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CONDITIONING STUDY (Jet Propulsion Lab.)  
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# Cooling Tower Water Conditioning Study

M. F. Humphrey  
K. R. French

December 15, 1979

National Aeronautics and  
Space Administration

Jet Propulsion Laboratory  
California Institute of Technology  
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## ACKNOWLEDGEMENT

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The Maintenance and Service Section is to be thanked as a whole for the energetic manner in which it gave of its time and material for this research project.

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## ABSTRACT

Successful elimination of cooling tower treatment chemicals has been accomplished at JPL. Three towers have functioned for long periods of time with ozone as the only treatment for the water. The water in the systems has been reused as much as thirty (30) times (cycles of concentration) without deleterious effects to the heat exchangers. Actual system blow-down was eliminated and the only makeup water added was that required to replace the evaporation and mist entrainment losses. Minimum water savings alone are approximately 75.1 l/kg/year (18,000 gal/ton/year). Cost estimates indicate that a savings of 55 percent was obtained on the JPL systems using ozone. [This amounts to a cost savings of approximately \$0.024/kg/yr (\$22.00/ton/year) including labor.]

A major problem experienced in the use of ozone for cooling tower applications was the difficulty of accurate concentration measurements. The ability to control the operational characteristics relies on easily and accurately determined concentration levels. Present methods of detection are subject to inaccuracies because of interfering materials and the rapid destruction of the ozone.

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## SECTION I

### INTRODUCTION

#### A. BACKGROUND

In 1976 a study was initiated by the NASA Water and Liquid Waste Treatment Advisory Task Group (WLWTATG) to study the chemical treatment of cooling tower waters. The study was initiated by a desire to unify the many different materials used by the various NASA centers. Results of this initial Phase I work indicated that all the chemical materials examined were effective in treating cooling tower waters, if administered according to the manufacturer's recommendations (Reference 1-1).

During the Phase I chemical investigations, a nonchemical treatment system was also examined. This system consisted of an electrical device, located in the make-up water line, and a small ozone generator in the recycle line. Initial use of this system proved very effective in removing scale and maintaining a sanitized and descaled condition. Later it was determined that the electrical device was ineffective and only the ozone, injected into the tower water, was producing the desired scale control. Ozonation appeared to work for a time and then failed. It became evident that additional work would be required to define and resolve the ozonation problems.

#### B. DISCUSSION

Ozone (See Appendix A) is the strongest oxidizing agent available for use in pollution control and water treatment. It has been in general use in Europe for over 70 years to disinfect, deodorize, and decolorize potable water. Ozone has been proposed and used in conjunction with other devices and chemicals for cooling tower applications. However, most utilized the ozone as a disinfectant to replace chlorine and other types of nonoxidizing biocides. Several American entrepreneurs have marketed cooling tower treatment systems containing ozone generating capabilities coupled with other methods to prevent corrosion and control scaling.

Past cooling tower studies have shown that a major cause of scaling can be related to the organic and biological content of the water in the system (Reference 1-2). It was theorized that if control of these materials could be maintained, the system would be free of scale deposition and corrosion. One simple approach to the control of the organic materials was destruction by the use of ozone. Ozone is a powerful oxidizer and is known to be able to destroy most organic and biological contaminants with the production of carbon dioxide (CO<sub>2</sub>). This CO<sub>2</sub>, dissolved in the water, can combine with the soluble calcium ion to form a precipitate or it can force the equilibrium back to the more soluble calcium bicarbonate salt. In either case, the net result is the prevention of scale buildup in the system by removing slimy organic materials; these materials function as a matrix that holds the precipitated hardness components in the heat exchanger tubes. With destruction of this organic



mucilage, the calcium carbonate clumps into small nodules that can be removed as sand from the reservoir basin.

Experience in the Federal Republic of Germany (Reference 1-3) has shown that the growth of microorganisms can be accelerated in waste water previously ozonated. This indicates a breakup of the more refractory materials into shorter chain molecules. Water clarity may be related to these short chain materials that cause "microflocculation" of the organics into hardness components after "conditioning" with ozone. Ozone appears to be able to modify the natural humic acid components into synthetic-like polymers that provide these flocculation properties. These polymers can also trap hardness materials within the formed floc. More polar components are formed during ozonation, which change the adsorbability characteristics of the precipitated hardness materials. Inorganic materials such as iron, aluminum, and manganese present in the water are oxidized by ozone to hydroxides. These hydroxides can also act as coagulants. Negatively charged colloids entering the cooling tower in the air stream can be neutralized by  $O_3$ , which can act with a positive charge. Thus contaminating materials are removed by the combination of decomposition, oxidation, charge neutralization, and flocculation.

A Phase II program was designed and submitted to the WLWTATG, requesting that ozone be examined as the sole cooling tower treatment material. Cost estimations indicated major savings in energy, water consumption, and chemicals could be realized if ozone alone could be shown to be an effective treatment. Additional savings would be realized by the standardization of treatment at all NASA centers.

## SECTION II

### OBJECTIVE AND RELATED QUESTIONS

The objective of the original Phase II plan included a provision for studying the effectivities of nonchemical water treating devices. In view of the excellent results being obtained with the ozonation experimentation, a request to eliminate the nonchemical devices was made and granted.

Specifically, the Phase II effort was authorized and begun with the objective of evaluating and characterizing the most effective methods of using ozone. Additional questions were also to be addressed during the program such as:

- (1) How effective is ozone and how long can its effectivity be maintained?
- (2) How can ozone be added to the system, how can it be monitored?
- (3) What materials will withstand ozone?
- (4) How many cycles of water concentration use can be maintained?
- (5) What are the effective concentrations in the water?
- (6) Can low-cost ozonation equipment be constructed?

During this Phase II study, the engineering consultant firm at Brown and Caldwell (Reference 2-1) approached JPL and requested the right to examine the cooling tower ozone experiments. The study was funded by the Electric Power Research Institute (EPRI) in San Francisco, to ascertain the implications of ozone treatment for power plant use. Several sites were being surveyed that used ozone in various ways including some in conjunction with electrical devices. Principal subjects of the Brown and Caldwell study were: NBC Studios, Burbank, California; JPL, Pasadena, California; Bullock's Department Store, Sherman Oaks, California; Bullock's Main Department Store, Los Angeles, California; and Duke University Medical Center, Durham, North Carolina.

