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# OZONE TREATMENT OF WASTE EFFLUENT

by

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# FOREWORD

The Water Resources Research Institute has provided the administrative coordination for this study and organized the interdisciplinary team that conducted the investigation. It is the Institute policy to make available the results of significant water related research conducted in Idaho's universities and colleges. The Institute neither endorses nor rejects the findings of the authors. It does recommend careful consideration of the accumulated facts by those who are assuredly going to continue to investigate this important field.

# ABSTRACT

A portable ozone test unit was designed and built for use in treating liquid materials with ozone. Due to its powerful oxidation properties, ozone has a great deal of potential as a treatment system for liquid waste materials and water supplies. The portable test unit was constructed so that it could easily be transported to a field site for testing.

Several applications used the ozone test unit. It was found that the dark brown, odorous wastes effluent from a kraft pulp mill could be satisfactorily decolorized and deodorized by the ozone. In addition, it was found that the material after ozonation was more biodegradable than before ozonation.

The ozone test unit was also used to treat potable water supplies to remove iron and manganese and to reduce off odors and tastes. Tests run on the Moscow, Idaho, water supply demonstrated that ozone could effectively remove high concentrations of both iron and manganese (1-5 mg/1 Fe and 0.1 - 1 mg/1Mg).

# ACKNOWLEDGMENTS

Several graduate students of the Chemical Engineering Department at the University of Idaho were major contributors to this project and should be acknowledged. They are Mr. Harvey L. Harding, Mr. Michael A. Smith and Mr. A. Wesley Langeland.

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# INTRODUCTION

As the needs for more and better quality water become increasingly acute, it follows that better methods must be developed to treat water, particularly waste water effluents from many industrial processes. For large water-consuming organizations, multiple use of water is not only desirable but is becoming a necessity in many regions.

Common treatment systems, normally consisting of primary solids settling followed by secondary biological degradation, are not sufficient in many cases to reduce the inorganic and organic substances in the waste water effluents to a level that the water can be either re-used in the process or discharged into a water way without adverse effects. Biological systems have their limitations in the reduction of organic compounds since the microorganisms and their enzyme systems must be capable of attacking the contaminants. In many cases the components have complex structures such as unsaturated carbon ring structures which are not easily attacked by the microorganisms. Also the contaminants may be toxic to most biological specimens. Thus, biological systems may be relatively ineffective on many industrial wastes.

Ozone has been known for many years as a powerful chemical oxidant second only to fluorine. It is able to sever unsaturated cyclic carbon compounds to form much simpler straight chain molecules which are much easier to attack biologically. Eisenhauer (1) reports that the ozonation of phenol produces three molecules of oxalic acid for each molecule of phenol if the reaction is carried to completion. Thus, ozone has promise as an agent to oxidize a wide variety of waste materials such as petroleum refining, pulp and paper, polymer production and similar wastes normally containing complex organic chemicals. In addition ozone can oxidize inorganic materials such as iron and manganese and thus can be used for water supply treatment particularly for decolorizing, deodorizing and sterilizing the water system (2). The powerful oxidizing capacity of ozone is one of the few ways of effectively removing very small amounts of organic material which cause off odors and color in water.

From time to time interest has been expressed in ozone treatment of water systems but the cost has been relatively high and the economic and/or legal incentive to use such treatment was lacking. However, water quality standards are rapidly becoming more stringent and the price of ozone has dropped due to better generation methods and lower cost oxygen supplies. Ozone may well be an attractive treatment alternative for more sophisticated treatment requirements.

## PORTABLE OZONE TEST UNIT

Partially financed by funds obtained through the Idaho Water Resources Research Institute, a portable ozone test unit was designed and built (3). The purpose of developing the unit was to have an experimental testing facility that could be used rapidly and easily to determine if ozone would be of value in the treatment of a particular liquid material.

The unit was designed so that it could be readily taken to a field site and the material tested without elaborate preparation. The ozone test facility developed was basically self-contained and comprised of an ozone generator, an oxygen feed source, an ozone-liquid contact system, a reactor, a feed pump, temperature measurement and control equipment, pH measurement, flow meters and other auxiliary equipment. A schematic diagram of the ozone test unit is given in Figure 1 and a photograph of the finished unit in Figure 2.

