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**OZONATION FOR DESTRUCTION OF CYANIDE IN  
CANADIAN GOLD MILL EFFLUENTS -  
A PRELIMINARY EVALUATION**

G.I. Mathieu

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OZONATION FOR DESTRUCTION OF CYANIDE IN CANADIAN  
GOLD MILL EFFLUENTS - A PRELIMINARY EVALUATION \*

by

G.I. Mathieu \*\*

ABSTRACT

A literature search was made to determine whether ozonation would be technically and economically attractive for the treatment of cyanide-bearing gold mill effluents. The publications covered in this survey were those concerned with (1) recent advances in ozone generation and gas-liquid contacting devices of interest to cyanide oxidation, (2) conditions for a rapid and complete decomposition by ozone of both simple and complex cyanides commonly found in gold mine effluents and (3) cost of ozonation under these conditions. This state-of-the-art review shows that ozonation might be a valid alternative to conventional methods of cyanide detoxification of gold mill effluents. The ozonation process at the time of writing is relatively high in capital cost but low in operating cost compared with conventional processes.

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\* Minerals Research Program, Processing Contribution No. 41

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UNE PREMIERE ETUDE DE L'OZONISATION  
COMME MOYEN POUR DETRUIRE LE CYANURE DANS LES EFFLUENTS  
DE MINES AURIFERES CANADIENNES

par  
G.I. Mathieu\*

SOMMAIRE

L'auteur a parcouru différentes publications dans le but de savoir si l'ozonisation pouvait être un moyen technique et économique souhaitable pour le traitement d'effluents aurifères miniers porteurs de cyanure. La littérature examinée, pour cette étude, traitait 1) des récents progrès faits dans les domaines de la production d'ozone et des dispositifs gaz-liquide agissant par contact, dont l'intérêt se porte sur l'oxydation du cyanure, 2) des conditions nécessaires à l'ozone pour décomposer rapidement et complètement les cyanures simples et complexes qu'on retrouve habituellement dans les effluents de mines d'or, et 3) du coût de l'ozonisation dans ces conditions. Cet examen démontra que l'ozonisation pourrait être une alternative valable aux méthodes classiques de détoxification des effluents de mine d'or du cyanure, surtout que ses frais d'opération sont moins dispendieux, bien que les frais d'établissement premier le soient.

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## INTRODUCTION

In 1955, Thorp <sup>(1)</sup> compiled the first bibliography on ozone technology. He listed 980 patents and 266 papers dealing with generation of ozone and its applications to industry. Klein <sup>(2)</sup> of the Illinois Institute of Technology Research Institute has estimated that another 3000 papers were published on this subject in the following 20 years, or some 150 per year. The International Ozone Institute, founded in 1973, in its monthly newsletter (OZO News) is now listing all the recent publications related to ozone, which cumulate at the rate of 50 per month or 600 per year.

The recent interest in ozone technology was partly attributed by Adams <sup>(3)</sup> to governmental requirement for removal of refractory constituents from industrial waste waters. He noted that ozonation possesses the potential of treating organics and inorganics which are resistant to other methods. Among these, he listed phenols, oils, ammonia and cyanides, both simple and complex. McLean <sup>(4)</sup> added detergents, sulphides and sulphites to this list.

Government regulatory action in various countries has served as an incentive to manufacturers to build larger and better ozonators. In U.S.A., seven companies are now fabricating large ozonation units, namely, Crane Co., Chromalloy American Corp., Emery Industries Inc., W.R. Grace Co., Welsbach Corp., Ozone Research and Equipment Corp., and Pollution Control Industries Company. In Europe, at least twelve companies produce

large ozonators. Japan has one large-scale manufacturer, while Canada has two subsidiaries of French companies dealing in ozone equipment, namely Dégrémont Canada Ltée and Compagnie Canadienne des Eaux et de l'Ozone Ltée. Several of these companies now advertise high-frequency ozonators developed along a new concept discovered by the Great Britain Electricity Council Research Centre and licensed in the U.K. to Mather and Platt, London. The British high frequency ozonator was called the "Capenhurst". Its features and advantages are given in the company literature and in an article by McLean<sup>(4)</sup>. The use of high frequency has resulted in more than doubling the normal ozone output and concentration, while both the capital and operating costs have been substantially reduced (Figure in Appendix 1)\*.

Although these features and other advances in ozone technology have induced several industries, particularly those in the fields of metal plating<sup>(5,6)</sup> and film processing<sup>(6,7)</sup>, to reconsider ozonation for cyanide destruction in their waste water, the technique up to now has been practically disregarded by gold mines using the cyanidation process.

#### THE PROBLEM OF OZONATION OF CYANIDE EFFLUENTS

This indifference could be attributed to the fact that ozonation of waste water is a complex process and that its economical

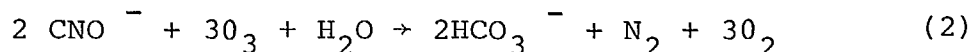
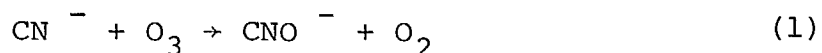
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\*NOTE: Further economies are predicted by Accelerators Inc. with the development of their new "electron accelerator/dynactor ozonator" announced in OZO News of November, 1976

application depends on several factors not previously fully determined or understood i.e.,

- 1) reaction mechanism and its rate
- 2) ozone concentration and rate of application necessary to achieve the desired chemical oxidation
- 3) technique for an effective contact between ozone gas and impurities in solution
- 4) optimum pH and temperature of waste water
- 5) effect of nature and concentration of secondary constituents present in waste water and reacting with ozone.

Recent literature has clarified a few of these points but others remain open to question. Evans <sup>(8)</sup> has suggested two principal mechanisms of ozone oxidation. The first considers an electrophilic attack by ozone, while the other involves ozone-initiated oxidation whereby ozone serves as the reaction initiator and oxygen is also a reactant. In the case of cyanide decomposition, it was found that oxygen can participate in the reaction <sup>(9)</sup>. The ozone-oxidation of cyanide according to Green and Smith <sup>(10)</sup> proceeds in two stages as follows:



The first reaction is extremely rapid while the second is slower but could be catalyzed by traces of copper, manganese, nickel and other transition metal ions. The presence of some of these in gold mill effluents would thus influence the speed of the



cyanide decomposition reaction.

It has been demonstrated in France and reported by Diaper<sup>(11)</sup> that higher concentration of ozone could result in important saving of this chemical in cyanide oxidation. Less than half of the ozone was effectively used at a concentration of 7 g O<sub>3</sub>/cu m while 80% of the ozone reacted with cyanide when the ozone concentration reached 26 g/cu m, with the remainder being lost in the atmosphere. Much higher ozone concentrations are now possible, but have not been investigated with regard to cyanide decomposition. According to Stahl<sup>(12)</sup>, the loss of ozone in exhaust gases is heavily dependent on the effectiveness of gas-liquid contacting devices. He identified four main types of these, namely, the spray tower, the packed beds, the bubble plate or sieve plate columns (an intermediate case to 1 and 2), and the gas dispersion within a liquid. A description of each type is given in Stahl's paper along with its advantages and disadvantages<sup>(12)</sup>. Some specific applications are discussed in detail, e.g., municipal water purification, odour and colour removal, etc. Although his study does not make any recommendation as to the best contacting device for cyanide decomposition, it is inferred from his general observation that the spray system would be a logical choice if the reaction time could be reduced to a few minutes. This was achieved in limited test work by the author when using the film layer purifying chamber (FLPC) spray contacting device and pure cyanide solutions<sup>(9)</sup>.

Garrison<sup>(13)</sup> observed that the cyanide decomposition by

ozone is speeded up by higher temperature while Bollyky<sup>(5)</sup> reported that the reaction is more rapid in highly alkaline solution, but quantitative data on these aspects are scarce.

Briefly, the reaction rates and parameters of ozone-oxidation cannot easily be predicted quantitatively and these should be determined experimentally on different industrial waste waters. This is particularly true in the case of gold mill effluents, since these have various compositions and contain several species of cyanide complexes. These effluents also contain metal ions which are readily oxidizable by ozone. This would result, not only in greater purification of water, but also in a higher ozone consumption. On the other hand, some of the cations present in mill effluents may have a beneficial catalytic effect on the oxidation reaction.

An assessment of the value of ozonation for treating some Canadian gold mill effluents would thus have necessitated actual test work on the complex cyanide solutions to answer some of the above questions. Since this was not done, results from treating cyanide wastes in other industrial fields will have to be reviewed to evaluate its potential application for mining effluents. This review also emphasizes recent discoveries in ozone technology and chemistry which show promise for this process as an alternative to treating cyanide - bearing gold mill effluents.

## RECENT FEATURES IN OZONE TECHNOLOGY AND CHEMISTRY

Early ozone generators operated at 19,000 to 20,000 volts and 60 Hz. In some of the newer designs, the power supply generates high frequency of 2000 Hz at 10,000 to 14,000 volts for much greater ozone production at higher concentrations. The use of high frequency in ozone generators was rendered possible by the recent advances in solid state frequency inverter construction, by precision manufacturing of dielectric and electrodes, and by utilizing cooling systems with higher efficiency.

Mather and Platt<sup>(14)</sup>, the manufacturer of the high frequency Capenhurst ozonator developed by the Great Britain Electricity Council Research Centre, forecasts for its 1000-Hz unit considerable economy in installation cost and plant size with reductions in ozonator volume by a factor of 6:1 and in floor area requirement by a factor of 25:1. PCI Ozone Corporation<sup>(15)</sup> now has units operating at 2000 cycles per second, which are said to increase the ozone production per square foot of electrode area by 10 times over that of 60-Hz units of the same size. Ozone concentrations of 3%, 5% and 6-8% by weight are obtained from the new PCI generators when the carrying gas is air, oxygen enriched air (40% O<sub>2</sub>) and oxygen, respectively.

The possibility of producing ozone at much higher concentrations should be very advantageous in cyanide treatment, as indicated by the work of Sondak and Dodge<sup>(16)</sup> who reported reductions of more than 50% in ozonation time when the inlet

ozone concentration increased from 6.7 - 8.3 mg/l to 24.6 - 26.8 mg/l (Appendix 2). For instance, for a three-fold increase in ozone concentration they show a reduction of ozonation time from 21 minutes to 8 minutes for a quasi-complete elimination of potassium cyanide in aqueous solution. Since the authors also observed that the increase in the rate of the cyanide decomposition was much more pronounced at the higher inlet ozone concentrations, the use of high-frequency ozonators to boost the ozone concentration to a further degree appears even more attractive.

