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Evaluation of Ozone Treatment in Air Conditioning Cooling Towers

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ABSTRACT

Ozone is a potential alternative to chlorine and proprietary chemicals for treating cooling tower circulating water systems at electric power plants. This study surveyed air conditioning cooling tower systems which have used ozone treatment for the past few years. The performance of these systems and the implications of using ozone treatment in electric power plants were examined.

Several sites were surveyed. Makeup and circulating water samples were taken at four sites using ozone treatment. The samples were analyzed for general mineral content, including parameters which affect chemical scaling. At two of these sites, cooling tower systems using proprietary chemical treatments were sampled for comparison. At selected sites, trihalomethanes, total plate counts, oxidant residuals, and trace metals were measured.

The results indicate that ozone treatment warrants further study for application at electric power plants. For the ozone systems sampled, biological fouling was apparently controlled. The ozone systems operated at conditions far exceeding conventional chemical scale limitations. As a result chemicals were apparently precipitated, but seemingly settled out in the cooling tower basins rather than fouling heat exchange surfaces. The failure of one system operating at elevated water temperatures indicates that the limits of ozone treatment must be determined before this technology is applied at electric power plants.

EPRI PERSPECTIVE

PROJECT DESCRIPTION

This report documents the results from an evaluation of the application of ozone to air conditioning cooling tower recirculating water systems. Purported experiences of extraordinarily high cycles of concentration being sustained by cooling tower systems treated solely with ozone prompted this investigation.

Makeup and circulating water samples were taken on four towers that had used ozone treatment for the past few years. The system was shown to be operating, in a clean condition, at conditions far exceeding conventional chemical scale limitations.

Further research is planned. The Office of Water Research and Technology (OWRT), U.S. Department of Interior, and the California State Water Resources Control Board's Office of Water Recycling (OWR) is contemplating a jointly sponsored pilot study of the chemistry and process limitations of ozonated-cooling systems. If the approach shows promise, the results will be integrated with EPRI Research Project (RP) 1261-1, Treatment of Closed Cycle Cooling Water, for comparative evaluation against other conventional treatment alternatives.

PROJECT OBJECTIVES

This study had three objectives. The primary objective was to confirm, through direct observation and measurement, reports that the use of ozone in air conditioning cooling tower operations effectively prevented chemical deposition on heat transfer surfaces. The second was to determine whether the technology was applicable to utility cooling water systems. Finally, based on the results derived and sound technical conclusions, recommendations for further research and developmental work were to be defined.

PROJECT RESULTS

The effectiveness of ozone treatment for controlling mineral scale deposition as well as biofilm formation was confirmed. High cycles of dissolved salt concentra-

tion in air conditioning cooling water systems were indeed attainable. Despite the positive results, uncertainties remain. The study postulates that superior performance of ozonated cooling tower recirculating waters is directly attributable to ozone. However, the observation is not conclusive. Similar results may be possible with varied chemical treatments and plant operating parameters. Ozone's apparent effectiveness may be a synergistic effect of several different parameters, such as water characteristics, temperature, or hydraulic velocity. Thus, whether these results can be translated to utility cooling tower performances remains in doubt. These uncertainties are expected to be resolved through the OWRT and OWR joint project.

With increasing regulatory pressure for utilities to eliminate chlorine as a biofouling control agent in cooling waters, and to move toward zero aqueous discharge from power plants, the prospects of this technology are exciting. Ozonation has the potential of offering a technically and economically attractive option for simultaneous abatement of biofouling and scaling on heat exchange surfaces. To accomplish this goal, further research is recommended. This includes (1) participation in the related OWRT and OWR research program, (2) coordination of the results of this and subsequent studies with RP1261, and (3) demonstration of the fully developed process at a utility site.

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SUMMARY

Currently accepted practice for controlling scale, corrosion and fouling in cooling tower systems is through the use of chemical addition and the control of cycles of concentration. Chlorine is usually used for control of biological growths. Recent concerns over chlorine residuals and trihalomethanes in wastewater discharges, including cooling tower blowdowns, have led to evaluation of alternatives to chlorine. Ozone is one of these alternatives. Although the reasons why are not immediately apparent, experience with ozone systems has indicated that ozone may also be effective in controlling chemical scaling.

One manufacturer, Source Gas Analyzers, Inc. (SGA), of Garden Grove, California, states that its water treatment system, which uses ozone, can be employed as the sole source of treatment for control of biological and chemical fouling in low temperature heat exchange systems and furthermore, that cooling tower systems using this treatment can operate with no blowdown. Thus, SGA claims, low temperature systems using ozone can be operated with greatly reduced water and power consumption and reduced chemical and labor costs. In a report (1) SGA has identified several sites in southern California where ozone is successfully used in cooling towers servicing air conditioning systems. Maximum water temperatures in such systems are typically about 90°F.

To our knowledge ozone has not been used to treat cooling tower systems at electric power generating stations. However, were ozone treatment to be as effective at electric power generating sites as SGA claims it is with air conditioning systems then similar benefits would occur and at a very large scale. There is justifiable reluctance to proceed directly with ozone testing at power generating stations, even if the claims made by SGA can be verified. For example, water temperatures may be different than water temperatures in air conditioning systems and scale-up problems may also be encountered. Thus, results obtained in air conditioning systems may not be directly translatable to power generating stations. A more cautious step-by-step approach to the issue was instead adopted.

The Electric Power Research Institute (EPRI) contracted with the firm of Brown and Caldwell to conduct a preliminary investigation into the current use of ozone in air conditioning systems. The objectives of the investigation were to survey several operations where ozone treatment is now used, to determine whether claims made by SGA are confirmed in practice and to provide a technical basis for a subsequent large-scale comparison of ozone and proprietary chemical treatment at an electric power generating station, if such a test seems warranted.

As previously mentioned, there are several sites in southern California where ozone is used to treat air conditioning systems. Visits were arranged at four locations (Bullock's main store in Los Angeles, Bullock's Store in Sherman Oaks, NBC Studios in Burbank, and the Jet Propulsion Laboratory of the California Institute of Technology in Pasadena) with full sampling programs carried out at the latter three. In addition an ozone system at Duke University in Durham, North Carolina, was sampled by the Duke Power Company of Charlotte, North Carolina. Both the Jet Propulsion Laboratory (JPL) and Duke University operate cooling towers which use proprietary chemicals in addition to those towers using ozone treatment. Towers using proprietory chemicals were also sampled to provide a basis for comparison with ozone treatment.

Makeup and circulating waters were analyzed at all installations sampled. Parameters measured in the field were temperature, pH, and for selected sites, oxidant residual. Parameters measured in the laboratory were those which could affect scaling (magnesium, calcium, silica, sulfate, inorganic carbon and phosphate) and other major anions and cations needed to perform an anion-cation balance. Standard plate counts, total organic carbon, trihalomethanes (THMs) and trace metal concentrations were measured for selected samples.

Users were generally pleased with ozone treatment. Most felt it was a great improvement over the proprietary chemicals previously used. Some expressed dissatisfaction with the durability and reliability of the SGA ozonator, however. For example, JPL had completely rebuilt its SGA ozonator and was using ozonators of its own design in most recent installations. Problems were experienced only when the ozone generators failed. When this happened, fouling problems (judged to be of biological origin) appeared within about five days. Circulating water in the ozone systems was generally clear in appearance, although occasionally colored. The physical appearance of the ozone treated towers was generally good, with visible scaling and biological growths limited to the outer edges of the

tower packing, in areas of alternating wetting and drying. Personnel indicated no heat transfer problems with the heat exchange units. All systems sampled were operating at no blowdown at the time of the site visits. The ozone dose was roughly estimated for all ozone treatment systems, with the maximum dose believed to be about 0.03 mg/l, based on circulating water flow.

Plate counts observed for ozone-treated circulating waters (7,000-54,000 colonies/ml) were relatively low compared to some rule-of-thumb limitations which have been applied to circulating waters. This in itself is not sufficient evidence to establish that biofouling was controlled. This can only be established by inspection of the heat exchange surfaces; these were not inspected during this survey. However the relatively low plate count numbers, the good clarity of the circulating water, the apparent cleanliness of the cooling towers and continued good operation of the air conditioning systems all suggest that biofouling is not a major problem with the ozonated systems surveyed.

From chemical analyses of makeup and circulating waters we calculated that ozone systems were operating at 30 to 50 cycles of concentration and at conditions far exceeding conventional scale control limits. The calculations indicated that significant quantities of calcium, magnesium, silica and alkalinity were removed from the circulating waters. For example 73 percent of the calcium, 27 percent of the magnesium, 73 percent of the silica and 96 percent of the alkalinity entering the NBC Studios cooling system in the makeup water appeared to be removed in the cooling circuit. Similiar trends, with somewhat different removals were seen in other ozonated systems (and also noted in one of the systems using proprietory chemicals). As indicated, the most plausible mechanism for removal of calcium, magnesium, silica and alkalinity is chemical precipitation. The precipitates, however, do not appear to interfere with the heat transfer process by adhering to heat exchange surfaces, since, according to operating personnel, air conditioning performance does not degrade with the passage of time. We surmise that the precipitates are continuously removed by mud separators (if the cooling circuit is equipped with such devices) and/or accumulate in other sections of the cooling circuit, most likely the cooling tower basin, where quiescent conditions allow them to settle out. The accumulated solids are then removed when the cooling system is periodically cleaned.

We should emphasize that the above statements with respect to chemical scaling are hypotheses and have not been proven. Removal calculations are based on materials balances thus are technically sound but the calculated mass of materials "removed" has not been verified by actual weighing and chemical analyses of the precipitated solids, i.e., a closure of the balance has not been obtained. To do so would require investigative effort far beyond the scope of this project. The "conclusions" with respect to scaling represent our best effort to analyze the limited data available.

Nitrates appear to accumulate in circulating waters beyond levels which could be achieved by simple concentration, both in ozonated systems and systems using proprietary chemicals. While nitrates in discharges are not normally regulated, this is a potential problem for sites where blowdown is discharged into nitrogen-sensitive receiving waters or waters which serve as a water supply. The excess nitrate accumulated in ozonated systems is believed due to dissolution of nitrogen oxides produced during ozone generation. Excess nitrate accumulations in systems treated with proprietary chemicals could be as the result of addition with treatment chemicals or possibly the result of the reaction of chlorine (a component of the proprietary treatments) with ammonia derived from decomposing bacteria or algae. If the latter mechanism is operative, the route by which nitrogen for nitrate production enters the system (besides in the makeup water) is with bacteria scrubbed from the air or by fixation of atmospheric nitrogen by algae.

Oxidant residuals were found in all circulating systems using ozone in which an analysis for these species was made. The residuals measured are not believed to be ozone because ozone is too reactive in aqueous media to exist by itself for more than a few minutes. The identities of the residuals present were not established because the test used is not specific for any particular oxidant. Ozone can react with chloride and bromide ions to form hypochlorous and hypobromous acids. Both bromide and chloride were present in the waters analyzed. Hypobromous acid formation is thermodynamically favored for the conditions evaluated. Replacement of chlorine by ozone does not appear to eliminate the oxidant residual problem.

Trihalomethanes (THMs) were significantly removed in all systems in which analyses for these species were made, including the systems using proprietary chemicals. Two of the five makeup waters examined had total THMs (the sum of

chloroform, dibromochloromethane, bromodichloromethane and bromoform) exceeding 100 ug/l, which is the tentative EPA standard for drinking water. However, total THMs concentrations were much below 100 ug/l in each of the five circulating waters in which THMs analyses were made. Therefore, removal of THMs was significant. Percent total THMs removals were highest for systems operating at highest cycles of concentration. Possible reasons for this are increased opportunity for THMs outgassing to the atmosphere or increased opportunity for destruction via ozonation as circulating water residence time increases. These results imply that total THMs do not build up to problem levels in cooling towers.

Data from the Duke University site suggest that the trace metals iron and zinc were removed in ozone systems. Chromium and arsenic accumulated to levels greater than could be achieved by simple concentration. Data with respect to other trace elements (cadmium, mercury, nickel, lead, and selenium) are ambiguous because concentrations of these elements in the makeup water were below limits of detection. The possibilities for removal of many of these elements seems great however, due to the high concentration driving force for precipitation.

The physical condition (turbidity, suspended solids and plate counts) of the circulating waters treated with ozone was superior to the physical condition of the circulating waters using proprietary chemicals even though the operating conditions for the former were far more severe. However, we cannot say with certainty that ozone treatment is "better" than the proprietary treatments used. It is possible that similar results might have been obtained with chlorine alone, different proprietary chemicals, different doses of the same proprietary chemicals, or operation at higher cycles of concentration. While it is not possible to state unequivocally that ozone treatment is better, the evidence suggests that ozone treatment is working at the sites visited.

The apparent success of the ozone systems sampled is to some extent counter-balanced by the failure of an ozone system at the University of California at Los Angeles (UCLA). This system failed prior to the start of this study and was removed from service, thus we were not able to determine the reason or reasons for its failure. It is noteworthy, however, that circulating water temperatures in this system (which serviced a lithium bromide air conditioning unit) were higher and circulating water temperature rises across the condenser were substantially greater than those observed in the other ozonated systems studied.

While there is insufficient evidence to conclude that failure of the UCLA system was caused by temperature related factors there are reasons to be concerned about the viability of ozone treatment for systems which operate at higher temperatures and greater temperature rises than the ozone systems sampled. It is believed that circulating water temperatures and temperature rises in electric power cooling systems exceed their counterparts in the air conditioning systems sampled, at least part of the time. Thus the apparently good results obtained in low-temperature air conditioning systems may not necessarily be reproduced at electric power stations.

We recommend that the use of ozone in cooling tower systems be further pursued. The possibilities for beneficial application of this technology are intriguing. The most striking potential benefits to electrical utilities appear to be:

1. Potential cost reductions

   --If systems using ozone can operate at higher cycles of concentration than currently possible, the volume of makeup water required per unit of cooling would be reduced as well as the volume of blowdown for treatment and disposal.

   --While ozone as a biocide is more costly than chlorine, ozone alone might be less costly than combinations of chlorine and scale inhibitors needed to give equivalent treatment.

   --Ozone treatment of the circulating water may reduce or possibly eliminate costly makeup water treatments, e.g., lime softening of municipal wastewater effluents to be used for cooling purposes.

2. Any required blowdown may be less noxious because:

   --Fewer halogenated hydrocarbons may form and those which do may be less toxic than those produced with chlorine treatment.

   --Oxidant residuals may be less.

   --Trace metals mass emissions may be less.

Immediate full-scale testing at a power generating station is not recommended. Present understanding of the technology is insufficient and the penalities for failure too severe. Further studies of a low-risk nature should be pursued instead. The thrust of the next phase of testing should be to pave the way for eventual testing at a full-scale electric power-generating station. The study should:

1. Seek to identify process limits in systems which operate at temperatures used at electric power generating stations. Testing would

ideally be carried out at a facility where process variables could be controlled by the investigator and where penalities for process failure would not be great.

2. Determine constituent removal mechanisms and the degree to which constituents can be removed.

3. If removal of calcium, magnesium, silica and alkalinity is by precipitation, determine why the precipitated solids apparently do not adhere to heat transfer surfaces.

4. Determine if ozone is unique in its effect in cooling systems or if chlorine, properly applied, has the same effect.

5. Identify oxidant residuals created by ozonation, and if possible, their relative toxicity.

6. Identify electrical generating stations where a full-scale ozone testing program could be carried out, if warranted.

7. Provide preliminary engineering designs and cost analyses for ozone treatment systems for power generating stations identified in Item 6.

Section 1

INTRODUCTION

Currently accepted practice for controlling scale, corrosion, and fouling in cooling towers is through the use of chemical additives and the control of the cycles of concentration. Chlorine is normally used for control of biological growths. Recent concerns over chlorine residuals and trihalomethanes in wastewater discharges, including cooling tower blowdowns, have led to evaluations of alternatives to chlorination. Ozone is one of these alternatives. Although the reasons why are not immediately apparent, experience with ozone systems has indicated that ozone may also be effective in the control of chemical scaling. Thus ozone may, under certain circumstances, be used as the sole chemical treatment for control of biological and chemical fouling.

BACKGROUND

Ozone has not been used for treatment of cooling tower circulating water systems at electric utility power plants. Within the last few years, however, ozone systems have been installed at several commercial buildings for controlling biological and chemical fouling in air conditioning cooling tower systems. One manufacturer of ozone systems is Source Gas Analyzers, Inc. (SGA) of Garden Grove, California. SGA states that if its water treatment system is used, these cooling systems can operate with no blowdown and the treatment is comparable in effectiveness to any proper chemical water treatment program (1).

STUDY OBJECTIVES

The objectives of this study were to survey several operations where ozone treatment is being used, to determine whether claims made by SGA are confirmed in practice, and to provide a technical basis for a subsequent large-scale comparison of ozone and proprietary chemical treatment at an electric utility power plant, if such a test seems warranted.

Specific objectives included:

1. Obtain and analyze makeup and circulating water samples from towers using ozone and, if available, samples from cooling towers at the same site using proprietary chemicals.

2. Determine the cycles of concentration obtained in each cooling tower and evaluate the scaling potential of each circulating water.

3. Obtain samples of solids removed from sidestream solids separation devices, if possible, and determine their composition.

4. Measure the oxidant residuals and trihalomethane levels in the makeup and circulating waters and evaluate their significance.

5. Evaluate the implications of using ozone treatment in cooling tower systems at electric power utilities.

6. Recommend additional work required before a large-scale demonstration can be carried out at an electric utility power-generating station.

Section 2

OZONE IN COOLING TOWER CIRCULATING WATER TREATMENT

Ozone is a powerful oxidant which has been used as in the treatment of water supplies in Europe since the beginning of this century. It has been used sparingly in the United States because of its high capital and operating costs and because it does not maintain an oxidant residual in drinking water. With the advent of less costly and more efficient ozone generators, ozone is receiving renewed attention in the wastewater field (2).

PROPERTIES OF OZONE

Ozone is an allotrope of oxygen. It is an unstable gas with a characteristic pungent odor. Because it is unstable it cannot be stored and must be generated on site. Ozone is normally generated by passing dry oxygen or air through a high voltage (4,000-30,000 volts) electric discharge gap, i.e., a corona discharge.

Ozone is a strong oxidizing agent and produces biological effects similar to those achieved with chlorine. The major differences between ozone and chlorine include (2,3):

1. Ozone is a stronger oxidizing agent and hence is a more potent germicide and viricide than chlorine. On a mass basis, ozone is a more effective disinfectant than chlorine by a factor of ten or greater.

2. Ozone is much more reactive than chlorine. This results in a greater oxidant demand in waters containing reduced inorganics, such as ferrous iron, sulfides, chlorides, bromides, and organic substances.

3. Ozone is about five times less soluble in water than chlorine.

4. Ozone is believed to be effective over a wider pH and temperature range than chlorine. Little is known about these effects however.

Free radicals ($HO^{\bullet}$ and $HO_2^{\bullet}$) form when ozone decomposes in pure water. These free radicals are believed to be the principal reacting species. Higher pH and carbonate concentrations favor free radical formation.

CLAIMS ABOUT OZONE TREATMENT

SGA has made certain claims about its ozone treatment (1). The major claim is that with ozone treatment cooling towers can be operated without blowdown. Thus, circulating water composition would be controlled by other mechanisms, e.g., evaporation, drift and precipitation. SGA believes that biological growths "are the bonding mechanism between the precipitating solids, such as calcium carbonate, and the heat exchanger tubes." According to SGA, if biological growths are not allowed to establish themselves, the precipitated chemicals cannot adhere to heat exchange surfaces and instead settle in quiescent areas such as the cooling tower basin. Precipitated chemicals, along with other solids and debris scrubbed from the air must be removed from the system either manually or mechanically by a separation device. SGA does not claim that ozone prevents precipitation.

SGA also has used a colloid neutralizer to neutralize colloidal particles in the makeup. This was claimed to prevent "hard calcium carbonate from forming by removing nuclei around which the positive calcium ions and negative bicarbonates cling to form 'hard' scale." SGA no longer claims that the colloid neutralizer is necessary for its system, and this device will not be discussed further.

EXPERIENCE WITH OZONE IN AIR CONDITIONING COOLING TOWER SYSTEMS

Several SGA systems have been installed for cooling tower circulating water systems used with air conditioning units. In these systems condenser outlet water temperatures are typically 90°F with condenser inlet water temperatures in the 80°F to 84°F range. SGA systems have been installed at NBC Studios in Burbank, California, and several Bullock's department stores in Southern California. Ozone treatment for similar air conditioning circulating water systems have also been installed and tested at the Jet Propulsion Laborabory (JPL) of the California Institute of Technology in Pasadena, California (4). Another installation at Duke University Medical Center in Durham, North Carolina, is being evaluated by Duke Power Company of Charlotte, North Carolina. Both JPL and Duke University operate cooling towers which use proprietary chemicals in addition to cooling towers using ozone treatment. Comparisons of ozone and proprietary chemical conditioning can be made at these sites.