Some basic characteristics of the unit are as follows:

| | |
|---|---|
| reactor volume: | 2 gal |
| reactor residence time: | 1 - 20 min |
| feed rate: | 0 - 1. 5 gpm |
| ozone production: | 12 grams/hr |

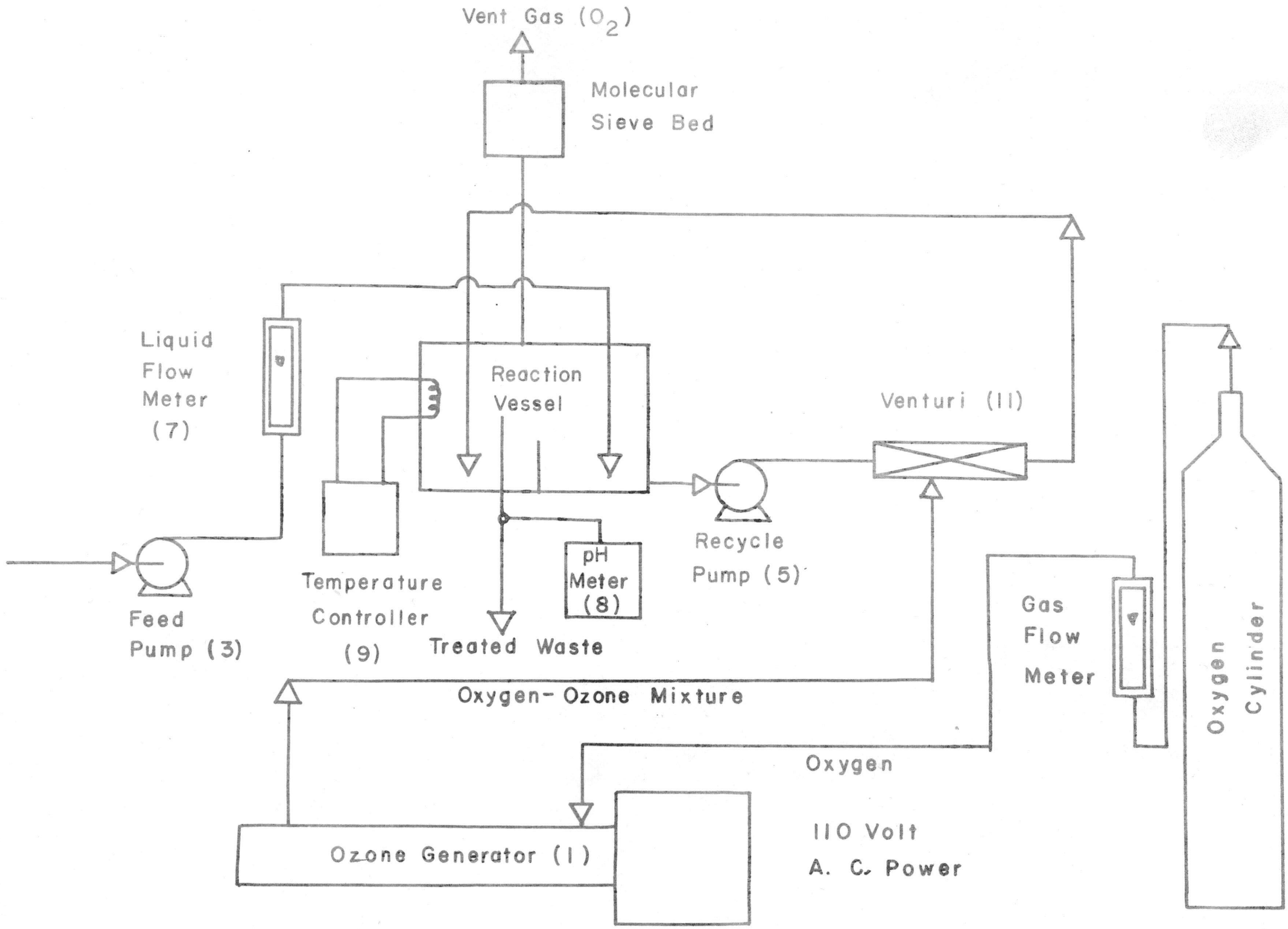


Fig. 1. Schematic flow diagram of portable test unit

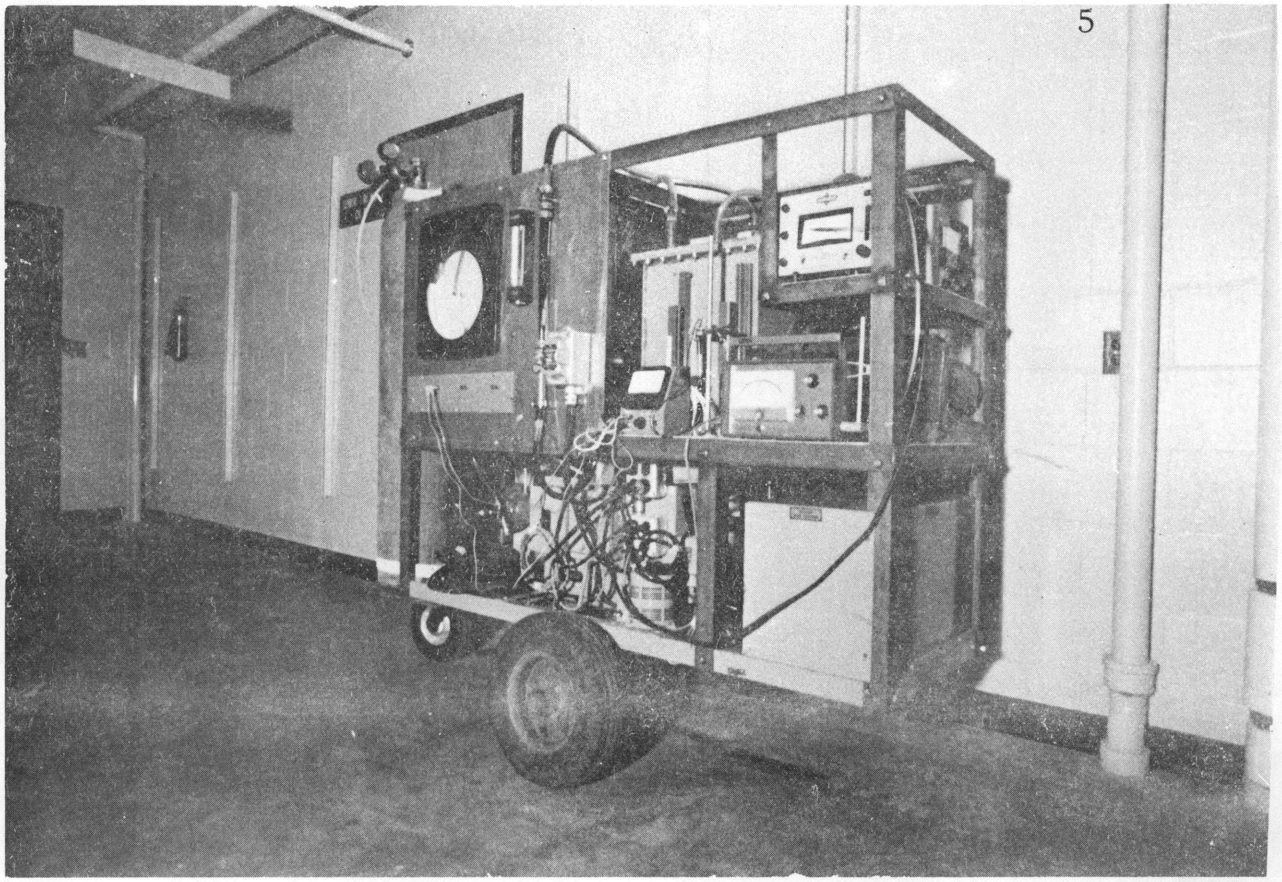

Figure 2. Photograph of Experimental Apparatus

A venturi type gas-liquid contacting device was used to keep the size of the unit as small as possible and still have good transfer of the ozone to the liquid system. The recirculation system devised provided for the ozone contact with the liquid to be independent of the flow through the system (and the reaction residence time).

As can be seen from Figure 2, the unit is portable and can be transported in the back of a pickup truck or van for long distances or towed for short distances. The unit operated quite satisfactorily in a variety of applications. For its operation the only requirements are a source of 110-volt electricity, cooling water for the ozonator, and a supply of the medium to be treated. The feed pump is a positive displacement type and no auxiliary pumps are needed for the supply.

