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OZONATION OF SECONDARY EFFLUENT
FOR COLOR REMOVAL

by

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A Thesis submitted to the
Faculty of the Department of Paper Science & Engineering
in partial fulfillment
of the
Degree of Bachelor of Science

Western Michigan University
Kalamazoo, Michigan

ABSTRACT

The purpose of this study was to determine the effect of various ozone concentrations when applied to secondary kraft effluent in regards to color removal. The influence of effluent temperature upon the color removal capabilities of ozone was also investigated to determine the optimal ozone reaction temperature or the temperature which would result in the greatest color reduction at a given ozone concentration.

The study was conducted by injecting ozone at three different concentrations of 20, 30 and 40 mg/liter into a temperature controlled column of secondary kraft effluent obtained from S. U. Warren Company in Muskegon, Michigan. The temperature was adjusted to maintain levels of 70, 80, and 90°F ($\pm 2^\circ\text{F}$). This resulted in nine separate runs of various ozone concentrations and temperature combinations.

These runs were evaluated in terms of spectroscopic adsorption using the Perkin-Elmer UV-VIS spectrophotometer.

This study indicated that increasing levels of ozone addition cause greater color removal, but at a decreasing rate. In every case, the greatest color removal was obtained with an addition of 40 mg/liter.

Also, effluent temperature had an effect on the color removal efficiency of ozone. The maximum efficiency was obtained at a temperature of 80°F.

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INTRODUCTION

One serious problem confronting our environment is that of colorization of the lakes, rivers, and streams caused by industrial wastes. Research concerning various color removal techniques for effluents began about thirty years ago in the United States. The research was a direct result of complaints by the public of colorization in small streams by pulp and paper mill effluents. The research was not a result of governmental pressure to clean up the streams. However, most states now have specific color regulations which must be met.

Four major methods have evolved from this research. They are chemical co-precipitation by the use of alum, ferric chloride, or massive lime treatment; adsorption methods which require powdered or granular carbon; reverse osmosis by the use of a semipermeable membrane; and chemical oxidation using various liquid and gas oxidants. All of these methods have serious drawbacks and it is only a matter of determining which will have the fewest undesirable effects when applied to an existing effluent treatment system.

Chemical co-precipitation is effective in removing color from effluent but produces a sludge disposal problem. Adsorption methods which use carbon or synthetic resins are usually quite costly and can only be used where a high effluent flow rate justifies the high capital expenditure. Reverse osmosis results in very low flux rates and present membrane life falls short

of that required for large scale commercial applications. Chemical oxidation usually results in high power for generation or chemical costs.

Oxonation, a form of chemical oxidation, was examined by this project to determine its pure color removal capabilities.

A satisfactory ozone treatment would result in many advantages and benefits not found in the other processes. In addition to its color removal capabilities, ozone treatment would substantially reduces the COD and turbidity of effluent and provide a high degree of disinfection. After ozonation, effluents would be completely saturated with oxygen due to the ozone breakdown and thus the need for a post-aeration step would be eliminated. Also, since sludge would not be generated in ozonation as in the chemical coprecipitation method, secondary clarifiers and dewatering equipment would not be required.

These advantages alone are enough to justify an investigation into the possibility of replacing present color removal processes with the ozone addition method and hopefully many new advantages will be discovered as interest and research develop in this new area.

LITERATURE SURVEY

The literature is full of such terms as "resistant" and "refractory" to describe materials that are not removed by waste treatment methods, whether these methods be conventional or advanced.

The point is that, in view of today's needs and tomorrow's necessarily more stringent requirements, the quantity of materials remaining after treatment must be reduced. Although advances are being made to extend the potential of the conventional treatment methods, their potential has a limited value.

Chemical oxidation has the potential for removing from wastewaters those organic materials which are resistant to other methods whether those methods are biological or the longer train of processes known as tertiary (or advanced) treatment. Chemical oxidants such as ozone have not been generally considered for color removal in wastewater treatment because of the expense of materials and related costs and because of the lack of demand for such vigorous treatment in the past.