Mr. Fred Dumpel of NBC Studios, Mr. Alan Bywater of Bullock's and Mr. Marshall Humphrey of JPL were contacted to discuss their experiences with ozone treatment. These discussions indicated that the circulating water systems using ozone

operated well without blowdown and that users were generally satisfied with the results. Periodic cleaning of the cooling tower basins and periodic checking to ensure the ozonator is operating properly are required. If the ozonator fails for any reason and the failure is not observed and corrected, fouling of the condenser (judged to be of biological origin) begins in about five days. All users reported ozone treatment to be a significant improvement over previous treatments with proprietary chemicals and had, when initiated, cleaned up previously accumulated biological and chemical scale.

An SGA treatment system was installed at the University of California at Los Angeles (UCLA) for a cooling tower circulating water system which services a lithium bromide (LiBr) absorption air conditioning system. The high temperature in the circulating water system is around 120°F. Operation of this system was discussed with Mr. Ben Budworth of UCLA's Physical Plant Department. Details of this conversation are included in Appendix B. Operation at this facility, which lasted from January 1978 to July 1978, was not successful. High temperatures were observed several times on the vapor side of the condenser, indicating the occurrence of fouling. Heavy chemical precipitation, believed to be calcium carbonate, was found in the tower basin in June. SGA suggested that a larger ozonator and twice a month cleaning of the tower basin would correct the problems. However, UCLA elected to remove the SGA system and return to its original acid-chromate treatment. Manpower for cleaning the basins was apparently a major factor.

Section 3

SAMPLING AND ANALYSES

On September 13 and 14, 1978, visits were made to several sites in Southern California where ozone treatment is being used. On September 22, 1978, the system at Duke University in Durham, North Carolina was visited. Details of site visits are discussed in Section 4 and Appendix A.

At each site makeup and circulating waters were grab sampled. Sludge samples were taken where available. A separate circulating water sample was taken and filtered at the site. Field data were taken at the same time samples were collected. The samples were taken back to the laboratory and analyzed. Analytical and field data then became the basis for subsequent evaluations of cooling tower performance.

Parameters measured in the field were temperature, pH and for selected sites, oxidant residual. Parameters measured in the laboratory were those which affect scaling (magnesium, calcium, silica, sulfate, inorganic carbon and phosphate) and other major anions and cations (e.g., sodium, potassium, chloride and nitrate) needed to perform an anion-cation balance. In addition, standard plate counts, total organic carbon, and total dissolved and suspended solids were measured for each circulating water. Trihalomethanes and trace metal concentrations were measured for selected samples.

Sludge samples were either not available or of insufficient size to allow analyses. Therefore no sludge composition data were obtained.

Details of the sampling and analytical procedures are discussed in Appendix C.

Section 4

COOLING TOWER CIRCULATING WATER EVALUATION

Water samples were obtained from five locations where ozone is being used for cooling tower circulating water treatment. At two sites, towers using proprietary chemical treatments were available and samples were taken from these for comparison. The results of the site visits and chemical analyses are discussed below. More detailed notes on the site visits are included in Appendix A.

NBC STUDIOS, BURBANK, CALIFORNIA

NBC Studios were visited on September 13, 1978.

Cooling Tower and Ozone System Description

Four Baltimore Aircoil towers connected in parallel service a refrigeration system of 2,200 tons capacity. A small stream of water is taken from the tower basin, ozonated and then returned to the basin. Ozone is injected into this loop through a venturi device; about 20 feet of 1-1/2 inch schedule 40 PVC pipe provides contact before the water is returned to the basin. The cooling system is reported to run at zero blowdown and at the time of the site visit was indeed operating in this manner.

A rough estimate of ozone dose can be made based on general industry practice. Assuming flow in the sidestream circuit to be economic velocity (7 feet/sec or 45 gpm), that the ozonater is operating at 35 scfh (flowmeter reading at the time of the visit) with 1 weight percent ozone production (5.8 g/hr) and that all the ozone produced is dissolved, the ozone dose applied to the sidestream is 0.6 mg/l. Ozone dose, based on estimated full cooling tower circulation flow of 6,600 gpm (assuming 3 gpm per ton of refrigeration for a full heat load of 2,200 tons) is 0.004 mg/l.

Further system details are provided in Appendix A.

Sampling and Analyses

The makeup water is from a private well which also is the potable water source for NBC Studios. The makeup water sample was taken from a potable water tap. The circulating water samples were taken from the high temperature side of the condenser of a 750-ton Carrier refrigeration unit.

The results of the laboratory and field analyses of the makeup and circulating waters are summarized in Table 4-1. Analytical procedures used are described in Appendix C.

Observations

The following general observations can be made:

1. The circulating water is quite concentrated, with a total dissolved solids of 13,400 mg/l. Sulfate and chloride are the principal anions and sodium is the predominant cation. There is little suspended material in the water.

2. Concentration factors for selected ions are shown in Table 4-1. The concentration factor is defined as the concentration of component X in the unfiltered circulating water divided by the concentration of component X in the makeup water. Apparent cycles of concentration are equal to the concentration factors of conserved components i.e., those components whose concentrations in the circulating water derive solely as the result of concentrating the makeup water. These are to be distinguished from nonconserved constituents, whose concentrations in the circulating water are affected by factors other than simple concentration, e.g., inputs as the result of scrubbing of materials from the atmosphere, by corrosion or as treatment chemicals or by losses due to outgassing or by precipitation of components from solution. Based on chloride, sulfate, potassium and sodium concentrations, we estimate that the NBC towers were operating at 46 cycles of concentration when sampled. These species were used to make the estimate because it was expected or shown that they would be conserved being nonvolatile, unlikely (except for sulfate) to precipitate and not generally added by corrosion. Although such materials could be scrubbed from the atmosphere or added with treatment chemicals the extent of such inputs could not be ascertained, thus they were assumed to be zero. The significance of the cycles of concentration term is that it provides a baseline against which the appearance or disappearance of nonconservative species can be measured. This is explained in detail in Attachment D, and further amplified in Item 3 (next).

3. We estimate that 73,27,73 and 96 percent of the calcium, magnesium, silica and total alkalinity, respectively, in the makeup water were removed from the cooling water. The basis for these estimates is Eq. 4-1.

$$\text{FRACT} = 1 - \frac{F}{\text{CYCLES}} \qquad (4\text{-}1)$$

Table 4-1
ANALYSES OF MAKEUP AND CIRCULATING WATERS FOR NBC STUDIOS

Constituent	Unfiltered Makeup Water	Unfiltered Circulating Water	Filtered Circulating Water	Concentration Factor[a]
Principal constituents				
Chloride, mg/l[b]	56	2,500		44.6
Sulfate, mg/l	126	5,550	5,340	44.0
Bicarbonate, mg/l	146	255	258	
Carbonate, mg/l	0	14	17	
Nitrate, as N, mg/l	0.64	104		162
Sodium, mg/l	56	2,600		46.4
Potassium, mg/l	3.8	190		50
Calcium, mg/l	50	620	620	12.4
Magnesium, mg/l	20	670	670	33.5
Silica, as SiO_2, mg/l	10	124	116	12.4
Total dissolved solids, mg/l	380	13,400		35.3
Phenolpthalein alkalinity, as $CaCO_3$, mg/l	0	12	14	
Total alkalinity, as $CaCO_3$, mg/l	120	233	240	1.9
pH, units	7.9	8.7		
Specific conductance, µmho/cm at 25°C	660	13,500		
Other constituents				
Ammonia, as N, mg/l	<0.05	<0.05		
Bromide, mg/l	<0.1	7.2		
Copper, mg/l	0.08	0.08		
Iron, mg/l	0.03	0.13		
Organic nitrogen, as N, mg/l	0.18	5.4		
Total organic carbon, mg/l	6	7		
Total phosphate, as PO_4, mg/l	<0.03	<0.03		
Total plate count, number/ml		54,000		
Total suspended solids, mg/l		6		
Total trihalomethanes, µg/l	110 ± 28.7	12.5 ± 3.3		0.1
Field measurements				
Temperature, °C	20.5	29.5[c]		
pH, units	9.1 - 8.8[d]	8.8		
Oxidant residual, as Cl, mg/l	1.5	1.0		

[a] Concentration in unfiltered circulating water divided by concentration in unfiltered makeup water.

[b] Constituents expressed as stated molecule, e.g., chloride, mg/l, as chloride, unless otherwise indicated.

[c] Hot side of Carrier unit.

[d] Measured pH drifted downward with time.

Where:

FRACT = fraction of component X in the makeup water which is removed;

F = concentration factor, defined previously;

CYCLES = cycles of concentration, defined previously.

Equation 4-1 is derived in Appendix D.

It is assumed that these components have been precipitated from solution since component concentration products (e.g., $Ca^{+2} \times CO_3^{-2}$) are near and in some cases exceed chemical scaling limitations found in the literature (6, 7). Sulfate, which could combine with calcium to form $CaSO_4$, apparently does not precipate under these conditions. Note that extensive work, well beyond the scope of this project, would be required to definitively confirm the fate of the missing constituents. This work would involve a mass balance, which includes measurements of the rate of constituent inflows, outflows and accumulation. In this report we have assumed calcium, magnesium, silica, and alkalinity and have been removed by precipitation, since it is by far the most plausible removal mechanism. Therefore subsequent discussions of removal of these constituents will be in terms of precipitation.

4. The precipitated materials apparently do not circulate within the cooling circuit as a slurry as indicated by near equal concentrations of constituents in the filtered and unfiltered circulating waters. Thus, precipitated materials are assumed to be accumulating within the cooling circuit. The precipitated materials do not appear to be accumulating in the condenser since according to NBC personnel, heat transfer and refrigeration efficiency have not degraded with time. This suggests the precipitated materials are being settled out in the cooling tower to be removed when the system is periodically cleaned. Current practice of NBC Studios is to clean the cooling tower every 6 to 9 months. We calculate that the cooling tower basins could easily hold 6 to 9 months worth of precipitate. We should note, however, the rate at which the solids are reported to accumulate is less than the rate calculated (see Appendix D).

5. Nitrate is accumulating in the circulating water above levels which can be achieved by simple concentration. Diaper (8) and Kinnon (9) indicate that nitrogen oxides (e.g., N_2O_5) are produced during ozone generation, particularly if the air fed to the generator is not dry. N_2O_5 reacts with water to form HNO_3. This could account for higher than anticipated nitrate levels.

6. Oxidant residuals were 1.5 and 1.0 mg/l for the makeup and circulating waters, respectively. The result for the circulating water was unexpectedly high. This is discussed later in Section 6, Implications for Electric Power Utilities. Note that the bromide concentration in the circulating water was 7.2 mg/l and that ozone reacts with bromide ion to produce hypobromous acid, which would measure as a residual.

7. Using Eq. 4-1, removal of total trihalomethanes (sum of chloroform, dibromochloromethane, bromodichloromethane and bromoform) is calculated

at 99.8 percent. Thus a significant reduction in total trihalomethanes is apparently achieved within the cooling circuit. Possible removal mechanisms are outgassing and destruction by ozonation.

8. The standard plate count for the circulating water sample was 54,000 colonies/ml. It is difficult to state whether or not biofouling was controlled on the basis of this number. While the water was clear in appearance and there were no slimes on the visible sections of the tower, we did not inspect the condenser tubes thus cannot say biofouling was absent with 100 percent certainty. Discussions with a representative of a firm which markets water treatment chemicals indicated the correlation between plate counts and condenser condition are reasonable for individual systems, but that correlations seem to vary from system to system (10). As an example, some condensers may operate with no problems with circulating water plate counts of 10^6/ml while others will be fouled at that level. As a rough rule of thumb, over 10^6 colonies/ml is considered cause for concern, the range 10^5-10^6 colonies/ml is considered a gray area and under 10^5 colonies/ml is usually acceptable. Based on these criteria, the plate count for the sample of NBC studies circulating water was "acceptable." This, plus the clarity of the water, absence of visible bioslimes and continued satisfactory operation of the air conditioning system suggests that biofouling was controlled.

JET PROPULSION LABORATORY, PASADENA, CALIFORNIA

The Jet Propulsion Laboratory (JPL) of the California Institute of technology was visited on September 14, 1978.

Cooling Towers and Ozone System Descriptions

Two cooling tower systems were evaluated, one using ozone treatment and the other using a proprietary chemical treatment. The proprietary treatment is believed by JPL personnel to consist of trichloryl triazine, phosphonates and "other" dispersants. Two other cooling tower systems using ozone treatment were inspected. These two latter systems are described in Appendix A.

The tower using ozone treatment is of wooden construction and services a refrigeration system of 250 tons capacity. A small stream of water is taken from the tower basin, ozonated and then returned to the basin. Ozone is injected into this sidestream through a venturi device; about 20 feet of 1-1/2 inch PVC pipe provides contact before the water is returned to the basin. The cooling tower is operated without blowdown.

According to JPL personnel, the ozonator has a capacity of 5.4 g/hr. A rough estimate of the ozone dose applied is 0.5 mg/l to the sidestream and 0.03 mg/l to

the circulating water. This is based on 45 gpm flow in the sidestream (economic velocity of 7 fps), ozonator operated at full capacity, and a circulating water flow rate of 750 gpm (3 gpm per ton of refrigeration).

The tower using the proprietary chemical treatment is also of wooden construction and services a refrigeration system of 280 tons capacity. This tower operates with blowdown and is run at lower cycles of concentration than the tower using ozone treatment. We estimate the circulating water flow rate to be 840 gpm (based on 3 gpm per ton of refrigeration capacity). Treatment chemicals are leached from solid chemicals floating in the makeup water sump.

Sampling and Analyses

The makeup water source is a private well which also is the potable water source for JPL. The makeup water sample was taken from a tap adjacent to the two cooling towers. The circulating water samples were taken from sample points in the circulating systems on the warm side of the condensers.

Results of the laboratory and field analyses for the ozone treated system and the chemically treated system are summarized in Table 4-2 and Table 4-3, respectively. Makeup water analyses are included in each table for comparison.

Observations

The following general observations can be made:

1. The circulating water for the system using ozone treatment is reasonably concentrated, with a total dissolved solids concentration of 3,330 mg/l. Sulfate and chloride are the principal anions and magnesium and sodium are the major cations.

   The circulating water for the chemically treated system is less concentrated, with a total dissolved solids concentration of 1,620 mg/l. Bicarbonate and sulfate are the major anions and magnesium, sodium, and calcium, in that order, are the predominant cations.

   There is little suspended matter in either circulating water.

2. Based on chloride, sulfate, sodium and potassium, we estimate that the system using ozone treatment is maintaining 30 cycles of concentration. On the same basis, we estimate that the system using chemical treatment is maintaining about 10.5 cycles of concentration.

3. We estimate that 97 percent of the calcium, 45 percent of the magnesium, 84 percent of the silica, and 90 percent of the total alkalinity in the makeup water are removed within the cooling circuit of the ozone-treated system. For the system treated with proprietary chemicals, about 71 percent of the calcium, 33 percent of the

Table 4-2
ANALYSES OF MAKEUP AND CIRCULATING WATERS FOR JPL OZONE TOWER

Constituent	Unfiltered Makeup Water	Unfiltered Circulating Water	Filtered Circulating Water	Concentration Factor[a]
Principal constituents				
Chloride, mg/l[b]	14	459		32.8
Sulfate, mg/l	34	1,120	1,031	32.9
Bicarbonate, mg/l	224	490	540	
Carbonate, mg/l	0	102	79	
Nitrate, as N, mg/l	0.95	68		71.6
Sodium, mg/l	19	540		28.4
Potassium, mg/l	3.5	91		26
Calcium, mg/l	49	49	49	1.0
Magnesium, mg/l	20	330	330	16.5
Silica, as SiO_2, mg/l	23	111	107	4.8
Total dissolved solids, mg/l	260	3,330		12.8
Phenolpthalein alkalinity, as $CaCO_3$, mg/l	0	85	65	
Total alkalinity, as $CaCO_3$, mg/l	184	572	572	3.1
pH, units	7.9	9.2		
Specific conductance, µmho/cm at 25°C	470	4,290		
Other constituents				
Ammonia, as N, mg/l	<0.05	<0.05		
Bromide, mg/l	0.10	0.80		
Copper, mg/l	<0.01	0.01		
Organic nitrogen, as N, mg/l	<0.05	3.2		
Total organic carbon, mg/l	4	6		
Total phosphate, as PO_4, mg/l	<0.03	0.26		
Total plate count, number/ml		7,200		
Total suspended solids, mg/l		6		
Total trihalomethanes, µg/l	<118.7±34.2	<14.7±3.9		0.1
Field measurements				
Temperature, °C	23	29.5		
pH, units	8.38	8.82		
Oxidant residual, as Cl, mg/l	1.8	0.8		

[a] Concentration in unfiltered circulating water divided by concentration in unfiltered makeup water.

[b] Constituents expressed as stated molecule, e.g., chloride, mg/l, as chloride, unless otherwise indicated.

Table 4-3
ANALYSES OF MAKEUP AND CIRCULATING WATERS FOR JPL CHEMICAL TOWER

Constituent	Unfiltered Makeup Water	Unfiltered Circulating Water	Filtered Circulating Water	Concentration Factor[a]
Principal constituents				
Chloride, mg/l[b]	14	180		12.9
Sulfate, mg/l	34	350	312	10.3
Bicarbonate, mg/l	224	499	468	
Carbonate, mg/l	0	78	48	
Nitrate, as N, mg/l	0.95	25		26.3
Sodium, mg/l	19	190		10.0
Potassium, mg/l	3.5	31		8.9
Calcium, mg/l	49	150	140	3.1
Magnesium, mg/l	20	140	140	7.0
Silica, as SiO_2, mg/l	23	86	86	3.7
Total dissolved solids, mg/l	260	1,620		6.2
Phenolpthalein alkalinity, as $CaCO_3$, mg/l	0	65	39	
Total alkalinity, as $CaCO_3$, mg/l	184	540	461	2.9
pH, units	7.9	8.9		
Specific conductance, µmho/cm at 25°C	470	2,170		
Other constituents				
Ammonia, as N, mg/l	<0.05	<0.05		
Bromide, mg/l	0.10	<0.1		
Copper, mg/l	<0.01	0.40		
Organic nitrogen, as N, mg/l	<0.05	32		
Total organic carbon, mg/l	4	43		
Total phosphate, as PO_4, mg/l	<0.03	3.7		
Total plate count, number/ml		43,000		
Total suspended solids, mg/l		10		
Total trihalomethanes, µg/l	<118.7 ± 34.2	<13.6 ± 3.6		0.1
Field measurements				
Temperature, °C	23	27.7		
pH, units	8.38	8.71		
Oxidant residual, as Cl, mg/l	1.8	2.1		

[a]Concentration in unfiltered circulating water divided by concentration in unfiltered makeup water.

[b]Constituents expressed as stated molecule, e.g., chloride, mg/l, as chloride, unless otherwise indicated.

magnesium, 64 percent of the silica, and 72 percent of the total alkalinity is being removed. Sulfate does not appear to be removed in these systems.

4. Nitrates are accumulating in the circulating water of both ozone and chemically treated systems above levels which can be achieved by simple concentration. Nitrate levels in the ozone-treated system were 2.4 times greater than could be attributed to concentration; in the system using proprietary chemicals, they were 2.5 times greater. As indicated previously, the excess nitrate in ozone-treated systems may be produced as a result of the dissolution of nitrogen oxides evolved during ozone generation.

   There are several plausible explanations for the apparent excess nitrates observed in systems using proprietary chemicals. One explanation is that nitrate is a component of the proprietary treatment chemicals. However, since the composition of these chemicals is unknown, this cannot be verified. An alternative explanation is that nitrate is produced as the result of the reaction of ammonia and/or nitrite with chlorine (chlorine is a component of the proprietary treatments). Nitrate can be produced as a side reaction of breakpoint chlorination (3). Note, however, the concentration of ammonia and nitrite in JPL's makeup water is insufficient to account for the excees nitrate accumulated in the circulating water (See Appendix C for nitrite analyses). A third mechanism by which excees nitrate could be produced is decomposition of algae or bacteria to release organic nitrogen, degradation of the organic nitrogen to ammonia, then nitrate productions as the result of the ammonia-chlorine reaction just discussed. If the latter mechanism is operative, the route by which nitrogen for nitrate production enters the system (besides in the makeup water) is with bacteria scrubbed from the air or by fixation of atmospheric nitrogen by algae. Biological nitrification seems unlikely, as the nitrifying organisms are extremely sensitive and not likely to survive chlorine treatment.