# APPLICATIONS

The portable ozone test unit was used for several applications - namely the decolorization and deodorization of kraft pulp mill wastes and the removal of iron and manganese from a water supply and the deodorization of a water supply.

## Pulp Mill Wastes

Some of the most extensive work using the ozone test unit has been done on the treatment of kraft pulp mill effluents. The pulping and bleaching process produce a relatively large quantity of highly pungent, dark brown colored waste water. The contaminating materials originate from lignin and lignin derivatives which are complex organic materials containing phenolic structures and other configurations which are not easily biodegraded. Thus, the waste water from a pulp mill can pass through normal primary and secondary treatment facilities without the color and odor being significantly reduced. In fact, the color may become worse.

The effluent from the Potlatch Forests Incorporated kraft pulp mill at Lewiston, Idaho, was treated with the ozone test unit (2). Actually several different streams were tested -- the waste from the bleach plant, from the total plant, from the primary clarifier and from an extended aeration secondary system. Little differences were noted between the streams with regard to color reduction, odor removal and COD reduction. Thus, the bulk of the data was taken on the primary clarifier output material. The results are as follows.

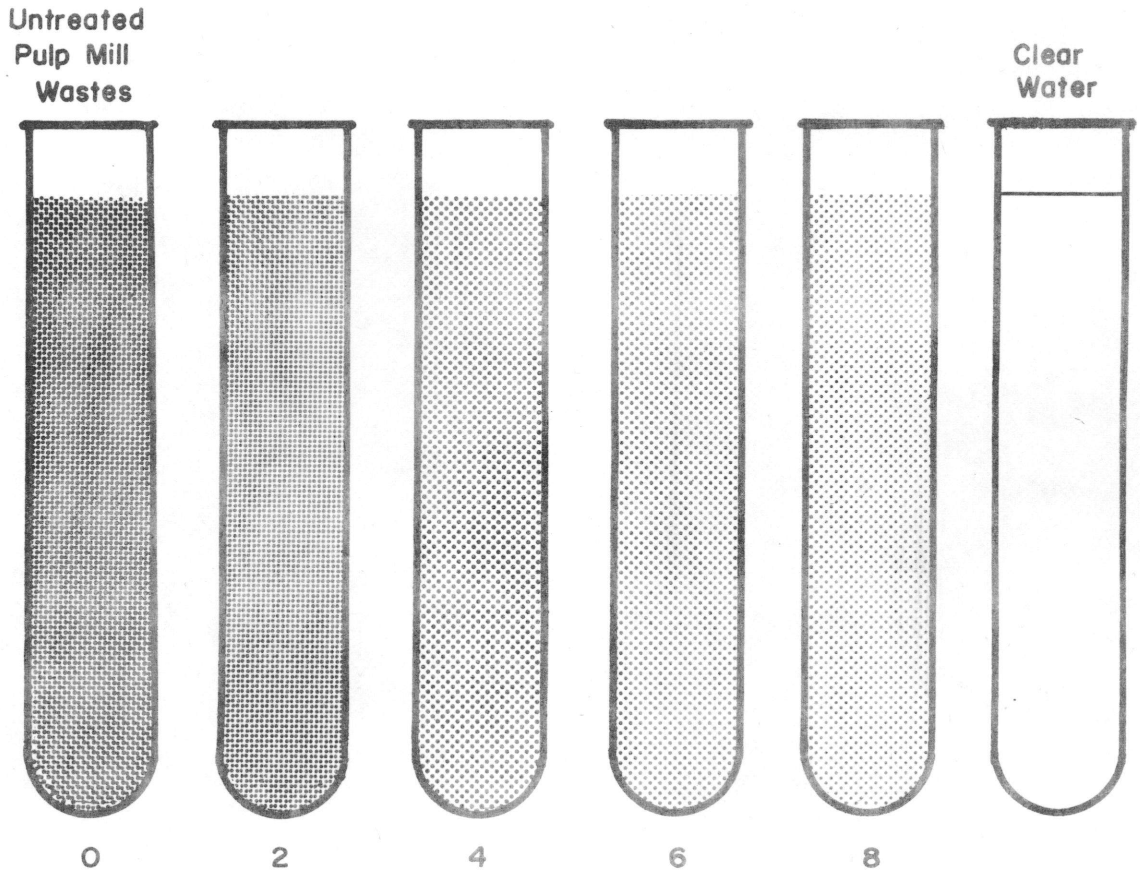


Figure 3: Color of Ozonated Kraft Mill Wastes
at 2-Minute Intervals

The color of the sulfate liquor dramatically changed from a dark chocolate brown to a light straw yellow in about five minutes of reactor resistance time. A draftsman's interpretation of the time lapse color photograph shows the color transition presented in Figure 3.