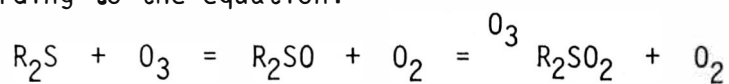
However, it is not generally realized or accepted that since the degree of treatment must be enhanced, there must be an increase in capital expenditure. It is likely, though, that the cost of this treatment will not be beyond the limits of economic acceptability.

The desirable characteristics of a chemical oxidant are that it is easily and economically available and that it not contribute secondary

pollutants to the waste stream (1). The oxidative destruction of both organic and inorganic compounds - resulting in the formation of carbon dioxide, water, and oxygenated fragments of the original molecule - occurs by bond fission. According to Bailey, this may be accomplished via two paths: homolytic reactions, in which the electron pairs are disrupted and one of the electrons is transferred to the oxidant; and the heterolytic reactions, in which the electron pair is transferred or partially transferred as a unit to the oxidizing substance (2). As a chemical oxidant, ozone has no equal, and given sufficient time will react with any and all organic materials common in dyes, bleach plant, and pulping operations which contribute most of the color in the waste stream.

The possible reactions of molecular oxygen can be broadly classified as oxygen insertive or noninsertive reactions (3). These are reactions in which oxygen itself combines with the substrate, and reactions in which oxygen merely serves as an oxidizing agent. Since the processes occur more or less spontaneously, they are referred to as "autoxidations" (4). However, the rates of reaction are too slow to be of any value in waste treatment with the exception of biological systems. It is probable that autoxidation mechanisms proceed via free radical including chain mechanisms once the production of the free radical has been initiated. Autoxidation is not necessarily a chain reaction, but the interpretation of some reactions can be made only on that basis.

According to Murray, the reactions of ozone as an oxidant appear to be of at least two distinct types (5). One involves an electrophillic attack by ozone; the other an ozone-initiated oxidation in which ozone serves as the reaction initiator and oxygen is the principal reactant. Examples of electrophillic attack by ozone are the reactions with tertiary amines, phosphines, arsines, sulfides, and sulfoxides (6). Decomposition of the substrate sometimes results. As an example, consider the ozone oxidation of a dialkyl sulfide which reacts according to the equation:



The well controlled attack of ozone on the sulfur molecule is explained by Whiting on the assumption that a terminal oxygen of the ozone molecule executes an electrophillic attack on the sulfur, forming a new bond with sulfur (7). The other two atoms of oxygen are liberated as molecular oxygen. Examples of ozone-initiated reactions are the oxidative reactions of ozone with aldehydes, ketones, alcohols, ethers, and saturated hydrocarbon groupings. In these reactions, ozone behaves as a radical reagent in an autoxidation process by mobilizing an additional number of oxygen molecules.

All of these reactions are important when trying to describe the processes by which ozone may be used to remove color from secondary kraft effluent. This is because kraft effluent will usually be a composite of pulping products such as lignosulfide, methylmercaptins, dissolved sugars which result in alcohols, and numerous phenols. Also,

some diazo compounds which are used in dyeing may be present along with inorganic salts used in the papermaking process.

The first use of ozone was for waste water sterilization, when in 1893, Schneller, Vander Sleen, and Tindal constructed an industrial apparatus at Oudshoorn in Holland for the sterilization of Rhine water after sedimentation and filtration (8). Otto ozone equipment was initially used in 1907 in Nice in the first major installation for the sterilization of a public water supply (9). Ozonation might have become universal for disinfection in water treatment except for the introduction in this country of cheap chlorine gas, a product of World War I research in poison gases. In Europe and other places, ozone for disinfection remained the method of choice and by 1936, there were more than one hundred installations in France alone (10).

In this country - aside from the city of Whiting, Indiana which used ozone in pretreatment for removal of taste, odor, and color from Lake Michigan water; and Philadelphia, Pennsylvania which used ozone to remove taste, odor, and manganese from Schuylkill River water - there have been no major ozone installations for municipal or industrial waste water or water treatment, and chlorination remains the principal method (11).

