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An Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies

Executive Summary

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AN ASSESSMENT OF OZONE AND CHLORINE DIOXIDE TECHNOLOGIES FOR TREATMENT OF MUNICIPAL WATER SUPPLIES

Executive Summary

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This report is an executive summary of a state-of-the-art survey of municipal water treatment practices involving the use of ozone and chlorine dioxide in Europe, Canada, and the United States. The study was sponsored by the Water Supply Research Division of the EPA Municipal Environmental Research Laboratory in an effort to assess the performance of advanced water treatment techniques for use in the production of drinking water. It is hoped that this report will be interesting and helpful to those active in water supply treatment.

Francis T. Mayo, Director
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SUMMARY

In 1974, the Safe Drinking Water Act (PL 93-523) was enacted by the U.S. Congress. This act was necessary to update the U.S. Public Health Standards of 1962 and to reflect results of research and development of sophisticated monitored techniques which revealed that many communities water supplies were unsafe. The Act directed the U.S. EPA to develop standards and promulgate regulations for several classes of substances found in drinking water supplies. Also the EPA was directed to support research on treatment technologies that would allow public water systems to treat their waters to the quality mandated by the new standards. As part of its overall mission, the EPA's Municipal Environmental Research Laboratory, Drinking Water Research Division funded this study dealing with the use of ozone and chlorine dioxide technologies in drinking water treatment.

Many of the countries of Europe have long been faced with the necessity of producing safe drinking water from chemically polluted raw water sources. As a result, there has been extensive development of drinking water treatment technologies in Europe, particularly related to the usage of ozone and chlorine dioxide as oxidants, and use of granular activated carbon as a filtration/adsorption process. The study summarized herein, and available in complete form from EPA, involved a comprehensive review of European, Canadian, and U.S. practices on the use of ozone and chlorine dioxide as process oxidants in the treatment of municipal drinking water supplies. Some study of the use of granular activated carbon with preozonation, or "biological activated carbon" (BAC), was carried out. Further study of the BAC process now underway will result in additional data on this process by late 1978.

This executive summary covers in abbreviated form each of the principal topics of the full report. Emphasis in the summary, and in the full report, is given to the fundamental uses and engineering design of ozone/chlorine dioxide systems. A detailed treatise on the chemistry of the two oxidants and their reactions with various classes of organic compounds is included in the full report. Data from extensive questionnaires and on site surveys of several hundred drinking water utilities are included in the full report and summarized herein.

The results of this study indicate that ozone, chlorine dioxide, and ozonation followed by GAC are being employed successfully by a large number of European and some Canadian water utilites to deal with the problems of trihalomethanes, synthetic organic chemicals, bacterial disinfection, viral inactivation, and other substances in raw water supplies. Europeans in particular employ ozone for a wide variety of applications which cannot be accomplished on a practical basis by other treatment techniques. Ozone, in conjunction with granular activated carbon, was found to be highly effective in removing organic chemical contaminants.

CONTENTS

Summary iv

Figures vii

Tables ix

Acknowledgments x

1. Introduction 1

Basis for the Ozone/Chlorine Dioxide Study 1
Scope of the Study and How it Was Conducted 2
Principal Results of The Study 4
Principal Recommendations of the Study 6

2. Water Treatment Philosophies 7

Introduction 7
European Water Treatment Philosophies 7
Canadian Water Treatment Philosophies 12

3. Ozone 13

Introduction and Background 13
Properties and Reactions of Ozone 15
Public Health Aspects of Ozonation 15
Operational Experiences With Ozone 16
Site Visits 21
Engineering Aspects of Ozonation Equipment and Processes 25
Ozone Measurement and Control 35
Operation and Maintenance 40
Costs/Benefits of Ozonation 41
Conclusions 41

4. Biological Activated Carbon 44

Introduction 44
Fundamental Principles 44
European BAC Practices 45
Conclusions 45

CONTENTS (continued)

5. Chlorine Dioxide 47

Introduction. 47
Preparation of Chlorine Dioxide 48
Oxidation Products of Chlorine Dioxide. 48
Usage of Chlorine Dioxide in the United States. 51
Usage of Chlorine Dioxide in Europe 55
Design of Chlorine Dioxide Systems. 56
Costs for Producing Chlorine Dioxide. 59
Conclusions 61

Appendix A 62

Condensed Bibliography. 62

Appendix B 66

List of U.S. Ozone Manufacturers. 66

FIGURES

Number		Page
1	Typical Points of Application of Ozone in Drinking Water Processes	11
2	Bank of Ozone Generators	14
2a	Internal Arrangement of a Typical Horizontal Tube Type Ozonator	14
3	Ozone System at Choisy-le-Roi, France	24
4	Sipplinger Berg, West Germany Water Treatment Plant on Lake Constance	26
5	The Four Basic Components of the Ozonation Process	27
6	Low-Pressure Gas Preparation System	28
7	Air Feed Desiccation System, Annet-sur-Marne, France	29
8	Modular Ozone Generator With Power Supply and Control System	30
9	Interior of a Tubular Ozonator in Operation	32
10	Typical Details of Horizontal Tube-Type Ozone Generator	34
11	Parallel Plate Ozonators at Konstanz Waterworks, West Germany	36
12	Interior of Individual Plate Ozonator	36
13	Turbine Contactor at Zurich, Switzerland, Lengg Plant	37
14	Ozone Diffuser System Layout and Bubble Pattern	38
15	Chlorine Dioxide Generation From Acid and Sodium Chlorite at Lengg Plant, Zurich, Switzerland	49

FIGURES (continued)

16 Preparation of Chlorine Dioxide From Gaseous Chlorine and Sodium Chlorite at Tailfer, Belgium 50

17 Photographs of Typical U.S. Chlorine Dioxide Generation Systems. 53

18 Gaseous Chlorine-Sodium Chlorite Chlorine Dioxide Generation System 57

19 The CIFEC System. 58

TABLES

Number		Page
1	Operational Plants Using Ozone -- 1977	9
2	Applications of Ozone in Water Treatment	10
3	European Plants Inspected by Site Visit Team	22
4	Canadian Ozone Plants Visited.	23
5	Costs of Ozonation at European Drinking Water Plants . . .	42
6	U.S. Chlorine Dioxide Plants Visited	52

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Mr. G. Wade Miller, PTI Director of Environmental Programs, was the Principal Investigator on the project. He was assisted by Dr. R. G. Rice of Jacobs Engineering Group, Inc.; C. Michael Robson, P.E., of Purdue University and the City of Indianapolis; Ronald L. Scullin, P.E., of Public Technology, Inc.; Dr. Wolfgang Kühn of the Engler-Bunte Institute of the University of Karlsruhe, Federal Republic of Germany; and Dr.Harold Wolf of the Department of Environmental Engineering, Texas A & M University.

The project team was assisted greatly by Daniel Houck, P.E., who was primarily responsible for condensing the large report into this Executive Summary.

SECTION 1

INTRODUCTION

BASIS FOR THE OZONE/CHLORINE DIOXIDE STUDY

In 1975, the results of the National Organics Reconnaissance Survey (NORS) revealed the presence of potentially carcinogenic organic compounds in the drinking water supplies of each of the 80 cities surveyed. The compounds identified were all halogenated organics of the trihalomethane group, including chloroform. The carcinogenicity of chloroform in rats and mice was confirmed in a National Cancer Institute study published in 1976. In 1977, another survey of drinking water supplies, this time in 113 communities, was conducted. This survey, the National Organics Monitoring Survey (NOMS) included analyses for trihalomethanes for an entire year and quantified a number of other synthetic organic compounds found in water. The NOMS also demonstrated that trihalomethanes could form in finished water on the way to the customer's tap, as a result of chlorine disinfection, and that other potentially carcinogenic compounds could exceed the concentration of chloroform.

The densely populated and heavily industrialized countries of Western Europe have been faced with the problem of industrial effluents containing potentially harmful synthetic organic compounds for some time. Consequently, considerable effort has been expended in Europe, particularly in France, the Netherlands, West Germany, Belgium, and Switzerland to develop improved drinking water processes for the production of chemically safe drinking water.

The fact that ozone and chlorine dioxide, and often activated carbon, are widely used for treating drinking water in Europe and Canada, has been known for years in the U.S. Europeans, in particular, favor ozone for a wide variety of reasons, some linked to aesthetic values and some related to the need and desire to render highly polluted raw water sources safe. Europeans judge their drinking water by the absence of taste and odor; by contrast, Americans expect a slight taste of chlorine disinfectant and are reassured by the presence of this taste that the water is safe. Europeans have been faced with the necessity of using water which has already been used for a variety of industrial and domestic purposes Americans are finding themselves having to deal with this same problem more frequently.

Interest in these advanced treatment techniques used by other countries has been stimulated by a heightened awareness of the presence of potentially harmful substances in many U.S. drinking water supplies. The enactment of the Safe Drinking Water Act of 1974, also has contributed greatly to this increased interest. The Act reflects updated knowledge and technology which

has allowed the water treatment community to learn more about the substances contained in drinking water; this body of knowledge in turn has led to the establishment of more stringent criteria for drinking water quality, intended to protect the public health. The Safe Drinking Water Act specifically mandates the establishment of maximum contaminant levels for a number of microbiological, chemical and physical substances and mandates a program of investigation of treatment technologies which will permit attainment of new drinking water standards. Thus, as part of its responsibilities under this Act, the U.S. EPA has funded the study of the two drinking water treatment technologies summarized herein.

SCOPE OF THE STUDY AND HOW IT WAS CONDUCTED

In carrying out this study four approaches were used to collect a large amount of data in a relatively short period of time:

- A review of the international literature on ozone, chlorine dioxide, and organic oxidation products resulting from their use.

- Development of working relationships with the manufacturers of ozonation and chlorine dioxide equipment, the International Ozone Institute, European water research institutes, and drawing heavily on these sources for plant locations and plant data.

- Direct contact via detailed questionnaires with a large fraction of those water treatment plants in the U.S., Canada and Europe using either ozone or chlorine dioxide or both in their process scheme.

- Field visits to a substantial number of plants in the U.S., Canada and Europe by a multi disciplinary study team.

The literature review resulted in the identification of over 310 publications, reports and articles in the subject area. Where necessary, foreign language publications were translated.

For marketing and research/development reasons, equipment manufacturers normally keep good records on installed equipment. Thus, manufacturers often are an excellent source of information on plant locations and on operational data for the plants. Particularly in Europe and Canada, manufacturers and large water companies* were a major source of information. They forwarded detailed cost information, filled out questionnaires, helped to arrange for site visits, often accompanied the site visit team, and answered many

*In France, there are large water companies that design, construct and operate numerous water treatment plants through the use of contractual arrangements with local governments.

detailed questions posed by the study team. A list of the principal U.S. manufacturers of ozonation equipment is included as an Appendix of this report.

The International Ozone Institute (IOI) is the principal scientific organization for ozonation manufacturers, researchers and users. The IOI has chapters in Canada and most European countries. Extensive data were contributed by the IOI to this study.

After identifying a large number of plants to be contacted in the U.S., Canada and Europe, detailed questionnaires were prepared in English, French and German and distributed. Often questionnaire distribution was aided by manufacturers and water companies, consultants active in the field, professional associations, regulatory officials and consultants to the program. The questionnaires requested data in the following categories:

General Plant Information

- Plant location and contact person
- Plant capacity
- Basic process flow sheet
- Purpose of ozonation
- History of plant and history of ozonation use

Ozonation System

- Feed gas source and gas preparation system
- Design parameters of ozone generation system
- Design parameters of ozone contacting system
- Power consumption data

Analytical Procedures and Monitoring for Ozone Control

- Ozone dosage data; how and where it is measured
- Analytical procedures used to monitor the ozone process
- Removal of specific compounds by the ozone process and final products of the process
- Use of residual disinfectant
- Ozonation process controls and operating experience

Plant Water Quality

- Source of raw water and analyses performed
- Tests conducted on finished water

Chlorine Dioxide

- Purpose of chlorine dioxide usage
- Method of generation
- Analytical methods for chlorine dioxide monitoring

For plants which used chlorine dioxide and not ozone a separate questionnaire was prepared. Similar to the ozone questionnaire, the chlorine dioxide questionnaire asked detailed questions about the design, operation, monitoring and costs associated with chlorine dioxide usage. When it was determined that a plant using ozone also used chlorine dioxide, a follow-up mailing of the chlorine dioxide questionnaire was carried out.

Aggregating all of the data from the questionnaires plus information from the other sources discussed above, the plants of greatest interest were selected for field visitation. In Europe and Canada, principal emphasis was placed on plants which used ozonation, since many of these aso used chlorine dioxide. Twenty plants in Europe, 6 plants in Canada, and 13 plants in the U.S. were visited, the latter for the purpose of observing chlorine dioxide usage. The results of the field tests are summarized in Sections 3 and 5 of this document.

PRINCIPAL RESULTS OF THE STUDY

The findings of this study are summarized below:

- Ozone has many useful functions other than disinfection. It is misleading to perceive ozone merely as a disinfectant. As an oxidant, ozone is currently used to remove or break down taste, odor, algae, organic compounds (phenol, detergents, pesticides, etc.), cyanide, sulfides, iron, manganese, turbidity and flocculate micropollutants (soluble organics), and to inactivate viruses. Ozone also is used as a disinfectant but rarely in the context of an "either-or" alternative disinfectant to chlorine. It is normal to follow ozone as the primary disinfectant with a small dosage (up to 0.6 mg/l) of chlorine or chlorine dioxide. This practice assures a residual of disinfectant to protect the distribution system against bacterial regrowth.

- The European approach to water treatment is based on a somewhat different philosophy of treating water, which has led to the use of different water treatment technologies. The cornerstone of the European philosophy is the desire to produce waters which are free from undesirable tastes, including chlorinous tastes. The goal is to obtain water supplies which require little or no treatment such as pure ground waters. Failing this, the goal is to treat other water supplies to a quality equivalent to that of a pure groundwater. Thus, emphasis is placed on both chemical removal plus strict bacteriological and virological standards, as opposed to the U.S. where the main emphasis to date has been in producing bacteriologically safe water.

- Ozone and chlorine dioxide are well established technologies in Europe. Use of ozone for treating drinking water also is well established in the Province of Quebec, Canada, the Soviet Union, and to a lesser degree in Japan. Ozone is not widely used or understood by water system practitioners in the U.S. Chlorine dioxide is widely used in the U.S., but is generally not being used optimally. Little consistency is evident in its application and the study team encountered numerous U.S. plants where the generation and/or application of chlorine dioxide is poorly understood.

- Properly designed and operated ozonation system components (electrical power supply, gas preparation, ozone generation, ozone contacting) have an established history of reliable performance and low maintenance service in Europe. Competent, routine maintenance is a basic necessity, however, for reasonably troublefree performance.

- In the absence of halogenated organic compounds, granular activated carbon can be operated in a steady state mode with only infrequent regeneration using preozonation. Aerobic bacterial growth in the activated carbon beds is promoted by ozonating the processed water prior to the carbon contactors. This results in the growth of a fixed biomass within the filter which works in conjunction with the activated carbon to remove organics and ammonia. Activated carbon systems with preozonation have been operated in Europe for up to 2.5 years without need of regeneration. The study includes a section on the process, popularly referred to as Biological Activated Carbon. Further work to determine the performance, engineering parameters and costs of BAC are being studied by the EPA and will be available in the future.

- Pure chlorine dioxide, though more expensive than chlorine, does not form trihalomethanes. As a final disinfectant, it exhibits a longer lasting residual in distribution systems and, because it is used in lower concentrations, imparts little or no taste to the product water.

- Chlorine dioxide is widely applied in Europe and the U.S. The technology, especially in Europe, is well established. The U.S. plants which responded to the questionnaire and/or were visited by the study team largely displayed inadequate monitoring control and understanding of the process with the result that the chemical was often not being generated or applied properly.

PRINCIPAL RECOMMENDATIONS OF THE STUDY

- An in-depth cost analysis of the use of ozone as a unit process capable of performing a number of useful functions is needed. Various combinations of air preparation, generation, contacting, and off-gas use or destruction systems should be studied.

- Epidemiological studies of populations using drinking water treated with chlorine dioxide and ozone should be conducted. Research directed at determining whether or not the chlorite ion is toxic, and at what levels, would be a part of that study. Toxicity of residual ozone in water is of little import because of its short half life in water.

- Technical assistance should be made available to those municipalities currently using chlorine dioxide in order to assure that it is being used properly and in safe concentrations. This could be provided by EPA, supported by expert assistance by contractors as needed.

- Granular activated carbon with preozonation appears to have great potential for use in U.S. water treatment. Pilot projects on this treatment combination should be initiated to determine its effectiveness for organics and/or ammonia removal. Engineering and cost details of currently operating BAC plants in Europe should be developed.

- A thorough investigation of the potential savings in activated carbon regeneration costs resulting from extended life of the biological activated carbon also should be investigated.

SECTION 2

WATER TREATMENT PHILOSOPHIES

INTRODUCTION

Water treatment approaches in Europe, and to a lesser extent, Canada, are markedly different than U.S. practices. In Europe, this is a result of strongly held concepts of drinking water quality. Although variations exist from country to country in actual practices, the philosophy of approach is quite similar.

Summarized herein are philosophies and the results of questionnaire surveys conducted in Europe and Canada.

EUROPEAN WATER TREATMENT PHILOSOPHIES

As one result of the study, several fundamental areas were found in which European and American drinking water treatment differ significantly. These areas include a different set of philosophies of treating drinking water from which, in turn, have evolved the use of several drinking water technologies.

The cornerstone of European water treatment philosophy is the desire to produce drinking waters that are free from chlorinous or other undesirable tastes, and which are chemically and bacteriologically safe. The philosophy has been best summarized by Professor Dr. Heinrich Sonthimer, Director of the Engler-Bunte Water Research Institute at the University of Karlsruhe, Federal Republic of Germany, and a noted authority on the treatment of polluted surface waters. Professor Sontheimer states simply that "in Germany we prefer not to have to treat water, but if we do have to treat it, then we treat it to a quality equivalent to that of a pure, unpolluted groundwater." This sentiment is echoed by other European drinking water experts in France, The Netherlands, Belgium and Switzerland.

The most striking difference between U.S. and European practices is the concentration on bacteriological quality of water in the U.S. as an indicator of safety. The Europeans, while concerned with bacteriological and virological safety of water, are much more concerned with chemical contamination. Europeans are brought up with the understanding that when there are any unnatural tastes in water (especially chlorine tastes) the water is contaminated. Many urban dwelling Americans are brought up with the understanding that when chlorine cannot be tasted, the water may be contaminated. Therein lies one of the major reasons for the difference in approaches in treating water supplies. Americans use relatively heavy dosages of chlorine in the

water to assure bacteriological (but not necessarily chemical) safety; Europeans reduce the chlorine demand of water (insuring chemical safety) so that the residual chlorine used to maintain bacteriological safety in the distribution systems will be so small as to be tasteless in the water.

Waters that do not need to be treated, such as pure groundwaters, exhibit a number of chemical and biological parameters which have been adopted as goals for treating German drinking waters. Two significant parameters are Total Organic Carbon (TOC) and oxidant demand (chlorine demand). If a German surface water supply is to be treated, then the product water first must satisfy these two parameters, then other standards. The TOC must be less than 2 mg/l and oxidant demand (chlorine demand) less than 0.5 mg/l. In other words, if the water demands more than 0.5 mg/l of chlorine to produce a stable residual for German distribution systems, then the water treatment process must be modified so that a higher quality drinking water is produced.

Similarly, Switzerland, The Netherlands, France, Austria and other western European countries are searching continually for groundwater supplies or water from mountainous areas which is relatively pure and requires little or no treatment prior to distribution. Several major European cities, do not treat their water supplies at all; no chemicals are added. If the source of raw water supply is polluted, however, as is the case of the Rhine in northern Germany and the Seine downstream of Paris, Europeans are prepared to utilize a range of technologies to produce a chemically and bacteriolgically safe drinking water. Each water is analyzed for pollutants and subjected to the treatment train that will remove them most effectively. Many of these techniques are physical in nature (settling, adsorption, microstraining, ozonation*) as opposed to the addition of chemicals.