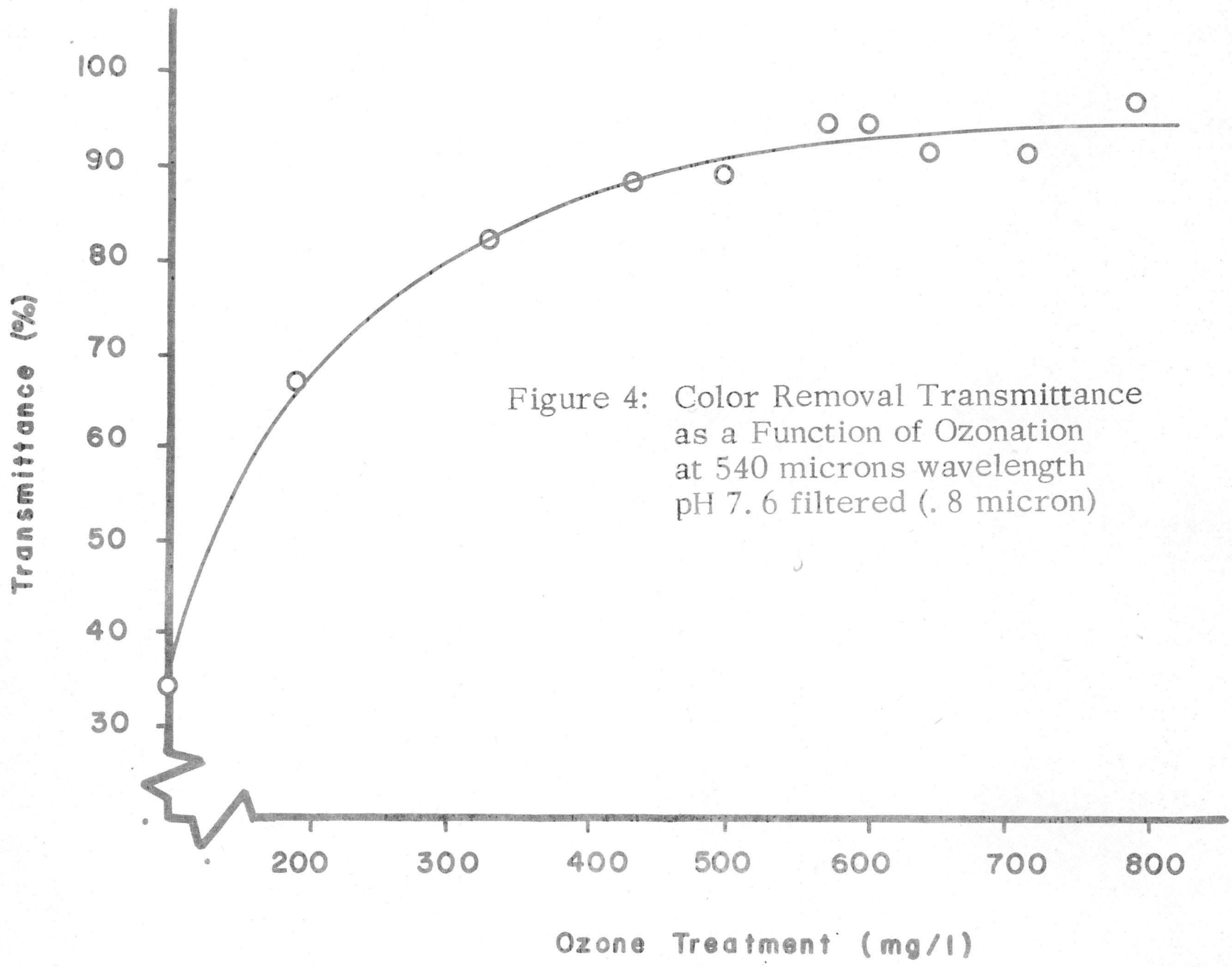


Figure 4: Color Removal Transmittance as a Function of Ozonation at 540 microns wavelength pH 7. 6 filtered (. 8 micron)

A more quantitative description of the color change is given in Figure 4 which plots the light transmittance of the sample after various contact periods. While the waste material is undergoing this color change, the strong sulfur laden odor disappears entirely.