5. Oxidant residuals in the circulating waters were 0.8 mg/l for the ozone-treated system and 2.1 mg/l for the chemically treated system; this is compared to 1.8 mg/l for the makeup water.

6. Total trihalomethanes were reduced from a makeup water concentration of about 119 ug/l to about 15 ug/l for the ozone-treated system and about 14 ug/l for the chemically treated system. Because the tower using ozone treatment is maintained at three times the cycles of concentration of the other tower, a greater percentage of the total trihalomethanes applied are removed even through the circulating water concentration is slightly higher.

7. Standard plate counts indicate about 7,200 colonies/ml for the ozone-treated circulating water and about 43,000 colonies/ml for the chemically treated circulating water. This, plus the clarity of the water, absence of visible bioslimes and continued good operation of the air conditioning systems suggest that biological growth is being controlled. We were not able to inspect the condenser tubes to verify this, however.

BULLOCK'S DEPARTMENT STORE, SHERMAN OAKS, CALIFORNIA

Bullock's Sherman Oaks store was visited and sampled on September 14, 1978.

Cooling Tower and Ozone System Description

A Marley Double-Flow Aquatower, of wooden construction, is connected to a refrigeration system of 600 tons capacity. A small stream of water is taken from the tower basin, ozonated and then returned to the basin. Ozone is injected into the system through the suction side of the sidestream circulating pump. About 20 feet of 1-1/2 inch PVC pipe provides contact before the water is returned to the basin. The cooling system is purported to run at zero blowdown and at the time of the site visit was being operated in this manner.

A rough estimate of the ozone dose can be made. Based on an air flow of 25 scfh and a sidestream flow of 45 gpm in the 1-1/2 inch line, the ozone dose applied to the sidestream would be about 0.4 mg/l. We estimate the maximum circulating flow rate to be 1,800 gpm (based on 3 gpm per ton of refrigeration capacity) and the corresponding ozone dose based on the circulation rate to be 0.01 mg/l.

Sampling and Analyses

The makeup water is from the potable water source serving the Sherman Oaks area. The makeup water samples ware taken from a tap on the roof near the cooling tower. The circulating water samples were taken from a sample tap on the tower basin.

Laboratory and field analyses of the makeup and circulating waters are summarized in Table 4-4.

Observations

The following general observations can be made:

1. The circulating water is mildly concentrated, with total dissolved solids of 1,830 mg/l. Sulfate and chloride are the major anions and sodium is the major cation. The total suspended solids of 46 mg/l, while not excessively high, was the highest value observed during this survey.

2. Based on chloride, sodium, and potassium, we estimate that this system is maintaining about 30 cycles of concentration.

3. We estimate that about 46 percent of the calcium, 34 percent of the magnesium, 70 percent of the silica, and 55 percent of the total alkalinity are removed within the cooling circuit. Sulfate does not appear to be removed from the system.

4. Nitrates are accumulating in the circulating water above levels which can be achieved by simple concentration.

Table 4-4
ANALYSES OF MAKEUP AND CIRCULATING WATERS AT BULLOCKS SHERMAN OAKS STORE

Constituent	Unfiltered Makeup Water	Unfiltered Circulating Water	Filtered Circulating Water	Concentration Factor[a]
Principal constituents[b]				
Chloride, mg/l	6.8	245		36.0
Sulfate, mg/l	9.0	480	472	53.3
Bicarbonate, mg/l	75	299	378	
Carbonate, mg/l	3.8	64	59	
Nitrate, as N, mg/l	0.18	24		133
Sodium, mg/l	15	440		29.3
Potassium, mg/l	2.8	66		23.6
Calcium, mg/l	17	87	87	5.1
Magnesium, mg/l	2.4	30	30	12.5
Silica, as SiO_2, mg/l	16	115	103	7.2
Total dissolved solids, mg/l	96	1,830		19.1
Phenolpthalein alkalinity, as $CaCO_3$, mg/l	3	53	49	
Total alkalinity, as $CaCO_3$, mg/l	68	352	408	5.2
pH, units	8.2	9.1		
Specific conductance, µmho/cm at 25°C	190	2,520		
Other constituents				
Ammonia, as N, mg/l	<0.05	<0.05		
Bromide, mg/l	0.86	0.36		
Copper, mg/l	0.08	0.4		
Organic nitrogen, as N, mg/l	0.24	3.2		
Total organic carbon, mg/l	5	33		
Total phosphate, as PO_4, mg/l	0.23	1.0		
Total plate count, number/ml		30,000		
Total suspended solids, mg/l		46		
Total trihalomethanes, µg/l	<52.2 ± 16.1	<3.3 ± 0.4		0.1
Field measurements				
Temperature, °C		24.5		
pH, units	9.0 - 8.6[c]	9.1		
Oxidant residual, as Cl, mg/l	0.2	0.2		

[a]Concentration in unfiltered circulating water divided by concentration in unfiltered makeup water.

[b]Constituents expressed as stated molecule, e.g., chloride, mg/l as chloride, unless otherwise indicated.

[c]Measured pH drifted downward with time.

5. Oxidant residuals for both the makeup water and the circulating water were 0.2 mg/l.

6. Total trihalomethanes were reduced from a makeup water concentration of about 52 ug/l to about 3 ug/l. The reductions are similar to those observed at other towers.

7. The standard plate count of 30,000 colonies/ml is in line with plate counts observed in other systems treated with ozone.

BULLOCK'S MAIN DEPARTMENT STORE, LOS ANGELES, CALIFORNIA

Bullock's main store was visited and sampled on September 13, 1978. However, after sampling was completed, it was determined that the ozonator for the evaporative cooling system sampled was not working and further, that only two cycles of concentration were being maintained. These samples were analyzed only for total plate count and trihalomethanes. Notes on the visit are included in Appendix A. This system has been reported to operate satisfactorily with ozone treatment when the ozonator is on-line.

DUKE UNIVERSITY MEDICAL CENTER

Duke University Medical Center was visited and the cooling system sampled on September 22, 1978, by a representative of the Duke Power Company.

Cooling Towers and Ozone System Descriptions

Three Binks cooling towers were evaluated. The first tower was treated with ozone and the other two with a proprietary chemical. Each cooling tower services a refrigeration system of approximately 250 tons capacity. The two towers using the proprietary chemical treatment are coupled, as described in Appendix A. There is no intentional blowdown from the cooling tower using ozone.

A small stream of water is taken from the tower basin, ozonated, then returned to the basin. Ozone is injected into this sidestream through the suction of its circulating pump. A mud separator is installed just downstream of the sidestream circulating pump.

A rough estimate of the ozone dose can be made. Based on an air flow of 20 scfh and a sidestream flow of 45 gpm (assuming a 1-1/2 inch line), the ozone dose applied to the sidestream would be about 0.3 mg/l. We estimate the maximum circulating water rate to be 750 gpm (based on 3 gpm per ton of refrigeration capacity) and the corresponding ozone dose based on the circulation rate to be about 0.02 mg/l.

Sampling and Analyses

The makeup water is from a lake which is the City of Durham's water supply. The makeup water samples were taken from a tap in the makeup water line. The circulating water samples were grab samples taken from the cooling tower basins.

Duke Power and Brown and Caldwell conducted separate analyses on the samples taken. Tables 4-5, 4-6 and 4-7 list results of laboratory analyses and field measurements for samples taken from the ozone-treated system, chemical tower No. 1, and chemical tower No. 2, respectively. Makeup water analyses are included in each table for comparison against the circulating water analyses. Note the laboratory analyses listed in Tables 4-5, 4-6 and 4-7 are those performed by Brown and Caldwell; the field measurements were performed by Duke Power. Laboratory analyses performed by Duke Power are tabulated in Duke Power's trip report (Appendix A). Brown and Caldwell's analyses are also listed in the latter tables for comparison. A summary of the analysis for ten trace metals in the makeup water and each circulating water is shown in Table 4-8. These analyses were performed by Duke Power.

Observations

The following general observations can be made:

1. The circulating water for the ozone treatment system is reasonably concentrated, with a total dissolved solids concentration of 2,630 mg/l. Sulfates and chlorides are the principal anions, while sodium is the major cation.

   The circulating water for the chemically treated system is less concentrated, with an average total dissolved solids concentration of 238 mg/l for the two towers. Bicarbonate is the major anion, and sodium and potassium are the predominant cations.

   The suspended solids concentration is 4 to 9 times greater in the chemically treated system than in the ozone-treated system.

2. Based on chloride, sulfate, sodium and potassium, we estimate the ozone treatment system was maintaining 44 cycles of concentration. Based on chloride, sulfate and sodium, we estimate that the proprietary chemical system was maintaining 2.3 cycles of concentration.

3. We estimate that about 46 percent of the calcium, 34 percent of the magnesium, 70 percent of the silica and 54 percent of the total alkalinity entering in the makeup water were removed from the cooling water of the ozone-treated system. Essentially, no removal was occurring in the systems treated with proprietary chemicals.

4. Nitrates were accumulating in the circulating water of both ozone and chemically treated systems above levels which could be achieved by simple concentration. Nitrate levels in the ozone treatment system

Table 4-5
ANALYSES OF MAKEUP AND CIRCULATING WATERS FOR DUKE UNIVERSITY OZONE TOWER[a]

Constituent	Unfiltered Makeup Water	Unfiltered Circulating Water	Filtered Circulating Water	Concentration Factor[b]
Principal constituents				
Chloride, mg/l[c]	8.0	390		48.8
Sulfate, mg/l	15	743	740	49.5
Bicarbonate, mg/l	34	549	544	
Carbonate, mg/l	0	66	49	
Nitrate, as N, mg/l	0.08	5.3		66.2
Sodium, mg/l	15	620		41.3
Potassium, mg/l	2.2	82		37.2
Calcium, mg/l	5.5	130		23.6
Magnesium, mg/l	1.8	52		28.8
Silica, as SiO_2, mg/l	11	146	137	13.3
Total dissolved solids, mg/l	74	2,630		35.5
Phenolpthalein alkalinity, as $CaCO_3$, mg/l	0	54	40	
Total alkalinity, as $CaCO_3$, mg/l	28	560	528	20.0
pH, units	6.5	8.8		
Specific conductance, µmho/cm at 25°C	161	4,026		
Other constituents				
Ammonia, as N, mg/l	<0.05	0.11		
Bromide, mg/l	<1	<1		
Copper, mg/l	<0.01	0.09		
Iron, mg/l	0.03	0.15		
Organic nitrogen, as N, mg/l	0.12	4.0		
Total organic carbon, mg/l	6	60		
Total phosphate, as PO_4, mg/l	0.77	3.5		
Total plate count, number/ml		-		
Total suspended solids, mg/l		6		
Total volalite solids, µg/l				
Field measurements				
Temperature, °C		25		
pH, units	7.7	8.9		
Oxidant residual, as Cl, mg/l				

[a]Analytical results listed in this table were by Brown and Caldwell, field measurements by Duke Power.

[b]Concentration in unfiltered circulating water divided by concentration in unfiltered makeup water.

[c]Constituents expressed as stated molecule, e.g., chloride, mg/l as chloride, unless otherwise indicated.

Table 4-6
ANALYSES OF MAKEUP AND CIRCULATING WATERS FOR DUKE UNIVERSITY PROPRIETARY CHEMICAL TOWER NO. 1[a]

Constituent	Unfiltered Makeup Water	Unfiltered Circulating Water	Filtered Circulating Water	Concentration Factor[b]
Principal constituents				
Chloride, mg/l[c]	8	20		2.5
Sulfate, mg/l	15	37	36	2.5
Bicarbonate, mg/l	34	99	99	
Carbonate, mg/l	0	0	0	
Nitrate, as N, mg/l	0.08	0.40		5
Sodium, mg/l	15	29		1.9
Potassium, mg/l	2.2	39		17.7
Calcium, mg/l	5.5	12	12	2.2
Magnesium, mg/l	1.8	4.3	4.2	2.4
Silica, as SiO_2, mg/l	11	21	21	1.9
Total dissolved solids, mg/l	74	234		3.2
Phenolpthalein alkalinity, as $CaCO_3$, mg/l	0	0	0	
Total alkalinity, as $CaCO_3$, mg/l	28	82	82	2.9
pH, units	6.5	6.6		
Specific conductance, µmho/cm at 25°C	161	387		
Other constituents				
Ammonia, as N, mg/l	<0.05	<0.05		
Bromide, mg/l	<1	<1		
Copper, mg/l	<0.01	0.14		
Iron, mg/l	0.03	0.75		
Organic nitrogen, as N, mg/l	0.12	1.5		
Total organic carbon, mg/l	6	20		
Total phosphate, as PO_4, mg/l	0.77	4.5	2.1	5.8
Total plate count, number/ml				
Total suspended solids, mg/l		24		
Total volalite organics, µg/l				
Field measurements				
Temperature, °C		22		
pH, units	7.7	7.9		
Oxidant residual, as Cl, mg/l				

[a]Analytical results listed in this table are by Brown and Caldwell, field measurements by Duke Power.

[b]Concentration in unfiltered circulating water divided by concentration in unfiltered makeup water.

[c]Constituents expressed as stated molecule, e.g., chloride, mg/l, as chloride, unless otherwise indicated.

Table 4-7
ANALYSES OF MAKEUP AND CIRCULATING WATERS FOR DUKE UNIVERSITY PROPRIETARY CHEMICAL TOWER NO. 2[a]

Constituent	Unfiltered Makeup Water	Unfiltered Circulating Water	Filtered Circulating Water	Concentration Factor[b]
Principal constituents				
Chloride, mg/l[c]	8.0	24		3.0
Sulfate, mg/l	15	35	35	2.3
Bicarbonate, mg/l	34	97	92	
Carbonate, mg/l	0	0	0	
Nitrate, as N, mg/l	0.08	0.41		5.1
Sodium, mg/l	15	30		2.0
Potassium, mg/l	2.2	39		17.7
Calcium, mg/l	5.5	12	12	2.2
Magnesium, mg/l	1.8	4.2	4.2	2.3
Silica, as SiO_2, mg/l	11	22	21	2.0
Total dissolved solids, mg/l	74	242		3.3
Phenolpthalein alkalinity, as $CaCO_3$, mg/l	0	0	0	
Total alkalinity, as $CaCO_3$, mg/l	28	80	76	2.9
pH, units	6.5	6.7		
Specific conductance, µmho/cm at 25°C	161	370		
Other constituents				
Ammonia, as N, mg/l	<0.05	<0.05		
Bromide, mg/l	<1	<1		
Copper, mg/l	<0.01	0.20		
Iron, mg/l	0.03	1.9		
Organic nitrogen, as N, mg/l	0.12	1.6		
Total organic carbon, mg/l	6	28		
Total phosphate, as PO_4, mg/l	0.77	2.7		
Total plate count, number/ml				
Total suspended solids, mg/l		58		
Total volalite organics, µg/l				
Field measurements				
Temperature, °C		22		
pH, units	7.7	7.8		
Oxidant residual, as Cl, mg/l				

[a]Analytical results listed in this table are by Brown and Caldwell, field measurements by Duke Power.

[b]Concentration in unfiltered circulating water divided by concentration in unfiltered makeup water.

[c]Constituents expressed as stated molecule, e.g., chloride, mg/l, as chloride, unless otherwise indicated.

Table 4-8
TRACE METAL ANALYSES OF MAKEUP AND CIRCULATING WATERS AT DUKE UNIVERSITY[a,b]

Constituent	Makeup Water	Ozone Tower	Chemical Tower No. 1	Chemical Tower No. 2
Arsenic[c]	<2	158 (>79)[d]	3.7 (>1.8)	6.1 (>3.1)
Cadmium	<0.2	2.1 (>10)	4.1 (>20)	3.9 (>19)
Chromium	<0.5	100 (>200)	13.3 (>17)	8.7 (>26)
Copper	1.7	79 (46)	79 (47)	140 (82)
Iron	5.5	68 (12)	400 (43)	900 (164)
Mercury	<2	6 (>3)	<2 (-)	2 (-)
Nickel	<5	8 (>1.6)	<5 (-)	<5 (-)
Lead	<1	7 (>7)	27 (>27)	54 (>54)
Selenium	<10	6 (-)	<5 (-)	<5 (-)
Zinc	136	100 (0.7)	5,200 (38)	5,400 (40)

[a]Sampled and analyzed by Duke Power Company.

[b]All concentrations in µg/l.

[c]Constituents expressed as stated molecule, e.g., arsenic, mg/l, as arsenic.

[d]Calculated concentration factor in parenthesis.

were 1.5 times greater than could be attributed to concentration; in the chemically treated system they were 2.2 times greater. Possible reasons for excess nitrate production in such systems were presented in the discussion of the JPL results.

5. Table 4-8 shows that of ten trace metals measured, five (arsenic, chromium, mercury, nickel, and selenium) had higher concentrations in the ozone-treated system than in the chemically treated system. Another four (cadmium, iron, lead, and zinc) had lower concentrations in the ozone-treated system. Copper concentration was about the same in both systems.

   A more meaningful analysis may be obtained, however, by observing calculated concentrations factors for the various metals (shown in parentheses in Table 4-8). For systems using proprietary chemicals, concentration factors for cadmium, chromium, zinc, copper, iron, and lead exceeded cycles of concentration (about 2.3 cycles). Thus, in these systems, metals accumulated in the circulating water to greater concentrations than could be achieved by simple concentration. Possible metal sources are corrosion of materials, treatment chemicals or materials scrubbed from the air. No conclusions can be drawn concerning the fate of arsenic, mercury, nickel and selenium. Concentration factors could not be calculated because concentrations of these materials in the makeup water were below detection limits.

   For the ozone-treated system, concentration factors for zinc and iron were less than cycles of concentration (about 44 cycles) indicating these materials were removed, most likely by precipitation. Arsenic and chromium increased to greater levels than could be achieved by simple concentration. Copper appeared to be neither removed nor excessively accumulated. No conclusions can be drawn concerning the fate of cadmium, mercury, nickel, selenium, or lead. Concentration factors could not be calculated because concentrations of those materials in the makeup water were below detection limits.

Section 5

DISCUSSION OF RESULTS

The most striking aspect of this survey was the apparent ability of many of the cooling systems to remove constituents from the cooling water, presumably by precipitation, without scaling of heat transfer surfaces. Table 5-1 summarizes removal data for species which could be precipitated, as well as for trihalomethanes, which are problably removed by different mechanisms.

Table 5-1
CALCULATED CONSTITUENT REMOVAL FROM COOLING WATERS

Cooling Systems	Apparent Cycles of Concentration	Constituent Removal, Percent					
		Ca	Mg	SiO_2	Alk	TDS	THMs
Ozonated							
NBC	46	73	27	73	96	23	>99
JPL	30	97	45	84	90	57	>99
Bullock's Sherman Oaks	30	46	34	70	55	36	>99
Bullock's main store	2						90
Duke University	44	46	34	70	54	19	
Nonozonated							
JPL	10.5	71	33	64	72	41	99
Duke University 1	2.3	4	(4)[a]	17	(26)[a]	(39)[a]	
Duke University 2	2.4	8	4	17	(21)[a]	(38)[a]	

[a]Calculated gain

Note constituent removal was not limited to the ozonated systems. Removal also occurred in the JPL system treated with proprietary chemicals; however removals were not so large as obtained in the JPL system. Where ozonated systems and systems using proprietory systems were operated side-by-side the ozonated systems appeared to operate as well or better under what seem to be substantially more severe scaling conditions.

However we cannot say with any certainty that ozone treatment is "better" than the proprietary treatments used. It is possible that the latter systems, operated at the same cycles of concentration as the ozonated towers, would have worked equally as well, i.e, the same quantity of scalants would have been removed without fouling the heat exchanger. We have no way of knowing this, however. While the cooling systems were operated in parallel they were not operated at identical cycles of concentration. The data on hand does not allow resolution of the question as to how much more effective ozone is, if more effective at all. The strongest claim for ozone is its performance in apparently cleaning up and subsequent successful operation of systems which had previously performed poorly when treated with proprietory chemicals. This in itself is not conclusive, since the proprietory treatments used were not documented. It is possible that better proprietory programs would have done as well as ozone treatment.