At least 1039 municipal water plants in 29 countries worldwide use ozone for some purpose (Table 1). Most of these plants are located in Europe. France has 593 plants (Nice, France has employed ozonation continuously since 1906), Switzerland has 150, Germany has 136, and Austria has 42. By contrast, there are only four ozonation plants currently in operation in the U.S. (Whiting, Indiana; Strasburg, Pennsylvania; Monroe, Michigan; Bay City, Michigan) with one additional under construction (Saratoga, Wyoming). Canada currently has 20, all but one located in the Province of Quebec.

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* Ozonation is viewed by Germans as being a natural product and not a chemical since it reverts back to oxygen and thus does not remain in the water.

TABLE 1. OPERATIONAL PLANTS USING OZONE -- 1977

Country	Number of Plants
France	593
Switzerland	150
Germany	136
Austria	42
Canada	23*
England	18
The Netherlands	12
Belgium	9
Poland	6
Spain	6
USA	5
Italy	5
Japan	4
Denmark	4
Russia	4
Norway	3
Sweden	3
Algeria	2
Syria	2
Bulgaria	2
Mexico	2
Finland	1
Hungary	1
Corsica	1
Ireland	1
Czechoslovakia	1
Singapore	1
Portugal	1
Morocco	1
Total	1,039

*Includes expansions. Actual number of operating plants in Canada equals 20, with 3 more under construction

Ozone, as applied in Europe, is used for many purposes (Table 2), color removal, taste and odor removal, turbidity reduction, organics removal, microflocculation, iron and manganese oxidation, bacterial disinfection and viral inactivation being the most prevalant. Most of these applications are based upon ozone's high oxidizing power (it is the second most powerful oxidant available on a commercial scale). Ozone is introduced at different points in the water treatment process, depending on its intended application(s). When used for iron and manganese oxidation or to induce flocculation, it usually is introduced at an initial point, and when used for taste and odor removal it is introduced at an intermediate point. When used for

viral inactivation or bacterial disinfection, it is introduced near the end of the water treatment process, sometimes as the terminal step. In several plants visited, multiple uses of ozone were observed, i.e., iron and manganese oxidation and/or microflocculation in the initial treatment stages and organics oxidation and/or disinfection near the end of the treatment processes. Figure 1 shows a standard water treatment process with the points of application of ozone for the purposes listed in Table 2.

TABLE 2. APPLICATIONS OF OZONE IN WATER TREATMENT

Bacterial Disinfection
Viral Inactivation
Oxidation of Soluble Iron and/or Manganese
Decomplexing Organically-Bound Manganese (Oxidation)
Color Removal (Oxidation)
Taste Removal (Oxidation)
Odor Removal (Oxidation)
Algae Removal (Oxidation)
Removal of Organics (Oxidation)
  such as Pesticides
  Detergents
  Phenols
Removal of Cyanides (Oxidation)
Suspended Solids Removal (Oxidation)
Preparation of Granular Activated Carbon for Enhanced Biodegradability of Ammonia and Dissolved Organics

In European water treatment practices, ozone is seldom considered simply as an either-or "alternate disinfectant to chlorination", especially outside of France. Instead it is recognized first for its ability to oxidize a variety of materials and to inactivate viruses. In many plants the bacterial disinfection capability of ozone is a secondary benefit which is provided when ozone is installed for another primary purpose.

Ozonation is seldom used as a terminal step because of its short half-life in water. It usually is followed by the addition of small dosages (less than 0.6 mg/l) of chlorine or chlorine dioxide. Ozone causes chemical transformations of dissolved organic compounds in the water, making them more easily biodegradable and thus providing food for bacteria. This condition can lead to bacterial regrowths in water distribution systems. Ozone can be used as a terminal step if the dissolved organic carbon concentration of water to be distributed is less than 0.2 mg/l. Also, ammonia should not be present, otherwise regrowth of nitro-bacteria can occur.

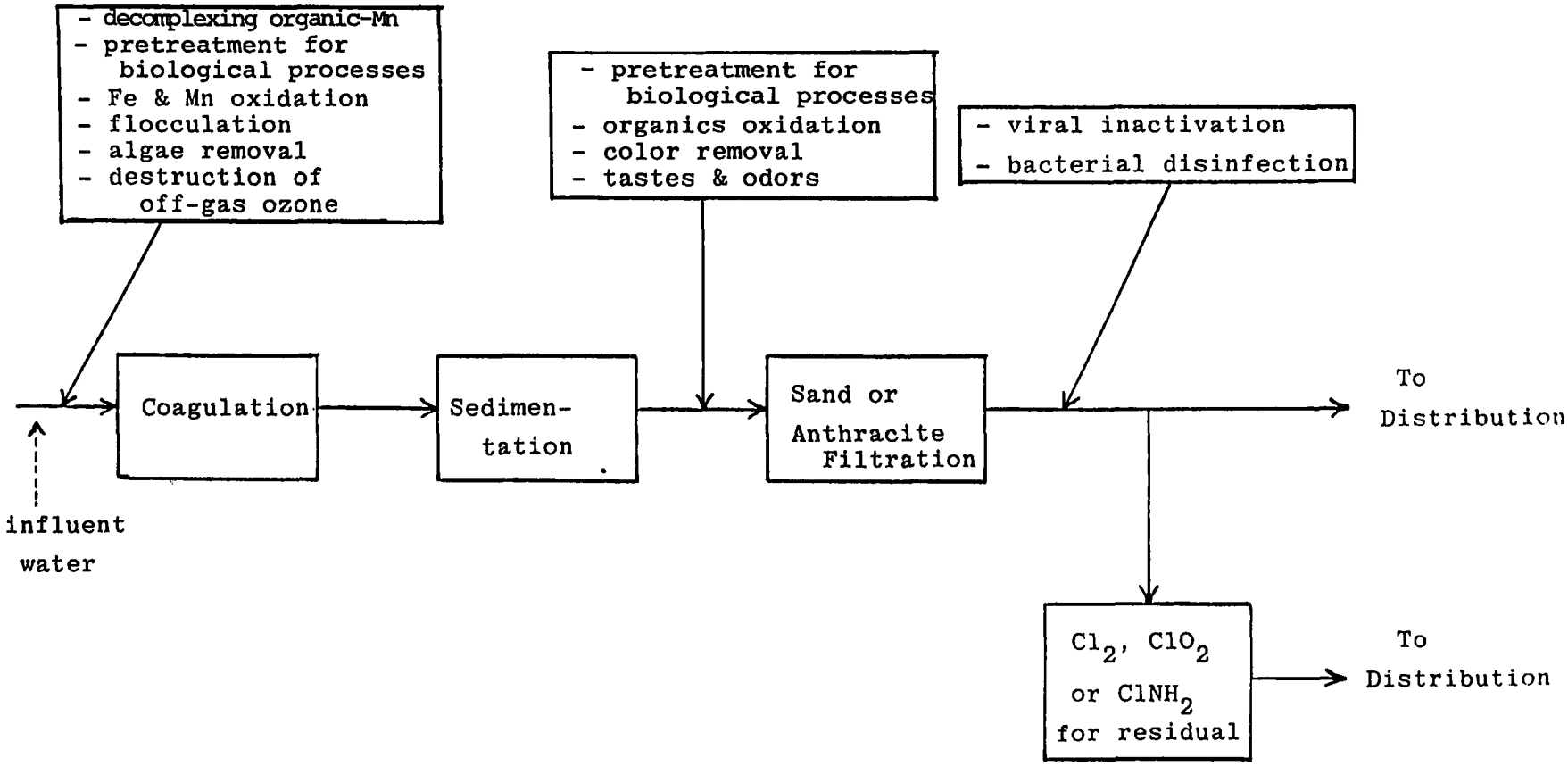


Figure 1. Typical Points of Application of Ozone in Drinking Water Processes

CANADIAN WATER TREATMENT PHILOSOPHIES

There appears to be no unified national water treatment philosophy as such in Canada, but there are voluntary recommended national drinking water standards. Each province decides whether to follow the Canadian Drinking Water Standards, as developed in 1968 by a joint committee representing each of the country's provinces. These standards parallel in some respects the U.S. standards and a revision of the current standards in 1978 is expected to reflect some of the provisions of the U.S. Safe Drinking Water Act of 1974 (PL 93-523).

The two most populous Canadian provinces, Ontario and Quebec, are the only two known to use ozone or chlorine dioxide to any appreciable extent. There are currently 20 plants in Canada which use ozone, 19 of which are in Quebec. Ten plants use chlorine dioxide and all are located in Ontario.

The philosophy of ozone usage in Canada evolved from a need to deal with seasonal taste and odor problems, plus the disinfection needs of surface water supplies. Ozone has been viewed in Canada as an alternate for both chlorine disinfection and activated carbon treatment. For example, some Canadian water treatment experts have pointed out that ozone costs are comparable to those of chlorine plus activated carbon, and ozone provides side benefits of decolorization, superior appearance and improved taste and odor characteristics. Chlorine dioxide is used in Canada largely because of its superior characteristics in destroying tastes and odors from phenolic compounds.

SECTION 3

OZONE

INTRODUCTION & BACKGROUND

Ozone was first discovered by Van Marun, a Dutch philosopher in 1785 when he noticed a characteristic odor in the air around his electrostatic machine. In 1840, Schonbein reported the odor as a new substance and gave it the name ozone, as derived from the Greek world "Ozein", meaning to smell.

Present day commercial ozonation equipment largely evolved from an apparatus designed by Werner von Siemens in 1857 in Germany. The Siemens ozonator has been developed into the present tube type ozone generators which use glass tubes coated internally with a metal dielectric and individual tube cooling with water, all housed in a cylindrical body. (Figures 2 and 3)

There are many variations in ozone generator design, including plate type units which feature parallel plates rather than tubes, but all of the units operate on the silent corona discharge principle by using the oxygen in air (or pure oxygen feed) to form ozone. All ozone generators produce heat which must be minimized in order to maximize ozone production.

The earliest use of ozone as a germicide occurred in 1886 in France, when de Meritens demonstrated that diluted ozonized air could sterilize polluted water. Pilot studies followed and in 1893 the first drinking water treatment plant to employ ozone was erected at Oudshorrn, Holland. Other plants quickly followed at Wiesbaden (1901) and Paderborn (1902) in Germany. In 1906, the Nice, France plant was constructed using ozone for disinfection. Nice has used ozone continuously to the present. Today there are more than 1000 drinking water treatment plants using ozone for one or more purposes.

In Canada, the first ozonation plant was built in Ste-Therese, Quebec Province in 1956. There are now 20 ozonation plants in Canada, with three more under construction including the largest drinking water treatment ozone system in the world at Montreal, Canada.

In the U.S., the first ozonation plant was started at Whiting, Indiana in 1941 for taste and odor control.

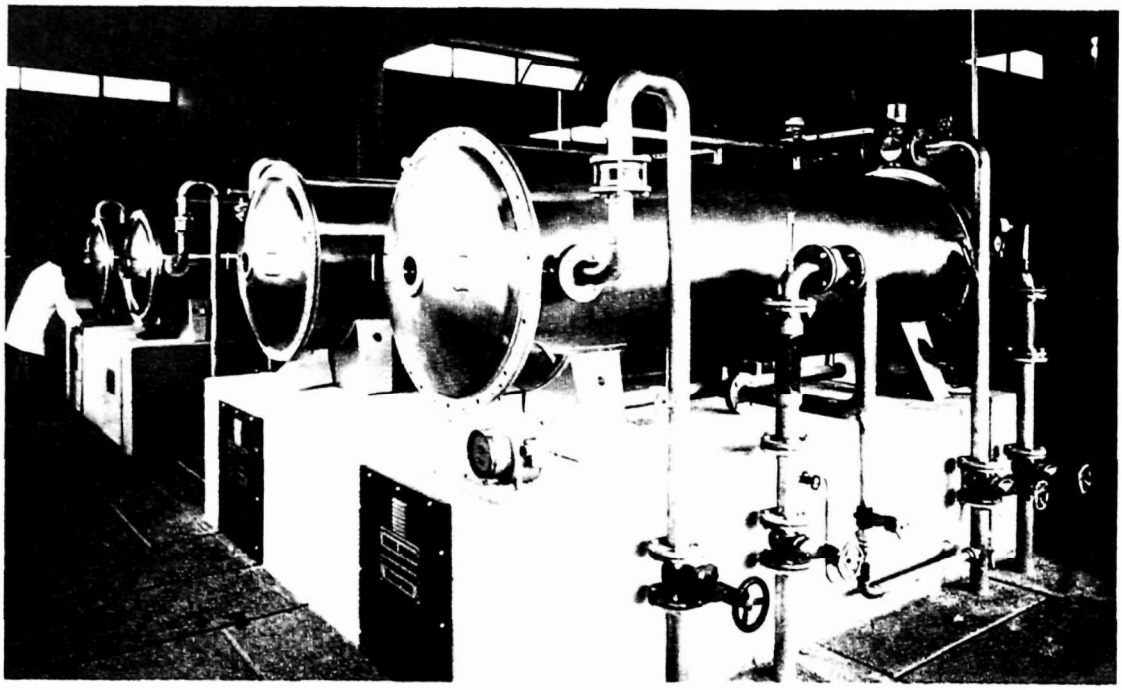


Figure 2. Bank of Ozone Generators

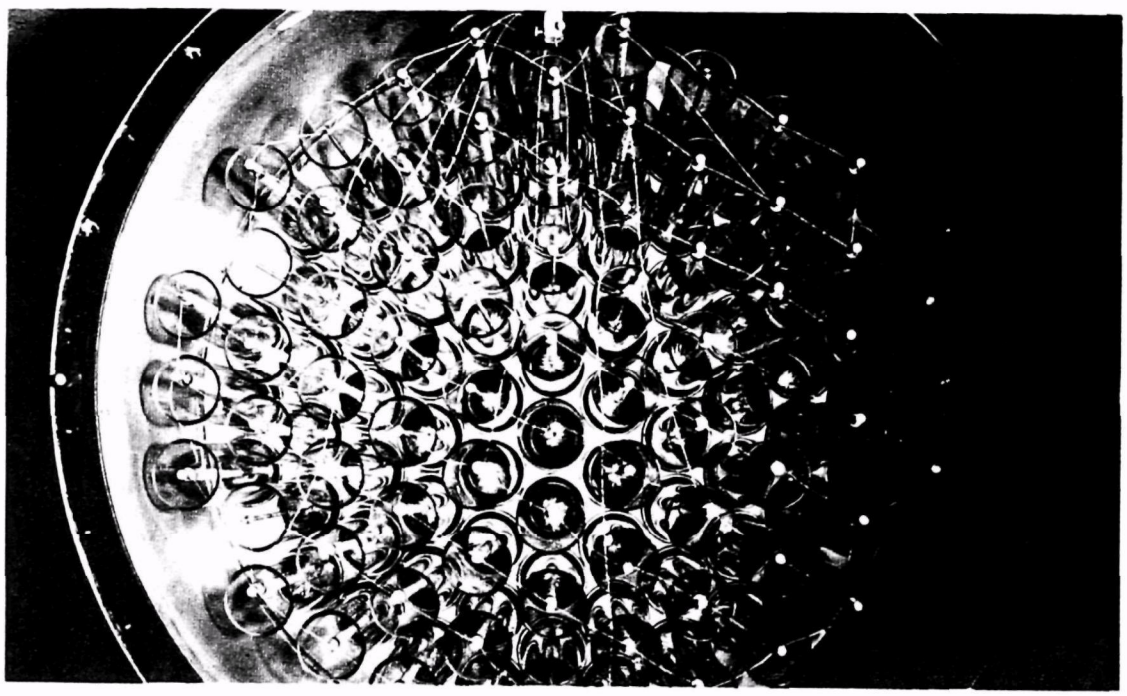


Figure 2a. Internal Arrangement of a Typical Horizontal Tube Type Ozonator

PROPERTIES AND REACTIONS OF OZONE

Ozone is an unstable gas which boils at minus 112 degrees Celsius (atmospheric pressure), is partly soluble in water (about 20 times the solubility of oxygen), and has a characteristic penetrating odor, readily detectable by humans at concentrations as low as 0.01 to 0.05 ppm. Ozone is the most powerful oxidant currently in use for water treatment. Commercial generation equipment produces ozone in concentrations of 1 to 3% in air (2 to 6% in oxygen). Ozone is relatively unstable in a water solution but is considerably more stable in air, particularly dry, cool air.

Because it is a powerful oxidant, ozone will react with a wide variety of organic materials. Ozone oxidizes phenol to oxalic and acetic acids. Ozone oxidizes trihalomethane (THM) compounds to a limited degree under the proper pH conditions and also reduces their concentration by air stripping. Trihalomethanes also are oxidized by ozone in the presence of ultraviolet light. More significantly, oxidation with ozone does not lead to the formation of THM's as does chlorination. A combination of ozone and ultraviolet radiation destroys DDT, PCB's, malathion and other pesticides, but requires high dosages and extended contact times not normally encountered in drinking water treatment plants. Ozonized organic materials are generally more biodegradable and adsorbable than the starting, unoxidized compounds. If ozonation is used as the terminal treatment step in water containing significant amounts of dissolved organics, bacterial regrowth in the distribution system can occur. Thus ozonation generally is not used as the final treatment step but is followed by granular activated carbon filtration and possibly the addition of a residual disinfectant.

Oxidation of humic materials, the precursors of trihalomethanes, can be accomplished by ozonation. Studies have shown that, given proper conditions, there is significant reduction in THM formation when ozone is applied prior to a chlorination step.

PUBLIC HEALTH ASPECTS OF OZONATION

Ozone has been shown to be effective against viruses. The French have adopted a standard for the use of ozone to inactivate viruses. When an ozone residual of 0.4 mg/l can be measured four minutes after the initial ozone demand has been satisfied, viral inactivation is assured. This characteristic, along with its freedom from THM formation, is of major significance in considering the public health aspects of ozonation. In addition, when ozone is coupled with granular activated carbon filtration, a high degree of removal of organic compounds, some of which may be potentially carcinogenic, can be achieved.

There is a paucity of data for assessing the public health implications of ozone usage. Only a limited amount of study has been carried out on the toxicity of the oxidation products of ozone and the removal of specific compounds by ozonation. During the study, some data were obtained regarding ozone reactions on specific compounds, but the data are quite limited. Further research efforts are planned for the study of ozonation end products. Data on

the removal of specific organics by the BAC process is being developed at the Rouen Plant in northwestern France. Preliminary results indicate that the first ozonation step (applied dosage 1 mg/l, contact time 3 minutes) results in a 63% quantitative decrease, and the sand filtration and carbon adsorption yields an additional 13% decrease in the total mass of the infrequent organics. The post treatment step (1 mg/l dosage, contact time 12 minutes) accounts for a 9% decrease, for an aggregate decrease of 85% through the process. Later data for the plant indicate even better results.

By way of summary, the evidence available does not indicate any untoward health hazards associated with the use of ozone, either alone or in conjunction with granular activated carbon. Some questions regarding the possible release of endotoxins by the BAC process should be answered with further research, and there is a need for better research data on the products of ozone oxidation of organic compounds.

OPERATIONAL EXPERIENCES WITH OZONE

Extensive information on current practices, engineering and costs was obtained during the course of the study, primarily from three sources:

Questionnaire responses
Equipment manufacturers/Integrated Water Companies
Site visits

Questionnaire responses provided variable amounts of data on many plants, as discussed below. Using other data supplied by ozonation equipment manufacturers and large integrated companies, together with questionnaire data, literature search data, and assistance from other professionals and organizations, sites were selected for visitation. Questionnaire responses and site visit results are summarized below.