In his study on ozone solubility in water and on ferricyanide decomposition by ozonation, Garrison<sup>(5)</sup> suggested that the increase in oxidation rate obtained at a higher ozone concentration in the carrying gas could be attributed to:

- (1) larger absorption of ozone by water when in contact with gas at higher ozone concentration (see graphs in Appendix 3);
- (2) greater oxidation power resulting from higher ozone concentration (see curves in Appendix 4).

When the ozone concentration in the carrying gas increases from 1.3 to 2.6% by weight, its solubility in the contacted water increases from 3.5 to 7 mg/l within a short time to enhance the oxidation (Appendix 3). Also, an increase of ozone content in the carrying gas from 1% to 5% was found necessary to increase destruction of ferricyanide, a very refractory complex, from 25 to 70%. Further decomposition of ferricyanide required the use of ultra-violet lighting, as shown also by the set of curves in Appendix 4. The effect of higher ozone concentration on a mixture

of simple and complex cyanides of the type found in gold mill effluents is still to be determined, but is likely to be beneficial.

Newly designed air-cooled ozone generators have been put on the market by W.R. Grace and Company. After using some of these, Garrison et al.<sup>(6)</sup> had this to say: "the new generation of air-cooled ozonators substantially reduces cost, decreases maintenance and improves reliability compared to water-cooled generators commonly in use". Klein<sup>(2)</sup> in his study on ozone generators foresees economy in plant size and operating cost for the new air-cooled ozonators, the extent of which will be determined by long-term experience.

Another development which could influence future treatment of cyanide waste water by ozonation is the recent introduction on the market of contactors in which the contaminated water is sprayed into a gas chamber containing ozone instead of by bubbling gas into the water. Two types of such devices, namely, the "cyclonic spray scrubber (CSC)" and the "film layer purifying chamber (FLPC)" are illustrated in Appendices 5 and 6. Cyanide oxidation with these contacting systems, is said to be considerably faster and more complete due to continuous formation of fresh surfaces of waste water directly exposed to ambient oxygen-ozone. Limited test work with the FLPC device has indicated a nearly total cyanide destruction of 105 ppm  $\text{CN}^-$  within three minutes, which is faster than any literature data in the case of conventional contacting methods for a corresponding level of cyanide concentration. According to Bowers<sup>(17)</sup>, the main advantage of the

spray contacting system is a better gas distribution system through the waste water stream resulting in a more complete oxidation. In his study on ozone contacting systems, Stahl recommended spray devices for efficiency and economy in capital cost when the reaction is fast enough to limit the contact stages to a reasonable number<sup>(11)</sup>. However, in the absence of reliable data on ozone solubility, diffusiveness and mass transfer coefficients, he stressed the importance in almost every case of piloting for a sufficient length of time to obtain the basic data for cost and scale-up computation with confidence. This advice is particularly valid in the case of ozonation of gold mill cyanide effluents because of their variable composition of cyanides and other impurities.

After discussing another aspect of ozonation, i.e., the consumption of ozone for cyanide destruction, Diaper<sup>(11)</sup> came to a similar conclusion and summarized his views as follows: "In the treatment of industrial wastes, it is generally assumed that 1.5 parts of ozone will be required for the destruction of each part of cyanide. However, because other chemical compounds in the effluent could materially alter this requirement, it is necessary to carry out laboratory tests in all cases". J. Roley has reported in a private communication that he succeeded in destroying one part of cyanide with one part of ozone in treating a sample of bleed solution from Giant Yellowknife Mines Ltd. containing 450 ppm cyanide of which about 220 ppm were metal-

cyano complexes. Only 2 ppm, probably in the form of ferricyanide, were left in the solution after 20 minutes of conventional bubbling ozonation for a decomposition rate of more than 22 ppm/minute. This value indicated that the reaction was probably autocatalytic, as will be seen later.

In his work on the kinetics of ozonation of cyanides, Kanderwall showed that the reaction rate constant is more than doubled when  $\text{Cu}^{++}$  ions in small quantities (less than 20 ppm) are added as catalyst to the oxidation reaction<sup>(18)</sup> Eiring found that copper also reduced the ozone consumption to only 70-75% of the stoichiometric amount for complete oxidation reaction<sup>(19)</sup>. The presence of nickel and manganese ions also proved to be beneficial, but to a lesser degree. Appendix 7 compares the effect of various catalysts. Serota attributed the economy of ozone in the catalytic oxidation to the participation of the whole three atom-molecules of ozone in the reaction (equation 3) rather than only one atom as indicated in equation 4<sup>(20)</sup>:



The theoretical weight ratio for the first stage of decomposition of one part of cyanide in equation (3) is 0.62 part of ozone while according to equation (4) 1.85 parts of ozone would be needed. This view has been confirmed recently by Chen of the University of Southern Illinois who wrote in OZO News of November 1976: "The catalyst not only speeds up the ozonolysis reaction but also increases the efficiency of ozone: It appears that all

three atoms from each ozone molecule takes part in the oxidation process when the catalyst is present, whereas only one atom participates when the catalyst is absent". He also added that "the use of catalyst (and ultrasound) in ozonation doubles the efficiency of ozone, thereby cutting in half the amount of ozone required as well as the costs of ozone, and will prove especially valuable in the treatment of industrial wastes which are heavily polluted".

Another factor favourable to ozonation of cyanide solutions from gold mills is their high pH. Selm<sup>(21)</sup> makes this an essential condition of decomposition of cyanates and of cyanide complexes. Eiring<sup>(18)</sup> observed about a 50% increase in the rate of oxidation by ozone when the pH increased from a 9-11 range to 12-13 by adding lime.

Most observations regarding enhancement of cyanide oxidation by ozone reported in literature prior to 1973 have been checked and confirmed by the Ore Dressing Group of Sumitomo Metal and Mining Company<sup>(22)</sup>. In their search for parameters favourable to cyanide decomposition, they have retained a combination of high pH and the use of 1 ppm of  $\text{Cu}^{++}$  as catalyst for a three-fold increase in the oxidation rate, as shown by the following selected results.



TABLE 1  
Effect of pH and Cu Ions on Cyanide  
Decomposition by Ozone

Cu <sup>++</sup> mg/l	pH	CN <sup>-</sup> level (mg/l)		CN <sup>-</sup> destruction mg/min	Time min
		Initial	Residual		
None	8	103	8.9	6.3	15
None	10	103	0.5	6.8	15
None	12	103	0.1	6.9	15
1	10	103	<0.1	20.6	5
1	12	103	<0.1	20.6	5

All the above findings should be examined in detail and used in a profitable manner in the potential ozonation treatment of the Canadian gold mill effluents.

The response of several cyanides to oxidation by the action of ozone is recorded in the literature. Selm<sup>(21)</sup> reported that oxidation of alkali simple cyanides by ozone is rapid and complete. This was confirmed by several others. Eiring<sup>(23)</sup> recorded ozone-oxidation of copper, zinc and nickel cyanide complexes. To this list, Garrison<sup>(6)</sup> added those of cadmium and iron. The rate of cyanide decomposition, albeit dependent on temperature, ozone and cyanide concentration, and other conditions, was generally considered to be fast for simple cyanides and copper cyanide, intermediate in the case of zinc and nickel cyanides, slow for cadmium and very slow for iron complexes. An order of magnitude for the depletion of 50-100 ppm of these cyanides under favourable conditions in an ozone bubbling system would be as follows:

>15 minutes for alkali and copper cyanides, 15-30 minutes for nickel and zinc cyanides, 30-60 minutes for cadmium cyanide, and <60 minutes for iron cyanides. Slower reactions are often

accompanied by higher ozone consumption, as illustrated in Appendix 8. It is worthwhile to stress again that the ozone oxidation reaction rate can be increased considerably and its consumption significantly diminished by the use of appropriate catalysts, suitable pH, higher concentration of ozone and better contacting devices.

Recent advances in ozone technology and understanding of the cyanide-ozone oxidation chemistry have illustrated conditions for rapid and complete destruction of both simple and complex cyanides. These facts have not received the attention of the gold mining industry. Also, with the exception of a Japanese study <sup>(22)</sup> and a few recent Russian papers <sup>(24,25,26)</sup> very little has been published on applications in this field.

Although a Research Group of Sumitomo Metal Engineering Co. published a report "Cyanide Refining Waste Water Treatment with Ozone at the Konomai Mine" their investigation devoted only six out of seventy tests to the treatment of the Merrill Press filtrate after diluting it to about 110 ppm CN<sup>-</sup>. Other analyses of this cyanide waste water were:

<u>Cu</u>	<u>Zn</u>	<u>Fe</u>	<u>Mn</u>
7.7 ppm	41.4 ppm	0.14 ppm	<0.1 ppm

Despite the limited number of tests on the diluted cyanide effluent and the lack of any attempt to optimize, the results were significant with good cyanide destruction as shown in Table 2:

TABLE 2

Results of Ozone Treatment of Konamai  
Mine Merrill Press Liquid (Diluted) (22)

pH		CN (mg/l)		Time min	CN destruction rate mg/min		O <sub>3</sub> mg/l	
Initial	Final	Initial	Final		Average	Increment	Blown in	Absorbed in
11.9	11.5	109	65.3	3	14.5	14.5	130	130
11.9	11.1	109	34.9	5	14.8	15.2	215	215
11.9	9.9	109	9.6	7	14.2	12.1	300	300
11.9	9.0	109	0.5	10	10.8	3.6	430	349
11.9	8.7	109	0.3	12	9.1	0.1	515	365
11.9	8.6	109	0.3	15	7.2	0.0	645	400

The 99.5% cyanide decomposition obtained in 10 minutes is particularly encouraging in view of the shortcomings and adverse conditions of the tests, namely:

- (1) utilization of a low frequency ozonator  
(W. R. Grace Model L0A-2 delivering ozonized air at only 1% O<sub>3</sub> concentration by weight),
- (2) the use of a conventional air bubbling contact system,
- (3) lack of pH adjustment to prevent its decrease to a level at which the reaction rate is rather low (see incremental CN destruction rate at pH between 8.6 and 9.0),
- (4) lack of devices to enhance the destruction of the residual 0.3 ppm CN present as iron cyano-complexes, e.g., ultraviolet lighting

or ultrasonic vibrations as recommended by Garrison (13) and Fridman<sup>(27)</sup>, respectively.