Recently, concern has been expressed concerning the possible toxic effects resulting from the discharge of chlorinated municipal and industrial wastes, which could adversely effect aquatic life in a receiving stream (12). In the search for alternatives to chlorine,

ozone is being considered. Although the literature on ozone disinfection is plentiful, the work has generally been done in pure aqueous and single culture systems. Despite these simplifications, variations in experimental conditions usually preceed any comparisons of results, and such data, having no relation to reality, cannot be extended to a practical situation.

As a result, the literature can be only generalized. The use of ozone results in disinfection but not necessarily sterilization. There appears to be a threshold dose which must be exceeded (13). According to Whitson, this threshold dose is a function of the ozone demand of the waste, which in turn, is an inverse function of the degree of treatment prior to ozone application. Satisfying the ozone demand and disinfection are believed to occur simultaneously. Therefore, a greater degree of pretreatment is advantageous in two ways. One, the ozone demand is reduced by the removal of the more easily oxidizable substrate; and two, clumps which shield the organisms from the disinfectant are removed.

Although the disinfection of potable water is the largest application of ozone, other uses of ozone have been made in the treatment of water. It is used for taste and odor control and for residual color reduction after conventional water purification by flocculation, sedimentation, and rapid sand filtration. Recently, Diaper has applied ozone more fundamentally, following discovery of its extremely effective action on organic colloids, in the "Micellization/Demicellation" process and in the "Microzone" process (14). These processes result from an attempt to

economize on the more conventional treatment processes. The intended result was to achieve a higher quality of water at a lower overall cost, and offset the higher capital cost of ozonation equipment when compared to the cost of eliminated processes and chlorination treatment. Laboratory and pilot plant studies have brought about the development of an ozonation/coagulation/filtration process. The M/D process is particularly suitable for surface waters containing organic matter that is often difficult to coagulate and requires uneconomical doses of electrolytes.

In the contemporary uses of ozone, Maass has summarized the principal applications in sterilization of water, taste and odor control, iron and manganese removal and color reduction (15). He initially installed ozone equipment at the Midland, Michigan waste treatment plant in order to evaluate its efficiency in deodorizing the exhaust from the vacuume filtration system. The trial was so successful in reducing sulfide odor that ozone is treating the exhaust from the sludge tank buildings and the remaining open facilities have been covered with styro-foam domes for exhaust gas ozonation.

In the United States, the interest in ozonation has been directed toward using not only the disinfection powers of the chemical but also its oxidation potential for color removal. Chemical oxidation as a unit process has never been practiced for color removal in wastewater treatment. Chemical oxidation may be applicable to many situations; one, as an alternative to carbon adsorption for use as a tertiary treatment process

and when carbon adsorption and regeneration cannot be economically justified; two, as a process to supplement carbon or synthetic resin adsorption; three, to extend the capabilities of intermediate treatment plants; and four, to enhance effluent quality in high-value reuse situations (16).

In evaluating the oxidative potential of ozone, there have been only a few laboratory studies of its effect on wastewater constituents.

Beuscher and Ryckman used ozone to reduce foaming of ABS, accompanied by an 80% reduction in COD (17). In 1966, they built a 2700 gallon/hour pilot plant in Ridbridge, England. The pilot plant provided variable combinations of microstraining, prechlorination, ozonation, coagulation, and rapid sand filtration for the treatment of settled, biologically treated effluent. This M/D process employs the following three stages of treatment:

1. Microstraining for primary filtration.
2. M/D to produce filterable microflocs.
3. Rapid sand filtration to eliminate the microflocs.

Ozone is used in the second stage to bring about the disruption of the colloidal state by attacking the hydrophillic grouping of organic molecular chains for the production of colloidal micelles. The production of micellization after ozonation is shown by the development of colloidal turbidity. The negatively charged micelles require an electrolyte to demicellize the water and the microflocs are then sand filtered. The process produces a final effluent low in suspended solids,

clear and colorless. Concentrations of ammonia were unaffected but nitrate was oxidized reducing nutrient output which has a tremendous effect on stream and lake alga growth.