Summary of Data From European Ozone Questionnaires

Eleven hundred niney-two (1192) questionnaires were mailed to municipal water plants in western Europe in mid-1977. These questionnaires asked for detailed information on various aspects of ozone usage. Questionnaires were mailed to plants in France, The Federal Republic of Germany (FRG), Switzerland, Austria, Belgium, the Netherlands, and Great Britain. Questionnaire mailings and responses by country are as follows:

Country	Mailed	Received	Estimated Total Municipal Plants Using Ozone
France	300	63	593
Germany	835	31	136
Great Britain	15	9	18
The Netherlands	10	7	12
Austria	11	5	42
Switzerland	20	9	150
Belgium	1	1	9
Total	1192	122	900

Great Britain--

Fifteen questionnaires were mailed to British plants using ozone and six responses were received. There are 18 water plants in Great Britain known to be using ozone. Most have used ozone only a few years. The plants responding averaged 105,000 cu m/day in size, and ranged in size from 5,000 cu m/day to 450,000 cu m/day. The primary application of ozone in Great Britain is for color removal. Each of the six plants responding indicated ozone use for this purpose. Other uses indicated include: bacterial disinfection (2 plants); iron and manganese oxidation (2 plants); taste and odor removal (1 plant); and viral inactivation (1 plant).

Treatment processes vary. Ozone is used after a filtration step in each of the six plants. In four of the plants microstraining is the filtration method used. Chlorine is used as a final disinfectant in each of the six plants. In 3 of 6 plants chlorination follows ozonation with no filtration step in between.

Five of the six reporting plants use tube type water cooled ozone generators. Ozone contacting methods include diffusers (3 plants), injectors (2 plants) and turbine (1 plant). Off-gas treatment is practiced at five of the six reporting plants.

Power consumption for ozone generation and application (including air preparation, generation, contacting, and off-gas treatment) averaged 29.7 kwh/kg of ozone produced among the responding plants.

Ozone dosage averaged 2.37 mg/l for the four plants that responded to that portion of the questionnaire. It should be noted that chlorine dioxide and ozone are not used jointly in any British plant. Chlorine dioxide is often used as a distinct unit process, added stepwise to insure a better oxidant residual.

The Netherlands--

Questionnaires were mailed to 10 major plants in The Netherlands using ozone. Seven were returned. Most of the Dutch plants which responded have been using ozone for less than five years.

The prevalent water treatment approach is that physical and biological treatment processes are preferred. Chemicals and disinfecting agents are used only in cases where they are unavoidable. Chlorine dioxide currently is not used. Chlorine is used as a terminal disinfecting agent although many plants indicate plans to switch to chlorine dioxide in the future.

The plants responding to the questionnaire are relatively large, averaging 49,500 cu m/day. The range in size is from 1000 cu m/day to 120,000 cu m/day. The primary application of ozone appears to be for color removal (6 plants), taste removal (6 plants), and odor removal (4 plants). Other applications are for bacterial disinfection (2 plants), viral inactivation (2 plants), organics removal (3 plants) and as a filtration aid (1 plant). Ozone dosages range from 0.23 mg/l to 5 mg/l. Average dosage for seven plants was 2.59 mg/l.

Each of the seven reporting plants uses tube type water cooled ozonators. Most of the plants use submerged turbines for contacting ozone. Five of seven plants practice off-gas destruction.

Power consumption ranges from 17 to 20 kwh/kg of ozone produced at the Houdsweg plant to 50 kwh/kg of ozone produced at the Engelse Werks plant.

Chlorine is used as a final disinfectant in 3 of the 7 plants; a fourth applies 0.2 mg/l sodium hypochlorite. Ozone is used as the terminal step in the Engelse Werk plant. In the other two plants, sand filtration is the terminal step and immediately follows the ozonation process.

Austria--

There are 42 municipal water plants in Austria currently using ozone. Questionnaires were mailed to 11 large water companies in Austria which serve 50% of the Austrian people. Five questionnaires were returned from water companies in Salzburg, St. Polten and Linz. Ozone has been used in the five facilities an average of 6.6 years, with the oldest plant having used ozone for 12 years. Plants range in size from 4,000 cu m/day to 48,000 cu m/day, average size being 21,000 cu m/day.

Bacterial disinfection is the main purpose of ozonation. Other applications indicated are for viral inactivation (2 plants), color removal (1 plant), and organics removal (1 plant).

Ozone dosages are relatively low, ranging from 0.06 mg/l to 1.2 mg/l, averaging 0.48 mg/l for the five plants reporting data. The low dosage can be attributed to the high raw water quality. The water source for each of the plants is deep wells.

Ozone generators in three plants are tube type, water cooled units. In the other two plants, plate type water cooled units are used. Contacting is by injection in three plants, and by a surface aeration device at the other two plants. Most of the plants reported that some type of off-gas destruction is practiced.

Power consumption for ozone production, contacting, and off-gas treatment averages 34.4 kwh/kg of ozone produced. Consumption ranges from 16 kwh/kg at the two St. Polten plants to 55 kwh/kg at the Salzburg City Waterworks.

The only oxidant other than ozone used in the five Austrian plants is chlorine (at one plant). In four of the five plants, ozonation is the only treatment of the water. The fifth plant applies ozone and then adds 0.8 mg/l of the sodium hypochlorite.

Switzerland--

There are approximately 150 water plants in Switzerland which use ozone. Many of these are very small plants. Questionnaires were not mailed to all plants, but rather to 20 representative waterworks which serve more than one

million people. Nine of 20 questionnaires were completed and returned. Five of the nine plants have been using ozone for more than 10 years; averaging period of usage is about 12 years.

The plants reporting data range in size from about 2,500 cu m/day (Waterworks Alstatten) to the Lengg Plant in Zürich which has a capacity of 250,000 cu m/day. Average plant size for the nine plants is about 65,600 cu m/day.

Ozone is used for several purposes, among them bacterial disinfection (7 plants), viral inactivation (7 plants), odor removal (7 plants), taste removal (6 plants) and organics removal (4 plants). Ozone dosage reported ranged from 0.3 to 1.5 mg/l.

Five of nine plants have tube type, water cooled ozone generators. The other four have plate type, water cooled generators. Contacting is accomplished in a number of methods: submerged turbines (4 plants), injector (3 plants), porous tubes (2 plants). Most of the plants did not treat contactor off-gases.

Average power consumption for ozone generation and contacting for the five plants reporting data is about 33.5 kwh/kg.

Six of nine plants use chlorine dioxide as a terminal step. It is estimated that 80% of the Swiss plants which use ozone also use chlorine dioxide as a final disinfectant. Chlorine dioxide is applied in very small amounts. Chlorine is used as a disinfectant at two plants. Ozone is the only treatment applied at the small (2500 cu m/day) Alstatten plant.

Four plants report the use of granular activated carbon directly following ozonation.

Federal Republic of Germany--

There are approximately 136 municipal waterworks in West Germany which use ozone. Thirty-one of these waterworks responded to a questionnaire.

Ozone usage in West Germany is more varied than in any other country. Purposes of ozonation, dosage, methods of contacting, and a number of manufacturers supplying equipment do not fall into a consistent pattern as is the case in other countries. Power consumption also varies greatly. The average period that ozone has been installed in the German plants responding is only 7.6 years, though ozone has been used in the Düsseldorf water plants since the mid 1950's. Plants using ozone in West Germany range in size from 1000 cu m/day to 648,000 cu m/day.

Ozone is used for many purposes in West Germany. Twenty-four of the 31 plants indicate its use for organics removal, taste (13 plants), viral inactivation (8 plants), iron oxidation (7 plants), manganese oxidation (6 plants), odor removal (7 plants), turbidity reduction (6 plants), and color removal (5 plants). Ozone dosages range from 0.15 mg/l at the Diez/Lahn plant to 5.7 mg/l at the Osterode plant.

Twenty-six facilities have tube type, water cooled generators while five use plate type, water cooled generators. Contacting of ozone with the water stream is accomplished mainly by means of injection (21 of 31 plants). Other methods are submerged turbine (2 plants), packed column (3 plants), and porous tubes (1 plant). Less than half of the reporting plants practice off gas destruction.

Power consumption for ozone generation, air preparation, contacting and off gas treatment appears to be higher at some West German plants than in other countries surveyed. However, the lowest power consumption cited (15 kwh/kg) is at Duisberg, the only known municipal water plant that produces ozone from oxygen.

For final disinfection, 9 plants use chlorine dioxide, 8 use chlorine and 2 use sodium hypochlorite. Nine plants apply ozone as their only treatment step. In 3 other plants, ozone is the only oxidant used. Ten of the 31 reporting plants use granular activated carbon (GAC) as an adsorbent. In every case, GAC follows the ozonation step.

France--

Ozone is used in approximately 600 French water plants. Questionnaires were mailed to 300 of these plants and a total of 63 completed questionnaires were received.

Ozone usage for water treatment began in France in 1906. While there are 10 plants that have used ozone for more than 10 years (the oldest having used ozone for 52 years), the average period of use among the responding plants is about 8 years. The average size of plants responding to the questionnaire is 29,100 cu m/day. Sizes ranged from 350 cu m/day to 240,000 cu m/day. Unlike West Germany, most of the plants use surface water as a raw water source. Forty-three of 63 plants indicated use of surface water as a raw water source.

The primary purposes cited for ozone use are bacterial disinfection (59 plants), viral inactivation (35 plants), taste removal (31 plants), and organics removal (24 plants). Other indicated uses include color removal (18 plants), turbidity reduction (10 plants), iron removal (7 plants) and manganese removal (5 plants). Ozone dosages range from 0.15 mg/l to 10 mg/l.

Most of the plants use tube type, water cooled generators. Only nine indicated usage of plate type, water cooled units. Contacting is accomplished primarily by porous plate diffusers, this method being used in 44 plants. Injectors are used in 10 plants, packed columns in 3 plants and spray towers in 2 plants. Most of the plants reporting do not practice off-gas destruction.

Power consumption is fairly consistent for the 33 plants that reported power data. Average power consumption is 31.3 kwh/kg of ozone generated for the total ozonation unit process.

Chlorine is used as a final disinfecting agent in 26 plants. Chlorine dioxide is used in 13 plants. In twenty-two of 63 plants, ozone is the only oxidant used and often it is the terminal step.

The classic French water treatment process is remarkably similar to the U.S. "conventional" process. The process used in many plants involves prechlorination, coagulation, sedimentation, filtration, ozonation, and use of chlorine or chlorine dioxide as a terminal treatment step. The only marked difference is the ozonation step. This allows smaller quantities of chlorine to be used as the residual disinfectant. Normally less than 1 mg/l of chlorine is added, or less than 0.6 mg/l of chlorine dioxide for purposes providing a protective residual for the distribution system.

Summary of Data From Canadian Ozone Questionnaires

Eighteen questionnaires were distributed in Canada, and all were completed and returned. These comprise all of the plants in Canada using ozone with the exception of a plant at Frobisher Bay in the Northwest Territories, and the Chomedey Plant at Laval, Quebec. Data for the latter were obtained at the time of the plant visits. The study provides a data summary for each of the responding Canadian plants.

Energy consumption for ozone treatment reported by the Canadian plants falls mainly in the 20 to 30 kwh/kg range. One older plant, Ile Perrot, reported 45 kwh/kg whereas one of the newest Canadian plants, Pierrefonds, reported 18 kwh/kg. Off-gas destruction is not normally practiced in Canada.

Porous diffusers and injectors are the most widely used form of ozone contacting. Only one plant, Ile Perrot, uses a submerged turbine. Contact times, where given, ranged from 5 to 20 minutes with most plants reporting contact times of 2 to 10 minutes. The Roberval plant practices two stage ozonation, utilizing ozone to enhance coagulation and then later for disinfection.

SITE VISITS

A significant portion of the report is based on findings and observations made during site visits to twenty municipal water treatment plants in Europe and seven plants in Canada which use ozone. The 20 plants in four European countries were visited in May 1977 by a team of scientists and engineers. In August 1977, this team inspected seven plants in the Province of Quebec, Canada. Tables 3 and 4 lists the plants visited in Europe and Canada along with some of their pertinent characteristics.

Plants were selected on the basis of variability and uniqueness of ozone application, size, and ozone treatment train variability. The site visit team inspected plants in Europe ranging in size from Annet-sur-Marne (25,000 cu m/day) in France to one of the largest plants in West Germany, Sipplinger Berg (648,000 cu m/day) (Figure 4).

TABLE 3. EUROPEAN PLANTS INSPECTED BY SITE VISIT TEAM

Name	Location	Design Capacity (cu m/day)	Ozone Generator Manufacturer	Ozone Generator Type
Choisy-le-Roi	Paris suburbs	800,000	Trailigaz	Tube
Morsang-sur-Seine	Paris suburbs	150,000	Degrémont	Tube
Rouen-la-Chapelle	NW of Paris	30,000	Trailigaz	Tube
Aubergenville	NW of Paris	100,000	Welsbach	Tube
Neuilly-sur-Marne	Paris suburbs	600,000	Trailigaz	Tube
Annet-sur-Marne	Paris suburbs	25,000	Trailigaz	Tube
Clairfont	Toulouse	110,000	Trailigaz	Tube
Super-Rimiez	Nice	90,000	Trailigaz	Tube
Tailfer	Brussels	260,000	Trailigaz	Tube
Holthausen	Düsseldorf	192,000	Herrmann	Tube
Flehe	Düsseldorf	88,000	Herrmann	Tube
Am Staad	Düsseldorf	144,000	Herrmann	Tube
Dohne	Mülheim	48,000	Trailigaz	Tube
Wuppertal	Wuppertal	168,000	Herrmann	Tube
Wittlaer III	Duisburg	48,000	Demag	Tube
Lengg	Zürich	250,000	Kerag	Tube
Kreuzlingen	Kreuzlingen (Switzerland)	34,560	Sauter	Otto Plate
Konstanz	Konstanz (Germany)	50,000	CEO (Trailigaz)	Otto Plate
Sipplinger Berg	Sipplingen (Germany)	648,000	Herrmann	Tube
Langenau	near Ulm (Germany)	198,700	Degrémont	Tube

TABLE 4. CANADIAN OZONE PLANTS VISITED

Name	Design Capacity (cu m/day)	Ozone Generator Manufacturer	Ozone Generator Type
Quebec City	218,000	Trailigaz	Otto
Sherbrooke	98,862	Degremont	Tube
Ile Perrot	6,800	Welsbach	Tube
Pierrefonds	95,500	Trailigaz	Tube
St. Denis sur Richelieu	27,300	PCI	Otto
Laval (Chomedey)	176,900	Welsbach	Tube

Plants containing ozone equipment supplied by each of the major European manufacturers were inspected. These included Trailigaz and Degremont of France, Gebruder Herrmann and Demag of Germany, and KERAG and Sauter Corporation of Switzerland. Plants using U.S. manufactured and Canadian made equipment also were observed in Europe (Welsbach) and Canada (Welsbach, PCI Ozone, and Degremont Infilco Ltd). These manufacturers provided substantial information on ozone installations and operational data.

The only operating municipal plant (Düisburg, Germany) using oxygen as the starting material for ozone production was visited. Five plants in the Dusseldorf area which practice river sand bank filtration and which place heavy emphasis on the use of ozone plus activated carbon were inspected. The newest concepts in German drinking water practice were viewed at the Dohne plant in Mulheim near Dusseldorf. In southern Germany, the Langenau plant, which uses ozone primarily for microflocculation, followed by activated carbon, was visited.

Rouen-la-Chapelle, located about 70 miles northwest of Paris, uses two stage ozonation, and is the first French plant to use biological activated carbon (BAC). This process began operating at Rouen in early 1976. Two plants in southern France using ozone as the terminal step in the process, Clairfont in Toulouse and Super Rimiez in Nice, were visited. Several plants having highly sophisticated control systems were visited. The most notable ones in this category were Neuilly-sur-Marne, (600,000 cu m/day) in the Paris suburbs and Kreuzlingen on the Bodensee (Lake of Constance) in northern Switzerland.

Ozone systems that had been in operation for a number of years were also of interest. Choisy-le-Roi in Paris (Figure 3) has had its current system in operation for more than 10 years. Holthausen (Düsseldorf) has been operating ozonation and granular activated carbon systems for 20 years.

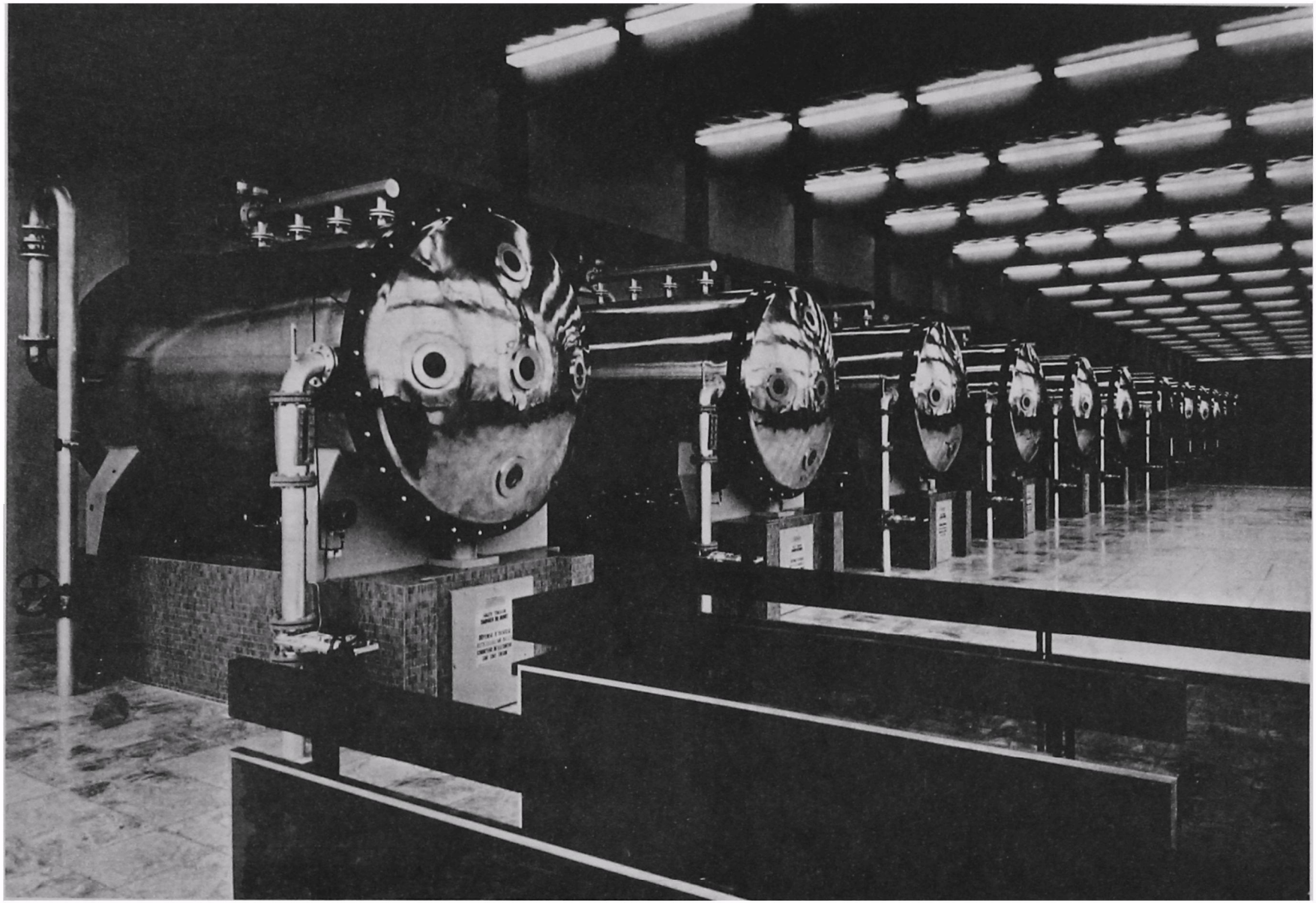


Figure 3. Ozone System at Choisy-le-Roi, France

Six of 19 operating plants in the province of Quebec, using ozone, were visited. A seventh, the new Charles-J. des Baillets plant in Montreal, scheduled to go on-line in 1980, also was visited. The largest ozone plant in Canada, Quebec City (218,000 cu m/day), was inspected. The other five visited were Sherbrooke, Pierrefonds, Laval-Chomedey, St. Denis, and Ile Perrot. Pierrefonds and Sherbrooke are the two newest ozone facilities in Canada and thus represent the most recent efforts in North American practices of the French technology. St. Denis is a very small plant (27,000 cu m/day, 7.2 mgd) that has PCI ozone equipment. Ile Perrot is an older small system that has a Welsbach ozonator. The Chomedey plant, located in the City of Laval, is rated at 39 million Imperial gallons per day (177,990 cu m/day), but only 114,000 cu m/day is treated with ozone for taste and odor control. The older part of the plant produces 63,890 cu m/day and uses powdered activated carbon for taste and odor control. The newer side uses ozone for the same purpose.

