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INVESTIGATION OF AN OZONE-FILTER SYSTEM FOR COLOR AND IRON REMOVAL AT LOW TEMPERATURES

INSTITUTE OF WATER RESOURCES

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NOTICE

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INTRODUCTION

The application of ozonation as a disinfectant and as a treatment process for both water and wastewater has been increasing in recent years. The study of ozone application to Arctic and subarctic waters, which are normally at low temperatures, has been limited. Many portions of the Alaskan Arctic and subarctic are plagued with waters which exceed the 1962 Drinking Water Standards for one or more parameters. The iron content and color of the water are among the most common offenders. This project was directed toward the examination of a method for water treatment utilizing ozone to meet the iron and color limits for drinking water. The three principle objectives of the project were:

- (1) to examine the effect of ozone on several known qualities of water,
- (2) to examine the effect of ozone on representative samples of surface and ground water, and
- (3) to develop a laboratory scale system for iron and color removal utilizing ozone followed by sand filtration.

Utilization of ozone treatment on subarctic waters was initially investigated by Reid and Potworowski (1973) in their report, "Ozone Treats Arctic Waters," submitted to the U.S. Army Cold Regions Research and Engineering Laboratory through the Arctic Health Research Center.

Deactivation of the Arctic Health Research Center left the report incomplete. Consequently, it lacked any quantifiable information regarding the ability of ozone to remove organically complexed iron and color. On the basis of the examined literature and the work of Reid and Potworowski (1973), it was determined that ozonation could effectively remove iron and color and required further investigation to evaluate its actual feasibility.

REVIEW OF LITERATURE

Historically, interior and northern Alaska's subarctic and Arctic water supplies are plagued by unacceptable water quality (Reid and Potworowski, 1973). Organically complexed iron and color are the most common nuisances. Summarizing a report by Smith (1973) submitted to the U.S. Army Cold Regions Research and Engineering Laboratory through the Arctic Health Research Center, the surface waters from the permafrost regions of Alaska range in color from 0 to 80 units and in iron from 0 to 4.6 mg Fe/liter. Data ranges are due in part to seasonal variations and sample locations. Intermittent permafrost areas demonstrates similar values for surface waters. Ground water data for intermittent permafrost areas exhibit color values as high as 500 units and iron concentrations over 150 mg/l. The present recommended maximum set in the U.S. Public Health Service Drinking Water Standards (1962) for iron is 0.3 mg/l Fe/liter and a color limit of 15 units.

The problems associated with these drinking water contaminants are essentially insurmountable for the individual homeowner. In recent years, various attempts have been made to facilitate the removal of these drinking water contaminants. These include carbon filtration, hypochlorite, lime, lime-alum, contact filtration, ion exchange, and reverse osmosis. Unfortunately, successful treatment using these conventional methods proved to be difficult (Smith, 1973).

Ozone Chemistry

At standard temperatures ozone is a highly unstable gas. At the low concentrations at which it is normally produced, it appears colorless with a pungent characteristic odor (similar to chlorine) from which its name is derived (Greek origin). It is an allotropic form of oxygen with a molecular formula of O_3 . Its structure is an obtuse angle with a central oxygen bonded to two equidistant oxygen. Its resonance structures can be written as:



In addition to being a potent germicide, ozone resembles its parent compound oxygen in that it is a powerful oxidant of both organic and inorganic compounds. Only three oxidizing agents (F_2 , F_2O , and O) are considered more powerful.

The solubility of ozone in water is dependent on temperature and pressure. Figures I and II show how solubility varies with temperature and pressure, respectively. Ozone's solubility in water is higher than oxygen, but still relatively low.

One of the major limitations of ozone-related research is the analytical methods of determining ozone in water. The most widely accepted method of ozone determination was presented by Birdsall, et al. (1952). This technique involves the oxidation of potassium iodide in an acid solution by the following reaction:

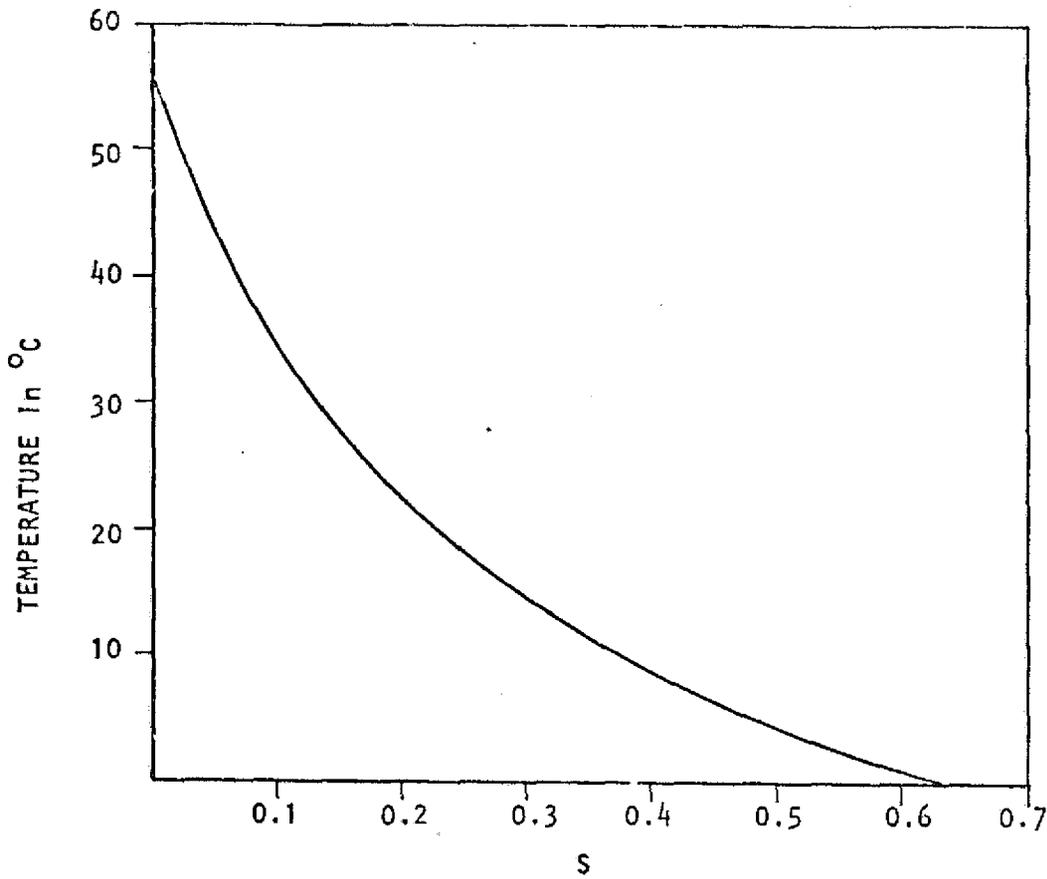


FIGURE I EFFECT OF TEMPERATURE ON S VALUE
From O'Donovan, 1965

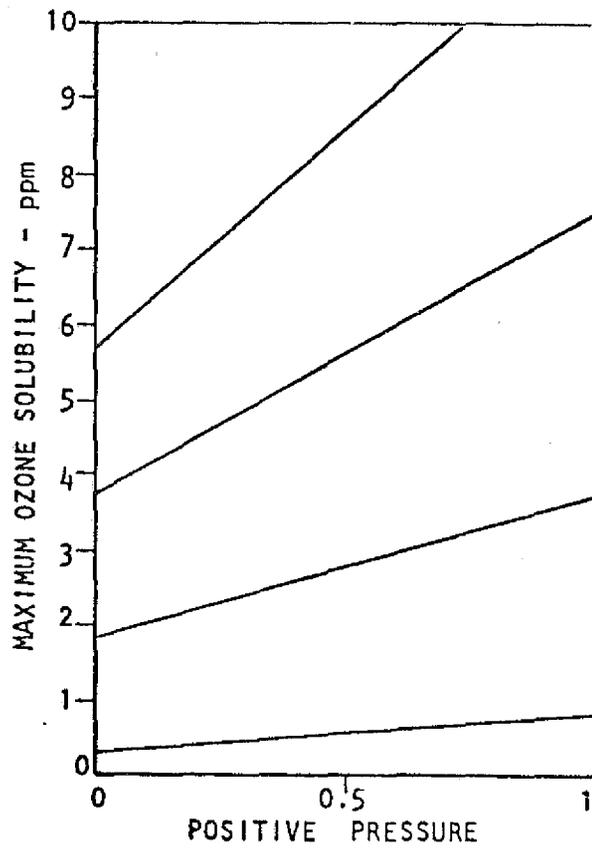
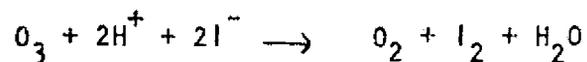
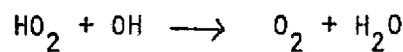
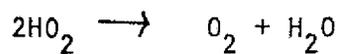
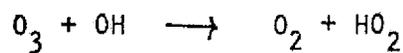
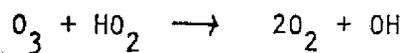
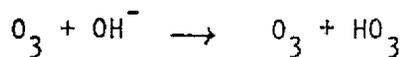


FIGURE II EFFECT OF PRESSURE ON OZONE SOLUBILITY AT 0°C
From O'Donovan, 1965



This method is limited due to the interference of most oxidants such as oxygen and chlorine. Several other analytical methods for the determination of ozone in water were described by Evans (1972).

Decomposition of ozone depends on surface reactions, which act as catalysts. Catalytic activity depends on the degree of subdivision, crystal structure, and the presence or absence of water moisture. A half-life as long as 100 hours can be obtained in clean inert containers such as glass and stainless steel. When associated with aqueous solutions, the decomposition rate is more rapid because of the catalyzing effect of the hydroxyl ion. The reaction, as presented by Manley, et al. (1967), is:



The actual reaction and decay rate of ozone in water is dependent on oxidizable substances present and natural decomposition. Reid and Potworowski (1973) determined decay rates to be 0.093 and 0.065 mg/l of ozone per minute for distilled water and pre-reacted distilled water, respectively. These investigations were performed under sterile laboratory conditions, which are not the case in field installations.

O'Donovan (1965) reported a non-linear ozone decomposition rate which was initially about 0.07 mg/l of ozone per minute. The rate of decomposition declined with time.

Aqueous Chemistry of Iron

Even though iron has the ability to exist in eight oxidation states ranging from Fe(-2), and Fe(+6), the commonly existing valence states are Fe(0), Fe(+2), and Fe(+3). The Fe(+2) and Fe(+3) species are of importance in the aqueous environment.

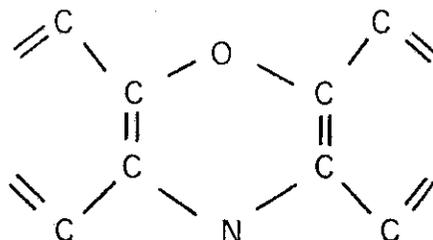
Solubility of Fe(+3) is essentially negligible in the absence of organic complexing agents. Its limited solubility is determined by the amorphous ferric hydroxide, ferric oxide or ferric oxide hydroxide solubility. The solubility of iron is dependent on the redox potential (Eh) and the hydrogen ion concentration (pH). The ferrous ion (occurring as Fe(+2), FeOH^+ , and $\text{Fe}(\text{OH})_3^-$) solubility is determined by the ferrous hydroxide, ferrous carbonate, and ferrous sulfide solubility. Consequently, high concentrations of soluble iron(II) species are contained in ground-water supplies where iron-bearing strata are indigenous. Upon the introduction of oxygen, the soluble iron(II) is oxidized and precipitated as $\text{Fe}(\text{OH})_3$, Fe_2O_3 , and occasionally FePO_4 . Similarly, in the absence of oxygen, ferric iron can be reduced to the soluble ferrous form.

Few surface waters contain soluble iron. Those that do are usually derived from eutrophic lakes and reservoirs where the dissolved oxygen of the stagnant hypolimnetic zones is depleted and deposited iron minerals are returned to solution. The process becomes cyclic as seasonal lake overturns and stratification occur, causing periods of high and low dissolved oxygen content, respectively. Due to the long winters and

resulting ice cover which prevents reaeration, dissolved oxygen is appreciably reduced. The change in the oxidation-reduction potential results in the release of ferrous iron into solution. When such waters are used as a municipal water supply, the problem becomes acute during late winter and spring break-up as the ferrous iron concentration reaches a maximum. The problem itself suggests a feasible solution, since ferrous iron can be readily aerated and precipitated.

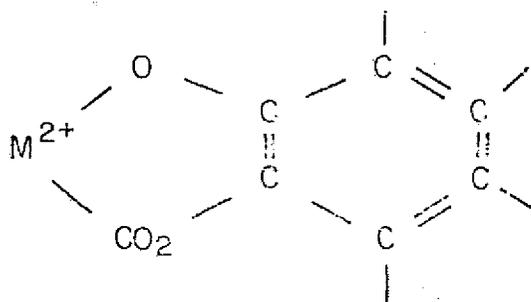
Iron removal difficulties are increased in natural waters containing organic pollutants that act as complexing agents. The worst of these is humic acid and its related compounds, which are formed through vegetation decomposition and are resistant to degradation. They are defined as any organic acids that are insoluble in alcohol and organic solvents.

The average molecular weight of humic acids appears to cover the range of 300 to 300,000 and has been the subject of much discussion (Oldham and Gloyna, 1965). In studies of interactions of iron with soil organic acids, Oldham and Gloyna (1965) indicated the average molecular weight of iron-complexing humic acid to be approximately 620 grams per mole. All humic acids exhibit similar composition, structure, and chemical properties. They usually contain some protein-like material and a carbohydrate fraction. Literature further suggests the likelihood of -O- and -N- linkages (Manahan, 1972):



Humic acid has the ability to bind or complex exchangeable cations such as metal ions and H^+ . At low pH's the complex's stability is reduced due to the hydrogen ion competition. This concurs with the results of Oldham and Gloyna (1965), at least for the ferrous iron where no complexing was evident at a pH of 5. Manley and Niegowski (1967) reported 50 mg/l of iron was complexed at a pH of 7. It was also concluded that the complexation of ferric iron is governed by an equilibrium constant, whereas the ferrous iron reaction is complete. Polarography and infrared analyses verify Oldham and Gloyna's theory that ferrous and ferric complexation occurs by different mechanisms.

Iron bonding or complexation occurs in one of two ways. The weaker bonding theory is used to explain what occurs between $-CO_2$ groups and the metal ion. The more stable version is that wherein a chelate bond is formed between the metal ion and both a $-CO_2H$ group and a $-OH$ group (Manahan, 1972):



Complexation of ferric iron occurs at lower pH's, which suggests that it has a higher ability to complex and would be favored over ferrous complexation.

The ability of humic acids to complex iron species is an important factor in the role of iron transport. Similarly, it is interesting to note that "color" in natural waters has been shown to be associated with

humic acid. Therefore, the successful removal of these stable organo-metallic complexes will similarly aid in the reduction of color.

Nature of Organic Color in Natural Waters

Organic color, yellow-brown in appearance, is very common in natural waters throughout Alaska. Extensive research, utilizing various methods, has been concerned with color removal processes. The actual chemical structure of these organic pollutants has remained somewhat a mystery. Various terms have been attached to organic color including tannins, lignins, and humic acids.

The origin of organic color is in the multitude of organic molecules that compose the native vegetation of a particular area. The vegetation in all stages of decomposition supplies the necessary organic molecules available for aqueous extraction. The extraction occurs upon contact between the water and vegetation debris and soils containing organic matter. Degree of extraction is dependent on pH, water temperature, contact period, and type and quantity of organic matter. The extraction method gives evidence of the acidic properties of color molecules. The color molecules are believed to consist of only carbon, oxygen, hydrogen, and occasionally traces of nitrogen.

Black and Christman (1963) in their article on colored surface water characteristics suggest that the presence of color is due to light scattering and fluorescence. This contradicts the molecular adsorption of light energy theory.