While it is not possible to state unequivocally that ozone treatment is better, the evidence suggests that ozone treatment is working at the sites visited. It is of interest to speculate why. Some investigator's (1, 11) suggest that biological slimes are the glue which enhances binding of precipitates and other solid debris to surfaces, i.e., once a slime layer has formed, attachment of other solids becomes much easier. If this is so, then chemical scaling will be less in systems in which biological activity is minimized. Thus there may be a correlation between the rather low plate counts observed in ozonated systems and the apparent absence of chemical scaling. The notion of bioslimes as "glue" is supported by the observation that previously deposited chemical scale was sloughed from cooling circuit apparatus shortly after initiation of ozone treatment. The most plausible mechanism for release of such materials is attack on the biological binder; attack on the chemical solids themselves seems much less likely.

On the other hand, it is possible that condenser scaling is unrelated to the presence or absence of biological films, i.e., there is no substance to the biological glue theory. For example, one cannot reasonably argue that the elimination of biofilms precludes chemical scaling. Examples of chemical scaling without biological assistance are abundant, e.g., the controlled deposition of $CaCO_3$ in water pipes to prevent corrosion. Thus other mechanisms may be responsible for the apparent absence of condenser scaling in low temperature ozonated systems. This might be the result of the way that the ozone is applied. Investigators at the both Duke University and southern California sites noted high foaming when withdrawing samples from the ozonated water circulating line

just downstream from the ozone injection point. Ions are known to concentrate in foams; indeed foam fractionation is one way of removing trace elements from aqueous solution. Thus, it is not illogical that foams generated in the ozonated water circulating loop could serve as sites for chemical precipitation, with the precipitates later settling out when the foam breaks down. Using this logic, one might argue that the most favorable conditions for precipitation are no longer at the condenser surface but in the ozonated water circulating loop and that precipitation has been simply displaced to an area where it does no harm.

Obviously this study has not resolved which mechanisms are responsible for the apparent absence of condenser scaling. Future studies should be pointed toward elucidating such mechanisms, since successful operation of cooling systems using ozone depends on controlling the right factors.

Another phenomena observed was the removal of trihalomenthanes (THMs) in all cooling systems in which analyses for these compounds were made. Concentrations of chloroform, dibromochloromethane, bromodichloromethane, bromoform and total THMs (which is the sum of these four compounds) in the makeup and circulating waters examined are summarized in Table 5-2. Makeup and circulating waters were also analyzed for 1,1,1 trichloroethane, trichloroethylene, benzene, and toulene; the results of these analyses are contained in Appendix C. Two of the five makeup waters examined had total THMs concentrations greater than 100 ug/l, which is the tentative Environmental Protection Agency standard for drinking water. However the total THMs concentration for all five circulating waters was much below 100 ug/l. Therefore the removal of THMs was significant.

Percent total THMs removals were highest for systems which operated at the highest cycles of concentrations. For example, THMs removal exceeded 99 percent for systems which operated at 30 cycles of concentration and above. THMs removals were less for systems which operated at fewer cycles of concentration. This is probably related to circulating water residence time, which increases as the cycles of concentration increase. As residence time increases, opportunity for THMs loss by outgassing or destruction via ozeration also increases.

Dibromochloromethane was removed to a lesser extent than other THMs. At NBC Studios, the concentration increased from not detectable in the makeup water to 4.5 ug/l in the circulating water. The makeup water at NBC Studios had a high bromodichloromethane concentration (43.0 ug/l) and it is possible that some of this compound was converted to dibromochloromethane by ozonation of the circulating water.

Table 5-2
TRIHALOMETHANE CONCENTRATIONS IN SELECTED MAKEUP AND CIRCULATING WATERS[a]

Sample Identification	Chloroform	Dibromochloromethane	Bromodichloromethane	Bromoform	Total THM
NBC Studios					
Makeup water	66.0 ± 21.6[b]	ND[c]	43.0 ± 6.8	1.0 ± 0.3	110.0 ± 22.6
Circulating water	5.6 ± 1.8	4.5 ± 1.3	1.4 ± 0.2	<1.0	<25.5 ± 2.6
JPL					
Makeup water	87.0 ± 28.3	7.7 ± 2.2	23.0 ± 3.7	<1.0	<118.7 ± 28.6
Circulating waters					
Ozone tower	2.7 ± 0.9	9.0 ± 2.6	2.0 ± 0.4	<1.0	<14.7 ± 2.8
Chemical tower	7.4 ± 2.4	4.2 ± 1.2	<1.0	<1.0	<13.6 ± 2.7
Bullocks Sherman Oaks					
Makeup water	42.0 ± 13.5	5.3 ± 2.0	3.9 ± 0.6	<1.0	<52.2 ± 13.7
Circulating water	1.3 ± 0.4	<1.0	ND	<1.0	< 3.3 ± 0.4
Bullocks Main Store					
Makeup water[d]	6	7	20	1	34
Circulating water	<1	4.8 ± 1.4	ND	<1.0	<6.8 ± 1.4

[a] Trihalomethane concentration, µg/l.

[b] Mean ± standard deviation.

[c] ND = not detected.

[d] Estimate. No replicates available.

Section 6

IMPLICATIONS FOR ELECTRIC POWER UTILITIES

Results obtained in cooling tower circulating water systems used with air conditioning systems cannot be directly applied to similar systems at electric power utilities. The major differences between these applications are possible higher operating temperatures and temperature rises and the larger size of circulating water systems for electric power utilities. Implications of ozone treatment at electric power utilities are discussed below.

OPERATION AT INCREASED CYCLES OF CONCENTRATION

The ozone-treated circulating water systems evaluated in this study operated at high cycles of concentration, essentially without blowdown. While it is not clear that ozone-treated cooling tower systems could be operated at electric power plants without blowdown, these systems may be able to operate at higher cycles of concentration than previously used. Sidestream solids separation (e.g., hydrocyclones, sedimentation or filtration) may provide an adequate means of removing any chemical precipitates formed.

Operating at higher cycles of concentration would reduce the volume of makeup water required per unit of cooling and the volume of blowdown water for treatment and disposal. This would in turn reduce raw water, waste treatment and disposal costs. The magnitude of the savings depends upon the number of cycles used prior to changing to ozone treatment and the increase in cycles which could be obtained with the use of ozone.

BLOWDOWN QUALITY CONSIDERATIONS

Operating cooling tower systems at high cycles of concentration significantly affects the quality of the circulating water and hence the quality of the blowdown stream. This study indicates that both beneficial and adverse water quality effects were experienced at the high cycles of concentration achieved by systems using ozone.

Oxidant Residuals

The results of this study indicate that oxidant residuals may be expected with ozone treatment. The residuals measured are not believed to be ozone because ozone is too reactive in aqueous media to exist by itself for more than a few minutes. The identities of the residuals present were not established because the residual test used is not specific for any particular oxidant. Ozone can react with chloride and bromide ions to form hypochlorous and hypobromous acids. Both bromide and chloride were present in the waters analyzed. Bromide oxidation is thermodynamically favored for the conditions evaluated.

The implication for electric utilities is that ozone treatment may not eliminate the oxidant residual problem associated with chlorination, although the residual problem may be alleviated somewhat. A way of further reducing oxidant residuals may be required for discharges to receiving waters harboring sensitive biota. The oxidant residuals associated with ozonation require further study.

Trihalomethanes (THMs) Reduction

THMs were significantly removed in all systems in which analyses for these compounds were made. Total THMs concentrations were in fact less than the tentative EPA standard for drinking water (100 mg/l) for all circulating waters which were examined for these species. These results imply that total THMs buildup in cooling towers should not be a problem for electric utilities.

Trace Metal Reductions

Results of the analyses at the Duke University site indicate that for the systems treated with proprietary chemicals, cadmium, chromium, zinc, copper, iron, and lead accumulated to levels greater than could be achieved by simple concentration. Possible trace metals sources are corrosion of materials, treatment chemicals or materials scrubbed from the air. Zinc and iron were removed in ozone-treated systems. Chromium and arsenic accumulated to levels greater than could be achieved by simple concentration. Copper did not change; no conclusions could be drawn as to the fate of cadmium, nickel, mercury, selenium, or lead.

Analyses of samples taken at the southern California locations indicates that iron and copper were removed in ozonated systems and that copper accumulated in the system using proprietary chemicals.

It is difficult to make definitive statements concering the relative effectiveness of ozone and proprietary chemical treatments from such a small amount of data, some of which is ambiguous. However it seems reasonable to assume that systems (e.g., ozone) which operate at high cycles of concentration may be better suited for removal of trace metals because concentration provides the driving force for precipitation. In addition, many proprietary chemicals act as chelating agents, thus increasing the solubilities of metal compounds. Thus, ozone systems appear to hold the promise of superior trace metal reduction.

TEMPERATURE CONSIDERATIONS

Circulating water temperatures for the ozonated systems sampled in this study were in the 80-90°F range; circulating water temperature rises through the condensers were in the 5-8°F range. Circulating water temperatures in the ozonated system which failed at UCLA ranged from 86°F at the condenser inlet to 120°F at its outlet. The system at UCLA differed from the other ozonated systems in that:

1. On the average, water temperatures in the UCLA system were greater.
2. The temperature rise in the UCLA condenser was greater.

A logical argument for the UCLA system's failure may be advanced in terms of these observations. First, because precipitates are generally less soluble at elevated temperatures, higher average temperatures will tend to force the formation of more chemical solids. Second, a very abrupt temperature rise (by rapidly increasing supersaturation) serves to catalize the precipitation reaction, perhaps tending to localize it within the condenser. Alternative precipitation sites, e.g., foams produced in the ozonated water circulating line, may be less competitive under these circumstances and as a result, the condenser could quickly scale over. Thus there are reasons for concern about using ozone in systems which operate at different temperature conditions than the systems sampled. This naturally raises the question "what are circulating water temperature conditions at electric power generating stations?"

We have been unable to find much information about circulating water temperatures at electric power generating stations. Reference 7 indicates that most turbine condensers are designed for a maximum pressure of 5 inches of mercury, which corresponds to a condensing temperature of 134°F. This suggest 134°F as an upper limit on circulating water temperature. It is believed that most circulating water temperatures are significantly below this value, however.

We asked the Duke Power Company to describe the range of circulating water temperatures for one of their evaporative cooling towers. Duke Power provided the information shown in Table 6-1. This limited data indicate that circulating water temperatures and temperature rises do exceed their counterparts in the air conditioning systems sampled during this survey, at least part of the time. Thus the apparently good results obtained with low temperature ozonated systems sampled may not necessarily be reproduced at electric power plants.

Table 6-1
CIRCULATING WATER TEMPERATURES FOR SELECTED CONDITIONS
AT DUKE POWER COMPANY'S CLIFFSIDE UNIT 5
ELECTRIC POWER GENERATING STATION

Date	Condenser Inlet Water Temperature, °F	Condenser Outlet Water Temperature, °F	Circulating Water Rise Through Condenser, °F	Electric Load, MWe
January 23, 1979	66	89	23	535
August 4, 1978	86	115	29	572
Hot summer day, (date not specified)	83	105	22	511

Source: R. B. Thompson, Duke Power Company, (personal communication).
Note: Station capacity 572 MWe.

SCALE-UP CONSIDERATIONS

The cooling towers evaluated in this study serviced refrigeration loads ranging from 250 tons at JPL to 2200 tons at NBC Studios. One thousand tons of air conditioning capacity is approximately equal to the thermal load from the generation of one megawatt of electricity (MWe). Hence, the equivalent loads on these towers at rated capacity could range from 0.25 to 2.2 MWe.

Duke Power Company is considering the feasibility of a side-by-side comparison of ozone and proprietary chemical treatment on cooling towers servicing loads of 286 MWe each. This represents a scale-up in ozone treatment equipment of at least 120 times those systems examined in this study. We estimate that the SGA ozonators may have the capacity to produce up to 0.4 lb/day of ozone. For the comparison considered by Duke Power Company, at least 50 lb/day capacity would be

required, not including spare units. Actual dosages required for electric power plant application may be substantially higher because ozone demands may be greater and because ozone is less soluble at higher water temperatures. If a 0.5 mg/l dose of ozone based on circulating water flow is desired for a 286 MWe load, a capacity of over 800 lb/day ozone would be required. Units of this size are commerically available in the United States.

There are other design features which must be considered. The design of the ozone contacting (mixing) system is extremely important because of the limited solubility of ozone (3). In addition, the way in which ozone is applied may control in a critical way whether chemical precipitates produced adhere to heat exchange surfaces. Various configurations for applying ozone to cooling tower systems at electric power plants should be investigated to achieve the optimum design. If air is used for generating ozone, an efficient air dryer is required to maximize ozone production. For ozone generated with oxygen, which becomes attractive with larger units, safety and potential reuse of oxygen must be considered.

ECONOMIC CONSIDERATIONS

Although the objective of this study was to evaluate the effectiveness of ozone treatment, i.e., cost evaluation was not in the scope of work, costs must be considered in any large scale application. One study, which in 1975 compared ozone with other biocides for use in cooling water systems for electric power plants rated at 1220 MWe, concluded that intermittant chlorination using 1-ton chlorine cylinders was the most cost-effective method (5). Continuous low dose application of ozone was approximately 13 times as expensive and intermittent application was 4.5 times as expensive on a present worth basis. However the economic picture could change:

- If, by the use of ozone, other chemicals, such as scale inhibitors are not required, i.e., ozone treatment might be economically more attractive than the combination of chlorine and proprietary chemicals.
- If ozone treatment allows increased cycles of concentration, hence reduced costs for makeup water and for blowdown treatment and disposal.
- If ozonation allows reduction or elimination of makeup water treatments, e.g., lime softening of municipal wastewater effluents to be used for cooling purposes.

Section 7

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are drawn and recommendations made.

CONCLUSIONS

1. With regards to the ozonated water systems sampled during this study:

   --While heat exchange surfaces were not examined to verify the absence of biological fouling, the circulating waters' relatively low plate counts, their generally good clarity, the apparent cleanliness of the cooling towers and continued good operation of the air conditioning systems leads us to believe that biofouling is not a major problem with the systems surveyed.

   --The ozonated systems operated at conditions far exceeding conventional scale control limits. Constituent material balances on the cooling circuits suggest that substantial chemical precipitation was occurring. However the precipitates formed did not appear to interfere with the heat transfer process by adhering to heat exchange surfaces. They instead apparently settled out in quiescent areas, e.g., the cooling tower basin.

   --Nitrates accumulated in circulating waters beyond levels which could be achieved by simple concentration. High nitrate levels could cause problems where blowdown is discharged to nitrogen-sensitive receiving waters or to waters used as a drinking water supply.

   --Oxidant residuals were present in all circulating systems using ozone where the residuals analysis was made; thus replacement of chlorine treatment by ozone treatment does not appear to eliminate the oxidant residual problem. The identities and relative toxicities of the oxidant residuals found in the ozone systems sampled are not known.

   --Trihalomethanes appeared to be significantly removed in all cooling circuits in which these species were analyzed. In this study, the percentage of THMs in the makeup water which were removed in the cooling system varied from 90 to 99.8 percent, higher removals occurring in these systems operating at greater cycles of concentration.

   --For the systems sampled, ozone doses appeared to be not greater than 0.6 mg/l, based on flow in the ozonated sidestream and not greater than 0.03 mg/l, based on circulating water flow. The highest estimated ozone dose used corresponds to ozone requirements of roughly 0.5 grams per day per ton of cooling.

2. The physical condition (turbidity, suspended solids, plate counts) of the circulating waters treated with proprietary chemicals was poorer than the physical condition of the ozonated circulating waters even though the operating conditions for the latter were far more severe. However, we cannot say with any certainty that ozone treatment is "better" than the proprietary treatments used. It is possible that similar results might have been obtained with chlorine alone, different proprietary chemicals, different doses of the same proprietary chemicals, or operation at higher cycles of concentration. While it is not possible to state unequivocally that ozone treatment is better, the evidence suggests ozone treatment is working at the sites we sampled.

3. While ozone treatment appears to be successful in small cooling systems operating at low circulating water temperatures (80-90°F) and low temperature rises (5-8°F), there is insufficient evidence to conclude it will be as successful in larger systems operating at higher temperatures and temperature rises. The failure of an ozonated cooling system at UCLA serves as a warning against extrapolating the results of this study to different temperature conditions.

4. Ozone generators should be equipped with alarm systems to indicate generator failure. Many of the problems experienced at sites using ozone treatment are attributed to unobserved termination of the ozone supply.

RECOMMENDATIONS

1. We recommend that the use of ozone in cooling tower systems be further pursued. The possibilities for beneficial application of this technology in electric power cooling systems are intriguing. The most striking potential benefits appear to be:

   --Potential cost reductions

     --If systems using ozone can operate at higher cycles of concentration than currently possible, the volume of makeup water required per unit of cooling would be reduced as well as the volume of blowdown for treatment and disposal.

     --While ozone as a biocide is more costly than chlorine, ozone alone might be less costly than combinations of chlorine and scale inhibitors needed to give equivalent treatment.

     --Ozone treatment of the circulating water may reduce or possibly eliminate costly makeup water treatments, e.g., lime softening of municipal wastewater effluents to be used for cooling purposes.

   --Any required blowdown may be less noxious because:

     --Fewer halogenated hydrocarbons may form and those which do may be less toxic than those produced with chlorine treatment.

     --Oxidant residuals may be less.

     --Trace metals mass emissions may be less.

2. Immediate full-scale testing at a power generating station is not recommended. Present understanding of the technology is insufficient and the penalties for failure too severe. Further studies of a low risk nature should be pursued instead.

3. The thrust of the next phase of study should be to pave the way for eventual testing of ozone treatment at a full-scale electrical power generating station. A logical study sequence is:

   --Phase A. Identify process limits in systems which operate at temperature conditions used at electric power generating stations. Limits would be determined by operating at progressively more severe conditions until process failure occurred. Testing would ideally be carried out at a facility where process variables could be controlled by the investigator and where penalities for process failure would not be great.

   --Phase B. As part of the experimental program, mass balances (including the weighing of solids and solids analyses) should be carried out to determine the means by which various constituents are removed from the circulating water and the degrees of removal. If removal is by chemical precipitation, it should be determined why the precipitating solids do not adhere to heat transfer surfaces, if this is indeed the case. It should also be determined if ozone is unique in its effect in cooling systems or if chlorine, properly applied, will accomplish the same thing. Oxidant residuals should be identified and, if possible, relative toxicities determined.

   --Phase C. Identify electrical generating stations where a full-scale ozone testing program could be carried out, if warranted.

   --Phase D. Provide preliminary engineering designs and cost analyses for ozone treatment systems for the power generating stations identified in Phase C. Plans and costs would be based on experimental work carried out in Phases A and B.

Section 8

REFERENCES

1. J.D. Von Bargen "Study on Water Treatment System. Federated Department Stores." Source Gas Analyzers, Inc., no date.

2. R.L. Culp, G.M. Wesner and G.L. Culp. Handbook of Advanced Wastewater Treatment. Second Ed. New York: Van Nostrand Reinhold Company, 1978.

3. G.C. White. Disinfection of Wastewater and Water for Reuse. New York: Van Nostrand Reinhold Company, 1978.

4. M.F. Humphrey. "Cooling Tower Water Conditioning Study." Jet Propulsion Laboratory. California Institute of Technology. Report 5030-11. August 22, 1977.

5. H.W. Siegrist, D.G. Tuttle and S.B. Majumdar. "Technical and Economic Considerations of Biocide System Options for Cooling Water Systems: A Review." Proceedings of the Second International Symposium on Ozone Technology. Montreal, Canada. May 11-14, 1975. International Ozone Institute, 1976, pp. 632-649.

6. Selected Aspects of Waste Heat Management: A State-of-the-Art Study. Electric Power Research Institute, June 1976. FP-164.

7. U.S. Environmental Protection Agency. Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Steam Electric Power Generation Point Source Category. EPA 440/1-74-029a. October 1974.

8. E.W.J. Diaper. "Practical Aspects of Water and Wastewater Treatment by Ozone." Ozone in Water and Wastewater Treatment, F.L. Evans III (Ed). Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan. 1972.

9. R.N. Kinmen. "Ozone in Water Disinfection," Ozone in Water and Wastewater Treatment. F.L. Evans III (Ed). Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan. 1972.

10. S.G. Freymark. Olin Water Services, Overland Park, Kansas (personal communication).

11. G.C. White. Handbook of Chlorination. New York: Van Nostrand Reinhold Company, 1972.

Appendix A

NOTES ON VISITS TO COOLING TOWER INSTALLATIONS
USING OZONE WATER TREATMENT

The following are included in this Appendix:

1. "Notes on trip to Los Angeles to Observe and Sample Cooling Towers Using Ozone." Memorandum to file by Douglas Merrill and Joe Drago, Brown and Caldwell.