It is unfortunate that the Japanese study was not pursued along those lines and followed by an economic evaluation.

The same can be said about the published Russian studies. They claim good success in ozone oxidation of cyanide complexes of zinc, copper, nickel and iron in the waste water from Lemnogorskii, Zodskii and Zyryanovskii dressing plants, but give practically no information on the cost projections and economics of a full-scale application under optimum conditions. For instance, Chernobrov<sup>(24)</sup> in his paper on "Ozone Purification of Waste Water from Dressing Plant", has only this to say about test work on cyanide removal by ozone on the pilot plant at Zodskii: "Waste water from the processing of mixed ore from Zodskii deposit gave the following analysis (mg/l): copper - 20, zinc - 40, nickel -15, iron - 4-8.5, arsenic less than 0.4, antimony less than 1.5, lead - 16-20, thiocyanates - 9-10, and cyanides - 70-100 (free and bound in complexes). An ozone-oxygen mixture with a pH of 11 to 12 was used for the ozonization (37 - 56 mg/l of ozone). After 10 to 20 minutes there was a complete removal of simple and complex cyanides from the waste water. By the time a 100% dissociation of cyanides was achieved 90 - 98% of heavy metals (copper, zinc, nickel, lead) was removed. Pilot plant experiments at the Zodskii plant have shown that cyanide-containing waste water treated with ozone can be used for recycling"<sup>(24)</sup>.

The main features of the tests in the USSR appears to be the use of oxygen as carrying gas, the high concentration of ozone, the presence of transition metal ions (catalyst), and a favourable pH. These conditions are probably responsible for the rapid and complete destruction of all the cyanides. It is hoped that the very recent paper by Kvyastkovskii <sup>(25)</sup> on the use of catalysts for purification of cyanide containing waste waters with ozone and by Bespamyatov <sup>(26)</sup> on decomposition of cyanides from waste waters of concentration plant by ozonation (with separate use of non-ferrous metals) will go further on optimization and practicability of the ozonation method for purifying mill cyanide-barren effluents.

In the United States, the renewed interest on ozonation of cyanide wastes has prompted the Environment Protection Agency (EPA) to sponsor research and development programs on applications of the technique in the fields of metal finishing and photo-processing. Two typical projects are entitled "Ozone Treatment of Plating Waste Waters Containing Cyanide" and "Treatment of Complex Cyanide for Reuse and Disposal". Their respective objectives are described as follows:

- (1) "The principal objective is to demonstrate in a full-scale system the effectiveness of the ozonation process for the treatment of plating wastes containing cyanides. Further objectives are to optimize the key process parameters, establish operating and capital costs, and explore the possibility of producing treated effluent that would meet Federal standards".

(2) "The basic objective in this project is to research and develop methods for the treatment of cyanide waters from film processing for recovery and disposal. Recovery methods to be explored are ozonation and electrolytic oxidation. Treatment for disposal includes ozonation for destruction, precipitation of complex cyanide and chlorination".

Although these studies are not directly concerned with gold mill effluents, their results should generate further valuable up-to-date information on the behaviour of various cyanides in the presence of ozone and on the current cost of treating cyanide-containing waste water by ozonation.

It is probably the cost of ozonation, historically assumed to be high, that has prevented its consideration as a practical alternative to conventional oxidation of cyanides. Is this assumption still valid? An attempt will be made to answer this question by reviewing some past cost studies on cyanide decomposition by ozone. The lack of economic data in the specific field of gold mill effluents will make it necessary to extrapolate the trend in ozonation costs from other industrial sectors, the plating industry in particular.

#### COST OF CYANIDE OXIDATION BY OZONE

In 1961, Sondak and Dodge<sup>(14)</sup> estimated that the cost for treating by ozonation 100,000 gpd of copper plating waste waters with a total cyanide concentration of 200 ppm (along with 58 ppm Cu, 63 ppm Zn and 8 ppm Cd) would be nearly twice that of chlorine treatment (i.e., \$1.27 to \$1.38/lb of CN

destroyed for ozone versus 0.72/lb CN for chlorine). It should be noted that Sondak's study attributed some 50% of the ozonation cost to the amortization of a \$172,000 ozonator (See Appendix 9-1 for details).

In 1973, L. J. Bollyky<sup>(5)</sup> revised the figures of Sondak and Dodge and arrived at substantial reductions in both capital and operating costs for ozone treatment of cyanide wastes, as shown below:

<u>Nature of Cost</u>	<u>Sondak and Dodge(1961)</u>	<u>Bollyky(1973)</u>
Capital	\$194,500	\$ 65,500
Operating	\$ 211/day	\$ 78/day

However, the ozonation cost per lb of cyanide decomposed was still high at \$0.94 in Bollyky's estimates, because these were based on a 100,000 gpd plant treating effluent with only 100 ppm cyanide for which a 150 lb O<sub>3</sub>/day ozonator (Pollution Controls Industries Company Model B-150) was proposed. With 200 ppm CN, as in the case of Sondak and Dodge, economies of scale would have been possible for the ozonator capital cost per pound of O<sub>3</sub> produced, and therefore its amortization per pound of cyanide destroyed (which is a major operating cost) would have been reduced accordingly. Bollyky priced his PCI ozone generator at \$60,000, which was competitive with similar capacity ozonators from other manufacturers, e.g., Chromalloy listed in 1973 their Model P-128, 135 lb O<sub>3</sub>/day generator at \$51,350, but gave an abnormally low listing of \$5,500 for the auxiliary equipment (see Appendix 9-11).

The most up-to-date study made in Canada on ozone cost was that of the Department of Chemical Engineering, McMaster University, by Bowers, Netzer and Norman<sup>(17)</sup>. The great merit of their study was to consider the cost of ozone generation from either air or oxygen with part of the latter being retrieved from the exhaust gases. The possible use of oxygen is of interest not only because of its probable contribution to the oxidation but also due to its significant effect on power requirement, ozone yield and cost. Rosen<sup>(28)</sup> has established that the ozone yield from a 90% oxygen concentration is maximum and nearly triple that from air (see data and curve in Appendix 10).

Because of their great economic relevance to the Canadian situation, a summary of the findings of Bowers et al. has been computed along a pattern similar to those previously reported, but in greater detail, and is shown in Table 3.



TABLE 3

## SUMMARY OF CAPITAL INVESTMENT AND OPERATION COST FOR OZONE GENERATING PLANTS

Cost	Ozone Capacity	100 lb/day		200 lb/day		400 lb/day		800 lb/day	
	Carrying Gas	Air	Recycled Oxygen	Air	Recycled Oxygen	Air	Recycled Oxygen	Air	Recycled Oxygen
Capital \$	Ozoniser <sup>(1)</sup>	14,000	7,000	25,100	13,100	46,600	25,300	86,700	47,000
	Auxiliary Equipment & Construction <sup>(2)</sup>	13,300	9,500	21,500	15,100	34,100	25,000	53,100	39,700
	Total	27,300	16,500	46,600	28,200	80,700	50,300	139,800	86,700
Operating \$/lbO <sub>3</sub>	Power(at 0.75¢/KWH) <sup>(3)</sup>	0.087	0.052	0.087	0.052	0.087	0.052	0.087	0.052
	Labour <sup>(4)</sup>	0.018	0.012	0.022	0.015	0.027	0.019	0.034	0.024
	Maintenance, depreciation & Interest <sup>(5)</sup>	0.159	0.096	0.136	0.082	0.118	0.073	0.102	0.063
	Total	0.264	0.160*	0.245	0.149*	0.232	0.144*	0.223	0.139*
With Oxygen Lost & Replaced <sup>(6)</sup>	Total at 1%	-	0.291	-	0.226	-	0.186	-	0.171
	Total at 2%	-	0.376	-	0.261	-	0.198	-	0.183
	Total at 3%	-	0.438	-	0.293	-	0.215	-	0.197
	Total at 5%	-	0.486	-	0.319	-	0.248	-	0.207

\* Assuming no oxygen loss and replacement.

- (1) Basic cost from Welsback Corporation Bulletin No. 201 with an increase cost factor of 0.9 for higher capacities.
- (2) Basic cost from Manufacturers' literature with an increase cost factor of 0.67 for higher capacities. (29,30)
- (3) Industrial power cost in Ontario in 1973 (from R.Thomson, Ontario Hydro, Toronto).
- (4) Set at 1.8¢/lbO<sub>3</sub> from air and 1.2¢/lbO<sub>3</sub> from oxygen for 100 lbO<sub>3</sub>/day<sup>(31)</sup> capacity plus 25%, when doubling capacity<sup>(32)</sup>.
- (5) 6%, 7.3% and 8% of capital investment, respectively.
- (6) Replacement of oxygen cost is based on Union Carbide data for oxygen produced by its "Pressure Swing Adsorption" system (from R.M. Gilmour, Union Carbide Corp., Toronto).

Albeit very informative on the cost of ozone generation in the Canadian context, the data of Bowers et al. are difficult to extrapolate with reference to the treatment of gold mill effluents for the following reasons:

- (1) the contribution of oxygen to oxidation has to be determined for this particular case,
- (2) the losses of oxygen through leakage and gas bleeding to maintain good reactivity are unknown and
- (3) the ratio of the  $O_3$  to CN for destroying entirely the latter in complex forms and in the presence of several species of metal cations can vary considerably depending on the components in solution. Nevertheless, if we consider (i) that oxidation by oxygen is, at least, cheaper than by ozonation, (ii) that the maximum oxygen losses would be 5%, and (iii) that a conservative 2.5:1 ratio for  $O_3$  to CN would be necessary to destroy cyanides, the total operating cost of ozonation derived from Bower's estimates would be lower than \$0.80 per lb of cyanide decomposed for a 200 lb  $O_3$ /day plant evaluated at \$28,200. By using air instead of oxygen, the operating cost would be reduced to \$0.60 but the capital cost would increase to \$46,600. These are about 1/3 lower than Bollyky's estimates. Bowers used Welsback Corp. ozonators for his cost projections.

