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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A full-scale demonstration plant utilizing ozone/ultraviolet radiation for removal of cyanide from electroplating wastes was optimized and tested at Tinker Air Force Base, Oklahoma. The original design goal was to reduce cyanide concentrations to nondetectable limits in a waste stream (6.25 gallons per hour) containing up to 50,000 milligrams per liter cyanide. Study results are supplemented by a review of literature related to ozone oxidation. → over	

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20. ABSTRACT (CONCLUDED)

The report summarizes equipment operational and plant design deficiencies identified and corrected. Major problems included compressor breakdown, oil carry-over, inefficient air filters, inoperable dryers, inadequate ventillation, low power output from ozone generators and an inefficient ozone contact system.

The plant was tested in both batch and continuous feed modes. Many factors affected cyanide removal rates including residual reactor cyanide concentration, complex metal cyanides, ultraviolet radiation, elevated temperatures and air stream ozone concentration. A 99 percent cyanide removal efficiency was observed for waste fed at 6.2 gallons per hour containing 12,110 milligrams per liter cyanide of which 20 percent was complexed with metals. Operation and maintenance costs for the ozone and alkaline chlorination processes were $3.70 and $4.70 per pound of cyanide removed, respectively, at Tinker Air Force Base.

PREFACE

This report was prepared by SEARCH Inc., P.O. Box J, Norman, Oklahoma 73069, under Contract No. F08635-78C-0205 with the Air Force Civil and Environmental Engineering Development Office (CEEDO), Detachment 1, Armament Development and Test Center (ADTC)/ECW, Tyndall Air Force Base, Florida and Headquarters, Air Force Engineering and Services Center (HQ AFESC)/RDVC, Tyndall Air Force Base, Florida 32403, and covers work accomplished from 14 July 1978 to 30 September 1979. Capt Anthony M. Wachinski managed the program for HQ AFESC.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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ABBREVIATIONS AND SYMBOLS

AFB	Air Force Base
Ag	Silver ion
amps	Amperes
BOD	Biological Oxygen Demand
°C	Temperature, degrees centigrade
Cd	Cadmium ion
cm	Centimeter
CN^-	Cyanide ion
COD	Chemical Oxygen Demand
Cu	Copper ion
°F	Temperature, degrees farenheit
Fe	Iron ion
fps	Feet per second
ft	Feet
gph	Gallons per hour
gpm	Gallons per minute
hp	Horsepower
kg	Kilograms
kw	Kilowatts
kwh	Kilowatt hours
l	Liters
lb	Pounds
lph	Liters per hour
lps	Liters per second

ABBREVIATIONS AND SYMBOLS (continued)

lpm	Liters per minute
m	Meter
m^2	Square meters
mg	Milligrams
mgd	Million gallons per day
m^3/d	Cubic meters per day
mg/L	Milligrams per liter
mls	Milliliters
N	Newtons
Ni	Nickel
N/m^2	Newtons per square meter
O_2	Oxygen
O_3	Ozone
O_3/CN^-	Ratio of ozone added per cyanide removed, weight/weight
ppm	Parts per million
psig	Pounds per square inch guage
rpm	Revolutions per minute
S	Sulfur
SO_2	Sulfur dioxide
scfm	Standard cubic feet per minute
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UV	Ultraviolet radiation
Y	Ozone yield

ABBREVIATIONS AND SYMBOLS (completed)

yr	Years
Zn	Zinc ion
%	Percent
$	Dollars

SECTION I

INTRODUCTION

Chemical oxidation with ozone is an effective method for removing organic constituents from industrial waste streams. Many organic materials which are resistant to other treatment methods can be oxidized by ozone. Cyanide and phenol bearing wastes are two examples where chemical oxidation using ozone may prove advantageous (References 1 and 2). When highly complexed metal cyanide wastes are present, ultraviolet radiation can be used successfully to break down the complexes and speed the reaction with ozone (Reference 3).

This study investigates the use of ozone and ultraviolet light to treat strong cyanide and complexed metal cyanide wastes from electroplating operations at Tinker Air Force Base (Tinker AFB) in Oklahoma City, Oklahoma. A full-scale demonstration plant utilizing chemical oxidation with ozone was designed and constructed at the test site to treat 3,000 gallons per month (11,356 liters/month) of primarily nickel strip wastes with total cyanide concentrations of up to 50,000 milligrams per liter (mg/L). It was designed to operate 24 hours a day five days per week at a flow of 6.25 gallons per hour (gph), i.e., 23.7 liters per hour (lph). The original design goal for the system was no detectable cyanides in the plant effluent. Since start-up, the system was plagued with operational and maintenance problems. The ozone-cyanide plant never achieved its purported cyanide removal efficiencies. Subsequently, the plant was shut down.

In August 1976, the contractor performed a study to determine the efficiency and reliability of the ozone-cyanide system. Upon plant start-up, several operational problems prohibited evaluation of the treatment process. Some of the more significant problems initially encountered include compressor breakdown, oil carry-over into the air stream, inefficient prefilter operation, defective dryer operation, erratic functioning of the ozone generation system, ineffective mixing and transfer, diffuser plugging, excessive foaming, inoperative monitoring equipment and inadequate ventilation.

Subsequently, in August of 1978 the contractor initiated work to correct these and other problems, to redesign and optimize the system, and to test the modified system. This paper details the project work and results.

SECTION II

OZONE-CYANIDE PLANT DESCRIPTION

1. INTRODUCTION

A flow diagram of the ozone-contact system is presented in Figure 1. The system consists of three reactors in series with the required ancillary equipment. The ancillary equipment includes an air preparation system, an ozone generation system, and waste handling equipment. The system description in this section applies to the original components. The modifications made during the project are delineated in subsequent sections.

2. AIR PREPARATION SYSTEM

The air preparation system consists of compressors, dryers, filters, and ancillary equipment. Efficient operation of the ozonators requires a clean, dry air stream. The air is initially compressed to approximately 100 psig ($6.9\text{x}10^5$ N/m^2) with three 25 hp (18.6 KW) screw type compressors, each having a capacity of 100 scfm (47 l/s) at 100 psig ($6.9\text{x}10^5$ N/m^2). Each compressor is equipped with an air-cooled radiator, water cooled after-cooler, and receiving tank.

From the compressors the air passes through a prefilter to a dryer. The cartridge-type prefilter causes oil and water droplets to coalesce and be removed from the air stream. The dryers are self-regenerative and designed to dry the air stream to a dewpoint between -40°F and -50°F (-40°C and -45.6°C).

The air then flows through a cartridge-type filter to remove desiccant dust. Following the after filter a surge tank dampens any pressure-flow fluctuations. The final step in the air preparation is a pressure reducing valve designed to feed the air stream to the ozone generators at the desired 10 to 12 psig operating level.

3. OZONE GENERATION SYSTEM

The ozone generation system consists of six separately controlled modules of Lowther Plate generator cells, 30 cells to a module. The six modules of cells are placed two to a console, each with power control. Each module has a design output capacity of one pound per hour of ozone at an air stream ozone concentration of approximately 1 percent by weight.

4. WASTE HANDLING EQUIPMENT

The concentrated cyanide waste is delivered to the treatment system in portable-wheel-mounted tanks. The waste is transferred to a 1200-gallon (4542 liter) fiberglass storage tank. From the storage tank the waste is

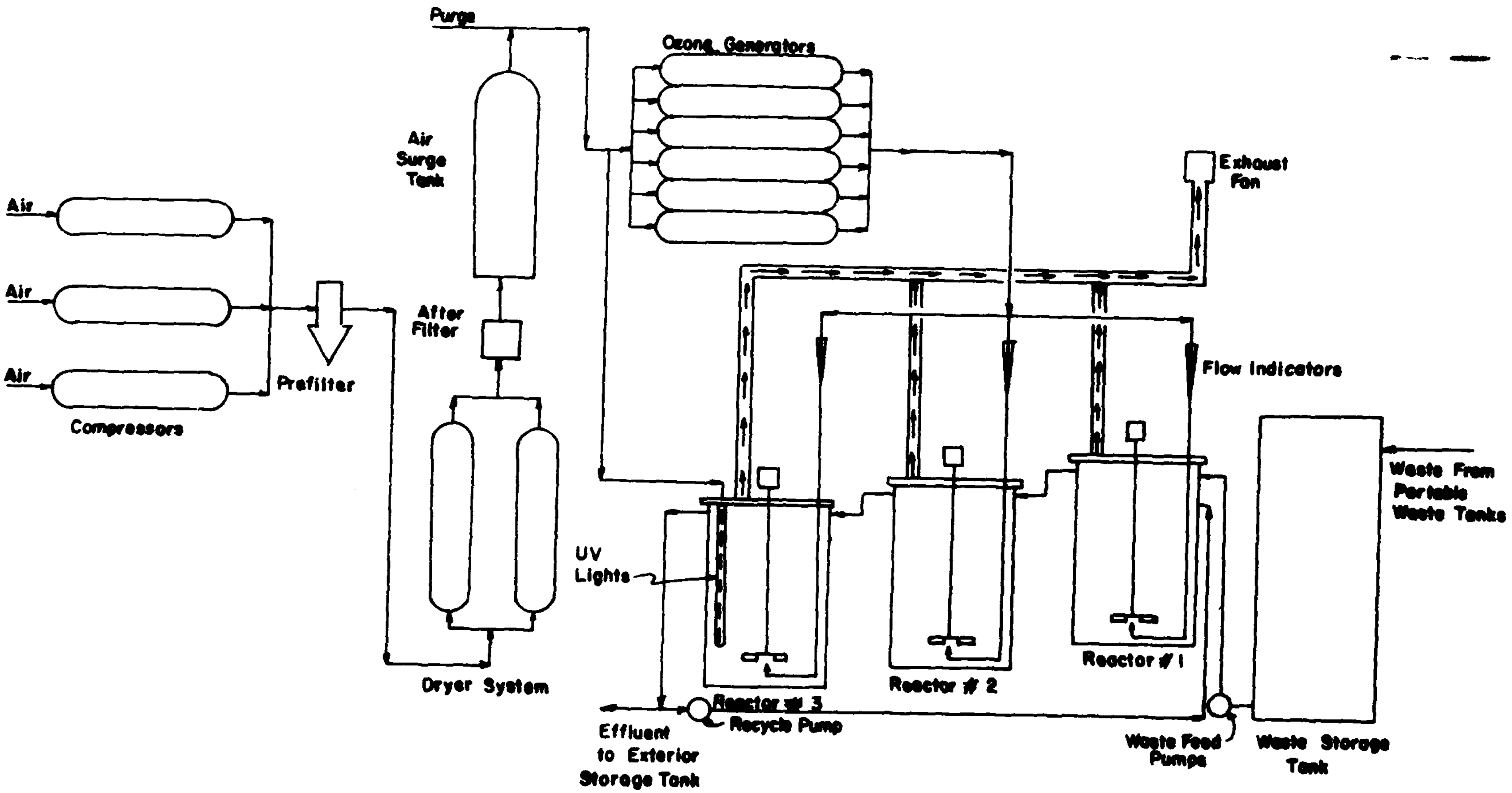

Figure 1 Flow Diagram For Cyanide Treatment Plant

pumped to the first reactor by adjustable flow-metering pumps. The waste flows from reactor 1 through reactors 2 and 3 by gravity. The reactors are 52 inches (132 centimeters) in diameter and at the 44-inch (112 centimeters) operating depth hold 400 gallons (1514 liters) of waste. The overflow from reactor 3 is piped to outside, underground storage tanks for subsequent final treatment through the industrial waste treatment facilities.

5. OZONE CONTACT SYSTEM

The air-ozone mixture is injected into the bottom of the reactors through porous diffusers. Each was originally equipped with a 3 hp (2.23 KW) mixer with 11-inch (28 centimeter), 6-bladed impeller. Design air flow rates to reactors 1, 2, and 3 are 112 scfm (53 l/s), 35 scfm (16.5 l/s), and 19 scfm (9 l/s) at 12 psig (82,740 N/m^2) respectively.

Gas escaping from the liquid surfaces in the reactors is collected in a ventilation system of PVC (Poly Vinyl Chloride) pipe and exhausted to the atmosphere by an electric-powered polypropylene fan.

Reactor 3 is equipped with two ultraviolet lamps placed in corex glass-wells. The ultraviolet (UV) lights are 42 inches (107 centimeters) long and rated at 4500 watts each.

SECTION III

LITERATURE REVIEW

1. OZONATION--THE PROCESS

Ozone is the triatomic form of oxygen (O_3) and is a very powerful oxidizing agent. Ozone is a highly unstable molecule and has a high tendency to revert back to the diatomic state (O_2). Ozone's principal virtue is that it is the most powerful oxidizing agent readily available to man. Only fluorine, fluorine oxides, and certain short-lived free radicals and atoms exhibit greater oxidizing power. Comparative oxidizing potential of water disinfectants has been calculated as: Ozone 2.5, chlorine 1.3, chlorine dioxide 1.25, and chloramine 0.9. In concentrations of a few ppm in water, ozone literally "burns out" a wide range of organic and oxygen-receptive, inorganic substances, such as bacteria, viruses, algae, cyanide, soluble ferrous and manganous salts, sulfides, sulfites, detergents, phenols, and oils. Its action is more rapid and thorough than that of comparable agents such as chlorine, and it disappears from water, leaving no aftertaste, odor, or residual, in less than half an hour (Reference 4). Ozonation is an excellent process for quickly destroying taste and odor-producing, organic substances, oxidizing manganese and iron, and sterilizing. It will accomplish reactions in 10 minutes that free residual chlorine requires hours to complete (Reference 4).

Ozonation has several advantages over other oxidation processes. According to Rosen (Reference 6), ozone has twice the oxidizing potential of the hypochlorite ion; and therefore, more complete oxidation can be expected from ozonation than from chlorination. One reason for this is that, unlike chlorine, ozone does not always have to be in solution before reacting. He states that in the case of disinfection, some evidence exists that the lysing reaction occurs between nascent ozone and the microorganisms. Other advantages are high residual dissolved-oxygen concentration in the effluent and oxidized products that are less toxic than chlorinated or unoxidized products (References 5, 6 and 7). Since ozone is generated on-site, no storage or handling of chemicals is required. Ozone reacts readily with unsaturated organic compounds and compounds possessing phenolic, aldehyde, cyanide, thiol, sulfide, and amine groups. The ozonation process lends itself to a continuous, automatic, tightly controlled operation; therefore, a relatively low capital cost, easily operated system with low maintenance requirements can be obtained (Reference 5).

Ozone has been used in many applications. These include: disinfection, reduction in BOD and COD from secondary effluents, oxidation of secondary sludge organics, odor control, complete physical/chemical treatment of primary effluent from municipal wastes, disinfection of combined stormwater overflows, and treatment of dye and phenolic wastes.

Ozone is the most rapid and effective agent available for the destruction of viruses in potable water treatment. In one study, the ozone dosage required to meet a standard of 200 fecal coliforms/100 mls ranged from 6 to 14 mg/L

(Reference 8). Data show that during this investigation, f_2 viruses were completely destroyed by ozone after a contact period of approximately 5 minutes. The bacteriophage f_2 was selected as a model virus by the investigators.

1.1 Ozone Generation

Ozone is produced when high-voltage alternating current is imposed across a discharge gap in the presence of an oxygen containing gas. This strongly endothermic reaction is accompanied by a rising temperature. Only about 10 percent of the energy supplied is used for ozone production; the remainder is lost primarily as heat. The reaction is temperature dependent. High temperatures cause rapid deterioration of the ozone-yield, and the dielectric characteristics can be effected to the point of causing failure. Also, at high temperature, the rate which ozone reverts back to oxygen is greatly accelerated. Therefore, an efficient heat transfer and removal system is imperative (Reference 7). The factors that effect ozone production are:

1. Dryness of air.
2. Power applied to electrodes.
3. Rate of air flow across electrode surfaces.
4. Pressure of air within ozonizer.
5. Frequency of electrical supply.
6. Temperature of the discharge gap.

Other factors being equal, the rate of air flow across, and the power applied to, the electrodes determines the concentration of ozone in the air stream and the quantity produced over a given period (Reference 9).

It is important that the gas stream be dry because ozone decomposition is accelerated by the presence of moisture. In addition, nitrogen in the gas stream can combine with oxygen, ozone, and water in the corona to produce nitric acids, which can damage the ozonator and further reduce ozone yields.

The composition of the oxygen containing feed-gas also has an effect on ozonator efficiency. Two to two-and-one-half times as much ozone can be produced from a stream of 100 percent oxygen as from a stream of air.

Variation in voltage affects the ozone yield (Y) and the useful life of the generator. The ozone-yield per area of electrode surface under optimum condition is calculated as follows (Reference 6):

$$Y/A \quad \frac{f \varepsilon V^2}{d}$$

Y = Ozone yield.
V = Voltage across the discharge gap (peak volts).
f = Frequency of the applied voltage.
ε = Dielectric constant.
d = Thickness of the dielectric.
A = Area of electrode surface.

As is evident from the equation, voltage variation is important because ozone-yield varies as the second power of the voltage.

1.2 Ozone Contacting System

Ozone-transfer to a water system requires a more elaborate system than does the more conventional oxidant chlorine. When chlorine gas is used for wastewater treatment, chlorine reacts rapidly with water resulting in homogeneous mixture that can easily be dispersed throughout the water under treatment. The ozone-air or oxygen mixture cannot be made into a solution. Therefore, it is necessary to form a gas-liquid emulsion between the water and the ozonated gas if high transfer rates are to be achieved. Several mechanisms or methods for gas-liquid contact have been tested. These include: gas injection systems, turbine mixers, porous diffusers, static mixers, film layer systems, hydrostatic injectors, vortex propellors, air dispersing impellers, liquid-circulating impellers and packed beds or columns (References 10, 11, and 12). The contactor is probably the most important component of the ozonation system in regards to the rate of gas transfer. The choice of the gas contactor is, or should be, dictated by the types of reactions to be promoted. Just as every wastewater is different so must the contactors be different. Rosen states that to design the contactor, the following must be considered (Reference 6):

1. The purpose of the system--disinfection, BOD or COD reduction.
2. Relative rates of possible competitive reactions--chemical oxidation, lysing bacteria, decomposition of ozone in aqueous solutions.
3. Mass transfer rates for ozone from gas to wastewater.
4. Characteristics of the wastewater--total SS, organic loading, pH, temperature.
5. Total operating pressure of the system.
6. Concentration of ozone used.
7. Contactor type--packed bed, sparged column, or sparged column with mixing.
8. Extent of treatment to determine number of contact stages--all stages may not be the same type.
9. Methods of gas dispersion and mixing within stages.
10. Configuration of contactors.
11. Points of gas-liquid contact.
12. Cocurrent or countercurrent mixing.

1.2.1 Materials of construction

Linde Division of Union Carbide Corporation studied the oxidative purification of secondary effluent with ozone. In their system, oxygen-containing ozone was fed into the injector to simultaneously affect complete mixing of the two phases and to induce high shear contact for improved mass transfer. They stated that adding the ozone to the effluent while in the injector gives a high mass transfer rate and high shear contacting at lower cost than with turbine agitation. This technique according to Linde has roughly doubled the rate of COD and TOC reduction (Reference 13).

Nebel et al., (Reference 8), in a study of ozone disinfection of secondary effluents using a static mixer to inject ozone rapidly into the Fort Southworth secondary effluent, found that disinfection occurred within 3 to 8 seconds, indicating extremely high rates of mass transfer.

Bowers (Reference 10), reported on three types of dispersion methods--gas injection systems, turbine mixers, porous diffusers and Film Layer Purifying Chamber System (FLPC). Table 1 summarizes the comparative merits of each system.

TABLE 1. COMPARISON OF OZONATION PROCESSES

Process	Type	Ozone Dose mg/liter	Power kwh/kg O_3	Comments
Otto	Total injection	2-3	---	Original European system--introduced 1930. High ozone losses 16%. Disadvantage is the cost of pumping water to top of contact tower.
Chlorator	Partial injection	10-20	10	Introduced 1955 as pilot plant 3/4 mgd (2838 m^3/d) scale. High ozone dosage made process uneconomic.
Van der Made	Diffuser	2-3	13	Original European system--introduced 1930. Ozone losses 16% but still a very common system--low concentration cost. Used in Philadelphia in 1957 for 26 mgd (98,410 m^3/d) installation.
Kerag	Emulsion Turbine	5	27	Introduced 1955 as pilot plant 3/4 mgd (2838 m^3/d) scale. Ozone losses 0.06%--excellent system but complex construction causes high cost.
FLPC	Liquid spray through ozone	---	---	1971 process-modular concept, may be installed direct in sewer lines resulting in low capital cost. Only operated on pilot scale to date.

Masschelein et al. (Reference 14) studied several techniques for dissolving and dispersing ozone in water. They stated that systems with circulating water were the most efficient among those examined, which included: porous diffusers, total injection system, Kerag System, helix-propeller, air-dispersing impeller, and a liquid-circulating aeration turbine.

Dissolution by forcing the ozonated gas through porous pipes placed at the bottom of a contact chamber is a widespread method for dispersing of ozone in water. For this system, ozonated-air can be injected into the chamber either cocurrently or countercurrently. The average residence time in each contact chamber for the system is approximately two minutes. The injection depth is at least 4 to 5m (13 to 16 ft). Pore openings of the diffusers range from 50 to 100 microns. The diffuser capacity ranges from 20 to 50 m^3 air/h/m^2 (66-164 ft^3/h/ft^2) porous surface. Countercurrent injection appears to be more effective than cocurrent injection. Ozone losses for countercurrent injection range from 10 to 15 percent.

The total injection system has been used in France since 1906. In this system the ozonated air is dispersed into the water at the top of a column. If an initial downflow velocity of more than 40 cm per second (1.3 fps) is attained, the air bubbles sink with the water flow. Dissolution is reached during this phase which is followed by a retention phase for action of the residual ozone. Percent losses vary from 2 to 8.3.

In the Kerag System, ozone is injected through a propeller just under the surface of the water. This system affects instant action of the ozonated air bubbles with the water rather than the delayed action of a residual ozone concentration. Ozone losses range from 20 to 30 percent. The method can be adapted to preozonation.

The helix-propeller is immersed to one-third of the vessel's depth, and a vortex is created by the rotation of the propeller at an appropriate velocity. The movement imparted to the liquid enables direct dissolution of ozone by swirling of the ozonated air into the vortex zone. The ozone losses amount to less than 10 percent. The major disadvantage is that it requires an appropriate regulation of the ozonated air pressure to the water flow in order to maintain a stable vortex. A destabilization of the vortex can cause a loss of the dissolving action, resulting in a sudden release of ozonated air.

An ozone injection system with a water recirculating impeller received only minimal coverage. In this system, contact time plays an important part in ozone dissolution and greatly influences the efficiency of the treatment. One to two recirculations of water were accomplished. As a consequence, two to three contacts of the water to incoming air result. The advantages of the process are:

1. Intimate contact of the water with the incoming ozonated air.
2. The yield of dissolution is good, and the recirculating process promotes concentrated-ozone-bubble water contact.