2. "Trip Report--notes on trip to Durham, North Carolina, Duke University Medical School to observe and sample cooling towers using either ozone or proprietary chemicals." forwarded by Duke Power Company, letter dated December 12, 1978.

ROUGH

MEMORANDUM 285-1

September 22, 1978

TO: FILES

FROM: DOUG MERRILL AND JOE DRAGO

SUBJECT: NOTES ON TRIP TO LOS ANGELES TO OBSERVE AND SAMPLE COOLING TOWERS USING OZONE

On September 13th and 14th, Joe Drago and Doug Merrill of the Walnut Creek Office visited several sites where ozone was being used for the control of biological and chemical scaling in cooling towers. Professor Jerome F. Thomas of U.C. Berkeley accompanied Drago and Merrill on the 13th. At each site, samples of make-up water and circulating water were taken. These samples will be subsequently analyzed for parameters as indicated on Attachment 1. Parameters measured in the field were pH, temperature and oxidant residual. The following notes summarize observations and measurements made at each site.

Bullock's Main Store, Los Angeles

We were shown the system by Mr. Alan Bywater of Bullock's Planning Department. Bullock's has eight evaporative condensers*, all serving a common refrigerant loop. Each individual condenser handles about 100 tons of refrigeration. Two ozone systems are provided, one system per four condensers. The ozonators and colloid

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*In evaporating condensing systems, the refrigerant condenser is located in and is part of the cooling tower itself. The system otherwise operates in the same fashion as conventional cooling towers.

neutralizers were supplied by Source Gas Analyzers (SGA) of Garden Grove, California. The ozone was injected into a line through which a small flow of tower circulating water was being pumped. The pump took suction from the evaporation condenser's basin and returned the ozonated water directly to the basin. The colloid neutralizers were installed in the make-up water lines. The ozonator could accept up to 50 SCFH of air and was using 25 SCFH when we observed it.

Mr. Bywater stated that they had used chemical treatments for many years, but that the results were unsatisfactory. They had then tried ozone treatment, with good results. The ozone system has now been on line for 11 months. During this time the condensers had "cleaned themselves up," i.e., much accumulated biomass and chemical scale had sloughed off. Mr. Bywater stated that the system was operated with zero blowdown. He indicated that if the ozonator failed for any reason, problems with biological fouling or chemical scaling appeared within four to five days. The condenser systems are cleaned by vacuuming out the dirt accumulated in the pan. The system is inspected once a month and cleaned if necessary.

We sampled one set of four towers. After we had completed sampling we discovered two things:

1) That water falling directly into the system's overflow lines created a large and unintentional bleed of the circulating water. The bleed was measured and amounted to about 2200 gpd. It thus appears that because of this previously undetected

bleed that cycles of concentration in this system are much less than anticipated. A rough measurement by Professor Thomas indicated that approximately 2 cycles were being maintained.

2) The ozonator was not working because of electrical problems; it may have been off for as long as two weeks, as indicated by maintenance tags saying fuses blowing out and breakers tripping, 9/1/78.

Because the ozonator was not working and because of the large unintentional circulating water bleed stream, this system was not typical of the system we wished to sample. Therefore, there is some question as to whether it is worthwhile to analyze the samples collected. We have decided to analyze for trihalomethanes and total bacterial counts, but to defer any other analyses on samples from this site until a need for analysis can be demonstrated. The samples will be stored in the meantime.

The ozonator for the other system was operating but was not generating ozone because the silica gel in the air drying unit (a small U-tube in the air feed line) was depleted. The silica gel was replaced by a maintenance man.

The following field measurements were made:

Field Measurements: Bullock's Main Store

Sample	pH	Temperature, °C.	Oxidant Residual, mg/l as Cl	Comment
Make-up H_2O	8.0 at time of sampling; drifted down to 7.6-7.7 with time	24	Not measured	
Circulating H_2O	-Condenser 3=8.8	-Condenser 1=32 -Condenser 2=35½ -Condenser 3=38-39 -Condenser 4=38-39	Not measured Not measured Not measured Not measured	
	-Unintentional bleed = 8.7	-Unintentional bleed = 33	Not measured	Cooled off during flow to measuring point

NBC Studios, Burbank

We were met by Mr. Fred Dumpel, Chief Engineer. He and Mr. Dick Collins, Senior Mechanical Engineer, took us around the system. NBC has a refrigeration system of approximately 2200 tons capacity, which utilizes 4 Baltimore Air Coil Cooling Towers. The towers appear to be of steel construction. There were three model 420C towers (serial numbers BAC-68-168M, BAC-68-169M, BAC-68-170M) and one model VLT-800 tower (serial number BAC-69-108M).

Ozone treatment has been used for four years, apparently with good success. Prior to that, chemical treatment had been used with little success. NBC personnel were quite pleased with the ozone system operation. They indicated that they begin to have fouling problems within a few days if ozone treatment is cut off. They claim that vacuuming of the towers is required every 6-9 months. There is no intentional blowdown from these towers. Cycles of concentration are controlled by evaporation and drift. There appears to be only

minor bleeds (leaks, splashing). The metal surfaces appeared to be in good shape (little corrosion or scaling), at least at the points we were able to inspect (one tower selected by NBC personnel). Some minor scaling was observed at the edges of the packing, where the surfaces were alternatively wet and dried, but this is to be expected. The circulating water was quite clear, but yellow, leading to speculation that iron levels might be high. This water will be analyzed for iron.

The ozonator and colloid neutralizer were supplied by SGA. They appeared to be similar to the system at Bullock's Main Store. Air rate to the ozonator was 35 SCFH. Neither Drago, Thomas nor I could smell ozone in the water immediately after the ozone injection point. However, Dick Collins could smell it. Professor Thomas could not smell ozone in gas feed line, either. NBC recognizes that the air supply to the ozonator must be dry in order for the ozonator to work effectively. They apparently use dry air in other services, thus having a source which they can tap for the ozonator. A silica gel U-tube is also provided, however.

The following field measurements were made:

Field Measurements at NBC Studios

Sample	pH	Temperature, °C	Oxidant residual, mg/l, as Cl
Make-up H_2O	9.1 initially, drifted down to 8.8	20.5	Sample 1 = 1.51 Sample 2 = 1.45 Sample 3 = 1.55
Circulating H_2O	8.8	29.5	Sample 1 = 1.10 Sample 2 = 0.96

Note that circulating water samples were taken on the hot side of the Carrier unit condenser for convenience, instead of out of the cooling towers directly.

Several oxidant residual determinations were measured to check repeatability, which was reasonably good. Oxidant residuals are expressed as chlorine; however, this does not imply the residual is chlorine. The test is not specific, rather a measure of materials in the water which can oxidize phenylarsine oxide under the conditions of the test. We were a little surprised to see an oxidant residual in the circulating water.

Mr. Dumpel also provided us with some water analyses done for the NBC system by the Mogul Corporation.

Professor Thomas made some rough hardness and alkalinity measurements of the circulating water. The hardness valves appeared to be very high (>3000 mg/l, as $CaCO_3$). An end point could not be reached, either because there is an exceptional hardness concentration, because of interferences, or possibly from chelating agents. Alkalinity in the cirulating water was approximately twice the alkalinity of the makeup water.

Jet Propulsion Laboratory, Pasadena

We were conducted around JPL's facility by Messrs. Marshall Humphrey, Ken French and Ron Howe. JPL currently has three cooling towers operating on ozone. In this report we are only going to analyze one ozone tower (tower 215). Information concerning the other towers is included in Attachment 2. Note that we intend to make a comparison between operations of tower 215 and another tower (tower 165) in which more conventional chemical treatment* is being used. Tower 215 serves a refrigeration system of 250 tons capacity. It is of wooden construction. The ozone treatment has been used in tower 215 for 18 months. Tower 165 is of wooden construction and serves a refrigeration system of 280 tons capacity.

The appearance of tower 215 (the ozone tower) was good. Some chemical scale and bioslime were visible at the outer edges of the tower fill, but this is expected due to alternate wetting and drying. The internals, at least as far in as could be reached, seemed fairly clean. Some hard, sandlike scale still adhered to the slats, but I believe that Humphrey said this was a residual from previous chemical treatments and was gradually being eroded away. Humphrey noted that when ozone treatment was started, sloughing of chemical and biological

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*Trichloryl triazine as biocide and a Calgon formulation for scaling and corrosion control. Mr. Humphrey believes the Calgon formulation to contain phosphonates and other dispersing agents.

scale previously accumulated was massive and that the tower pan had to be cleaned frequently. Cleaning is now done about every 4 months. There is an annual inspection. Humphrey also indicated that water flows for tower 215 were measured and that we could have access to these data.

TDS levels in the ozone tower fluctuate in the 2000-3000 mg/l range. The concentration is controlled by evaporation, draft and dilution by rainwater. There is no blowdown. They aren't able to get concentrations much above 3000 TDS. In contrast, tower 165 (chemical tower) circulating water TDS is controlled at about 700 mg/l (blowdown is used).

JPL has mounted copper and steel corrosion coupons in tower 215's circulating loop. The rate of corrosion is measured by instrument (a corrater, Magna Corporation, model 1130). The instrument's measurements are occasionally verified by removing and inspecting the coupons. Humphrey stated that the rate of corrosion is very low. JPL has analyzed the coatings on the steel coupons and found them to be Fe_3O_4 (not Fe_2O_3). Humphrey feels the Fe_3O_4 coatings protect the steel coupon.

JPL uses an ozone generator of its own design and manufacture, (essentially a complete rebuilding of the original SGA generator, necessitated by component failures). Capacity of the generator is 5.4 grams ozone/hr. They do not use a colloid neutralizer, as they feel it does not do what SGA claimed it to do; produce a soft nonadherent $CaCO_3$ scale. (A nonadherent scale <u>is</u> apparently generated however.) Ozone was injected into the suction of a pump which was recycling a

small stream of water from the tower basin back to the tower basin. JPL tries to maintain an ozone residual of 0.025 mg/l (at the refrigerant condensers?). The residual is measured by Hach Kit. They would like to be able to continuously monitor the residual, since ozone demand is affected by many variables, including temperature, organics concentration, etc., and thus the demand changes. They would like to be able to automatically supply a variable demand and I believe they are working on such a system. JPL uses silica beds to dry out air being fed to the ozonators. They indicated that teflon is the only plastic which stands up to ozone and they use teflon tubing in the gas lines. Other plastics which contact the ozone gas stream are eaten up in a few days. They also said that they had to keep on top of the ozone system. If it went down for any reason, they had problems (presumably biofouling or scaling) in a few days.

The following field measurements were made:

Field Measurements at JPL

Sample	pH	Temperature, $^{o}C.$	Oxidant residual, mg/l as Cl
Make-up H_2O	8.38	23	Sample 1 = 1.73 Sample 2 = 1.89
Circulating water, tower 215 (ozone)	8.82	Tower inf. = 29.5 Tower eff. = 26.5	0.76
Circulating water, tower 165 (chemical treatment)	8.71	Tower inf. = 27.7 Tower eff. = 24.0	2.07

Note: All circulating water samples taken from the warm side of the condenser.

Bullock's Sherman Oaks Store

We were shown the cooling tower by Mr. Fred Kimball of the store's maintenance department. This is a Marley Double Flow Aqua-tower, serial number 21-1-532. The system had been using ozone since June 1977. As the name implies, it is a two-celled tower, one fan for each cell. The circulating water distribution plates at the top of the towers were covered to prevent algae formation. The fan on one side (call it side B) was not operating while we were at the site. An opening had been made in the common wall between cells so that water should be, in theory, of the same composition in both cells. There may be some difference in composition; there didn't appear to be a lot of intermixing. We could tell this because the water temperatures in the two cells were quite different. Samples of circulating water were withdrawn from the side in which the fan was operating (side A). We were forced to make a choice between drawing samples from side A or side B, since there was no sample tap in the circulating loop which would allow sampling of the combined streams.

The appearance of the tower packing (wooden) was good. We also inspected some wooden slats which had been removed from the tower. They had been replaced shortly before our visit; they were in service for about 15 years with "other" treatments and 14 months with ozone. These slats were badly scaled.* It appears that ozonation was not able to clean up the slats to the degree desired, so they were simply replaced.

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*Joe took some photographs of the slats.

There is no blowdown in this system. We were not able to find any unintentional bleeds.

An SGA ozonator and colloid neutralizer are in operation. The ozonator can accept up to 50 SCFH of air. The ozonator was working, as indicated by a "sniff test," when tubing was disconnected from the generating apparatus. The ozone was injected into the suction of a pump which was recycling a small stream of water from the tower basin back to the tower basin. Mr. Kimball indicated that no problem had been experienced with pump seals. However, the ozone feed line previously became brittle and required replacement. Mr. Kimball indicated that many components in the ozone generator had required replacement.

The following field measurements were made:

Field Measurements at Bullock's Sherman Oaks Store

Sample	pH	Temperature, °C.	Oxidant residual, mg/l as Cl
Make-up H_2O	initially 9.0, drifts down to 8.6 with time		Sample 1 = 0.15 Sample 2 = 0.26
Circulating H_2O			
-Side A	9.08	24.5	Sample 1 = 0.18 Sample 2 = 0.16
-Side B		31-32	

As previously indicated circulating water sample was taken off a sample tap from the pan of Side A.

Note the oxidant residuals measured were much less in this system than measured at NBC Studios and at JPL. These measurements may be in error. I note that the amount of iodine required for the blank determination for these experiments was less than the iodine required at JPL and NBC. It should be the same for all; I may have made an error in reading the burette vernier.

ATTACHMENT 1

Parameter	Make-up H_2O	Circ. H_2O	Filtered Circ. H_2O	Sludge
Bicard-Carb. Alk	x	x	x	
Chlorides	x	x		
Calcium	x	x	x	
Magnesium	x	x	x	
Nitrate-N	x	x		
Ammonia-N	x	x		
Org.-N	x	x		
Potassium	x	x		
Silica	x	x	x	
Sodium	x	x		
Sulfate	x	x	x	
TDS	x	x		
pH	x	x		
Sp. Conductance	x	x		
Total inorganic carbon	x	x	x	
TOC	x	x		
Total Plate Count		JPL & Bullock's Sherman Oaks only		
TSS		x		
Cu		x		
Fe	NBC only	NBC only		
Br	x	x		
THM	x	x		
Total phosphate	x	x	x	

ATTACHMENT 2

Description of Other Towers Using Ozone at JPL

Tower 238

This tower is 1 year old and utilizes PVC fill and transite louvers. It has a galvanized steel frame. It has been on an ozone program for about 3 months. The tower is in good condition. The tower is manufactured by Marley Cooling Towers of Mission, Kansas; its serial number is 5-1173-76A. The tower operates on a system providing 300 tons of refrigeration. The circulating water is very clear. The circulating water TDS is controlled at 700 mg/l by blowdown, which is actuated by a TDS meter.

The ozonator is of JPL design and manufacture. They do not use a colloid neutralizer. Capacity of the ozorator is 8 grams ozone per hour. Ozone is injected into a plastic venturi located in a line through which a small stream of water was being recycled from the tower basin back to the tower basin.

Tower 200

This is a small tower located near a maintenance building. It services a refrigerator system of approximately 75 tons capacity. JPL designed and built the ozonator. Ozone is injected into a venturi located in a line through which a small stream of water was being recycled from the tower basin back to the tower basin. JPL had tried injecting ozone into the suction side of the feed pump, but the pump seals deteriorated within a few days. No colloid neutralizer is used. Ozone generation capacity is 4.2 grams per hour. Circulating water TDS is controlled at 1500 mg/l by a conductance meter hooked into a blowdown valve. Ozone demand in this system is fairly heavy because of organic fumes generated by the maintenance facility.

DUKE POWER COMPANY

STEAM PRODUCTION DEPT.
GENERAL OFFICES
422 SOUTH CHURCH STREET
CHARLOTTE, N. C. 28242

P. O. BOX 2178

TELEPHONE: AREA 704
373-4011

December 12, 1978

Brown and Caldwell
Consulting Engineers
1501 North Broadway
Walnut Creek, CA 94596

Attention: Douglas T. Merrill

Subject: Cooling Tower Operation
File: GS-254.00, 144.40, 701.20

Dear Mr. Merrill:

Attached is a copy of the trip report and preliminary comments on our study of the two cooling tower treatments, ozone and proprietary chemicals, at Duke University. Our results seem to confirm the JPL and NBC studio results when cooling towers are properly maintained on ozone treatment.

If you have further questions regarding this data, please advise.

Very truly yours,

R. B. Thompson

R. B. Thompson
System Power Chemist

STM/mp

Attachments

Trip report - notes on trip to Durham, North Carolina, Duke University Medical School to observe and sample cooling towers using either ozone or proprietary chemicals.

On September 22, 1978 Sherman Mayne of Duke Power Company visited the Duke University Medical School, Durham, North Carolina where ozone and proprietary chemicals were being used in separate cooling towers for the control of biological and chemical scaling. At the site, samples of make-up water and circulating water from the two towers on proprietary chemicals and one tower on ozone were taken. These samples were subsequently analyzed for the parameters listed in the attachments. Parameters measured in the field were pH, alkalinity, acidity, temperature (not calibrated) and conductivity values. The following notes and comments summarize the trip observations, plant site, and analytical determination of listed parameters.

I was shown the system by Mr. Clarence McClure of the Maintenance Department. This building within the hospital complex has a refrigeration system of approximately 750 tons capacity, which utilizes 3 Binks Manufacturing Company cooling towers. The three towers, each having a capacity of 250 tons, appears to be of steel construction.

Since June of 1978, one tower has been operated on ozone. After initial start-up difficulties for a period of about a month (ozone generator problems), the ozone system has been operating without further reported problems. The other two towers are being operated using proprietary chemicals to control scale and biological fouling problems. These towers are being operated in conjunction with one another. A schematic is attached showing the piping arrangement, the sampling location, and point of proprietary chemical addition. It should be noted from the schematic that proprietary chemicals are not added directly to the #2 tower. The chemicals must pass thru the #1 tower and #2 heat exchanger before entering the #2 tower.

The ozone system supplied by Source Gas Analyzers (SGA) of Garden Grove, California, was an ozone generator with a silica gel air dryer, a colloid neutralizer, and an open impeller centrifugal pump. The colloid neutralizer was installed in the make-up line to the system. The ozone was injected on the suction side of the pump thru which a portion of tower basin water was being pumped. The ozonated water was then returned to the basin. When the system was observed the ozonator was using 20 SCFH of air to produce the ozone.

The Duke University operating personnel stated that they have not had operating difficulties with the ozone system after the initial ozone generator problems. According to Duke University personnel, there is no intentional blowdown from the ozone tower. Based on the quantity of water used during the four day test period, the cycles of concentration were controlled by evaporation and drift. If one assumes 2 gpm of water evaporated per 100 tons of refrigeration during the mild temperature period in late September, the calculated water volume approximates the volume of water actually used.

Calculated water volume[1]

$$\frac{2 \text{ gallons}}{\text{minutes} - 100 \text{ tons}} \times \frac{60 \text{ minutes}}{1 \text{ hrs.}} \times 91.5 \text{ hrs.} \times 250 \text{ tons} = 27{,}450 \text{ gals.}$$

Measured water volume 22,675 gallons

1/ Refrigeration cycle use is based on 50% operation.

The data base collected from samples of make-up water and system recirculation water analyzed for selected parameters also confirmed the operation of the system with essentially no blowdown.

Before discussing the data base established for the three towers, the sampling protocol and use of the analytical results must be spelled out.

All samples were individual grab samples taken from the cooling basin. There was no large composite taken from which individual samples were then obtained. Portions of each grab sample were filtered thru a Whatman #40 filter paper to obtain a filtered sample. The only sample not taken from the cooling tower basin was the make-up water sample. The quantified parameter differences between the filtered and nonfiltered sample from the same location were not significant. In fact, the quantity of many of the parameters from filtered samples were equal to or slightly larger than from non-filtered samples from which the filtered sample was obtained. For this reason, the attached analytical results are an average of the two data points from the filtered and nonfiltered portions. The only parameter which did differ significantly between two samples taken at different times was TSS.

As was previously noted for the cooling tower being treated with ozone, the addition of ozone was continuous. However, for the #1 and #2 cooling towers, the addition of proprietary chemicals was on a shock basis. The frequency of addition was dependent upon the visual appearance of tower and recommendation of vendors. For this period of the year, the tower was being treated 2 to 3 times per week.