Utilizing various membrane filters, Black and Christman (1963) were able to determine that the majority of the color in the sample waters

tested was colloidal in nature, ranging in size from 3.5 to 10 μ in diameter. Simultaneously, pH was observed to have an irregular effect on color concentration by altering particle size and number of particles in suspension. No viable correlation between iron content and color concentration existed except that all samples contained substantial amounts of iron. Similarly, there was no uniformity between color concentration and organic carbon content, which are believed to be dependent on characteristics of contacted organic matter and contact time.

At present there appear to be two methods of isolating color materials from waters--freeze concentration and ion exchange. Both methods utilize degradative chemical studies. Christman and Ghassemi (1966) reported that oxidation with alkaline-copper oxide effectively degraded the complex color molecule to recognizable chemical structures. Both techniques involve time-consuming and complex identification methodology.

Luminescence of Organically Colored Water

Luminescence is the emission by a substance of electromagnetic radiation from another source and is composed of fluorescence and phosphorescence. Fluorescence is the radiation emitted as a result of, and only during, adsorption, whereas phosphorescence is that radiation emitted after adsorption.

Luminescence is of interest because it characterizes the luminescent molecule by the following features (Sinelnikov, 1969):

- (1) A chain of conjugated bonds.
- (2) Tautomerism.
- (3) A tendency toward ortho and paraquinoid ring formation.

- (4) Intramolecular hydrogen bonding formation.
- (5) Structural symmetry, such that the molecule configuration restricts the conversion of the excitable energy into kinetic energy.

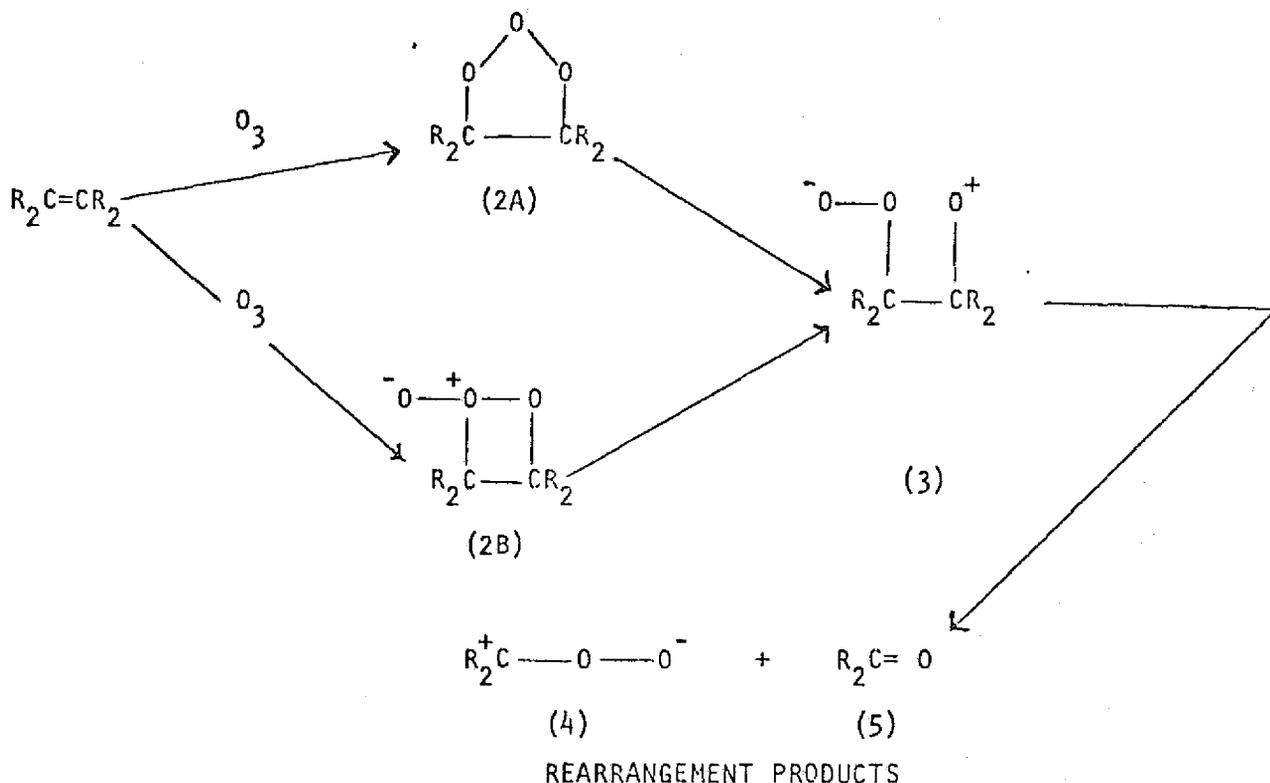
Because of the diverse possibilities of organic molecules, the recorded luminescence is characteristic of the individual water. Similarity between observed luminescence (samples) and known luminescence spectra (standard organic solutions) can aid in the identification of colored organics. Luminescence spectra also reflect changes occurring because of treatment or natural causes, or both.

With regard to organically colored water in Arctic areas, Reid and Potworowski (1973) indicated that the appropriate range of fluorescence was 440 to 460 $m\mu$ when excited by a source of 366 $m\mu$ using a primary filter number 7-60 and a secondary filter number 2-A. This is in relatively close agreement with Black and Christman's (1963) observed results of a maximum at 490 $m\mu$ with the combined excitation wavelengths of 365, 405, and 436 $m\mu$. Similarly, it was reported that fluorescence intensity varied with color concentration.

Ozonation of Organics

The complexation of iron by organic agents, especially humic acids, necessitates the understanding of organic oxidation by ozone. The possibility of breaking down these stable organic compounds by ozone oxidation would make the organic ligands monodentate in addition to the reduction of organic color. The oxidation products would then be more susceptible to hydroxyl bridging because of the increased freedom of motion exhibited.

Ozonolysis of unsaturated organic compounds occurs at the carbon-double bonds. The elucidation of the ozonolysis mechanism was made by Criegee in the 1950's when he proposed the following reactions (Evans, 1972; Manley and Niegowski, 1967):



Depending on the original attacking resonance form of ozone, the primary ozone-olefin addition product formed is either 2A or 2B. In theory the initial electrophilic attack takes place by a terminal oxygen. Then, depending on the completion of the attack by either the other terminal oxygen or the central oxygen (both being nucleophilic), primary ozonolysis products 2A and 2B are produced. The structure of 2B is felt to be more accurate because of its reduced stability in comparison to structure 2A. The primary addition product (2A or 2B) then decomposes to an unstable molozonide zwitterion (3). Stabilization of the zwitterion then occurs by splitting into a carbonyl compound (5) and another

zwitterion (4). These intermediates are termed "Rearrangement Products". The final observed ozonolysis products are dependent upon the zwitterion rearrangement product reacting with itself or other compounds present (solvents, etc.) In polar solvents such as water, the end product mixture usually contains aldehydes, acids, peroxides, and ozonides. The decomposition of humic acids has created end products containing such compounds as syring aldehyde and 3,5-dihydroxyl benzoic acid (Manahan, 1972). These products are in agreement with the proposed theoretical products. Similarly, the expected reduction of double-bond quantities is verified by the investigations of Reid and Potworowski (1973) where ozonation rapidly reduced the fluorescence.

Theoretical determination of end products is difficult. In addition to the vague and varied humic acid structure and numerous possible rearrangement product reactions, the ozonolysis products are temperature (thermally unstable) and pH dependent.

The ozonation of the highly stable colloidal dispersions responsible for the complexed iron and organic color results in microflocs that do not settle easily. Their removal is usually achieved by coagulant addition followed by a filtration process.

Ozonation Design Optimization

The dominant cost in ozonolysis is the cost of ozone generation. In addition, the optimum utilization of generated ozone affects the overall cost by reducing the amount of ozone required and hence the total generation cost.

The literature suggests the following variables as the major

parameters to be considered in design:

- (1) Residence time.
- (2) Temperature.
- (3) Ozone dosage and contact time.
- (4) Mixing (gas-liquid surface contact area per unit of ozone).

Furgason, et al. (1973) demonstrated that the reduction of color units is a function of ozone applied, and follows the pattern given in Figure III. As shown in Table I, color reduction is rapid for residence times less than 10 minutes and slows down thereafter.

Literature states that the presence of iron interferes with color reduction and conversely because of the interaction between the two. Therefore, it is pertinent to investigate the residence time to optimize the utilization of ozone.

In regard to color reduction, the suggested optimum reaction temperature was reported to be 85°F (Furgason, et al., 1973). The feasibility of treating Arctic waters is consequently reduced.

Suggested contact times and required dosages vary depending on treatment objective and water quality. Dosages range from 0.5 mg/l up to 9 mg/l as seen in Table II. Contact times usually do not exceed 20 minutes.

Recent design improvements in mixing techniques have increased the popularity of ozone treatment which was low because of inefficient methods. The key to successful introduction of ozone is to cause the formation of very fine bubbles, thereby increasing surface contact area per unit of ozone. Similarly, adsorption is seen to increase as the air-water ratio decreases, common commercial plant ratios used are 0.5 to 0.1 (O'Donovan, 1965). Two-stage ozone application also increases

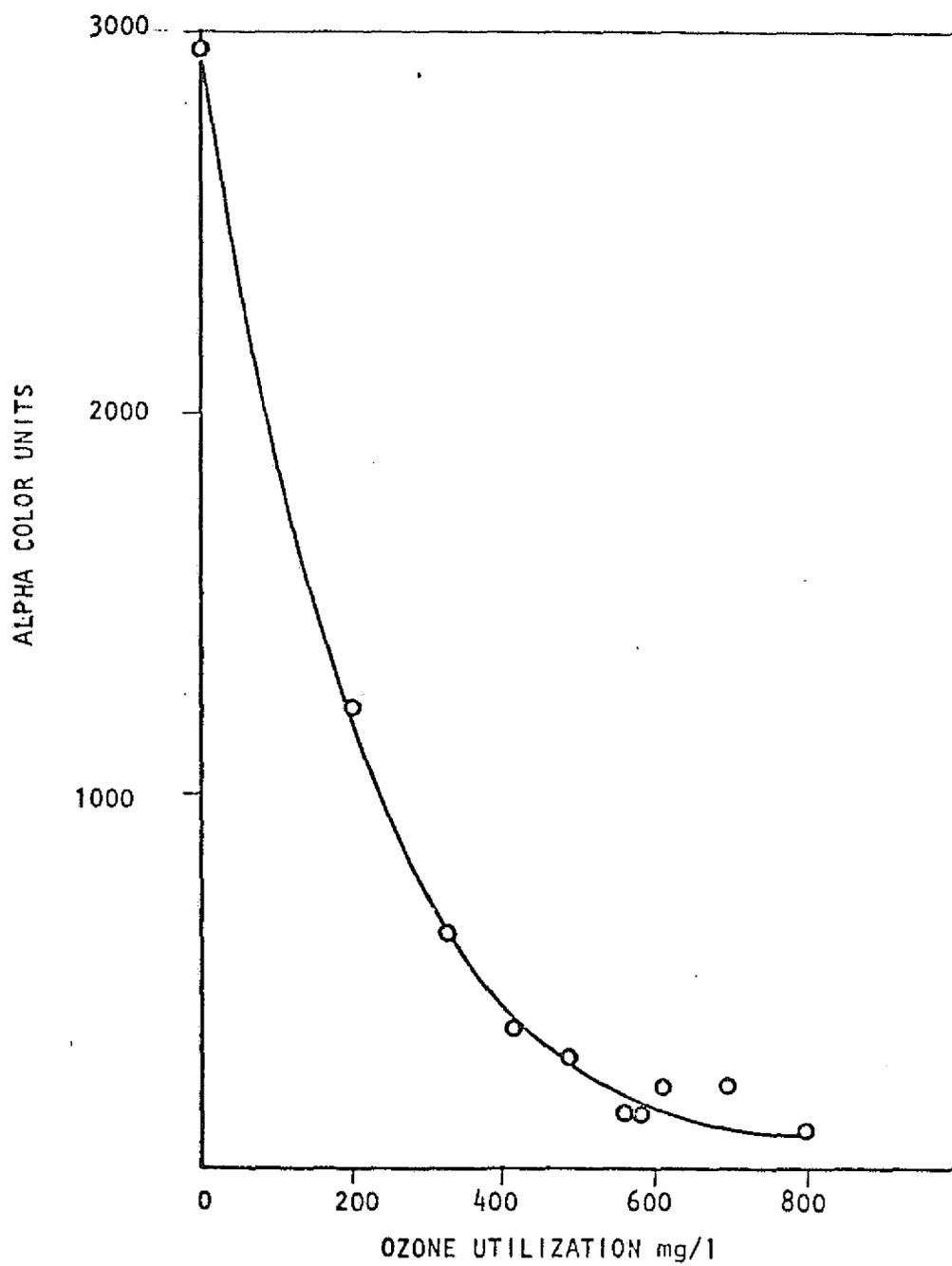


FIGURE III COLOR AS A FUNCTION OF DEGREE OF OZONATION

From Furgason, *et al.*, 1973

TABLE I
EFFECT OF RESIDENCE TIME ON COLOR REDUCTION

Residence Time min.	Color Units		
	Initial	Final	% Reduction
10	2050	740	64
18	2050	710	65
30	2050	340	83
45	2050	260	87
60	2050	260	87

(Applied dose = 340 mg/l)

From Furgason, et al., 1973.

TABLE II
OZONE DOSE REQUIREMENTS
FOR VARIOUS WATER TREATMENT OBJECTIVES

Raw Water Condition	Dose, mg/l
Virus Destruction	0.5 - 1.5
Taste and Odor Control	1 - 2
Iron and Manganese Removal	1 - 5
Color Removal	1 - 9
Good Bacterial Quality	0.25 - 0.5
Ground Water	0.5 - 1
Surface Water	2 - 3
Poor Bacterial Quality	
Surface Water	2.5 - 5

From Smith, 1973.

efficiency of introduction.

Three current techniques are the Otto partial-injection system, the Kerag system, and the diffuser system. The Otto partial-injection method sucks the ozone into the water because of a pressure loss across an injector. It is then carried to the bottom of a contact column. The high frequency rotation of the propeller in the Kerag system sucks the ozone through the propeller's hollow shaft. The diffuser system injects pressurized ozone through porous diffusers at the bottom of a deep contact tank.

Furgason, et al. (1973) analyzed two methods of gas liquid contact based on cost. One system used a venturi contactor outside the reaction vessel, whereas the other system used a contactor that was an integral part of the reactor. The estimated cost was reported lower for the system with the contactor within the reactor.

Operating costs depend on the quality of the water being treated and treatment objectives of the individual situation. Capital cost increases with dosage requirements as well as design flow capacity. Table II lists ozone dose requirements for various treatment objectives.

Operating costs are essentially determined by electrical costs for the design area. Assuming an electrical cost of \$0.01 per kwh and utilizing 0.028 kwh/gm of ozone, a dose of 1 mg of ozone per liter requires \$0.001 per 1000 gallons (Evans, 1972). Specific examples of ozone cost analysis exist in the literature, making it apparent that a cost analysis is necessary for each individual application.

Summary

Available literature on ozone treatment of Iron and color indicates the process is effective and can be economical, depending on electrical requirements, location, and local water characteristics.

The advantages and disadvantages of ozonation are as follows:

Advantages

- (1) Effective disinfectant and powerful germicide and viricide.
- (2) No taste and odor problems.
- (3) No ammonia interference.
- (4) Effective over a wide range of pH.
- (5) Effective at relative low concentrations.
- (6) Aids in reducing taste and odor problems.
- (7) Lowers BOD and COD.
- (8) No chemical transportation required.
- (9) Does not add to water salinity.

Disadvantages

- (1) High capital costs.
- (2) Low water solubility.
- (3) Generation required at the site.
- (4) High partial pressure generation danger exists.
- (5) No residual capacity.
- (6) Equipment design is critical.
- (7) Equipment sensitivity increases maintenance.
- (8) Higher operating cost than chlorine.
- (9) Difficult production adjustment to meet flow variations.