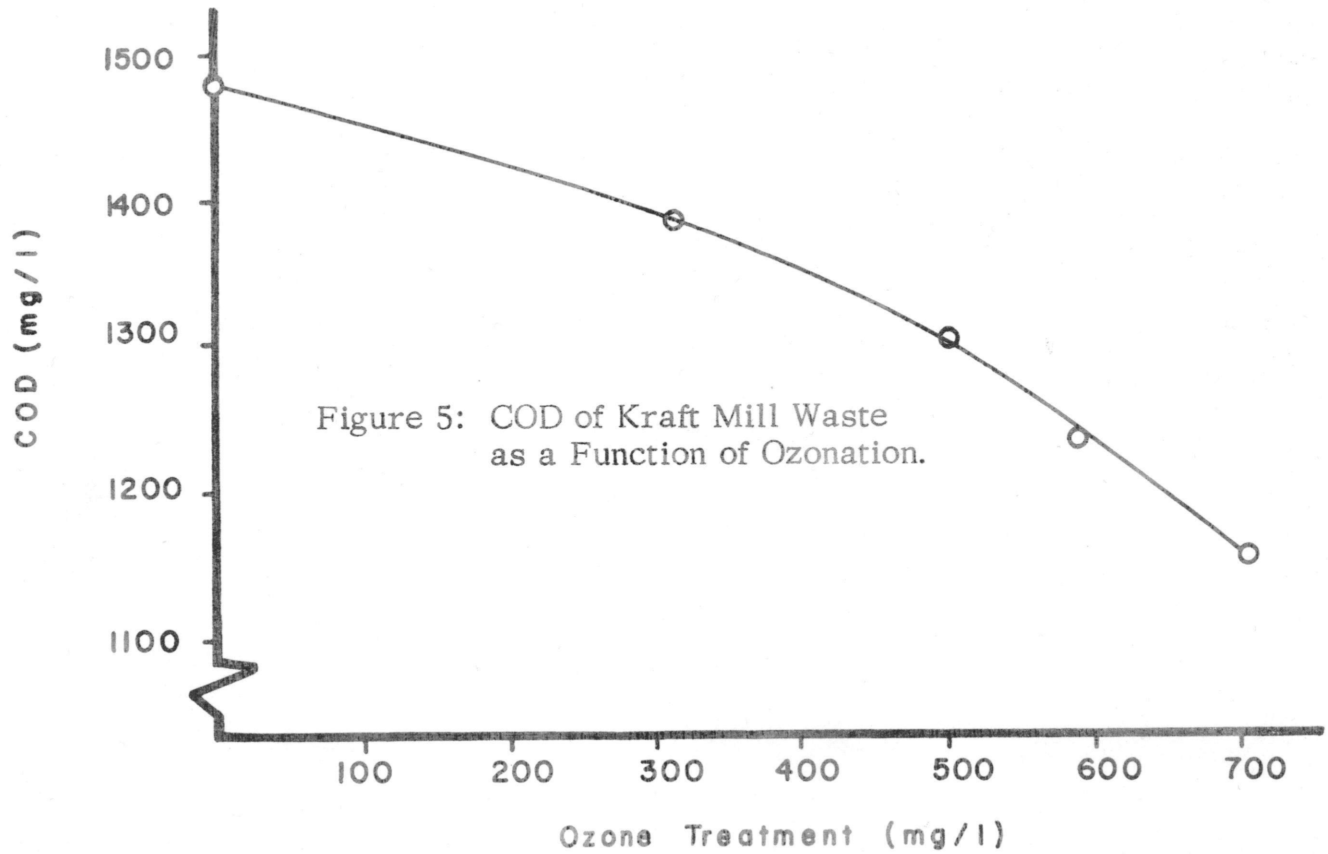


Figure 5: COD of Kraft Mill Waste as a Function of Ozonation.