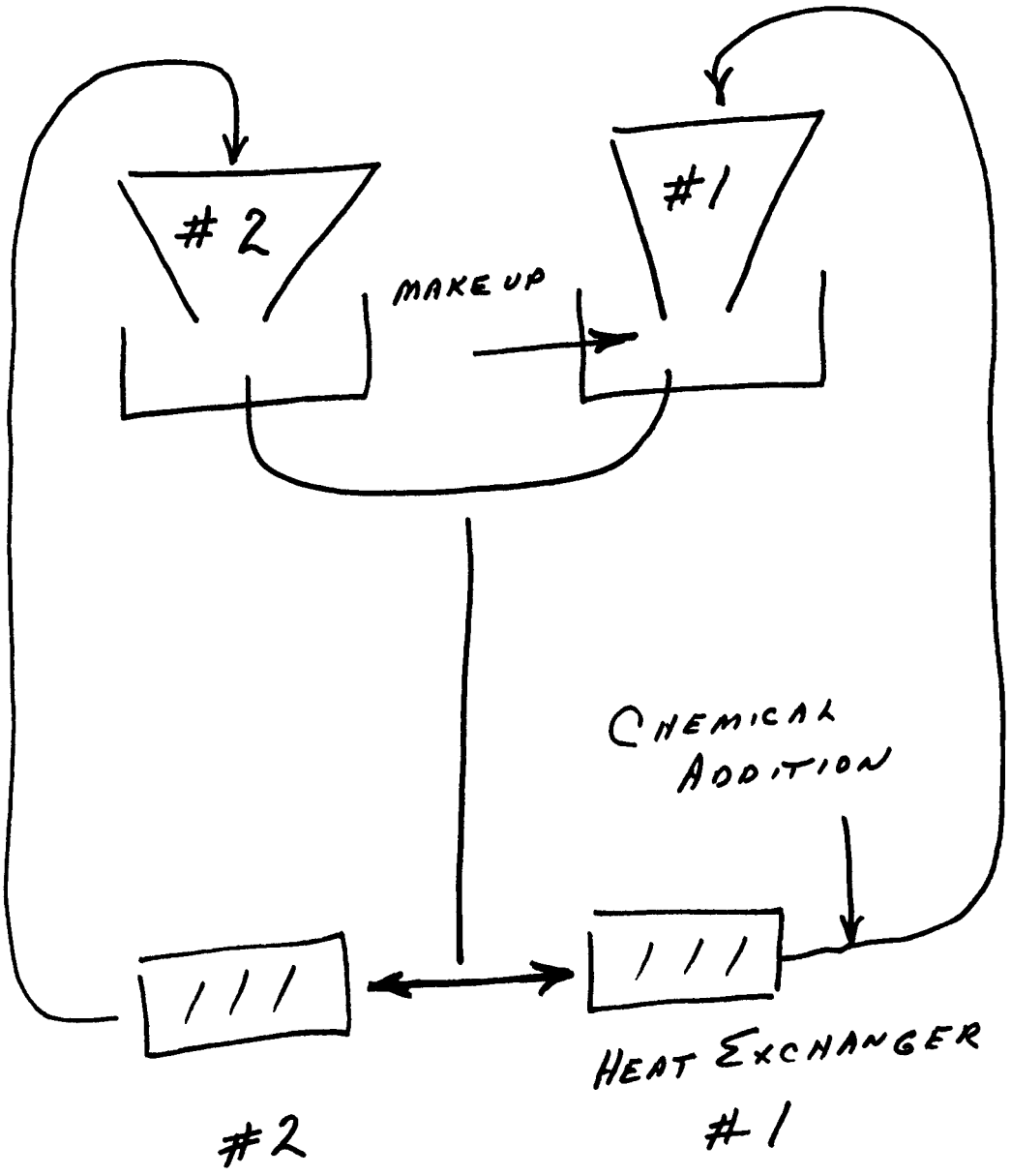
Just prior to sampling and during the sampling period for the #1 and #2 cooling towers, the towers were being treated with proprietary chemicals. As shown on the attached schematic, the #1 cooling tower is the first to receive the chemical dose. As noted by the appearance of the towers, the increased blowdown rate, and the suspended solids concentrations the #1 cooling tower was adequately treated to reduce algae and slime. The appearance of the #2 cooling tower with increased amounts of suspended solids resulting from sloughed off biological materials was in the process of being treated.

The comparison between identical cooling towers using ozone and proprietary chemicals to control biological and chemical scaling was noticeably evident. The circulating water in the ozone treated cooling tower had the appearance of clarified raw water with a low suspended solids concentration. The circulating water in the proprietary chemical treated tower was considerably darker in appearance having a light-gray color with suspended and settleable solids. The slimes adhering to the tower basins were also different in color and texture. The proprietary chemical treated tower had slimes which were green in color. A different appearance was noted for the ozone treated cooling tower. The remaining biomass which was smaller and less dense than the biomass in the proprietary chemical treated cooling tower was brown to black in color with an apparent inactive biomass.

COMMENT

The study comparing the operation of two cooling towers using proprietary chemicals and a similar tower using ozone to control biological and chemical scale at the same location all using the same makeup water source confirmed the applicability of ozone to cooling tower biofouling and scale control. Even though comparative operational costs were not determined during this study, the makeup water savings and no discharge to the sanitary sewer system are cost benefits which make the ozone system attractive.

Cooling System Schematic



11 21 21 150

Parameter		Make-up Water Duke	Make-up Water B&C	Cl_2 #1 Tower Duke	Cl_2 #1 Tower B&C	Cl_2 #2 Tower Duke	Cl_2 #2 Tower B&C	O_3 Circ. Tower Duke	O_3 Circ. Tower B&C
Silica (SiO_2)	ppm	11.3	110	29.9[1]	210	23.5[1]	210	134.7	1500
Arsenic	ppb	<2		3.7[1]		6.1[1]		158[1]	
Calcium	ppm	5.2	5.5	11[1]	12[1]	12[1]	12[1]	99[1]	130[1]
Cadmium	ppb	<0.2		4.1[1]		3.9[1]		2.1[1]	
Chromium	ppb	<0.5		8.7[1]		13.3[1]		100[1]	
Copper	ppb	1.7		79[1]		140[1]		79[1]	
Iron	ppb	5.5	30	400[1]	750	900[1]	1900	68	150
Mercury	ppb	<2		<2		<2		6[1]	
Magnesium	ppm	2.0	1.8	3.9[1]	4.3[1]	4.3[1]	4.2[1]	47[1]	52[1]
Manganese	ppm	<0.1							
Sodium	ppm	16	15	33[1]	29	37[1]	30	610[1]	620
Nickel	ppb	<5		<5[1]		<5[1]		8[1]	
Lead	ppb	<1		27[1]		54[1]		7	
Selenium	ppb	<10		<5[1]		<5[1]		6	
Zinc	ppm	0.136		5.2[1]		5.4[1]		0.1[1]	
Chloride	ppm	11	8	21	20	22	24	320	390
Sulfate	ppm	9	15	33	37	20	35	420	742
Nitrate - Nitrite	(as N) ppm	0.12	0.085	0.43	0.42	0.42	0.424	2.0	5.31
Kjeldahl N	(as N) ppm	<0.10	0.12	2.1	1.5	8.1	1.6	4.0	4.0
Ammonia (as N)	ppm	<0.01	<0.05	0.19	<0.05	0.15	<0.05	0.053	0.11
TSS	ppm	0.8		29 (0)[2]	24	340 (75)[2]	58	7 (6)[2]	6
Total PO_4 (as PO_4 - ppm) (soluble - as PO_4)			0.77	15.3	4.5C, 2.1F	23.0	2.7C, 2.5F	4.3	3.5
Orthophosphate	ppm	0.28		1.35		1.71		1.41	
Dissolved Solids (ppm)	Total			262		261		2548	
	Fixed			191		183		2166	
	Volatile			71		78		382	

1. Average of filtered and non-filtered samples. 2. Two TSS analyses listed. Second sample taken about 2 hrs after first sample.

Dev./Station _____ Unit _____ File No. _____

Subject _____ By _____ Date _____

Sheet No. ___ of ___ Problem No. _____ Checked By _____ Date _____

Duke University Cooling Tower Study

Parameter	Make-up Water	Ozone Tower	Chlorine Tower #1	Chlorine Tower #2
pH	7.7	8.9	7.9	7.8
Acidity to 8.3	—	—		
ml of base			0.23	0.11
N of base			0.0949	0.0949
Sample size, ml			100	100
Meq/liter - EPM			0.218	0.104
Mg/liter - $CaCO_3$			10.9	5.2
Alkalinity to 4.5	—			
ml of acid		9.43	1.41	1.48
N of acid		0.0923	0.0923	0.0923
Sample size, ml		100	100	100
Meq/liter - EPM		8.704	1.301	1.366
Mg/liter - $CaCO_3$		435.2	65.1	68.3
Alkalinity to 8.3	—			
ml of acid		1.84		
N of acid		0.0923		
Sample size, ml		100		
Meq/liter - EPM		1.698		
Mg/liter - $CaCO_3$		84.9		

Form 184 (5.76)

Form 184 (5-76)

Dev./Station

Subject

Sheet No. ___ of ___ Problem No. ___

Unit File No.

By Date

Checked By Date

DUKE UNIVERSITY COOLING TOWER STUDY

PARAMETER	MAKEUP WATER	OZONE TOWER	CHLORINE TOWER #1	CHLORINE TOWER #2	
CONDUCTIVITY (μmho's)	150	4500	350	325	
COOLING TOWER BASIN WATER - °C	—	25	22	22	THERMOMETER
WATER TEMPERATURE PRIOR TO ENTERING HEAT EXCHANGER		28.9 °C (84 °F)	26.7 (80°F)	26.7 (80°F)	TEMPERATURE PROBE
WATER TEMPERATURE IMMEDIATELY AFTER LEAVING HEAT EXCHANGER		31.7 (89°F)	31.1 (88°F)	30.0 (86°F)	TEMPERATURE PROBE
QUANTITY OF H_2O USED FROM 2:15 PM 9-18-78 TO 9:45 AM 9-22-78 (91.5 HOURS TOTAL)		22,675 GALS.	(METER NOT FUNCTIONING)		

TOWERS — BAKER MFG CO. — 250 TONS/EACH

Appendix B

MEMORANDUM ON FAILURE OF OZONE TREATED COOLING SYSTEM

This Appendix includes a memorandum to file by Douglas Merrill, Brown and Caldwell, entitled "Failure of Ozone System to Prevent Scaling in Cooling Tower at UCLA."

MEMORANDUM 285-1

September 1, 1978

TO: FILE 285-1

FROM: DOUG MERRILL DM

SUBJECT: FAILURE OF OZONE SYSTEM TO PREVENT SCALING IN COOLING TOWER AT UCLA

Joe Drago and I talked by telephone with Ben Budworth of UCLA's Physical Plant Department (Phone 213-825-1391). The conversation was about a cooling tower using an ozone system supplied by Source Gas Analyzers (SGA).

This tower services an air conditioning system using LiBr adsorption. Water is returned to the cooling tower in the range of 120°F and leaves the tower of something less than 86°F. The cooling tower system had been in service for 7 or 8 years previously, using acid-chromate treatment, with an algacide.

In January of this year an ozonation treatment system was installed by SGA. The system included a colloid neutralizer and a mud separator. pH was maintained just below 9.0. The cooling tower was operated at 40 cycles of concentration as indicated by chloride balance. There was no blowdown other than flushing the mud separator. Budworth indicated that only 10 cycles of concentration were calculated when TDS was used as the parameter for calculation.

At the end of March, temperatures in the vapor condenser began to increase, an indication of scaling in the condenser. When Budworth complained to SGA, they responded that the cooling tower wasn't being cleaned properly. SGA then came out and cleaned the tower and the system was restarted.

In June algae were found in the water distribution boxes located above the cooling tower, indicating that the biocidal action of the ozone was insufficient. SGA suggested that the boxes be covered, and they were. However, algae problems continued.

Temperatures within the condenser continued to rise. In late June, heavy chemical scaling was noted in the tower pan. The scale was removed, analyzed, and found to be $CaCO_3$. The scale was relatively hard; i.e., could not be hosed out. Thirty and ninety day corrosion coupons were completely scaled over. At about this time, the lower cooling tower slats became covered with algae.

SGA was again notified. They suggested that a bigger ozonator be installed and that the cooling tower be vacuumed out twice a month.

Budworth figured that vacuuming twice a month was more work than the system was worth, so he shut the ozone system down and returned to acid-chromate-algacide treatment. They are currently circulating a water of pH 5 to try to dissolve scale.

Budworth indicated that the mud separator had not done much separating.

DM:lnj

cc: Joe Drago

Appendix C

SAMPLING AND ANALYSES

The following are included in this Appendix:

1. A description of sampling and field measurement protocols.
2. A description of analytical techniques used.
3. Analytical data.

SAMPLING AND FIELD MEASUREMENTS

Sampling and field measurement protocols used in this study are detailed below.

Southern California Sites

Sample Collection. One 1-pint bottle with a preservative and one 5-pint bottle without preservatives were used for collecting unfiltered makeup water. Circulating water samples were collected in the same way. Sulfuric acid was the preservative, the nitrogen series (ammonia, organic nitrogen, nitrate and nitrite) the species preserved. One 1-pint bottle without preservatives was used to collect circulating water samples filtered through Whatman No. 2 filter paper. A small bacterial sampling bottle was used to collect samples to be analyzed for total plate counts and special glass vials, with teflon seals which are crimped in the field, were used to collect samples to be analyzed for trihalomethanes. These last two sets of samples were refrigerated.

Field Measurements. Measurements of temperature, pH and oxidant residuals were made in the field for each makeup and circulating water sampled. A 0-100°C thermometer was used for temperature measurements. A portable Leeds and Northrup pH meter with a combination pH-reference electrode was used to determine pH. Buffer solutions of pH 7 and 9 were used to standardize the meter. Total oxidant residuals were measured with a Fischer and Porter Model 17T1010 amperometric titrator, using the back titration method for total oxidant residual, as described in Fischer and Porter Bulletin 17T1010. This method is described below.

The conductance current between the titrator's electrodes is a function of the free residual halogen in solution. In the conventional forward titration for total oxidant (combined as well as free halogen), excess KI is added to the sample at controlled pH conditions. Elemental iodine is produced as the result of oxidation of KI by the combined and free oxidant residuals. The amount of iodine released is directly proportional to the total oxidant residual initially present. A reducing agent (in this analysis, 0.00564 N phenylarsine oxide) is then added, reducing the free iodine and also decreasing the conductance current. When the conductance current (as measured by a microammeter connected in series with the electrodes) can be no further decreased, the iodine has been completely reduced. The initial oxidant residual can then be related to the amount of titrant used. When the sample contains organic compounds which might interfere with the conventional forward titration, the back titration method is suggested. Since we had no way of knowing beforehand whether organics would be a problem, the back titration method was used. The procedure is:

1. Add 200 ml sample to the titrator beaker.

2. Add four eyedroppers of buffer (pH 4) to bring the sample into the pH range 3.5-4.5.

3. Add 10 drops of 5 percent KI.

4. Add sufficient phenylarsine oxide (PAO) to swamp any residual present. We used 5.0 ml of 0.00564N PAO.

5. Titrate the sample with iodine solution. Consumption of the excess PAO is indicated by the appearance of the conductance current.

6. Concentration of oxidant residual, as Cl, mg/l $= \frac{N\ (A-B)\ 35{,}450}{\text{sample volume, ml}}$;

   Where;

   N = normality of the iodine solution,

   A = volume of titrant required to titrate 5.0 ml of PAO,

   B = volume of titrant to titrate sample.

Duke University Medical Center

Sample Collection. All samples were individual grab samples rather than portions of a single composited sample. The makeup and circulated water samples subsequently analyzed by the Environmental Sciences Division of Brown and Caldwell were collected in bottles similar to those used for the southern California sites.

Field Measurements. Measurements of pH, alkalinity, acidity, temperature, and specific conductance were made in the field for the circulating waters. Measurements of pH and conductivity only were made for the makeup water. A 100°C thermometer was used for temperature measurements. A Beckman Phasar I pH meter with a combination electrode was used to determine pH. Buffer solutions of pH 7 and 10 were used to standardize the meter. Conductivity was measured with Dionic conductivity meter.

LABORATORY ANALYSES

Southern California Samples

Wet chemical analyses performed by Brown and Caldwell's laboratories generally followed Standard Methods for the Examination of Water and Wastewater (1). These are described in Table C-1. The trihalomethane analyses were performed by Foremost Food Company Research and Development Center of Dublin, California, using gas chromatography. A technique described by Lichtenberg (2) was followed. Copies of the laboratory reports on these analyses are included at the end of this Appendix.

Duke University Medical Center Samples

Analyses performed by Brown and Caldwell's laboratories are described in Table C-1. Chemical analyses performed by Duke Power generally followed Standard Methods for the Examination of Water and Wastewater (1). Trace metal analyses were by atomic absorption. Copies of the laboratory reports are included at the end of this Appendix.

REFERENCES

1. American Public Health Association. Standard Methods for the Examination of Water and Wastewater. 14th Edition. Washingtion, D.C., 1976.

2. B. Lichtenberg, EPA-670/4-74-009, November 1974.

Table C-1
ANALYTICAL METHODS USED BY BROWN AND CALDWELL LABORATORIES

Species	Description	Reference Source
Nitrite	Sulfanilic acid method	Section 420, Standard Methods[a]
Nitrate	Brucine method	Section 419D, Standard Methods
Chloride	Argentometric method	Section 408A, Standard Methods
Sulfate	Turbidimetric method	Section 427C, Standard Methods
Sodium, potassium, calcium, magnesium, iron, copper	Atomic absorption, Perkin-Elmer Model 503	Manufacturer's literature
Alkalinity	Titration with colorimetric end point	Section 403, Standard Methods
Dissolved residue	Material filtered through Reeves-Angel 934A filter, then evaporated at 180 C	Section 208B, Standard Methods
Total suspended solids	Material retained on Reeves-Angel 934A filter is dried at 105 C	Section 208D, Standard Methods
Ammonia	Distillation, followed by titration of distillate	Section 418A, Standard Methods
Organic nitrogen	Digestion with K_2SO_4/H_2SO_4/HgO, followed by distillation, then titration of distillate	Section 421, Standard Methods
Total phosphate	Ascorbic acid method, preceded by digestion with H_2SO_4/HNO_3	Section 425F, Standard Methods
Silica	Molybdosilicate method	Section 426B, Standard Methods
Conductivity	Yellow Springs Instruments, Model 31	Manufacturer's literature
pH	Corning pH meter 130	Manufacturer's literature
Fluoride	Potentiometric method	Section 414B, Standard Methods
Bromide	Colorimetric determination	Section 406, Standard Methods
Standard plate count	Incubation at 35 C for 48 hours	Section 907, Standard Methods
Total organic carbon	Infrared detection, Beckman Model 915	Manufacturer's literature
Total inorganic carbon	Infrared detection, Beckman Model 915	

[a]All references to Standard Methods are to Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 14th edition, Washington D.C., 1976.