The most recent study on the economics of treating cyanide wastes was reported by Goldstein <sup>(33)</sup> in Pollution Engineering of March 1976. Analysis of his data and extrapolation of his charts give the following comparative costs of ozonation versus chlorination for the destruction of 140 lb of

cyanide per day:

<u>Nature of Cost</u>	<u>Ozonation</u>	<u>Chlorination</u>
Capital	\$100,000 (2)	\$ 30,000
Operating (1)	0.74 (3)	1.90 (4)

(1) Including amortization plus interest at 20%, but not labour.  
 (2) Crane Co. Ozonator  
 (3) Electricity at 1¢/kWh  
 (4) Chlorine at 10.25¢/lb and caustic at 6¢/lb.

Since the chlorination process is more labour intensive than ozonation, we can conclude that the operating cost of the latter is about one third of the former. The fact that, 25 years ago the cost of ozonation per pound of cyanide decomposed was nearly twice that of chlorination, helps us appreciate the great progress of ozone technology. Unfortunately, ozonation still needs very large capital investment compared with the chlorination process, as shown in the above projections.

Although there are three full size plants using ozonation to destroy cyanides in the western world, namely, Boeing Corporation (Wichita, U.S.A.), Michelin (Clermont-Ferrand, France) and Courtaulds (Coventry, U.K.), this is not a great help in determining the costs and economics of the ozone treatment because these plants are not equipped with modern ozonators and, as far as is known, no details of operational costs have been published for any of these installations.

## SUMMARY AND CONCLUSIONS

This literature survey shows that considerable progress has been made during the past twenty five years in ozone technology and chemistry. Increase in the productivity of generators and an improvement in ozone-liquid contacting devices have been recorded by several authors. Methods to accelerate oxidation of cyanides by ozone have been discovered, e.g. use of catalyst, higher ozone concentration, control of pH and temperature, and utilization of ultrasonic vibration or ultraviolet lighting in conjunction with ozonation. Conditions have been established for the destruction of simple cyanides and most of the common complex metallo-cyanides (including ferricyanide) at concentration levels comparable to those existing in gold mill barren solutions. The projected costs of cyanide decomposition by ozone have also been surveyed and found to have a significant downward trend, e.g., from \$1.27/lb CN destroyed in 1961 to less than \$0.80/lb CN in 1976. The latter compares favourably with any other known process of cyanide destruction. This tendency and the great potential of cyanide waste treatment by ozonation was recognised by both researchers and scholars. For instance, Fridman<sup>(26)</sup> concluded his study on removal of cyanides from waste water as follows: "This (ozonation) appears to be the most promising of all methods for cyanide detoxification from an economic point of view", while Besselièvre<sup>(34)</sup> in his book on the treatment of industrial wastes has this to say: "Ozonation offers perhaps the cheapest method of destroying cyanide, all things considered,

because of the cost of producing ozone is low and the amount of ozone required per pound of cyanide is small".

More specifically, the advantages of ozonation over conventional cyanide oxidation were found to be:

- 1) a more rapid destruction of the cyanides, cyanates and thiocyanates and down to a level comparable with other oxidation techniques, i.e., less than 0.1 ppm in most of the cases,
- 2) a lower operating cost, recently established at some \$0.80 per lb of CN destroyed, for the necessary ozone generation,
- 3) absence of transportation, storage and handling of chemicals, minimum maintenance and man-power requirement, no residual chemical (e.g., chlorine) in treated water, etc.....
- 4) simplicity of the process (see typical flowsheets in Appendix 11).

The main disadvantages appear to be a high capital cost of ozonation equipment (likely to be over \$100,000 for an intermediate size plant with a capacity of 400 lb O<sub>3</sub> per day), a great economic sensitivity to amortization (depreciation and interest) and electrical energy costs, and a lack of actual experience in the use of ozonation of gold mill cyanide effluents. It must be noted that the above observations were thus mainly drawn from studies on treatment of cyanide waste waters originating from industries other than gold mines.

Lack of data on ozone treatment of gold mill effluent containing cyanide, therefore, does not allow a definitive conclusion on the value and economics of this particular application. As there are a number of gold producers in Canada using the cyanidation process, the technique should be investigated on their mill effluents. This should be aimed at adapting and even improving the recent findings on the cyanide destruction by ozone in related fields. It should be kept in mind in such a study that ozonation still has a very good future, with plenty of room for improvement. In spite of recent advances, the method of producing ozone by an electrical discharge is still inherently inefficient, with only about 15% of the energy supplied to the generation system being used to make ozone. The remainder is lost as light, sound and primarily as heat.

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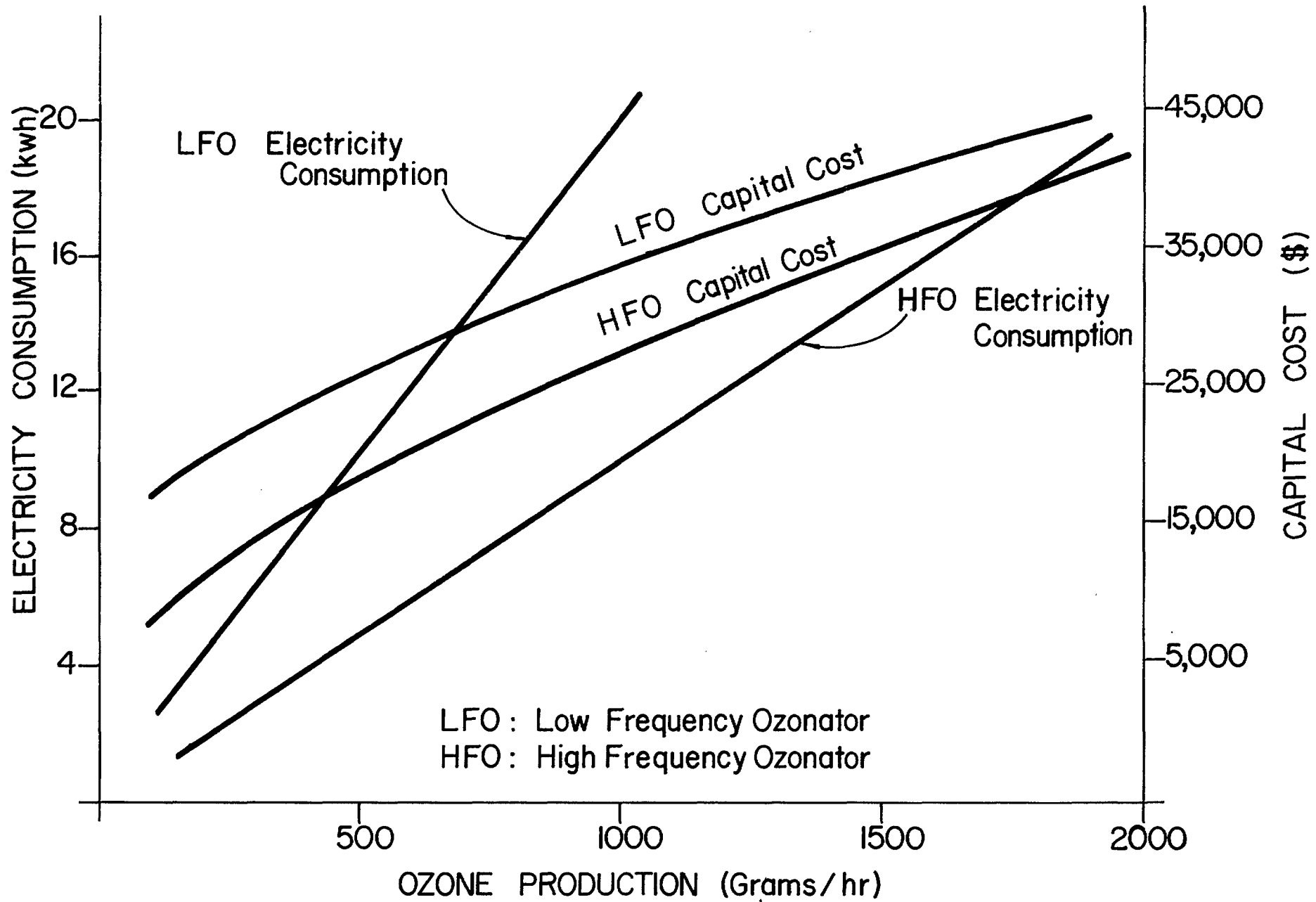
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Appendix 1 - Comparison of Capital Cost and Electricity Consumption with Low Frequency and High Frequency Ozonators



Appendix 2 - Effect of Ozone Concentration on Ozonation Time  
(After Sondak and Dodge)

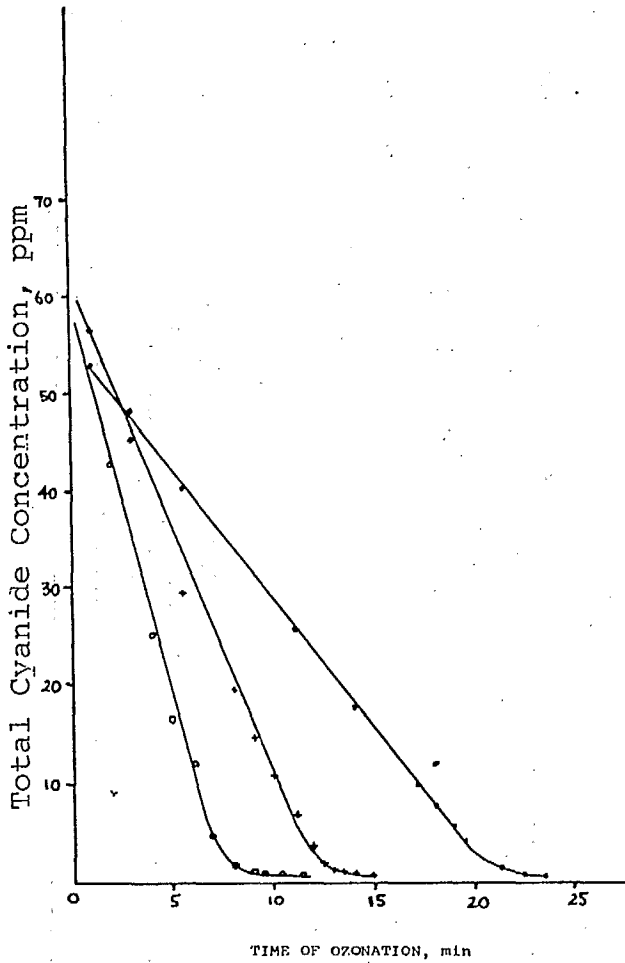


Fig. 2. Pure aqueous cyanide solution, total cyanide concentration versus time of ozonation at constant flow rate of ozonized-air, 30C but different inlet ozone concentrations.