The Brown and Caldwell study was designed to examine the following:

- (1) Material compositions of all make-up and recirculating waters, including scaling or corrosion parameters.
- (2) Methods of ozone addition and monitoring for control.
- (3) Concentrations and effects of trihalomethanes, oxidant residuals, trace metal contaminants, and biological populations.

Results of this testing program and the recommendations of Brown and Caldwell indicated that ozone treatment warrants further study for application at electric power plants. One very important conclusion of the Brown and Caldwell study is in agreement with JPL's findings (see

Section V), namely that the limits of applicable conditions must be determined, i.e., temperatures, concentrations, effects on the environment, and costs.

## SECTION III

### APPROACH AND PREPARATION

In a meeting with the JPL Plant Maintenance and Service Section of the Facilities Division, it was decided to utilize three standard cooling towers for this study. Towers were selected on the basis of size, type of construction, and ease with which results could be monitored in the associated heat-exchanger equipment. None of the towers were cleaned or chemically prepared in any way. Heat exchangers were cleaned with inhibited hydrochloric acid. The conditions of all the tube bundles were examined before placing the systems on ozone.

Cooling towers chosen for the study were of different sizes, i.e.,  $9.45 \times 10^8$ ,  $31.6 \times 10^8$ , and  $44.1 \times 10^8$  J (75, 250, and 350 tons), respectively. (The  $31.6 \times 10^8$  J (250-ton) tower (Number 215) had previously been placed on ozone as a result of the Phase I study.) Initial instrumentation and hook-ups were made as indicated in Figure 3-1. Progress and condition of the cooling towers during the experimentation were monitored and controlled as described in Subsections A through K (see Cooling Tower Summary, Appendix B).

#### A. TOWERS

The three towers chosen were of different constructions and also located in different service atmospheres.

- (1) Tower Number 200 [ $9.45 \times 10^8$  J (75 tons)]: a small air-conditioning system located near the facilities maintenance area in a very "dirty" atmosphere. This tower was subjected to hydrocarbon vapors from pipe cutting operations and solvent vapors from the paint shop. Construction was galvanized steel with plastic fill. Circulation in the system was 851.62 l/min (225 gal/min).
- (2) Tower Number 215 [ $31.6 \times 10^8$  J (250 tons)] (Figure 3-2): the tower is made of redwood. It has a shallow reservoir with a deeper sump feeding the recirculation pumps located a distance greater than 211.25 m (65 ft) away. This tower is located near a road with vehicular traffic.
- (3) Tower Number 238 [ $44.1 \times 10^8$  J (350 tons)] (Figure 3-3): two 15,874-kg (175-ton) towers operated together constitute this system. Construction is of galvanized steel with plastic fill. This system is located away from traffic and other sources of contamination.

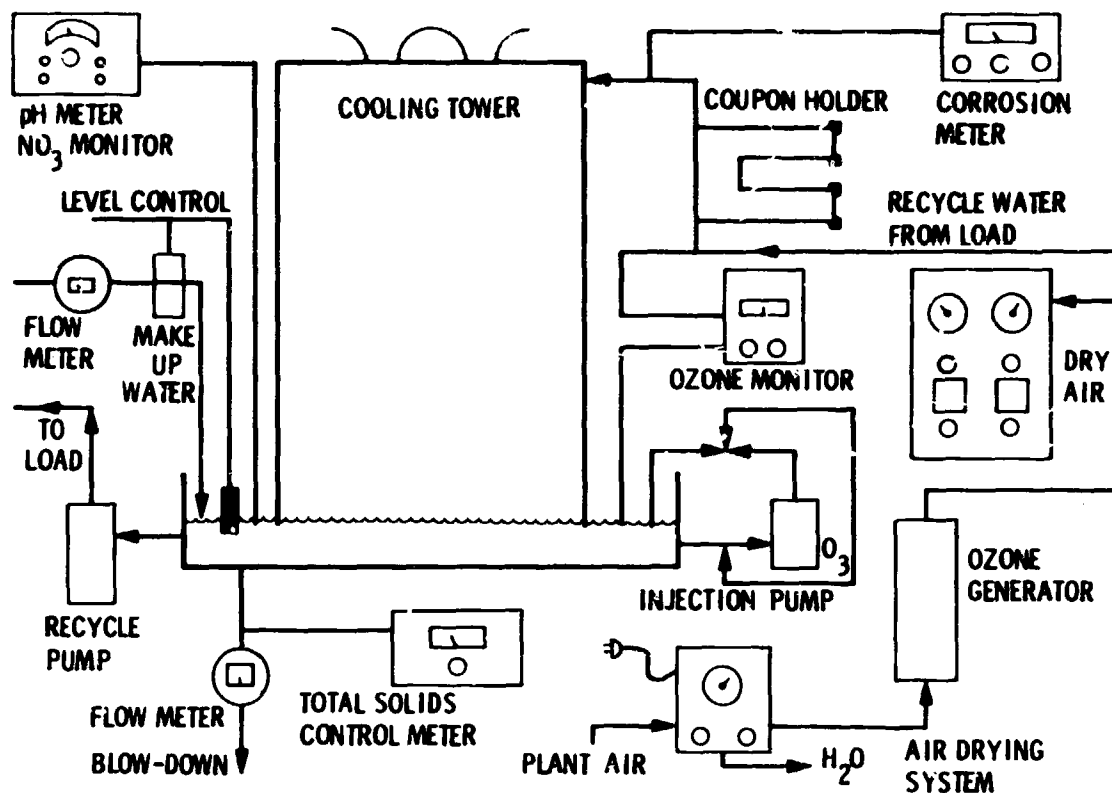


Figure 3-1. Representative Experimental System

B. OZONE GENERATION (SEE APPENDIX C)

Each tower system was equipped with an ozone generator as follows:

- (1) Tower Number 200: a small Source Gas Analyzers (SGA) ozone generator (producing 0.7 g/h of ozone) was installed. Because of the ozone demand of this location, the unit was rebuilt to produce 1.4 g/h. It was later substituted with a larger homemade unit able to produce 4.8 g/h.
- (2) Tower Number 215: This tower was originally equipped in April of 1977 with a Welsbach ozone generator capable of producing 4.0 g/h (Reference 3-1). It was later reequipped with an additional capacity of 1.4 g/h.
- (3) Tower Number 238: a Welsbach generator with a capacity of 8 g/h (Reference 3-1) was installed on this tower.

