	ND	ND
dissolved solids mg/l	180	4996
suspended solids mg/l	ND	29
total hardness mg/l	92	1682
cycles on chlorides		56.2
saturation index, 100 F	-0.49	+1.92

These results confirm the scale analysis results in that the amounts of calcium, magnesium, and silicon found in the cooling water are substantially below what would be expected based on the cycles obtained in the cooling tower.

Examination of the cooling tower distribution deck and basin on August 19, 1992, showed significant scale and deposition accumulation only on the heating coil. As shown by the two following photos, both the deck and basin were very clean. No evidence of the typical bulk precipitation and settling of hardness from the cooling water as reported in previous reviews of ozone treated zero discharge cooling towers was noted.

COOLING TOWER BASIN

A fourth set of water samples was obtained on August 19, 1992, in conjunction with the plant review and analyzed with the following results obtained.

Parameter	City/Makeup	Tower
pH su	7.40	8.40
total alkalinity mg/l	46	140
conductivity mmhos	214	10,000
calcium mg/l	24	281
magnesium mg/l	5.2	144
iron mg/l	0.03	0.40
copper mg/l	0.02	0.09
zinc mg/l	0.010	0.017
silicon mg/l	2.2	23.1
chloride mg/l	24.6	750
sulfate mg/l	12.4	512
nitrate mg/l	5.2	165
phosphate mg/l	ND	ND
dissolved solids mg/l	148	2868
total hardness mg/l	80.4	1295
cycles on chlorides		30.5
saturation index 100 F	-1.14	+1.69

These results confirm the first set of hard water makeup samples, showing that the calcium, magnesium, and silicon levels in the cycled water are substantially less than expected based on the cycles obtained.

Discussion/conclusion

Based on the results obtained during the study, we have concluded that ozone has no corrosion inhibition properties when applied to treatment of cooling water. Use of ozone as a stand alone water treatment program will result in corrosion rates ten to twenty times higher than could be obtained via use of proven corrosion control chemistry.

The past reports noting successful corrosion control via stand alone use of ozone are believed to be in error. It is our opinion, based on the decrease in corrosion rate found following the switch to hard water makeup in the present study, that the corrosion control effects attributed to ozone have been due solely to operation of the cooling tower systems under scaling conditions. It is generally accepted that operation under such conditions will result in a substantial decrease in corrosion rates due to formation of protective scales on metal surfaces.

In regards to the ability of ozone to control scale, the results obtained indicate that ozone has little or no ability to control scale formation on heat exchange surfaces. The reported bulk water precipitation of hardness, which has been used to explain the lack of scale on several zero discharge operation systems and provide a mass balance for the cooling system, was not observed during the present study. Scale, in contrast, was found to rapidly form on the test heat exchanger surface with no bulk precipitation observed.

Given the higher makeup water alkalinities in the Western United States, where the majority of the ozone studies have been carried out, it is likely that any bulk precipitation observed resulted from operation of the cooling tower with water chemistry similar to the classic "carbonate" cycle utilized for many years to control scale formation in boilers. If this is the case, the same results could be obtained in zero discharge systems without use of ozone.

Biological control of the cooling tower system was observed to be excellent, confirming the generally accepted fact that ozone is a very good oxidizing biocide which can be used on a stand alone basis. Use of ozone for biological control in zero discharge cooling towers should be carefully considered as it is one of the few biocides available which adds no dissolved solids to the cooling water. This consideration must also include evaluation of the local air pollution control regulations and plant health and safety based on our experience with ozone off gas release on the studied cooling system.