Studies were also performed using an air-dispersing impeller. In this system, ozone is injected into water flowing through baffled chambers. The average residence time in each chamber is two minutes. The impeller is placed five meters (16 ft) under the water level in the ozonation compartment. Total ozone loss from this system is between 10 and 15 percent. One big advantage of the process is its relatively low energy consumption.

A liquid-circulating aeration turbine was another method investigated (Reference 14). The turbine consists of a water circulating mill-wheel that mixes the ozonated air into the circulated water, and permits normal operation in the range of 50 to 170 percent of its total capacity. If less air is admitted to the system, more water is circulated. The advantage of the system is the excellent performance of the dissolution even when high residual ozone concentrations exist.

1.3 Gas Transfer

Ozonation is a transfer process requiring the efficient transfer of the maximum amount of ozone from the gas phase into the liquid phase. The film theory is commonly used to explain this process. Figure 2 shows this model.

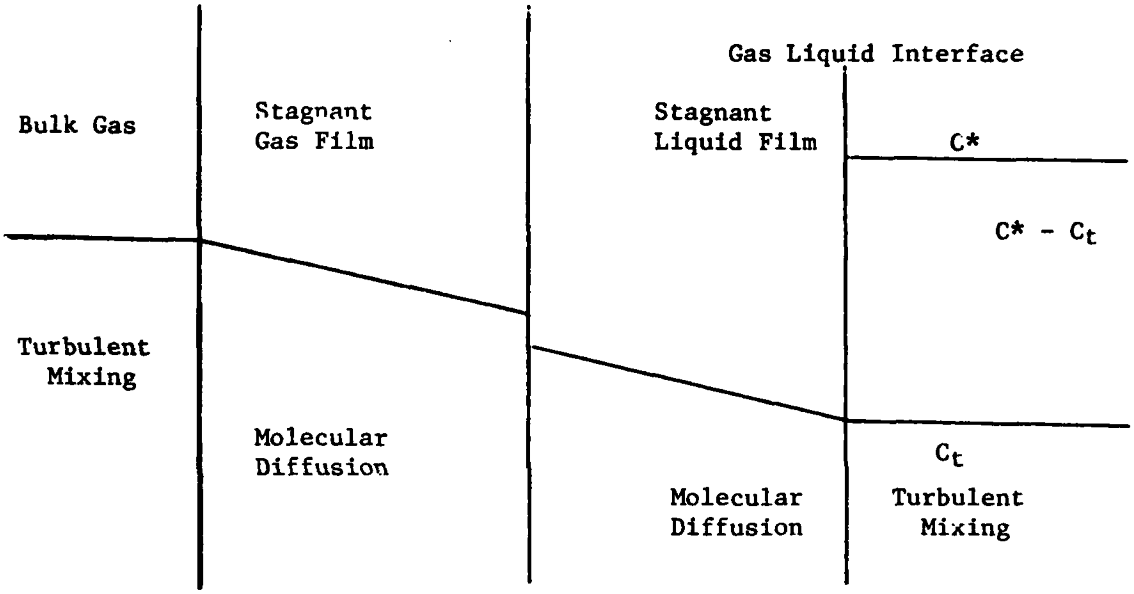

FIGURE 2. Film Theory Model

Ozone molecules are transferred to a liquid when the concentration in the liquid (C_t) is less than the concentration (C^*) in equilibrium with the partial pressure in the gas. Ozone molecules from the bulk-gas phase are continuously transferred to the stagnant gas film by turbulent mixing or eddy diffusion. Through molecular diffusion, they reach the gas-liquid interface where they dissolve into the stagnant liquid film. Finally, the ozone molecules diffuse through the liquid film and are transported to the bulk liquid by turbulent mixing.

The rate of ozone transfer by molecular diffusion is slow compared to turbulent mixing; therefore, the rate of transfer is controlled by the stagnant films. The rate of transfer across the stagnant films and into the liquid, when the ozone concentration in the liquid remains fairly constant, can be estimated on the basis of steady state conditions. For these conditions the following equations apply.

$$N = K_L a\ V\ (C^* - C_t) = K_G a\ V\ (\overline{P} - P^*) \qquad (1)$$

$$N + K_L A\ (C^* - C_t) = K_G A\ (\overline{P} - P^*) \qquad (2)$$

where

N = Rate at which ozone is transferred between phases (kg/hr).
$K_L a$, $K_G a$ = Overall volumetric mass transfer coefficient, liquid- and gas-phase basis respectively.
V = Volume of the system (1).
A = Area across which diffusion is taking place (m^2).
C_t = Concentration of ozone in the liquid phase (kg/1).
$\overline{P}$ = Partial pressure of ozone in the gas phase (N/m^2).
C^* = Equilibrium concentration corresponding to the partial pressure of ozone in the gas phase (Kg/1).
P^* = Equilibrium partial pressure corresponding to the concentration of ozone in the liquid phase (N/m^2).

If one studies the components of the mass transfer rate equations, the design parameters are apparent. For optimum reactions or transfer rates, a large interfacial surface area to gas-volume ratio must be developed. This ratio maximizes the diffusion area and can be accomplished by generating many small bubbles. In non-agitated vessels, the ozone transfer rate is a function of reactor depth. For agitated vessels, it is a function of the bubble retention time. Turbulence reduces the thickness of the stagnant film thereby decreasing the resistance to transfer and increasing the transfer rate. Turbulence is controlled by gas flow rates and by mixer power input. Another variable which controls the transfer rate is the ozone concentration gradient or the difference between the equilibrium concentration of ozone in the liquid phase (corresponding to the partial pressure in the gas phase) and the concentration in the liquid phase ($C^* - C$).

1.4 Mixing or Dispersion (Reference 15)

In gas-liquid dispersion operations, the size of the bubbles, and therefore the total interfacial area between the dispersed and continuous phases, vary with conditions and degree of agitation. New surface area must continually be created against the force of the interfacial tension, since bubbles are always coalescing and being redispersed. In most gas dispersion operations, bubbles rise through the liquid pool and escape from the surface. They must therefore be replaced by new ones.

In this dynamic situation the volume of gas held-up in the liquid pool is also a variable, depending upon the rate-of-rise of the bubbles and the volumetric feed rate. Statistical averages are used to characterize the system, since the hold up, interfacial area, and bubble diameter all vary with time and spacial location in the vessel.

Gas is normally fed to a reactor through the open end of a submerged pipe, perforated pipe, sparger, or porous ceramic or metal plate. In some systems the gas flow provides sufficient mixing while for others, a motor-driven turbine-impeller is required to adequately disperse the gas and circulate the liquid through the reactor.

For low gas holdups ($Z < 0.15$) the following empirical equations apply for dispersion into pure liquids by a six-bladed turbine impeller: The average bubble diameter $\overline{D}_s$ (Sauter mean diameter) in millimeters is given by:

$$\overline{D}_s = \frac{4.15\ (\sigma)^{0.6}}{(P/V)^{0.4}\ \rho_L^{\ 0.2}}\ Z^{0.5} + 0.9 \qquad (3)$$

$\overline{D}_s$ = Average bubble diameter (mm).
σ = Interfacial tension (g/s^2).
P/V = Power input per unit volume (g/mm - s^2).
ρ_L = Density of liquid (g/mm^3).
Z = Gas holdup.

The interfacial area a' (mm^{-1}) is given by:

$$a' = \frac{1.44\ (P/V)^{0.4}\ \rho_L^{\ 0.2}}{(\sigma)^{0.6}}\ (\overline{V}_s/Y_t)^{0.5} \qquad (4)$$

$\overline{V}_s$ = Superficial velocity of gas (m/s).
Y_t = Bubble rise velocity (m/s).

Combining Equations (3) and (4) leads to the following equation for Z:

$$Z = (\overline{V}_s Z/Y_t)^{0.5} + \left(\frac{0.216\ (\rho/V)^{0.4}\ \rho_L^{\ 0.2}}{(\sigma)^{0.6}}\right)(\overline{V}_s/Y_t)^{0.5} \qquad (5)$$

If the gas throughput to a turbine-agitated vessel is progressively increased, a point is eventually reached at which the impeller floods. If the gas flow is then reduced somewhat, the agitator begins to circulate the liquid and disperse the gas; this point is known as the redispersion point. The flow number N_Q,g, based on the gas flow rate q_g at the redispersion point, has been correlated by the Froude number to give:

$$N_Q,g = \frac{q_g}{n\ D_a^{\ 3}} = 0.194\ N_{Fr}^{\ 0.75} \qquad (6)$$

where

q_g = Volumetric gas flow rate (m^3/h).
n = Rotational speed (r/h).
D_a = Diameter of impeller (m).

$N_{Fr} = \frac{n^2 D_a}{g}$

g = Gravitational acceleration.

The power number $N_{p,g}$ at the redispersion point when N_{Fr} is between 0.2 and 1.0 has been found to be:

$$N_{p,g} = \frac{P_g g_c}{n^3 D_a^5 \rho_L} = 1.36 N_{Fr}^{-0.56} \qquad (7)$$

where

g_c = Newton's-law proportionality factor.

P_g = Power at gas redispersion point.

Equations (3) through (7) provide a basis for design of turbine agitated vessels for gas dispersion.

2. OZONATION OF CYANIDE WASTES

Tyler R. G. et al. (Reference 16) carried out experiments on ozonation of cyanide wastes. Wastes studied were cadmium cyanide solutions from one of the plating tanks of the Boeing Airplane Company. Cyanide content varied from 7.5 mg/L to 50.0 mg/L, with a pH range of 9.25 to 10.16. The studies were small scale using a laboratory-mode ozone generator. Ranges in ozone-applied/cyanide removed ratios (weight/weight) of 1.40/1 to 1.96/1 were reported. The authors found that most of the cyanide was oxidized rapidly as indicated in the typical test results shown in Table 2.

TABLE 2. RELATIONSHIP OF OZONE USED TO CYANIDE OXIDIZED
(Quantity = 1500 ml at 46 ppm CN^-)

Application Time (minutes)	Cyanide (CN^-) (p.p.m.)	pH	Ozone Used (grams)	
0	46.0	10.16	0	
5	7.0	8.2	0.0738	
8	2.8	7.5	0.118	Ozone
10	1.15	7.47	0.148	appeared in
15	0.92	7.40	0.222	air exhaust

The authors speculated that the change in reaction rate which occurred at the appearance of ozone in the exhaust air, was the point at which oxidation of the cyanate began. They postulated the following equations to describe the ozone/cyanide oxidation process:

$$2\ KCN + 2O_3 \rightleftharpoons 2\ KCNO + 2O_2$$

$$2\ KCNO + H_2O + 3O_3 \rightleftharpoons 2\ KHCO_3 + N_2 + 3O_2$$

$$2\ KCN + H_2O + 5O_3 \rightleftharpoons 2\ KHCO_3 + N_2 + SO_2$$

The authors concluded the following:

1. Cyanide wastes from metal treating industries can be satisfactorily and economically treated by ozonation.
2. The efficiency of the process is improved by maintaining the pH between 11.0 and 12.0 at the beginning of the treatment to allow complete oxidation to cyanate before the pH drops below 8.0.
3. Cyanide is oxidized by ozone through cyanate to nitrogen gas and bicarbonate.

Khandelwol, Bardunn, and Grove (Reference 17) investigated rates of oxidation of cyanide solutions by ozonized oxygen. The reaction rate constant more than doubled when copper II ions were added as a catalyst. Further increases in copper II concentration did not markedly effect the reaction rate. Also, the rate was not effected by copper sulfate, nitrate, acetate, sulfide, or by temperatures from 13°C to 30°C (55°F and 86°F). The following rate equation was given to quantify the ozonation of cyanide based on cyanide disappearance:

$$\frac{-d\ CN^-}{d\ t} = K\ [CN^-]^{\frac{1}{3}}$$

where

CN^- = Concentration (mg/L).
t = Reaction time (min.).
K = Reaction rate constant.

During the lab tests the concentration of the ozone in the gas phase was varied from 70 to 90 mg of ozone per liter of oxygen. Cylinder oxygen was used as feed gas to the generator. Feed solutions were made with potassium cyanide and initially contained 100 mg/L cyanide (CN^-).

Selm (Reference 18) reviewed the chemistry of ozonation of cyanides and cyanates, studied mass transfer kinetics using a laboratory scale column, and discussed the disadvantages of using chlorine for cyanide oxidation. He reported that the ozonation of cyanides involves two separate steps, i.e., oxidation of cyanide to cyanate, with subsequent destruction of the cyanate by either oxidation or hydrolysis. He concluded that the mechanisms of destruction of the cyanate ion were not well understood and that the predominate mechanism could not be identified. He found that, contrary to past reports, ozone could oxidize ferrocyanides, first to ferricyanides and then to ferric hydroxide sols. Selm also performed laboratory scale investigations of ozonation of the free cyanide ion using a borosilicate glass column 4 inches (10 centimeters) in diameter packed with 1/4-inch (0.6 centimeter) ceramic Intalox saddles. He reported that the oxidation of simple cyanides by ozone was rapid and complete, with the mass transfer of ozone into the liquid controlling and therefore, recommended the use of packed towers to provide adequate mass transfer time and surface area. Selm felt that a countercurrent absorbtion tower would provide more intimate contact and better mass transfer than a stirred batch reactors.

The following disadvantages of chemical oxidation using chlorine were discussed by Selm:

1. Chlorine must be used in considerable excess, 8 lbs. of chlorine per lb. of cyanide.
2. The use of excess chlorine may result in residual free chlorine which is toxic to biologic life in the receiving stream.
3. Chlorine is expensive. Freight and handling charges; chlorine equipment, loading equipment, feeders, dechlorination equipment, retention tanks, railroad spurs, storage rooms, and similar costs must be considered when comparisons are made.
4. Ozone is a more efficient oxidant than chlorine.

Studies of cyanides and cyanates were conducted at the chemical laboratory of the VODGEO Institution (Reference 19). The purpose of these studies was to determine the possibility of using ozonation for the purification of effluents containing cyanide compounds (Reference 19). The authors concluded that cyanide, at concentrations of 3-4 mg/L, is easily oxidized with ozone. The process is independent of pH within the 10.5 to 12 range, but the oxidation of cyanate is much slower with the maximum rate occurring at pH 12. Completed zinc cyanates are oxidized to simple soluble cyanides, while complexed copper cyanides are oxidized more easily, despite their higher stability (apparently due to secondary oxidation of cyanide by the copper ion). A similar phenomenon is observed in the ozonation of complex nickel cyanides. Hexacyanoferrates (II) are rapidly oxidized to hexacyanoferrates (III), but the latter are oxidized only slowly. Complex cobalt cyanides are resistant to oxidation with ozone. Finally, the authors concluded that ozonation as a purification method is simple, easily controlled, and lends itself to full automation. The purified effluent does not become contaminated with residuals, e.g., as occurs with hypochlorite.

Tests carried out in France on an effluent from a large metal finishing factory (Reference 20) showed that 25 mg/L of cyanide was destroyed with 80 to 90 mg/L of ozone. The test results showed that total destruction of cyanide is easily obtained, and that the process is economical when compared with other processes. Further, it was determined that the ozone/cyanide ratio decreased when both the concentration of cyanide increased and when the concentration of ozone in the air stream increased. Also, the mass of ozone escaping from the reactor decreased when the concentration of ozone in the air stream increased. The author found that 1 1/2 parts of ozone are required for the complete oxidation of each part cyanide.

Garrison et al. (Reference 21) performed lab and prototype-scale ozonation tests on actual Air Force plating and photographic wastes. The plating wastes consisted of "Melex" nickel strip, copper and cadmium. The photographic wastes consisted of ME-4 ferricyanide bleach and fixer. Table 3 presents analyses of the wastes studied.

For the lab-scale studies, a batch reactor with a 5.85 liter capacity was used. The reactor was provided with a variable speed mixer allowing power input variations through the range of 1 to 30 horsepower per 1000 gallons of solution.

An ozone generator capable of providing an ozone concentration of 0.5 percent to 10 percent by weight was used. The treatment characteristics of the system were studied by varying waste concentration, ozone concentration and feed rate.

The results of several lab-scale tests are summarized in Table 4. In Test 2, undiluted nickel strip cyanide waste (initial cyanide concentration 40,000 mg/L) was ozonated for 12 hours. After 12 hours, the cyanide concentration was reduced to 60 mg/L with 3.5 grams of ozone per gram of cyanide. The test was terminated after 26 hours (final cyanide concentration of 54 mg/L, final ozone/cyanide ratio 7.6 grams of ozone/gram of cyanide). Very little change in the cyanide concentration was noted during the last 14 hours (Figure 3). The authors concluded that the iron complexes slowed the reaction rate after 8 hours. The results of Test 3, run on a sample of nickel strip waste diluted with tap water are shown in Figure 4. The ozone usage was about 3.4 grams of ozone per gram of cyanide destroyed. In this test 8 additional hours of ozonation at temperature of 150°F (65.5°C) decreased the cyanide concentration to 0.26 mg/L (an additional ozone usage of 6,180 grams of ozone per gram of cyanide destroyed).

Test No. 5 depicts results obtained for full-strength copper-plating wastes. Again, further ozonation did not decrease the cyanide concentration. This residual was also explained by the cyanide complexed with iron. Diluted copper-plating wastewater was ozonated in Test No. 6 for 2.5 hours resulting in more than 99 percent removal of cyanide. At this point in the test, however, the reaction slowed and 16.5 additional hours of ozonation only reduced the cyanide concentration to 4 mg/L. An additional 19 hours of ozonation in the presence of UV radiation reduced the cyanide concentration to 0.36 mg/L.

Test No. 7 was performed on diluted photographic fixer wastes. The reaction was very slow and the ozone to cyanide ratio extremely high, indicating the stability of the iron cyanide complexes. The same results occurred in Test No. 8 for bleach cyanide wastewater.

Further tests on the bleach cyanide waste indicated that UV radiation could speed the reaction rate. In Test No. 9 (Table 4), three UV bulbs at 4 watts each were used. The reaction rate in the presence of UV light was much faster than the reaction rate using 1 percent ozone without UV light.

Further continuous-waste-feed tests were performed using a three stage prototype system. Each reactor was 12 inches (30.5 centimeters) in diameter and 16.5 feet (5 meters) tall. Six-15 watt UV lamps were mounted in each stage. Mixing was accomplished by a six-bladed disc impeller. A constant 10 hp/1000 gallons power-input was maintained. The system was designed to treat 15 gallons per day (gpd) of waste containing 4000 mg/L of cyanide. Typical of results was the run using nickel strip waste diluted to 4000 mg/L. For the test, 2.1 pounds of ozone were added, and 0.501 pounds of cyanide removed per day at equilibrium. This yeilded an O_3/CN^- ratio of about 4.0. The discharge contained less than 0.1 mg/L cyanide.

Some of the conclusions noted by the authors were:

1. In reactions with concentrated wastes, the rate of oxidation of the waste is limited by the rate at which ozone is transferred from the gas phase to the liquid phase, but in reactions with dilute wastes the rate of oxidation of the waste is limited by the chemical reaction rate.

TABLE 3. PROPERTIES OF ACTUAL AIR FORCE CYANIDE WASTES (Reference 21)

	Plating Wastes			Photo Wastes		
Property	Cadmium	Copper	Nickel Strip	Bleach	Fixer	
Total Cyanide (mg/L)	51,000	41,000	40,000	72,200	7,000	
pH	13.0	13.0	13.0	8.2	7.8	
Color	lt. yellow	none	dk. yellow	yellow	lt. yellow	
Metal Analysis (mg/L)						No. of Cyanide Ions Complexed with Each Metal
Iron	1,397	89.5	36.4	28,530	2,853	6
Cadmium	24,900	8.4	5.2	---	---	4
Copper	451	37,757	16.7	---	---	3
Nickel	317	21	1,755	---	---	4
Zinc	74	1.4	12.8	---	---	4
Chromium	5	2	1	---	---	4
Cobalt	3.4	2	5.9	---	---	4
Cyanide Complexed with Iron (calculated from iron content)						
mg/L	3,906	250	102	79,760	7,976	
% of total	7.66	.61	.26	100	100	

TABLE 4. SUMMARY OF SELECTED TEST RESULTS

Waste Tested	Test Ref. #	Initial CN^- (mg/L)	Initial pH	% Ozone by wt.	Final CN^- (mg/L)	Ratio of Ozone added Per Weight of CN^- Ion at Test Termination	Test Time Hours
Nickel Strip	1	65	10.8	1	< 0.7	3.0	--
Nickel Strip	2	40,000	13.0	5	60	3.0	12
Nickel Strip	3	3,200	11.8	3	20	3.4	12
Copper Plating	4	400	10.5	1	< .2	2.5	--
Copper Plating	5	41,000	--	5	180	2.4	8.5
Copper Plating	6	3,700	11.5	5	21	3.0	2.5
Fixer Waste	7	6	7.6	3	0.5	> 500	5.0
Bleach Cyanide	8	6	6.8	1.2	1.3	> 200	7.0
Bleach Cyanide	9	53	--	1.0	< .3	22	7.0