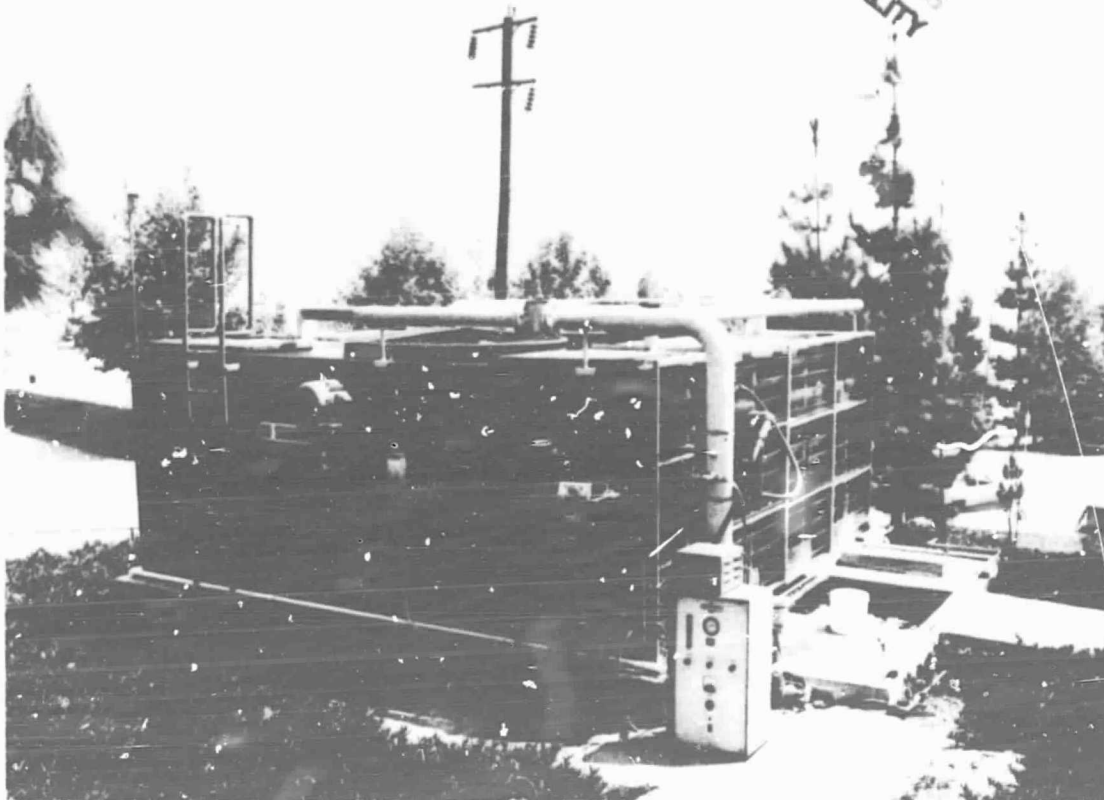


Figure 3-2. Tower Number 215

### C. AIR DRYING

After the program was begun, it was determined that dry air was essential to the production of ozone. Therefore the following equipment was procured, constructed, and installed on the towers as indicated:

- (1) Tower Number 200 and Tower Number 215: two 0.014-m (2-1/2-in) diameter by 0.923-m (3-ft) long glass desiccant tubes were constructed and filled with three pounds of silica gel (colored blue to indicate a dry condition - colored tan or pink when exhausted). These columns were attached to the ozonators with plumbing to allow one column to be used at a time. Semidry, plant-compressed air was run to the dryers. Provision was also made to remove and regenerate the silica gel when it indicated exhaustion.
- (2) Tower Number 238: this system utilized a purchased, refrigerated drying unit [Hankisan Model Number 8010, 0.2831 m<sup>2</sup>/min (10 SCFM) at 689,400 N/m<sup>2</sup> (100 psig) capacity]. Dry plant