ENGINEERING ASPECTS OF OZONATION EQUIPMENT AND PROCESSES

INTRODUCTION

Extensive data were obtained during the course of the study on engineering design, operation and costs of ozonation systems. Engineering design practices of ozonation systems vary widely by country and by equipment manufacturers, and there can be considerable variation among similar water treatment plants with regard to the efficiency of generation and contacting of ozone. Current U.S. waterworks design standards and texts provide little guidance for engineering design of ozonation systems. Manufacturers of ozonation equipment comprise the principal source of design information in the U.S. at present. Hence, one of the major goals of the study was to provide corroborating design information to allow a range of understanding and appreciation of the various design alternatives.

Ozonation systems consist of four major parts, plus ancilliary equipment. The major parts of the system (Figure 5) are:

a. Gas preparation unit
b. Electrical power unit
c. Ozone generator
d. Contactor, include off-gas treatment

Ancilliary systems include instruments and controls, safety equipment and equipment housing.

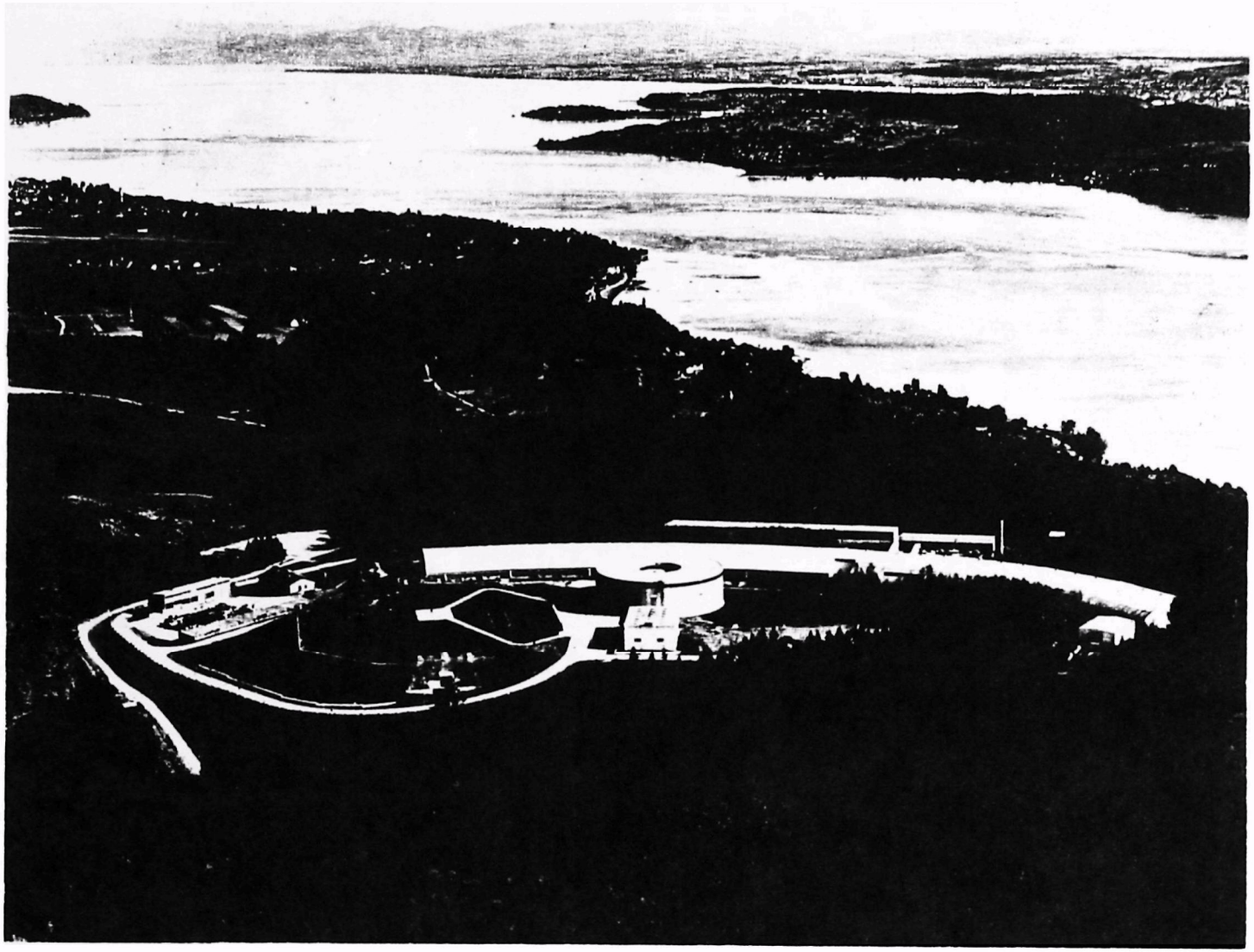


Figure 4. Sipplinger Berg, West Germany Water Treatment Plant on Lake Constance

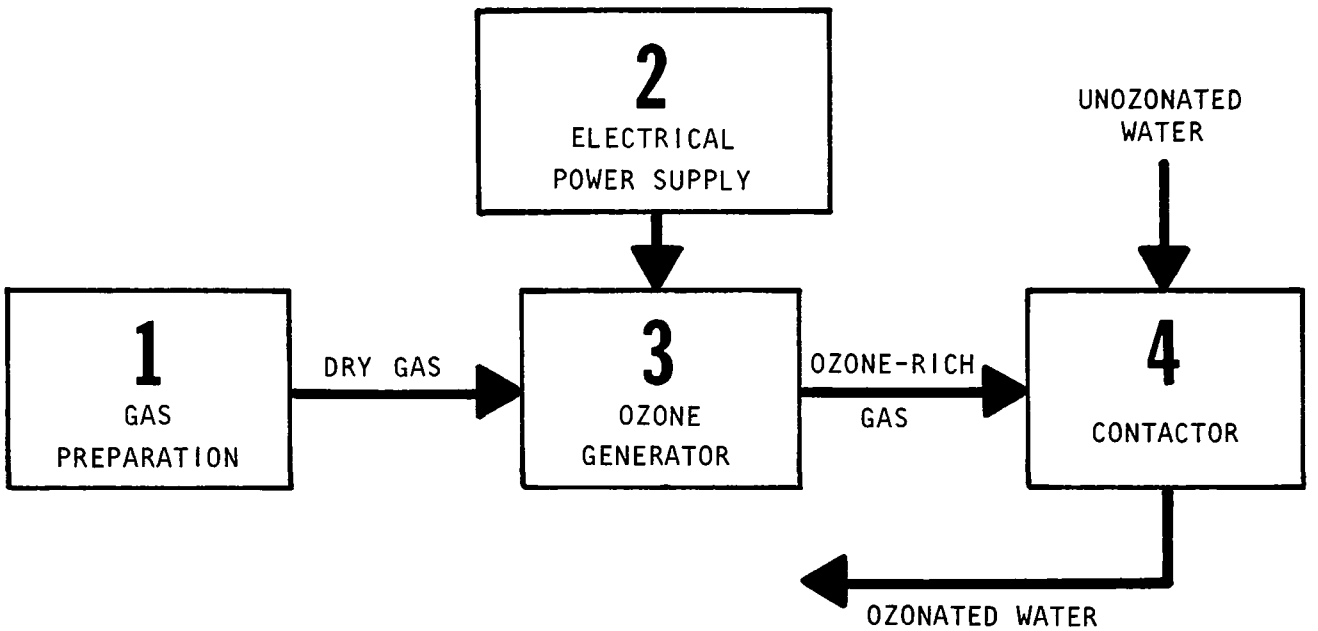


Figure 5. The Four Basic Components of the Ozonation Process

Gas Preparation

A high level of gas preparation, normally air, is required prior to ozone generation. Air must be dried in order to prevent formation of nitric acid and to increase the efficiency of ozone generation. The presence of moisture greatly accelerates the breakdown of ozone. Nitric acid, which will chemically attack the internal parts of the ozone generator, is formed when nitrogen combines with moisture in the corona discharge; thus, the introduction of moist air into the unit must be avoided. Selection of the air preparation system depends to some extent on the contacting system chosen. However, the gas preparation system normally will include refrigerant gas cooling and desiccant drying to a minimum dew point of minus 40 degrees Celsius. A dew point monitor or hygrometer appears to be an essential part of any air preparation system. A schematic of a low pressure air preparation system with turbine contacting is shown in Figure 6 and a gas drying system is shown in Figure 7.

Oxygen can be used to generate ozone with much greater efficiencies of conversion when the cost of producing the oxygen is not considered. The plant at Duisburg, Federal Republic of Germany, is the only operational municipal water treatment plant known which utilizes high purity

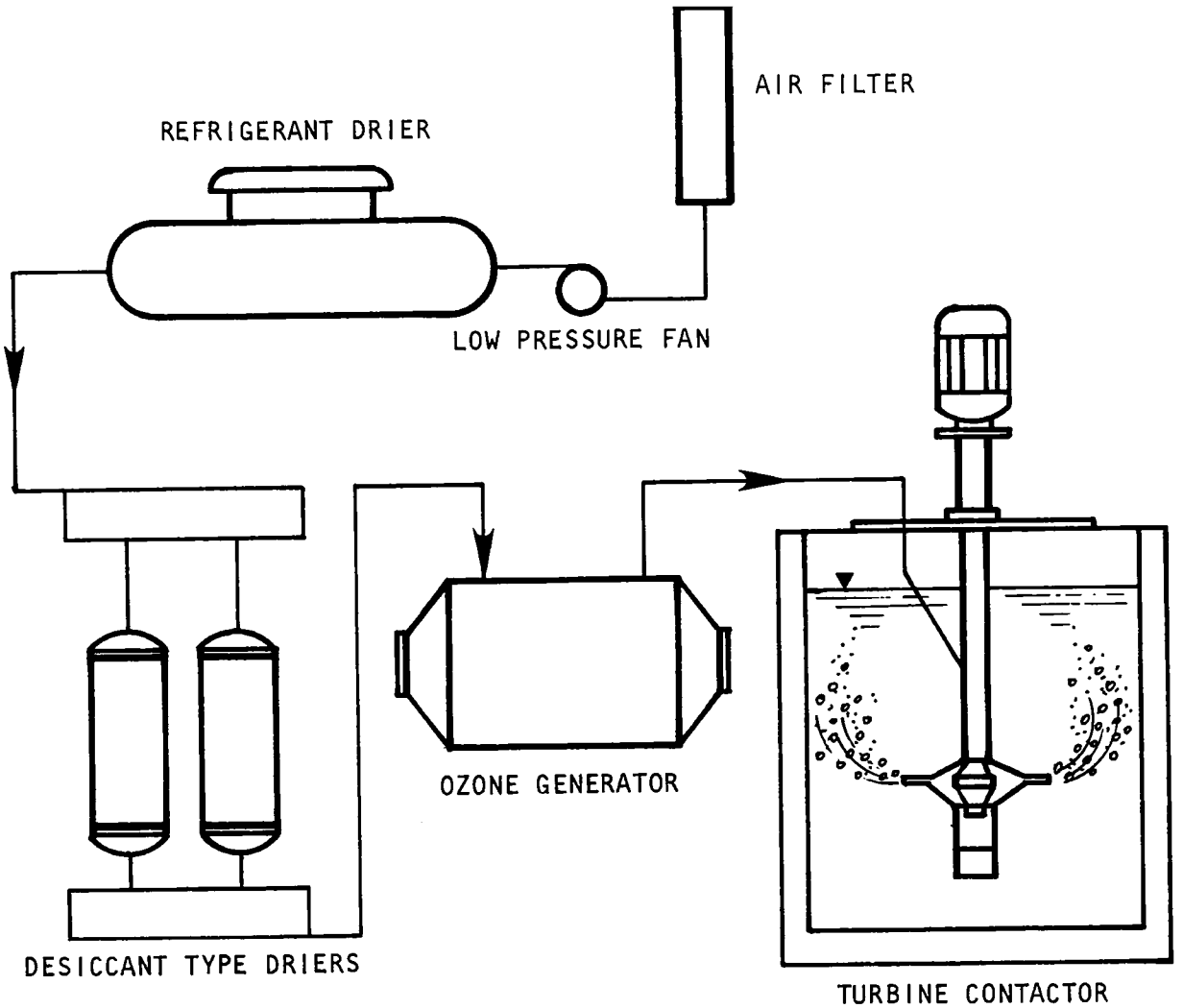


Figure 6. Low-Pressure Gas Preparation System

oxygen instead of air as the ozone generator feed gas, although the Tailfer plant of Brussels, Belgium, is installing this capability. This is contrary to United States wastewater ozonation practice, where it is frequently found that the use of high purity oxygen for both oxygen activated sludge treatment and ozone generation for disinfection is cost-effective.

Electrical Power Supply

Information available on the electrical power supply is limited. This part of the ozonation system was generally isolated and difficult to inspect in the plants visited, and the plant operators had little knowledge of power supply design. Manufacturers indicated that the power supply normally is considered integral to the ozonation unit and designs are proprietary. Thus, the information obtained in the study on electrical power supplies is of a

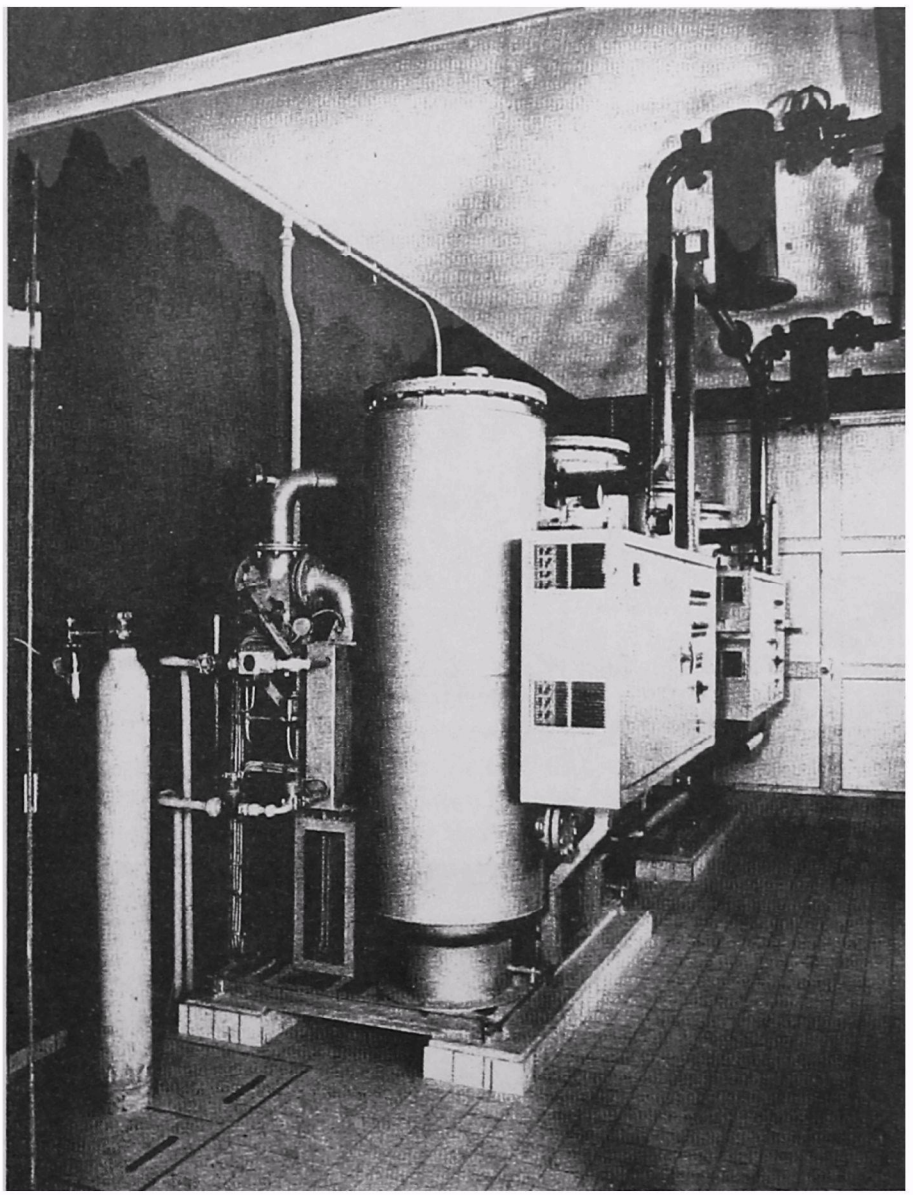


Figure 7. Air Feed Desiccation System
Annet-sur-Marne, France

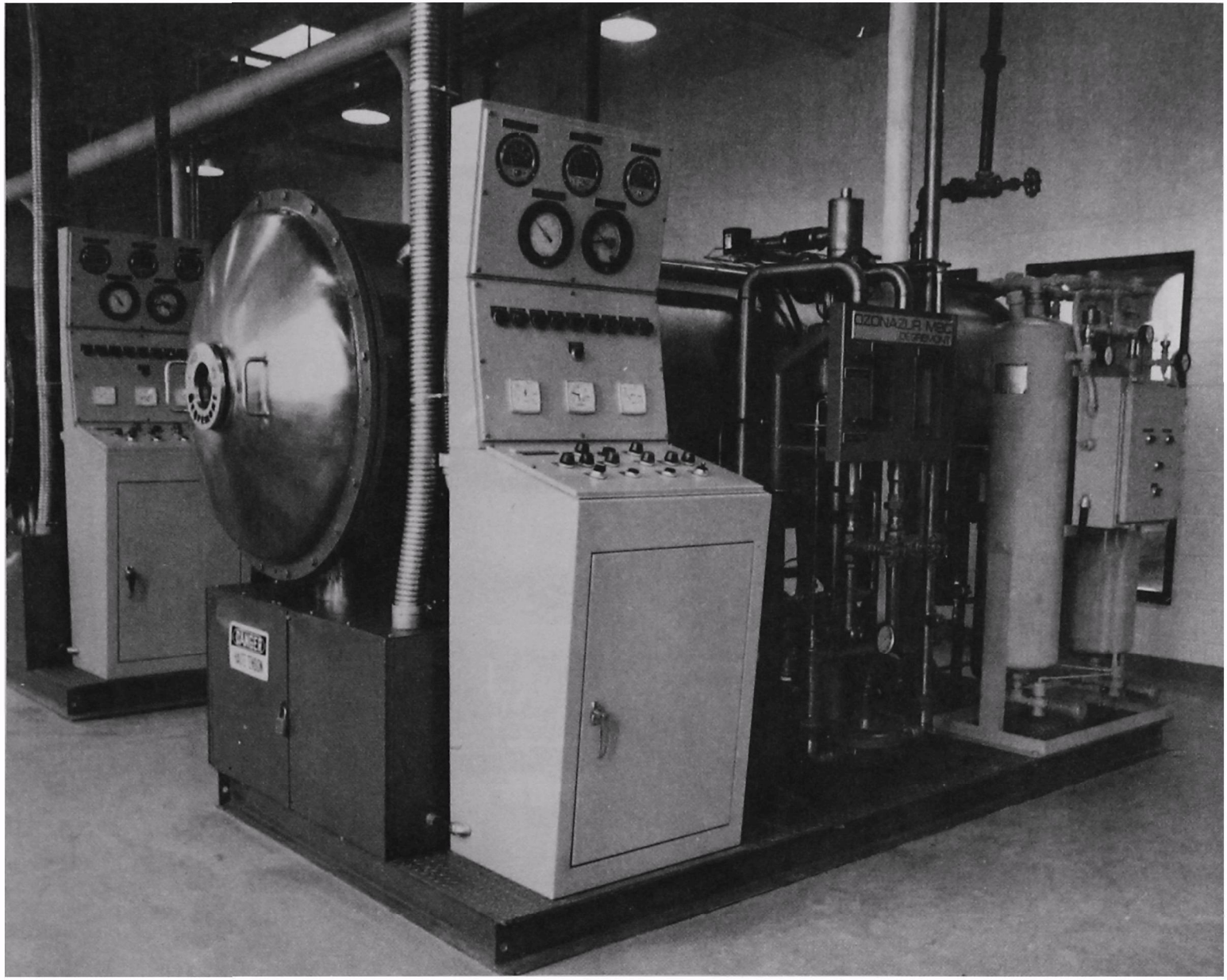


Figure 8. Modular Ozone Generator With Power Supply and Control System (Courtesy, Degremont)

general and theoretical nature rather than highly specific. Figure 8 shows a power supply system normally provided as part of the ozonation equipment.