The effect on the concentration of organic material as measured by the chemical oxygen demand COD was far less spectacular. In general with a treatment time of five minutes, the COD would be reduced up to 30% though normally in the range of a 10 - 15% reduction as illustrated in Figure 5. Even though the organic material itself was not greatly oxidized to $CO_2$, further testing of the ozonated material showed that it was more biodegradable than the unozonated material (4). This suggests that ozonation, if used, should not be a post or tertiary treatment but should precede the secondary biological treatment.

The tests using the portable ozone unit definitely substantiated the utility of ozone as a decolorizing and deodorizing agent for kraft pulp mill wastes. Preliminary estimates indicate that the costs involved for a full-sized plant would be in the range of \$.30/1000 gal. However, additional data must be taken to obtain a more accurate cost figure.

Iron and Manganese Removal

The ozone test unit was used to investigate the removal of iron and manganese from the well water supply of the City of Moscow, Idaho (5). Several shallow wells have iron contents of 5 mg/1 and manganese contents of 1 mg/1. Although the iron is relatively easy to remove, it is very difficult to remove such high concentrations of manganese from water supplies. Both iron and manganese can form insoluble oxides ($Fe_2O_3$ and $MnO_2$) which can readily be filtered out. The ferric oxide can be formed by using air or chlorine but manganese dioxide formation needs a stronger oxidant.

Samples of Moscow water were treated using the ozone test unit. It was verified that both the iron and manganese could be removed to below acceptable limits with an ozone contact time of less than one minute as given in Table 1. Further analysis of the system indicated that ozone treatment for iron and manganese removal would compete economically with a manganese greensand removal system and was less costly than a potassium permangate oxidation system. Currently the

Moscow City Council is contemplating the possibility of building a full-sized ozone water treatment plant.

Table 1

EFFECT OF OZONE ON IRON AND MANGANESE REMOVAL FROM MOSCOW WATER SYSTEM

| Run No. | Flow mg/sec | Sample | Unknown | Trans-mission % | PPM | Avg. PPM |
|---|---|---|---|---|---|---|
| | | | IRON | | | |
| Raw | | 1 | Iron | 25. 0 | 5. 000 | |
| | | 2 | | 25. 0 | 5. 000 | 5. 0000 |
| No. 12 | | 1 | Iron | 66. 0 | 0. 400 | |
| Filtered | 0. 167 | 2 | | 76. 0 | 0. 250 | 0. 3250 |
| No. 23 | | 1 | Iron | 76. 0 | 0. 250 | |
| Filtered | 0. 206 | 2 | | 79. 0 | 0. 225 | 0. 2375 |
| No. 34 | | 1 | Iron | 90. 0 | 0. 100 | |
| Filtered | 0. 201 | 2 | | 95. 0 | 0. 050 | 0. 0750 |
| | | | MANGANESE | | | |
| Raw | | 1 | Mn | 82. 5 | 0. 930 | |
| | | 2 | | (95) (4) | 0. 900 | 0. 9100 |
| No. 1 | | 1 | Mn | 96. 0 | 0. 265 | |
| Filtered | 0. 167 | 2 | | 96. 5 | 0. 210 | 0. 2375 |
| No. 2 | | 1 | Mn | 97. 0 | 0. 170 | |
| Filtered | 0. 206 | 2 | | 98. 0 | 0. 130 | 0. 1500 |
| No. 3 | | 1 | Mn | 98. 5 | 0. 090 | |
| Filtered | 0. 201 | 2 | | 98. 0 | 0. 130 | 0. 1100 |

## Water Deodorization

Small amounts of flavor and odor off-tastes are particularly troublesome in some applications such as food processing and beverage manufacturing. The portable ozone test unit was shipped to a major brewery of a national brand beer manufacturer to examine the use of ozone for elimination of trace tests and odors. As a result of these tests, the beer manufacturer is installing a full-sized plant to treat a portion of the brewery water.

# CONCLUSIONS

The portable ozonation unit developed in this project has demonstrated its ability to obtain information valuable in analyzing ozone as a possible water treatment method. Several other applications are currently being programmed for the unit mainly concerned with pulp mill wastes. The major limitation of the present unit is its ozone generation capacity which is quite low. When funds permit, a larger ozonator should be incorporated into the unit.

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