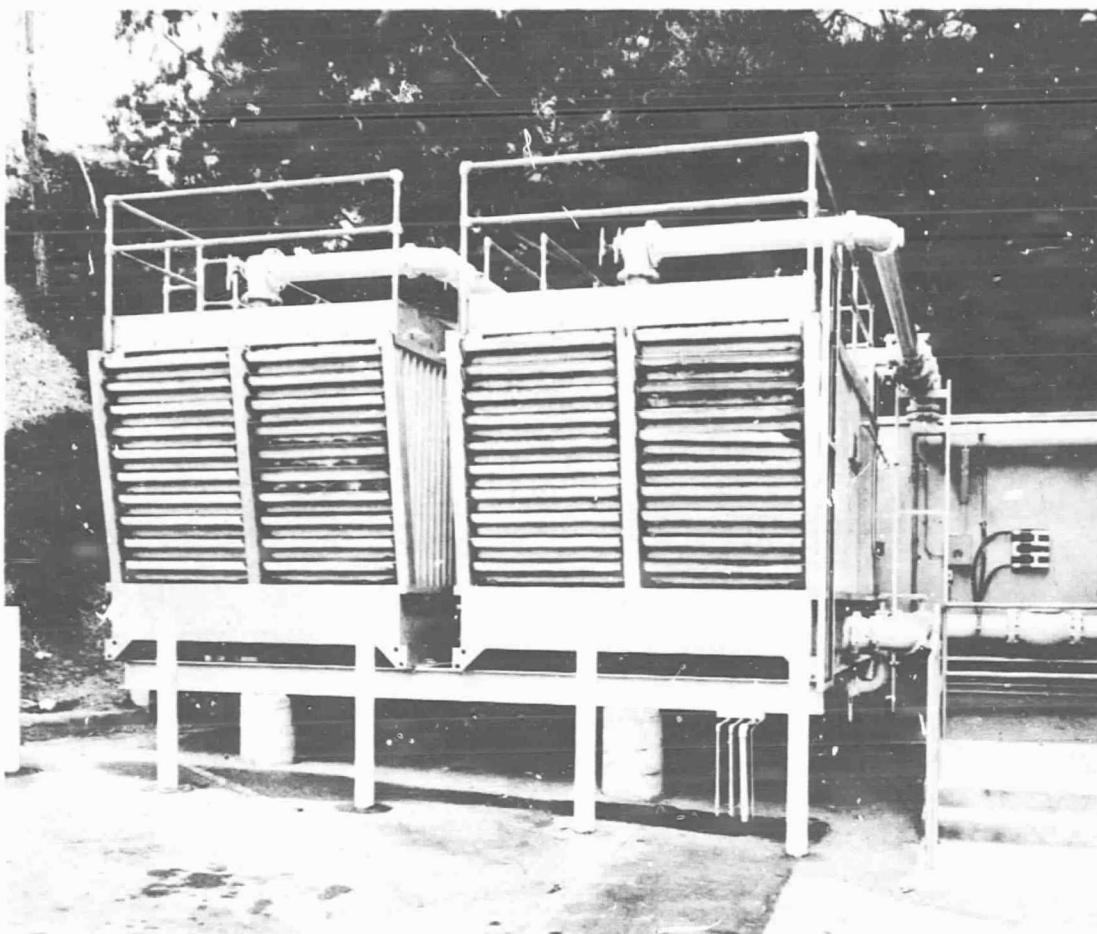


Figure 3-3. Cooling Tower Number 238

air was supplied to this unit and the air from the unit was run through a desiccant column described above.

#### D. CORROSION METER

A Magma Corratel was installed on Tower Number 215. Only one electrode probe assembly was supplied with the instrument so another one was constructed. This allowed both steel and copper corrosion rates to be determined. Relative corrosion rates could now be compared with the actual corrosion coupons.

#### E. CORROSION COUPONS

Each tower system had a corrosion coupon holder installed. Copper and steel coupons were used in the return flow lines from the heat exchangers.

#### F. OZONE INJECTION SYSTEMS

- (1) Tower Number 200: ozone was originally injected into the suction side of the recirculating pump used for the cooling tower. This was changed to a venturi aspirator fed into the tower reservoir through a small line on the pressure side of the recirculation pump.
- (2) Tower Number 215: ozone was injected into the suction side of a small 559.5-W (3/4-hp) centrifugal pump and recycled into the tower basin. Packing in the pump required frequent changing due to the sensitivity to ozone. A venturi aspirator was installed on the pressure side of a pump submerged in the sump and the ozone fed into the partial vacuum. This line discharged into the tower reservoir.
- (3) Tower Number 238: this system was originally set up with a recirculation pump feed but was later changed to the aspirator method to prevent ozone attack to the pump.

#### G. TOTAL SOLIDS CONTROL

Each cooling tower system had a small adjustable total dissolved solids controller (Presto-Tek) installed on the blow-down line. The device was set at different total solids on each tower.

#### H. FLOW METERS

Flow meters were installed on the make-up water lines of each tower.

#### I. pH

A pH was monitored in each tower using a portable instrument.

#### J. OZONE MONITOR

An efficient instrument for monitoring ozone could not be located; therefore, ozone concentrations were determined by two alternate methods:

- (1) A Hach ozone test kit (Model OZ-1): this kit based on orthotolidine (see Appendix D) produces an intense yellow color directly proportional to the ozone concentration. Interferences of iron and manganese were removed with sodium arsenite solution.
- (2) Iodometric titration: this method is more sensitive than the above test. It involves the oxidation of potassium iodide to iodine in acid solution (Reference 3-2).



K. WATER BACTERIA POPULATION MONITOR

A total-count test kit (Mogulab Kit II) was obtained for use in the field to monitor the disinfectant level of performance of the ozonated water in the towers.

## SECTION IV

### RESULTS

#### A. COOLING TOWER NUMBER 200 [ $9.45 \times 10^8$ -J (75-ton)]

This cooling tower was located in the maintenance area where it was subjected to paint solvent vapors and hydrocarbon materials from cutting oils. The system was outfitted with ozone on April 5, 1978, using a generator producing 0.7 grams of ozone per hour. Tubes in the heat exchanger had previously been cleaned (March 30, 1978) with inhibited acid. Little or no algae kill was experienced during the first week of operation at a generated ozone level of 0.010 mg/kg/h (9.3 mg/ton/h). Actual ozone concentration in the water was 0.010 mg/l. This low level of ozone was caused by the high ozone demand of the materials being drawn through the cooling tower water.

After a week of operation, the ozone generator was removed, torn down and rebuilt with a design developed at JPL. This modification doubled the ozone production to 0.020 mg/kg/h (18.7 mg/ton/h).

A total solids controller was installed on the blow-down line, and the recycling water set to a total dissolved solids (TDS) content of approximately 1000 mg/l. The system required flushing with sulfamic acid after one month of operation because of algae and scaling. Also, the ozone concentration could not be maintained. Troubles were also experienced with the design of the corona tube generators. Shorting developed at the high-voltage terminals, which necessitated redesigning the hardware and the method of attaching the leads.

By June of 1978, it was decided that the concentration of ozone was not sufficient to treat this system due to the high influx of oxidizable material. Therefore, another generator was installed and the produced ozone raised to a level of 0.070 mg/kg/h (64 mg/ton/h). This dosage proved sufficient to maintain a disinfected and clean system. It has been operating up to the present time.

Other problems were encountered that involved the feeding and mixing of the ozone into the water. This problem has not been completely solved; however, it was determined that the best method to date is to add the ozone by aspirator and not into the suction side of a pump.

Tower Number 200, after eight months of continuous operation on ozone, was drained and the reservoir cleaned of sand-like solids. The heat exchanger was inspected and found to be in good condition with little or no scaling (water in this system has been used for approximately 14 cycles [cycles of concentration]).

#### B. COOLING TOWER NUMBER 215 [ $31.6 \times 10^8$ -J (250-ton)]

All normal chemical treatment for this cooling tower was suspended in March of 1977. Ozone treatment was begun on April 13, 1977. Blow-down

on bleed water was turned off on May 10, 1977. This tower has been in continuous operation for 23 months without blow-down and with the scale water treatment accomplished with ozone. The cycles of concentration are approaching 33.