WASTEWATER ANALYSIS

BROWN AND CALDWELL
CONSULTING ENGINEERS
ENVIRONMENTAL SCIENCES DIVISION
1255 POWELL STREET
EMERYVILLE, CA 94608
PHONE (415) 428-2300

Log No. 23C1

Date Sampled 9/14/78
Date Received 9/15/78
Date Reported 10/11/78

Job No: 285-1

Report To: Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

cc. Doug Merrill

Steven A. Fisher
Laboratory Director

Sample Description: Bullock's , Sherman Oaks, make up water

Anions	Milligrams per liter	Milliequiv. per liter
Nitrite Nitrogen (as NO_2)	0.043	< 0.01
Nitrate Nitrogen (as NO_3)	0.81	0.01
Chloride	6.8	0.19
Sulfate (as SO_4)	9.0	0.25
Bicarbonate (as HCO_3)	75	1.23
Carbonate (as CO_3)	3.8	0.13
H. Phosphate (as HPO_4)	0.22	< 0.01
H_2 Phosphate (as H_2PO_4)	0.01	< 0.01
Total Milliequivalents per Liter		1.81

Cations	Milligrams per liter	Milliequiv. per liter
Ammonium Nitrogen (as NH_4)	< 0.06	< 0.01
Sodium	15	0.65
Potassium	2.8	0.07
Calcium	17	0.85
Magnesium	2.4	0.20
Total Milliequivalents per Liter		1.77

Determination	Milligrams per liter
Phenolphthalein Alkalinity (as $CaCO_3$)	3.2
Methyl Orange Alkalinity (as $CaCO_3$)	68
Calcium Hardness (as $CaCO_3$)	42
Magnesium Hardness (as $CaCO_3$)	9.9
Dissolved Residue, Evaporated at 180°C	96
Dissolved Residue, Calculated	111
Nitrite Nitrogen (as N)	0.013
Nitrate Nitrogen (as N)	0.18
Ammonia Nitrogen (as N)	< 0.05
Organic Nitrogen (as N)	0.24
Total Nitrogen (as N)	0.43
Total Phosphate (as PO_4)	0.23
Silica (as SiO_2)	16
Specific Conductance, micromhos at 25°C	190
pH	8.2
Sodium (as % Cations)	----

Determination	Milligrams per liter
Fluoride	----
Total Kjeldahl Nitrogen (as N)	0.24
Total Inorganic Carbon	13
Total Organic Carbon	5
Copper	0.08
Bromide	0.86
Turbidity (NTU)	----

WASTEWATER ANALYSIS

BROWN AND CALDWELL
CONSULTING ENGINEERS
ENVIRONMENTAL SCIENCES DIVISION
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EMERYVILLE, CA 94608
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Log No. 23C2

Date Sampled 9/14/78
Date Received 9/15/78
Date Reported 10/11/78

Job No: 285-1

Report To: Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

cc. Doug Merrill

Laboratory Director

Sample Description: Bullock's, Sherman Oaks, Circulating water

Anions	Milligrams per liter	Milliequiv. per liter
Nitrite Nitrogen (as NO_2)	0.039	< 0.01
Nitrate Nitrogen (as NO_3)	104	1.67
Chloride	250	7.05
Sulfate (as SO_4)	480	9.98
Bicarbonate (as HCO_3)	299	4.90
Carbonate (as CO_3)	64	2.13
H. Phosphate (as HPO_4)	1.0	0.02
H_2 Phosphate (as H_2PO_4)	0	0
Total Milliequivalents per Liter		25.75

Cations	Milligrams per liter	Milliequiv. per liter
Ammonium Nitrogen (as NH_4)	< 0.06	< 0.01
Sodium	440	19.14
Potassium	66	1.69
Calcium	87	4.34
Magnesium	30	2.47
Total Milliequivalents per Liter		27.64

Determination	Milligrams per liter
Phenolphthalein Alkalinity (as $CaCO_3$)	53
Methyl Orange Alkalinity (as $CaCO_3$)	352
Calcium Hardness (as $CaCO_3$)	218
Magnesium Hardness (as $CaCO_3$)	123
Dissolved Residue, Evaporated at 180°C	1830
Dissolved Residue, Calculated	1784
Nitrite Nitrogen (as N)	0.012
Nitrate Nitrogen (as N)	24
Ammonia Nitrogen (as N)	< 0.05
Organic Nitrogen (as N)	3.2
Total Nitrogen (as N)	27
Total Phosphate (as PO_4)	1.0
Silica (as SiO_2)	115
Specific Conductance, micromhos at 25°C	2520
pH	9.1
Sodium (as % Cations)	----

Determination	Milligrams per liter
Fluoride	----
Total Kjeldahl Nitrogen (as N)	3.2
Total Inorganic Carbon	77
Total Organic Carbon	33
Total Suspended Solids	46
Copper	0.40
Bromide	0.36
Estimated Standard Plate Count/ml	30000
Turbidity (NTU)	----

WASTEWATER ANALYSIS

BROWN AND CALDWELL
CONSULTING ENGINEERS
ENVIRONMENTAL SCIENCES DIVISION
1255 POWELL STREET
EMERYVILLE, CA 94608
PHONE (415) 428-2300

Log No. 23C3

Date Sampled 9/14/78
Date Received 9/15/78
Date Reported 10/11/78

Job No: 285-1

Report To: Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

cc. Doug Merrill

Laboratory Director

Sample Description: JPL, make up water

Anions	Milligrams per liter	Milliequiv. per liter
Nitrite Nitrogen (as NO_2)	0.008	< 0.01
Nitrate Nitrogen (as NO_3)	4.2	0.07
Chloride	14	0.39
Sulfate (as SO_4)	34	0.71
Bicarbonate (as HCO_3)	224	3.67
Carbonate (as CO_3)	0	0
H. Phosphate (as HPO_4)	< 0.03	< 0.01
H_2 Phosphate (as H_2PO_4)	0	0
Total Milliequivalents per Liter		4.84

Cations	Milligrams per liter	Milliequiv. per liter
Ammonium Nitrogen (as NH_4)	< 0.06	< 0.01
Sodium	19	0.83
Potassium	3.5	0.09
Calcium	49	2.45
Magnesium	20	1.64
Total Milliequivalents per Liter		5.01

Determination	Milligrams per liter
Phenolphthalein Alkalinity (as $CaCO_3$)	0
Methyl Orange Alkalinity (as $CaCO_3$)	184
Calcium Hardness (as $CaCO_3$)	123
Magnesium Hardness (as $CaCO_3$)	82
Dissolved Residue, Evaporated at 180°C	260
Dissolved Residue, Calculated	277
Nitrite Nitrogen (as N)	0.003
Nitrate Nitrogen (as N)	0.95
Ammonia Nitrogen (as N)	< 0.05
Organic Nitrogen (as N)	< 0.05
Total Nitrogen (as N)	0.95
Total Phosphate (as PO_4)	< 0.03
Silica (as SiO_2)	23
Specific Conductance, micromhos at 25°C	470
pH	7.9
Sodium (as % Cations)	----

Determination	Milligrams per liter
Fluoride	----
Total Kjeldahl Nitrogen (as N)	< 0.05
Total Inorganic Carbon	37
Total Organic Carbon	4
Copper	< 0.01
Bromide	0.10
Turbidity (NTU)	----

WASTEWATER ANALYSIS

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PHONE (415) 428-2300

Log No. 23C4

Date Sampled 9/14/78
Date Received 9/15/78
Date Reported 10/11/78

Job No: 285-1

Report To:
Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

cc.
Doug Merrill

Laboratory Director

Sample Description: JPL, Circulating water - Chem. Tower

Anions	Milligrams per liter	Milliequiv. per liter
Nitrite Nitrogen (as NO_2)	0.018	< 0.01
Nitrate Nitrogen (as NO_3)	121	1.95
Chloride	180	3.74
Sulfate (as SO_4)	350	7.28
Bicarbonate (as HCO_3)	499	8.18
Carbonate (as CO_3)	78	2.60
H. Phosphate (as HPO_4)	3.7	0.08
H_2 Phosphate (as H_2PO_4)	0	0
Total Milliequivalents per Liter		23.83

Cations	Milligrams per liter	Milliequiv. per liter
Ammonium Nitrogen (as NH_4)	< 0.06	< 0.01
Sodium	190	8.27
Potassium	31	0.79
Calcium	150	7.49
Magnesium [a]	140	11.51
Total Milliequivalents per Liter		28.06

Determination	Milligrams per liter
Phenolphthalein Alkalinity (as $CaCO_3$)	65
Methyl Orange Alkalinity (as $CaCO_3$)	540
Calcium Hardness (as $CaCO_3$)	375
Magnesium Hardness (as $CaCO_3$)	576
Dissolved Residue, Evaporated at 180°C	1620
Dissolved Residue, Calculated	1576
Nitrite Nitrogen (as N)	0.006
Nitrate Nitrogen (as N)	25
Ammonia Nitrogen (as N)	< 0.05
Organic Nitrogen (as N)	32
Total Nitrogen (as N)	57
Total Phosphate (as PO_4)	3.7
Silica (as SiO_2)	86
Specific Conductance, micromhos at 25°C	2170
pH	8.9
Sodium (as % Cations)	----

Determination	Milligrams per liter
Fluoride	----
Total Kjeldahl Nitrogen (as N)	32
Total Inorganic Carbon	97
Total Organic Carbon	43
Total Suspended Solids	10
Copper	0.40
Bromide	< 0.1
Estimated Standard Plate Count/ml	43000
Turbidity (NTU)	----

a) Magnesium by Titration = 117 mg/l

WASTEWATER ANALYSIS

BROWN AND CALDWELL
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Log No. 23C5

Date Sampled 9/14/78
Date Received 9/15/78
Date Reported 10/11/78

Job No: 285-1

Report To:
Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

cc. Doug Merrill

Laboratory Director

Sample Description: JPL, Circulating water - Ozone

Anions	Milligrams per liter	Milliequiv. per liter
Nitrite Nitrogen (as NO_2)	0.008	< 0.01
Nitrate Nitrogen (as NO_3)	300	4.83
Chloride	459	12.94
Sulfate (as SO_4)	1120	23.30
Bicarbonate (as HCO_3)	490	8.04
Carbonate (as CO_3)	102	3.40
H. Phosphate (as HPO_4)	0.26	0.01
H_2 Phosphate (as H_2PO_4)	0	0
Total Milliequivalents per Liter		52.52

Cations	Milligrams per liter	Milliequiv. per liter
Ammonium Nitrogen (as NH_4)	< 0.06	< 0.01
Sodium	540	23.49
Potassium	91	2.33
Calcium	49	2.45
Magnesium	330	27.13
Total Milliequivalents per Liter		55.40

Determination	Milligrams per liter
Phenolphthalein Alkalinity (as $CaCO_3$)	85
Methyl Orange Alkalinity (as $CaCO_3$)	572
Calcium Hardness (as $CaCO_3$)	123
Magnesium Hardness (as $CaCO_3$)	1358
Dissolved Residue, Evaporated at 180°C	3330
Dissolved Residue, Calculated	3344
Nitrite Nitrogen (as N)	0.003
Nitrate Nitrogen (as N)	68
Ammonia Nitrogen (as N)	< 0.05
Organic Nitrogen (as N)	3.2
Total Nitrogen (as N)	71
Total Phosphate (as PO_4)	0.26
Silica (as SiO_2)	111
Specific Conductance, micromhos at 25°C	4290
pH	9.2
Sodium (as % Cations)	----

Determination	Milligrams per liter
Fluoride	----
Total Kjeldahl Nitrogen (as N)	3.2
Total Inorganic Carbon	104
Total Organic Carbon	6
Total Suspended Solids	6
Copper	0.01
Bromide	0.80
Estimated Standard Plate Count/ml	7200
Turbidity (NTU)	----

WASTEWATER ANALYSIS

BROWN AND CALDWELL
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PHONE (415) 428-2300

Log No. 23C6

Date Sampled 9/14/78
Date Received 9/15/78
Date Reported 10/11/78

Job No: 285-1

Report To: Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

cc. Doug Merrill

Laboratory Director

Sample Description: NBC Studios, make up water

Anions	Milligrams per liter	Milliequiv. per liter
Nitrite Nitrogen (as NO_2)	0.008	< 0.01
Nitrate Nitrogen (as NO_3)	2.9	0.05
Chloride	56	1.58
Sulfate (as SO_4)	126	2.62
Bicarbonate (as HCO_3)	146	2.39
Carbonate (as CO_3)	0	0
H. Phosphate (as HPO_4)	< 0.03	< 0.01
H_2 Phosphate (as H_2PO_4)	0	0
Total Milliequivalents per Liter		6.64

Cations	Milligrams per liter	Milliequiv. per liter
Ammonium Nitrogen (as NH_4)	< 0.06	< 0.01
Sodium	56	2.44
Potassium	3.8	0.10
Calcium	50	2.50
Magnesium	20	1.64
Total Milliequivalents per Liter		6.68

Determination	Milligrams per liter
Phenolphthalein Alkalinity (as $CaCO_3$)	0
Methyl Orange Alkalinity (as $CaCO_3$)	120
Calcium Hardness (as $CaCO_3$)	125
Magnesium Hardness (as $CaCO_3$)	82
Dissolved Residue, Evaporated at 180°C	380
Dissolved Residue, Calculated	397
Nitrite Nitrogen (as N)	0.003
Nitrate Nitrogen (as N)	0.64
Ammonia Nitrogen (as N)	< 0.05
Organic Nitrogen (as N)	0.18
Total Nitrogen (as N)	0.82
Total Phosphate (as PO_4)	< 0.03
Silica (as SiO_2)	10
Specific Conductance, micromhos at 25°C	660
pH	7.9
Sodium (as % Cations)	----

Determination	Milligrams per liter
Fluoride	----
Total Kjeldahl Nitrogen (as N)	0.18
Total Inorganic Carbon	17
Total Organic Carbon	6
Bromide	< 0.1
Copper	0.08
Iron	0.03
Turbidity (NTU)	----

WASTEWATER ANALYSIS

BROWN AND CALDWELL
CONSULTING ENGINEERS
ENVIRONMENTAL SCIENCES DIVISION
1255 POWELL STREET
EMERYVILLE, CA 94608
PHONE (415) 428-2300

Log No. 23C7

Date Sampled 9/14/78
Date Received 9/15/78
Date Reported 10/11/78

Job No: 285-1

Report To:
Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

cc. Doug Merrill

Laboratory Director

Sample Description: NBC Studios, Circulating water

Anions	Milligrams per liter	Milliequiv. per liter
Nitrite Nitrogen (as NO_2)	0.015	< 0.01
Nitrate Nitrogen (as NO_3)	460	7.41
Chloride	2500	70.50
Sulfate (as SO_4)	5550	115.44
Bicarbonate (as HCO_3)	255	4.18
Carbonate (as CO_3)	14	0.47
H. Phosphate (as HPO_4)	< 0.03	< 0.01
H_2 Phosphate (as H_2PO_4)	0	0
Total Milliequivalents per Liter		198.00

Cations	Milligrams per liter	Milliequiv. per liter
Ammonium Nitrogen (as NH_4)	< 0.06	< 0.01
Sodium	2600	113.10
Potassium	190	4.86
Calcium	620	30.94
Magnesium	670	55.07
Total Milliequivalents per Liter		203.97

Determination	Milligrams per liter
Phenolphthalein Alkalinity (as $CaCO_3$)	12
Methyl Orange Alkalinity (as $CaCO_3$)	233
Calcium Hardness (as $CaCO_3$)	1550
Magnesium Hardness (as $CaCO_3$)	2760
Dissolved Residue, Evaporated at 180°C	13400
Dissolved Residue, Calculated	12854
Nitrite Nitrogen (as N)	0.005
Nitrate Nitrogen (as N)	104
Ammonia Nitrogen (as N)	< 0.05
Organic Nitrogen (as N)	5.4
Total Nitrogen (as N)	109
Total Phosphate (as PO_4)	< 0.03
Silica (as SiO_2)	124
Specific Conductance, micromhos at 25°C	13500
pH	8.7
Sodium (as % Cations)	----

Determination	Milligrams per liter
Fluoride	----
Total Kjeldahl Nitrogen (as N)	5.4
Total Inorganic Carbon	22
Total Organic Carbon	7
Total Suspended Solids	6
Bromide	7.2
Iron	0.13
Estimated Standard Plate Count/ml	54000
Turbidity (NTU)	----

BROWN AND CALDWELL
CONSULTING ENGINEERS
ENVIRONMENTAL SCIENCES DIVISION
428 JESSIE STREET
SAN FRANCISCO, CA 94103
PHONE (415) 777-1070

Log No. 23C
Date Sampled 9/14/78
Date Received 9/15/78
Date Reported 10/18/78

Job No: 285-1

Report To:
Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

Laboratory Supervisor

cc: Doug Merrill

Log No.	Sample Description
23C7	NBC Studios

Results (mg/l unless indicated otherwise)

Sample Log No.	23C7					
Copper	0.08					

BROWN AND CALDWELL
CONSULTING ENGINEERS
ENVIRONMENTAL SCIENCES DIVISION
1255 POWELL STREET
EMERYVILLE, CA 94608
PHONE (415) 428-2300

Log No. 23C

Date Sampled 9/14/78
Date Received 9/15/78
Date Reported 10/11/78

Job No: 285-1

Report To: Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

cc. Doug Merrill

Laboratory Director

Log No.	Sample Description
23C2	Filtered Circulating water: Bullocks, Sherman Oaks
23C4	JPL Chem. Tower
23C5	JPL Ozone
23C7	NBC Studios

Results (mg/l unless indicated otherwise)

Sample Log No.	23C2	23C4	23C5	23C7		
Phenolphthalein Alkalinity (as $CaCO_3$)	49	39	65	14		
Methyl Orange Alkalinity (as $CaCO_3$)	408	461	572	240		
Calcium	87	140	49	620		
Magnesium	30	140	330	670		
Silica (as SiO_2)	103	86	107	116		
Sulfate[a]	472	312	1031	5430		
Total Inorganic Carbon	91	105	118	46		
Total Phosphate (as PO_4)	0.53	3.7	0.17	< 0.03		

a) gravimetric analysis

BACTERIOLOGICAL EXAMINATION

BROWN AND CALDWELL
CONSULTING ENGINEERS
ENVIRONMENTAL SCIENCES DIVISION
428 JESSIE STREET
SAN FRANCISCO, CA 94103
PHONE (415) 777-1070

Date Reported 10/11/78

Job No: 285-1

Report To:
Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

Laboratory Supervisor

cc: Doug Merrill

Date Sampled	Date of Exam	Log No. and Source of Sample	Std Plate Count Bacteria per ml agar 35°C	Examination for Coliform Organisms						Coliform Organisms Most Probable Number per 100 ml	Quality at Time of Sampling
				Portions Examined		Presumptive Lactose Broth		Confirmed B.G.B.			
				Vol	No.	24 hr	48 hr	24 hr	48 hr		
9/13	9/15	23C9 - Circulating Water, Bullock's Main Store		10 ml							
			33000[a]	1.0 ml							
				0.1 ml							
				10 ml							
				1.0 ml							
				0.1 ml							
				10 ml							
				1.0 ml							
				0.1 ml							
				10 ml							
				1.0 ml							
				0.1 ml							
				10 ml							
				1.0 ml							
				0.1 ml							
				10 ml							
				1.0 ml							
				0.1 ml							
				10 ml							
				1.0 ml							
				0.1 ml							
				10 ml							
				1.0 ml							
				0.1 ml							

All Examinations Are Made In Accordance With *Standard Methods for the Examination of Water and Wastewater.*

Scheduled distribution system samples:

Number of samples ________

Number of samples with 3 or more tubes positive ________

Number of 10 ml tubes ________

Number of 10 ml tubes positive ________

a) Estimated

Analyst P. Sheppard

WASTEWATER ANALYSIS

BROWN AND CALDWELL
CONSULTING ENGINEERS
ENVIRONMENTAL SCIENCES DIVISION
1255 POWELL STREET
EMERYVILLE, CA 94608
PHONE (415) 428-2300

Log No. 26J1

Date Sampled 9/22/78
Date Received 10/06/78
Date Reported 11/07/78

Job No: 285-1

Report To: Mr. Joe Drago
Brown & Caldwell
1501 North Broadway
Walnut Creek, CA 94596

Laboratory Director

cc.
Doug Merrill

Sample Description (Duke Power Company) Make-up Water

Anions	Milligrams per liter	Milliequiv. per liter
Nitrite Nitrogen (as NO_2)	0.017	< 0.01
Nitrate Nitrogen (as NO_3)	0.35	0.01
Chloride	8.0	0.23
Sulfate (as SO_4)	15	0.31
Bicarbonate (as HCO_3)	34	0.56
Carbonate (as CO_3)	0	0
H. Phosphate (as HPO_4)	0.25	< 0.01
H_2 Phosphate (as H_2PO_4)	0.52	< 0.01
Total Milliequivalents per Liter		1.11

Cations	Milligrams per liter	Milliequiv. per liter
Ammonium Nitrogen (as NH_4)	< 0.06	< 0.01
Sodium	15	0.65
Potassium	2.2	0.06
Calcium	5.5	0.27
Magnesium	1.8	0.15
Total Milliequivalents per Liter		1.13

Determination	Milligrams per liter
Phenolphthalein Alkalinity (as $CaCO_3$)	0
Methyl Orange Alkalinity (as $CaCO_3$)	28
Calcium Hardness (as $CaCO_3$)	14
Magnesium Hardness (as $CaCO_3$)	7.4
Dissolved Residue, Evaporated at 180°C	74
Dissolved Residue, Calculated	76
Nitrite Nitrogen (as N)	0.005
Nitrate Nitrogen (as N)	0.08
Ammonia Nitrogen (as N)	< 0.05
Organic Nitrogen (as N)	0.12
Total Nitrogen (as N)	0.21
Total Phosphate (as PO_4)	0.77
Silica (as SiO_2)	11
Specific Conductance, micromhos at 25°C	161
pH	6.5
Sodium (as % Cations)	----

Determination	Milligrams per liter
Fluoride	----
Total Kjeldahl Nitrogen (as N)	0.12
Total Inorganic Carbon	7
Total Organic Carbon	6
Copper	< 0.01
Bromide	< 1
Turbidity (NTU)	0.25