EXPERIMENTAL METHODS

Ozone generation was achieved by passing oxygen gas through a corona arc discharge in Grace Models LG-L1 and LG-2-L2 Ozone Generators. Both units are air cooled and operable anywhere 110 volt, 60 cycle power is available.

Determination of generated gas flows were made utilizing the soap bubble technique as suggested by Reid and Potworowski (1973). The travel time of a soap bubble of gas through a 50 ml burette is measured and correlated to flow meter readings.

The actual quantity of ozone generated was calculated by the method of Birdsall, Jenkins, and Spadinger (1952) and as modified by Reid and Potworowski (1973). This procedure entails bubbling the oxygen-ozone mixture into a 5 percent potassium iodide solution at various flow rates and for various detention times. The potassium iodide solution was then acidified with sulfuric acid. The free iodine was then stoichiometrically titrated with 0.1N sodium thiosulfate. The quantity of ozone was then calculated by the following equation:

$$(\text{ml of thiosulfate})(N \text{ of thiosulfate})(24) = \text{mg of ozone}$$

and

$$[(1000)(\text{mg of ozone})] / (\text{sample volume in ml}) = \text{mg/l of ozone}$$

During titration, 2 ml of starch were added to aid in identification of titration end points. Calibration of both the LG-L1 and LG-2-L2 Grace model ozonators was performed regularly. The initial batch analyses required minimal gas flow rates and utilized the LG-L1 generator. A

graphical representation of these levels of generated ozone for various flow rates and contact times are shown in Figure IV. The continuous flow pilot studies required larger flow rates and utilized the LG-L1 or LG-2-L2, or both. It was observed that generating capacities varied depending on gas flow rates, bottled oxygen quality and operator adjustment. Therefore, to eliminate any possible error, the ozonator's generating capacity was calculated before and after the particular study at the utilized gas flow rate. Tables III and IV depict typical ozone generation at various gas flow rates.

Generated levels of ozone were also calculated for various oxygen feed pressures, utilizing the model LG-L1 generator. The lower oxygen feed pressures reduced the number of oxygen molecules present within the ozonator discharge gap. The arcing electrical current therefore affected a higher percentage of oxygen molecules. This resulted in a higher concentration of ozone in the reaction stream as shown in Figure V.

The powerful oxidizing characteristics of the generated ozone-oxygen mixture required positive confinement and control of the potentially toxic gas. Experimental procedure dictates that all generated gas be wasted into a potassium iodide trap. A secondary iodide trap was similarly used to insure the removal of any additional unreacted ozone in the gas stream. During experimental testing, the generated gas flow was diverted to the reaction vessel. The subsequent gas flow from the reaction vessel was wasted into a fresh potassium iodide trap for later assay to determine reacting ozone.

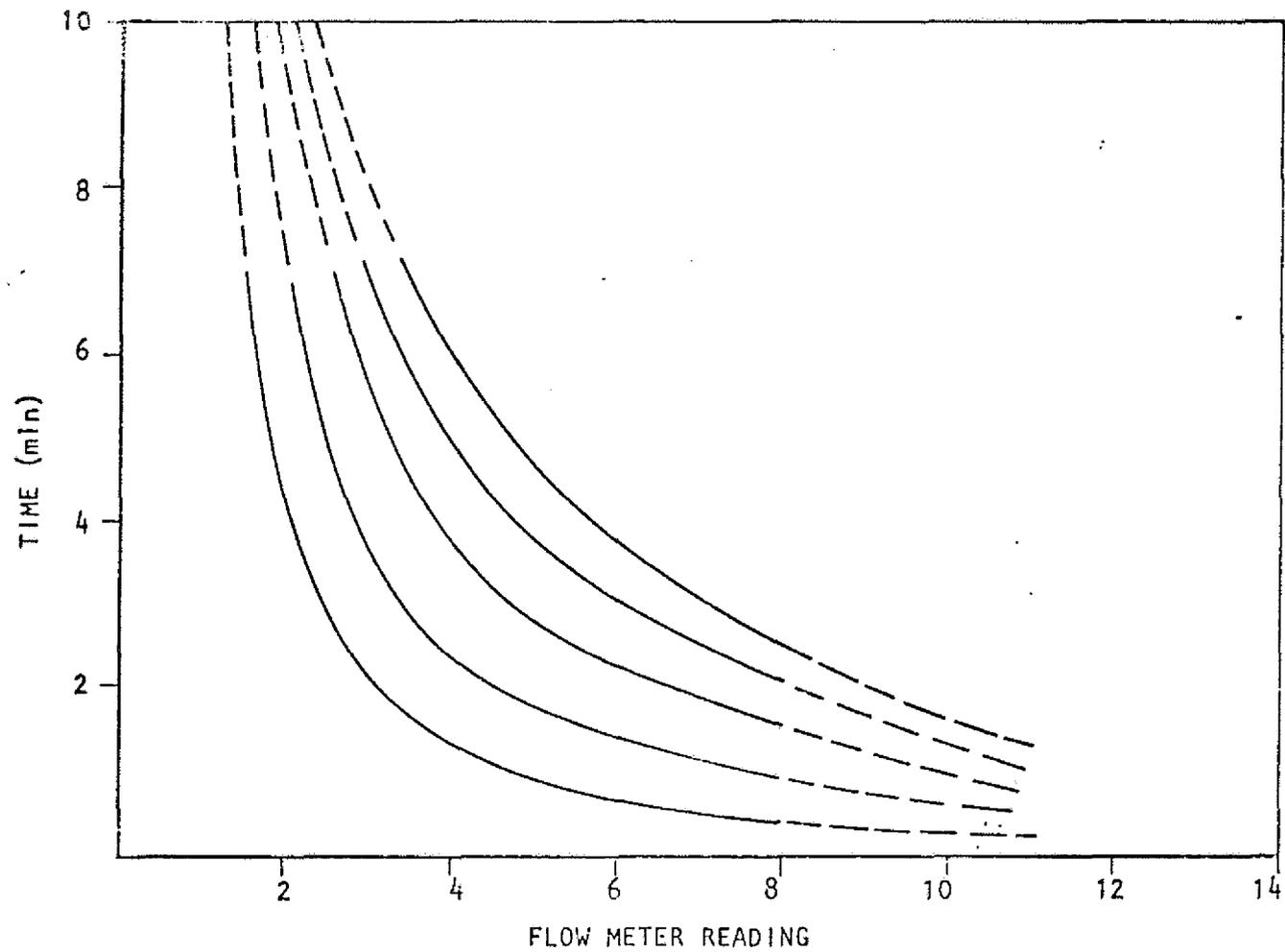


FIGURE IV REACTION TIME vs. ROTAMETER FLOW RATE
FOR VARIOUS LEVELS OF OZONE GENERATED

TABLE III
OZONE GENERATION
FOR VARIOUS FLOW RATES
(Model LG-L1)

Gas Flow Rate (SCFH)	Ozone Generation (mgO ₃ /SCF)
20	520
12.6	640
9.3	833
7.2	1080

TABLE IV
OZONE GENERATION
FOR VARIOUS FLOW RATES
(Model LG-2-L2)

Gas Flow Rate (SCFH)	Ozone Generation (mgO ₃ /SCF)
100	475
75	455
60	490
40	609

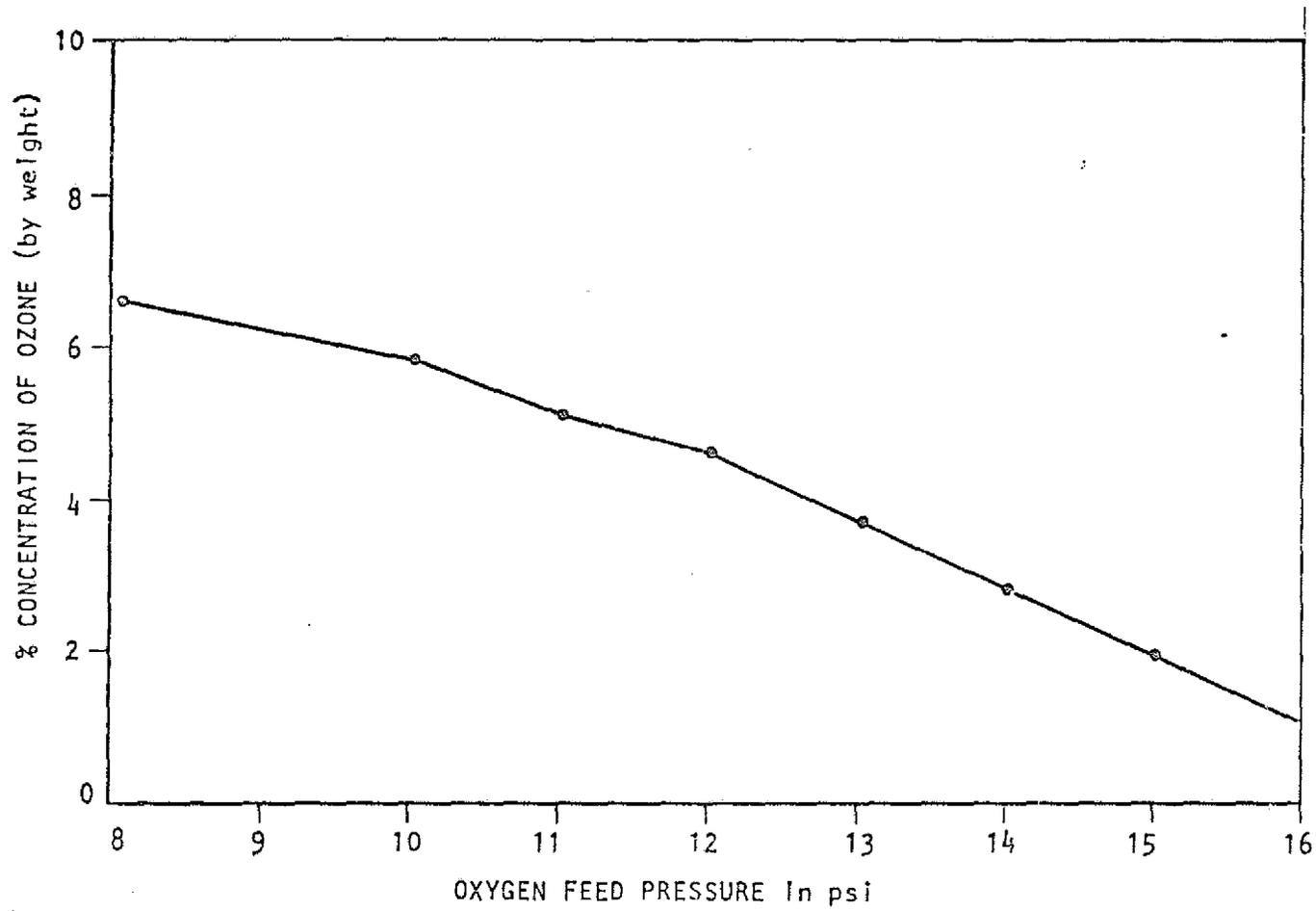


FIGURE V CHANGE IN OZONE CONCENTRATION (% by weight) IN REACTION STREAM AS AFFECTED BY OXYGEN FEED PRESSURE

The quantity of ozone that decomposes in the ozone-oxygen mixture prior to entering the reaction vessel is considered negligible. This is in accordance with the literature, which describes relatively long half-lives (20-100 hours) for ozone concentrations contained within non-reactive materials as utilized in the experimental apparatus.

Prior to experimentation, the ozonator was allowed to warm up by operation for a 15- to 20-minute period with the generated ozone being wasted into a potassium iodide trap. Following warm-up and experimental preparation, the generated ozone-oxygen mixture was diverted to the contact chamber at a desired flow rate. This initiated the contact period. The gas released from the contacting unit was wasted into an uncontaminated potassium iodide trap. This allowed accurate determinations of the quantity of ozone remaining in the gas mixture. Utilizing calibration data, the quantity of ozone reacted with the water sample could be determined by differences upon completion of the contact period.

Initial ozonation studies were performed utilizing a laboratory size batch contactor apparatus, a schematic of which is shown in Figure VI. This served to delineate the feasibility and roughly quantify ozonation with regard to the examined waters.

An attempt was made to investigate continuous flow contactors and to optimize the ozone utilization. The initial continuous flow unit consisted of a single-column contactor with a volume of 21 liters (see Figure VII). Gas-liquid flow was in the same direction (upward), with the gas injected by a double-headed diffuser stone located in the base