The tower condition is good. Heat exchangers have been examined every three months and are in excellent condition. Scaling can be detected on areas of the transite slats of the tower where the water evaporates. This is due to the high concentration of dissolved solids in the water. Hardness materials such as calcium carbonate are being precipitated in the tower reservoir as a sand. Periodic removal of this sand has been accomplished by vacuuming the basin.

Evaporation rate and drift rate have averaged approximately 11,355 liters (3000 gal) per day. This has caused a leveling off of the TDS in the system. It was desired to increase the TDS to a level comparable to the ozone treated towers at the National Broadcasting Company (NBC) (See Appendix E). NBC has been operating  $277 \times 10^8$ -J (2200-ton) cooling towers at a TDS level of 13,400 mg/l, with most of the TDS contributed by sodium chloride. Ozone is injected into the NBC recirculation water at an estimated rate of 0.0029 mg/kg/h (2.63 mg/ton/h). This concentration is only 10 percent of the JPL experience. It is believed that the high salinity content may be contributing to the operational capabilities at NBC. Another anomaly noted was in the comparison concentrations of nitrates between JPL and NBC. Air drying equipment is utilized at JPL whereas NBC does not appear to maintain a separate air drying capability (see Appendix F). Nitrogen compound accumulation at NBC seems to be 2-1/2 times that at JPL. Nitrate concentration can also contribute nutrients for algae growth, which will increase the overall ozone demand in the system.

Concentration of the dissolved solids in Tower Number 215 is being maintained at approximately 3000 mg/l. Ozone was initially injected at a rate of 0.017 mg/kg/h (16 mg/ton/h). This rate was found to be insufficient for this system as biological slimes developed. The rate of ozone addition was increased to 0.024 mg/kg/h (21.6 mg/ton/h) and the slimes disappeared. pH of the water increased to 8.0 and has remained constant.

As the TDS in the tower system increased, the indicated concentration of ozone increased in the recirculating water. It was theorized this was due to the oxidation of chlorides to chlorine. The stability of chlorine in the water is measured in hours due to the formation of hypochlorous acid, but ozone is decomposed very rapidly under the same conditions (see Appendix G).

#### C. COOLING TOWER NUMBER 238 [ $44.1 \times 10^8$ -J (350-ton)]

An 8-g/h ozone generator was installed on this tower on March 31, 1978. Plant air was piped into a refrigerated dryer. A total solids controller was placed on the blow-down line. It was desired to maintain a TDS level of approximately 700 mg/l in this system. The heat exchangers were cleaned before starting ozone but the tower was not cleaned. Six

days after an ozone rate of 0.025 mg/kg/h (23 mg/ton/h) was achieved, the scale coating on the plastic fill began falling off. Tower water became cloudy and the basin had to be vacuumed after nine days of running. Scale solids continued to be removed from the fill material and required several additional vacuumings.

Ozone was being injected into this tower through the suction side of a bronze, 559.5-W (3/4-hp) centrifugal pump. After two months of running, the pump had to be repaired because of ozone attack. The resistances of other materials are indicated in Appendix H. It was decided to inject the ozone with an aspirator on the pressure side of the pump. To date, this cooling tower and system has been functioning for nine continuous months without any chemicals or maintenance.

#### D. CORROSION

Coupon holders were built and installed on each of the three tower systems. Each holder contained mild steel and copper specimens. The following corrosion rates were obtained:

SPECIMEN, mm/yr (mils/yr)	Tower		
	No. 200	No. 215	No. 238
Copper	$0.88 \times 10^{-3}$ (0.0346)	$0.3 \times 10^{-3}$ (0.012)	$1.175 \times 10^{-3}$ (0.047)
Magna Corrator	<sub>a</sub>	<sub>a</sub>	<sub>a</sub>
Steel	0.055 (2.20)	0.042 (1.70)	0.04 (1.60)
Magna Corrator	<0.125 (<5.0)	<0.125 (<5.0)	<0.125 (<5.0)

<sup>a</sup>Too low to indicate.

Some pitting was observed upon cleaning the steel coupons. A white coating of calcium carbonate was observed on the uncleaned steel coupons along with patches of red iron oxide. The deposit observed on these coupons was different than that seen in the heat exchangers. Black iron oxide appears to be the material generated on the steel surfaces of the exchanger heads. Copper coupons appeared identical to the originals before exposure but slightly darker in color. The corrosion coupons confirmed the very low rate of attack with ozonated water. Water in the tower systems attains and maintains a pH of about 8.0 to 8.5.

#### E. OZONE CONCENTRATION

Problems have been encountered in monitoring the concentration of ozone in the waters of the towers. Using the orthotolidine reagent (see Appendix D), inconsistencies were noted between the iodometric titration, amperometric and the commercial test kit. An interesting observation noted was the effect of the TDS on the ozone concentration. As the TDS increased, so did the ozone concentration test results. Additional testing to determine the cause was beyond the scope of this study.

An ozone detecting electrode was noted in the literature, but the manufacturer (Delta Scientific) was unable to supply a unit for testing.

#### F. COST

A cost estimation and comparison was made for chemical versus ozone treatment, based on the actual experience generated over 21 months of Tower Number 215 operation. (See Appendix I.)

Four different chemical-type control functions are required for complete treatment in a chemical system. These categories of control are: pH, scale, corrosion, and biological. Control of the biological system may be the most critical. With most biological treatment materials, the biospecies develop resistance to the biocides. This condition requires "shocking" or alternating treatment with different materials. No resistance of the biota can be built up with ozone because the organisms are completely destroyed by the ozone.

The major cost difference appears to be the expenditure for excessive water usage. Using a blow-down rate of 0.00834 l/kg/h (2 gal/ton/h) (as recommended by a chemical water treating company) and a water cost of \$0.1666/l (\$0.63/1000 gal), ozone will save approximately \$0.012/kg/yr (\$11.00/ton/year) over chemical treatment. Labor costs were estimated from actual experience with a comparison tower (Number 165) being treated with chemical. Maintenance and clean-out were responsible for a difference of \$0.004/kg/yr (\$3.35/ton/yr). The total savings, including labor on the Number 215-size cooling tower systems was \$0.024/kg/yr (\$21.76/ton/yr).