Legend

Symbol	Run Number	Flow Rate ft <sup>3</sup> /min × 10 <sup>2</sup>	Inlet Ozone Conc. mg/l
•	12	3.19	8.35
×	15	4.30	14.9
○	18	4.66	26.8

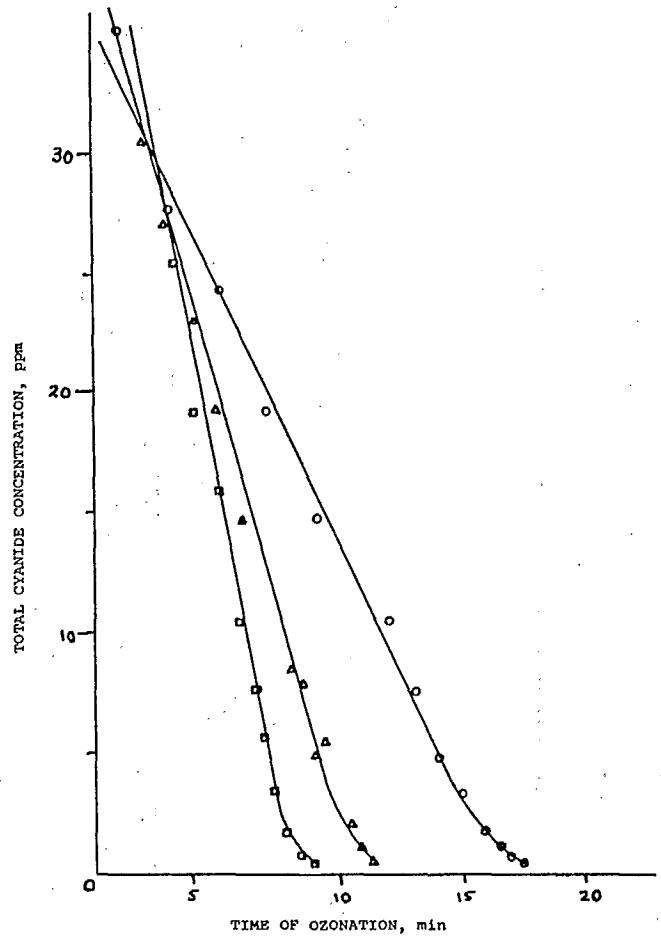
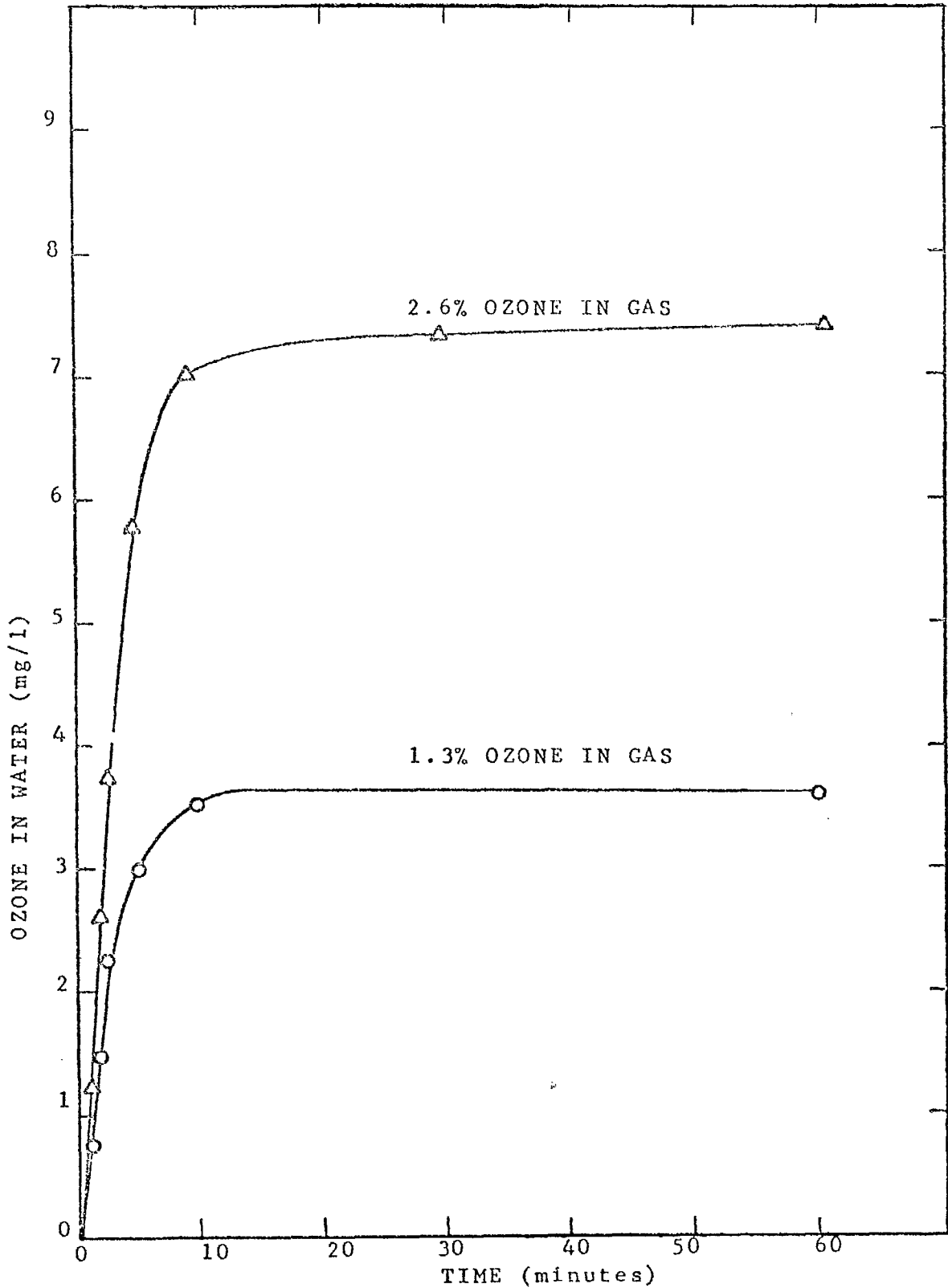


Fig. 3. Total cyanide concentration versus time of ozonation for copper plating solution at constant flow rate of ozonized-air, but different inlet ozone concentrations.

Legend

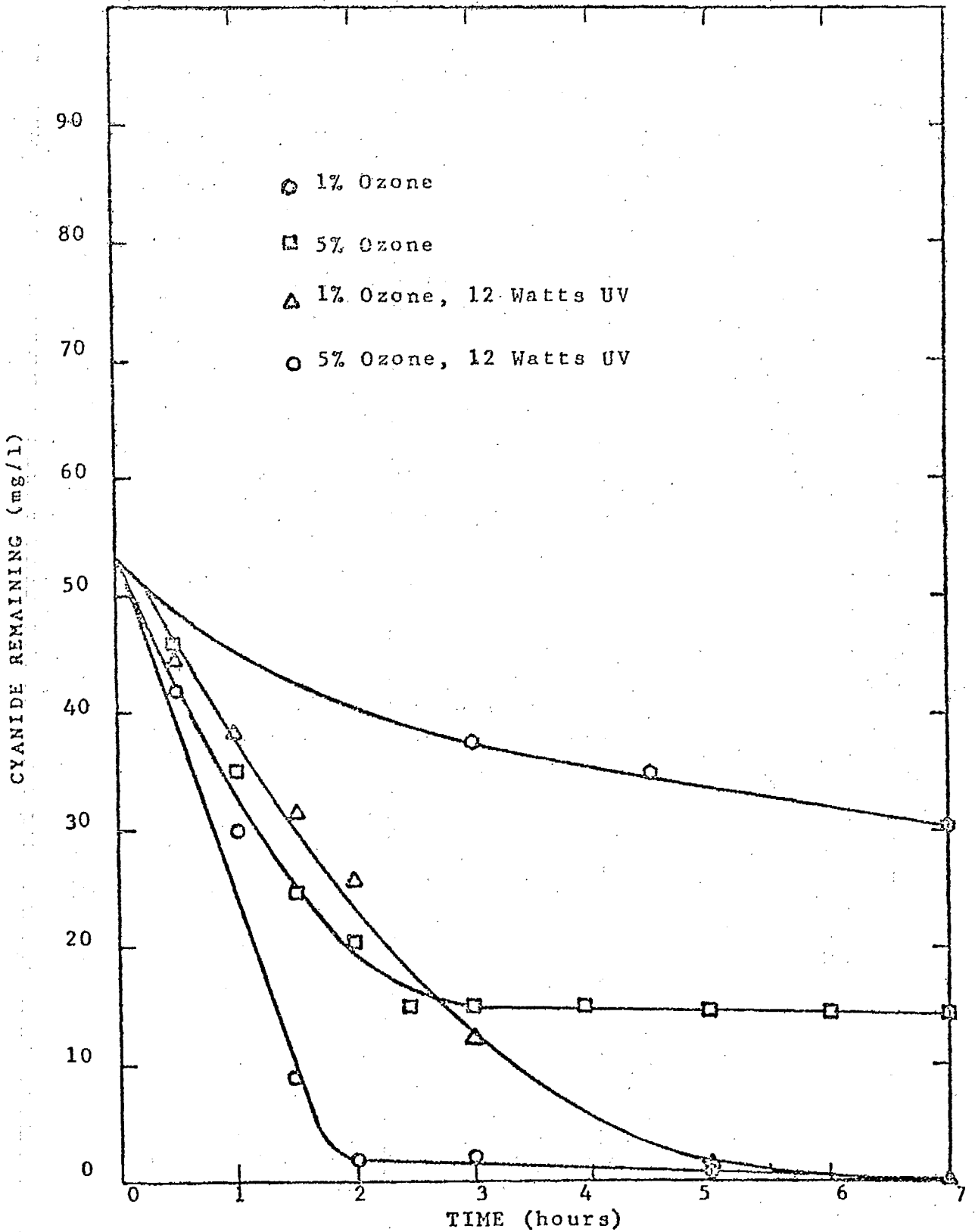
Symbol	Copper Plating Run Number	Flow Rate ft <sup>3</sup> /min × 10 <sup>2</sup>	Inlet Ozone Conc. mg/l
○	1	4.53	6.70
△	2	3.22	12.2
■	3	4.21	24.6