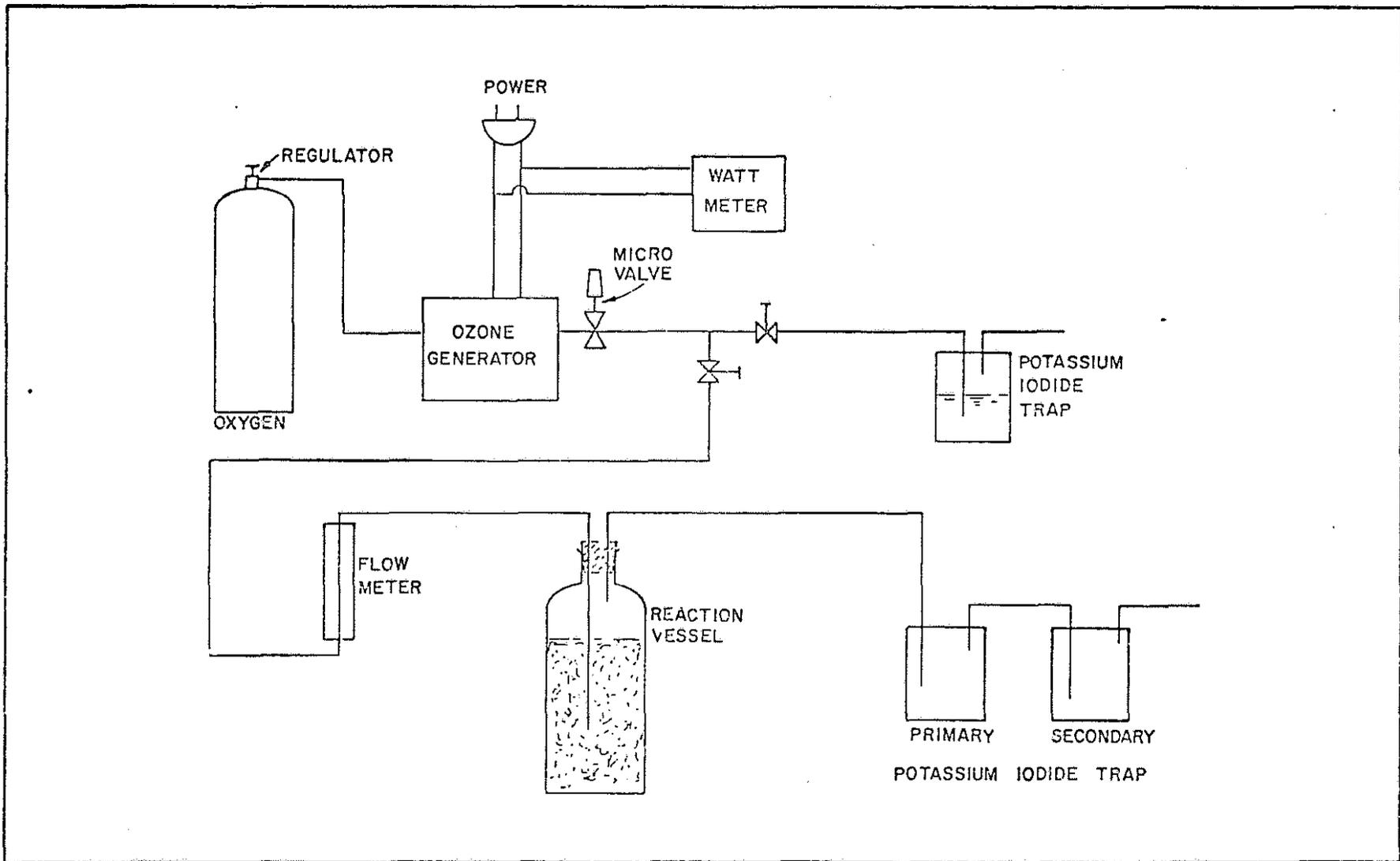


FIGURE VI SCHEMATIC DIAGRAM OF BATCH EXPERIMENTAL OZONATION EQUIPMENT

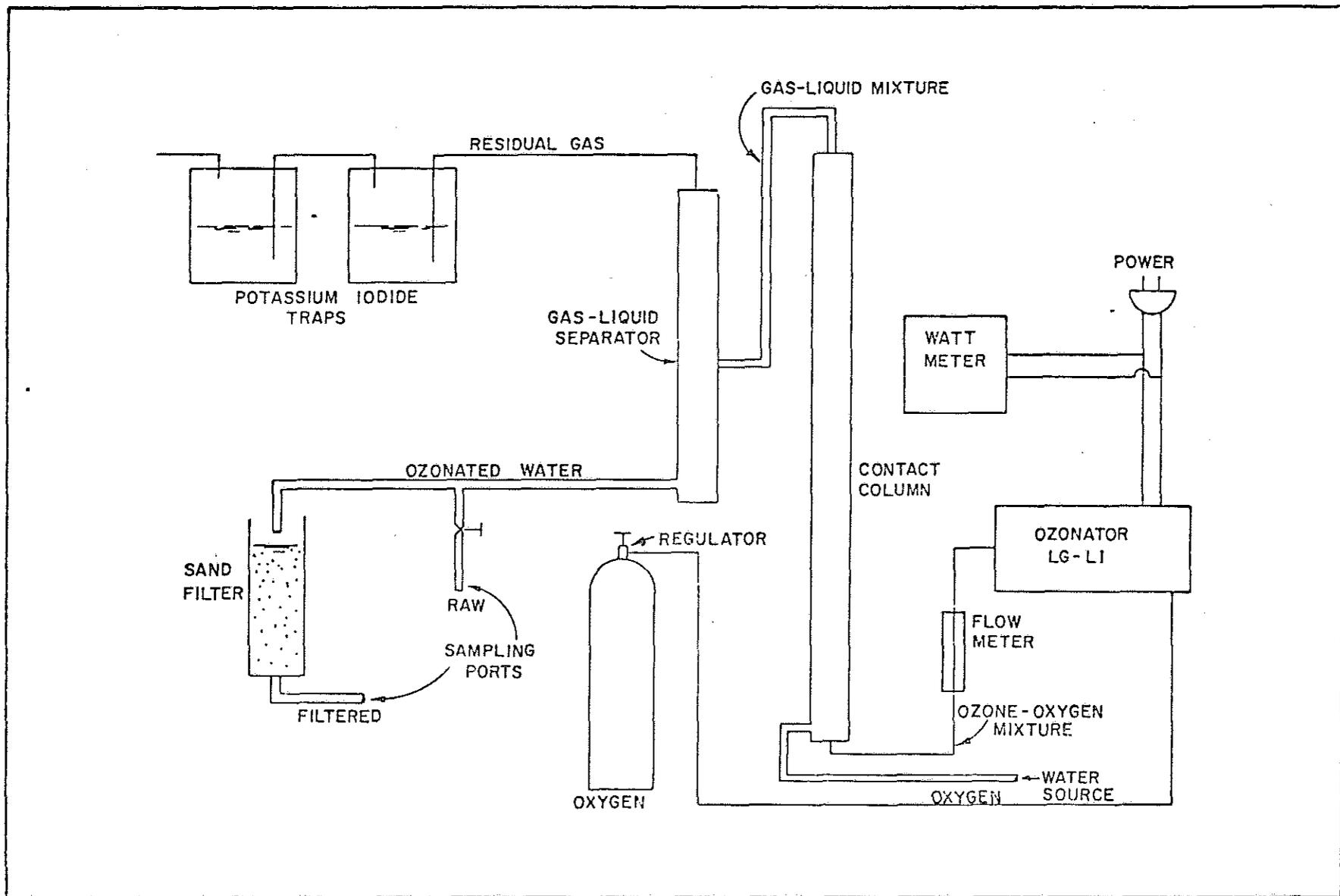


FIGURE VII

SINGLE COLUMN CONTINUOUS FLOW CONTACTOR

of the column. Gas and liquid flow rates were 10 - 20 scfh and 0.5 - 4.01 liters/min., respectively.

A second column was used as a gas-liquid separator by discharging the contactor effluent to the center of a second column. Residual gas was then collected at the top and wasted into an uncontaminated potassium iodide trap. The unit had the capacity to filter effluent via a typical gravity sand filter. This was performed to determine the ability of normal filtration to remove the characteristic precipitate.

The U.S. Public Health Service provided the investigators with a continuous-flow pilot unit, which was tested on-site in Kotzebue. Figures VIII and IX depict the unit. The gas and liquid are mixed via a positive injection head located on top of the innermost column. The velocity of the water forces the gas downward, maximizing the gas-water interface by dispersing the gas. The gas-water mixture then flows into the middle column where pressure forces the water up with the gas and over into the outermost column. This column acts as a gas-liquid separator, with the residual gas escaping from the top and the water draining off the bottom. The contactor unit utilized the LG-2-L2 model generator. The ratio of water-to-gas flow was somewhat constant to maintain the downward flow of the injected gas. Unfortunately, this was such that the water being tested could not be suitably treated. To establish comparable results regarding the positive injection method of gas-liquid contacting, the unit was modified. A baffled 150-gal. holding tank was utilized to recycle the ozonated water until treatment was effected.

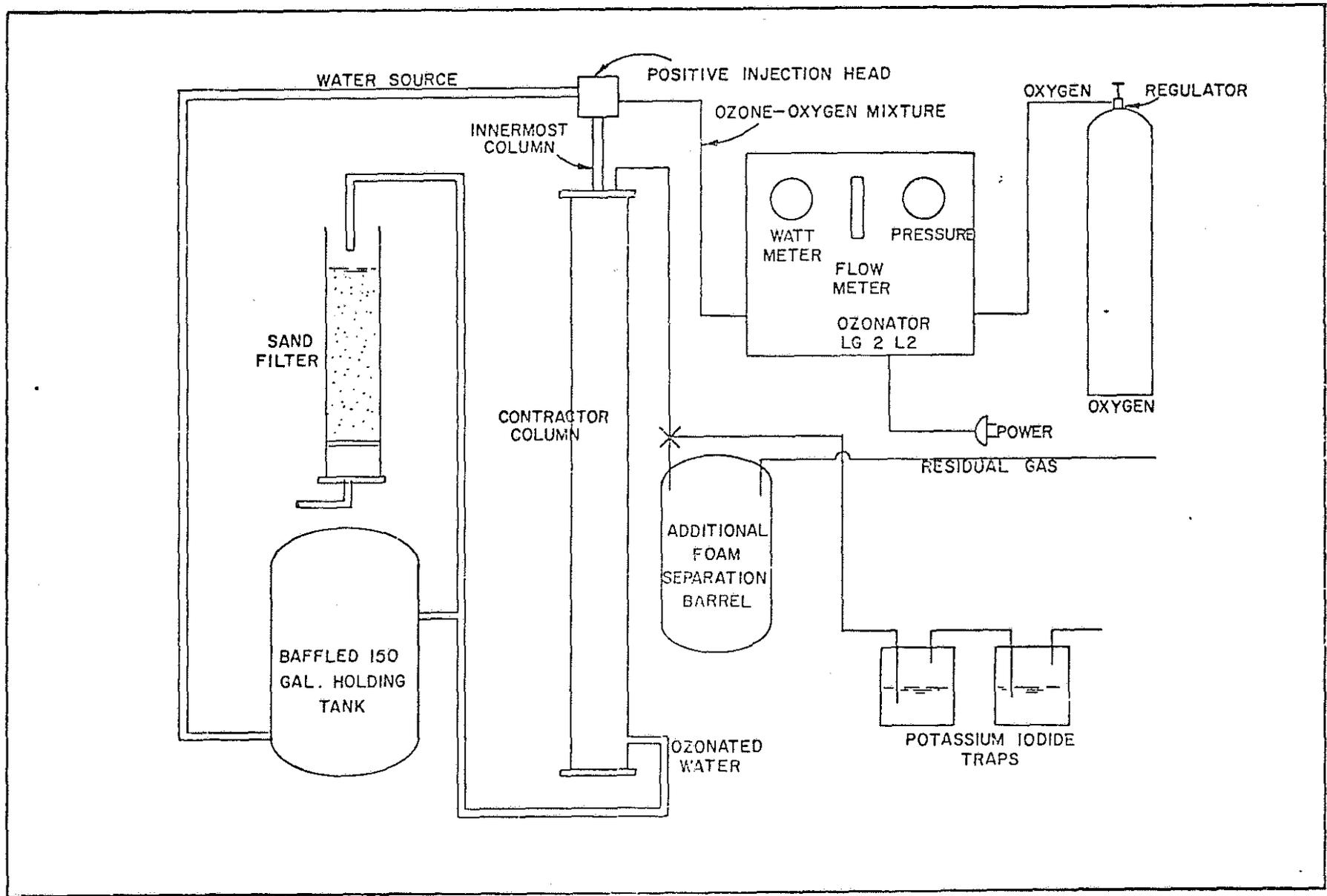


FIGURE VIII

POSITIVE INJECTION CONTACTOR - UNIT DESIGN

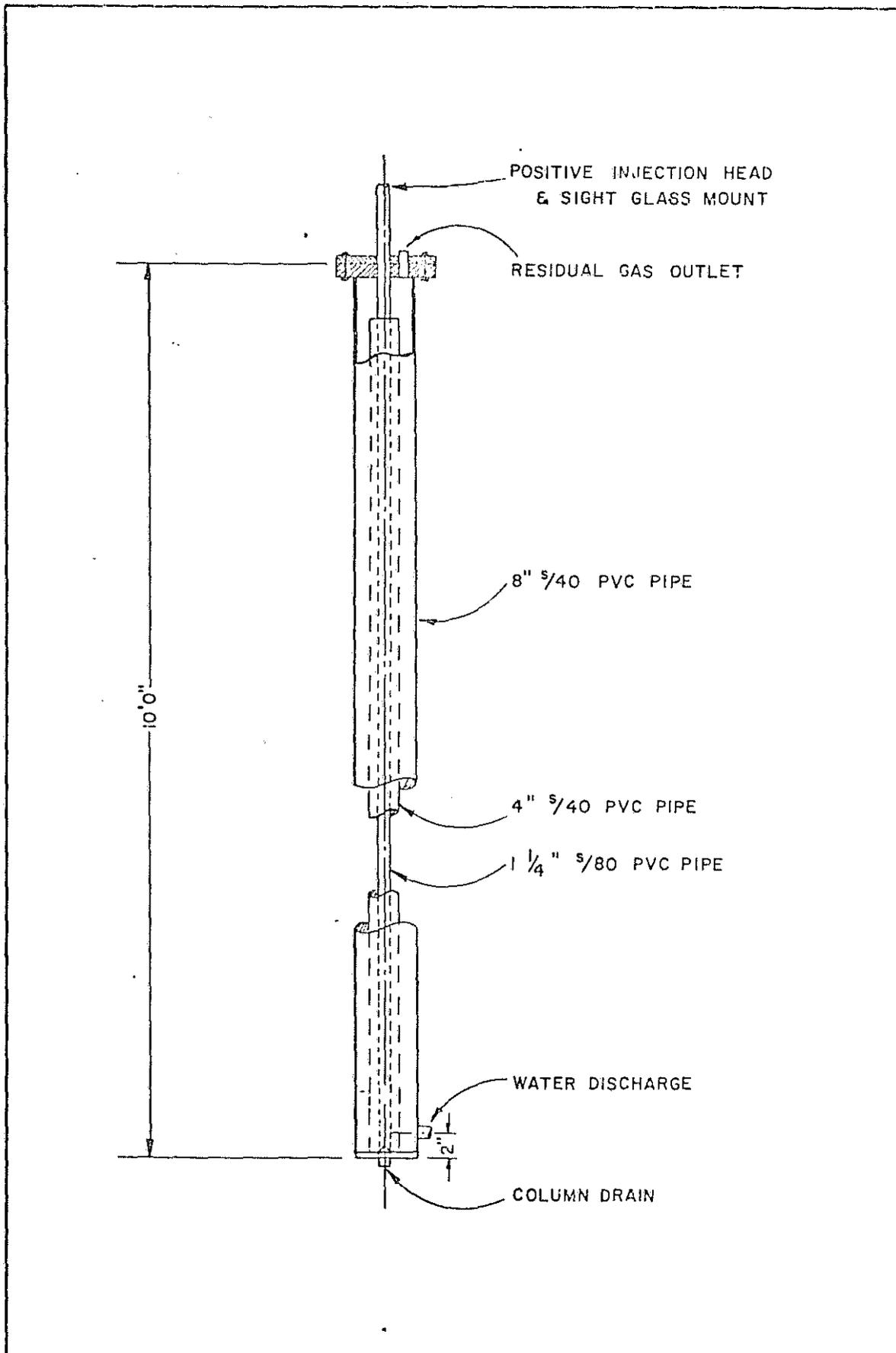


FIGURE IX POSITIVE INJECTION CONTACTOR - COLUMN DESIGN

One additional contactor design was investigated to obtain additional data on a continuous flow non-recycle unit. This consisted of utilizing the previous column design without the positive injection system. The liquid flow direction remained the same, whereas gas injection was achieved through eight diffusers located in the bottom of the columns. One diffuser was located in the innermost column and four in the outer column where the gas-liquid flow was countercurrent. In the middle column, there were three gas diffusers and the gas-liquid flow was co-current. Generated gas for the inner column was provided from LG-L1 model generator, while the larger model LG-2-L2 generator provided the gas for the outer column. Residual gas was collected from the top and the water drained off the bottom of the outer column. Maximization of the gas-liquid interface was not achieved in this unit due to the lack of diffusers available and the utilization of 5 ml pipettes in their place.

An associated 8-foot sand filter was utilized to investigate the feasibility of conventional sand filter removal of ozonation precipitates from all column configurations. Two and one-half feet of 20-30 mesh silica sand (ASTM C-109) was placed upon six inches of gravel, which rested on the underdrain within the column.

Power Requirements

Power requirements of the LG-L1 ozonator were initially determined in order to optimize the operational mode variables and ultimately for accurate economic determinations. Using a General Electric wattmeter, readings were recorded for various oxygen feed pressures and generated gas flow rates. Throughout all experimental analysis, power require-

ments were recorded continuously for both generators utilized.

When maintaining a constant oxygen feed pressure, it was observed that power requirements, (watt hours/gram of ozone), varied greatly. Tables V and VI depict the data for the LG-L1 and LG-2-L2 generators respectively. The variation is large in the lower operating range of the generator as observed in the presented data for the LG-L1 generator. An upper limit for the normal operation of both these generators appears to be 10 watt hours/gram of ozone produced.

Reduced oxygen feed pressures exhibited higher percentages of ozone to oxygen in the generated gas and increased power requirements as shown in Table VII. Below a 13 psig oxygen feed pressure, the amount of power utilized per unit of ozone produced begins to increase. The desirable operational mode was found to be between 13 and 15 psig oxygen feed pressure.

Water Analysis

Representative water samples were collected from surface waters in Kotzebue, Alaska, and from both ground and surface waters in the Fairbanks, Alaska, area. Accurate characterization of sampled waters was achieved by experimental analysis and available water quality literature.

Initial experimental analysis included the following:

- A. Chemical
 - 1. Iron
 - 2. Manganese

- B. Organic Constituents
 - 1. Chemical Oxygen Demand (COD)
 - 2. Total Organic Carbon (TOC)

TABLE V
POWER REQUIREMENTS FOR THE LG-LI OZONE GENERATOR

Gas Flow Rate (SCFH)	Watt Hour per gram of Ozone
0.36	191.0
0.85	62.5
1.50	30.5
2.33	18.0
9.5	5.94
15	5.06
20	4.24

TABLE VI
POWER REQUIREMENTS FOR THE LG-2-L2 OZONE GENERATOR

Gas Flow Rate (SCFH)	Watt Hour per gram of Ozone
40	8.62
60	7.14
75	5.9

TABLE VII
GENERATED OZONE CONCENTRATIONS AND
POWER REQUIREMENTS AT VARIOUS
OXYGEN FEED PRESSURES*

Oxygen Feed Pressure (psig)	Power Requirements (watts)	Generated Ozone Concentration Percent by weight
16	44	1.1
15	48	1.9
14	52	2.8
13	57	3.8
12	62	4.8
11	66	5.3
10	72	5.9
8	84	6.8

* Flow rate was held constant at 1.5 SCFH.