## SECTION V

### CONCLUSIONS AND RECOMMENDATIONS

Ozone has been shown to be an effective treatment for cooling-tower water. It was shown to attack and remove existing scale deposits. Since no adulterating chemicals were used, the blow-down and tower drift were ecologically acceptable. The water circulating in the tower basins was always crystal clear without objectionable odors. Raw-water usage was greatly reduced along with the energy and operational maintenance costs.

Actual mechanisms responsible for the workability of ozone are not known. There are indications that micro-organisms and the products of their metabolism are heavily involved in the scaling and corrosion processes, and it is possible that the products of ozone destruction are responsible for coagulated and precipitated hardness components. There is, however, a need to detect and monitor the ozonation operation. This experimentation utilized a continuous generation and injection into the system of small amounts of ozone. A more efficient system could be designed if the concentration could be automatically monitored and the production of ozone adjusted to the varying conditions of the system. Ambient atmospheric conditions should be related to tower conditions and used to control the ozone application. Because the application and use of ozone appears critical, a very important parameter is the fail-safe alarm. After a system has been acclimatized to ozone, any interruption in ozone service for more than approximately 48 hours (the exact time is not yet established) can cause extensive scaling. Some form of alarm or action signal (such as increasing blow-down flow) is required to prevent heat exchanger problems.

Efficient methods of injecting ozone in the system are also needed. To obtain maximum use of the smallest quantity of ozone, it is very important to obtain good and rapid mixing in the water. Most methods using bubbling or injection into a moving stream or pump are not sufficient. These methods are also contrary to Henry's law of mass transfer of gases into a liquid. When the bubble of ozone bursts at a water/air interface, the undissolved ozone is released into the gas phase and dissipated. As much as 30 percent of the ozone is lost in this way.

Ozone can be a great asset in reducing cooling tower costs and saving energy. It can also prevent the dumping of ecologically unacceptable material into waterways. The study of ozonation in cooling towers should be continued to:

- (1) Identify the limits of temperature, ambient conditions, and ozone concentrations on operational characteristics.
- (2) Monitor and detect ozone concentrations to allow adaptation to automatic control.
- (3) Examine the effects of ozone on the water and the materials produced. Oxidant residuals should be identified and relative toxicities determined.

- (4) Engineering evaluations and new designs for water-type cooling equipment and cost analyses should be generated.
- (5) Test ozonation in a larger-size system to determine scalability.

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APPENDIX A  
PROPERTIES OF OZONE

Ozone is a gas and a natural ingredient of the earth's atmosphere. It is generated by the action of solar ultraviolet light (short wavelengths) on oxygen atoms in the stratosphere. Ozone is also produced by natural electrical discharges such as lightning. Ozone is second only to fluorine in the electronegative oxidation potential and will oxidize most organic materials and a great many inorganic substances. Its reactions are very numerous. It is an ideal bactericide and virucide. The decomposition product of the unused or unreacted ozone is simply oxygen.

Ozone is an allotropic form of oxygen. An ozone molecule contains three atoms of oxygen whereas an oxygen molecule contains only two atoms. This extra oxygen atom produces the great differences in the properties of the two materials.

Due to the unstable nature of ozone, it must be produced where and when it is to be used. At present there is no known method of safely storing ozone. It has been liquidized but it is very sensitive to explosion in that state. There are three major methods for the production of ozone; (1) ultraviolet light, (2) electrical corona or spark discharge, and (3) the electrolysis of perchloric acid. Most commercial ozone generators operate on the more efficient silent electrical or corona discharge principal.

Oxygen can be used as the raw material for ozone production. It is usually used for commercial applications where cryogenic oxygen is available and where the unused oxygen can be recycled into the generation equipment.

For small operations where the oxygen cannot be recycled, air is the major raw material. When air is used for the production of ozone, it must be dry. Any moisture present in the feed air (as humidity) will reduce the amount of ozone produced. Moisture in the air acts as a catalyst for the fixation of nitrogen. As the concentration of moisture increases, the amount of nitrogen pentoxide ( $N_2O_5$ ) and nitrous oxide ( $N_2O$ ) produced increases, resulting in a decrease in the concentration of ozone. This  $N_2O_5$  can dissolve in moisture, producing nitric acid that can then attack metal surfaces of the system.

Ozone is not considered a dangerous poison because it can easily be detected by smell in low concentrations. It is a strong oxidizing agent, however, and low concentrations can produce nasal, bronchial, and pulmonary membrane damage. Toxicity is dependent upon two factors: concentration and length of exposure. The government has established a maximum concentration level for the gas as 0.1 ppm (by volume) for continuous exposure. Detection of ozone by odor occurs at 0.01 to 0.02 ppm. Long before a toxic concentration is reached, the symptomatic results of coughing, nausea, and eyewatering occur.

Properties of Pure Ozone

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Molecular weight	48
Boiling point, °C	-111.9
Freezing point, °C	-192.5
Critical temperature, °C	-12.1
Critical pressure, N/m <sup>2</sup> (atmospheres)	55.3 x 10 <sup>5</sup> (54.6)
Density, at 195.5°C, liquid g/ml	1.613
Density of gas at 0°C, 2.182 x 10 <sup>5</sup> N/m <sup>2</sup> (1 atm); gm/l	2.154
Heat capacity (C <sub>p</sub> ) at -111.9°C, J/°C/mole (cal/deg/mole)	33.47 (8)
Heat of vaporization at -111.9°C J/mole (cal/mole)	4,267 (3410)
Heat of formation (gas), J/mole (cal/mole)	142,256 (34,000)
Heat of formation (aqueous solution), J/mole (cal/mole)	134,725 (32,200)
Surface tension, N/cm (dynes/cm) at 182.7°C	38.1 x 10 <sup>-5</sup> (38.1)

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APPENDIX B  
COOLING TOWER SUMMARY SHEET