Appendix 3 - Effect of Ozone Concentration in Gas on Its Adsorption in Water (After Garrison)



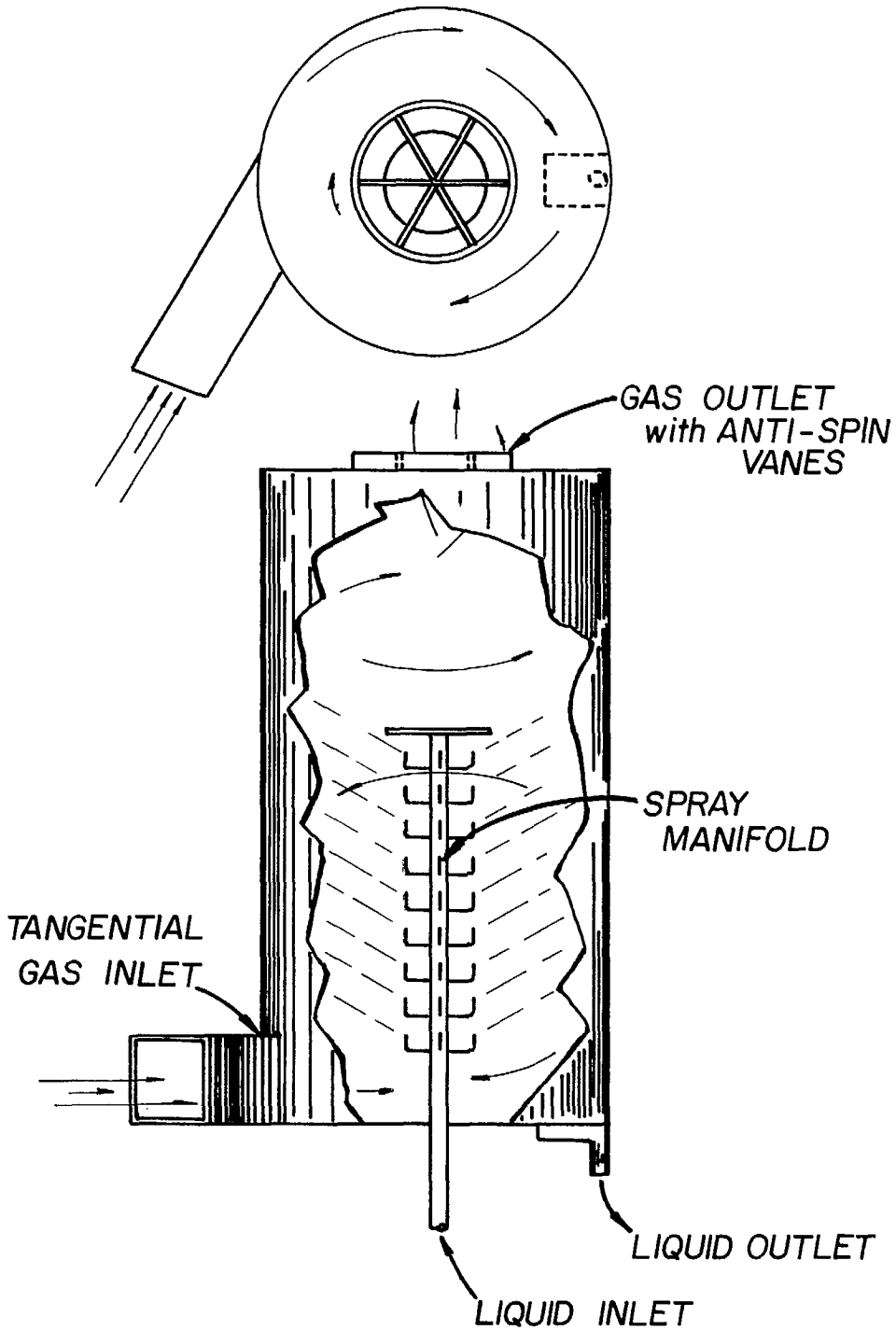
Absorption of Ozone into Pure Water at 25°C and pH 6.9

Appendix 4 - Effect of Ozone Concentration in Carrying Gas and Ultraviolet Light on Ferricyanide Decomposition (After Garrison)



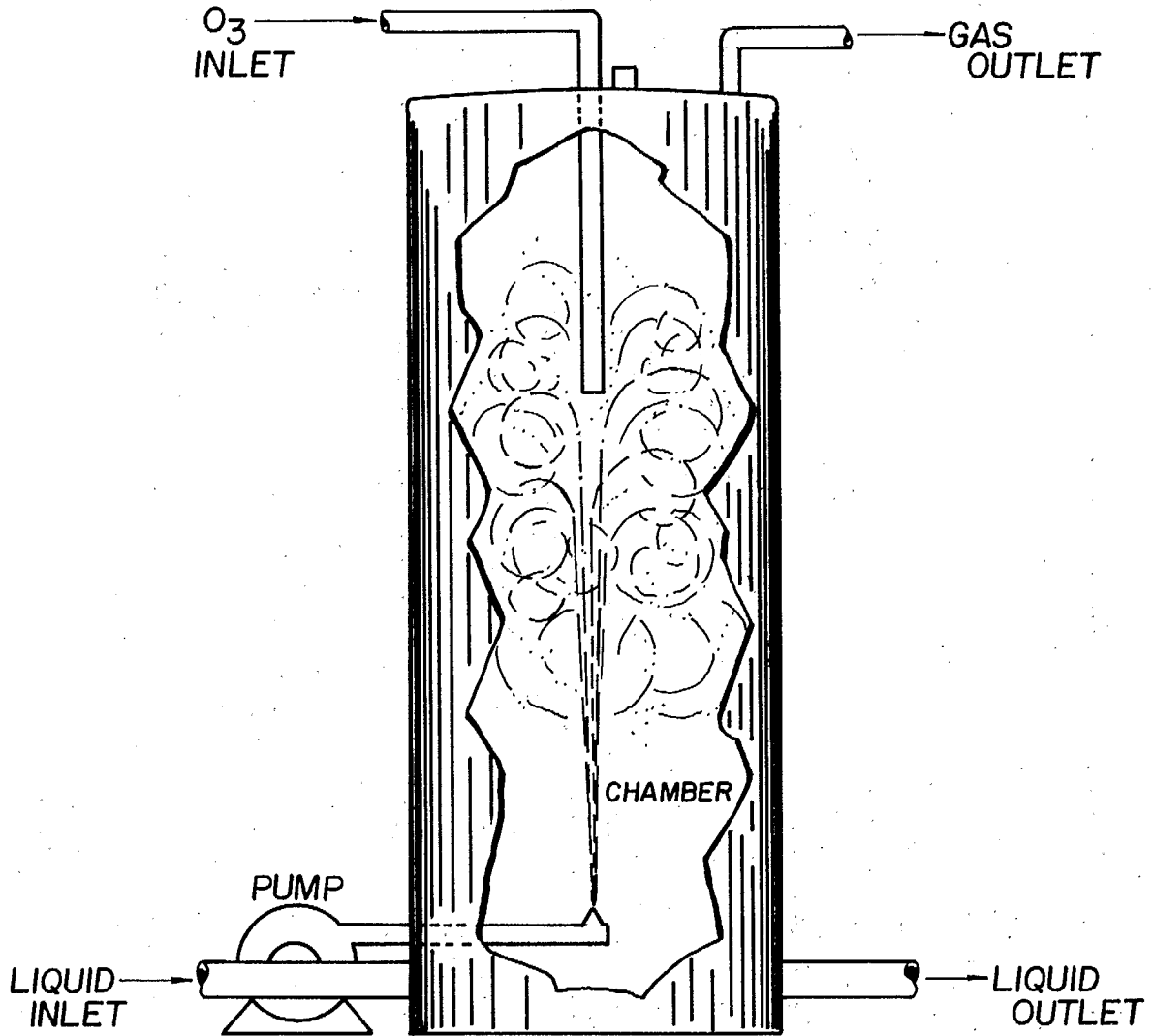
Effect of UV light and ozone Concentration on Ferricyanide at 77°F