Empirically, power consumption and ozone generation capacity are proportional to both voltage and frequency. Therefore, there are two ways to control the output of an ozone generator: vary voltage or vary frequency. Three common electrical power supply configurations are presently used in commercially available equipment:

- low frequency (60 hz), variable voltage
- medium frequency (600 hz), variable voltage
- fixed voltage, variable frequency

Constant low frequency, variable voltage is the most common power supply used. For larger systems, the 600 hz fixed frequency is often used because it allows doubled ozone production with no increase in ozone generator size, though at a higher power consumption for unit weight of ozone produced.

Little information has been developed in this study regarding power supply reliability. No general problems were identified, though there have been some difficulties with air cooled transformers. It is recommended that the ozone generator supplier be made responsible for providing the electrical power supply.

Ozone Generation

The silent electrical (corona) discharge method currently is considered to be the only practical method of generating ozone in plant scale quantities, and consequently was the only method covered in the study. Using this principle, a simple ozone generator can be constructed from a pair of electrodes separated by a gas space and a layer of glass insulator (Figure 9). An oxygen containing gas is passed through the empty space and a high voltage alternating current is applied. A corona discharge occurs across the gas space and ozone is created when a portion of the oxygen is ionized and then become associated with non ionized oxygen molecules.

$$\underset{\substack{\text{atmospheric}\\\text{oxygen}}}{O_2} + \underset{\text{electricity}}{e^-} \longrightarrow \underset{\substack{\text{ionized}\\\text{oxygen}}}{2(O)} + \text{heat}$$

$$2(O) + \underset{\substack{\text{non ionized}\\\text{oxygen}}}{2O_2} \longrightarrow 2O_3$$

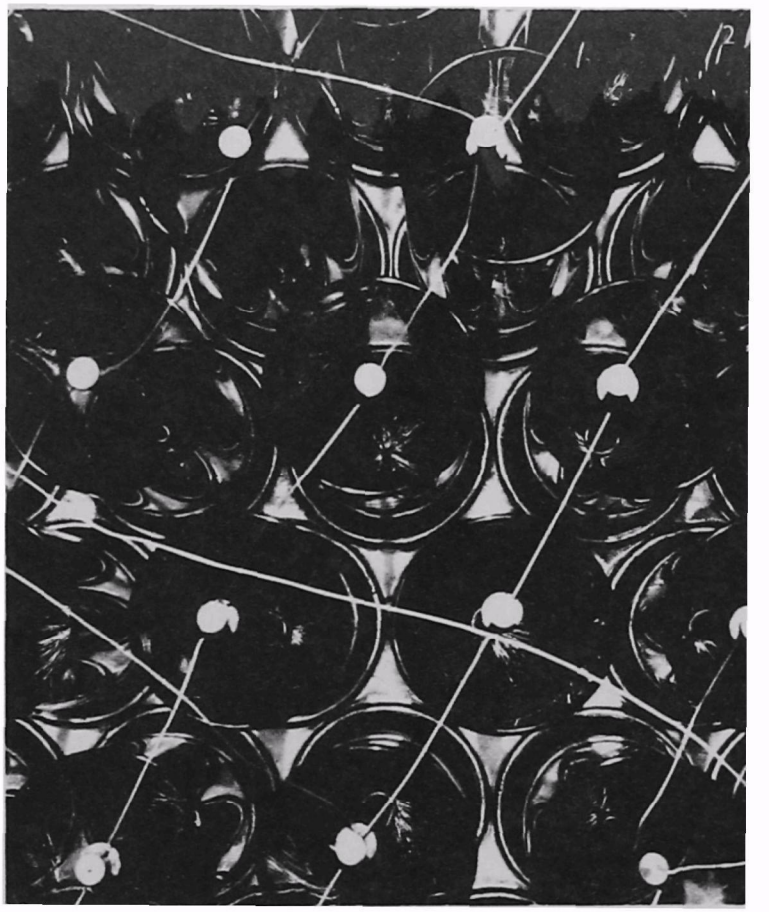


Figure 9. Interior of a Tubular Ozonator in Operation

This reaction is an equilibrium reaction; hence, newly formed ozone is simultaneously breaking down into molecular oxygen. Heat accelerates this breakdown and since most of the energy fed to the ozonator is lost in the form of heat, efficient cooling of the unit is a necessity. Most ozone generators are water cooled with the exception of the Lowther plate design, which uses air for cooling.

The various types of ozone generators observed and their manufacturers are as follows:

- Horizontal tube type, water cooled (Figure 10):

  Trailigaz, Degremont, Demag, Herrmann

- Vertical tube, water cooled:

  Kerag

- Vertical tube, double cooled (oil and water):

  PCI Ozone

- Plate, water cooled (Figure 11):

  Cie des Eaux et de l'Ozone (CEO), Sauter

- Lowther plate, air cooled (Figure 12):

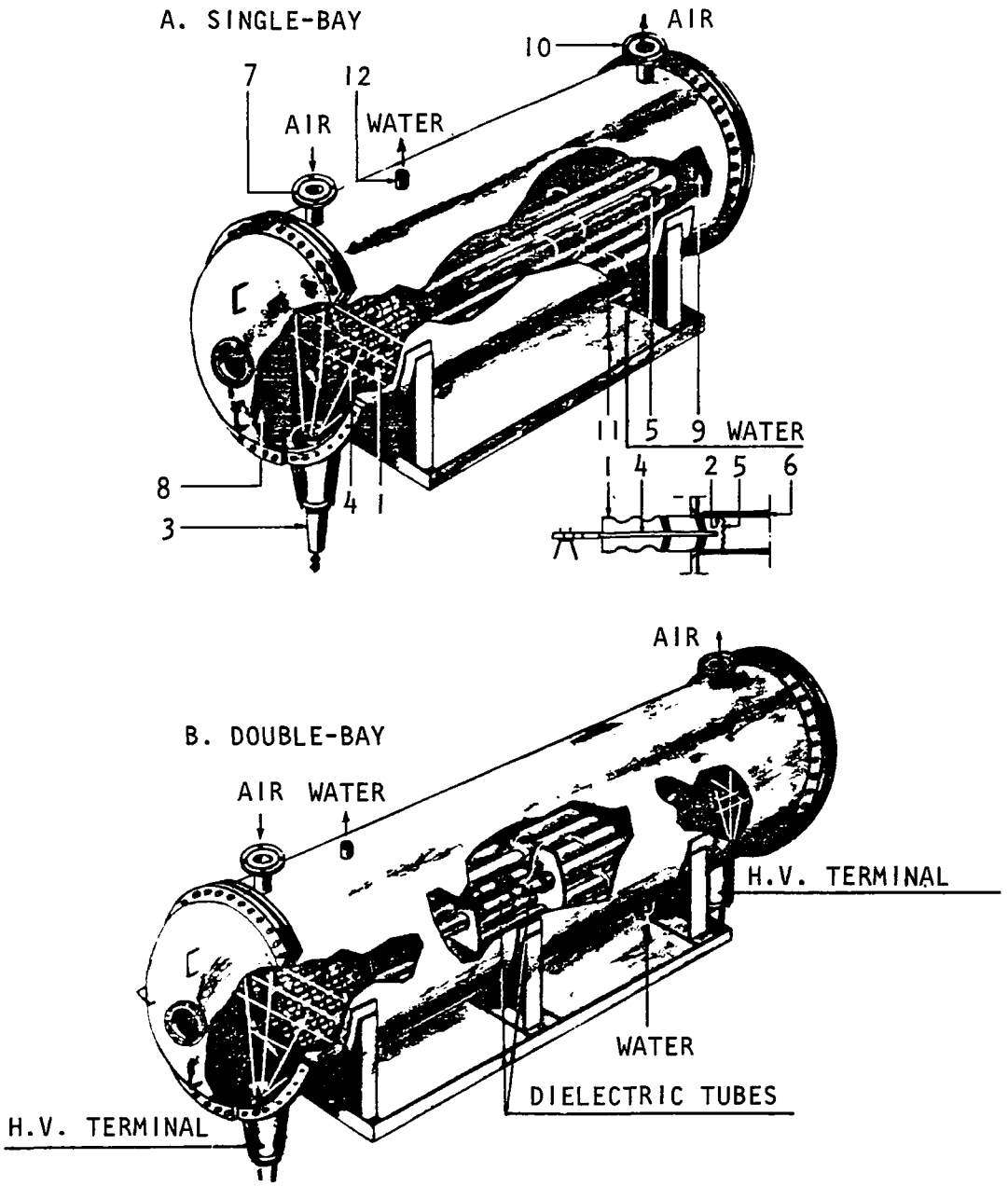
  Union Carbide

There are other manufacturing firms in Europe, Japan and the U.S., but installations with their equipment were not visited during this study. By far the most common type of ozonator in use is the horizontal tube type with water cooling (Figure 10). This unit is especially popular where larger size units are required. The water cooled plate units are frequently used in smaller plants but require considerably more floor space per unit of output than the tube type units. The air cooled Lowther plate unit is a relatively new design developed in the U.S. It appears to have the potential for simplifying the use of ozone generating equipment, but to date it has had little operating experience in water treatment plants.

Ozone Contacting

After generating the ozone, it must be mixed with the water stream being treated. The objective is to maximize the dissolution of ozone into the water at the lowest power costs and still accomplish the desired objective. The wide range of ozone contactor designs in operation in water treatment facilities includes the following:

- Multi-stage porous diffuser contactors
  - Single application of an ozone-rich gas stream
  - Application of "fresh" ozone gas to second and subsequent stages with off-gases being recycled to the first stage
- Eductor induced, ozone vacuum injector contactors
  - Total plant flow through eductor
  - Partial plant flow through eductor
- Turbine contactor
  - Positive pressure to turbine
  - Negative pressure to turbine



1. DIELECTRIC TUBE
2. METALLIC COATING
3. H.V. TERMINAL
4. CONTACT
5. CENTERING PIECE
6. IONIZATION GAP
7. AIR INLET
8. FRONT CHAMBER
9. REAR CHAMBER
10. AIR OUTLET
11. WATER INLET
12. WATER OUTLET

Figure 10. Typical Details of Horizontal Tube-Type Ozone Generator

- Packed bed contactors
  - Cocurrent water/ozone-rich gas flow
  - Countercurrent water/ozone-rich gas flow
- Two level diffuser contactor
  - Application of ozone-rich gas to lower chamber
  - Lower chamber off-gases applied to upper chamber

These contactors are described and illustrated in the large report. Diffuser contacting (Figure 13) is the most commonly used design particularly when ozone is used for disinfection. Turbine contacting (Figure 14) also is quite popular in Europe, particularly for mass transfer controlled reactions that do not require lengthy contact times.

Treatment of off-gas from the contactors is an important consideration. Methods used for off-gas treatment include dilution, destruction with granular activated carbon, thermal or catalytic destruction, and recycling.

OZONE MEASUREMENT AND CONTROL

Operational economics and good management practices require that high levels of control of the ozonation system be maintained. Depending upon specific process of applications of ozone, plant size, regulatory agency policy, and design philosophy, the control system may be simple or complex. The trend in France and Switzerland appears to be toward highly sophisticated and centralized control, examples being the small (30,000 cu m/day) remotely operated Kreuzlingen plant (Switzerland) and the large (600,000 cu m/day) Neuilly-sur-Marne plant near Paris, France. On the other hand, water treatment plants visited in the Federal Republic of Germany and in the Province of Quebec, Canada, employ a higher degree of local control and monitoring.

A number of parameters must be measured to provide a fully operable ozonation system; these include the following:

- There must be a means of providing a full temperature and pressure profile of the ozone generator feed-gas from the initial pressurization (by fan, blower, or compressor) to the ozone generator inlet.
- There must be a means of measuring the moisture content of the feed-gas to the ozone generator. This procedure should be conducted with a continuously monitoring dew point meter or hygrometer.

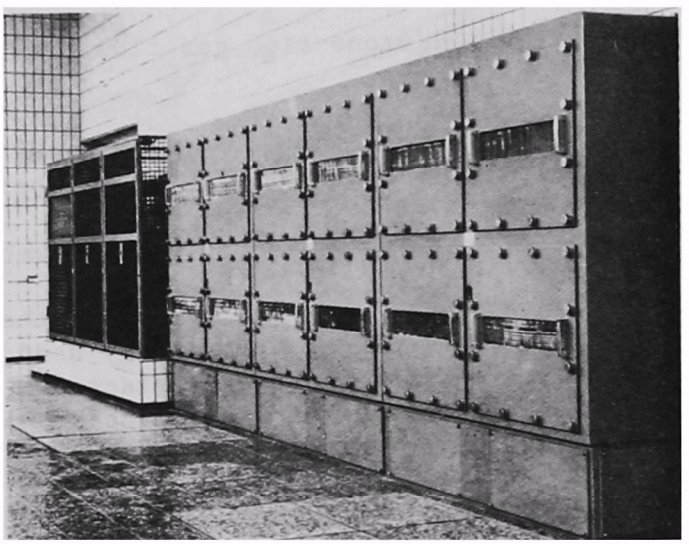


Figure 11. Parallel Plate Ozonators at Konstanz Waterworks, West Germany

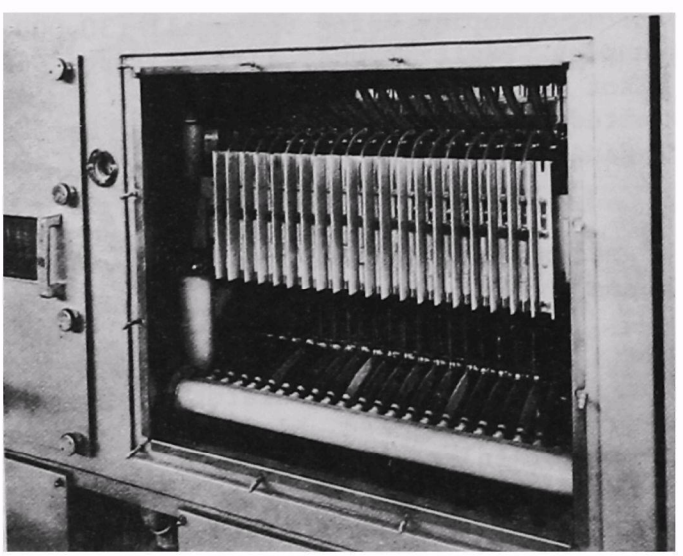


Figure 12. Interior of Individual Plate Ozonator

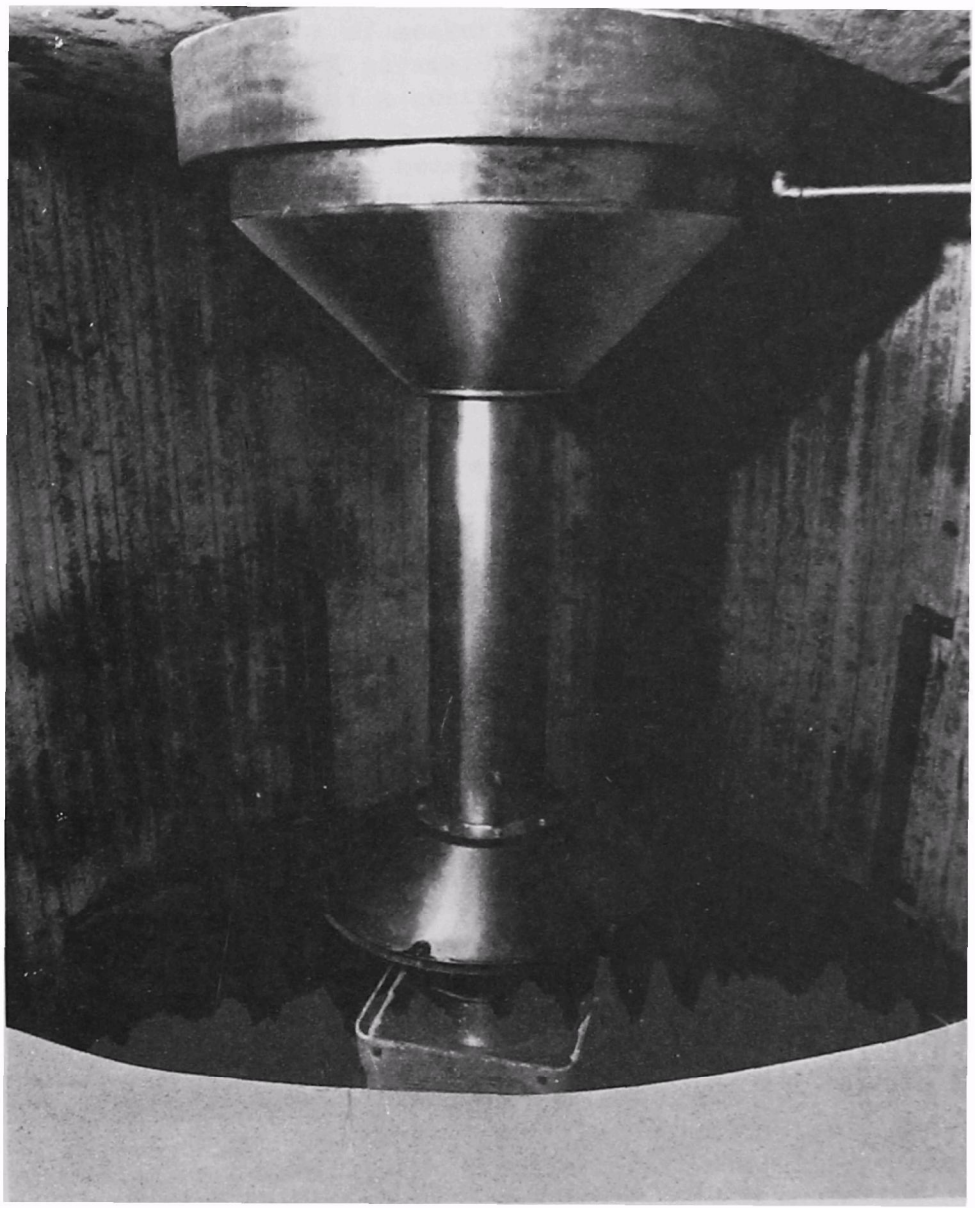


Figure 13. Turbine Contactor at Zurich, Switzerland, Lengg Plant

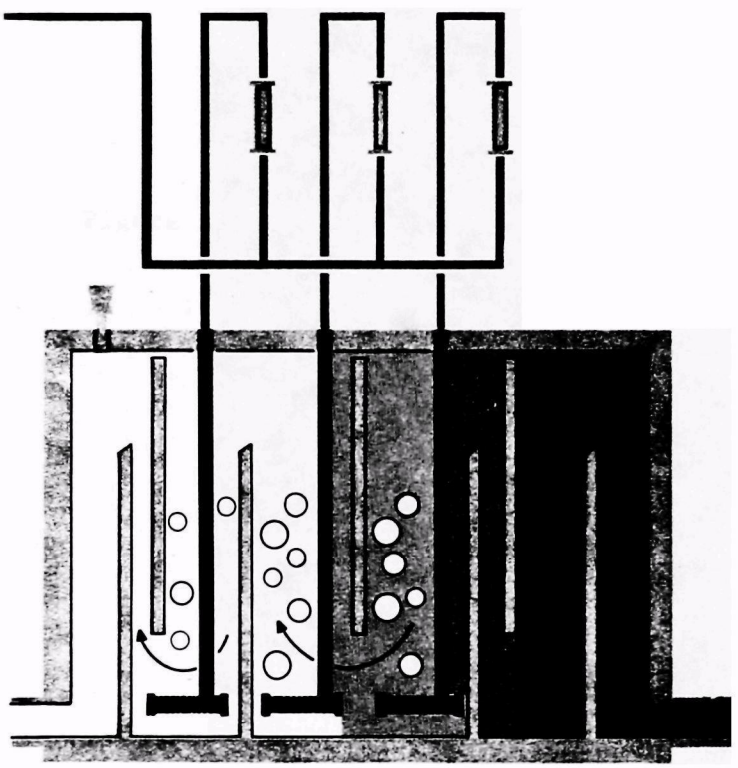


Figure 14. Ozone Diffuser System Layout and Bubble Pattern

- There must be a means of measuring the temperature, pressure, flow rate, and ozone concentration of the ozone-containing gas being discharged from all the ozone generators. This is the only effective method by which ozone dosage and the ozone production capacity of the ozone generator can be determined.