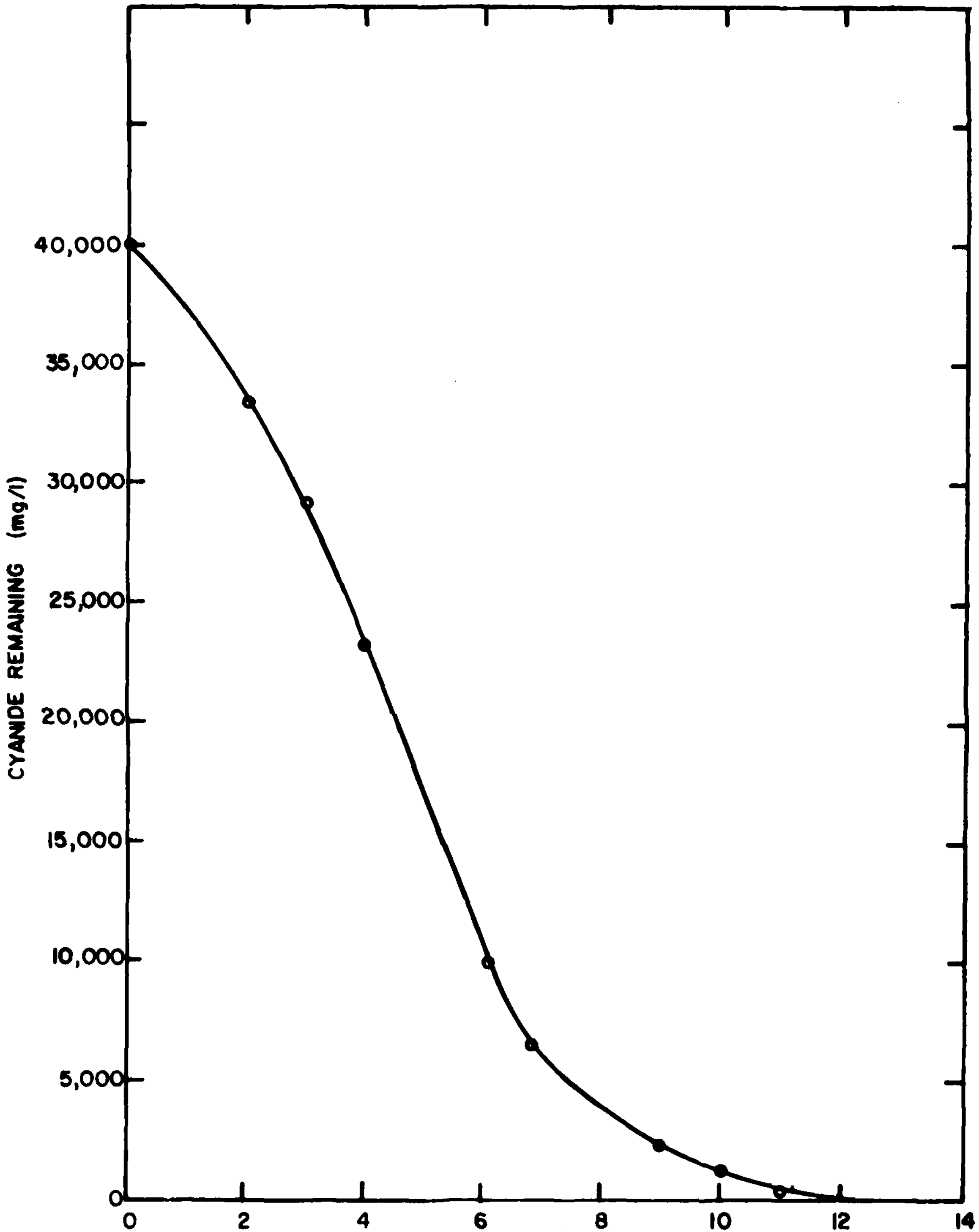

Figure 3 Ozonation of concentrated Nickel Strip Waste

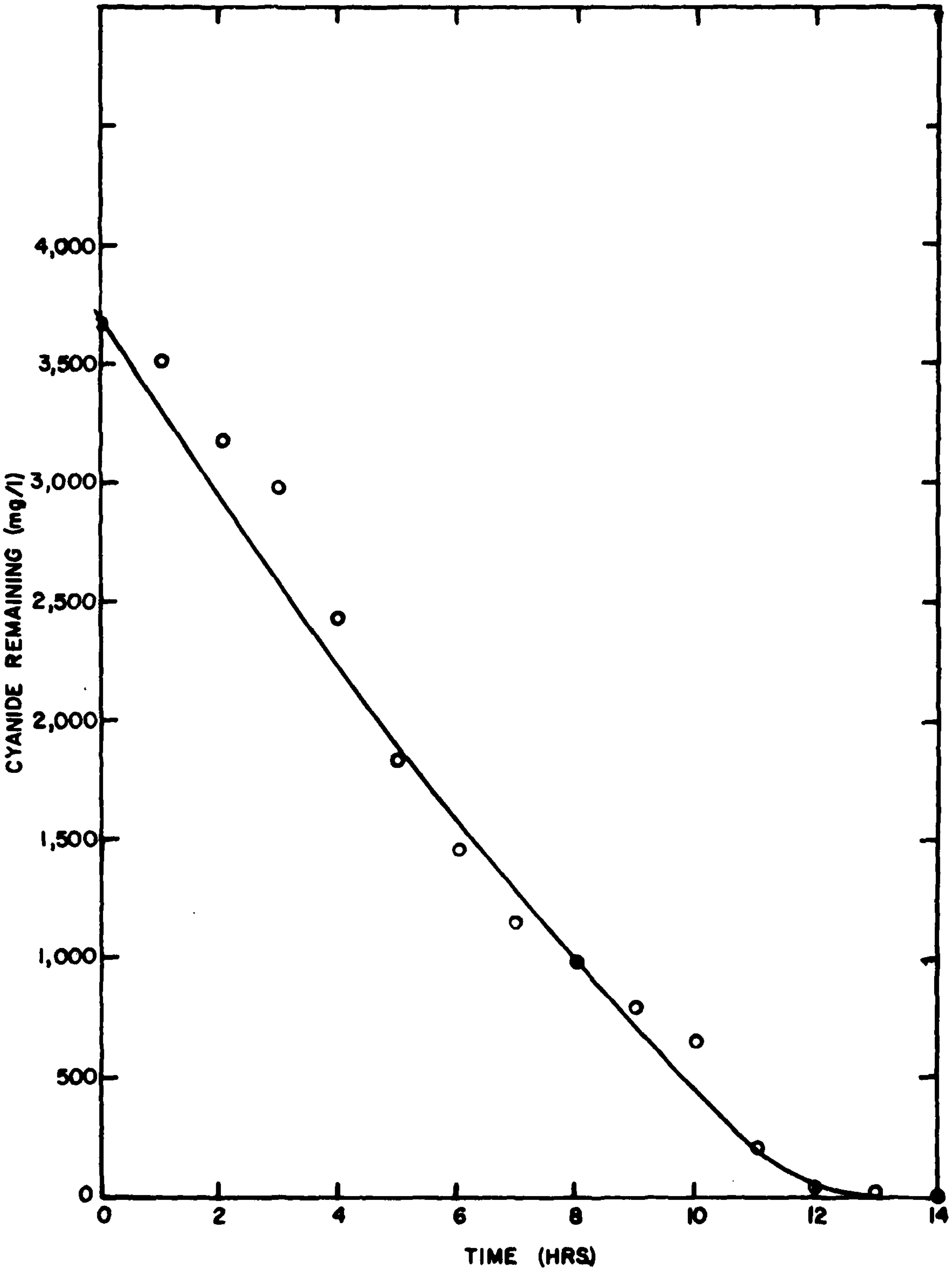

Figure 4 Ozonation of Medium Concentration Nickel Strip Waste

2. The staged ozone-reactor with UV is extremely effective in treating refractory compounds in wastewater such as ferricyanide complex.

3. The maximum reaction rate of ozone with iron cyanide occurs at pH 7.

4. Neither copper nor silver catalysts had any beneficial effect on the ozone cyanide process.

Bollyky (Reference 22) reported on an ozone treatment plant built to treat waste from copper, gold and silver plating operations. Two waste streams from the plant were treated: an alkaline cyanide waste stream flow of 6.75 gpm (25.6 L/min) containing a maximum concentration of 60 mg/L cyanide and an acid waste stream, waste flow 16 gpm (60.6 L/min) containing no detectable cyanide. The system consisted of an equalization tank, and one ozone reaction-tank for the pretreatment of the alkaline cyanide waste. The discharge from this system was flash-mixed with the acid waste and settled before discharge. Porous diffusers were used in the ozone reaction tank for both dispersion and mixing of the ozone feed-gas. No other form of mixing was provided. The ozone generator produced 20 pounds of ozone per day (9.1 kg of ozone/day). The plant was operated intermittently 16 hours per day for two weeks. Data from the first tests indicated that the cyanide concentration could be reduced from 15 mg/L to 0.08 mg/L in the cyanide treatment tank at an ozone dosage of 1 to 1.5 moles of ozone per mole cyanide. The following summarizes the author's conclusions.

1. Optimum ozone dosage was 1 to 1.5 mole O_3/mole cyanide.

2. Optimum pH range was 7.0 to 9.5.

3. Ozone treatment was safe.

4. Ozone treatment rapidly and economically destroyed copper and sodium cyanides.

However, due to many operational problems, the reliability of these results should be carefully evaluated.

3. OZONATION OF PHENOLIC WASTES

Ozonation of phenols proceeds very similarly to ozonation of cyanides. Both constituents are readily oxidized by ozone at comparable rates. Reactions appear to both be catalyzed by similar environments including, for example, high pH and the presence of ultraviolet radiation. Much more work has been done in the area of ozone oxidation of phenolic wastes than ozone oxidation of cyanide wastes. Therefore, a literature review of the history of ozone oxidation of phenolic wastes was deemed appropriate.

Leggett (Reference 23), and Marechal (Reference 24) received patents in 1920 and 1905 respectively on processes utilizing ozone as an oxidant for purifying phenolic wastes.

Niegowski (Reference 25) reported in a paper on the ozonation of phenolic wastewaters that efficient ozone-producing equipment of large capacity became available in the early 1950's making ozone highly competitive in price with other oxidants. In a pilot study, Niegowski found that oxidation with ozone appeared to be an economical method for phenol destruction in a variety of industrial wastes. He concluded that two parts of ozone were required for the total destruction of each part of phenol in laboratory-prepared solutions containing 100 mg/L phenol. The ozone air stream contained 1-2 percent ozone by weight. The same results were repeated for other homologs of phenol, namely O-Cresol and M-Cresol. Further tests on actual coke plant wastes and refinery wastes produced a wide range of ozone-phenol ratios for 99 percent removal of phenols (shown in Table 5). The variation in the ratios reflects differences in the composition of the wastes. Niegowski found a pH of 11.8 to be optimum for phenol ozonation. Complete ozonation of a 1000 mg/L pure-phenolic solution resulted in about 70 percent reduction in chemical oxygen demand (COD) with the production of intermediate products.

TABLE 5. OXIDATION OF PHENOLIC WASTES

Source	Initial Phenols, P.P.M.	Ozone Demand, P.P.M.	Ozone/ Phenol Ratio	Residual Phenols, P.P.M.
Coke Plant A	1,240	2,500	2.0	1.2
Coke Plant B	800	1,200	1.5	0.6
Coke Plant C	330	1,700	5.2	1.0
Coke Plant D	140	950	6.8	0.1
Coke Plant E	127	550	4.3	0.2
Coke Plant F	102	900	8.8	0.0
Coke Plant G	51	1,000	20	0.4
Coke Plant H	38	700	18	0.1
Chemical Plant*	290	400	1.4	0.3
Refinery A	605	750	1.3	0.3
Refinery B	11,600	11,000	1.0	2.5

*This waste contained 2,4-dichlorophenol. Results are expressed as 2,4-dichlorophenol.

In a later paper Niegowski (Reference 26) investigated ozonation of phenols in petroleum wastewaters. For a petroleum wastewater containing 600 mg/L phenols at pH 12, the ozone demand for complete phenol removal was less than one-half of the ozone demand at pH 7. For a refinery waste containing 11,600 mg/L phenol, an ozone/phenol ratio of one reduced the phenol concentration by 99 percent. Further tests on several refinery wastes containing other constituents exerting an ozone demand resulted in an average ozone requirement of about five parts of ozone per part of phenol. Niegowski concluded there were several advantages offered by ozone destruction of phenols, i.e., ozonation added only oxygen to the water, biochemical oxygen demand and chemical oxygen demand reductions accompanied phenol removal, and the toxicity due to phenols was reduced in the same proportion as the removal of phenols.

Hall and Nellist (Reference 27) concluded that ozonation of phenols in coke plant liquors was an efficient process for treating concentrations ranging from 100 to 2000 mg/L. Tests were run on spent liquors, which besides phenol, contained other chemicals oxidized by ozone, such as thiosulphates and thiocyanates. Wastewaters having an average phenol concentration of 1030 mg/L from 13 coke plants were ozonated in a laboratory pilot study. An average Ozone/Phenol ratio of 1.7 (range 0.7 to 2.8) was required to reduce the phenol concentration below 1 mg/L in each wastewater. The initial pH of the liquors averaged 7.5 while the final pH averaged 3.2 after phenol reduction. Further experiments indicated the ozone utilization efficiency could be increased 25 percent by raising the original pH to 10.0 (final pH in the latter tests averaged 7.8).

Labine (Reference 28) described a refinery treatment plant using biological oxidation and ozone for phenol removal. The biological system reduced the phenol concentration from 55 mg/L to about 0.38 mg/L. Ozonation then provided a polishing step, reducing the phenol concentration to 0.012 mg/L before discharge. The plant had to meet an effluent standard of 0.015 mg/L phenol. The design capacity of the system was 300 gpm. Around 190 lb/day of ozone was produced and diffused through carborundum plates for contact in the reactor.

Eisenhauer (Reference 29) performed a series of detailed laboratory studies on the ozonation of pure phenolic solutions. It was convincingly shown that catechol was the first intermediate oxidant product in phenolic ozonation. Further, it was shown that the phenolic degradation rate proceeded according to the following equation:

$$\ln \frac{Po}{Pt} = k \frac{Rt}{F^{1/3}}$$

where

P_o = Initial phenol concentration (mg/L).
P_t = Phenol concentration at time (mg/L).
R = Ozone dose rate (moles of ozone added/initial moles of phenol/minute).
t = Time (minutes).
F = Ozone gas flow rate (L/min).
k = Rate constant [moles phenol/mole ozone/bubble diameter (dm)].

Note: It can be shown the bubble diameter is directly proportional to $F^{1/3}$.

The value of the rate constant k at room temperature was determined to be 0.256. Eisenhauer concluded that the rate of phenol degradation by ozone oxidation could be increased by increasing the ozone concentration in the gas, increasing the gas flow rate, reducing gas bubble size, increasing gas bubble frequency, and increasing gas/liquid contact time.

In a later paper, Eisenhauer (Reference 30) showed that the rate constant k increased from 0.256 at an initial pH of 5.57 (as determined originally) to a value of 0.658 at pH 11.06. Thus, the reaction rate in the ozonation of phenols more than doubled. The major change occurred between an initial pH of 9.14 (k = 0.307) and 11.06 (k = 0.658). Further, within the reaction temperature range of 20°-50°C (68°-122°F) over a range of ozone flow rates and concentrations, there was no significant effect of temperature on the rate of phenol ozonation.

Kroop (Reference 31) found ozone effectively oxidizes phenols at pH values 11.0 to 11.5. Batch and continuous pilot studies indicated that 1.77 lbs ozone/lb phenol and 2.66 lbs ozone/lb phenol respectively, were required to affect 99 percent phenol reduction. Initial phenol concentrations between 2000 mg/L and 3000 mg/L, were measured in phenolic aircraft paint stripping wastewater from Vance AFB. In the continuous flow study, 99 percent phenol reduction was accompanied by 65 percent COD reduction, indicating the likely production of intermediate products. Kroop optimized the ozone dose-rate and pH; however, other optimization alternatives such as contact systems, temperature and UV radiation were not evaluated.

Pengle, Mauk and Payne (Reference 32) reported on UV/ozone oxidation of five chlorinated compounds: Pentachlorophenol, O-dichlorobenzine, dichlorobutane choroform and polychlorinated biphenyls. They found that the destruction of pentachlorophenol with UV/ozone proceeded more rapidly than with only ozone or UV. The authors compared this study to similar observances, where they reported monitoring Total Organic Carbon (TOC) and found that phenol is converted to CO_2 by UV/ozone at the stoichiometric rate at which ozone is added to the reactor. A refractory index (RFI) was defined which measures the difficulty of oxidation of a given compound by ozone.

$$\mathrm{RFI} = \frac{B^{\circ}_{c}\, t_{1/2}}{Ao}$$

where:

B°_{c} = Ozone supplied to $t_{1/2}$
$t_{1/2}$ = Time for one-half conversion of Ao
Ao = Initial amount of compound

Using the refractory index, a list was presented quantifying seventeen compounds. The least refractory compounds were potassium cyanide and phenol with RFI values of 0.41 and 0.44 respectively. Pentachlorophenol was listed as refractory with an RFI value of 1.6.

Bailey (Reference 33) reviewed past work on mechanisms of the ozone-phenol reaction. He concluded the most likely reaction pathway for ozonation of phenol was catechol to muconic acid.

SECTION IV

SYSTEM DEFICIENCIES, CORRECTIONS AND MODIFICATIONS

1. INTRODUCTION

Evaluation of equipment performance and reliability was an important objective of the study. Many operational problems were known to exist as a result of the preliminary investigation performed in August 1976. Based on these previous observations the initial phase of the study was directed toward correcting the problems already known to exist. This phase lasted approximately 4 months during which time some equipment was shipped back to the manufacturer for repair and work on other equipment was performed on site by bringing in service engineers from various companies or by contractor personnel. Many of the problems were related to inadequate maintenance and operation.

After the initial rehabilitation phase, the system was then operated to evaluate the corrections and identify other deficiencies. Efforts were made to correct both newly discovered problems and the old problems which still persisted. This second phase overlapped with the final study phase which involved testing the system and optimizing the cyanide treatment capabilities. As the second phase progressed the main emphasis shifted from correcting equipment problems to testing the system performance. The initial system operation was typically intermittent where often the system was shut down to correct a problem or install replacement equipment. Gradually, as emphasis shifted to testing, the operation became continuous, 24 hours per day throughout the week. For the entire study, Table 6 presents all system deficiencies, corrective measures, adjustments in operation and current status for all system unit operations. The remaining narrative in this section discusses the most troublesome problems encountered.

2. AIR PREPARATION SYSTEM

The first objective of the initial phase was to correct the problems in the air preparation system thereby providing a clean, dry air stream to the ozone generation system. This would eliminate some variables when evaluating and servicing the ozone generators. Field engineers from equipment manufacturers were brought in to service all components of the air-preparation system. As indicated in Table 6, most problems resulted from improper equipment maintenance and operation. The oil carry-over from the compressors was reduced by adding a catch-well below the prefilter to prevent coalesced oil from being reintrained into the air stream, replacing the cartridges in the prefilters, never allowing the compressor pressure to drop below 80 psig, continuously draining the compressor receivers, keeping the oil return lines unplugged and adjusting the water feed in the after coolers to keep the air stream discharge temperature below 80°F to optimize filter efficiency, operating more than one

TABLE 6. SYSTEM DEFICIENCIES AND CORRECTIVE ACTIONS

Deficiencies	Corrective Measures	Adjustments in Operation	Results and Current Status
Air Preparation System			
Compressors: Frequent breakdown. Excessive oil carry over. High air discharge temperature.	Completed servicing; Replaced belts. Replaced filters. Solvent cleaning. Cleaned oil return line.	Continuously drain receiver. Maintain minimum receiver pressure of 80 psig. Increased water feed to after coolers. Operate more than one compressor only when warranted by air flow rates. Maintain equal unit loading time during multiple compressor operation.	Some oil carry over still persists but much less. Problem is inherent to this type of compressor.
Prefilters: Inefficient oil removal.	Replaced cartridges. Added holding well. Additional filter installed.	More frequent cartridge replacement.	Some oil continues to bypass filters to ozone generator.
Dryers: Inoperable. Oil fouled desiccant.	Complete servicing: Cleaned and oiled valves. Replaced desiccant. Cleaned lines.	Continually monitor dewpoint in the air stream with continuous readout dewpointer with alarm. Clean and oil valves periodically.	Dryers consistently maintain dewpoint of -55°F in air stream.

TABLE 6. SYSTEM DEFICIENCIES AND CORRECTIVE ACTIONS (continued)

Deficiencies	Corrective Measures	Adjustments in Operation	Results and Current Status
Ozone Generation System			
Rectifier fuses frequently blow. Total power output at 50% of purported capability. Ozone leaks. Circuitry sensitive to temperature changes.	Complete servicing: Service engineer from equipment designer checked every component and could not identify the problem source initially. Run system to establish optimum operation procedure. Repaired all ozone leaks. Boosted primary voltage from 208v to 230v by installing buck boost transformers to each unit.	Maintain ambient temp. in range of 80-90°F for optimum equipment performance. Allow system to dry for extended period before start up. Clean rotometers once weekly.	Power output increased to design level. Increased voltage causing some breakers to trip. Breakers are being resized and replaced as problems arise.
Waste Handling Equipment			
Magnetic drive transfer pump inoperable.	Replace with new pump.		Problem resolved.
Crystallization of sodium carbonate in piping systems and metering pumps.	Repaired faulty room heaters.	Maintain ambient room temperature above 50°F.	Problem resolved.

TABLE 6. SYSTEM DEFICIENCIES AND CORRECTIVE ACTIONS (concluded)

Deficiencies	Corrective Measures	Adjustments in Operation	Results and Current Status
Ozone Contact System			
Diffuser plugging and breakage.	Replaced with open gas discharge 1-1/2 inch below turbine impellers.		Trouble free operation with good mixing and transfer.
Inadequate mixing and transfer in reactor 1, impeller flooded at gas flow rates above 60 scfm.	Replaced 3 HP mixed and 11 inch flat blade impeller with 7.5 HP variable speed mixer with 26 inch flat blade impeller.	Vary shaft speed depending upon gas flow rate.	Good mixing and transfer, speed can be adjusted to eliminate impeller flooding at all gas flow rates.
Coating of corex tubes housing UV lamps in reactor 3.	Cleaned tubes with dichromate/acid solution.	Remove tubes and clean once weekly.	Problem resolved.
Could not recycle waste from reactor 3.	Added piping, valves and metering pumps to recycle waste to reactors 1 and 2.		Advantages from recycling have been evaluated.
Excessive foaming.	Silicone defoaming agent.		Problem resolved.
Reactor ventilation system could not remove all gases from reactors.	Added a new polypropylene fan with greater capacity.	Clean reactor ventilation duct filters once weekly.	Problem resolved.
Off gases from reactors pulled back in building once exhausted.	Added stack 10' above building top.		Problem resolved.

compressor only when the required air flow rates exceed the capacity of one unit (100 scfm), maintaining equal unit loading time among the compressors during multiple compressor operation. These actions significantly reduced oil carry-over from the compressors.

The Oklahoma Publishing Company, Oklahoma City, utilizes the same compressors in its operation. This installation was visited during the study to evaluate the performance of its equipment. Observations and conversations with the maintenance supervisor clearly reveal oil carry-over from the compressors has been a big problem in the system for several years and is not resolved. Recently, new prefilters have been added to their system to reduce oil carry-over but evaluation is not complete.

During the last phase of the project an additional prefilter was installed. The filter was field tested for approximately three weeks during continuous system operation. Some oil carry-over to the ozone generators still occurred during this time. However, the filter did reduce the oil carry-over and provides additional protection for the desiccant. The filter was retained in the system.

In summary, the air preparation system was plagued with many problems, the majority of which resulted from improper operation and maintenance. Although oil carry-over has been greatly reduced during the project, some oil carry-over still persists and is currently the only operational problem in the system. A filtering system could not be identified which could completely eliminate oil carry-over.

It is not clear how detrimental oil carry-over is to the operation of the ozone generators or the dryers. During the project the dryers were operated continuously for more than two months with no decrease in efficiency. The ozone generators have also been operated continuously, but past electrical system component deficiencies have clouded the impact of oil carry-over on the generator performance. With the other generator deficiencies corrected, future evaluation would reveal the impact of the oil carry-over on ozone production. It is generally felt that oil carry-over could lower the ozone production of such a system. Future ozone system design should consider the use of an oil-free compressor system.

3. OZONE GENERATOR SYSTEM

With the air preparation system functioning, a field engineer serviced the ozone generation system. Initially, no substantial progress was made in correcting the operational problems with the ozone generators. The unresolved operational problems with this system after initial servicing included:

1. Power output of the generator system was approximately 50 percent of the purported design.
2. Rectifier fuzes protecting the solid state circuitry frequently blew.

The reduced power level of the ozone generator reduced the concentration of ozone in the air stream and limited total ozone output. During the project the problems were investigated further. The following equipment modifications were recommended for field tests on one of the generating units:

1. Boosting of the primary voltage.
2. Incorporating a more efficient silicon controlled rectifier (SCR) and diode design.
3. Using larger amperage rectifier fuses.