Appendix 5 - Illustration of the SCS Spray Tower  
Ozone Contacting System



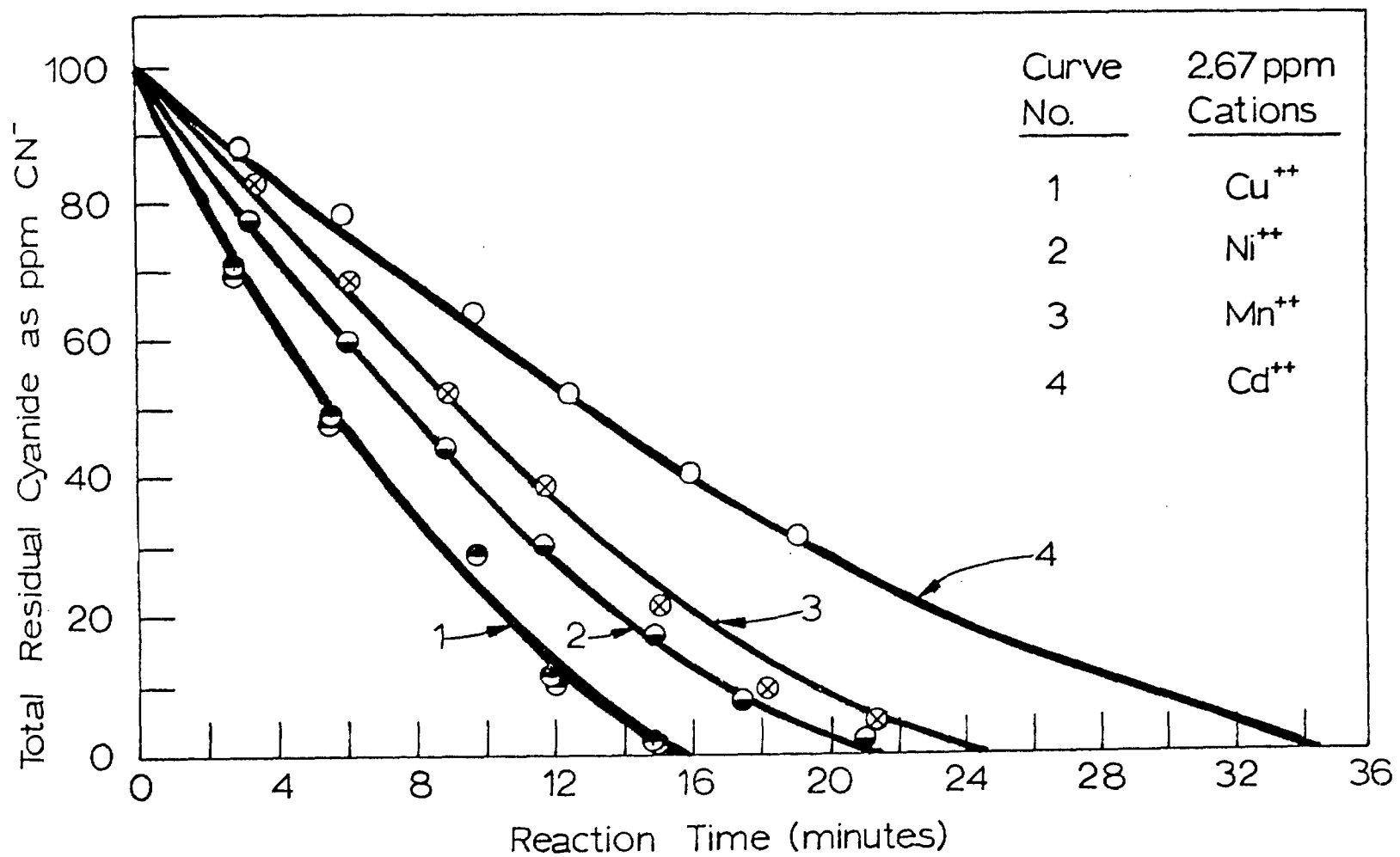
1 - CYCLONIC SPRAY SCRUBBER

Appendix 6 - Illustration of the FLPC Spray Tower  
Ozone Contacting System



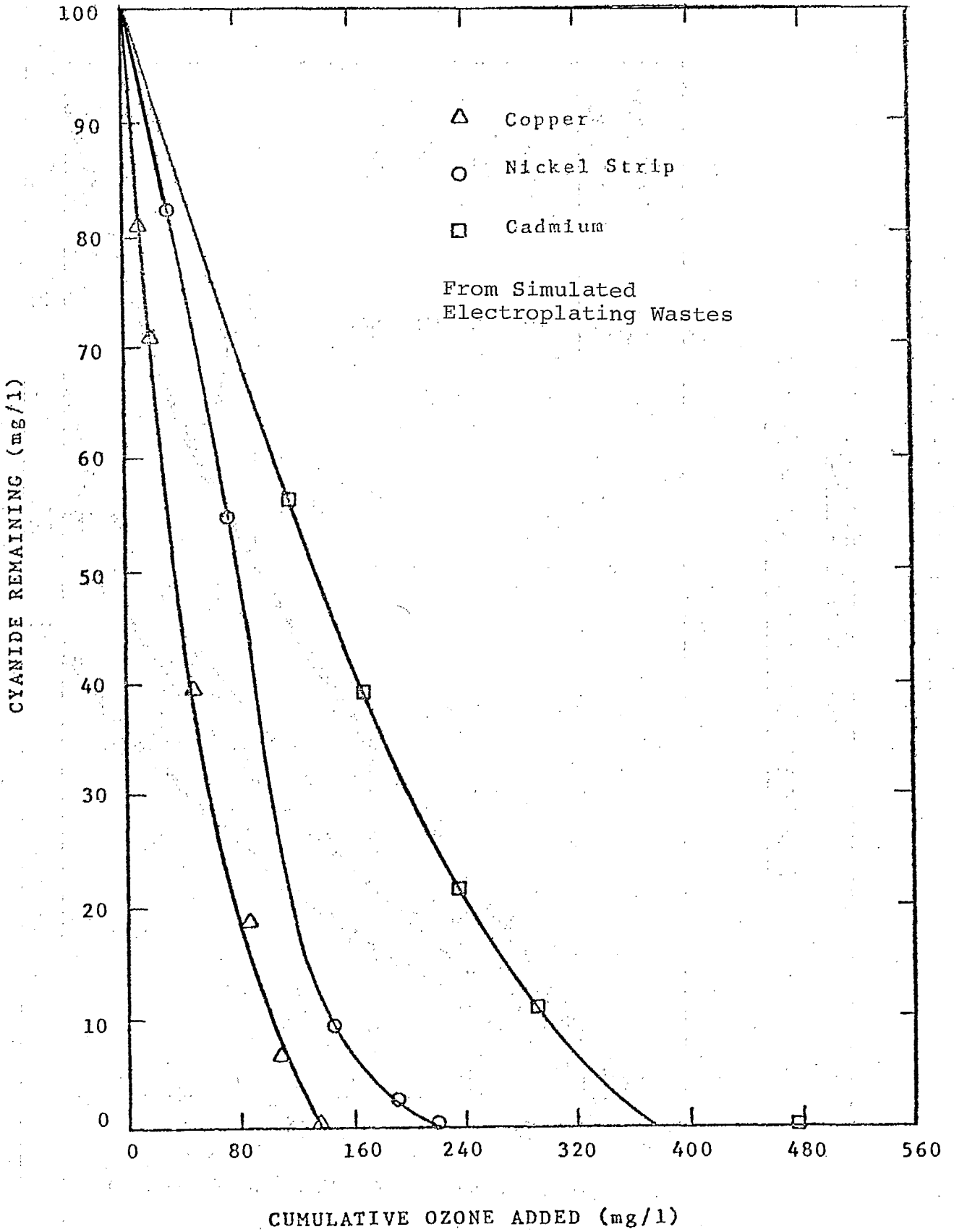
2-FILM LAYER PURIFYING CHAMBER

OZONATION of KCN  
Catalyzed by Various Metal Sulfates





Appendix 8 - Effect of the Nature of Cyanide on Ozone Consumption (after Garrison)



Appendix 9 - Cost Studies on Ozonation of Cyanide Wastewater  
 Illustrating the Downward Trend in the Cost of  
 the Process

I. Comparison of Investment Costs and Operating Expenses  
 for a 100,000 Gallon-per-day Plating Waste Disposal  
 Plant of 200ppm CN<sup>-</sup>, using Ozone or Chlorine (after  
 Sondak & Dodge, 1961).

Reactant .....	Ozone		Chlorine
	Batch Equipment..... Cost,\$	Continuous Cost,\$	Batch Cost,\$
Storage.....	2,000	-	16,000
Reaction.....	20,600	9,600	10,000
Hydrolyzer.....	25,400	6,000	-
Ozonator System.....	172,000	172,000	-
Tanks for Chemicals.	900	900	900
Pumps & Mixers.....	3,000	2,000	6,500
Piping.....	7,000	3,000	5,000
<b>Total.....</b>	<b>230,900</b>	<b>194,500</b>	<b>38,400</b>
<b>Operations</b>	<b>Cost, \$/Day</b>	<b>Cost, \$/Day</b>	<b>Cost, \$/Day</b>
Power			
Ozone.....	71.20	71.20	-
Pumping.....	0.60	0.60	5.00
Chemicals.....	32.60	32.60	94.50
Amortization *.....	126.00	106.60	21.35
<b>Total</b>	<b>230.40</b>	<b>211.00</b>	<b>120.85</b>

\* Including depreciation at 12% and interest on capital at 8%

Note: The estimates of Sondak & Dodge contain a hydrolysis  
 stage evaluated at about 10% of both capital and  
 operating costs.

Appendix 9 (Continuation)

II. Cost of Ozone Treatment of 100,000 Gallon-per-day  
of Cyanide Waste at 100ppm CN<sup>-</sup> (after Bollyky, 1973)

Capital Cost:	<u>100ppm</u>
Ozone Generating Equipment	\$60,000
Tanks & Controls & Piping & Pumps	5,500
	<hr/>
	\$65,500
Operating Cost: \$/day	
Power x 1.25¢* KWH	\$ 22
Chemical Cost	20
Labour 3 hr/wk \$5/hr	3
	<hr/>
	\$ 45
Amortization**	33
	<hr/>
Total	\$ 78