- There must be a means of measuring the power supplied to the ozone generators. The parameters measured include amperage, voltage, power, and, if a controllable variable, frequency.

- There must be a means of measuring the flow rate and temperature of the cooling water to all water cooled ozone generators. Reliable cooling is important to maintain constant ozone production, and to protect the dielectrics in the generation equipment.

- There must be a means to monitor the several cycles of the desiccant drier, particularly the thermal-swing unit.

Three obvious analytical needs are measurement of ozone concentrations in (1) the ozonized gas from the ozone generator, (2) the contactor off-gases, and (3) the residual ozone level in the ozonized water. Methods of ozone measurement observed during plant visitations include the following:

- Simple "sniff" test

- Draeger type detector tube

- Wet chemistry potassium iodide method

- Amperometric type instruments

- Gas phase chemiluminescence

- Ultraviolet radiation adsorption

Each of these methods is discussed in some detail in the study.

The use of control systems based on the measurements listed above vary considerably in the water treatment plants that were visited. The French plants using ozonation primarily for disinfection incorporate a closed-loop control system by which the residual ozone level in the contactor is used to control the amount of ozone supplied to maintain that ozone residual. The key to successful operation of such a system is an accurate and reliable residual ozone analyzer. On the other hand, the German ozonation systems which are used primarily for iron, manganese and/or organics oxidation are manually controlled through a periodic "sniff" test of off-gas from the holding tanks after ozonation.

At present, it appears that continuous residual ozone monitoring equipment may be successfully applied to water that has already received a high level of treatment. However, a more cautious approach must be taken with the application of continuous residual ozone monitoring equipment for water that has only received chemical clarification, because the ozone demand has not yet been satisfied and the residual is not as stable. Instrumentation for continuous monitoring of the ozone concentration in gas phases appears to be reliable.

Ozone production must be closely controlled because excess ozone cannot be stored, and changes in process demand must be responded to rapidly. Ozone production is costly, under ozonation may produce undesired effects, and over ozonation may require additional costs where off-gas destruction is used. The study discusses the following ozone production control methods:

- Manual Operation - Manual Sampling
- Manual Operation - Automatic Sampling
- Closed Loop Control - Automatic Sampling
- Closed Loop Control of Voltage/Frequency and Gas Flow Automation

OPERATION AND MAINTENANCE

The site visits verified in most cases the relatively low maintenance needs of ozonation equipment. The air preparation system requires frequent attention for air filter cleaning/changing and for assuring that the desiccant is drying the air properly. Both of these normally are simple operations.

Two factors which impact ozone generator operation and maintenance are the effectiveness of the air preparation system and the amount of time that the generator is required to operate at maximum capacity. Mainteance of the ozone generators commonly is scheduled once per year in the plants visited. However, many plants perform this maintenance every six months. Typically, one man-week is necessary to service an individual ozone generation unit of the horizontal tube type. Dielectric replacement due to failure as well as to breakage during maintenance may be as low as 1 to 2 percent. However, it appears reasonable to predict an average tube life of ten years if a feed gas dew point of minus 60 degrees Celsius is maintained and if the ozone generator is not required to operate for prolonged periods at its rated capacity. Plate type ozone generators use window glass as dielectrics. However, the same attention to air preparation is taken as with the more expensive glass or ceramic tubes in order to avoid costly down time.

Operation and maintenance of the ozone contactor also must be considered. Turbines require electricity to power the drive motors, while porous diffusers require regular inspection and maintenance to insure a uniform distribution of ozone rich gas in the contact chamber. Experience with maintenance of the ozone contact chambers in the Morsang-sur-Seine plant in France

(diffuser chambers) indicates that even after purging of the contact chambers with air, maintenance personnel entering the chambers should be equipped with a self-contained breathing apparatus, since the density of ozone is heavier than air and therefore is difficult to remove completely by air purging.

COSTS/BENEFITS OF OZONATION

Based on the field cost data acquired, the capital costs of ozonation systems can range from a low of $600/lb of ozone generation capacity/day for large systems to a high of $4000/lb capacity/day for relatively small systems. An added cost is housing for the system, which can range from approximately 20% to 33% of equipment costs.

Total capital and operating costs depending on energy demand, period of amortization, interest, subsystem components selected and cost of energy, were found to range from 1.75 cents to about 4 cents/1000 gallons of water treated based on the limited data available (see Table 5).

When one considers the versatility of ozone, its many applications, and its effectiveness in breaking down potentially harmful synthetic organic chemicals, these operating costs can be justified. Also, ozone combined with granular activated carbon has been demonstrated in Europe to be one of the most effective combinations known for the simultaneous removal of ammonia and dissolved organic compounds. This combination at the Dohne plant of Mulheim, Germany employs 3 mg/l dosages of ozone which has replaced prechlorination dosages of 30 to 50 mg/l. Prechlorination produced high concentrations of chlorinated organics, which required frequent reactivation of the Dohne GAC columns (every 6 to 8 weeks). Preozonation of granular activated carbon also can result in much longer time periods between GAC regeneration. Precise savings have not yet been investigated thoroughly.

CONCLUSIONS

- Ozonation for drinking water treatment is a well established and growing technology. Over 1000 operational plants throughout the world (most are in Europe) use ozone for one or more of a multiplicity of purposes, most of which are based upon its strong oxidizing power.

- As an oxidant, ozone currently is used to remove colors, tastes, odors, algae, organics (phenols, detergents, pesticides, etc.), cyanides, sulfides, iron, manganese, turbidity, to cause flocculation of micropollutants (soluble organics) and to inactivate viruses.

- Ozone also is used as a disinfectant, but seldom in the context of an either-or "alternative disinfectant to chlorine". It is normal to follow ozone as the primary disinfectant with a small dosage (up to 0.6 mg/l) of chlorine or chlorine dioxide, which provides a residual a residual for distribution systems.

TABLE 5. COSTS OF OZONATION AT EUROPEAN DRINKING WATER PLANTS

Plant	water treatment capacity (mgd)	ozone generation capacity (lbs/day)	capital cost of ozonation*	capital cost/lb of ozone generation capacity	amortization period (yrs.)	av. dosage of ozone (mg/l)	ozonation operating costs (c/1000 gal)**	electrical cost (¢/kwhr)
Tailfer Brussels Belgium	68.7	1267	$4,024,000	$2200	20	1.7	2.52	3.01
Lengg Zurich Switzerland	66	1742	$1,120,000	$ 643	20	1.5	1.75	2.0
Large Automated Paris Plant	-	-	-	-	20	2.5	2.76	2.1
Several French Plants	-	-	-	-	10	1.5-3.0	3.95	3.12

*includes air preparation equipment, ozone generation, ozone contacting, treatment of off-gas ozone, instrumentation, installation and housing for ozonation system (including contact system)

**includes operation, maintenance and amortization

Table 5. Costs of Ozonation at European Drinking Water Plants

- Under specific circumstances, ozonation can be used as the sole disinfectant. In addition to the obvious requirements (e.g., ozonation is the terminal treatment step and the distribution system must be free of contamination), the distribution system should be short and the residence time of treated water in the system also should be short. Ammonia should be absent and dissolved organic carbon should be less than 0.2 mg/l. It is also advantageous that the temperature of treated water be low, so as to reduce the potential for bacterial regrowth.

- Ozonation system components (electrical power supply, gas preparation, ozone generation, ozone contacting) operating in Europe are reliable and do not exhibit unusual equipment operation problems, provided that routine maintenance is performed.

- Costs of ozone treatment of drinking waters in Europe range from 1.75 cents to 4 cents/1000 gallons of water treated in operational plants visited. The range depends upon the specific uses of ozone, the amounts of ozone required, types of contacting employed, the type of equipment housing and degree of control instrumentation selected. Ozonation equipment normally is amortized over 20 years.

- Chemical evidence obtained to date does not indicate any untoward health hazard to be associated with the use of ozone.

- Organic oxidation products formed upon ozonation are non-halogenated, are more biodegradable than before oxidation, and usually are less toxic. However, some pesticides pass through intermediate stages of oxidation to produce more toxic materials.

- Formation of the same or similar non-halogenated, more toxic intermediates also can occur, with the use of oxidants other than ozone, for example chlorine and chlorine dioxide. Therefore, it is important in using any oxidant for water treatment to know the identity of dissolved organic matter present, the chemistry of intermediate oxidation stages, and to design sufficient oxidant into the process to guarantee that such intermediate stages are passed and potentially toxic intermediates are destroyed through oxidation.

- The sequential combination of ozonation, filtration, then granular activated carbon filtration is being employed in newer European water treatment plants to enhance removal of dissolved organics and ammonia simultaneously by means of the biological activity in the activated carbon. This process also is used for extending the useful life of granular activated carbon. Some European Biological Activated Carbon columns and/or beds have operated 2.5 years without having to be regenerated.

SECTION 4

BIOLOGICAL ACTIVATED CARBON

INTRODUCTION

Biological Activated Carbon (BAC) is a term used to describe processes by which granular activated carbon contactors are made biologically active. Dissolved oxygen (DO) is introduced before the carbon contactor in sufficient quantity to maintain aerobic conditions within the carbon. The availability of surface area within the carbon, plus dissolved oxygen and organic matter in the water stream, creates nearly ideal conditions for microbial growth. The microbes, in turn, metabolize dissolved organics, thereby acting as an organics removal process. The use of ozone before the carbon filters not only creates the needed oxygen rich environment, but the ozone also oxidizes the larger, less degradable organics into smaller molecules which are more easily biologically degraded.

Many of the advantages of biological activated carbon were first recognized by German water treatment scientists in the 1960's in drinking water plants along the Rhine River in the Dusseldorf area. Subsequently, BAC processes also have been installed in Swiss and French drinking water treatment plants, and are subjects of active pilot studies in Holland and Belgium. In the United States, the U. S. Environmental Protection Agency's Water Supply Research Laboratory in Cincinnati, Ohio has been testing a pilot BAC column since late 1976, although not continuously. EPA also is planning to fund three pilot plant studies in Fiscal Year 1978.

FUNDAMENTAL PRINCIPLES

At the present level of understanding of the BAC process, two mechanisms by which the process functions are proposed. It is thought that microbes are present both on the surface of the carbon and in the pores of the carbon surface. Organics passing through the process will be surface adsorbed and pore adsorbed. The surface adsorbed organics do not have to be firmly adsorbed, if they are biodegradable, in order to effect their removal from the water stream, as the surface microbes will quickly metabolize them. The less degradable organics are more slowly removed from the surface or pores by the microbes, thereby "regenerating" the carbon. Preozonation converts larger less biodegradable organics into smaller, more degradable organics, and charges the water stream with dissolved oxygen.

Critical to the functioning of the process is the adsorptive capacity of the granular activated carbon. Detention time in a carbon contactor is short, usually on the order of 15-30 minutes empty bed contact time. Thus, the surface area and pore volume of the carbon should be high.

Many organic materials are readily adsorbed onto GAC, but many others are not. For example, high molecular weight natural organic compounds, such as the humic acids, are poorly adsorbed by GAC. If, however, the water is preozonized, the humic acids are broken down into more readily adsorbable and biodegradable compounds. Other non polar and highly carbon adsorbable organic compounds upon ozonation become more polar and more biodegradable, but less adsorbable.

EUROPEAN BAC PRACTICES

Granular activated carbon was introduced into European drinking water treatment practices after 1945, initially for dechlorination and taste/odor control. Dechlorination was required whenever prechlorination was practiced, such as with waters containing ammonia and treated by breakpoint chlorination. Ammonia is effectively removed in this manner, but chlorinated organic compounds are produced.

Combinations of ozone and GAC were installed in plants near Dusseldorf, West Germany in the late 1950's, but the synergistic interaction of the two processes was not fully recognized until nearly ten years later.

The BAC process has been studied extensively at the Bremen, West Germany plant, on the River Weser. At Rouen, France, the process is being applied to successfully treat polluted deep well waters drawn adjacent to the Seine River. The Zürich, Switzerland system uses preozonation of granular activated carbon at its Lengg plant, and there have been considerable studies of the process in Holland. The U.S. EPA also has funded additional investigation of European BAC practices. The project is currently underway and hopefully will extend the data presented in this study.

At Mulheim, West Germany, a switch to BAC in mid 1977 resulted in significant improvements of final water quality. The Dohne plant treats polluted water from the Ruhr river, and had previously been removing ammonia by breakpoint chlorination. This resulted in the formation of halogenated organic compounds which were removed inadequately by the GAC systems, and also created a need for frequent GAC regeneration. By switching to BAC, the Dohne plant was able to attain equivalent nitrogen removals and improved dissolved organic carbon removals while eliminating the breakpoint chlorination process. At the time of this writing, over 13 months of running time had been accumulating on the GAC columns without regeneration. Previously, it was necessary to regenerate the carbon columns every 6 to 8 weeks.

CONCLUSIONS

- For optimum pollutant removals, granular activated carbon contactor depths should be 4 to 5 meters (13 to 16 feet) in depth. Empty bed contact times in the carbon contactor should be at least 15 minutes, and preferably 20 to 30 minutes, with a safety factor for pollutant surges.

- Dissolved oxygen (DO) in the effluent from the GAC contactor should be at least 2 mg/l and preferably exceed 3.5 mg/l, for optimal bacterial activity. Normally, sufficient DO is provided by the breakdown of ozone added for organic compound oxidation. If required, supplemental addition of DO is made prior to carbon filtration.

- BAC is an effective process for ammonia removal. In the absence of chlorinated organics, regeneration frequencies of the GAC reactors are low, possibly as high as 3 years between cycles. Plants using breakpoint chlorination before carbon contactors can expect to regenerate every 6 to 8 weeks under the worst conditions.

- BAC contactors generally require backwashing, due to buildup of solids and adhesion between carbon particles, as a result of bacterial action. A combination of air scouring and water backwashing has been found to be effective.

SECTION 5

CHLORINE DIOXIDE

INTRODUCTION

Chlorine dioxide was first discovered in 1811 by Sir Humphrey Davy, who prepared the compound by reacting potassium chlorate with hydrochloric acid. Other experimentation followed wherein it was determined that chlorine dioxide exhibited strong oxidizing and bleaching properties. In the 1930's, the Mathieson Alkali Works developed the first commercial process for preparing chlorine dioxide from sodium chlorate. By 1939, sodium chlorite was established as a commercial product for the generation of chlorine dioxide.

The use of chlorine dioxide expanded rapidly in the industrial sector. In 1944, chlorine dioxide was first applied for taste and odor control at a water treatment plant in Niagara Falls, New York. Other water plants recognized the benefits of using chlorine dioxide and its use increased rapidly. In 1958, a national survey determined that 56 U.S. water utilities were using chlorine dioxide. The number of plants using chlorine dioxide has grown more slowly since that time, to a total of 84 plants in 1977, as determined by a survey carried out as part of this study.

Currently, chlorine dioxide is most commonly used for bleaching in the pulp and paper industry. It is also used in large amounts by the textile industry, as well as for the bleaching of flour, fats, oils and waxes. In treating drinking water, chlorine dioxide is used in the United States for taste and odor control, decolorization, iron and manganese oxidation, oxidation of organics, disinfection and provision of residual disinfectant in water distribution systems. Of the 84 plants in the U.S. currently using chlorine dioxide, only one, Hamilton, Ohio, uses the chemical solely as a disinfectant. The principal use of chlorine dioxide in the U.S. is for taste and odor caused by phenolic compounds in the raw water supply.

Chlorine dioxide is a yellow green gas and is soluble in water at room temperature to about 2.9 g/liter chlorine dioxide (at 30 mm mercury partial pressure) or more than 10 g/l in chilled water. The boiling point of liquid chlorine dioxide is 11 degrees Celsius and the melting point is minus 59 degrees Celsius. Chlorine dioxide has a density of 2.4 (air=1). The oxidant is normally used in a water solution and is five times more soluble in water than chlorine gas. Also, chlorine dioxide does not react with water as does chlorine. Chlorine dioxide is quite volatile and therefore can be stripped easily from a water solution by aeration.

The compound has a disagreeable odor, similar to that of chlorine gas, and is detectable by the human nose at 17 ppm. Chlorine dioxide is distinctly irritating to the respiratory tract at a concentration of 45 ppm in air. Concentrations of chlorine dioxide in air above 11% can be mildly explosive. Chlorine dioxide as a gas or liquid may be readily decomposed upon exposure to ultraviolet light. It also is sensitive to temperature and pressure which are two reasons why chlorine dioxide is generally not shipped in bulk concentrated quantities.

Chlorine dioxide has a much greater oxidative capacity than chlorine and therefore is a more effective oxidant in lower concentrations. Chlorine dioxide also maintains an active residual longer in potable water than does chlorine. Chlorine dioxide does not react with ammonia or with trihalomethane precursors when prepared with no free residual chlorine.

PREPARATION OF CHLORINE DIOXIDE

Chlorine dioxide is prepared from feedstock chemicals by a variety of methods, depending on quantity needed and the safety limitations in handling the various feedstock chemicals. The most common processes are:

From Sodium Chlorite ($NaClO_2$):

- Acid and sodium chlorite
- Gaseous chlorine and sodium chlorite
- Sodium hypochlorite, acid and sodium chlorite

From Sodium Chlorate ($NaClO_3$):

- The suphur dioxide process
- The methanol process
- The Hooker R-2 Process
- The Hooker SVP (R) Process

The first group of processes are more adaptable to water utility operations and therefore are more commonly used. The second group of processes are frequently used by industry where the quantities produced are much greater than in water utitilies. U.S. and European water utilities usually prepare chlorine dioxide using sodium chlorite and gaseous chlorine (Figure 15) rather than acid, although the acid based process is used extensively in Switzerland (Figure 16).

OXIDATION PRODUCTS OF CHLORINE DIOXIDE

The study presents a detailed review of the literature and current analysis of current knowledge on the oxidation products of chlorine dioxide. Some of the reactions and conclusions regarding oxidation products and chlorine dioxide are listed below.

- Regardless of the oxidant employed, many (if not all) of the same organic oxidation products will be present in the water or wastewater at the same treatment point. More significantly in the case of chlorine, these same (non-halogenated) oxidation products have been present all along.