Based on these recommendations, an ozpac module was selected for field testing the effect of boosting the primary voltage from the current 208 volts to 230 volts. This was accomplished by installing two Acme buck boost transformers in the ozpac module. Ozpac module no. 4 was selected for testing. Under the pressure levels and air flow rates tested, the maximum power ranges previously achieved for the ozpac were 20 to 22 amperes (amps) and 240 to 245 volts. After installation of the buck boost transformer in the ozpac module, the power in the unit could be increased to 40 amps and 250 volts.

From the favorable results of the field test, buck boost transformers were installed in each of the ozpac modules. Also, to lower the current in the three-phase system, the ozone-module cooling fans were rewired from 115 volts to 230 volts. With these modifications completed, the system was operated for two weeks to evaluate the changes.

During the two-week testing period the power output of each unit increased to the maximum values possible. As a result of the greater power levels, some of the breakers in the system would trip. The ozpac generation system has four sets of breakers, any of which are subject to overloading and tripping. These consist of:

1. Main power breaker before the 208 volt transformer.
2. Main control box breaker after the 208 volt transformer.
3. Individual control box breakers for each of the six ozone modules.
4. Individual cabinet breakers for each of the six ozone modules.

Table 7 summarizes the breakers which have tripped to date, conditions under which the breakers tripped, corrective actions and current status. As indicated in the table, one breaker has not been replaced.

With the buck booster transformers installed, data were collected to establish the ozone production capabilities of the system. Due to problems with the breakers, ozone production at total system power exceeding approximately 200 amps has not been established. Figure 5 depicts two curves for ozone concentration versus total system power. The curves were established under varying air flow conditions while maintaining the same system pressure. The higher flow rate 155 scfm (73 l/s) coincides with the maximum system design flow rate. The lower flow rate is typical of a setting used at lower cyanide concentrations. These curves can be used for approximate adjustment of the ozone generation system to achieve a desired ozone output. However, the ozone production in a module at a given power setting will vary. For example, at a system flow rate of 113 scfm (53 l/s) the following variance was measured:

TABLE 7. OZONE GENERATOR PERFORMANCE

Breaker Event Identification (Chronological Order)	Typical Condition at Time Breaker Tripped	Corrective Action	Current Status
Ozpac No. 4 Console breaker	Field test, unit at 35 amps.	Balanced phase current in ozpac No. 4.	No further problems.
Ozpac No. 5, Indicator Control box breaker	All ozpac units operating at 25 amps.	Selected replacement breaker.	No further problems.
Main power control box breaker before 208-v transformer	Ozpac units 1, 2, 3, 4, and 6 operating at 30 amps, unit 5 at 20 amps.	Replaced 480 v., 90 amp breaker with 480 v., 100 amp breaker.	No further problems.
Main control box breaker after 208-v transformer	Ozpac units 1 at 35 amps, 2 at 30 amps, 3 at 40 amps, 4 at 40 amps, 5 at 25 amps, 6 at 40 amps.	Selected replacement breaker.	Not installed.

Power Settings (amps)							
Ozpac 1	Ozpac 2	Ozpac 3	Ozpac 4	Ozpac 5	Ozpac 6	Total Amps	Ozone Concentration Percent by Weight
25	20	25	25	20	25	140	0.49
30	25	30	0	25	30	140	0.52

During operation of the ozone generation system, it was observed that the power output of the system would decrease by approximately one-third when the ambient air temperature fell below 75°F. Optimum power output for the system occurs when the ambient temperature is maintained between 85°F and 95°F.

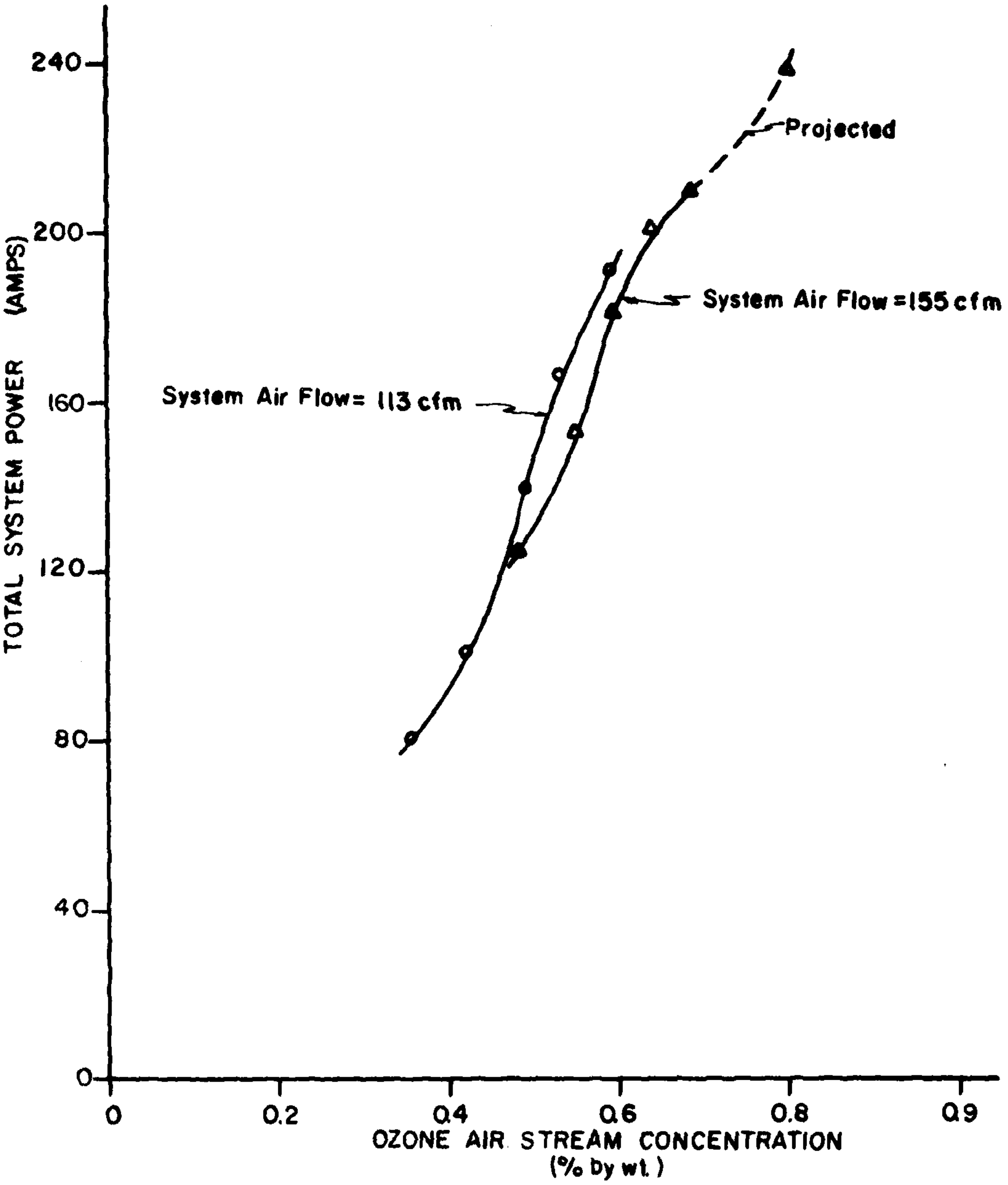

Figure 5 Ozone air stream concentration vs. total system power

SECTION V

SYSTEM OPERATION AND MONITORING

1. METHODS AND PROCEDURES

With all components of the ozone cyanide system functioning, a program of continuous operation and monitoring was initiated. The objectives were to identify and correct unknown equipment deficiencies, establish system treatment capabilities, optimize system performance, document system reliability, and project Operating and Maintenance (O&M) costs. The system would be continuously operated 24 hours per day five days per week for approximately eight weeks. An operator was continuously present during system operation.

The monitoring schedule presented in Table 8 was adhered to during continuous operation. All analyses followed the procedures outlined in the 14th edition of Standard Methods for the Examination of Water and Wastewater (Reference 34).

All cyanide analyses included the initial sample distillation procedure as outlined in Reference 34. One hour of distillation was found to consistently result in greater than 95 percent recovery of all cyanides. The major difficulties in performing the cyanide analyses were maintaining an appropriate bubble rate during distillation and accurately standardizing the silver nitrate titrant. During the study duplicate samples analyzed by a certified independent laboratory for quality control of the analytical procedures indicated close agreement.

The percent concentration of ozone in the air stream was determined by metering an air stream sample (50 to 70 ml/min) into a train of three bottles containing a 2 percent potassium iodide solution. The train insured that no ozone escaped undetected. The titration was performed with standard sodium thiosulfate solution.

In addition to maintaining the monitoring schedule in Table 8, the operators continuously checked the performance of all equipment. Detailed daily logs were maintained.

All monitoring data were recorded on special coding forms for easy keypunching and eventual computer compilation and data analyses.

TABLE 8. OZONE-CYANIDE SYSTEM MONITORING SCHEDULE

Unit Operation	System Variable Monitored	Minimum Monitoring Frequency
Air Preparation System	Air Stream Dewpoint	Once every 3 hours
Ozone Generation System (6 modules)	Voltage	Once every hour
	Amperage	Once every hour
	Air flow rate	Once every hour
	Pressure	Once every hour
	Ozone concentration in air stream	Once every 3 hours
	Air stream temperature	Once every 3 hours
Reactors (3)	Air flow rate	Once every 4 hours
	Waste inflow rate	Once every 4 hours
	Recycle flow	Once every 4 hours
	Reactor pH	Once every 4 hours
	Reactor temperature	Once every 4 hours
	Reactor total CN	Once every 4 hours
Others	Influent total CN	Once daily
	Influent flow	Twice daily
	Ambient air temperature	Once every 3 hours

SECTION VI

RESULTS

1. INTRODUCTION

The results presented in this section cover the equivalent of more than two months of continuous operation of the ozone-cyanide system. Typically the system was operated 24 hours per day five days per week while testing. The exception to this mode of operation was an initial batch study performed on reactor 1 in which the system was operated on a day to day basis for a period equivalent to approximately two days of continuous operation.

The approach during operation of the system was to adhere closely to initial design recommendations for equipment operation, including air flow rates and waste feed rates. Air stream ozone concentration during operation was kept at a maximum as limited by the performance of the ozone generators. One original design recommendation which was not followed was the addition of 4 parts of make-up water (25 gph) to each part of waste added to the system in reactor 1. Instead, make-up water was added only to offset evaporation losses which totaled approximately 4 gph as measured in the study. Under conditions of continuous operation the make-up water was added to reactor 3.

The objectives of testing were to establish the treatment capabilities and equipment reliabilities of the system. Another objective was modification of operational procedures to obtain optimum performance. The testing procedure involved evaluation of both batch and continuous system operation under various system parameter conditions. In each of the following discussions the reactors are differentiated by the numbers assigned in the flow diagram (Figure 1).

2. BATCH TEST OF REACTOR 1

The first test was a batch operation of reactor 1 on an intermittent basis. During this test the original 3 hp (2.2 kw) mixer was mounted on reactor 1. The porous diffusers had been replaced with an open-end pipe discharging 1.5 inches (3.8 cm) below the mixer impeller. One objective was to provide background information on operational performance of the 3 hp (2.2 kw) mixer for later comparison with the replacement variable speed mixer. Also, this test would yield initial insight into the treatability of the strong cyanide waste using the full-scale ozone system.

The reactor was filled with cyanide waste having a total concentration of 27,000 mg/L. The waste had an initial pH of 12.8. The cumulative length of the run was 46 hours. Concentration of cyanide in reactor 1 versus time is plotted in Figure 6. During the first 20 hours of operation the average air flow to reactor 1 was 68 scfm (32 l/s) with a 0.85 percent ozone by weight concentration. This resulted in 38 lbs. of cyanide removed with the addition of 52 lbs. of ozone or a ratio of 1.4 pounds of ozone added per pound of cyanide removed (O_3/CN^- removed). For the final 26 hours of operation the air flow rate to reactor 1 and air stream ozone concentration were 59 scfm (28 l/s)

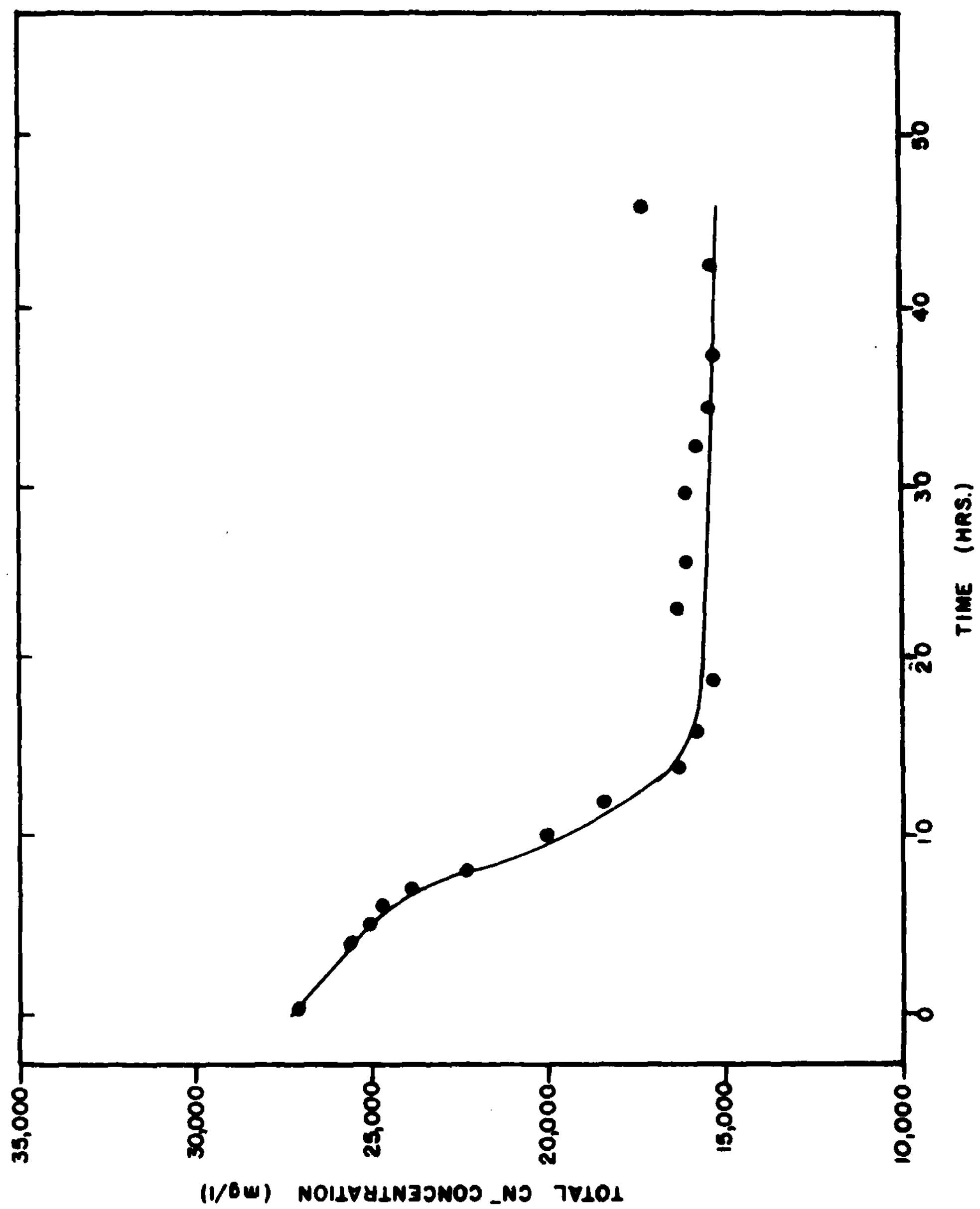

Figure 6 Batch Treatment of Waste in Reactor I

and 0.60 percent ozone by weight, respectively. During the final 29 hours no cyanide was removed. The average temperature in the reactor was 62°F (16.7°C). The pH of the waste in reactor 1 at the end of the test was 10.9.

Analyses of metals present in the waste in reactor 1 (Table 9) indicated a significant amount of the cyanide remaining was not complexed. From the metal analyses the concentration of complexed metal cyanide present in the waste of reaction 1 was calculated to be 6,950 mg/L (Table 9). The calculations were performed using the number of cyanide ions known (Reference 1) to complex with each metal to convert the metal concentration to the equivalent complexed metal cyanide concentration. The total cyanide concentration remaining at the end of the test was approximately 15,000 mg/L.

In summary, an initial, rapid removal rate of cyanide was followed by a period of virtually no change in cyanide concentration. Further, the limiting concentration was not totally explainable by complexed metal cyanides present. It is likely the limiting concentration resulted from other competing side reactions with ozone.

TABLE 9. METALS ANALYSES OF WASTE IN REACTOR 1 AND ASSOCIATED CYANIDE COMPLEX CONCENTRATION

Metal	Concentration (mg/L)	No. Cyanide Ions Complexed with Each Metal	Calculated Concentration of Complexed Metal Cyanide (mg/L)
Iron	480	6	1337
Zinc	96	4	154
Nickel	1480	4	2609
Cadmium	1920	4	1783
Copper	405	3	494
Silver	1184	2	570

3. BATCH TREATMENT OPERATIONS OF ALL REACTORS

The system was operated continuously 24 hours per day for five days, with the waste in each of the three reactors treated on a batch basis. At the time of this test, all diffusers in the reactors had been replaced by an open end pipe 1.5 inches (3.8 cm) below the mixer impellers. Also, the 3 hp (2.2 kw) mixer on reactor 1 had been replaced with the 7.5 hp (5.6 kw) variable-speed mixer. The UV lamps in reactor 3 were operated continuously during this test. Reactor 1 was filled with untreated plating waste (total cyanide concentration 62,500 mg/L). The waste in reactors 2 and 3 was a mixture of partially treated and untreated wastewater with total cyanide concentrations of 20,000 and 25,000 mg/L, respectively. Other test conditions are given in Table 10. Changes in cyanide concentrations during the test are shown in Figures 7, 8, and 9.