In a laboratory investigation supporting the Ridbridge project, Gardner & Montgomery studied the effect of ozonation alone on the chemical composition of sewage effluents over a wide range of temperatures and ozone doses (18). The results of the study were:

- I. Ten minutes ozonation reduced organic carbon only slightly. One hour ozonation effected a 27% reduction when 94mg/l ozone was absorbed.
- II. Thirty to sixty minutes ozonation caused a reduction in the BOD; the samples were likely saturated with dissolved oxygen.
- III. The COD reduction in mg/l was approximately equal to one half the amount of ozone absorbed.
- IV. Color reduction was directly related to ozone input yet not determinable because of the necessity of using unfiltered effluent.
- V. Nitrate was oxidized; organic nitrogen was slightly reduced; ammonia concentrations were unaffected.
- VI. Removals of phenol, pesticides, and detergents were in agreement with the removals found by other investigators.

The Air Reduction Company used trickling filter effluent which was alum clarified and sand filtered to produce an influent with a reduced

ozone demand (19). This study determined that the operation of a six stage contactor and a one hour retention time reduced the COD from 32 to 13 mg/l and reduced the TOC from 12 to 9 mg/l. It was demonstrated that ozone efficiency for TOC and COD reduction increased with increasing levels in the sample, indicating that the more readily oxidizable organic compounds in the effluent consume ozone more readily. Only when oxidation leads to the formation of carbon dioxide, is there a reduction in the TOC. Cost estimates, based on the design of six stage cocurrent contacting system for 1, 10, and 100 MGD plants, assuming 80% ozone utilization, compared favorably with those for activated carbon treatment plants.

Improvements in ozone generation equipment are claimed by Chromalloy American Corporation. They are claiming that its new Purogen Activated Oxygen system overcomes ozone's two main drawbacks; instability and high power costs (20). A new system developed by Purification Sciences includes a low cost ozone generator based on corona discharge and a new approach for mixing the ozone with the waste.

EXPERIMENTAL DESIGN

Objective

The purpose of this experiment was to determine the effect and efficiency of varying amounts of ozone at three different temperatures on color reduction.

As a result of knowledge obtained through a review of the literature concerning ozonation and chemical oxidation, this experiment was guided along the lines of evaluation of kraft mill secondary effluent. The effluent was obtained from the outlet of the secondary clarifiers at S.D. Warren Company in Muskegon, Michigan. This type of effluent was selected because it exemplifies the current trend in the paper industry.

Procedure

Before this study was undertaken, a calibration curve of the Cochran Ozonator was determined that related the amount of ozone produced at a given amperage and flow rate of compressed air. This calibration was accomplished by leaving the amperage constant at about 0.8 amps and adjusting the flow rate of air. The ozone produced was then extracted through a 200 ml gas bottle filled with 2% KI which was titrated against 0.1 N $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 10 ml of 1N H_2SO_4 to give mg/l of ozone. A calibrated aspirator bottle was used to give a constant gas sample volume.

The process set-up is shown in Figure 1 and the calibration curve is shown in Figure 2.

Once the calibration of the ozonator was completed, the experiment was conducted. This was done by injecting ozone into 7 liters of the unfiltered kraft secondary effluent through a scintered glass diffuser at the base of a six inch diameter plexiglass column. Three different concentrations were used. They were 20 mg/liter, 30 mg/liter and 40 mg/liter. The retention or contact time was 15 minutes. At each of these concentrations, the effect of effluent temperature was also studied. The temperatures of interest were 70°F, 80°F, and 90°F. These temperatures were maintained within a two degree limit by immersing a 3/4 in. glass "U" tube connected to a steam outlet into the column below the ozone diffuser. Because the reaction rate of ozone is so great, metal heating elements are not recommended.