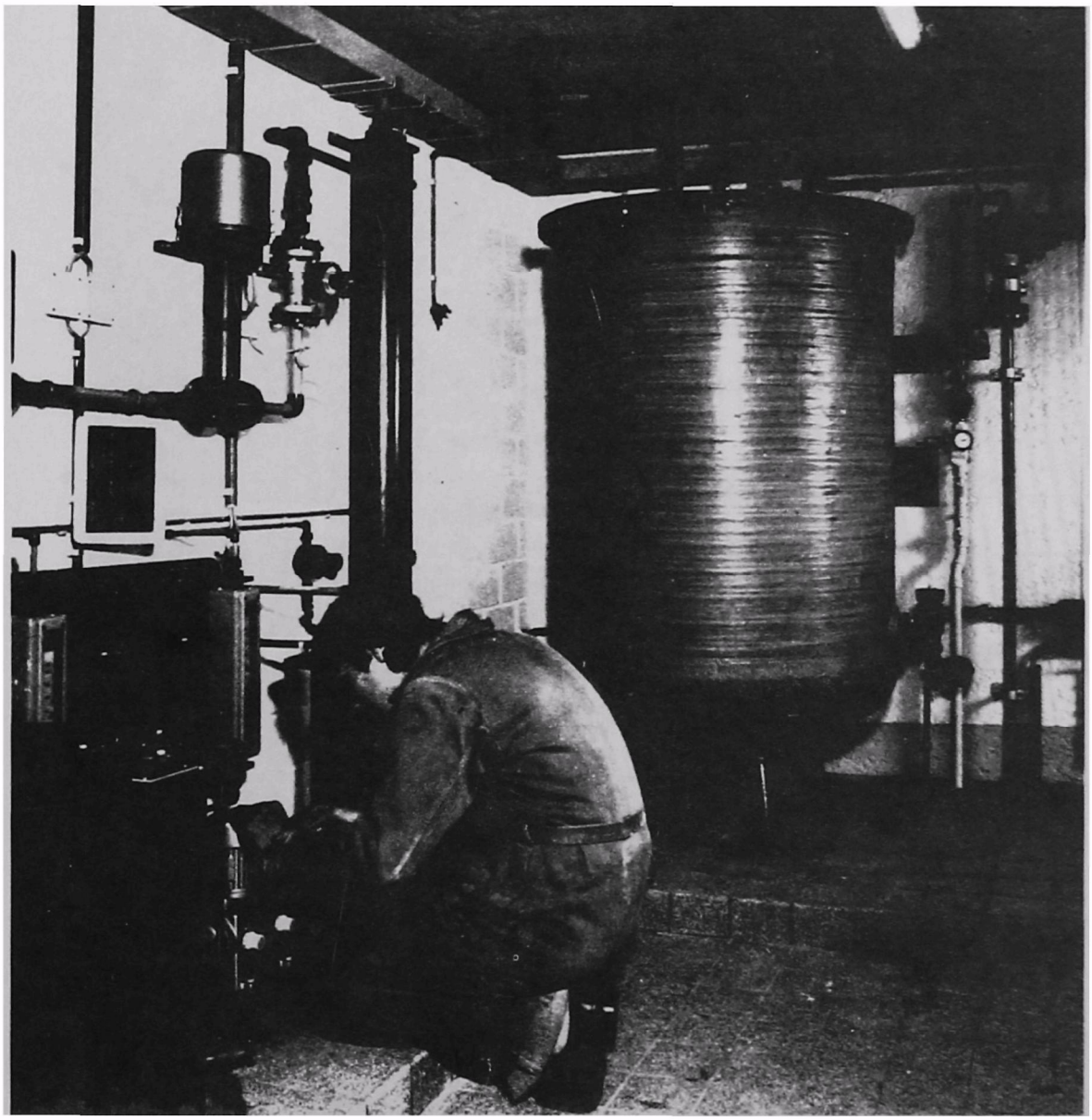


Figure 15. Chlorine Dioxide Generation From Acid and Sodium Chlorite at Lengg Plant, Zurich, Switzerland

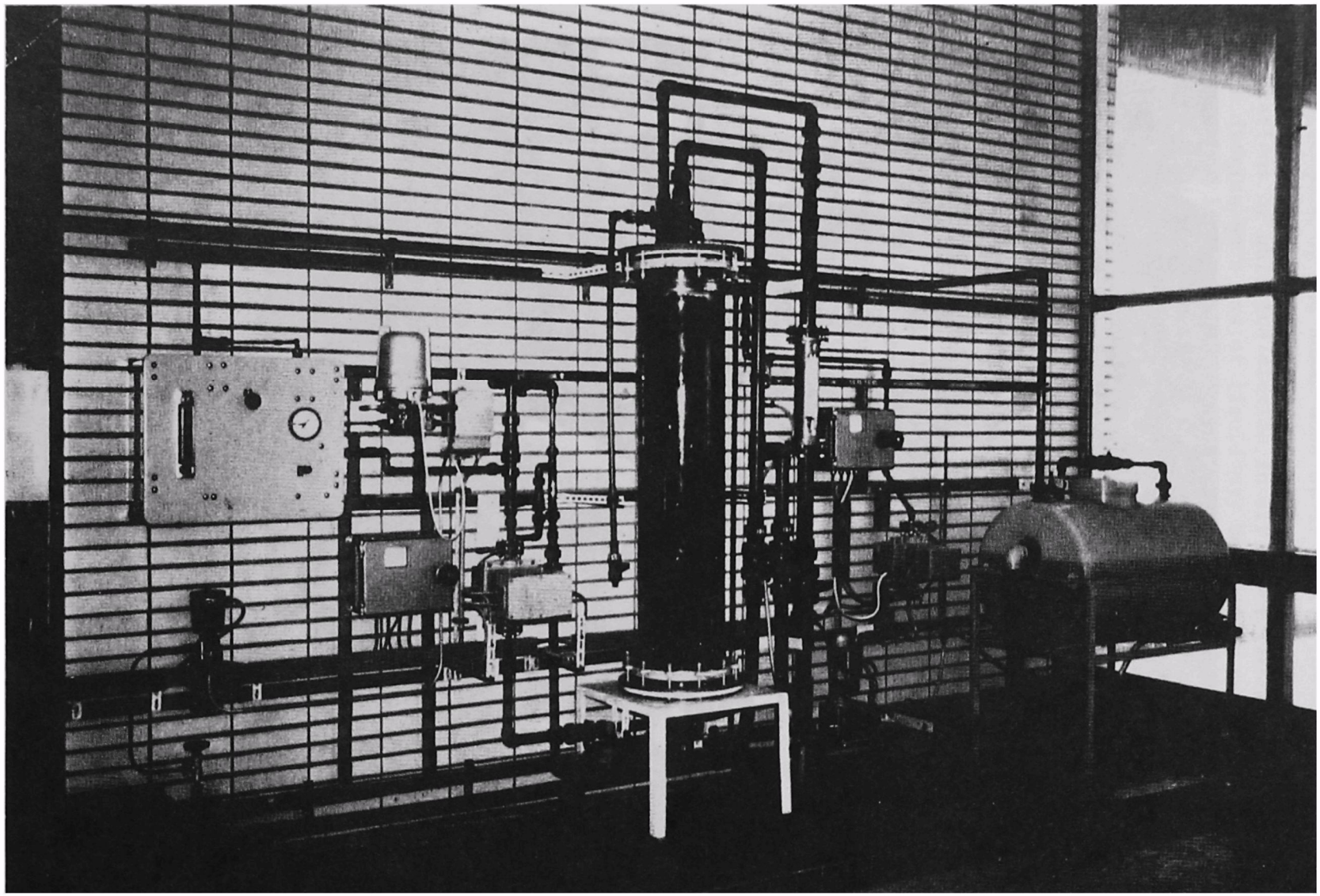


Figure 16. Preparation of Chlorine Dioxide From Gaseous Chlorine and Sodium Chlorite

- Oxidation of phenols with chlorine dioxide or chlorine produces chlorinated aromatic intermediates before ring rupture.

- Oxidation of phenols with ozone or chlorine dioxide produces oxidized aromatic compounds as intermediates, which undergo ring rupture upon treatment with more oxidant and/or longer reaction times. In many cases, the same, non-chlorinated, ring-ruptured aliphatic products are produced using ozone or chlorine dioxide.

- In oxidizing organic materials, chlorine dioxide can revert back to chlorite ion. In the presence of excess chlorine (or other strong oxidant) chlorite can be preoxidized to chlorine dioxide.

- Using large excesses of chlorine dioxide over the organic materials appears to favor oxidation reactions (without chlorination), but slight excesses appear to favor chlorination.

- When excess free chlorine is present with the chlorine dioxide, chlorinated organics usually are produced, but in lower yields, depending upon the concentration of chlorine and its reactivity with the particular organic(s) involved.

- Treatment of organic compounds with pure chlorine dioxide containing no excess free chlorine produces oxidation products containing no chlorine in some cases, but products containing chlorine in others.

- Under drinking water plant treatment conditions, humic materials and/or resorcinol do not produce trihalomethanes with chlorine dioxide even when a slight excess of chlorine (1-2%) is present.

- Saturated aliphatic compounds are not reactive with chlorine dioxide. Alcohols are oxidized to the corresponding acids.

USAGE OF CHLORINE DIOXIDE IN THE UNITED STATES

Summary of U.S. Questionnaire Results

Using data from chemical suppliers and other sources, 105 questionnaires were sent to plants which were thought to be using chlorine dioxide or which had used it in the past. The water utilities provided information on plant capacity, treatment processes, multiple uses of chlorine dioxide, method of production, and methods of analyzing and monitoring chlorine dioxide in the system. Most plants using chlorine dioxide have been in service at least 15 years are less than 5 mgd in size, and generally are located in the southeastern (EPA Region 4) and midwestern (EPA Region 5) parts of the United States. The most frequent usage of chlorine dioxide

reported was for the control of taste and odor in water supplies (47 responses), followed by disinfection and provision of an oxidant residual in the water distribution system (22 responses), iron/manganese control (18 responses), and oxidation of organic chemicals (12 responses). Those plants using chlorine dioxide for taste and odor control cited phenols and algae as the primary source of these problems.

The common method of chlorine dioxide generation in U.S. water plants is by the gaseous chlorine/sodium chlorite method. One U.S. plant uses the acid method and three use the hypochlorite method. All of the plants reportedly using the gaseous chlorine method use single pass chlorination equipment; none use the multiple pass chlorine enrichment system used by some European plants.

Few plants offered any information on monitoring and analysis of chlorine dioxide. Those that did reported that only the gross measurement of total oxidants (chlorine and chlorine dioxide) is monitored in the finished water. Few plants monitor the actual chlorine dioxide concentration which is added to plant water, rather production rates are determined by the weight of chemical reagents used for the generation process. Production efficiencies are rarely monitored.

Summary of U.S. Plant Visits

During the months of September and October 1977, 13 water treatment plants in the United States were visited. The purpose of these visits was to learn first hand information about the engineering and operational aspects of chlorine dioxide in water treatment operations. Of the thirteen plants visited, five were located in Georgia, five in Ohio, and one each in West Virginia, Kentucky and Michigan. These plants represent a cross section of the use of chlorine dioxide in United States water treatment works. Data collected were similar to that requested by the questionnaire, but in greater detail, plus considerable information on engineering and operation of chlorine dioxide systems. The plants visited are listed in Table 6:

TABLE 6. U.S. WATER TREATMENT PLANTS VISITED WHICH USE CHLORINE DIOXIDE

Columbus, Ohio
Newark, Ohio
Bethesda, Ohio
Hamilton, Ohio
Toledo, Ohio
Atlanta, Georgia
  Chattahoochee Plant
  Hemphill Plant
Carrollton, Georgia
Fayetteville, Georgia
Marietta, Georgia
Wheeling, West Virgina
Covington, Kentucky
Ann Arbor, Michigan

Most of the plants visited use chlorine dioxide to control taste and odor problems or for manganese reduction in the raw water. Twelve of the thirteen plants use the gaseous chlorine and sodium chlorite process for chlorine dioxide generation. The reactor units for chlorine dioxide generation typically are made of PVC and have viewing ports where the color of the chlorine dioxide formed can be viewed. (Figure 17)

There is little monitoring in U.S. plants of the production efficiency or the chlorine dioxide concentration in the finished water. Hamilton, Ohio is the only plant which analyzes for chlorine dioxide in the finished water. Likewise, there is little routine monitoring and control of the processes. As a result, the conversion efficiency and the chlorine dioxide actually produced varies from plant to plant. There appears to be a lack of understanding of what can and does happen when chlorine and chlorine dioxide are mixed in different ratios. Manufacturers of chlorine dioxide generation systems recommend a 1:1 feed ratio by weight of chlorine and sodium chlorite. A number of plants feed excess chlorine, however. Chlorine is needed to depress the pH to a point where conversion efficiencies of 80-95% can be obtained. If the chlorine is recycled, as is the case in one French manufacturer's system, the pH is depressed to 2.7 or less and conversion efficiencies of 98-100% are said to be obtained. In a once pass through system, if excess chlorine is added, the resulting free residual chlorine can 1) lead to the formation of THM's and/or 2) negate the purpose of using chlorine dioxide. If sodium chlorite is not converted to chlorine dioxide, the potentially harmful chlorite ion remains in the water. If too much chlorine is added (or not mixed properly), free residual chlorine will result.

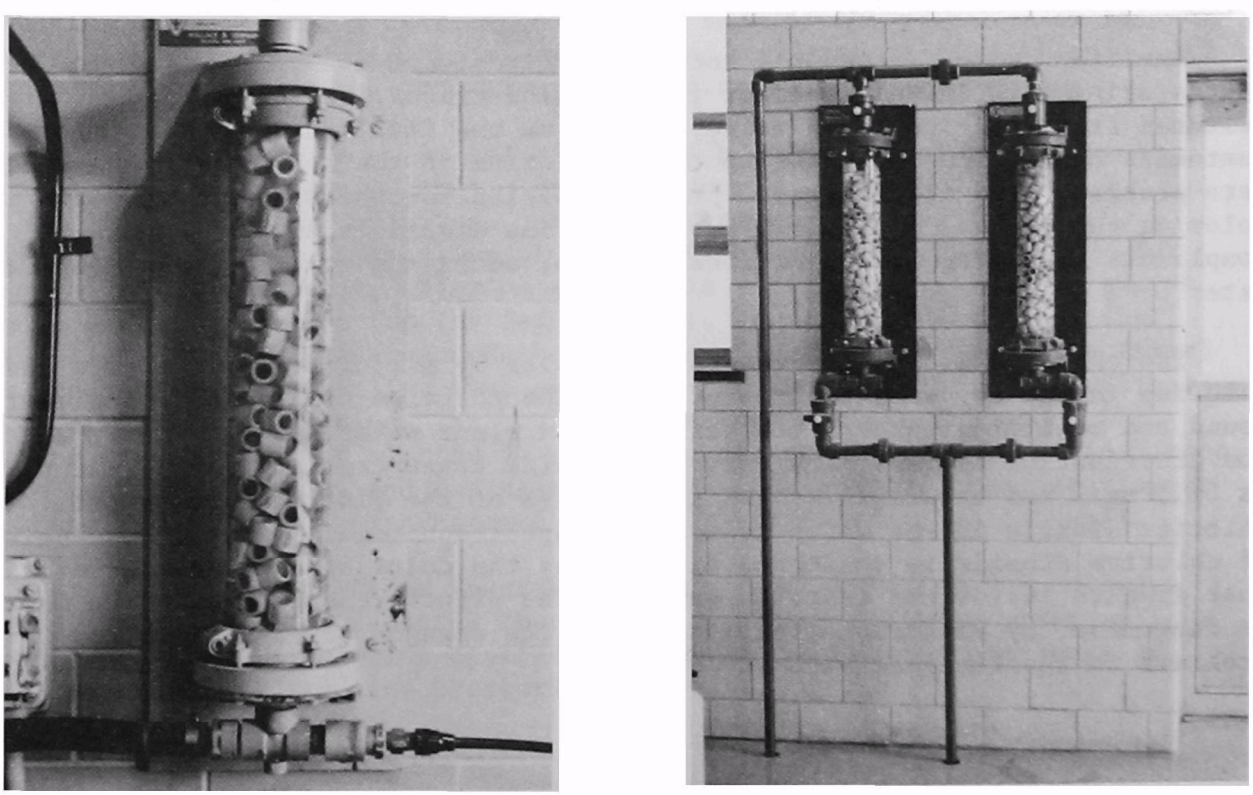


Figure 17. Photographs of Typical U.S. Chlorine Dioxide Generation Systems.

The Ann Arbor water treatment plant uses the acid-sodium chlorite method for chlorine dioxide production. It is the only plant of 84 water treatment plants using chlorine dioxide in the United States that uses this method. The oxidant is added to control taste and odor problems at the 16 mgd facility. These year-round problems are reportedly caused by actinomycetes in the Huron River.

The chlorine dioxide is generated on-site by mixing sodium chlorite ($NaClO_2$) and hydrochloric acid (HCl) in a dry weight ratio of 6.1:1, respectively. The pH of the discharge of the chlorine dioxide reaction vessel is monitored periodically to ensure proper acidity inside the vessel for efficient chlorine dioxide generation. Otherwise the production of chlorine dioxide is monitored visually by the richness of the dark-brown color which appears through the transparent reaction vessel. The efficiency of chlorine dioxide addition is gauged by the absence of tastes and odors in the finished water.

Ann Arbor uses the acid/sodium chlorite method because of the lower costs for operating and maintaining the overall generating system. The pH of the chlorine dioxide generation is better controlled with the acid-sodium chlorite method. Liquid chlorine storage and feed facilities were removed in 1975 when the plant switched to a liquid sodium hypochlorite (NaOCl) chemical feed system for disinfection.

The cost of aqueous HCl, which is 31.45 HCl by weight, is $8.95/100 pounds ($0.20/kg) and $NaClO_2$ which is 80% pure, costs $78.70/100 pounds ($1.75/kg). The chlorine dioxide is added ahead of the sand filters and costs approximately 16¢/1000 gallons (4.23¢/cu.m) of water treated. (1977)

Hamilton, Ohio is the only known water treatment plant in the United States using chlorine dioxide for final disinfection. This 15 mgd plant switched from chlorine to chlorine dioxide as the final disinfectant when customers complained about the taste of chlorine in the tap water. There also were problems with iron bacteria in the distribution mains which were discoloring the water. Since 1972, when chlorine dioxide addition began, the complaints regarding the objectional tastes, odors and colors in the finished water have reportedly ceased.

The chlorine dioxide is generated on-site by mixing sodium chlorite and chlorine in the dry weight ratio of 1:1. The chlorine dioxide is added year round and monitored three times daily in the plant water and once daily in the distribution system. The chlorine dioxide concentration leaving the plant is 0.15 mg/l and 0.10 mg/l at the extremities of the distribution system. The chlorine dioxide in the water is measured spectrophotometrically. Production of chlorine dioxide is monitored visually by the color of the chlorine dioxide that appears inside the reaction vessel. The effectiveness of chlorine dioxide is determined by bacteriological tests and the absence of taste and odor problems in the finished water.

USAGE OF CHLORINE DIOXIDE IN EUROPE

Summary of European Chlorine Dioxide Questionnaire Results

Substantial data were obtained on chlorine dioxide usage in Europe. It is estimated that approximately 495 European water treatment plants currently are using chlorine dioxide. Questionnaires were mailed to plants in West Germany, France, Great Britain, Switzerland, and Austria. Forty-four responding plants were in West Germany, 23 in France, 5 in Great Britain, and 2 plants in Austria responded.

Unlike the U.S. practice, chlorine dioxide is used in Europe principally for bacterial disinfection and provision of a long lasting, low oxidant residual in the distribution system. This was particularly true in West Germany, Austria, and Great Britain. French plants cited a variety of reasons for using chlorine dioxide, principally bacterial disinfection, taste/odor control and organics oxidation. The British cited taste/odor control as a principal reason for chlorine dioxide usage.