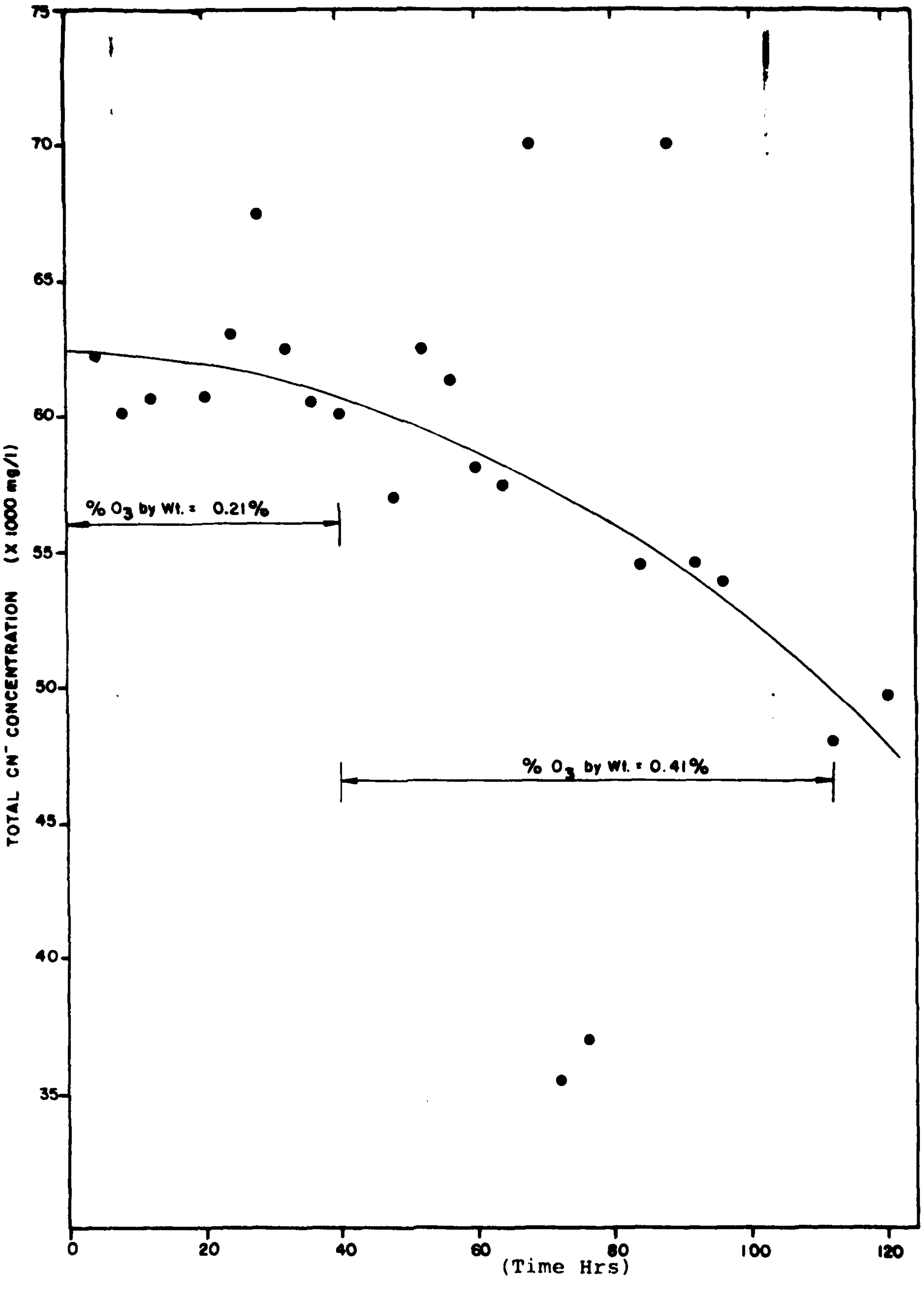

Figure 7 Batch Treatment of CN Waste in Reactor I

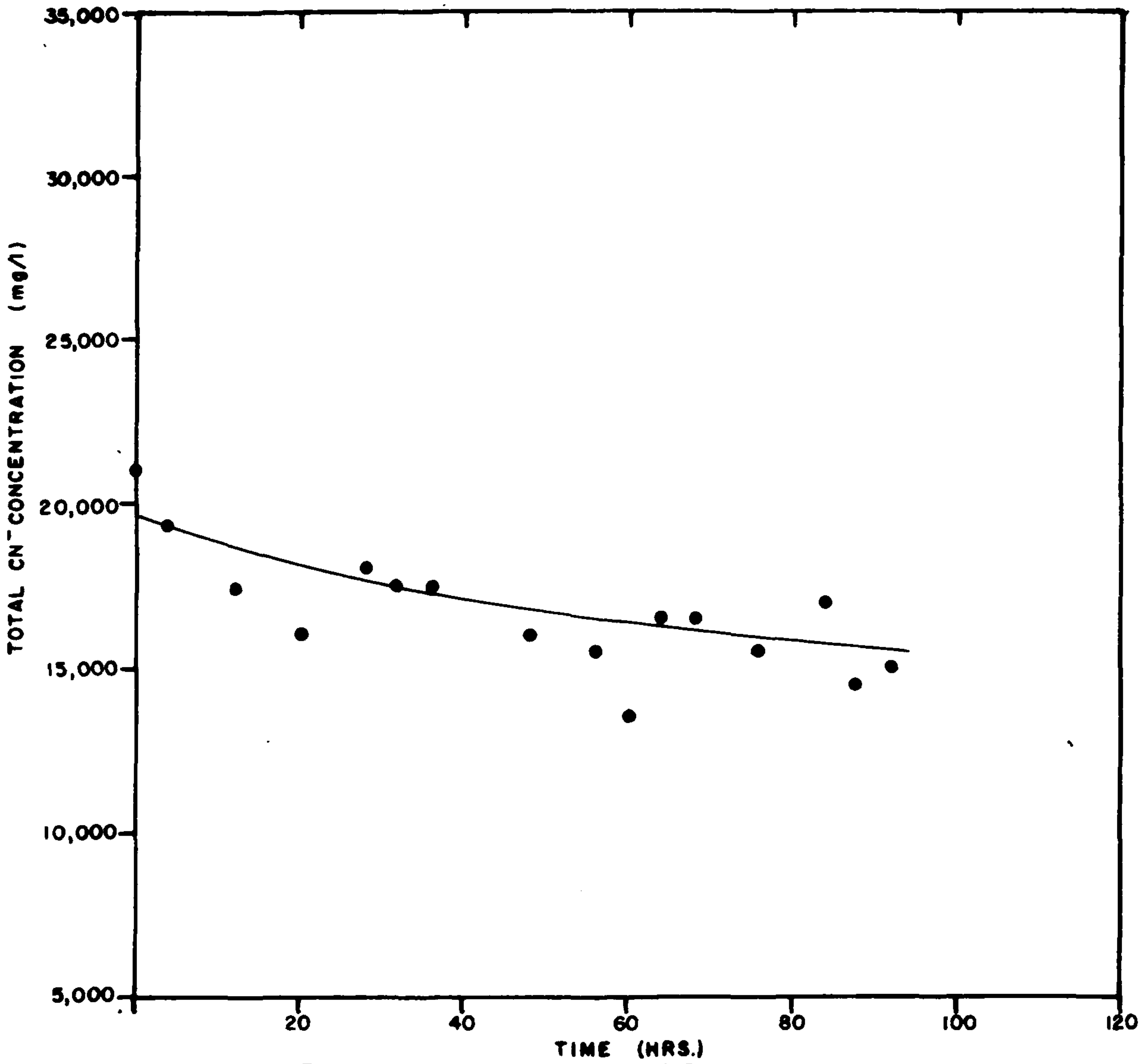

Figure 8 Batch Treatment of CN Waste in Reactor 2

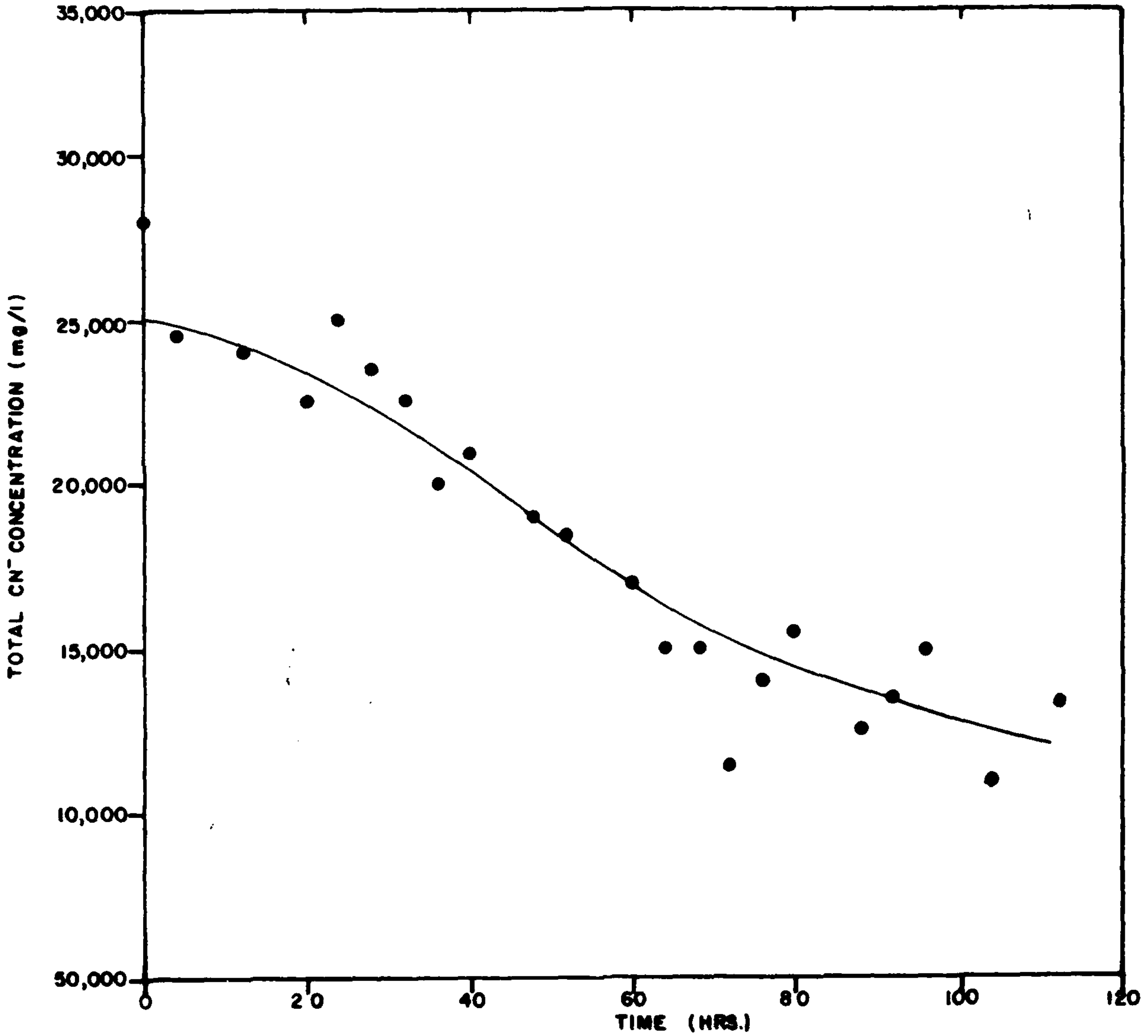

Figure 9 Batch Treatment of CN Waste in Reactor 3

TABLE 10. BATCH TREATMENT OF ALL REACTORS

Reactor	Initial Cyanide Concentration (mg/L)	pH Initial/ Final	Average Reactor Temp. (°F/°C)
1	62,500	13.3/13.4	78/25.6
2	20,000	12.8/12.7	80/26.7
3	25,000	12.8/10.2	118/47.8

The ozone concentration in the air stream and air flow rates to the reactors were significantly different for the first 40 hours as compared to the rest of the testing period. The average ozone concentration in the air stream during the first 40 hours was 0.21 percent by weight and 0.41 percent by weight for the remaining test period. Average air flow rates to reactors 1, 2, and 3 for the initial 40 hour period were 109 scfm (51 l/s), 31 scfm (14.6), and 17 scfm (8 l/s) respectively. These rates were decreased to averages of 53 scfm (25 l/s), 14 scfm (616 l/s), and 13 scfm (6 l/s) respectively, for the second phase of the test. The operational settings were dictated more by equipment performance than by preferential selection. During each of the two test phases the ozone concentrations and reactor flows varied only slightly.

Inspection of the data indicates some initial scatter at the higher cyanide concentrations. These incidents are small in number compared to the total data. Obtaining a representative sample was more difficult at high cyanide concentrations due to the sample size limitation. Dilution techniques and other quality control methods, including duplicate samples analysis at an independent laboratory, were effective in minimizing the scatter. However, all data obtained in the study are presented in this report.

Mass balances were computed from the results for each of the reactors. For reactor 1 during the first 40 hours, 6 pounds (1800 mg/L) of cyanide were removed (Figure 7). For the same period, 42 pounds (19 kg) ozone were added to reactor 1. The next 72 hours of operation resulted in 39 pounds (17.7 kg) (12,000 mg/L) of cyanide removed in reactor 1 while 72 pounds (32.7 kg) of ozone were added. This yields O_3/CN^- removed ratios of 7.0 and 2.0 for the two test phases. These results demonstrate the ozone utilization efficiency was increased by increasing the concentration of ozone in the air stream. The overall O_3/CN^- removed-ratio for the entire test period was 2.7. During the test period the mixer shaft speed was maintained at 80 rpm.

An analysis of the metals concentrations in the waste added to reactor 1 was performed. The concentrations were 499 mg/L Fe, 254 mg/L Zn, 1110 mg/L Ni, 387 mg/L Cd, 455 mg/L Cu, and 722 mg/L Ag. From the analyses the concentrations of cyanide complexed with the metals was calculated to be 4800 mg/L. The calculations were performed in the same manner as shown in Table 9. This indicates the cyanide present in the waste added to reactor 1 was primarily in the uncomplexed form.

Figure 8 shows no significant change in removal rates for reactor 2 from the first 40 hour period to the second phase of the test. The concentration of cyanide in reactor 2 was reduced approximately 4000 mg/L. 13 pounds (5.9 kg) of cyanide were removed during the first 90 hours of testing, and 27 pounds (12.2 kg) of ozone were added to the reactor to give an O_3/CN^- removed-ratio of 2.0. The results indicate efficient transfer of ozone in reactor 2 occurred at both the high and the low flow rates.

The change in cyanide concentration for reactor 3 is presented in Figure 9. The two UV lamps were operated continuously during the entire test. For the first 40 hours, 15 pounds (6.8 kg) of cyanide (4500 mg/L) were removed in reactor 3 and 7 pounds (3.2 kg) of ozone added. In the next 72 hours, 27 pounds (12.3 kg) of cyanide (8000 mg/L) were removed and 17 lbs. (7.7 kg) of ozone added. This yielded O_3/CN^- removed-ratios of 0.47 and 0.63, respectively for the two successive phases. The overall O_3/CN^- removed-ratio was 0.57. Figure 9 shows that the removal of cyanide in the first and second phases was controlled mainly by the quantity of ozone added and not transfer efficiency. The slight increase in the O_3/CN^- removed-ratio in the second phase is likely a combination of effects produced from decreased cyanide concentrations and second stage cyanate oxidation reactions by the ozone. It is also significant to recognize that reactor 3 had the highest cyanide removal rates, indicating the benefits of ultraviolet radiation. It is further noted that the benefits derived from radiation occurred when the majority of the cyanide in reactor 3 was in the uncomplexed form. The increased reactor temperature was significant in speeding the decomposition of ozone and the production of free radicals. Various research in the past has indicated free radicals and ions formed by ozone decomposition are likely the chief reaction species (References 35, 36, and 37).

4. SYSTEM BATCH OPERATION WITH CONTINUOUS RECYCLE FLOW

The system was operated during this test with no raw waste introduced to the reactors but with flow from reactor 3 continuously recycled to reactor 1. Table 11 summarizes the test conditions for each reactor. Initial concentrations of cyanides in reactors 1, 2, and 3 were 39,000 mg/L, 18,000 mg/L, and 8,300 mg/L, respectively. The test period was 103.5 hours with continuous operation. The average ozone concentration in the air stream was 0.52 percent by weight. The test was conducted with little variation in the average ozone concentration and air flow rates. The UV lamps in reactor 3 were used for the entire test period. Recycle flow from reactor 3 to reactor 1 averaged 5.6 gph (0.35 l/m). Cyanide concentrations as a function of cumulative test time are plotted in Figures 10, 11, and 12 for reactors 1, 2, and 3, respectively. The test was terminated after 103.5 hours of operation when large volumes of unreacted ozone were emitted from reactor 1.

From the data, mass balances for the entire system and each reactor were computed for the test period. The total system cyanide was reduced by 156 pounds (71 kg), which is equivalent to 72 percent of the cyanide present at the beginning of the test. A total of 323 pounds (147 kg) of ozone were added to the reactors. Thus the O_3/CN^- removed-ratio was 2.1.

From Figure 10, it is apparent that a steady decrease in cyanide concentration occurred in reactor 1 during the test period. When the test was terminated, the concentration of cyanide in reactor 1 was 3100 mg/L. As noted

TABLE 11. SYSTEM BATCH OPERATION WITH CONTINUOUS RECYCLE

Reactor	Initial Cyanide Concentration (mg/L)	pH Initial/Final	Air Flow Rate (scfm/L per sec)	Average Reactor Temperature (°F/°C)
1	39,000	13.0/9.7	85/40	90/32.2
2	18,000	12.3/10.6	32/15	87/30.6
3	8,300	10.0/9.8	14/6.6	115/46.1

previously, the test was terminated when large volumes of unreacted ozone were observed to be coming off of reactor 1. Subsequent metal analyses reported concentrations of 466 mg/l Fe, 118 mg/l Zn, 1110 mg/l Ni, 410 mg/l Cd, and 520 mg/l Cu to be present in the treated waste. From the metal analyses the concentration of cyanide complexed with these metals was calculated to be 4460 mg/l. Thus, when unreacted ozone was detected in the off gas, the cyanide remaining in reactor 1 was in the complexed form. This test illustrated that ozone alone is much less effective in oxidizing complexed metal cyanides than free cyanides. Foaming in reactor 1 also increased substantially at the lower cyanide concentration. Silicone defoaming agent was found to be very effective in controlling foaming in reactor 1 when most of the ozone was being reacted, but was much less effective when the unreacted ozone was emitted. The mass balance computations indicated 89 pounds (41 kg) cyanide were removed in reactor 1 during the test period. This represents 57 percent of the total cyanide removed in the system [156 pounds (71 kg)] and is 41 percent of the cyanide [218 pounds (99 kg)] initially present in the system at the beginning of the test. A total of 210 pounds (95.5 kg) of ozone were added to reactor 1. The O_3/CN^- removed-ratio was 2.4. The mixer speed during the test was 80 rpm.

Mass balance compurations indicate less cyanide was removed in reactor 2 than reactor 1. Total cyanide removed in reactor 2 was calculated to be 42 pounds (19.1 kg) which accounts for 27 percent of the total cyanide removed, and is 19 percent of the initial cyanide in the system. During the test 78 pounds (35.5 kg) of ozone were added to reactor 2. Thus the O_3/CN^- removed-ratio for reactor 2 (1.9) was less than reactor 1. This indicated that efficient contact and transfer was occurring in reactor 2 during the test, and suggested that the mixer speed in reactor 1 should be increased. Removals in reactor 2 could be increased by increasing the ozone mass flow rate. From Figure 11 the final concentration of cyanide in reactor 2 at test termination was still considerably greater than the computed complexed cyanide concentration.

Figure 12 indicates that a rapid decrease of cyanide concentration occurrence in reactor 3 down to approximately 500 mg/L. The reactor concentration then remained relatively constant for the remaining portion of the test period. The limiting concentration was about equal to the computed concentration of complexed cyanides (4460 mg/L) calculated from the metals analyses.