Evaluation

The only supplementary test used to evaluate the color removal potential of ozone was color adsorption using the Perkin-Elmer UV-VIS spectrophotometer.

The final ozonated samples were filtered through a #3 Whatman filter paper to remove the suspended solids. It was not possible to remove all of the suspended material and the final color had a slightly "apparent" value rather than a purely "absolute" value. The pH of the

samples were adjusted to a value of 7 using concentrated H_2SO_4 and NaOH as required. The samples were then placed in the spectrophotometer using the 1 cm sample cells and the adsorption measured at a wave length of 465 mu with a 0.225 mm slit width. Distilled water was used as the standard reference solution of zero adsorption.

An identical procedure was followed on the nonozonated samples so that a percentage color reduction figure could be calculated.

Precaution

All of the work with ozone was performed under a fume hood as there was no way of determining the unreacted residual ozone.

Also, no rubber or metal fitting could come into contact with the unreacted ozone in the system. All fittings and other pieces of equipment such as flow meters and the like were constructed of glass, Tygon, or stainless steel.

EXPERIMENTAL RESULTS AND CONCLUSIONS

The data gathered showed that an ozone addition rate of 40 mg/liter produced the greatest color reduction (i.e., ca. 34% of original color at 70°F to 45.8% at 80°F while 20 mg/liter of ozone produced the least effect (i.e., ca. 22.9% of original color at 70°F to 38.8% at 80°F). This relationship is shown in Figure 4. This is hyperbolic in nature and expresses the difficulty and extremely large amounts of ozone required to remove the final color producing elements.

This leveling effect was probably the result of the decrease in the number of easily oxidizable sites contributing to color reduction and the fact that increased residual ozone concentration (a result of the decrease in bonding sites with the color producing bodies) causes the ozone molecules to react with each other. This reaction produces oxygen which is a much weaker oxidizing agent and greatly reduces the color removing capabilities of this method.

The data also indicated that an effluent temperature of 80°F caused the greatest color removal and that temperatures above and below this value have a lesser effect. This result is shown by Figures 3 and 4 in the Appendix.

This relationship can partially be explained as the result of a greater number of oxygen molecules adhering to the outer surface of

the ozone bubble. The temperature at which this regression begins is a function of the amount of oxygen present and the pressure of the system.

Analysis of the data indicated that 25 mg/liter of ozone was the most efficient rate of addition (i.e., ca. 24% to 35% color reduction at all temperatures) when considering power requirements. This was determined by considering which point on Figures 3 and 4 gave the greatest change in slope.

Cost estimates showed that assuming 20 million gallons per day of effluent from an integrated bleached kraft mill, power costs would approach \$81,000 per year for an ozone addition rate of 25 mg/liter at 80°F resulting in a color reduction of 42% over the untreated effluent. These figures were based on 2.5¢/kwh which is the approximate cost of power supplied to medium sized industrial users, by public utility companies.

The significance of this method is illustrated by the fact that it is capable of reducing effluent appearing as a dark opaque liquid to one which approximates the appearance of a glass of weak tea and the results have emphatically highlighted the value of ozonation as a tertiary treatment, when considering cost and final color evaluation when compared to other current treatment methods. The value of this practice in a production situation would have to be determined from a practical and economic viewpoint in order to ascertain its overall