As in the U.S., the principal method of chlorine dioxide preparation is the gaseous chlorine/sodium chlorite process. Dosages at all of the plants reporting were quite low, often about 0.3 mg/l and seldom exceeding 0.6 mg/l.

Summary of European Chlorine Dioxide Plant Visits

During May 1977, the site visit team toured 15 European water treatment plants which employ chlorine dioxide. Four of the plants were in France, one in Belgium, eight in Germany, and two were in Switzerland. All but two of the plants use ozonation in addition to chlorine dioxide.

In general Europeans use chlorine dioxide only when chlorine cannot be used, mainly because of cost. In Europe, chlorine dioxide costs 3 to 3.5 times more than chlorine. The two primary processes for which chlorine dioxide is utilized are in pretreatment and post-treatment. For example, in pretreatment, chlorine dioxide is utilized at the Paris suburb plants of Choisy-le-Roi (on the Seine River), Neuilly-sur-Marne (on the Marne River), and at Annet-sur-Marne (upstream of Paris on the Marne River) for breaking up organically bound manganese and iron and for presterilization of water before filtration. At Toulouse, in southwestern France on the Garonne River, chlorine dioxide is used in pretreatment for presterilization, taste and odor control, and for color removal. Dosages of chlorine dioxide employed in Europe for pretreatment generally range from 1 to 1.5 mg/l.

At the Tailfer plant in Brussels Belgium, both chlorine and chlorine dioxide are used in pretreating Meuse River waters. Chlorine presterilizes the raw water while chlorine dioxide decomposes the organic complexes of iron and manganese and also presterilizes.

In Germany and Switzerland, chlorine dioxide is used only for post-treatment at the 10 water treatment plants visited in these countries. Germans and Swiss use a maximum of 0.3 mg/l of chlorine or chlorine dioxide to provide a residual in the distribution systems. This dosage level provides trace amounts of chlorine or chlorine dioxide in the distribution systems. The tacit rule in these countries is that if finished water leaving the plant requires greater than 0.3 mg/l residual chlorine or chlorine dioxide to provide stable residuals in the distribution system, then the existing water treatment process must be modified to reduce oxidant demand until this level of oxidant demand is attained. German water treatment plants can add as much as 0.6 mg/l of chlorine or chlorine dioxide to attain residuals.

In post-treatment, chlorine dioxide is used only at Choisy-le-Roi and Annet-sur-Marne of the plants visited in France and Belgium.

Four methods of generating chlorine dioxide on-site at European drinking water treatment plants were observed:

1. Addition of chlorine gas to water, followed by addition of excess chlorine solution to aqueous solution of sodium chlorite.

2. Addition of chlorine gas to water under pressure, then addition of this solution under pressure to aqueous solution of sodium chlorite under pressure.

3. Addition of chlorine gas to water and recirculation of this aqeuous solution in a closed loop with continued addition of chlorine until a pH below 2.7 has been attained. Then addition of this pH 2.7 solution to aqueous solutions of sodium chlorite.

4. Addition of HCl solution to aqueous solution of sodium chlorite.

DESIGN OF CHLORINE DIOXIDE SYSTEMS

The study included considerable review of the engineering details of chlorine dioxide generation systems. The gaseous chlorine/sodium chlorite and acid sodium/chlorite systems are the principal systems in use today. The multiple pass enrichment technique, a recently developed variation of the gaseous chlorine approach is rapidly being adopted in Europe because of superior efficiency. The acid based process is less popular, principally due to the difficulties and safety related problems of handling concentrated acids. Both processes use a similar chlorine dioxide reactor, usually a cylindrical vessel constructed from Pyrex glass of polyvinyl chloride (PVC). Typically, the reactor is 36 to 42 inches high, 8 inches in diameter and packed with Raschig rings. The feedstock chemicals are usually added at the bottom of the vessel and flow upward, being mixed by the packed column of rings.

The Gaseous Chlorine-Sodium Chlorite System

This approach uses aqueous chlorine and aqueous sodium chlorite to produce a mixture of chlorine dioxide and chlorine (commonly as HOCl). Figure 18 is a schematic of such a system, which consists of a chlorine dioxide generator, a gas chlorin ator, a storage reservoir for liquid sodium chlorite, and a chemical metering pump. (Sodium chlorite solution can be prepared from commercially available dry chemical by adding it to water.) The recommended feed ratio of chlorine to sodium chlorite is 1:1 by weight. Additional chlorine can be injected into the reactor vessel without changing the overall production of chlorine dioxide.

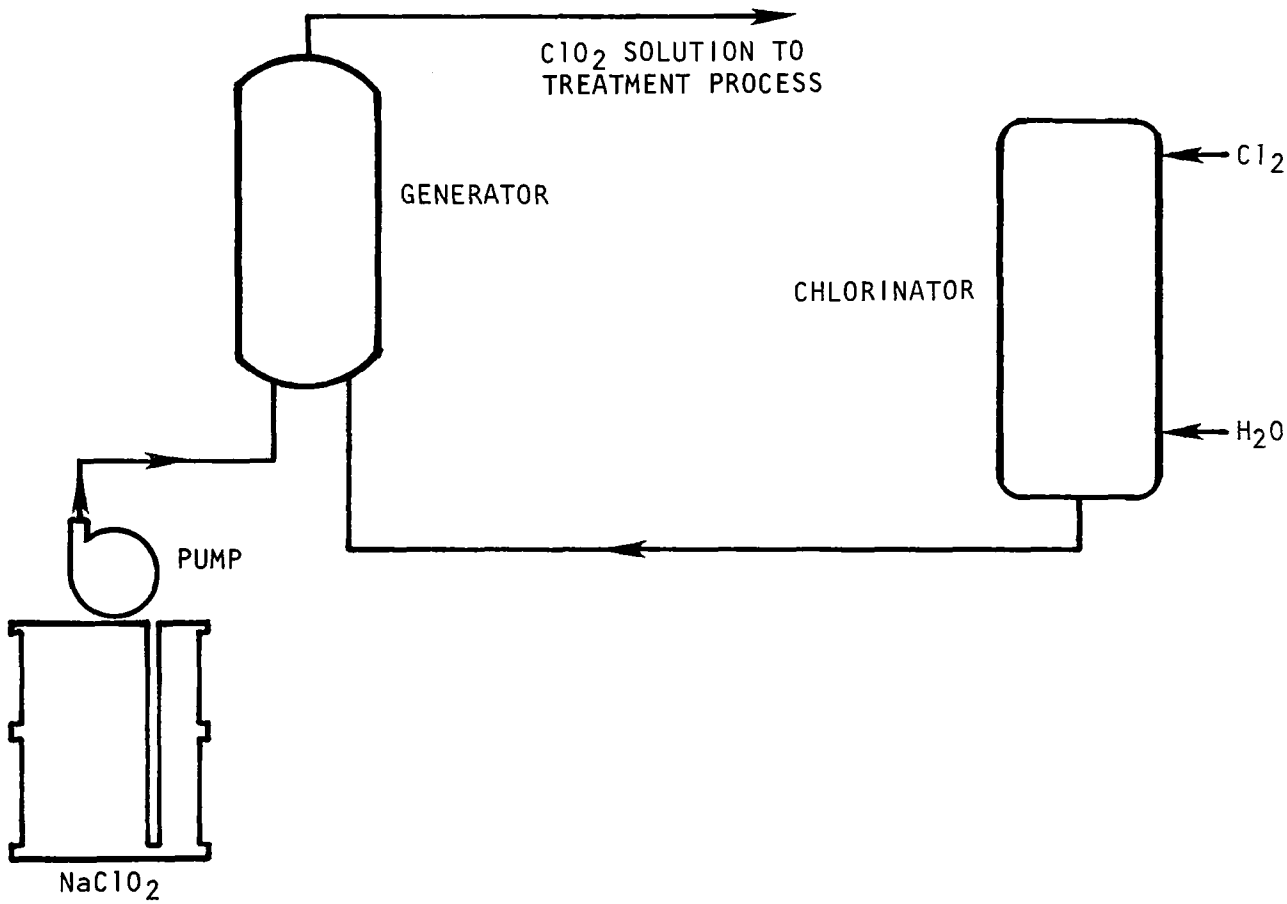


Figure 18. Gaseous Chlorine-Sodium Chlorite Chlorine Dioxide Generation System.

A disadvantage of this process is the limitation of the "single pass" gas chlorination. Unless increased pressure is used, this equipment is not able to achieve higher concentrations of chlorine as an aid to a more complete and controllable reaction with the chlorite ion. A French firm, CIFEC, has developed a variation of this process using a multiple pass enrichment loop on the chlorinator to achieve a much higher concentration of chlorine and thereby quickly attain the optimum pH for maximum conversion to chlorine dioxide. (Figure 19)

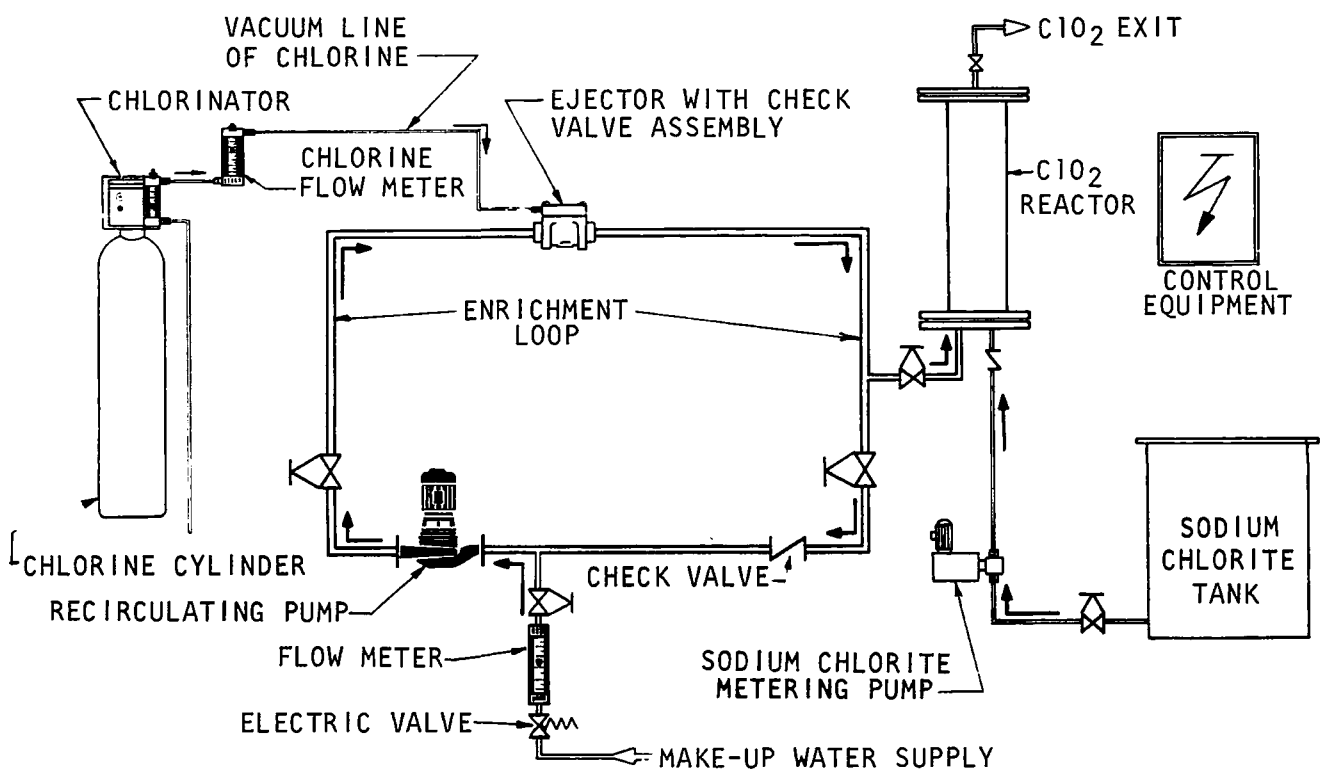


Figure 19. The CIFEC System

The purpose of the multiple pass recirculation system is to allow enrichment of the chlorine solution to a level of 5 to 6 g/l. At this concentration the pH of the solution will drop to 3.0 and thereby provide the low pH level necessary for efficient chlorine dioxide production. A "single pass"results in a chlorine concentration in water of about 1 g/l, which produces a pH of 4 to 5. If sodium chlorite solution is added at this pH, only a 60% yield of chlorine dioxide reportedly is obtained. The remainder is unreacted chlorine (in solution) and chlorite ion. When upwards of 100% yield of chlorine dioxide is achieved, there is virtually no free chlorite or free chlorine carrying over into the product water.

The CIFEC system can be designed for variable feed rates with automatic control by an analytical monitor. This method has the advantages of eliminating the chlorine dioxide storage reservoir. The production of the CIFEC system can be varied by 20 equal increments of production. A 10 kg/hr (530 lbs/day) reactor can be varied in 0.5 kg/hr (26.5 lbs/day) steps over the range of 0-10 kg/hr, and this can be accomplished by automatic control with the monitor located in the main plant control panel.

Wallace and Tiernan offer a new single pass system which is pressurized to produce a higher concentration of aqueous chlorine for chlorine dioxide production. Gaseous chlorine is injected into feed water at about 7 bars (102 psi). With a chlorine concentration of 5 g/l produced, the pH of the solution is reduced and chlorine dioxide is said to be produced quantitatively. The chlorine dioxide solution is then diluted to 10 to 20 mg/l (as chlorine dioxide) for water treatment operations.

The Acid - Sodium Chlorite System

The combination of acid and sodium chlorite produces an aqueous solutions of chlorine dioxide without production of significant amounts of free chlorine. The acid based process avoids the difficulty of differentiating between chlorine and chlorine dioxide for establishing an oxidant residual.

Figure 20 illustrates the chlorine dioxide production schematic for the Lengg Waterworks of Zürich, Switzerland by the acid/sodium chlorite procedure. This system uses liquid chemicals as the feed stock. Each tank has a level sensor to avoid overfilling. The tanks are installed below ground in concrete bunkers which are capable of withstanding an explosion. There are no floor drains in these bunkers, and any spillage must be pumped with corrosion resistant pumps. Primary and backup sensors with alarms warn of any spillage.

Because of the potential explosiveness, these chemicals are diluted prior to the production of chlorine dioxide. The dilution is carried out on a batch basis which is controlled by level monitors. Proportionate quantities of softened dilution water along with the chemical reagents are pumped to mixing vessels by means of calibrated double metering pumps. After the reactor is properly filled, an agitator within the container mixes the solution for 15 minutes. Dilutions of 9% HCl and 7.5% sodium chlorite are produced in the chemical preparation process. The chlorine dioxide is subsequently manufacturered on a batch basis. The final strength of the solution is about 20%, 90-95% of this is chlorine dioxide, and 4-7% is chlorine.

COSTS FOR PRODUCING CHLORINE DIOXIDE

The cost for generating chlorine dioxide on-site is primarily dependent on what method is used to generate the oxidant. There are other factors that affect capital and O/M costs for on-site chlorine dioxide production. These include:

- rate of chlorine dioxide production

- level of automation
- back up equipment
- availability of existing equipment to be incorporated into a chlorine dioxide system
- chemical storage facilities
- type of chemical reagent--liquid, powdered, drums, tank car, rail car, etc.
- size and frequency of chemical shipments
- experience of plant operators

Although it is difficult to assign cost figures to chlorine dioxide production because it is a site-specific assessment, chlorine dioxide production generally follows an economy of scale. Larger plants that generate chlorine dioxide on-site normally can produce it pound for pound less than smaller water treatment plants. However, the larger plants will typically incur higher capital costs for chlorine dioxide production because of higher levels of system automation, chemical storage facilities, stand by equipment, etc.

The gaseous chlorine and sodium chlorite method is the most popular chlorine dioxide generation technique in the U.S., Canada, and Europe. Because few plants actually use the minimum practicable amount of chemicals in this process, chemical costs have been estimated on the basis of stoichiometric production. On this basis, chlorine dioxide produced from gaseous chlorine and sodium chlorite costs approximately $1.35 to $2.00 per pound in chlorine dioxide in the United States. The cost for the acid and sodium chlorite process is $1.80 to $2.60 per pound chlorine dioxide. These estimates are based on 1977 dollars.

Capital costs for a chlorine dioxide system are largely dependent on the type of chlorine dioxide process and the degree of sophistication desired. Plants which have gaseous chlorine capability can install chlorine dioxide generation equipment relatively inexpensively. At the other end of the scale, the relatively efficient and sophisticated CIFEC system can be quite expensive.

The major equipment components needed for a relatively simple chlorine dioxide system, along with their estimated 1977 costs, are tabulated below.

	Capital Cost (U.S. dollars)
Chlorine Dioxide Reactor	650 - 1200
Chemical Feed Pumps (each)	400 - 800
Chemical Storage Tanks (up to 250 gallons)	
Gas Chlorinator (500 lbs/day to 2000 lbs/day)	1700 - 4000
Weighing Scale for Chlorine	350 - 500

For a 10-15 mgd plant, a typical gaseous chlorine based chlorine dioxide could cost $3000 to $4000 for materials and another $3000 to $5000 for installation.

In Europe, the CIFEC system is becoming quite popular for generating chlorine dioxide at water treatment plants. The manufacturer reports that the capital cost for a 20 kg chlorine dioxide/hr (1058 pounds chlorine dioxide/day) CIFEC system is about $100,000 (1977). Installation costs are not included. A 200 g chlorine dioxide/hr (11 pounds/day) CIFEC system costs about $24,000 (1977).

CONCLUSIONS

- Chlorine dioxide, when free of chlorine, does not form trihalomethane compounds in drinking water processes. It is less likely than chlorine to form chlorinated compounds with most organic substances commonly found in raw water supplies.

- Chlorine dioxide is effective in oxidizing organic complexes of iron and manganese, imparts no taste and odor to the treated water, and provides a very stable, long lasting oxidant residual.

- The technology of chlorine dioxide generation is well established and recent innovations have increased process efficiency. There are no unduly hazardous aspects in the operation of most chlorine dioxide systems when operated with care.

- The European plants visited, and those responding to the questionnaire, appeared for the most part to understand and properly apply the chemical. By contrast, many of the U.S. plants surveyed and/or visited demonstrated a limited understanding of the process, often leading to incorrect and inefficient operation of the chlorine dioxide system.

- The cost of producing and using chlorine dioxide is considerably higher than that of chlorine in both the U.S. and Europe. Consequently, its use generally is limited to those locations where chlorine cannot meet process needs.

Appendix A

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Appendix B

LIST OF OZONE EQUIPMENT MANUFACTURERS

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Alron Industries
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Brown, Boveri & Co., Ltd.
CH-5401
Zurich, Switzerland

Chemie und Filter GmbH
Verfahrenstechnik KG
D-6900
Heidelberg, Germany

Crane-Cochrane
P.O. Box 191
King of Prussia
Pennsylvania 19406

D-3 Company
4935 McConnell Avenue
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Los Angeles, California 90066

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183 Ave. du 18 Juin 1940
92400 Rueil-Malmaison
Paris, France

Degremont Infilco, Ltd.
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California 94080

Welbach-Trailigaz Ozone Systems
Corporation
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Philadelphia, Pennslyvania 19129

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(Please read Instructions on the reverse before completing)

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16. ABSTRACT

This executive summary covers in abbreviated form each of the principal topics of the full report. Emphasis in the summary, and in the full report, is given to the fundamental uses and engineering design of ozone/chlorine dioxide systems. A limited discussion of Biological Activated Carbon is included. Data from extensive questionnaires and from site surveys of several hundred drinking water utilities are included in the full report and summarized herein.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ozone, Water supply, Water treatment devices, Engineering costs	Chlorine dioxide, Oxidation products, Drinking water treatment, Engineering design, Biological activated carbon, Canada, Western Europe, United States	13B

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