Parameter	Cooling Tower Number		
	200	215	238
Size, J (tons)	9.45 x 10 <sup>8</sup> (75)	31.6 x 10 <sup>8</sup> (250)	44.1 x 10 <sup>8</sup> (350)
O <sub>3</sub> date started	3/28/78	6/9/77	5/31/78
Duration (to date), month	12	21	10
System volume, liters (gal)	757 (200)	12,869 (3400)	9,273 (2450)
Recirculation rate, L/min (gal/min)	852 (225)	2,838 (750)	5,677 (1500)
Ozone injection, mg/kg/h (mg/ton/h)	0.07 (64)	0.024 (21.6)	0.025 (23)
TDS (set), mg/l	1200	3000	750
Air supply for drying	Plant air, silica gel (heat regenerated)	Plant air, silica gel (heat regenerated)	Plant air, silica gel, refrigeration (heat regenerated) 8.0
O <sub>3</sub> generation capacity, gm/h	4.8	5.4	8.0
Corrosion coupons	Copper and steel	Copper and steel	Copper and steel
O <sub>3</sub> injection system	Aspirator	Submerged pump, aspirator	Recirculation pump, aspirator
Tower construction	Gal. steel, plastic fill	Wood, transite fill	Gal. steel, plastic fill
TDS, conductivity and pH, turbidity and Δ temp	Monitored daily	Monitored daily	Monitored daily
Water consumption, average L/day (gal/day)	2270 (600)	11,355 (3000)	Not determined
Heat exchangers, Δ temp	Recorded daily (normal)	Recorded daily (normal)	Recorded daily (normal)

APPENDIX C  
OZONE GENERATORS USED

Parameter	Welsbach		SGA <sup>a</sup>		JPL Unit <sup>b</sup>
	T-408	T-816	As received	Rebuilt	
Rate of ozone production, gm/h					
From dry air at 1% by wt. <sup>c</sup>	4	8	0.7	3.2	4.8
From O <sub>2</sub> at 1.75% by wt.	8	16	1.4	6.4	9.6
Feed gas 55.1 x 10 <sup>3</sup> N/m <sup>2</sup> (8 psig) pressure, m <sup>3</sup> /min (SCFM)	0.0037 (0.13)	0.0074 (0.26)	-	-	-
Cooling water, l/h (gal/h)	18.9 (5)	37.85 (10)	Air cooled	Air cooled	Air cooled
Electrical					
Power, watts	120	240	30	90	150
Volts	115	115	115	115	Varied
Cycles/s	60	60	300	300	60
kWh/kg (kWh/lb)	6.18 (13.62)	6.18 (13.62)	8.83 (19.45)	5.76 (12.7)	6.45 (14.2)
Type Discharge	Brush	Brush	Corona	Corona	Corona

<sup>a</sup>SGA - Source Gas Analyzer Company.

<sup>b</sup>Unit designed and built by JPL.

<sup>c</sup>Ozone concentrations in air can be increased to 4% (or higher) by varying the following: dew point of the air, frequency of the electrical, power, primary voltage, and/or the air flow rate and the cooling capacity of the unit.

APPENDIX D  
OZONE TEST



(From Reference 3-2: orthotolidine)

A. General

In the ozone determination, iron and manganese oxides interfere. A solution of sodium arsenite is used to prevent these materials from interfering.

Reagent orthotolidine: 1.35 g of orthotolidine dihydrochloride is dissolved in 500 ml of distilled water. This solution is then added to a solution of 350 ml of distilled water and 150 ml of concentrated hydrochloric acid. The reagent is stored in dark bottles.

Sodium thiosulphate solution, chlorine neutralizer: dissolve 10 g of sodium thiosulphate in 1000 ml of distilled water.

Sodium arsenite solution: dissolve 5 grams of sodium arsenite ( $\text{NaAsO}_2$ ) in 1000 ml of distilled water.

B. Test

A 50-ml sample is obtained and treated as follows:

- (1) 2 ml of sodium thiosulphate solution is added and the bottle shaken.
- (2) 5 ml of orthotolidine reagent added and the sample shaken.
- (3) If interfering materials of iron or manganese are present, 1 ml of sodium arsenite solution is required.
- (4) Repeat the above reagent additions in 50 ml of tap water blank.
- (5) Compare colors of the two samples on a spectrophotometer at 400 to 450 m. The spectrophotometer must be previously standardized with known concentrations. The color developed by this test approximates the color and intensity developed by chlorine.

APPENDIX E  
WATER ANALYSES RESULTS

Parameter	Test Comparison						
	1	2	3	4	5	6	7
Alkalinity P <sup>a</sup> (CaCO <sub>3</sub> ), mg/l	0	84	-	2.4	5.0	30	12
Alkalinity M <sup>b</sup> (CaCO <sub>3</sub> ), mg/l	184	572	-	2.4	6.4	180	233
Calcium hardness, mg/l	123	123	359	80	27	162	620
Magnesium hardness, mg/l	82	1328	-	45	879	25	670
Total dissolved solids, mg/l	260	3330	-	252	3052	280	13,400
Silica, mg/l	23	111	118	8	70	4	125
pH	7.9	9.2	8.9	7.8	9.0	7.8	8.7
Nitrate, mg/l	0.95	71	-	20	290	-	104
Chloride, mg/l	14	459	100	21	469	15	2500

Test No.:

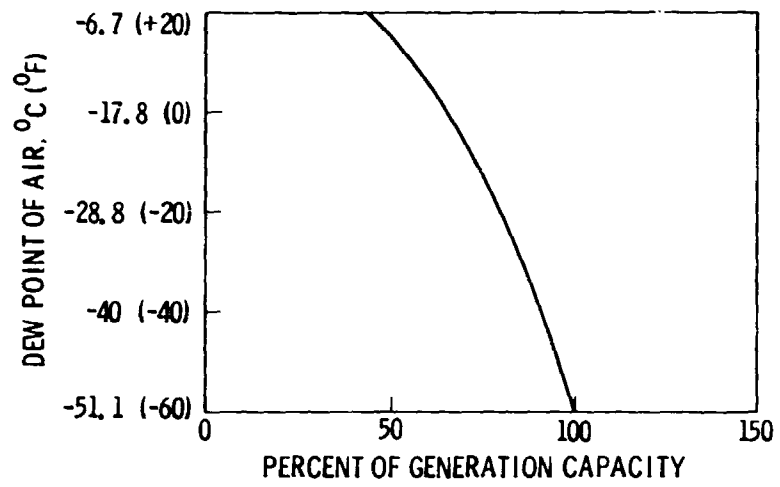
1. JPL make up water - Brown and Caldwell tested.
2. Tower No. 215 water - Brown and Caldwell tested.
3. Tower No. 215 - Calgon tested.
4. JPL make up water - JPL tested.
5. Tower No. 215 - JPL tested.
6. JPL previous make up water - JPL tested.
7. NBC cooling tower water - Brown and Caldwell tested.