C. Physical

1. Color
2. pH
3. Alkalinity
4. Fluorescence

Upon ample characterization and familiarization of sample waters, continuous testing was restricted to iron, manganese and color.

A Turner Model III Fluorometer was used to measure sample fluorescence before and after ozonation. The expected reduction of fluorescence as reported by Reid and Potworowski (1973), was regarded as indicative of conjugated bond reduction due to ozonolysis. Similarly, fluorescence spectra observed aided in characterizing collected water samples.

Prior to analysis of water samples, filtration was performed. The filtration procedure entailed utilizing a standard 0.45 micron filter. Following filtration, color analysis was performed with standard Nessler tubes, thereby indicating unfilterable or true color.

Iron and manganese analyses were determined using atomic absorption spectrophotometry techniques (Methods for Chemical Analysis of Water and Wastes, 1971). The remaining parameters were determined following the 13th edition of Standard Methods (1971).

Sampling of the Fairbanks area water supplies was as demand necessitated. Kotzebue area samples were collected by the U.S. Public Health Service and periodically sent to Fairbanks for analysis.

Accurate characterization of the organometallic humic acid fraction is complex and time-consuming. Time alone made this characterization impossible within the scope of this investigation.

CHARACTERIZATION OF RAW WATERS

To adequately interpret ozonation results from batch analysis, it was necessary to characterize the selected Arctic and subarctic water supplies. Previously reported water quality literature was utilized whenever available. In addition, experimental analyses were performed to substantiate reported values. The quality differences between surface and ground waters were dealt with individually.

Arctic Surface Water

Arctic surface water samples were collected from the supply reservoir at Kotzebue, Alaska. This Arctic reservoir typifies the characteristics of Arctic surface waters as reported in the literature. In addition, its year round accessibility made it desirable as a sampling site. The erratic and limited baseline information available for this water supply necessitated a thorough sampling program. Sampling was carried out regularly through late winter and spring breakup. This time period provides the poorest water quality from Arctic and subarctic surface supplies.

In addition to iron and color, samples were analyzed for hydrogen ion concentration (pH), total organic carbon (TOC), chemical oxygen demand (COD), manganese, and alkalinity. These experimental results, except for manganese, are presented in Table VIII. Manganese was not included in the table since the values were below recommended levels.

TABLE VIII
RESULTS OF KOTZEBUE SURFACE WATER SAMPLE ANALYSES *

Sample Date	pH	C.O.D. (mg/l)	T.O.C. (mg/l C)	Color (Color Units)	Iron (mg/l Fe)
4/02/74	--	30.7	73	225	3.1
4/08/74	--	50	64	200	4.5
4/10/74	--	31	68	200	2.6
4/12/74	6.4	51	67	200	1.5
4/15/74	6.5	65	68	190	2.0
4/18/74	6.3	73	65	200	1.7
4/22/74	6.1	73	66	225	2.2
4/26/74	6.0	69	66	225	0.5
4/28/74	6.2	80	65	215	1.0
5/01/74	6.2	73	65	250	1.5
5/03/74	6.4	69	65	250	3.1
5/05/74	6.5	84	73	275	---
5/08/74	6.4	82	66	200	6.7
5/11/74	6.5	65	58	150	3.3
5/14/74	6.9	121	62	150	4.2
5/16/74	6.4	77	57	125	2.4
5/17/74	6.3	99	67	175	3.8
5/24/74	6.3	95	59	100	2.6
5/28/74	--	--	60	200	---
AVERAGES	6.4	71.5	65	197	2.8

* Alkalinity remained constant throughout the sampling period, =64 mg/l as CaCO_3 .

Iron, manganese, and color were determined prior to and following sample aeration with oxygen and filtration of the associated precipitate. Manganese levels were found to be in trace amounts throughout the sampling period and subsequently eliminated from further analysis. The procedure of before and after aeration analysis enabled identification of the readily oxidizable versus highly complexed iron and color. Figures X and XI graphically depict iron and color content before and after oxygen aeration and filtration.

The arithmetic average of iron content before and after oxygen aeration was 2.8 mg/l and 1.9 mg/l, respectively. This is a 32 percent reduction in the mean value. Similarly, true color values exhibited a 35 percent reduction in the mean value due to oxygen aeration.

The failure to oxidize sufficient quantities of iron demonstrates the presence of iron-complexing molecules that resist normal oxidation procedures. In addition, the close resemblance between percent iron and color reduction due to oxygen aeration substantiates the idea that organic color and available metallic ions interact by forming organic metallic molecules, which do not permit simple oxidation.

Utilization of powdered carbon to remove the contaminating color and iron was experimentally investigated for additional characterization purposes. A 100 gram per liter carbon slurry (Norit A decolorizing carbon), standard jar test equipment and one liter test samples composed the experimental method. Removal of complexed iron and color below acceptable standards required a powdered carbon dosage of 12,000 mg/l.

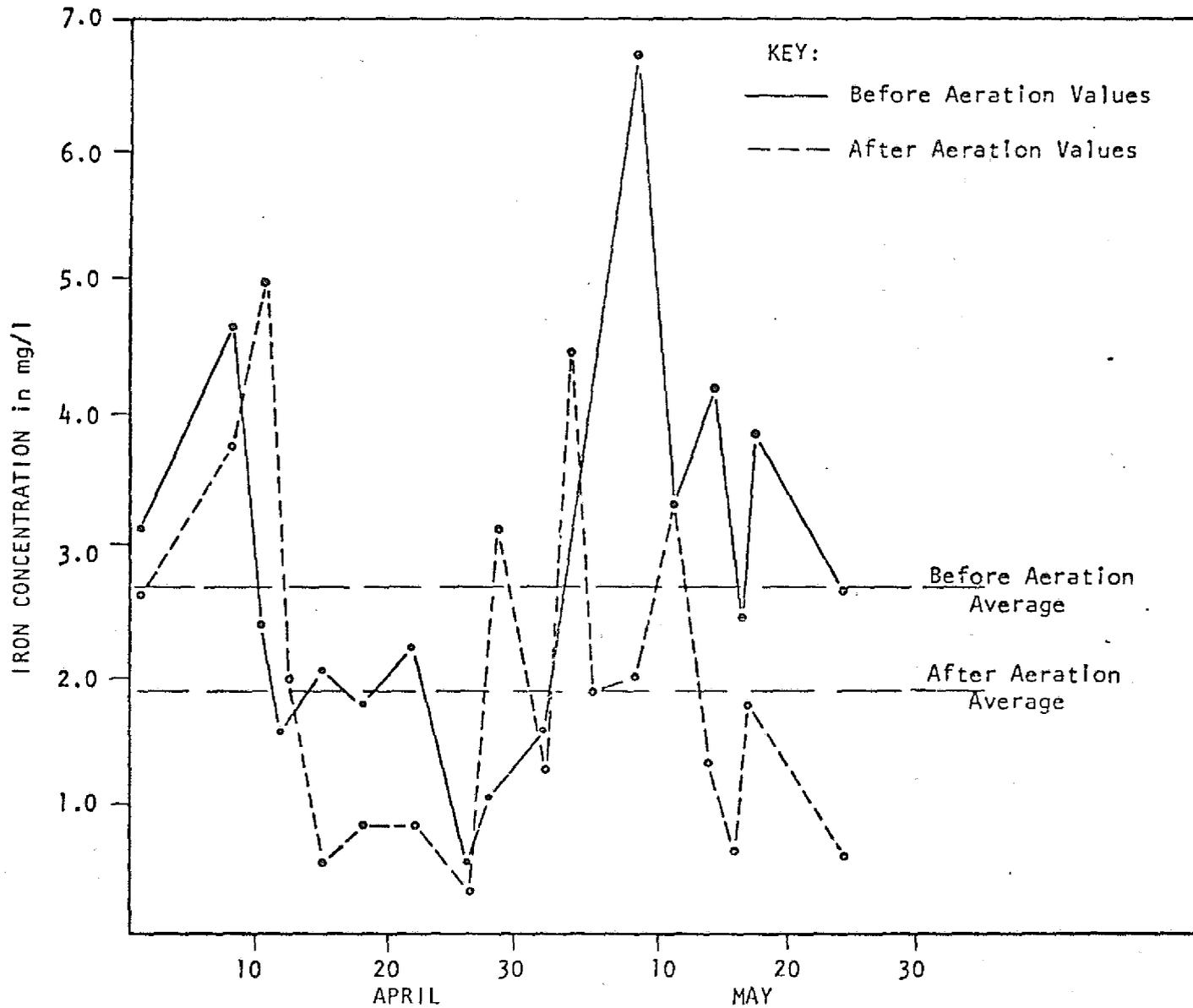


FIGURE X IRON CONTENT OF KOTZEBUE WATER SUPPLIES - BEFORE AND AFTER AERATION

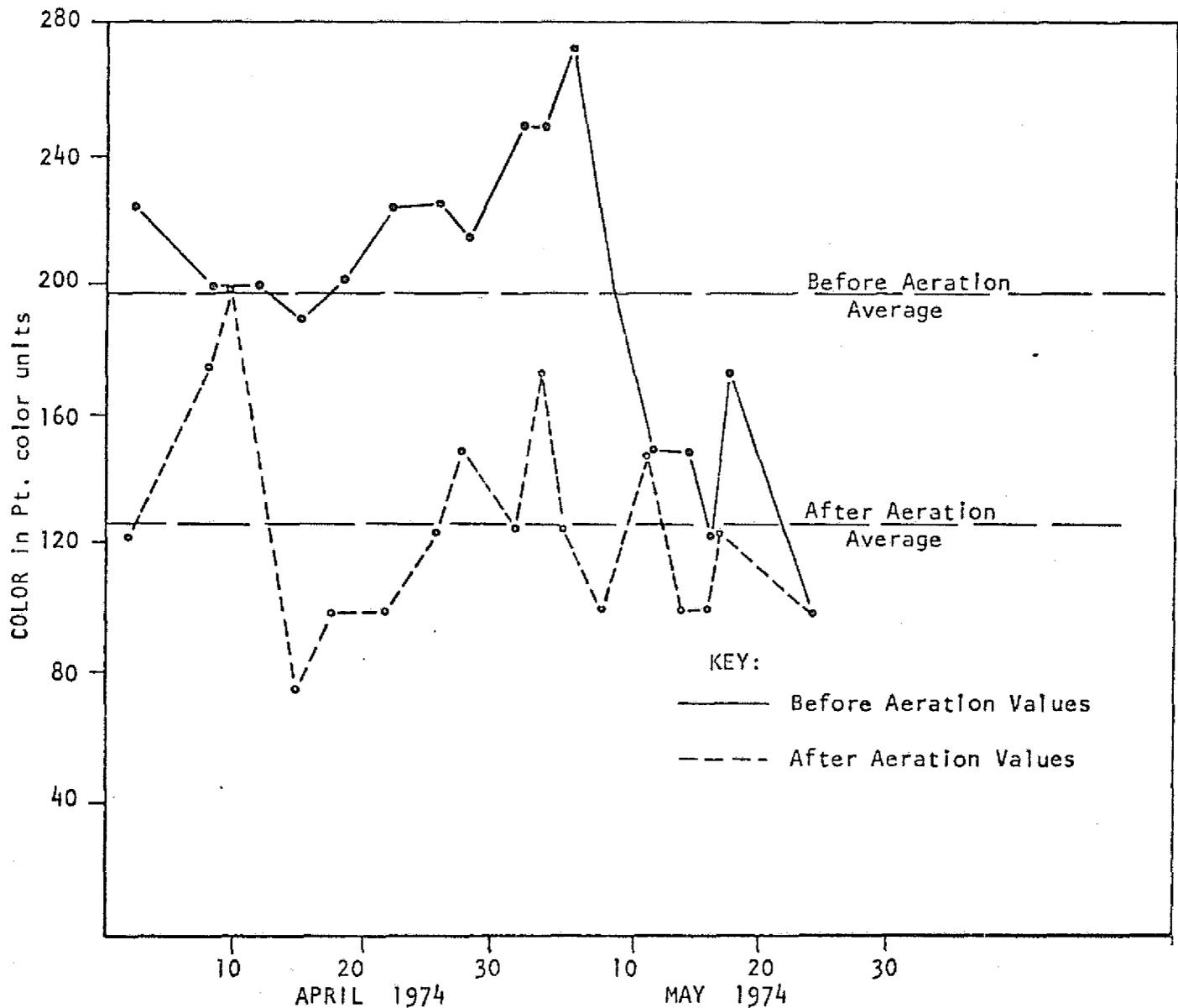


FIGURE XI COLOR CONTENT OF KOTZEBUE WATER SAMPLES - BEFORE AND AFTER AERATION

Subarctic Ground Water

Ground water sampling locations were selected from available sources near Fairbanks, Alaska. This was necessitated by the limited utilization and availability of ground water sources farther north. In addition, a recently completed ground water quality survey of the Fairbanks area facilitated accurate characterization and selection of appropriate wells (Smith and Casper, 1974).

In keeping with the chosen parameters, iron and color, Smith and Casper (1974) reported that iron and color correlations in ground water are very high. Nearly 95 percent of the consumers who reported color also indicated iron as a problem. The average consumer, however, easily confuses true color of water and iron-induced or apparent color. Of the 106 ground waters analyzed, only 15 exhibited true color. The average color value of these 15 ground waters was 24 color units. This relatively low average and limited existence suggests negligible amounts of organically complexing molecules. This is as expected with the understanding that organometallic complexes are formed essentially via humic acids, which are leached from vegetative detritus and are usually not present in ground water aquifers.

Seven samples reporting true color and iron values in the earlier study were selected for sampling. Of the samples tested, only one exhibited values above standards for color and/or iron upon aeration and filtration. Levels of manganese, however, remained essentially unaffected by aeration and filtration. Tabulation of sampled ground water characterization is demonstrated in Table IX.

TABLE IX

RESULTS OF GROUND WATER SAMPLE ANALYSES

Sample Identifica- tion	IRON (mg/l)		MANGANESE (mg/l)		True Color After Aeration
	Raw Sample	After Aeration	Raw Sample	After Aeration	
A	16.0	0.3	1.1	1.0	15
B	16.0	0.3	2.7	2.5	15
C	3.8	0.3	0.8	0.6	15
D	7.0	0.3	2.0	1.6	15
E	18.0	3.2	0.5	0.5	35
F	10	0.3	1.2	1.0	15

Subarctic Surface Water

The subarctic surface water chosen was Smith Lake located west of Fairbanks, Alaska. The selection was limited to one source because of time restrictions and the respective seasonal difficulties in obtaining samples. Color values were as expected, exhibiting average color values of 175. Iron and manganese were low with values of less than 0.25 and 0.06 mg/l, respectively.

RESULTS OF BATCH ANALYSIS

Bulk water samples collected and characterized during the sampling period were utilized for ozonation analysis of subarctic and Arctic water supplies. Parameters investigated were color, iron, manganese, TOC, and fluorescence. Generated gas flow rate and ozonation contact period were the experimental variables. In addition, the effect of water sample temperature and intermediate filtration on ozonation capabilities were examined.

Arctic Surface Water Iron and Color Reduction

Ozonation periods were varied from 30 seconds up to 30 minutes. Generated gas flow rates were varied from 0.17 to 1.1 liters per minute, while sample size and temperature were maintained at 200 ml and 25 degrees Celsius, respectively. Following ozonation, all samples were filtered using a standard 0.45 micron membrane filter and stored in 250 ml polyurethane bottles prior to chemical analysis. Figures XII and XIII are graphical representations of the observed experimental data for iron and color removal utilizing ozone.