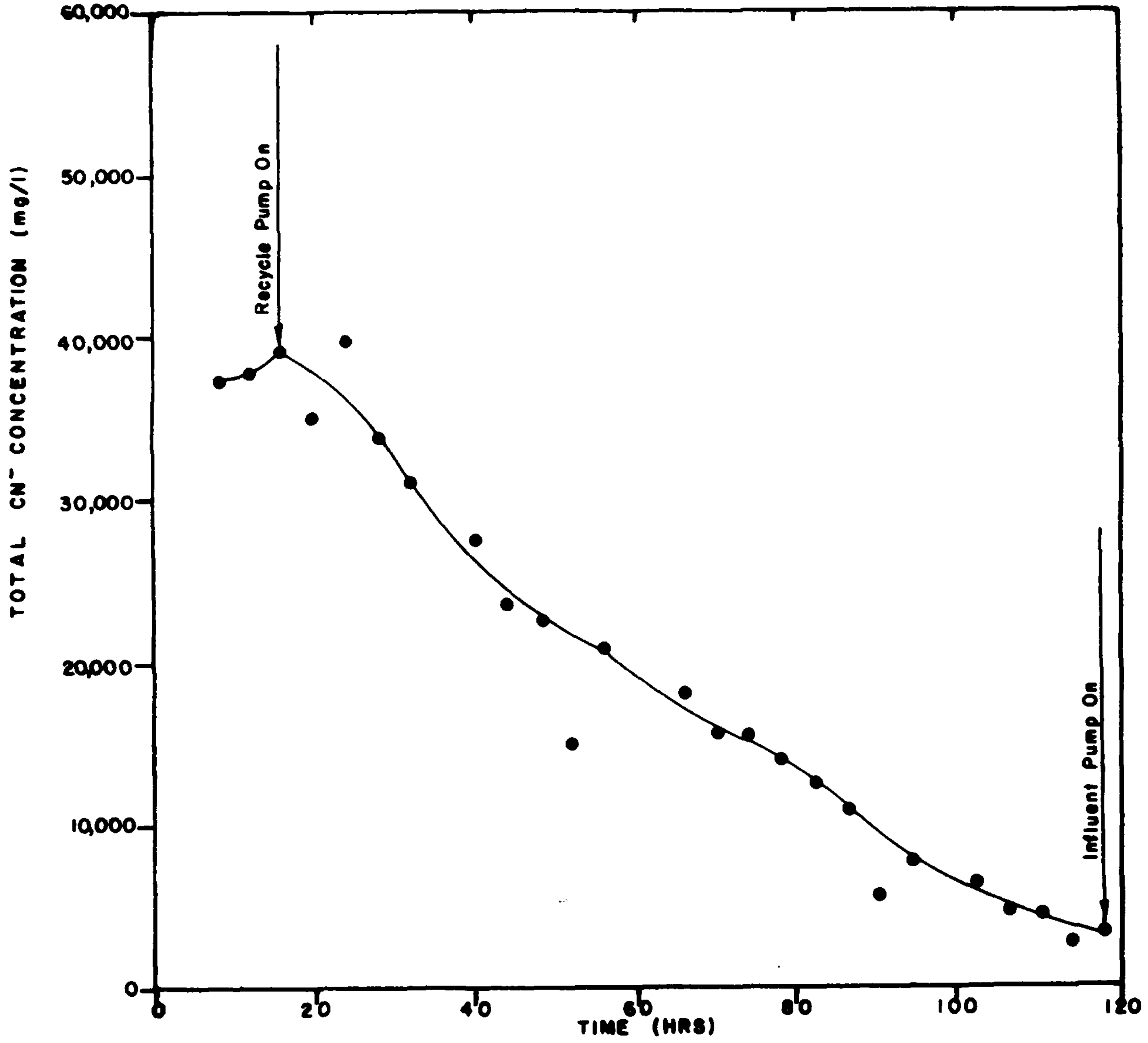

Figure 10 Batch Treatment of CN Waste in Reactor I With Continuous Recycle

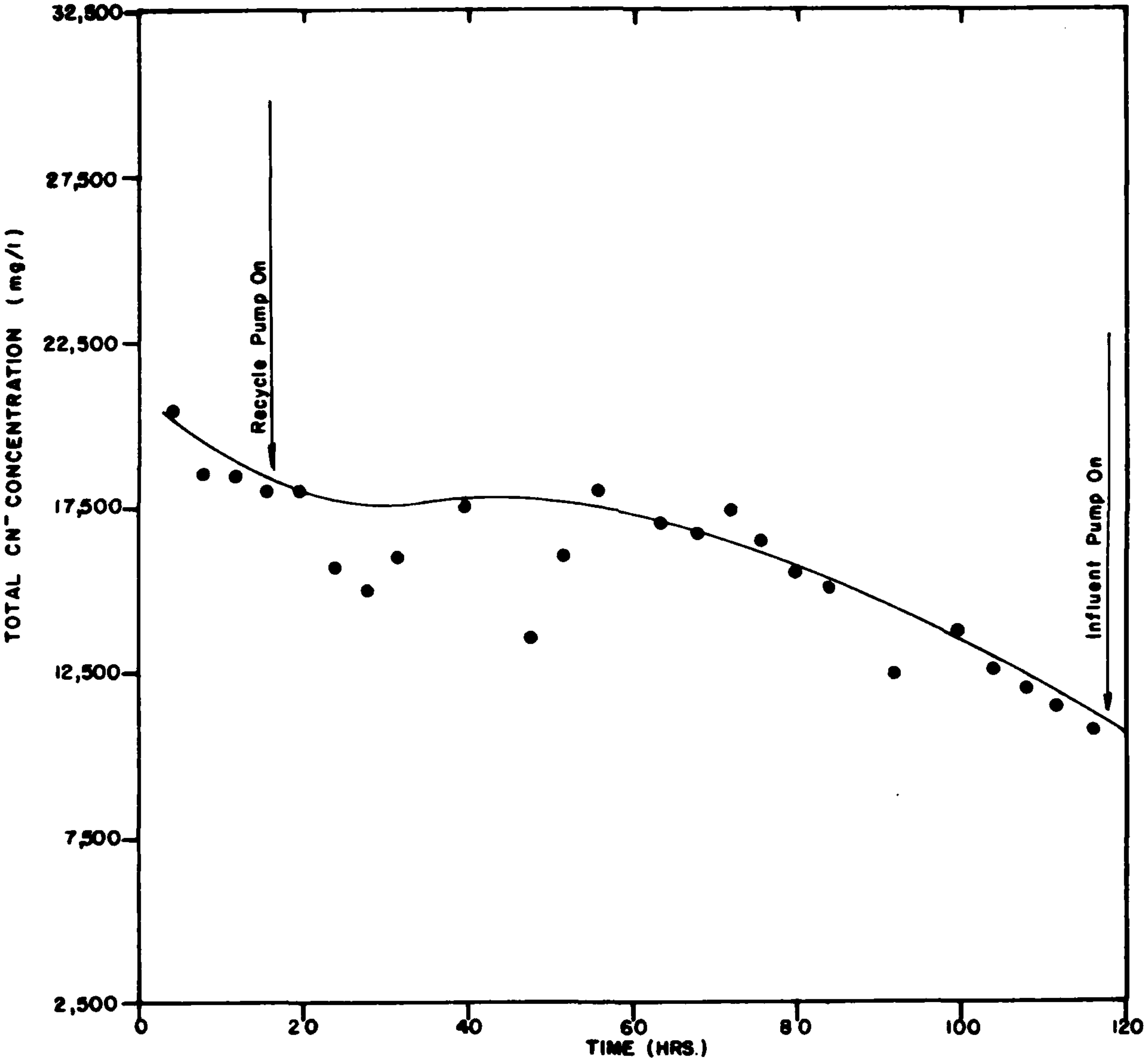

Figure 11 Batch Treatment of CN Waste in Reactor 2 With Continuous Recycle

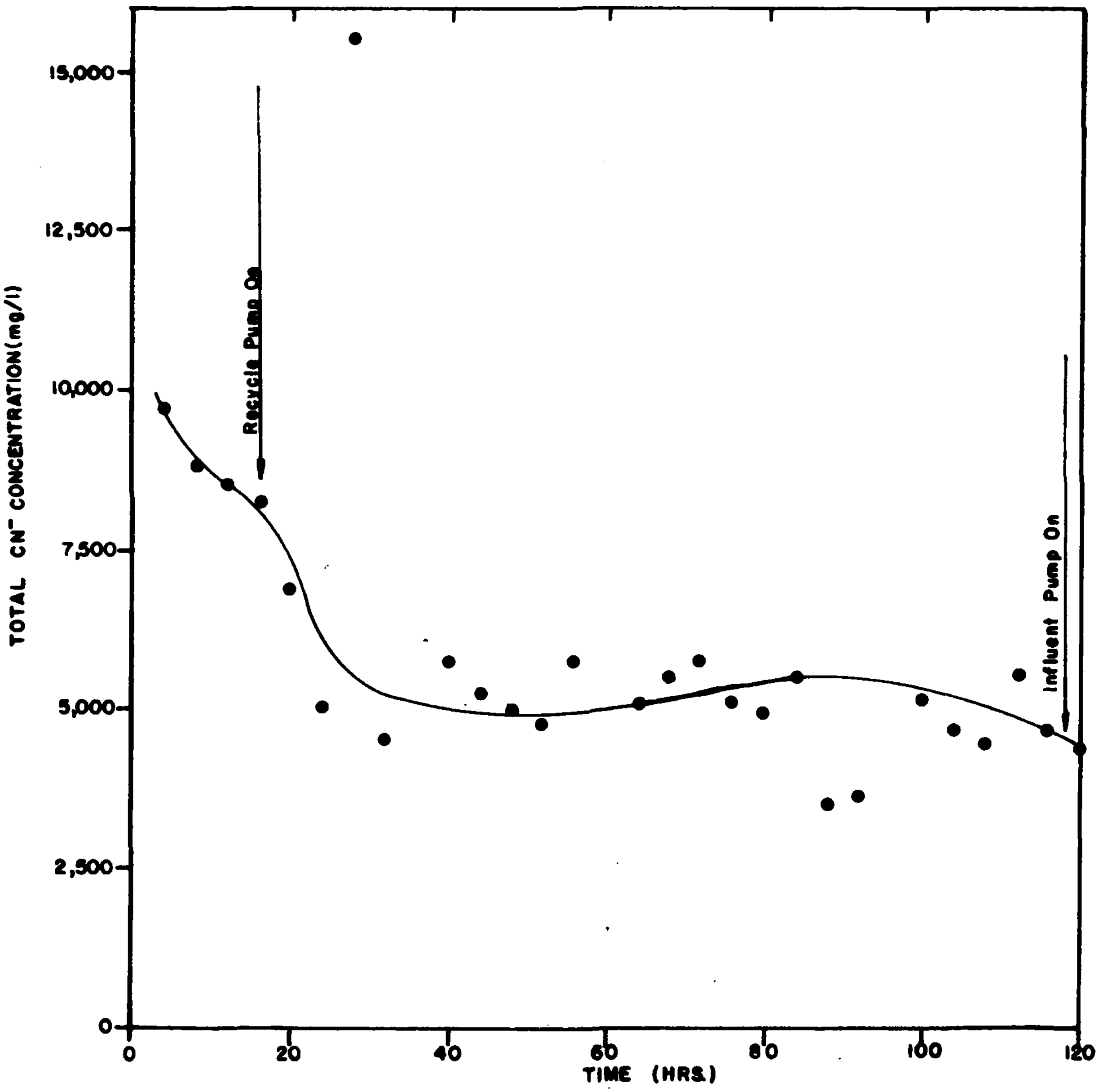

Figure 12 · Batch Treatment of CN Waste in Reactor 3 With Continuous Recycle

Once the concentration in reactor 3 leveled off, all free cyanide entering reactor 3 was quickly oxidized. From the mass balance computations, 25 pounds (11.4 kg) of cyanide were removed in reactor 3 during the test. The cyanide removed was 16 percent of the total cyanide removed during the test, and 11 percent of the cyanide initially present in the system. The O_3/CN^- removed-ratio of 1.4 for reactor 3 was less than those for either reactor 1 or reactor 2 but greater than previous values for reactor 3 under batch conditions at higher cyanide concentrations. The high percentage of complexed cyanides present in reactor 3 accounted for the ratio increase.

5. CONTINUOUS OPERATION WITH RECYCLE FLOW

When ozone began coming off reactor 1 the previous test was terminated. The mixer speed on reactor 1 was slowed to 70 rpm. Simultaneously, continuous metering of raw cyanide waste to reactor 1 began. Recycling of waste from reactor 3 to reactor 1 continued. This marked the beginning of the continuous operation of the system. The incoming raw waste had an initial cyanide concentration of 41,800 mg/L and a pH of 13.3. After 28 hours of operation the mixer speed on reactor 1 was increased to 90 rpm. The cyanide concentration of the incoming flow was 38,500 mg/L after 46 hours, after which it began to decrease more rapidly to 20,000 mg/L at 62 hours and to 12,500 mg/L at 86 hours from the start of the test. The decrease occurred when the supply of high concentration cyanide waste ran low and waste with lower cyanide concentration was added to the waste storage tank. The system approached equilibrium approximately 12 hours into the test. This discussion is limited to the first 50 or so hours or that time when the incoming raw waste cyanide concentration was essentially constant.

Concentration of cyanide for each of the reactors and for the raw effluent during the test are displayed in Figure 13. The average influent flow was 6.45 gph (0.4 l/m) and average recycle flow was 5.61 gph (0.35 l/m). Ozone concentration was lower than previous outputs in other tests due to problems with ozone generators. Table 12 summarizes other test conditions. The UV lamps in reactor 3 were operated throughout the test period.

TABLE 12. CONTINUOUS OPERATION WITH RECYCLE FLOW

Reactor	Equilibrium Cyanide Concentration (mg/L)	pH Initial/Final	Air Flow Rate (scfm/L per sec)	Average Reactor Temperature (°F/°C)
1	14,000	10.2/10.3	79/37	90/32.2
2	11,000	10.3/9.9	26/12.2	85/29.4
3	5,300	9.8/9.7	14/6.6	120/48.9

Figure 13 shows that the cyanide concentration in reactor 1 gradually increased for the first 12 hours then leveled off at approximately 14,000 mg/L. The concentration remained fairly constant and then began to decrease after 50

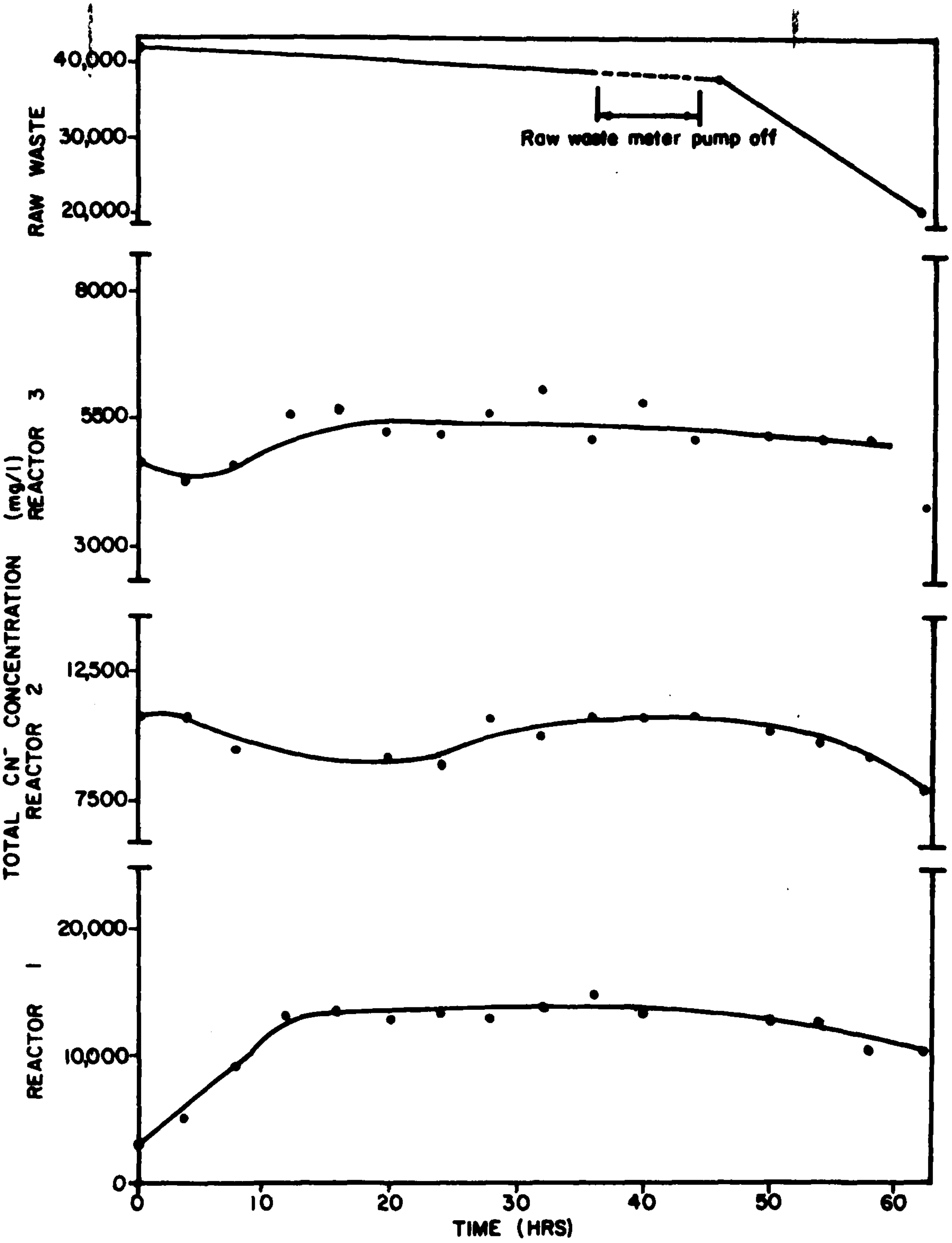

Figure 13 Treatment of CN waste with continuous Inflow and Recycle

hours as the influent cyanide concentration began to drop rapidly due to dilution with other waste as explained previously. The graph for influent concentration indicates very little change from the beginning of the test to 46 hours. At equilibrium the average influenct was 40,125 mg/L. A mass balance of total cyanide into and out of reactor 1 including the recycle flow must be made to determine the true removal efficiency. The recycle flow was 5.61 gph with approximately 5300 mg/L cyanide. From the mass balance computations, reactor 1 was removing 1.1 lbs of cyanide per 2.4 lbs. of cyanide added each hour or 46 percent of the incoming cyanide. Ozone was added to reactor 1 at the rate of 1.3 pounds per hour (0.6 kg/hr) giving an O_3/CN^- removed-ratio of 1.2. The ozone utilization efficiency was high, indicating good mixing and transfer. An increase in the air stream ozone concentration increased the ozone mass flow rate and improved the cyanide removal efficiency.

After the concentration of cyanide in reactor 1 leveled off, the cyanide concentration in reactor 2 began to reach equilibrium and was at equilibrium approximately 36 hours with a cyanide concentration of approximately 11,000 mg/L. The inflow to reactor 2 was approximately 11.1 gph. The inflow had a total cyanide concentration of 14,000 mg/L. This indicated 0.3 pounds of cyanide (0.14 kg/hr) were removed for each 1.3 pounds of cyanide added per hour (0.6 kg/hr) or 23 percent of the incoming cyanide to reactor 2. Ozone was added at the rate of 0.43 pounds per hour (0.2 kg/hr) giving an O_3/CN^- removed-ratio of 1.4. The cyanide concentration in reactor 2 eventually began to drop after 50 hours as the effects of decreasing waste strength began to be present.

Reactor 3 was able to reach equilibrium during the test since the initial concentrations were already relatively close to equilibrium values. From Figure 13 the cyanide concentration in reactor 3 leveled off to approximately 5300 mg/L after 30 hours. The incoming waste had a concentration of 11,000 mg/L and a flow rate of 10.6 gph (0.7 l/s). Make-up water at an average rate of 3.1 gph (0.20 l/s) was added to reactor 3 for evaporation losses in the system. Total outflow from reactor 3 was approximately 11.7 gph (0.75 l/s) (subtracting reactor evaporation losses). Mass balance computations indicate 0.45 lbs. cyanide per hour (0.2 kg/hr) was removed in reactor 3 with 0.97 lbs. of cyanide per hour (0.44 kg/hr) added. Thus 46 percent of the cyanide entering reactor 3 was removed. The O_3/CN^- removed-ratio was 0.50 based on 0.22 pounds (0.1 kg/hr) of ozone added per hour. Again the advantages of the UV radiation are apparent from the high ozone utilization efficiency. The limiting concentration in reactor 3 was approximately equivalent to the complexed cyanide concentration calculated from the metals analyses.

A mass balance of the system during equilibrium indicates 86 percent of the incoming cyanide was removed. Ozone at 0.36 percent by weight in the air stream was added at a rate of 1.93 pounds per hour (0.88 kg/hr) while cyanide was being removed at a rate of 1.85 pounds (0.84 kg/hr) per hour giving an overall O_3/CN^- removed-ratio of approximately 1.0.

6. BATCH TREATMENT OF COMPLEXED CYANIDE

The previous tests indicated that the reaction of ozone with cyanide slowed when the cyanide concentration approached levels equal to the complexed cyanide concentration calculated from the metals analyses. Treatment of the complexed cyanide needed further clarification. Following the previous test, cyanide concentrations in reactors 2 and 3 were reduced by ozonation to concentrations less than 5000 mg/L, and a series of batch tests performed on these two reactors to clarify the complexed cyanide removal characteristics. During these tests, the percent ozone in the air stream was increased to a maximum by operating the ozone generator at minimum flow rates.

Results from the first batch test are presented in Figure 14. Table 13 summarizes various test conditions. The initial cyanide concentrations in both reactors were below the levels of complexed cyanide calculated from the metals analyses (Figure 14). The test was continued for 20 hours, and the UV lamps in reactor 3 were on throughout the test. The average ozone concentration in the air stream was 0.91 percent by weight. Mass balances performed on reactor 2 for the test indicated 3.3 pounds (1.5 kg) of cyanide were removed and 10.2 pounds (4.6 kg) of ozone added. For reactor 3, it was calculated that 7.0 pounds (3.2 kg) of cyanide were removed and 21.2 pounds (9.6 kg) of ozone were added. The O_3/CN^- removed-ratios for reactors 2 and 3 were 3.1 and 3.0, respectively. The graphs in Figure 14 indicate no cyanide was removed in reactor 2 once a concentration of approximately 2700 mg/L was reached, 8 hours after the test began. This was in contrast to reactor 3 where removals were still proceeding at this concentration. This indicated that the UV radiation was effective in breaking-down the complexed metal cyanides. From the high O_3/CN^- removed-ratios, it is clear the ozone was not being used as efficiently as observed in previous tests on waste with greater cyanide concentrations present. For example, the value of 3.0 for O_3/CN^- measured in this test for reactor 3 can be compared to a value of about 0.5 for reactor 3 in previous tests. The removal of the complexed cyanides was apparently reaction rate limiting. Clearly UV radiation is very effective in increasing the destruction of cyanide complexed with metals.

TABLE 13. BATCH TREATMENT OF COMPLEXED CYANIDE

Reactor	Initial pH	Air Flow Rate (scfm/L per sec.)	Average Reactor Temperature (°F/°C)
2	10.2	14.8/7	95/35
3	10.2	25.1/11.8	126/52.2

The batch operation was continued for reactor 3 until a concentration of 1260 mg/L total cyanide was achieved. During this time, the cyanide removal rate continued to decrease. Approximately 24 hours of time was required to decrease the concentration of cyanides in reactor 3 from 1700 to 1260 mg/L. The average ozone concentration in the air stream was 0.87 percent by weight. The air flow to reactor 3 averaged 20.4 scfm (9.3 l/s). In all, 1.5 pounds (0.7 kg) of cyanide were removed and 19 pounds (8.6 kg) of ozone added. The pH at the end of the test was 10.3. Most of the cyanide present in the waste was complexed with iron since iron-cyanide complexes are very stable, and the metals analyses presented previously indicated that approximately 1400 mg/L of cyanide could be complexed with the iron in the waste.

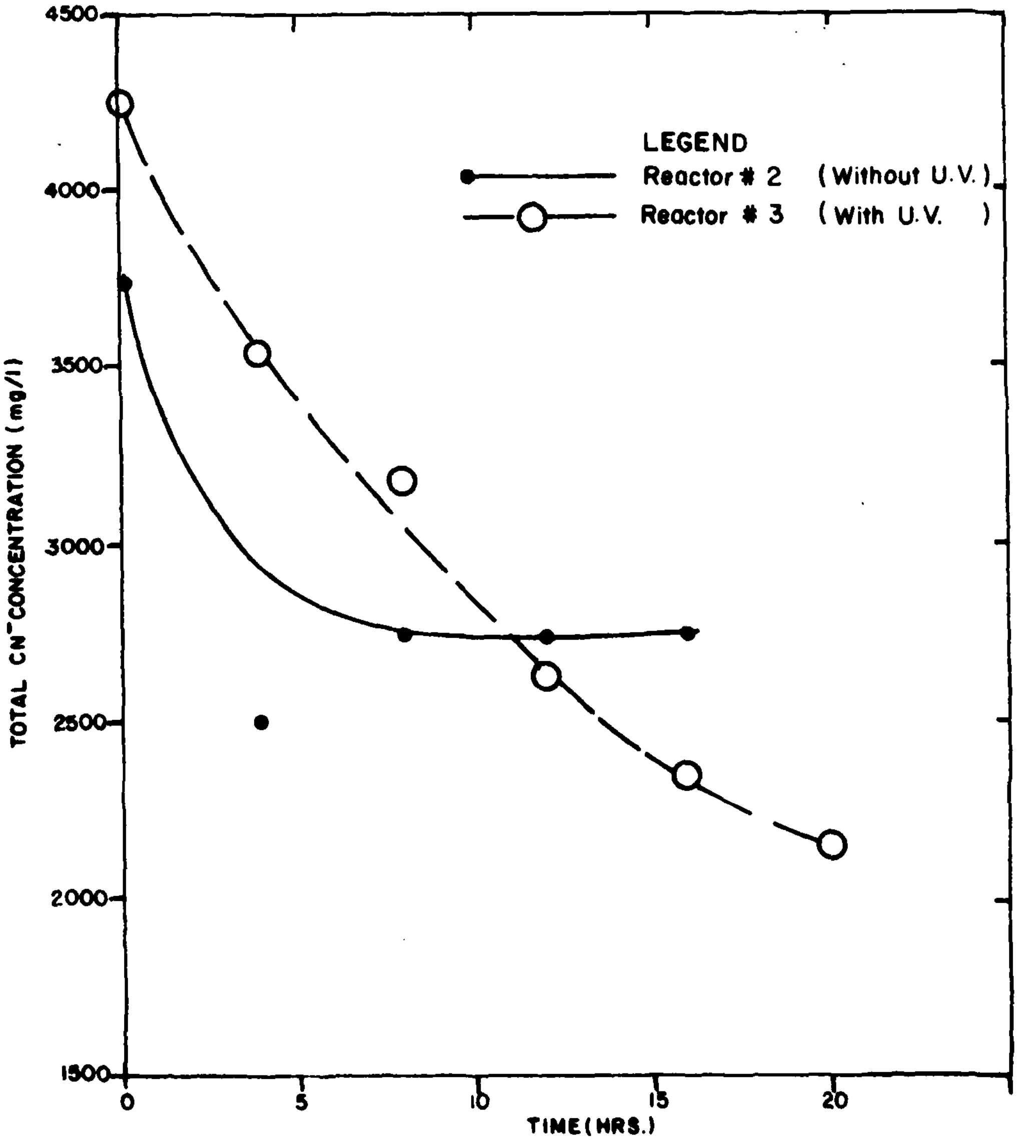

Figure 14 Ozonation of Complexed Metal Cyanide

At this point, it was decided to investigate the effect of concentration and pH adjustment on the removal rates. It was felt that dilution of the waste would increase the penetration from the UV lamps. First, 75 percent of the waste in reactor 3 was discharged, then the reactor was refilled with tap water. After dilution the cyanide concentration in reactor 3 was 370 mg/L and the pH was 10.4. For the following test, air flow to reactor 3 was 21 scfm (9.9 l/s) and had an average ozone concentration of 0.92 percent by weight. The average temperature of the reactor was 120°F (48.9°C). The test was continued for 11 hours. The cyanide concentrations are presented in the first part of Figure 15. During the test 0.60 lbs. (0.3 kg) of cyanide were removed and 9.55 lbs. (4.3 kg) of ozone were added for a O_3/CN^- removed rate of 16. The removal rate for this test was 0.054 lbs. (0.02 kg) of cyanide per hour compared to 0.062 lbs (0.03 kg) of cyanide per hour for the previous test without dilution. Thus lowering the concentration was not beneficial.

The next batch test involved reducing the pH of the diluted waste and continuing the treatment. It is noted a period of 20 days passed from the end of the dilution study to the beginning of this test. The pH in reactor 3 was adjusted from 10.1 to 7.0 by adding 30 liters of concentrated sulfuric acid (H_2SO_4). The cyanide concentration in reactor 3 after pH adjustment was 210 mg/L. Air flow and ozone concentration to reactor 3 averaged 21 scfm and 0.93 percent, by weight, respectively. The results of the test are shown in the second part of Figure 15. During the first 4 hours, the pH increased to 8.9 and was adjusted back to 7.0 with H_2SO_4. No drop in cyanide concentration was detected until 9 hours of treatment. The concentration of cyanide continued to decrease to approximately 75 mg/L when the removal rate slowed significantly. During the period of more rapid removals approximately 0.42 lbs. of cyanide was removed in a 10 hour period. Thus the pH adjustment did not increase the removal rates. However, it was observed that lowering the pH to 7.0 resulted in the formation of a very good floc which rapidly settled. The solids consisted primarily of metal hydroxides formed once the cyanide complexes were broken. Typical data for solids build up and composition are given in Section 7.

After 40 days, continuous batch testing of reactor 3 was resumed for a period of approximately 32 hours. At the start of this final batch test, the pH in reactor 3 was 5.7. The initial cyanide concentration was 81 mg/L. Air flow and ozone concentration averaged 20 scfm (9.4 l/s) and 0.76 percent by weight, respectively, during the test. Cyanide concentration versus cumulative test time is plotted in Figure 16.

The data show the cyanide concentration initially decreased to 35 mg/L after four hours of treatment, followed by a period in which the cyanide concentration decreased very little. After 16 hours of testing, the pH had decreased to 3.9 in reactor 3 and was adjusted to 7.0 by adding NaOH. At the end of 32 hours the pH decreased once more to 4.2. During the test, 22 lbs. (10 kg) of ozone were added amd 0.18 lbs (0.08 kg) of cyanide removed in reactor 3, giving an O_3/CN^- removed-ratio of 122. The temperature in reactor 3 averaged 125°F (51.7°C). These results indicate certain metal cyanide complexes, primarily iron/cyanide complexes, are very resistant to treatment by ozone oxidation, even with UV radiation present.