<sup>a</sup> Phenolphthalein end point.

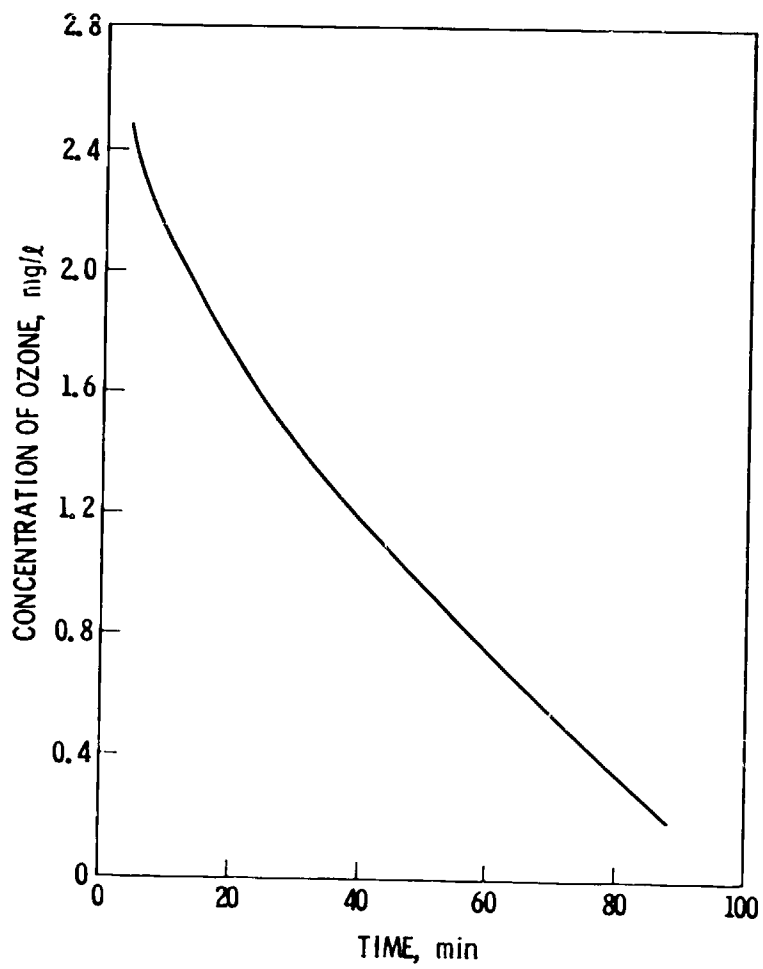
<sup>b</sup> Methyl-orange end point.

APPENDIX F

OZONE PRODUCTION vs AIR  
DRYNESS (CORONA-TYPE GENERATORS)  
(Reference F-1)



APPENDIX G  
DECOMPOSITION OF OZONE IN  
WATER (20°)  
(Reference F-1)



APPENDIX H  
EFFECTS OF OZONE ON VARIOUS  
MATERIALS



Material	Comment
Bronze	No apparent attack - some darkening.
Copper	Blackened by oxidation, surface is passivated by copper oxide.
Brass	Ozone removes the zinc leaving a porous copper.
Iron and steel	Surface oxidation, but little corrosion attack. Surface passivated.
Aluminum	Some alloys are easily attacked and oxidized.
Stainless steel	
AISI 400 series AISI 300 series	Generally acceptable wet or dry. Generally acceptable wet or dry.
Zinc and galvanizing	Completely unacceptable.
Plastics	Only Teflon can withstand constant use at high concentrations.
Rubber	Ethylene-propylene copolymer is only material acceptable.
Wood	Lignin of wood can be attacked at high O <sub>3</sub> concentrations.
Ceramics and glass	Acceptable at all concentrations.
Copper catalyzes the destruction of ozone.	

APPENDIX I  
COST ESTIMATION COMPARISON

Chemical vs Ozone Treatment Based on 31.6 x 10<sup>8</sup>-J (250-ton) Tower No. 215 (Experimental Unit)

Functions	Chemical System Bleed at 0.60 l/J/h (2 gal/ton/h), \$/J/h (\$/ton/h)	Total	Ozone System, \$/J/h (\$/ton/h)	Total
I. Chemicals				
Antiscale	0.24 x 10 <sup>-6</sup> (3.04)		0	
Anticorrosion	0.19 x 10 <sup>-6</sup> (2.48)		0	
Biocide	0.98 x 10 <sup>-6</sup> (1.24)		0	
Acid (pH)	0.02 x 10 <sup>-6</sup> (0.26)		0	
		1.43 x 10 <sup>-6</sup> (7.02)		
II. Water Usage				
Blow-down 0.6 l/J/h (2 gal/ton/h)	0.87 x 10 <sup>-6</sup> (11.03)			0
Basin Water Flush				
Acid Cleaning				
Water	0.04 x 10 <sup>-6</sup> (0.45)		0.02 x 10 <sup>-6</sup> (0.30)	
Acid	0.03 x 10 <sup>-6</sup> (0.32)		0.01 x 10 <sup>-6</sup> (0.21)	
		0.54 x 10 <sup>-6</sup> (11.80)		0.06 x 10 <sup>-6</sup> (1.81)
III. Electrical				
		0.01 x 10 <sup>-6</sup> (0.12)		0.11 x 10 <sup>-6</sup> (1.41)

Chemical vs Ozone Treatment Based on  $31.6 \times 10^8$ -J (250-ton) Tower No. 215 (Experimental Unit) (Continuation 1)

Functions	Chemical System Bleed at $0.60 \text{ l/J/h}$ (2 gal/ton/h), \$/J/h (\$/ton/h)	Total	Ozone System, \$/J/h (\$/ton/h)	Total
IV. Amortization				
Equipment		$0.56 \times 10^{-6}$ (7.04)		$0.42 \times 10^{-6}$ (5.36)
V. Labor				
Maintenance and monitoring		$1.05 \times 10^{-6}$ (13.28)		$0.79 \times 10^{-6}$ (9.93)
Grand Total		$3.12 \times 10^{-6}$ (39.26)		$1.39 \times 10^{-6}$ (17.50)