Tables X and XI summarize the experimental data showing the necessary operating characteristics to effect efficient iron and color removal respectively. Required dosages of utilized ozone (mg/l) varied greatly, ranging from 90 to 350 and from 65 to 350 for iron and color, respectively. This data demonstrates that the lower batch experimental gas flow rates require less ozone (mg/l) to effect adequate treatment, necessitate a greater time and power requirement, and waste a higher percentage of

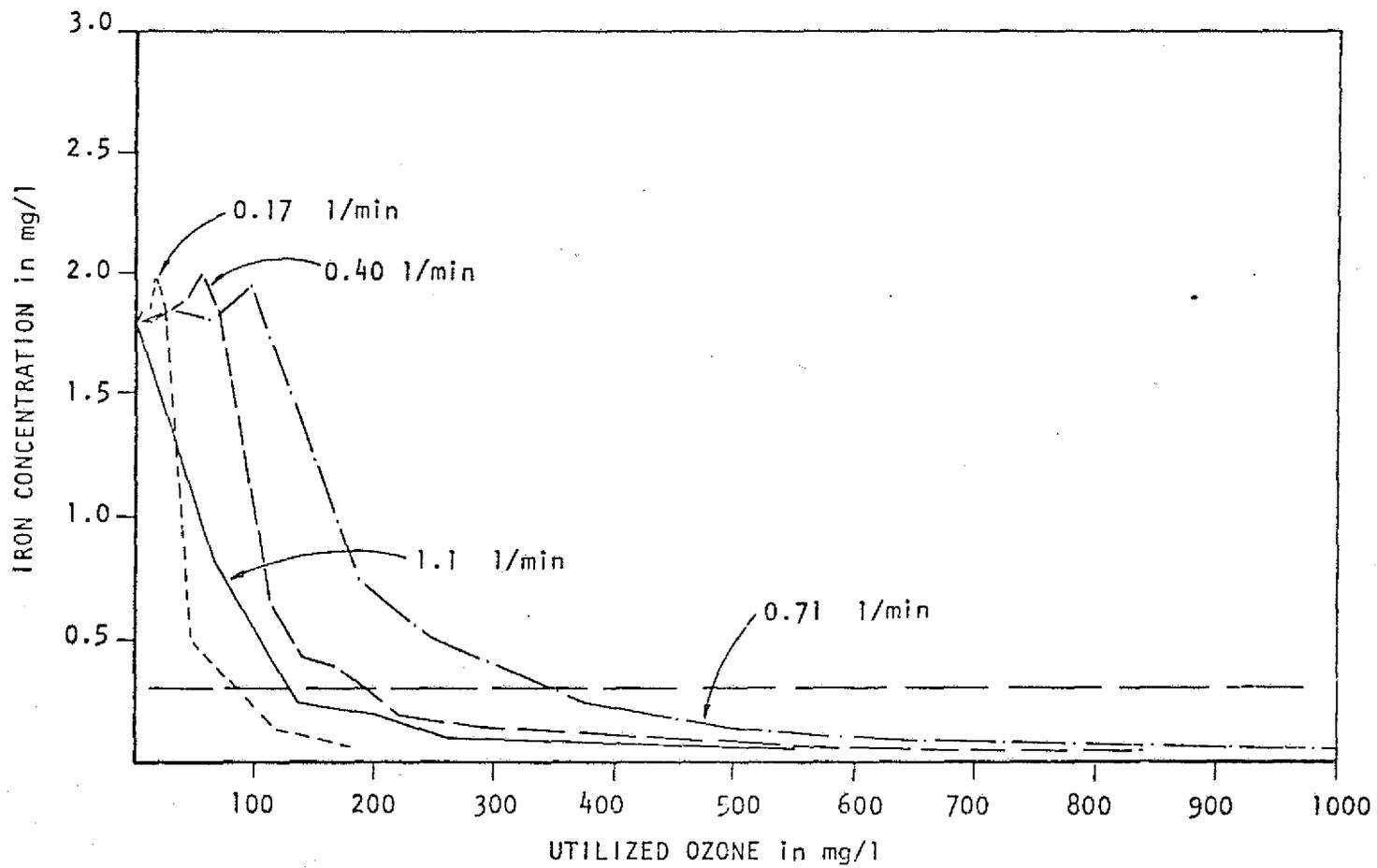


FIGURE XII IRON CONCENTRATION vs. mg/l OF UTILIZED OZONE FOR VARIOUS GAS FLOW RATES (BATCH ANALYSIS)

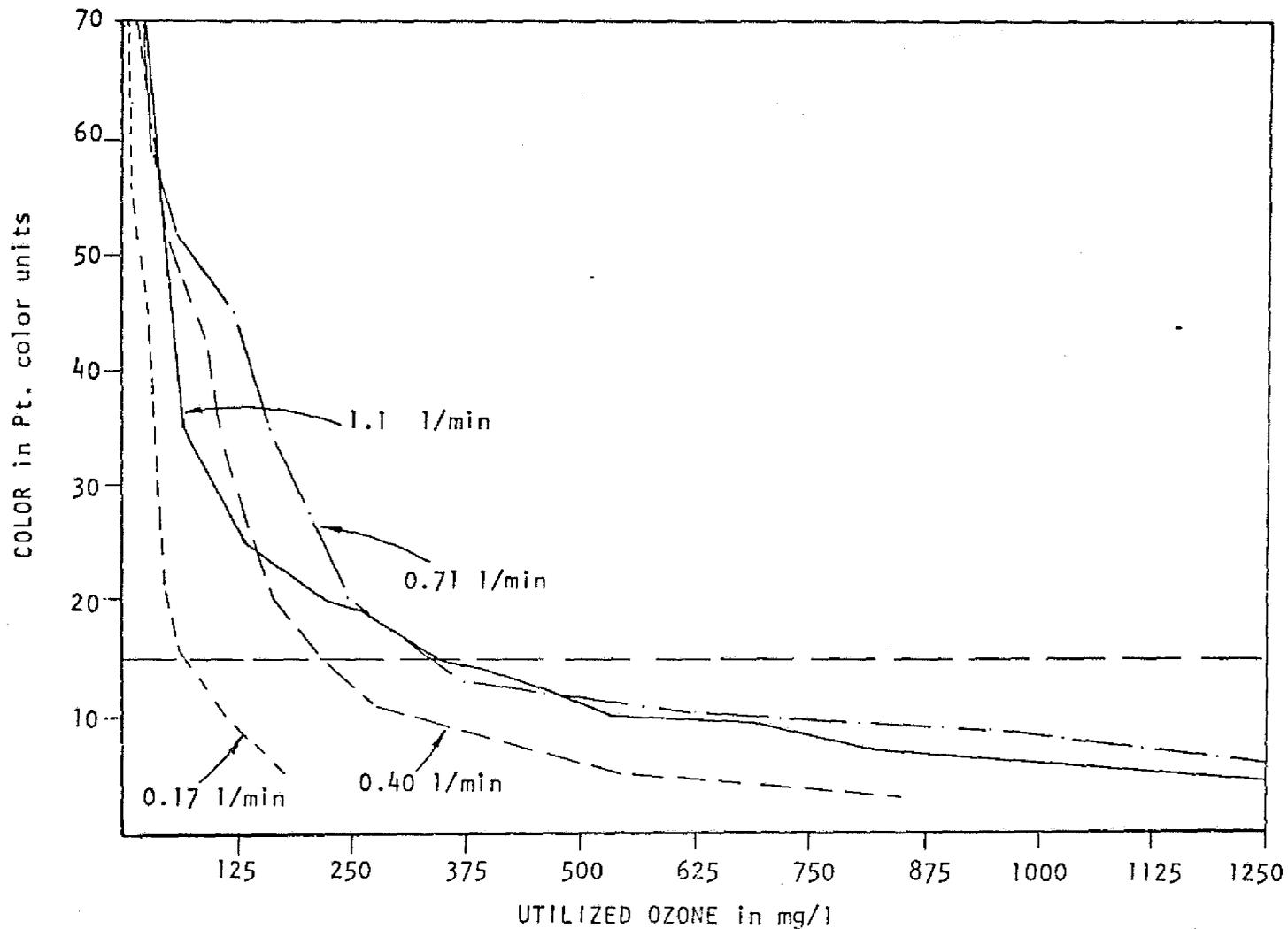


FIGURE XIII COLOR vs. mg/l OZONE UTILIZED FOR VARIOUS GAS FLOW RATES (BATCH ANALYSIS)

TABLE X
 BATCH ANALYSIS RESULTS FOR FOUR OZONATION
 FLOW RATES TO EFFECT IRON REMOVAL
 BELOW 0.3 MG/L

Flow Rate (liter/min)	Contact Time (minutes)	Ozone Applied (mg O ₃ /l)	Percentage of Ozone Utilized	Ozone Utilized (mg O ₃ /l)
0.17	15	321	28%	90
0.40	6.8	452	42%	190
0.71	5.5	795	44%	350
1.1	0.9	236	55%	130

TABLE XI
 BATCH ANALYSIS RESULTS FOR FOUR OZONATION
 FLOW RATES TO EFFECT COLOR REMOVAL
 BELOW 15 UNITS

Flow Rate (liter/min)	Contact Time (minutes)	Ozone Applied (mg O ₃ /l)	Percentage of Ozone Utilized	Ozone Utilized (mg O ₃ /l)
0.17	10.8	232	28%	65
0.40	7.8	523	42%	220
0.71	5.6	795	44%	350
1.1	2.5	636	55%	350

ozone. In batch studies, the limited available ozone at lower flow rates optimizes the probability of a reaction. In addition, at higher flow rates, the created interference between surplus ozone molecules and the subsequent catalization effect of the hydroxyl ion, increases the decay rate and reduces utilization of generated ozone.

Figure XII demonstrates measurable ion concentrations increased above the level in the raw sample following initial short ozonation periods. This deviation was observed at all investigated flow rates except the highest and constituted an 18 percent increase in measurable iron that was unfilterable. It appears that initial ozonation releases additional unfilterable but measurable iron from the organo-metallic complex. The disappearance of this peak at the higher flow rate simply exhibits the more rapid oxidation of this quantity of iron into a filterable precipitate.

It is worthwhile to note that batch investigations of ozone generation demonstrated a similar irregularity between the highest gas flow rate and the pattern set by the other three flow rates. Grams of ozone needed to effect treatment showed a rapid leveling off of the grams required in contrast to the increasing pattern set by the lower three gas flow rates. The inefficient characteristics of the batch contacting apparatus could possibly explain this irregularity. The observed disparity does suggest a reduction of ozone required at higher flow rates if gas-liquid contacting equipment are optimized. It is felt that this would further substantiate the belief that batch results lack any importance beyond simple verification of the reduction feasibility for a particular contaminate. Furthermore, it stresses the importance of optimizing reaction

chamber design and scale experimentation of design with the particular water to determine the economics of the process.

Additional Batch Investigations

Ozonated batch samples were analyzed for fluorescence levels as indicative of conjugate bond and color concentrations. Figure XIV demonstrates the observed fluorescence reduction due to sample ozonation. This further substantiates the connection between color concentration and conjugate bonded molecules.

Organic carbon reduction was measured by analyzing ozonated samples for total organic carbon (TOC) levels. Figure XV exhibits the observed total organic carbon reduction due to ozonation. An overall average reduction of 38 percent was effected, with a leveling off at approximately 17 mg/l TOC.

The effect of sample temperature on ozonation efficiency was investigated for iron and color removal. Figures XVI and XVII depict the experimental results for iron and color removal, respectively. Results showed that iron and color removal was more effective at higher temperatures, which is in agreement with published literature. In addition, the effect appears to be linear, especially with the case of color removal. Within the range of 10 to 50 degrees Celsius, a 10-degree increase in temperature effects the additional removal of 6 units of color and 0.17 mg/l of iron for the sample water tested.

Initially, it was felt that intermediate filtration of produced precipitate during ozonation might increase the effective utilization of generated ozone by eliminating any precipitate which might interfere

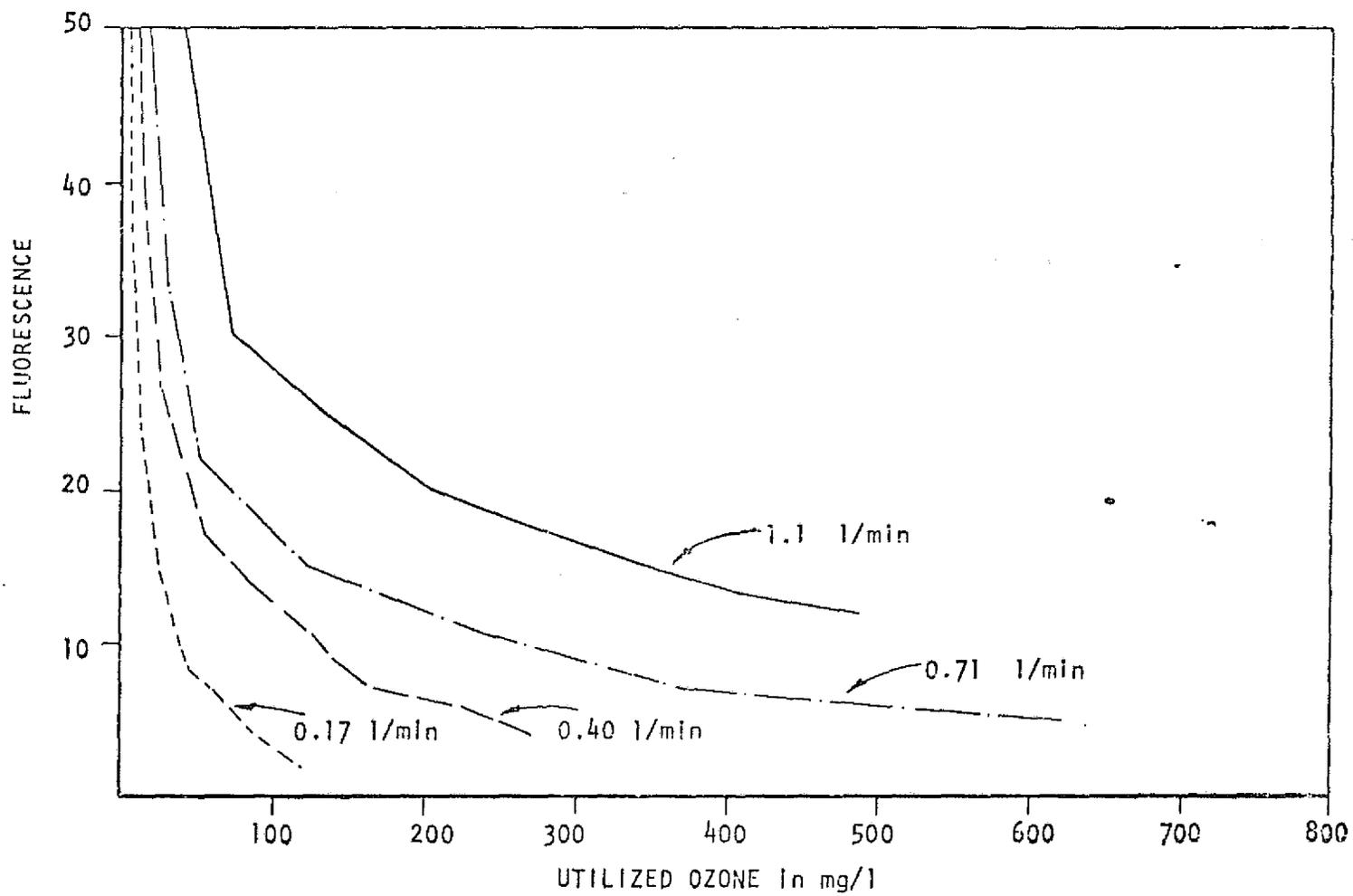


FIGURE XIV

FLUORESCENCE vs. UTILIZED OZONE In mg/l
FOR VARIOUS GAS FLOW RATES (BATCH ANALYSIS)