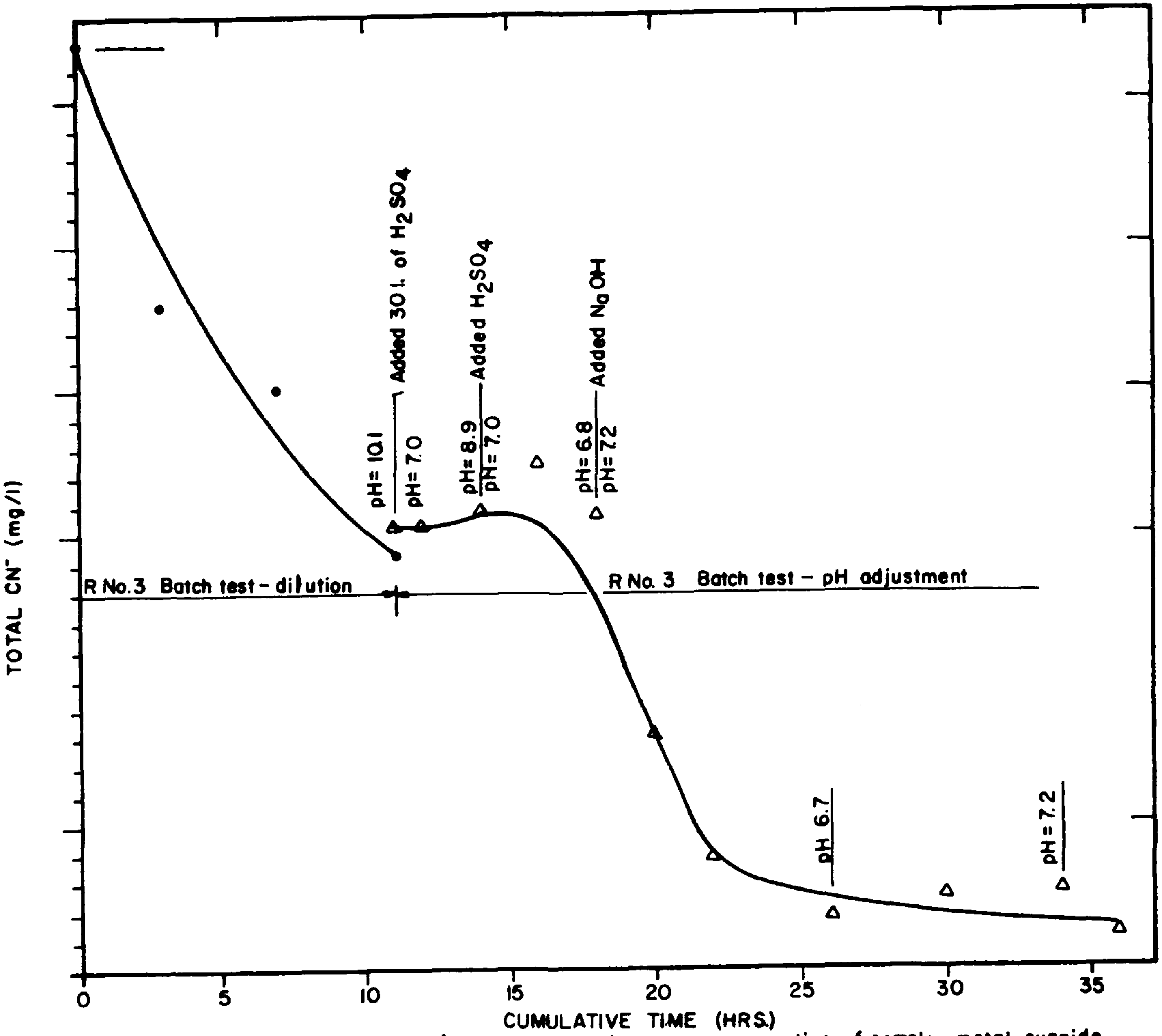

Figure 15 Effect of dilution and pH adjustment on ozonation of complex metal cyanide

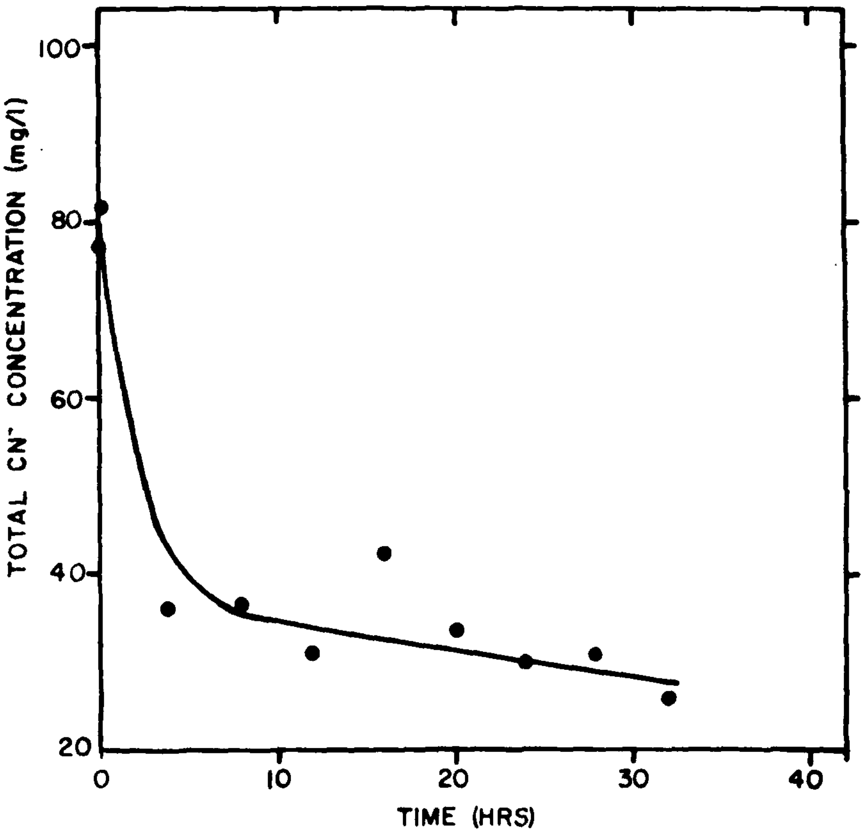

Figure 16 Batch treatment of reactor 3 at low CN^- concentration

7. CONTINUOUS SYSTEM OPERATION

The final system configuration tested was continuous operation. No waste was recycled during this testing phase. Prior to the test, buck boost transformers were installed in each ozpac unit to increase the primary voltage from 208 volts to 230 volts, thereby increasing the system's power output capabilities and ozone production. Fresh cyanide waste was used for the test. During the test, the cyanide concentration of the incoming waste remained virtually constant, at 12,110 mg/L. The average pH of the raw waste was 12.3. The test spanned two consecutive weeks with continuous 24 hour operation except during the weekend when the system was shut-down. Thus the discussion which follows is presented as two separate phases coinciding with each week of the two week period.

Concentration of cyanide for each reactor and for the raw influent during the first week of testing is presented in Figure 17. The average influent flow was 6.29 gph (0.4 l/m). Test conditions are summarized in Table 14. Air flow to reactor 2 was discontinued after 17 hours of testing when the mixer motor for reactor 2 quit functioning properly. The mixer speed for reactor 1 was 90 rpm throughout the test. The average ozone concentration in the air stream was 0.60 percent by weight. The UV lamps in reactor 3 were operated throughout the test period.

From Figure 17, the cyanide concentration in reactor 1 began to level off at approximately 1050 mg/L after 20 hours of continuous operation. Reactor 1 was removing 91 percent of the cyanide present in the incoming waste. From mass balance computations reactor 1 was removing 0.58 lbs (0.26 kg) of cyanide per 2.0 lbs. (0.91 kg) of ozone added each hour. This is equivalent to an O_3/CN^- removed-ratio of 3.4. Metal concentrations in the raw waste entering reactor 1 were 135 mg/L Fe, 30 mg/L Zn, 200 mg/L Ni, 500 mg/L Cd, and 958 mg/L Cu. The concentration of cyanide complexed with the metals was calculated as 2409 mg/L. These results indicated all free cyanide present in the raw waste was removed in reactor 1. Further, reactor 1 was removing at least 50 percent of the cyanide present in complexed form. These observations and a relatively high O_3/CN^- removed-ratio of 3.4 computed for reactor 1 indicates the process was reaction-rate limiting.

TABLE 14. CONTINUOUS SYSTEM OPERATION

Reactor	Equilibrium Cyanide Concentration (mg/L)	Average pH	Air Flow Rate (scfm/L per sec)
1	1050	10.5	73.7/34.6
2	--	--	17.3/8.1
3	120	10.3	19.8/9.3

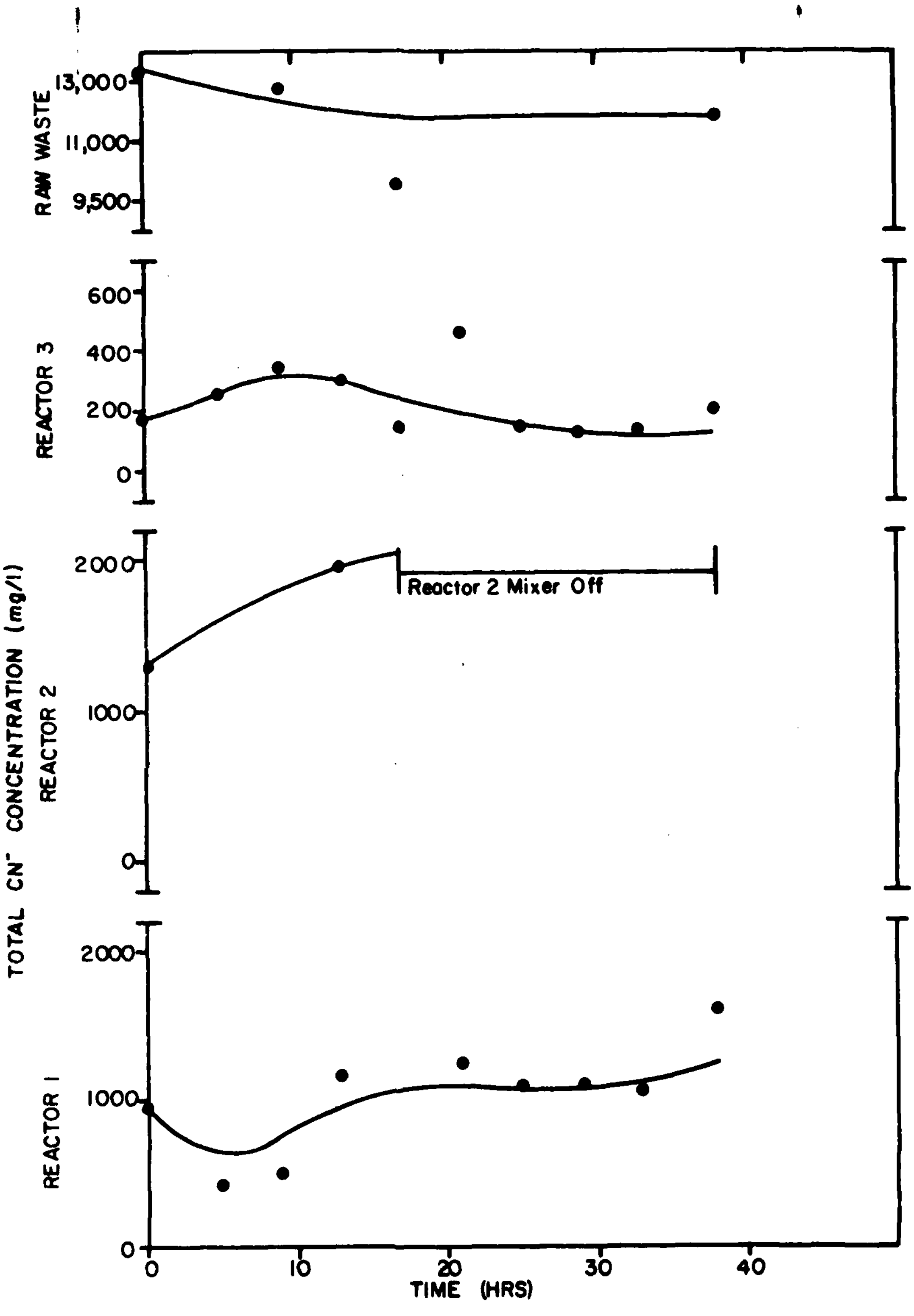

Figure 17 Treatment of CN^- waste with continuous inflow

The cyanide concentration in reactor 2 had not reached equilibrium when the mixer motor malfunctioned. At this point, air flow to reactor 2 was discontinued. The motor was replaced before the next test began.

Figure 17 shows that cyanide concentration in reactor 3 reached equilibrium approximately 24 hours after the test began. The equilibrium concentration of cyanide in reactor 3 was 120 mg/L. The incoming waste had a cyanide concentration of approximately 1050 mg/L. Therefore, 89 percent of the cyanide entering reactor 3 was removed and 8 percent of the cyanide present in the raw waste (12,110 mg/L) was oxidized in reactor 3. Mass balance computations indicated 0.53 lbs. (0.74 kg) of ozone were added for each 0.05 lbs. (0.02 kg) of cyanide removed per hour, or a O_3/CN^- removed-ratio of 10.6. Again, it was observed that the complexed metal cyanide present in the waste are limiting the reaction rate in reactor 3.

The system was shut down for the weekend and the test was resumed the following Monday. Before the beginning of the next test period, the mixer on reactor 2 was replaced. Test results for the second week of continuous operation are presented in Figure 18. The average raw waste flow during the second week was 6.17 gph (0.4 l/m). Other test conditions are summarized in Table 15. The previous week's results indicated that the mass flow of ozone was not limiting the cyanide removal-rate, but rather that the complexed metal cyanide reaction was the limiting factor. Thus the ozone concentration was lowered slightly during the second week to further evaluate this observation. The average air stream ozone concentration was 0.49 percent by weight. The UV lamps were operated continuously in reactor 3.

From Figure 18 the concentration of cyanide in reactor 1 remained fairly constant throughout the test. The average cyanide concentration in reactor 1 was 904 mg/L. Reactor 1 was removing 93 percent of the incoming cyanide. Ozone was added at a rate of 1.6 lbs (0.7 kg) per hour and cyanide removed at a rate of 0.58 lbs. (0.26 kg) per hour (an O_3/CN^- removed-ratio of 2.8). Although the rate is relatively high, it is still less than the previous test rate of 3.4 for reactor 1. This further illustrated the influence of the complexed metal cyanide present in limiting the removal rates. Lowering the air stream ozone mass flow rate increased the ozone utilization efficiency without decreasing the overall removal rate in reactor 1.

TABLE 15. CONTINUOUS SYSTEM OPERATION

Reactor	Equilibrium Cyanide Concentration (mg/L)	Average pH	Air Flow Rate (scfm/L per sec.)	Average Reactor Temp. (°F/°C)
1	904	10.3	74.2/34.9	89/31.7
2	1100	10.1	15.6/7.3	92/33.3
3	200	10.4	19.2/9.0	127/52.8

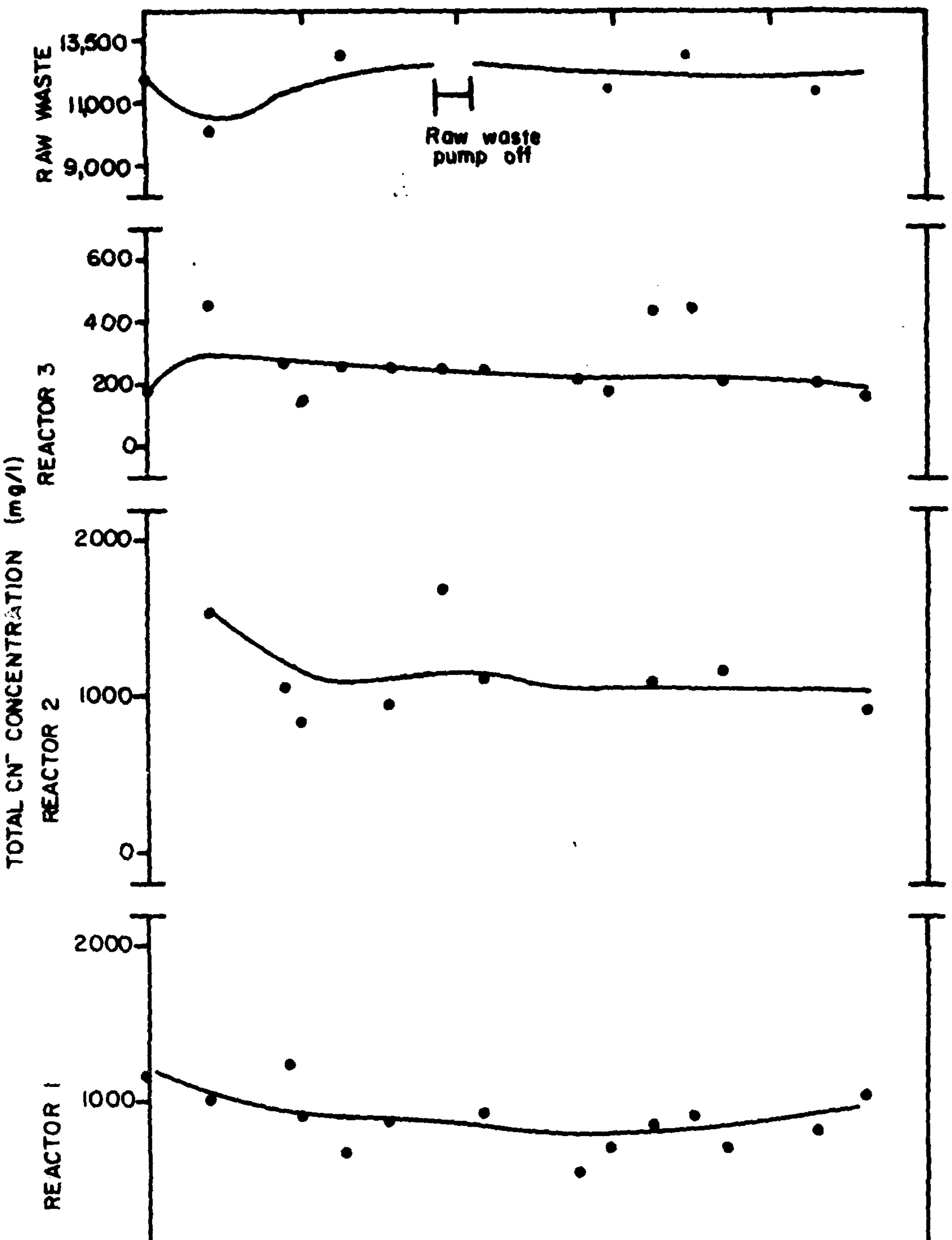

Figure 18 Treatment of CN⁻ waste with continuous inflow

The cyanide concentration in reactor 2 began to level off after 30 hours of operation to around 1100 mg/L. This indicated that no cyanide removal was occurring in reactor 2. From the metals analysis, all cyanide entering reactor 2 was in the complexed form and no free cyanide was present. The ineffectiveness of reactor 2 in removing the complexed cyanide resulted in large quantities of ozone being released in the off gas from reactor 2.

In contrast to reactor 2, the complexed cyanide was more effectively removed in reactor 3 as evidenced in Figure 18. The cyanide concentration was reduced to approximately 200 mg/L throughout the test in reactor 3. Ozone was added to reactor 3 at a rate of 0.42 lbs (0.2 kg) per hour and cyanide removed at a rate of 0.05 lbs. (0.02 kg) per hour or an O_3/CN^- removed rate of 8.4. The ozone utilization efficiency was increased by decreasing the ozone mass flow rate from the previous test value. Radiation was very effective in increasing the removal rates in reactor 3 when compared to reactor 2.

For the two weeks of testing, the ozone-cyanide system was able to consistently remove 99 percent of the cyanide from the waste stream. In reactor 1, 92 percent of the cyanide was removed including all the free cyanide present and the more easily oxidizable complexed cyanide present. All the cyanide entering reactor 2 was in the complexed form and essentially no treatment occurred through reactor 2. The remaining 7 percent of the cyanide removal occurred in reactor 3, where UV radiation was effective in breaking down the complexed metal cyanide.

In the system, suspended solids concentration increased during treatment. The raw waste contained 10 mg/L TSS whereas the waste exiting reactor 1 contained 8300 mg/L TSS. The solids formed readily settled and consolidated. Analysis of the sludge indicated 24.2 percent on a dry weight basis consisted of Fe, Zn, Ni, Cd, Co, and Cu. Relative contributions for the metals were 3.45 percent Fe, 0.975 percent Zn, 10.75 percent Ni, 6.57 percent Cd, 0.0158 percent Co and 2.475 percent Cu.

SECTION VII

EVALUATION OF CYANIDE TREATABILITY

1. INTRODUCTION

In ozone oxidation of cyanide wastewaters, several factors were found to influence the overall efficiency of the system during the study. Many of these were previously identified and included; for example, ozone mass flow rate, ozone air stream concentration, radiation and cyanide concentration remaining. At a given time in the treatment process, circumstances will dictate which of these parameters are controlling the cyanide removal rates. In this section, factors effecting treatment efficiency are evaluated further in order to establish criteria for optimum system performance.

A graphical methodology is presented to establish regions in which the treatment rates are dependent upon cyanide concentration remaining in the reactor. The influence of ozone concentration and other parameters are also clarified. These observations are compared with previous work in the literature. Finally, reaction rates for batch processes are computed and a comparison of the effects of radiation and elevated temperatures is presented.

2. EVALUATION OF FACTORS CONTROLLING TREATMENT EFFICIENCIES

For many of the test runs discussed in the previous sections, graphs were prepared depicting the results in terms of parameters which reflect process efficiency. One of the parameters used is the change in reactor cyanide concentration per incremental time period (cyanide removed/unit time as pounds per hour). This parameter reflects changes in the rate of cyanide removals but does not reflect the other main process parameter, ozone. Thus, the parameter defined as reactor change in cyanide concentration per unit time per quantity of ozone added to the system per unit time (cyanide removed/unit time/ozone added/unit time) is represented by the symbol CN^-/O_3 and used throughout the section as a means of incorporating ozone in the evaluation of process efficiency.

2.1 Removal Rates at High Reactor Cyanide Concentrations

The first graph, Figure 19, depicts the cyanide removal rates measured during a batch test of reactor 2. The cyanide concentrations in the reactor were high during the test, varying from 20,000 mg/L to 15,000 mg/L. A bar type graph has been used to show the removal rates. An interpretation of the figure is that the area under the bar in a specified time period represents the amount of cyanide (lbs.) removed in the reactor. For the high cyanide concentrations studied, the bar graph was found to be a good method to illustrate the changes in the system efficiency parameters and is used for this purpose throughout the section.