WASTEWATER ANALYSIS

BROWN AND CALDWELL
CONSULTING ENGINEERS
ENVIRONMENTAL SCIENCES DIVISION
1255 POWELL STREET
EMERYVILLE, CA 94608
PHONE (415) 428-2300

Log No. 26J2

Date Sampled 9/22/78
Date Received 10/06/78
Date Reported 11/07/78

Job No: 285-1

Report To:
Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

Laboratory Director

cc.
Doug Merrill

Sample Description (Duke Power Company) Proprietary Treatment Circulation #1

Anions	Milligrams per liter	Milliequiv. per liter
Nitrite Nitrogen (as NO_2)	0.068	< 0.01
Nitrate Nitrogen (as NO_3)	1.8	0.03
Chloride	20	0.56
Sulfate (as SO_4)	37	0.77
Bicarbonate (as HCO_3)	99	1.62
Carbonate (as CO_3)	0	0
H. Phosphate (as HPO_4)	1.7	0.04
H_2 Phosphate (as H_2PO_4)	2.8	0.03
Total Milliequivalents per Liter		3.05

Cations	Milligrams per liter	Milliequiv. per liter
Ammonium Nitrogen (as NH_4)	< 0.06	< 0.01
Sodium	29	1.26
Potassium	39	1.00
Calcium	12	0.60
Magnesium	4.3	0.35
Total Milliequivalents per Liter		3.21

Determination	Milligrams per liter
Phenolphthalein Alkalinity (as $CaCO_3$)	0
Methyl Orange Alkalinity (as $CaCO_3$)	82
Calcium Hardness (as $CaCO_3$)	30
Magnesium Hardness (as $CaCO_3$)	18
Dissolved Residue, Evaporated at 180°C	234
Dissolved Residue, Calculated	217
Nitrite Nitrogen (as N)	0.02
Nitrate Nitrogen (as N)	0.40
Ammonia Nitrogen (as N)	< 0.05
Organic Nitrogen (as N)	1.5
Total Nitrogen (as N)	1.92
Total Phosphate (as PO_4)	4.5
Silica (as SiO_2)	21
Specific Conductance, micromhos at 25°C	387
pH	6.6
Sodium (as % Cations)	----

Determination	Milligrams per liter
Fluoride	----
Total Kjeldahl Nitrogen (as N)	1.5
Total Inorganic Carbon	16
Total Organic Carbon	20
Total Suspended Solids	24
Copper	0.14
Bromide	< 1
Turbidity (NTU)	12

WASTEWATER ANALYSIS

BROWN AND CALDWELL
CONSULTING ENGINEERS
ENVIRONMENTAL SCIENCES DIVISION
1255 POWELL STREET
EMERYVILLE, CA 94608
PHONE (415) 428-2300

Log No. 26J3

Date Sampled 9/22/78
Date Received 10/06/78
Date Reported 11/07/78

Job No: 285-1

Report To: Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

Steven A. Fisher
Laboratory Director

cc. Doug Merrill

Sample Description (Duke Power Company) Proprietary Treatment Circulation #2

Anions	Milligrams per liter	Milliequiv. per liter
Nitrite Nitrogen (as NO_2)	0.045	< 0.01
Nitrate Nitrogen (as NO_3)	1.8	0.03
Chloride	24	0.68
Sulfate (as SO_4)	35	0.73
Bicarbonate (as HCO_3)	97	1.59
Carbonate (as CO_3)	0	0
H. Phosphate (as HPO_4)	1.2	0.02
H_2 Phosphate (as H_2PO_4)	1.5	0.02
Total Milliequivalents per Liter		3.07
Cations	**Milligrams per liter**	**Milliequiv. per liter**
Ammonium Nitrogen (as NH_4)	< 0.06	< 0.01
Sodium	30	1.31
Potassium	39	1.00
Calcium	12	0.60
Magnesium	4.2	0.35
Total Milliequivalents per Liter		3.26

Determination	Milligrams per liter
Phenolphthalein Alkalinity (as $CaCO_3$)	0
Methyl Orange Alkalinity (as $CaCO_3$)	80
Calcium Hardness (as $CaCO_3$)	30
Magnesium Hardness (as $CaCO_3$)	17
Dissolved Residue, Evaporated at 180°C	242
Dissolved Residue, Calculated	219
Nitrite Nitrogen (as N)	0.014
Nitrate Nitrogen (as N)	0.41
Ammonia Nitrogen (as N)	< 0.05
Organic Nitrogen (as N)	1.6
Total Nitrogen (as N)	2.02
Total Phosphate (as PO_4)	2.7
Silica (as SiO_2)	22
Specific Conductance, micromhos at 25°C	370
pH	6.7
Sodium (as % Cations)	----

Determination	Milligrams per liter
Fluoride	----
Total Kjeldahl Nitrogen (as N)	1.6
Total Inorganic Carbon	17
Total Organic Carbon	28
Total Suspended Solids	58
Copper	0.20
Bromide	< 1
Turbidity (NTU)	25

WASTEWATER ANALYSIS

BROWN AND CALDWELL
CONSULTING ENGINEERS
ENVIRONMENTAL SCIENCES DIVISION
1255 POWELL STREET
EMERYVILLE, CA 94608
PHONE (415) 428-2300

Log No. 26J4

Date Sampled 9/22/78
Date Received 10/06/78
Date Reported 11/07/78

Job No: 285-1

Report To:
Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

Laboratory Director

cc.
Doug Merrill

Sample Description (Duke Power Company) Ozone Treatment Circulation

Anions	Milligrams per liter	Milliequiv. per liter
Nitrite Nitrogen (as NO_2)	0.032	< 0.01
Nitrate Nitrogen (as NO_3)	24	0.39
Chloride	390	11.00
Sulfate (as SO_4)	743	15.45
Bicarbonate (as HCO_3)	549	9.00
Carbonate (as CO_3)	65	2.16
H. Phosphate (as HPO_4)	3.5	0.07
H_2 Phosphate (as H_2PO_4)	0	< 0.01
Total Milliequivalents per Liter		38.07

Cations	Milligrams per liter	Milliequiv. per liter
Ammonium Nitrogen (as NH_4)	0.14	< 0.01
Sodium	620	26.97
Potassium	82	2.10
Calcium	130	6.49
Magnesium	52	4.27
Total Milliequivalents per Liter		39.83

Determination	Milligrams per liter
Phenolphthalein Alkalinity (as $CaCO_3$)	54
Methyl Orange Alkalinity (as $CaCO_3$)	560
Calcium Hardness (as $CaCO_3$)	325
Magnesium Hardness (as $CaCO_3$)	214
Dissolved Residue, Evaporated at 180°C	2630
Dissolved Residue, Calculated	2526
Nitrite Nitrogen (as N)	0.010
Nitrate Nitrogen (as N)	5.3
Ammonia Nitrogen (as N)	0.110
Organic Nitrogen (as N)	4.0
Total Nitrogen (as N)	9.41
Total Phosphate (as PO_4)	3.5
Silica (as SiO_2)	146
Specific Conductance, micromhos at 25°C	4026
pH	8.8
Sodium (as % Cations)	----

Determination	Milligrams per liter
Fluoride	----
Total Kjeldahl Nitrogen (as N)	4.1
Total Inorganic Carbon	95
Total Organic Carbon	60
Total Suspended Solids	6
Copper	0.09
Bromide	< 1
Turbidity (NTU)	1.5

BROWN AND CALDWELL
CONSULTING ENGINEERS
ENVIRONMENTAL SCIENCES DIVISION
1255 POWELL STREET
EMERYVILLE, CA 94608
PHONE (415) 428-2300

Log No. 26J

Date Sampled 9/22/78
Date Received 10/06/78
Date Reported 11/07/78

Job No: 285-1

Report To:
Mr. Joe Drago
Brown and Caldwell
1501 North Broadway
Walnut Creek, CA 94596

Laboratory Director

cc.
Doug Merrill

Log No.	Sample Description
26J2	Duke Power Co., Filtered Circulation Water: Proprietary Treatment #1
26J3	Proprietary Treatment #2
26J4	Ozone Treatment

Results (mg/l unless indicated otherwise)

Sample Log No.	26J2	26J3	26J4			
Phenolphthalein Alkalinity (as $CaCO_3$)	0	0	17			
Methyl Orange Alkalinity (as $CaCO_3$)	82	76	479			
Calcium	12	12	130			
Magnesium	4.2	4.2	51			
Silica (as SiO_2)	21	21	137			
Sulfate	36	35	740			
Total Inorganic Carbon	17	18	96			
Total Phosphate (as PO_4)	2.1	2.5	3.5			

Foremost FOODS COMPANY
RESEARCH AND DEVELOPMENT CENTER
6363 CLARK AVENUE • DUBLIN, CALIFORNIA 94566
P.O. BOX 2277 TELEPHONE: AREA 415 - 828-1440

September 25, 1978
Reference: WR-79156

Mr. Ted Slyvester
Brown & Caldwell
Environmental Sciences Division
428 Jessie
San Francisco, CA

Dear Mr. Slyvester:

We have analyzed for volatile organics the nine water samples you submitted September 18, 1978. The results are submitted in Table I.

Please note that the results for sample 23C8 are estimates only.

Analyzed by,

Barbara I. Spruce
Chemist
Water Research

Approved by,

Warren C. Steele, Ph.D.
Project Leader
Water Research

BIS/WCS/dp
Attachment

cc: W.A. Hoskins,
Mgr. Contract Research
951-RI (12)

TABLE I. ANALYTICAL RESULTS

	CONCENTRATION, ppb								
SAMPLE IDENTIFICATION	23C1[a]	23C2[b]	23C3[c]	23C4[d]	23C5[e]	23C6[f]	23C7[g]	23C8[1,h]	23C9[i]
CHLOROFORM	42.0 ± 13.5	1.3 ± 0.4	87.0 ± 28.3	7.4 ± 2.4	2.7 ± 0.9	66.0 ± 21.6	5.6 ± 1.8	6	<1.0
1,1,1 TRICHLOROETHANE	<1.0	≈2	<1.0	<1.0	<1.0	<1.0	<1.0	<1	<1.0
BROMODICHLOROMETHANE	3.9 ± 0.6	ND	23.0 ± 3.7	<1.0	2.0 ± 0.4	43.0 ± 6.8	1.4 ± 0.2	20	ND
TRICHLOROETHYLENE	≈3	≈3	≈1	≈2	≈2	≈7	≈2	≈6	≈4
BENZENE	ND	ND	<1.0	ND	ND	<1.0	ND	<1	ND
DIBROMOCHLOROMETHANE	5.3 ± 2.0	<1.0	7.7 ± 2.2	4.2 ± 1.2	9.0 ± 2.6	ND	4.5 ± 1.3	7	4.8±1.4
BROMOFORM	<1.0	<1.0	<1.0	<1.0	<1.0	1.0 ± 0.3	<1.0	1	<1.0
TOLUENE	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1	<1.0

ND - not detected

[1] No area counts given due to instrument malfunction, concentrations are estimates only. No duplicates were submitted.

[a] Bullock's Sherman Oaks makeup water

[b] Bullock's Sherman Oaks circulating water

[c] JPL makeup water

[d] JPL circulating water-proprietary chemical tower

[e] JPL circulating water-ozone treated

[f] NBC Studios, makeup water

[g] NBC Studios, circulating water

[h] Bullock's main store makeup water

[i] Bullock's main store circulating water

Appendix D

MATERIAL BALANCE CALCULATIONS

The following are included in this Appendix:

1. Derivation of a formula for determining component X removed in the cooling circuit as a fraction of component X which entered in the makeup water; also an example of how the formula is used.

2. A calculation to determine if the cooling tower basins at NBC studios could hold all the chemical solids which could be precipitated during the periods between cleanings.

DERIVE A FORMULA FOR DETERMINING COMPONENT X REMOVED IN THE COOLING CIRCUIT AS A FRACTION OF COMPONENT X WHICH ENTERED IN THE MAKEUP WATER.

1. For component X, Eq. 1 is a steady state material balance on the circulating water. Within the limits of the steady state assumption, the balance is rigorous.

$$Q_m C_m + I = C_c (Q_b + Q_d + Q_s) + P \qquad (1)$$

Where:

Q_m = Makeup water flow, volume/time;

Q_b = Blowdown rate, volume/time;

Q_d = Drift loss, volume/time;

Q_s = Loss by splashing and leakage, volume/time;

C_m = Concentration of component X in the makeup water, mass/volume;

C_c = Concentration of component X in the circulating water, blowdown, drift, splashing and leakage, mass/volume;

P = Rate at which component X is removed from the cooling water by mechanisms other than blowdown, drift, splashing and leakage, e.g., precipitation or outgassing, mass/time;

I = Rate at which component X is added to the cooling water by sources other than the makeup water, e.g., scrubbing of materials from the atmosphere, by corrosion or as a treatment chemical, mass/time.

2. The amount of any component removed from the cooling water by precipitation or outgassing is defined by rearranging Eq. 1.

$$P = Q_m C_m + I - C_c (Q_b + Q_d + Q_s) \quad (2)$$

3. The ratio of the mass of component removed to its mass in the makeup water is obtained by dividing Eq. 2 by $Q_m C_m$.

$$FRACT = 1 - \frac{I}{Q_m C_m} - \left(\frac{C_c}{C_m}\right)\left(\frac{Q_b + Q_d + Q_s}{Q_m}\right) \quad (3)$$

Where;

FRACT = Fraction of component X in the makeup water which has been removed by precipitation or outgassing.

4. The ratio $\frac{C_c}{C_m}$ is defined as the concentration fractor F. This ratio can be determined by rearranging Eq. 1.

$$F = \frac{C_c}{C_m} = \frac{Q_m C_m + I - P}{C_m (Q_b + Q_d + Q_s)} \quad (4)$$

5. For the conserved component, i.e., a component whose concentration is affected only by simple concentration of the makeup water, I and P are zero. For these components, the concentration factor is known as the Cycles of Concentration (CYCLES).

$$CYCLES = \frac{C_c^*}{C_m^*} = \frac{Q_m}{Q_b + Q_d + Q_s} \quad (5)$$

Where:

C_c^* = Concentration of a conserved component in the circulating water, mass/volume;

C_m^* = Concentration of the same component in the makeup water, mass/volume.

The significance of the CYCLES term is that it provides a baseline measurement against which the appearance or disappearance of potentially nonconserved substances can be measured.

6. Substitute the definitions of F and CYCLES established in Eqs. 4 and 5 into Eq. 3.

$$FRACT = 1 - \frac{I}{Q_m C_m} - \frac{F}{CYCLES} \quad (6)$$

7. Eq. 6 is rigorous within the limits of the steady state assumption, but in this study could not be used since the rate at which materials were scrubbed from the atmosphere, added with proprietary chemicals or by corrosion (I) was not known. I was thus neglected, i.e., set equal to zero; the result is Eq. 7, which was used for all constituent removal calculations.

$$FRACT = 1 - \frac{F}{CYCLES} \quad (7)$$

Eq. 7 will be in error to the extent that I is not zero and the system deviates from the steady state. Nonvolatile, nonreactive species such as sodium, potassium and chloride were assumed conserved and used to calculate CYCLES.

8. Eq. 7 can be used to calculate removals of potentially nonconserved elements, such as calcium and magnesium. The basic approach is:

   a. First, calculate CYCLES for assumed conserved elements. For example, CYCLES, i.e., $\frac{C_c^*}{C_m^*}$, for chloride, sulfate, sodium and potassium for NBC Studios samples are calculated at 44.6, 44.0, 46.2, and 50.0, respectively. That they are not exactly the same may reflect small analytical errors or the fact that I or P may not be zero for each component. However, they are certainly sufficiently close for the purposes of this calculation. CYCLES is calculated as an average of the four values; CYCLES = 46.

   b. Next, determine the concentration factor for the potentially nonconserved species in question; for example:

      F for calcium is $\frac{620}{50} = 12.4$.

   c. Calculate FRACT, using Eq. 7:

      For calcium, FRACT = $1 - \frac{12.4}{46.0} = 0.73$.

      Seventy-three percent of the calcium which entered with the makeup water is estimated to be precipitated from solution.

Note that the fate of various species can be quickly discerned by glancing at the concentration factors. Species with concentration factors less than those of conserved elements have been removed, e.g., calcium, magnesium, alkalinity and

silica. Those with concentration factors greater then those of conserved elements have accumulated to values exceeding those which may be accounted for by simple concentration, e.g., nitrate.

COULD THE COOLING TOWER BASINS AT NBC STUDIOS HOLD ALL THE CHEMICAL SOLIDS WHICH COULD BE PRECIPITATED DURING THE PERIOD BETWEEN CLEANINGS?

1. Water balance

$$Q_m = Q_b + Q_d + Q_s + Q_e \tag{8}$$

where:

Q_m, Q_b, Q_d, and Q_s are as defined before, Q_e = evaporation, volume/time.

2. From Eq. 5, for conservative species, $\text{CYCLES} = \dfrac{Q_m}{Q_b + Q_d + Q_s}$.

3. Therefore;

a. $Q_b + Q_d + Q_s = \dfrac{Q_m}{\text{CYCLES}}$

b. $Q_m = \dfrac{Q_m}{\text{CYCLES}} + Q_e$

c. $Q_m \left(1 - \dfrac{1}{\text{CYCLES}}\right) = Q_e$

d. $Q_m = Q_e \left(\dfrac{\text{CYCLES}}{\text{CYCLES} - 1}\right)$ (9)

4. Rule of thumb: 3 gpm of water are evaporated for every 100 tons of refrigeration. Assume that on the average, NBC operates at half of its 2,200-ton capacity. Therefore, total evaporation in 9 months is:

$$\frac{3 \text{ gal}}{\text{min } 100 \text{ tons}} \times \frac{2{,}200 \text{ tons}}{2} \times \frac{1{,}440 \text{ min}}{\text{day}} \times \frac{30 \text{ days}}{\text{month}} \times 9 \text{ months}$$

$= 1.28 \times 10^7$ gal.

5. Assume 46 cycles of concentration are used. This was the condition for NBC at the time of sampling. By Eq. 9, $Q_m = 1.28 \times 10^7 \left(\dfrac{46}{46 - 1}\right)$ $= 1.31 \times 10^7$ gal.

6. The NBC analysis indicates the following conditions:

Constituent	Makeup water concentration, mg/l	Percent removal in tower	Milligrams removed per liter makeup water
Calcium	50	73	37
Magnesium	20	27	5.4
Alkalinity	120	96	115 as $CaCO_3$, 69 as CO_3^{-2}
Silica	10	73	7.3

Assume that calcium, magnesium and alkalinity are removed as magnesium calcium carbonate, where $MgCO_3$ is 20 percent of the compound. The formation of $Ca_4Mg(CO_3)_5$ is plausible as calcium, magnesium and carbonate are removed from NBC waters in the approximate molar ratios of 4:1:5. Silica is assumed to precipitate as SiO_2.

7. Mass removed per liter of makeup water fed = 37 + 5.4 + 69 + 7.3 = 119 mg/l.

8. According to NBC personnel, the period between cleanings is about 9 months. Total pounds of material removed from the makeup water over this period $= 1.31 \times 10^7$ gal $\times 3.785 \frac{l}{gal} \times 119 \frac{mg}{l} \times \frac{lb}{4.54 \times 10^5 mg}$ = 13,000 lbs. Assuming all solids settle in the tower basin, the settled material is 50 percent solids and 50 percent water, and its bulk specific gravity is 1.05, then the volume of precipitate which accumulates over a period of 9 months $= 13{,}000$ lb $\times \frac{lb\ slurry}{0.50\ lb\ solids} \times \frac{ft^3\ slurry}{1.05(62.4)lb\ slurry} = 396\ ft^3$.

9. According to NBC Studios personnel, three of the towers have basins which are flat pans 151 inches long by 109 inches wide with water depths of about 24 inches. The fourth tower basin has a vee bottom and is 290 inches long by 109 inches wide with water depth from the bottom of the vee of 34 inches. To simplify calculations, assume the fourth basin is flat. Total basin area is then roughly $\frac{3(109 \times 151) + (109 \times 290)}{144} = 562\ ft^2$. If the slurry was spread uniformly its depth would be $\frac{396}{562} \times 12 = 8.5$ inches. The basins could hold this amount of material very easily. Note, however, that NBC Studios personnel claim to remove much less than this when cleaning the basins, perhaps as little as an inch or two. This illustrates the difficulties which can arise when one attempts to simulate nine months of activity with calculations based on one grab sample. Clearly, calculations can only be verified by a long-term mass balance.