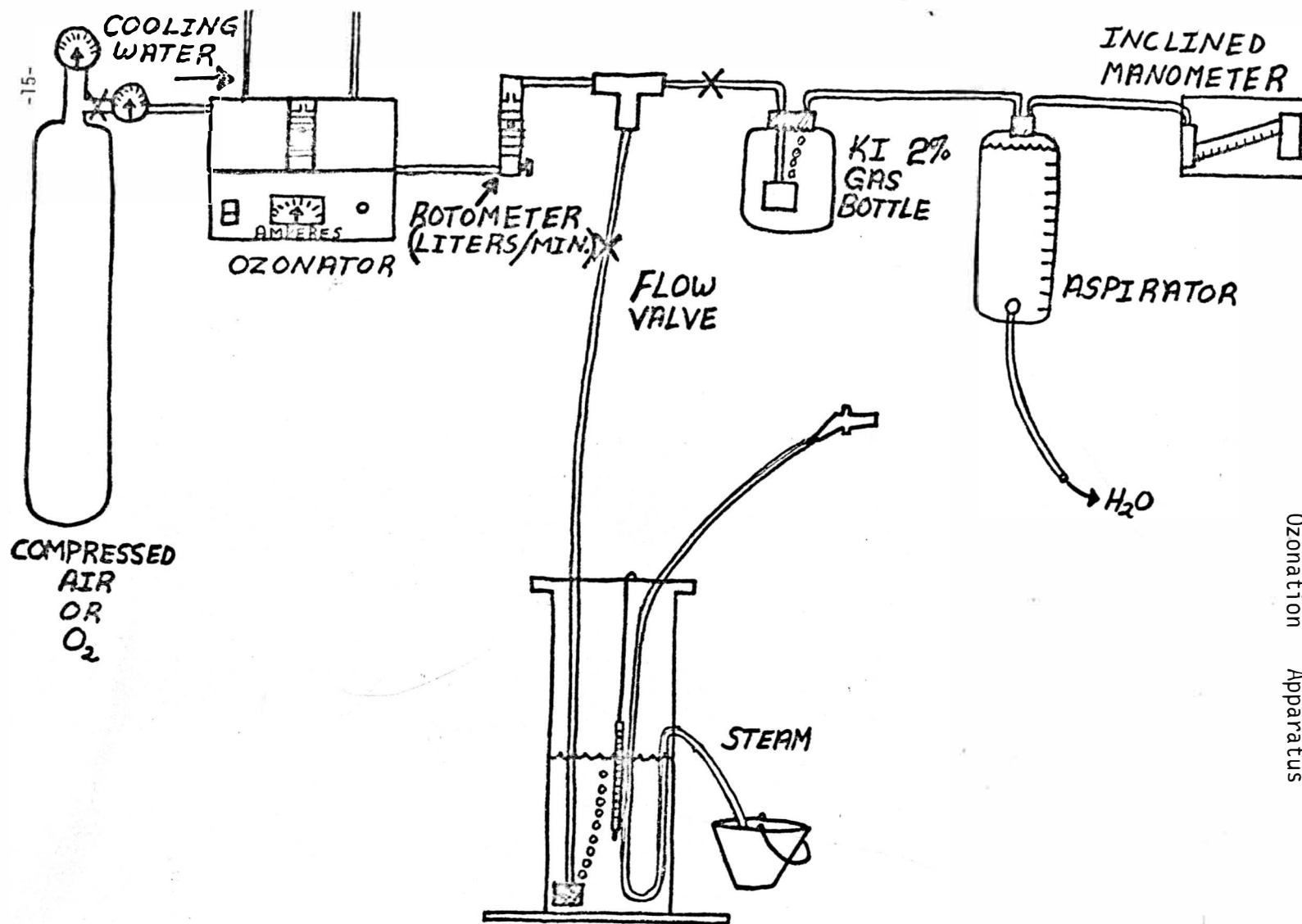
benefit. Perhaps today's technology could enhance the benefit and render it an even more interesting innovation.

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Ozonation Apparatus

Figure 1

TABLE I

<u>Run</u>	<u>Temperature ± 2°F</u>	<u>mg O₃/l</u>	<u>Ozonator Setting (AMPS)</u>	<u>Final Adsorbance</u>	<u>Final Color (ppm)</u>	<u>% Color Reduction</u>
I	70°F	0	0	.213	930	0
II	70°F	20	.2575	.162	717	22.9
III	70°F	30	.3450	.140	626	32.7
IV	70°F	40	.4600	.145	614	34.0
V	80°F	20	.2575	.128	569	38.8
VI	80°F	30	.3450	.113	517	44.3
VII	80°F	40	.4600	.110	504	45.8
VIII	90°F	20	.2575	.136	613	34.1
IX	90°F	30	.3450	.117	548	41.1
X	90°F	40	.4600	.115	535	42.5