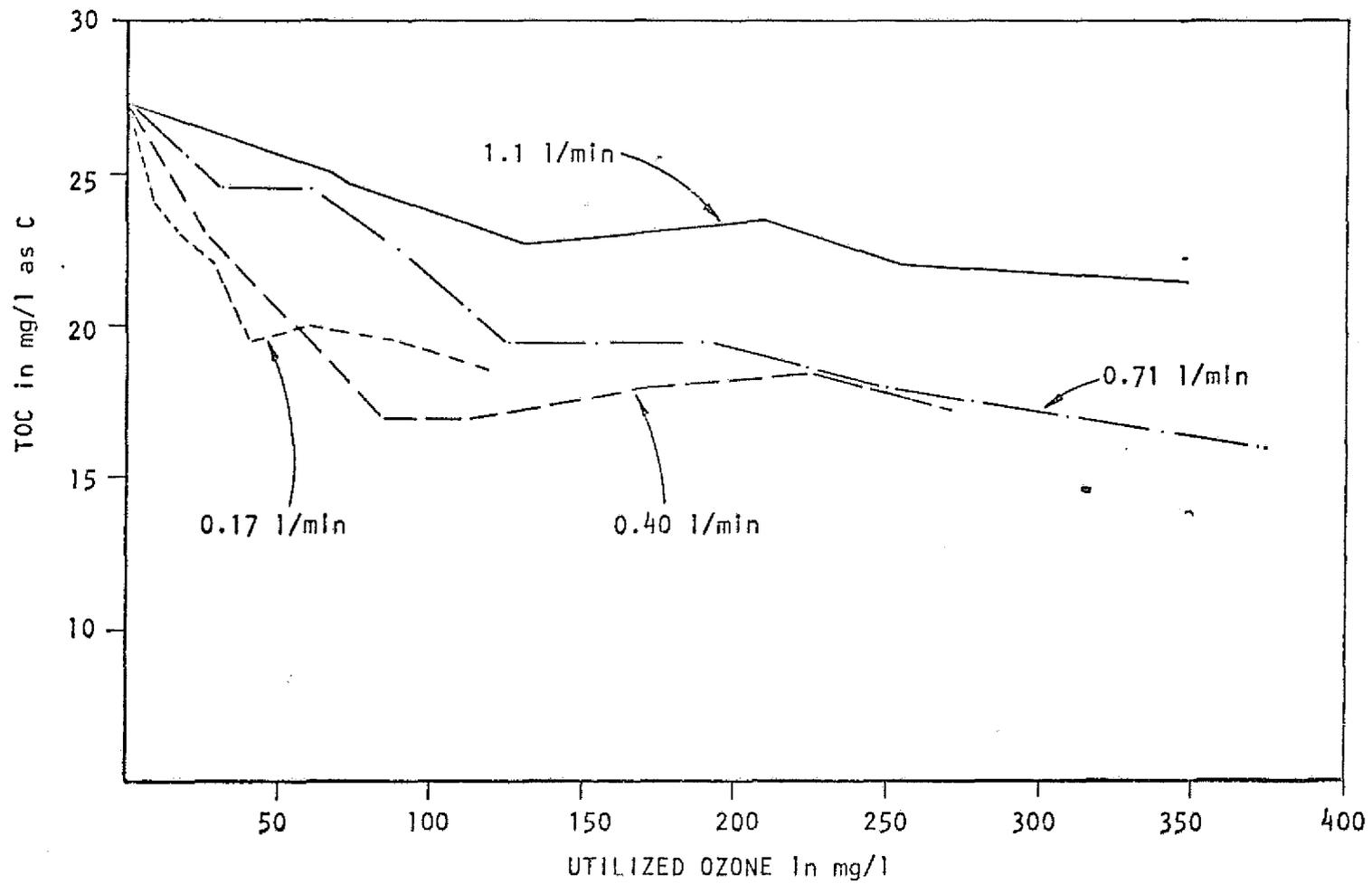


FIGURE XV TOTAL ORGANIC CARBON vs. mg/l OF UTILIZED OZONE FOR VARIOUS GAS FLOW RATES (BATCH ANALYSIS)

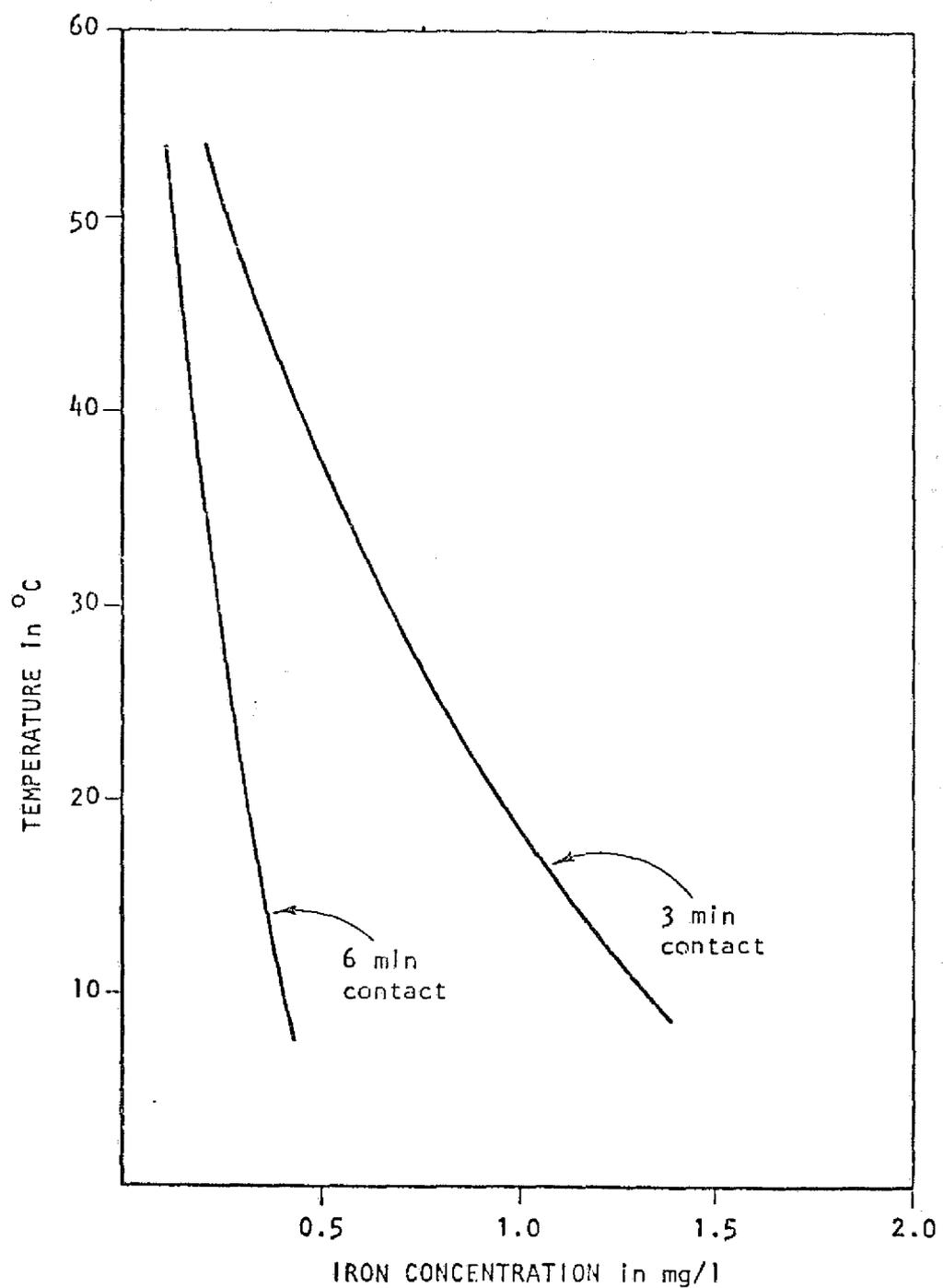


FIGURE XVI EFFECT OF SAMPLE TEMPERATURE ON IRON REDUCTION UTILIZING OZONE FOR TWO CONTACT TIMES

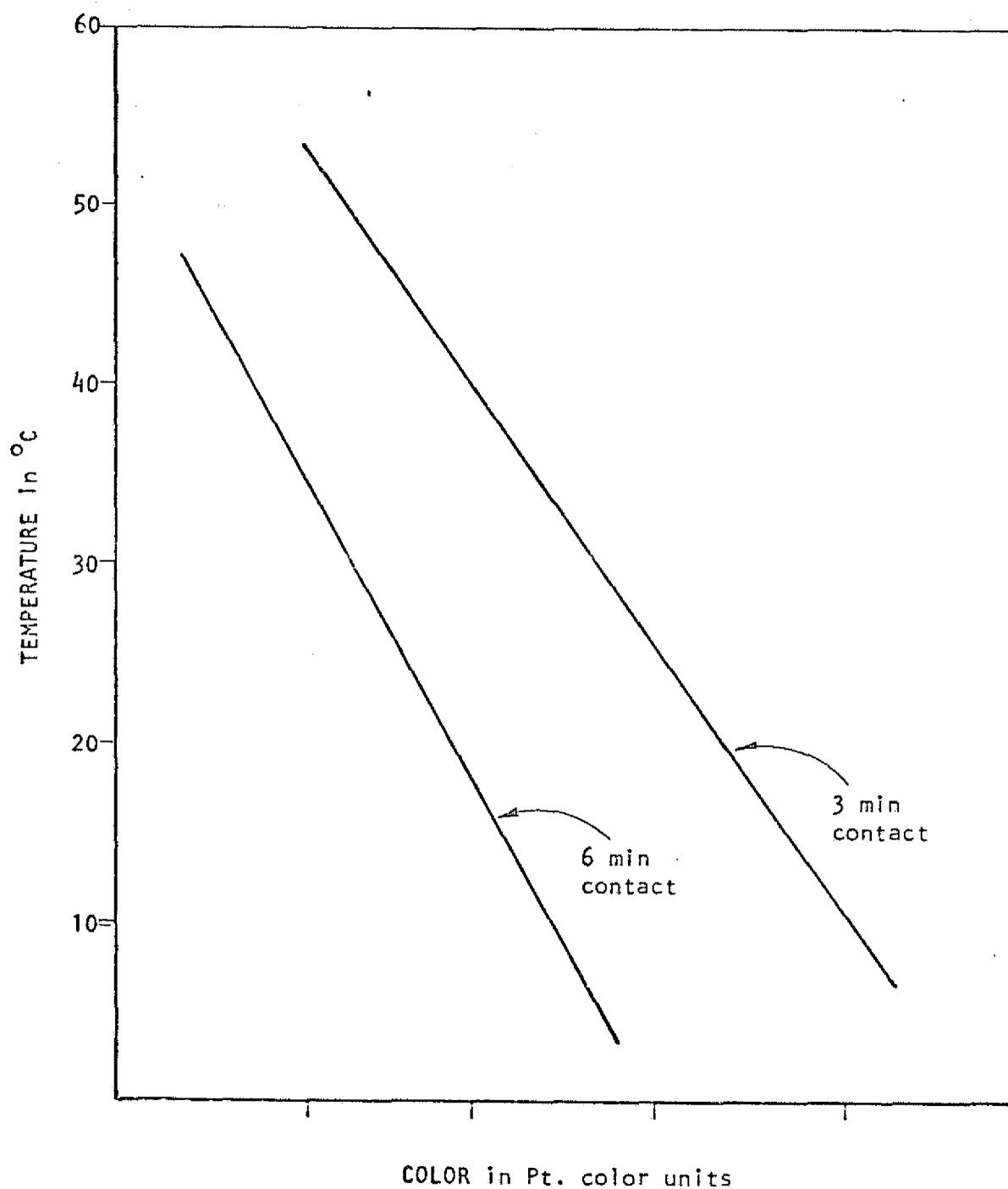


FIGURE XVII EFFECT OF SAMPLE TEMPERATURE ON COLOR REDUCTION UTILIZING OZONE FOR TWO CONTACT TIMES

with further ozonation. Upon experimental investigation, intermediate filtration was shown to have no observable effect on overall utilization of ozone for the sample waters tested.

As a final verification of the ability of ozonation to remove organically complexed iron and color, the samples that were used to characterize the Arctic surface water from Kotzebue were ozonated. From the previous batch results, a contact period of 8 minutes, gas flow rate of 0.75 liters/minute, and a sample size of 200 ml was utilized. In all cases, which covered a sampling period from April to June, 1974, the product water contents of iron and color was below U.S. Public Health Standards of 0.3 mg/l and 15 units, respectively.

Observation showed that ozonation of filtered raw water containing complexed iron created a very fine red precipitate. Various ozonated samples were passed through a conventional sand filter containing 20-30 mesh silica sand in an attempt to remove the precipitate. While a 0.45 micron filter successfully removed it, the precipitate was too fine for removal by the conventional sand filter.

Subarctic Ground Water Batch Analysis Results

The characterization of ground waters revealed that there was little to be achieved from ozonation of these water supplies. Simple aeration followed by filtration in all cases except one adequately removed contaminating color and iron concentrations. Manganese levels, however, were essentially unaffected by aeration. Ozonation was therefore examined to delineate its affect on the levels of manganese.

Ozonation contact times were at 3-minute intervals up to 15 minutes. Subsequent sample analysis showed that the initial 3-minute contact period, equivalent to a dosage of 10 mg ozone per liter, was sufficient to adequately effect removal of manganese and any remaining iron or color. The longer contact periods had no additional effect on the remaining levels of manganese. Tabulated results of the sample analyses are presented in Table XII.

TABLE XII
 TABULATED RESULTS OF
 GROUND WATER OZONATION ANALYSIS

Sample Identifica- tion	Iron (mg/l)		Color		Manganese (mg/l)	
	After Aeration	After Ozone	After Aeration	After Ozone	After Aeration	After Ozone
A	< 0.3	< 0.3	< 15	< 15	1.0	< 0.1
B	< 0.3	< 0.3	< 15	< 15	2.5	< 0.3
C	< 0.3	< 0.3	< 15	< 15	0.6	< 0.3
D	< 0.3	< 0.3	< 15	< 15	1.6	< 0.4
E	3.2	< 0.3	35	< 15	0.5	< 0.1
F	< 0.3	< 0.3	< 15	< 15	1.0	< 0.3

EXPERIMENTAL CONTACTOR RESULTS

The results of continuous flow contactor studies have been divided into three subsections to allow individual discussion of the three types of units examined.

Single Column Continuous Contactor

The initial single column continuous flow contactor was utilized to treat the subarctic surface water studied. This raw water was characterized by low levels of iron and manganese. Minimum required dosages ranged between 219 mg ozone per liter up to 290 mg ozone per liter depending on the gas flow rate to obtain adequate color reduction. These relatively high dosages and variations are a result of inefficient design. Detention time of the water was a minimum of 35.2 minutes. This long detention time allows excessive amounts of gaseous ozone in the liquid state to decay due to the catalyzing effect of the hydroxyl ion present. This increased the amount of utilized ozone to above normal. From Reid and Potworowski's (1973) decay rate determinations, this could amount to 70 mg ozone per liter. In addition, the residual ozone averaged 10 mg ozone per liter. Therefore, the observed dosage can only be viewed as quantitative with regards to the applied and utilized dosage.

The treated water exhibited the absence of any filterable oxidation products. This indicates that the presence of color-complexed iron and manganese increases the difficulty of color removal and forms the filterable precipitate upon oxidation.

Positive Injection Continuous Contactor

This unit was tested on location in Kotzebue, Alaska, with the previously characterized surface water. The positive injection head was unable to supply a sufficient quantity of ozone to effect treatment in one pass. A baffled 150-gallon holding tank was utilized to recycle the once ozonated water until treatment was effected. Figures XVIII and XIX depict a graphical representation of the observed iron and color reduction, respectively, for the three gas flow rates examined. Plotted points represent average iron and color levels for each theoretical circulation through the unit. The small disparity observed between runs is explained by possible short-circuiting through the baffled 150-gallon holding tank. Table XIII summarizes the actual amount of ozone applied and utilized, and the overall power consumption. The observed amount of applied ozone required supports the importance of optimizing contactor design. The utilized quantity of ozone was 75 percent less than the average of all of the batch analyses. The percent of ozone utilized in the continuous contactor increased from 30 to 55 percent up to 75 to 80 percent. Power consumption was decreased. This reduction was due in part to the more efficient production of ozone from the LG-2-L2 generator.