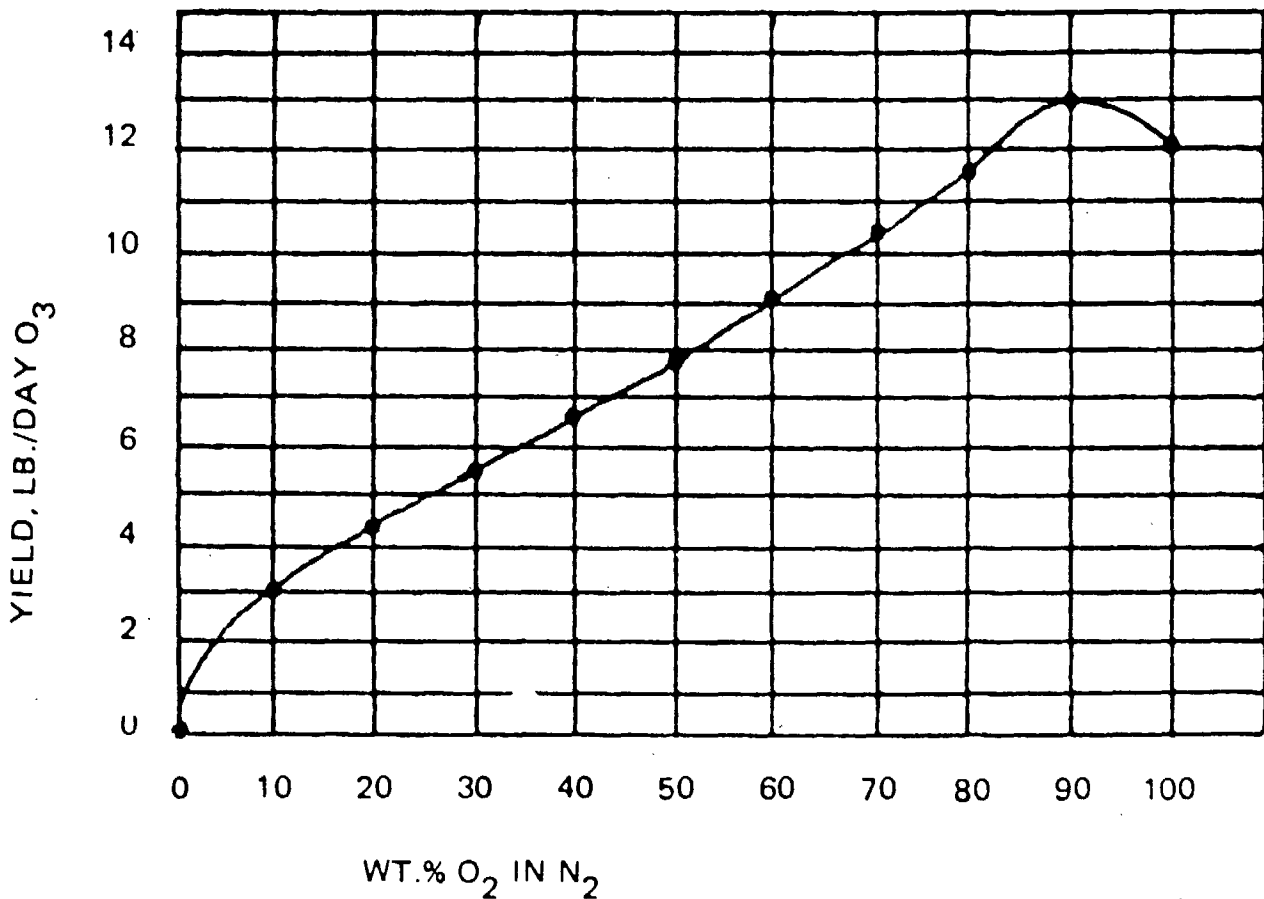
\* Corrected from 2.5 ¢ KWH

\*\* Including depreciation at 12% and interest on capital at 8%.

Appendix 10 - Effect of Oxygen on Power Requirement and Ozone Yield (after Rosen)

### Ozone Generator Power Requirements\*

Type	Air Feed kwhr/lb	Oxygen Feed kwhr/lb
Otto	10.2	—
Tube	7.5-10	3.75-5.0
Lowther	6.3-8.8	2.5-3.5

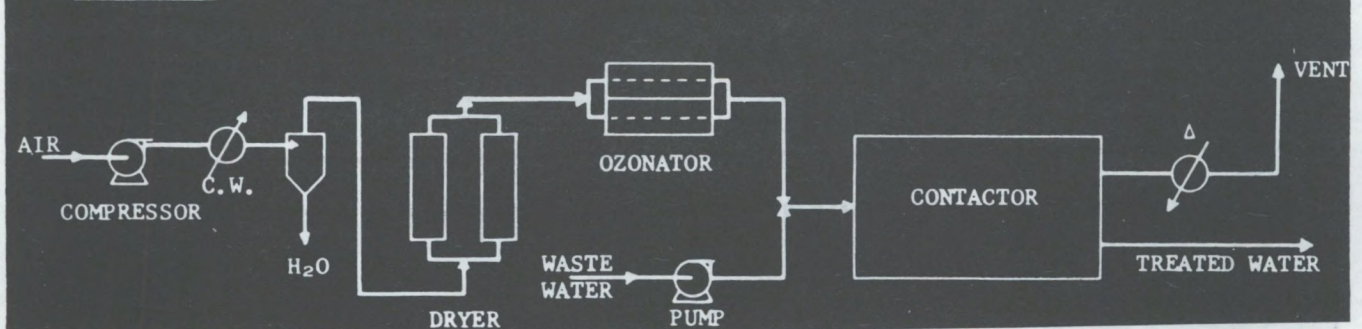


Effect of nitrogen on ozone yield (Lowther generator)

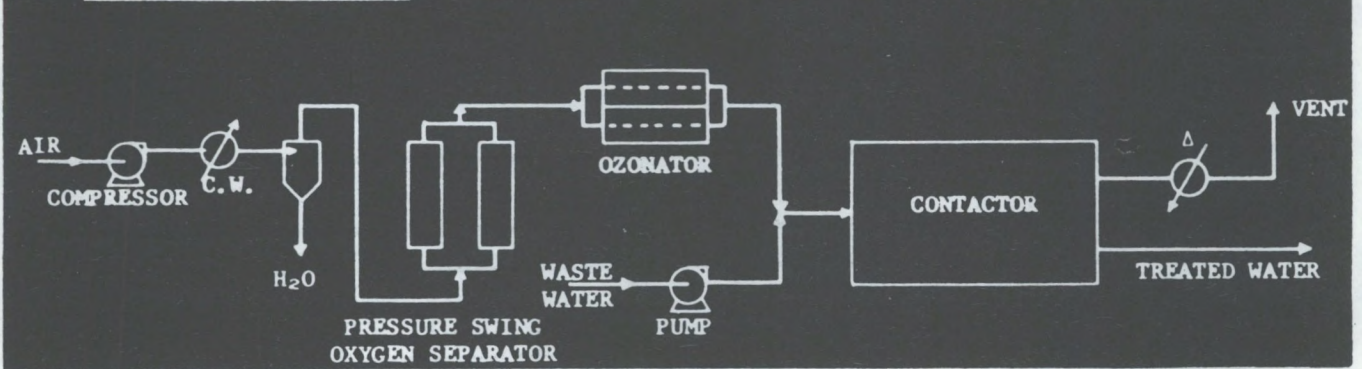
Note: The Lowther generator is the basic type used for construction of high frequency units.

Appendix 11 - Typical Flowsheets for Ozonation of Waste Waters

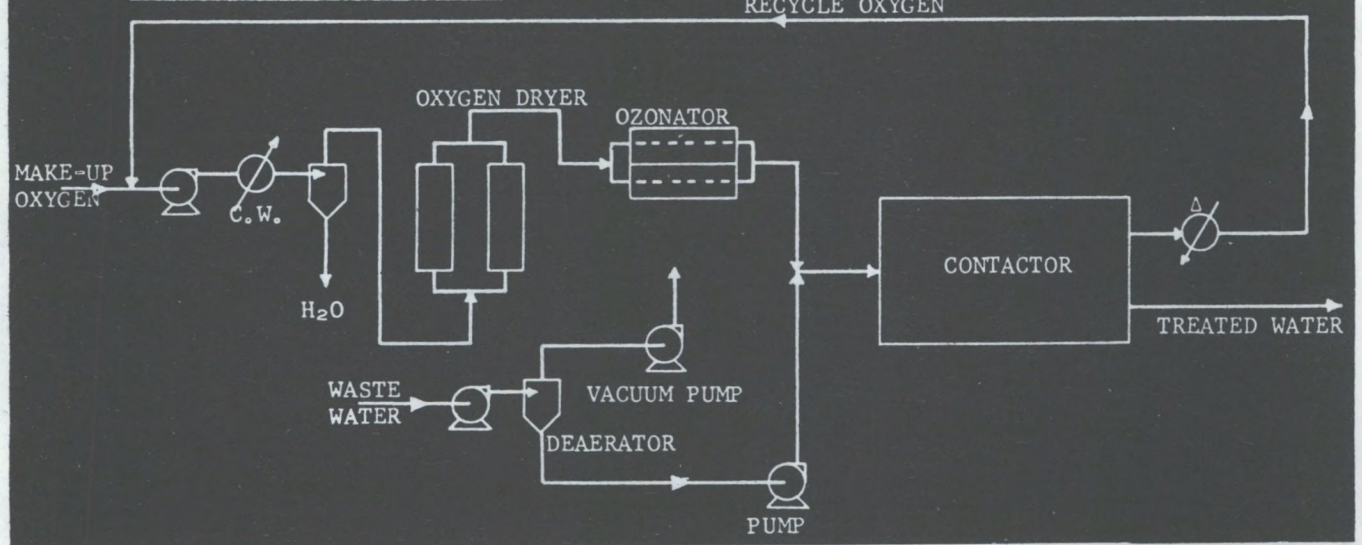
(I) AIR SYSTEM



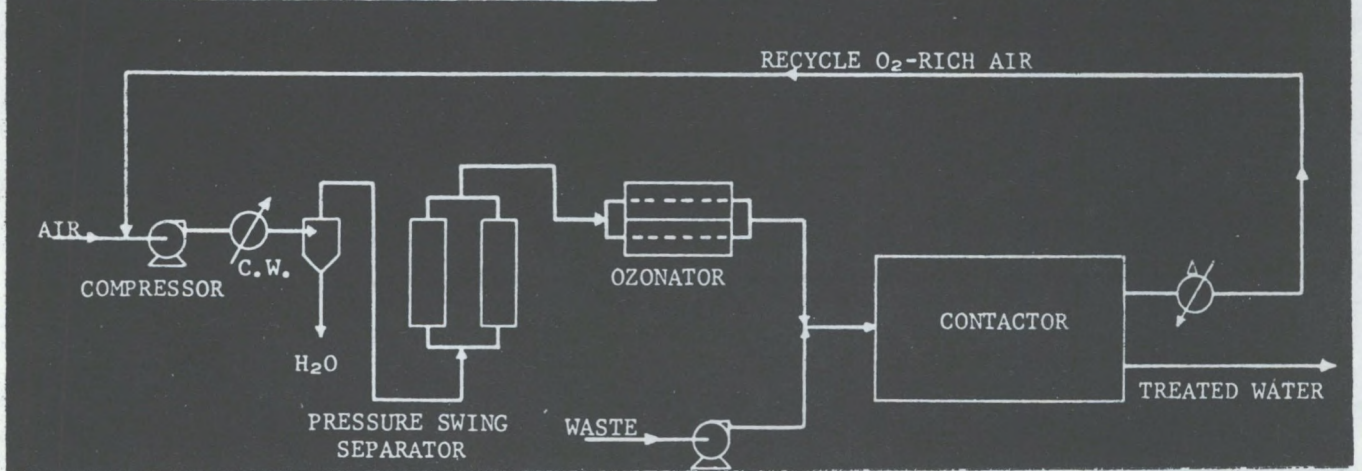
(II) OXYGEN-RICH AIR SYSTEM



(III) OXYGEN WITH RECYCLE SYSTEM



(IV) OXYGEN-RICH AIR, WITH RECYCLE SYSTEM



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