Figure 2

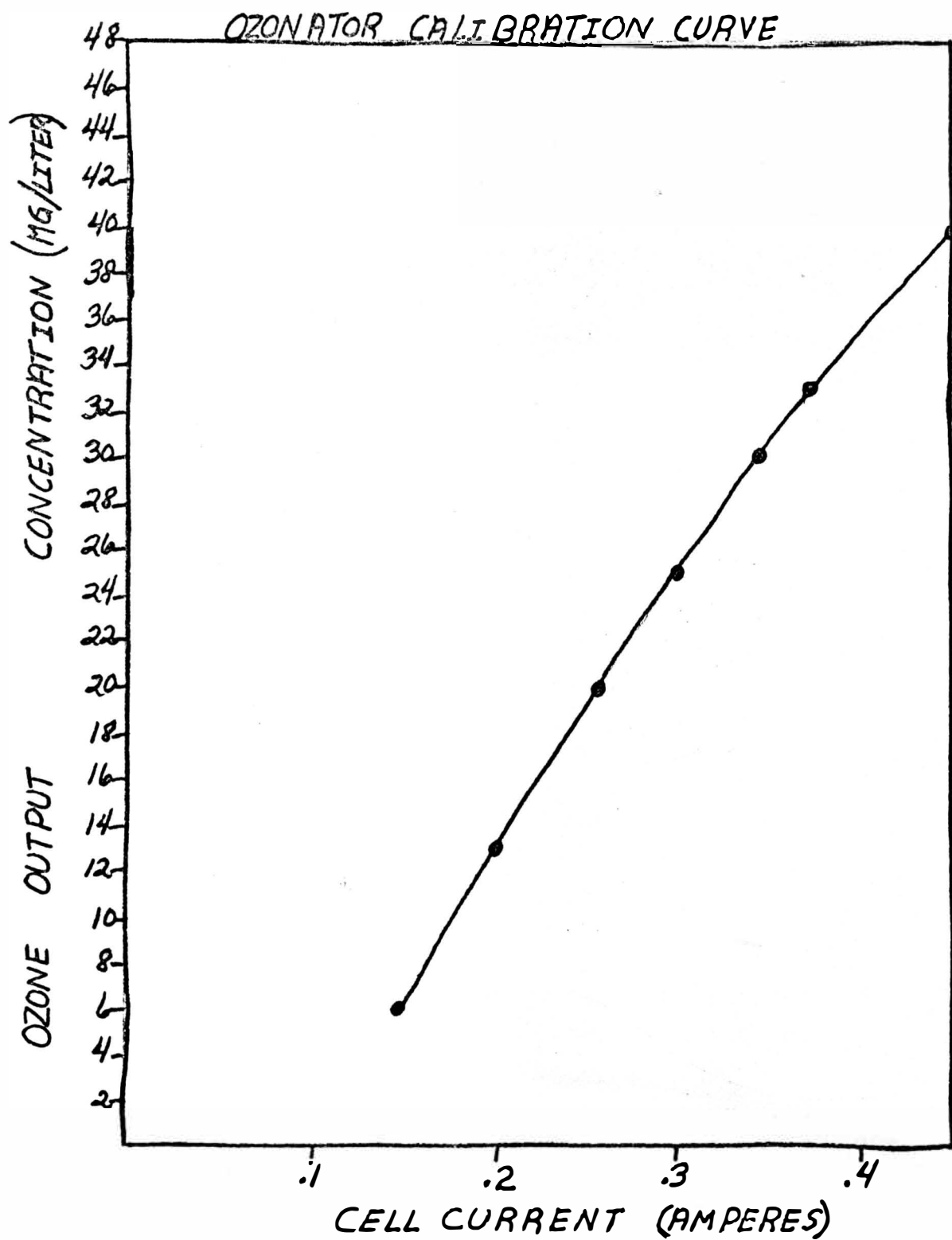