The quantity of ozone in the residual gas stream at various times was calculated and is presented in Table XIV. As expected, the quantity of ozone utilized decreases as adequate treatment is gradually effected. This fact, and the quantity of ozone required to remove the color and iron from Arctic surface waters, suggest a multi-column contacting design would be more efficient with respect to ozone utilization.

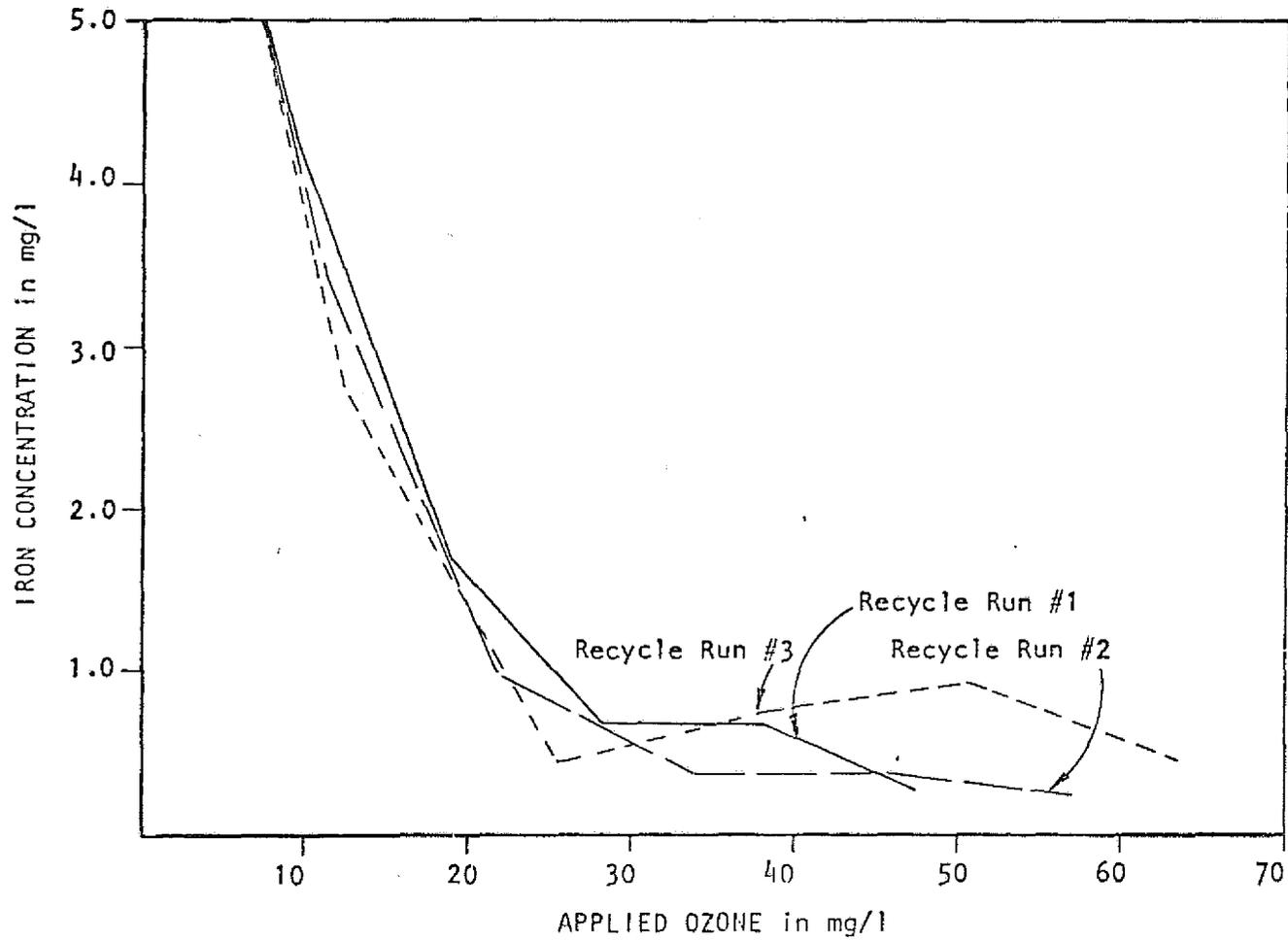


FIGURE XVIII IRON vs. APPLIED OZONE FOR RECYCLE TEST RUNS

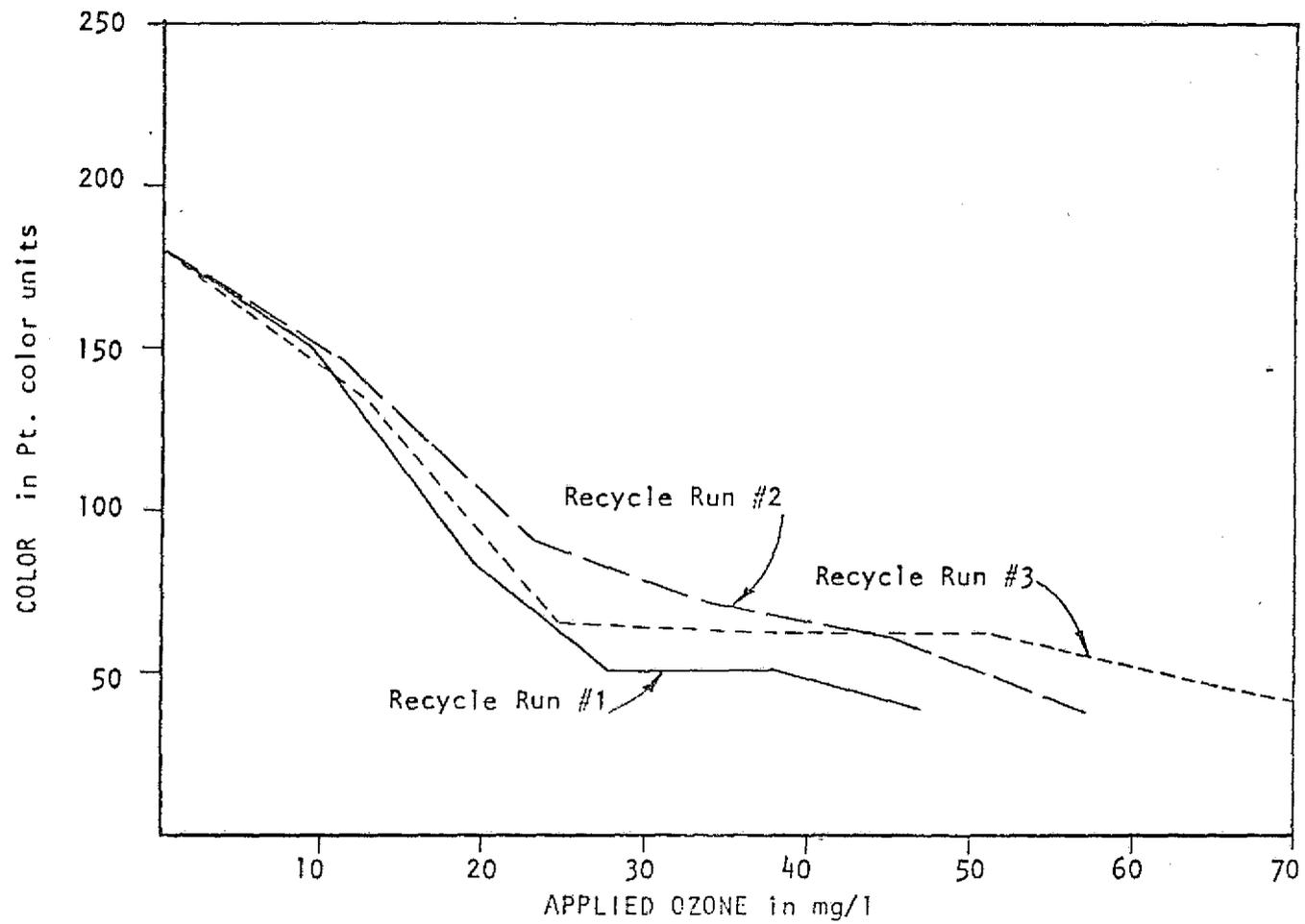


FIGURE XIX COLOR vs. APPLIED OZONE FOR RECYCLE TEST RUNS

TABLE XIII
 POSITIVE INJECTION CONTINUOUS CONTACTOR
 TEST RESULTS

Run No.	Gas Flow Rate (SCFH)	Ozone Applied (mg O ₃ /l)	Percentage of Ozone Utilized	Ozone Utilized (mg O ₃ /l)
1	40	57.1	75%	42.8
2	60	57.3	76%	43.5
3	75	63.9	79%	50.5
AVERAGE		59.4		45.6

TABLE XIV
 OZONE IN RESIDUAL GAS STREAM

Circulation No.	Percent of Ozone Applied That is Utilized		
	Recycle Run #1	Recycle Run #2	Recycle Run #3
1	96	89	93
2	86	81	85
3	80	73	80
4	72	65	71
5	62	--	68
6	57	--	--

Regardless of the individual contactor design, the gas-liquid flow between columns should be countercurrent, the first column being fed raw water and residual gas from the previous column. The last column would be discharging treated water and a once reacted gas stream that would be used to contact the next to last column. The number of columns would be dependent on flow rate, contact time, contactor design, generation capacity, and ozone utilization efficiency.

In addition to iron and color, samples were analyzed for manganese. Initial raw water concentrations were observed to be 0.2 mg/l, which were in agreement with the Public Health routine water analysis conducted locally. However, subsequent ozonated samples demonstrated a rapid increase of measurable manganese. When 10 to 15 mg ozone per liter was applied, the manganese concentration leveled off at 0.9 to 1.0 mg/l. Additional dosages of ozone failed to decrease or increase the amount of manganese in the treated and filtered sample. The additional soluble manganese, which proved unremovable, constituted a 450 percent increase. After ozonation the concentration of manganese was well above the USPHS recommended level of 0.05 mg/l. It is evident that the ozonation process liberated manganese that was complexed with the colored organic molecule into a measurable but unremovable state.

Continuous Gas Diffusion Contactor

This design allowed continuous flow, discharging acceptable treated water with one pass through the unit. The equipment and time were not available to optimize the liquid-gas dispersion as was previously seen with the positive injection design. Therefore, the results only serve to verify the feasibility of acceptable treatment with one pass through the

contactor. Table XV lists the various results for the two test runs. The relatively higher levels of ozone utilization (133 to 267 mg ozone per liter) and residual iron and color indicate the less efficient contactor design in comparison to the positive injection head. This is partly due to a much longer detention time within the contactor which allows excessive amounts of gaseous ozone in the liquid state to decay naturally. A short detention time with optimum gas-liquid dispersion represents the most efficient utilization of generated ozone. Regardless of the unit's lack of utilization efficiency, it has shown that adequate treatment can be affected with a continuous flow contactor.

TABLE XV

CONTINUOUS GAS DIFFUSION CONTACTOR RESULTS

	Run #1 (1 gal/min)	Run #2 ($\frac{1}{2}$ gal/min)
Applied Ozone Dosage	196 mg O_3 /l	392 mg O_3 /l
Utilized Ozone Dosage	133 mg O_3 /l	267 mg O_3 /l
Percent Utilized	68%	68%
Iron	0.35 mg O_3 /l	0.07-0.14 mg O_3 /l
Color	35	10 - 20
WH/1000 gals (applied)	4.17	8.33

OPERATING COSTS

The operating costs include consideration of power consumption, required dosage, and the location of the source of water to be treated.

Power consumption per gram of ozone produced varied (Tables V and VI). Generally, less than 10 watt hours per gram of ozone was required under normal operating conditions. This value is somewhat lower than that reported by Evans (1972) of 28 watt hours per gram and by Manley and Niegowski (1967) of 66 watt hours per gram of ozone. The difference may be due to source gas differences, more efficient generation or testing apparatus and procedure. This type of difference makes it necessary to limit further discussion to the performance of the units used in this study. It is important to note that only after proper generator sizing, selection and testing at the installation location and with refinement of dosage requirements can accurate electrical costs be delineated. The observed minimum dosage of 59 mg ozone per liter is far in excess of the reported dosage of 1 - 9 mg ozone per liter for color removal (Smith, 1973). In addition, seasonal variation of the quality of Arctic and subarctic surface waters compromise the attempt at quantifying the required dosage. It is possible, using the data presented to make an estimate of the maximum ozone per liter requirements of the surface water supply in Kotzebue, Alaska, and from Smith Lake, west of Fairbanks. Treatment systems designed to treat these two waters would be oversized for the operating conditions during 9 to 10 months of the year. Also the need for coagulation,

sedimentation and possibly filtration operations in the case of the Kotzebue water must be realized. These costs have not been determined.

For Kotzebue's surface water supply it is estimated that a minimum of 2.23 kilowatt hours per 1000 gallons of water would be required assuming 10 watt-hours per gram of ozone generated and 59 mg ozone per liter treated. Using the power requirements reported by Manley and Niegowski (1967), 14.72 kilowatt-hours per 1000 gallons treated would be required. At \$0.10 per kilowatt-hour the costs are \$0.22 and \$1.47 per 1000 gallons treated, respectively. The difference in these values is so great it is recommended that where detailed information of the operating cost of the ozonation system is required, a year-long pilot study be conducted.

This study also shows the need for additional work on the removal of the precipitate. The conventional gravity filter system did not perform satisfactorily. The use of conventional coagulation, sedimentation and filtration with ozonation may be feasible; however, very careful cost analyses would be needed. The use of finer pore filter media may reduce or eliminate the need for coagulation and sedimentation.

Another aspect requiring further study is the benefit of ozone with regard to the destruction of microorganisms including viruses. This side benefit, along with the reported reduction in chlorine requirements could be used in the justification of the possibly more expensive system.

CONCLUSIONS

- (1) The Arctic and subarctic organometallically contaminated water supplies can be treated effectively with ozone for iron and color removal. Observed minimum dosage was 59 mg of ozone per liter for Arctic surface waters. The inherent surface water parameters variation, however, cause water quality fluctuations that compromise these quantifiable results.
- (2) Generator, contactor, and design locations inconsistencies necessitate individual investigations to accurately delineate operating costs.
- (3) The ozone oxidized precipitate is not removable with a conventional sand filter, but is retained on a 0.45 micron filter. To facilitate precipitate removal, therefore, additional treatment would be necessary.
- (4) The concentration of color and iron in the examined Arctic surface water was reduced by 30 percent by simple aeration and passage through a 0.45 micron filter and required 12,000 mg/l of powdered carbon to effect acceptable treatment.
- (5) Ozonated Arctic surface waters showed a 38 percent reduction in total organic carbon.
- (6) The ozonation of some water supplies released additional measurable complexed quantities of iron and manganese. The additional iron was further ozone-oxidized and precipitated, whereas the manganese, with further ozonation, was unaffected.

- (7) Examined ground waters contained minimal amounts of organometallic complexes. Simple aeration and filtration was usually sufficient to effectively remove any iron and color. Manganese, however, was not affected and required a maximum dosage of 10 mg ozone per liter for adequate treatment.
- (8) Positive injection gas dispersion increased ozone utilization by 60 percent and reduced the required dosage by 75 percent to the observed minimum dosage of 59 mg ozone per liter. This contactor and results verified the importance of efficient gas-liquid dispersion and short detention time.
- (9) The quantity of ozone in the residual gas stream increased as the ozonation of the contaminants was effected, suggesting a multi-column countercurrent positive injection contactor to obtain optimum utilization of generated ozone.
- (10) With equal applications of ozone to the Arctic surface water, an additional 6 units of color and 0.17 mg/l of iron were oxidized for each 10°C water temperature rise between 10 and 50°C.
- (11) For ozonation of the Arctic surface water supply using the results of these, would require a 2.23 kilowatt hours per 1000 gallons. Up to 14.72 kilowatt hours per 1000 gallons would be required using published power per gram of ozone data.

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