Figure 3

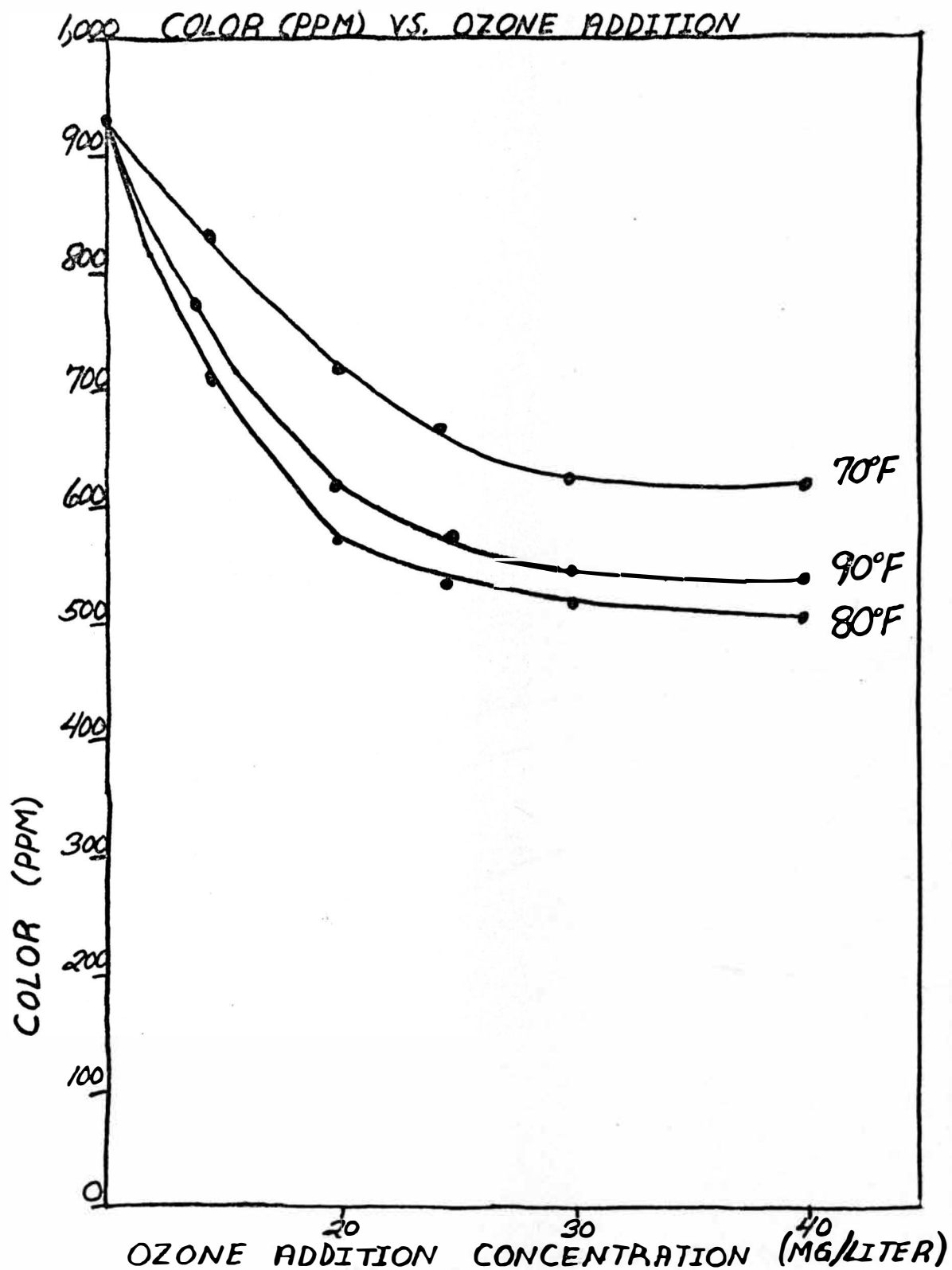


Figure 4