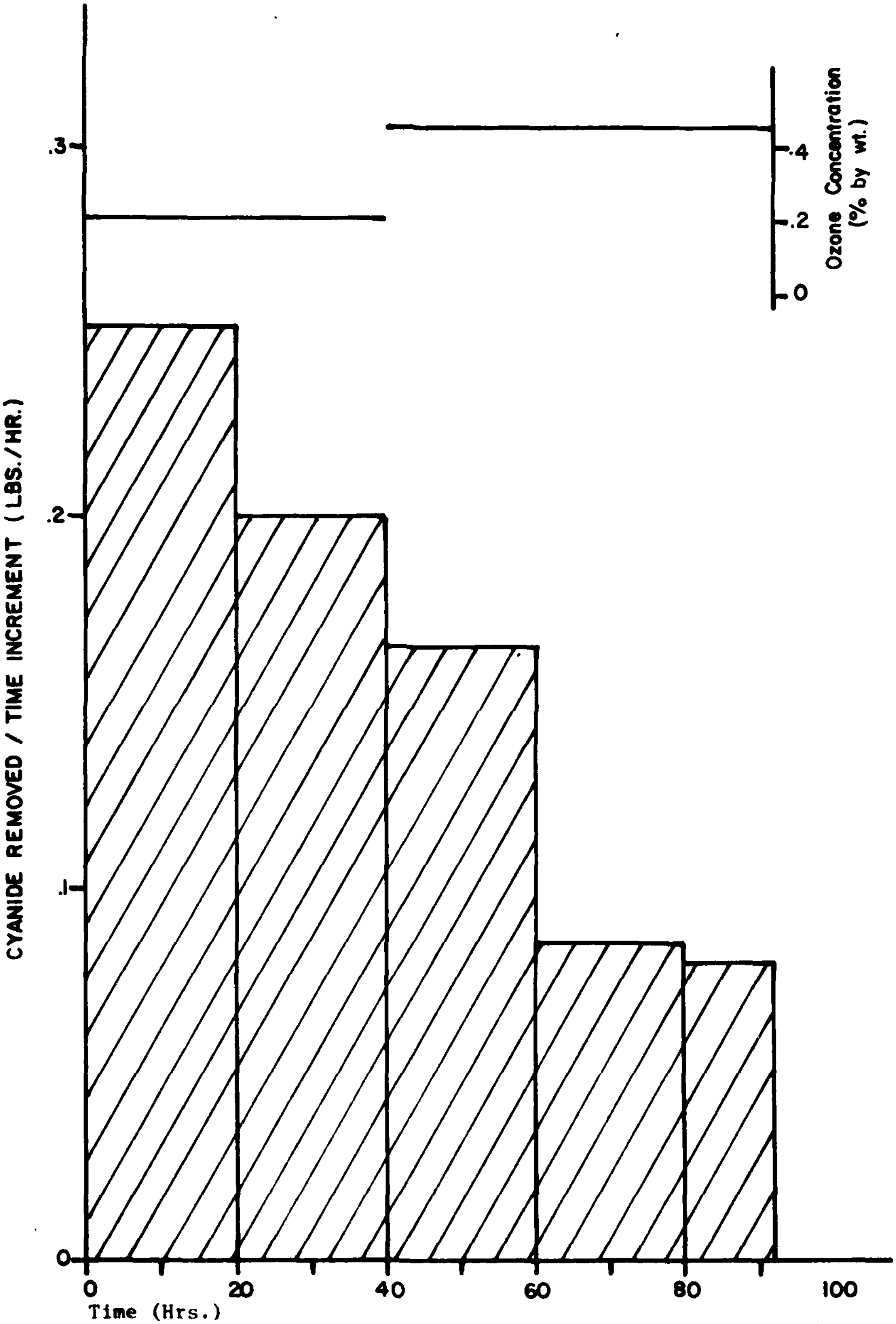

Figure 19 Cyanide removal rates during a batch test of reactor 2

During the first incremental test period the figure shows cyanide was removed at a rate of 0.25 lbs/hr. (0.11 kg/hr). Afterwards, the cyanide removal rates progressively declined. A graph showing ozone concentration during the test is also depicted in Figure 19 and indicates the concentration remained constant for the first 40 hours, increasing to a second plateau for the remainder of the test period. The removal rates continued to follow a decreasing pattern with constant and increasing ozone concentrations. Thus, the rate of cyanide removal appears dependent upon residual cyanide concentration.

For the same test, Figure 20 represents the changes in process efficiency reflected by the CN^-/O_3 parameter previously defined. Ozone mass-flow rate for the test period is also depicted. The ozone mass flow decreased at the same time the ozone concentration was increased (40 hrs.). This occurred since the reactor air flow rate was decreased. Figure 20 shows process efficiency (as measured by the parameter CN^-/O_3) did not decrease at this time even though the cyanide removal rates had decreased. This suggests optimizing the process in terms of ozone utilization efficiency can be accomplished by adjusting the ozone mass-flow during treatment to coincide with cyanide removal rates. The lower limit for the adjustment would be controlled by maintaining the process efficiency (CN^-/O_3) and cyanide removal rate at the maximum practical level.

2.2 Removal Rates at High Cyanide Concentrations with Ultraviolet Radiation Present

Figure 21 presents the variation in cyanide removal rates which occurred during a batch test of reactor 3 (which contains ultraviolet lamps). Cyanide concentration varied from 25,000 to 12,000 mg/L. The initial cyanide removal rates were slow, then greatly increased after 20 hours of testing. An increase in the ozone concentration at the 40 hour period was accompanied by a further increase in removal rates. After about 50 hours, the removal rates followed the same declining curve observed for the test in reactor 2 while constant levels of ozone concentration were maintained. Thus, as in the previous section, the reaction in this region is dependent on residual cyanide concentration. For reactors 2 and 3, the reactor cyanide concentrations were generally above 15,000 mg/L in this region.

Figure 22 shows the variation in process efficiency (CN^-/O_3) and ozone mass flow rate during the test. The process efficiency decreased slightly as the ozone concentration and mass flow was initially increased. As noted above, the removal rates correspondingly increased at this point. Thus optimization of the process can be accomplished by maintaining a practical balance between these two operation parameters. The changes occurred as the ozone concentration was increased from 0.21 percent to 0.46 percent by weight. At 0.46 percent ozone, the process efficiency continued to decrease until approximately 90 hours into the test. At this point the process efficiency was increased by decreasing the ozone concentration to 0.34 percent by weight. From Figure 21, this decrease did not cause the removal rate pattern to change.

The process efficiency plots for the batch tests of reactors 2 and 3 are superimposed in Figure 23. The ozone concentrations were the same during both tests. Also, reactor cyanide concentrations were both high, i.e.,

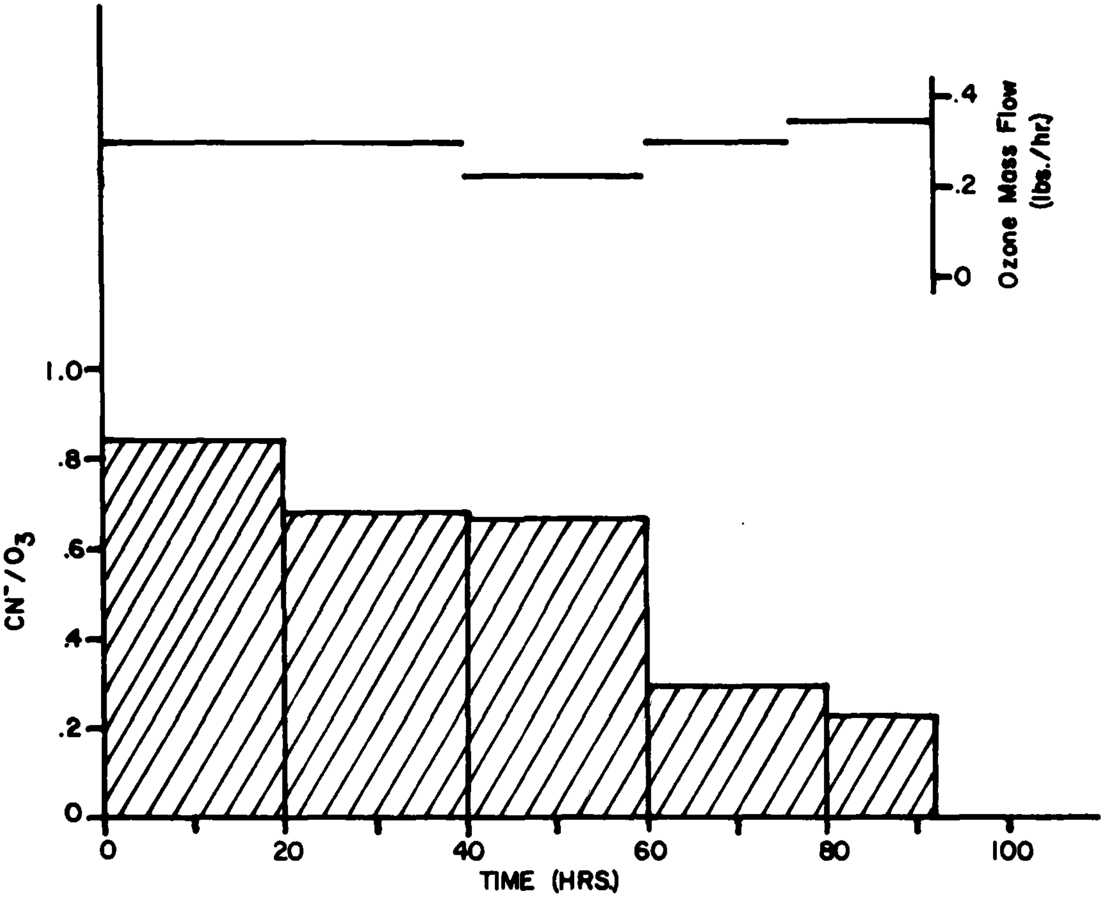

Figure 20 Changes in process efficiency at high reactor CN^- concentrations

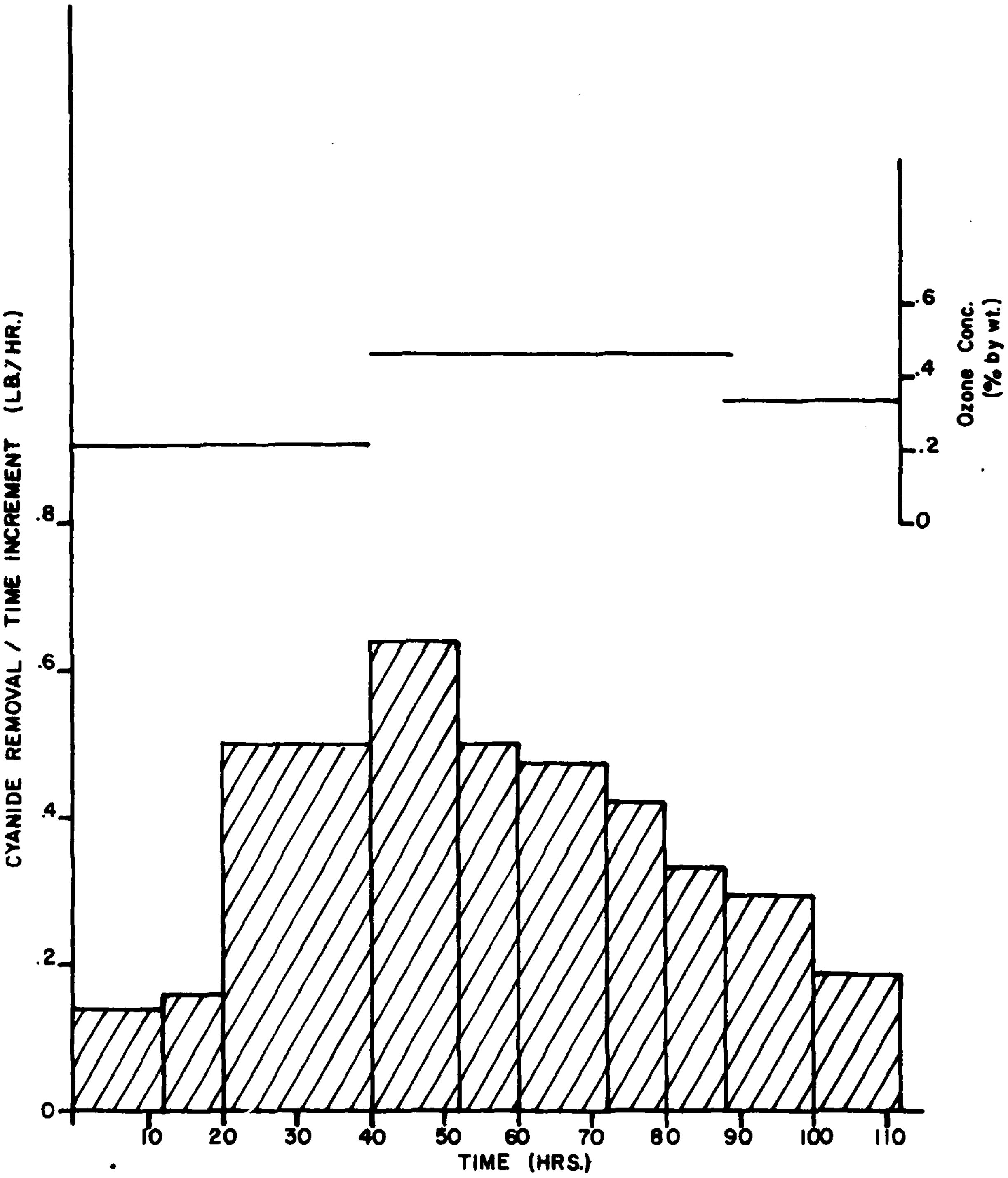

Figure 21 Cyanide removal rates during a batch test of reactor 3

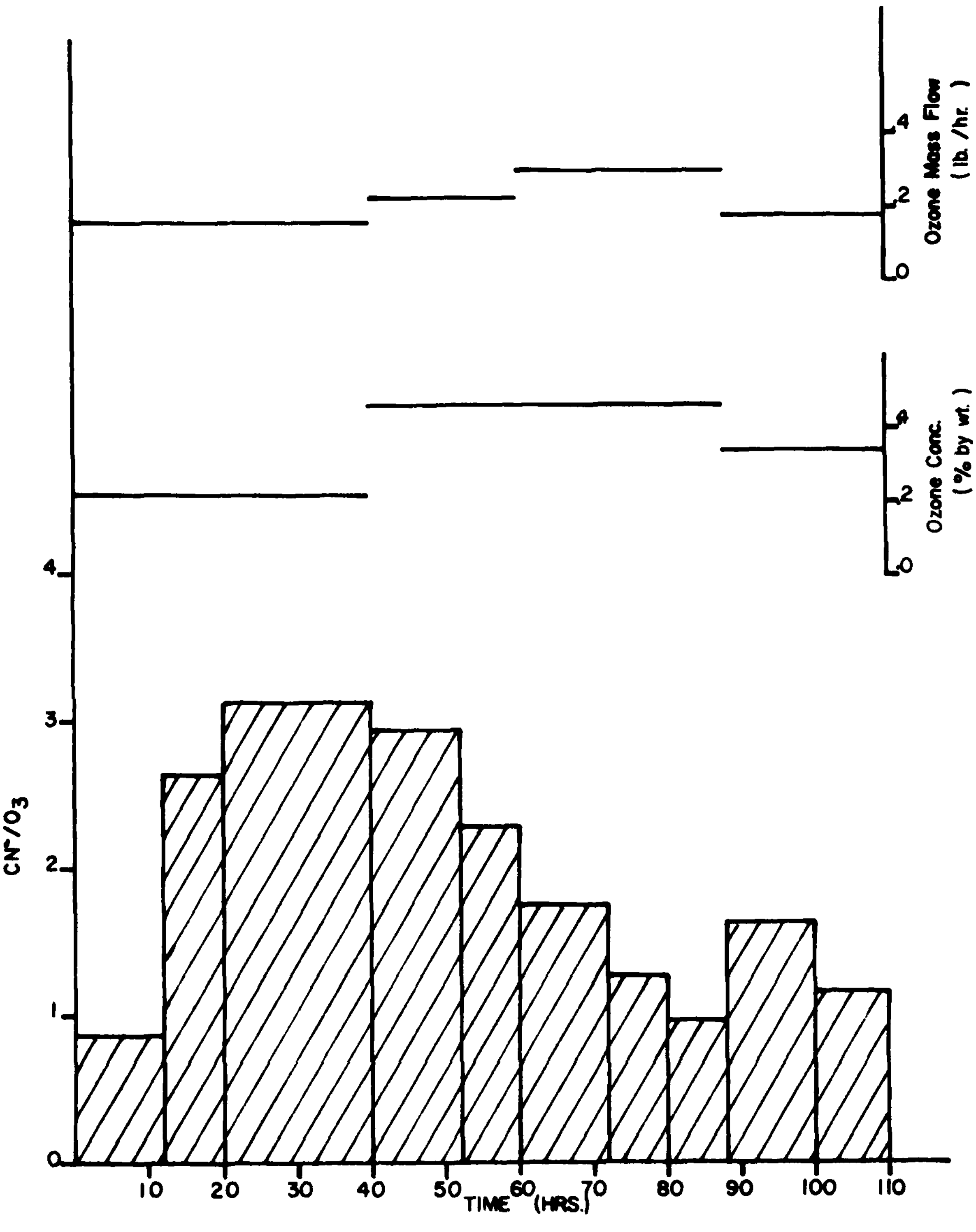

Figure 22 Value of the ratio CN⁻/ O_3 during a batch test of reactor 3

initially 20,000 mg/L. During the initial 12 hours, the reactor process efficiencies were the same. At the 12 hour point, reactor 3 took a significant jump, indicating that the elevated temperatures resulting from ultraviolet radiation could play a significant role in the ozone/cyanide process efficiency. The reactor temperatures at the point were 26°C and 52°C (78.8°F and 125.6°F) for reactor 2 and 3, respectively. Figure 23 further illustrates the process efficiencies in reactor 3 are significantly greater than reactor 2 during the remainder of the test period. As the reactor test conditions are the same, it was concluded that UV radiation, associated elevated temperatures improve the ozone/cyanide efficiency for high free cyanide concentrations quantitatively by a factor of 4 to 5.

2.3 Initially Increasing Cyanide Removal Rates at High Cyanide Concentrations

During the study, an initial period of relatively slow removal rates occurred for some of the cyanide waste treated, followed by gradually increasing rates. This was especially true for raw, untreated wastes. These periods were of a significant duration to warrant consideration in the system design phase. Figure 24 depicts such an example for a batch-treatment test of reactor 1. The waste, at the beginning of the test, was untreated with a total cyanide concentration of 63,000 mg/L. The graph indicates very low removal rates of 0.1 lb. CN^-/hr. to 0.2 lb. CN^-/hr. were achieved during the initial 20 hours of treatment. Also, the figure indicates that the rates continuously increased during the 100 hour plus batch test. Figure 25 shows the associated process efficiencies during the test, which also increased proportionately. Further, the reactor pH did not change during the test period and appears unrelated to the cyanide removal rate. Based on these observations, one can conclude that secondary carbon source was most likely present in the waste and was preferentially oxidized by the ozone.

A review of the literature indicated that this phenomena had not been adequately considered previously in evaluating the ozone process. Figures 3 and 4 in the literature review present the only published curves found depicting ozonation of highly concentrated nickel strip cyanide waste (Reference 3). Both graphs indicate an initial period of slow removal rates followed by increasing rates. Data from Figure 3 were used to construct Figure 26 which depicts the associated removal rates in the test time increments. The figure clearly shows that the same pattern initially occurred as is observed in Figure 24 for reactor 1.

These observations indicate that initial slow reaction rates constitute a significant impact on the process efficiency. Future process designs for ozonation of cyanide wastes should include consideration of this fact.

2.4 Process Parameters at Equilibrium Conditions During Continuous Operation

As noted previously, equilibrium was obtained during the study under continuous waste inflow/outflow conditions. Process parameter values computed during continuous operation are shown in Table 16. The ozone mass flow rates for the three tests varied from 1.3 to 2.0 pounds (0.6 to 0.91 kg) of

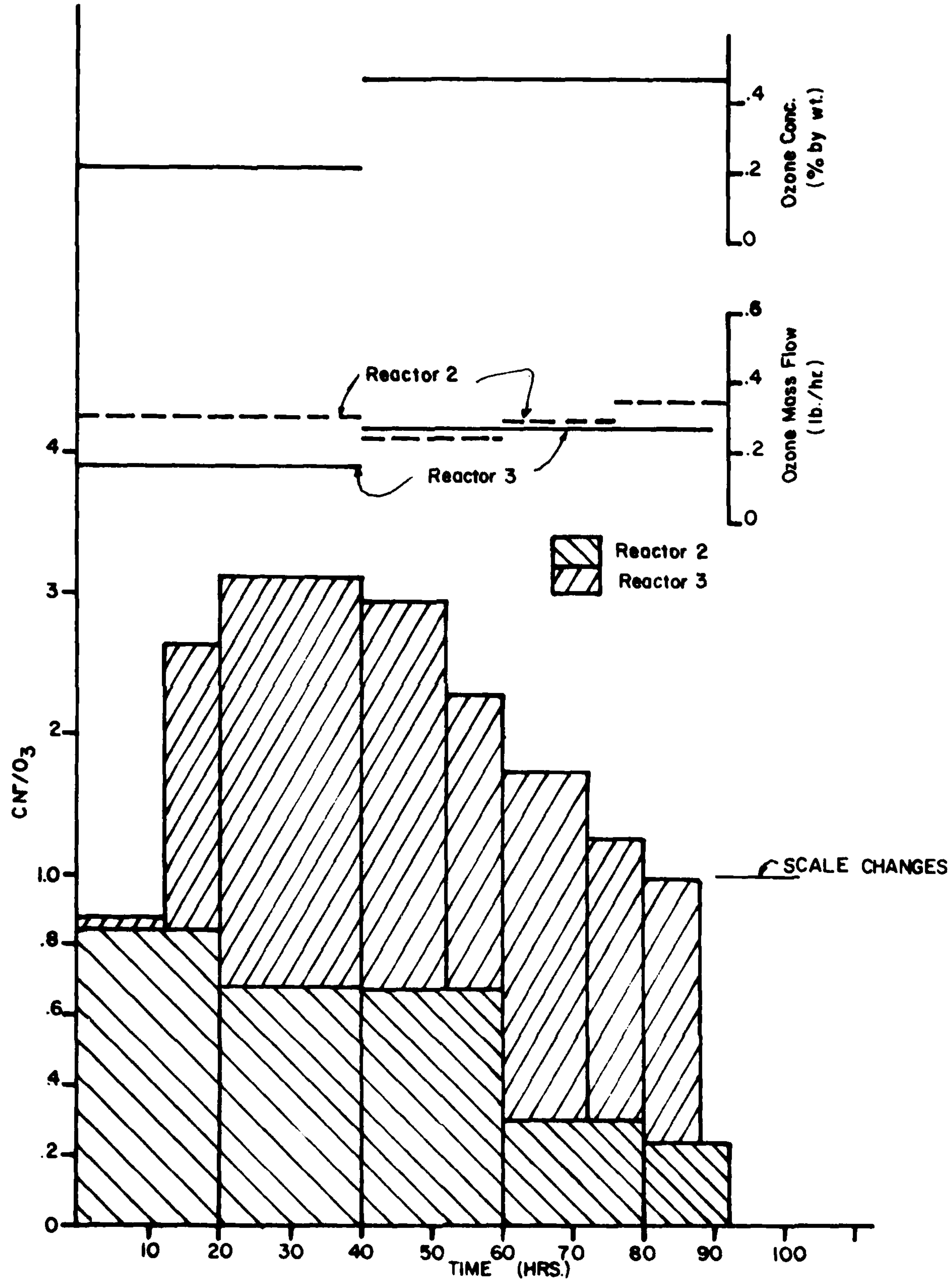

Figure 23 Comparison of $CN^{-}O_3$ for reactors 2&3

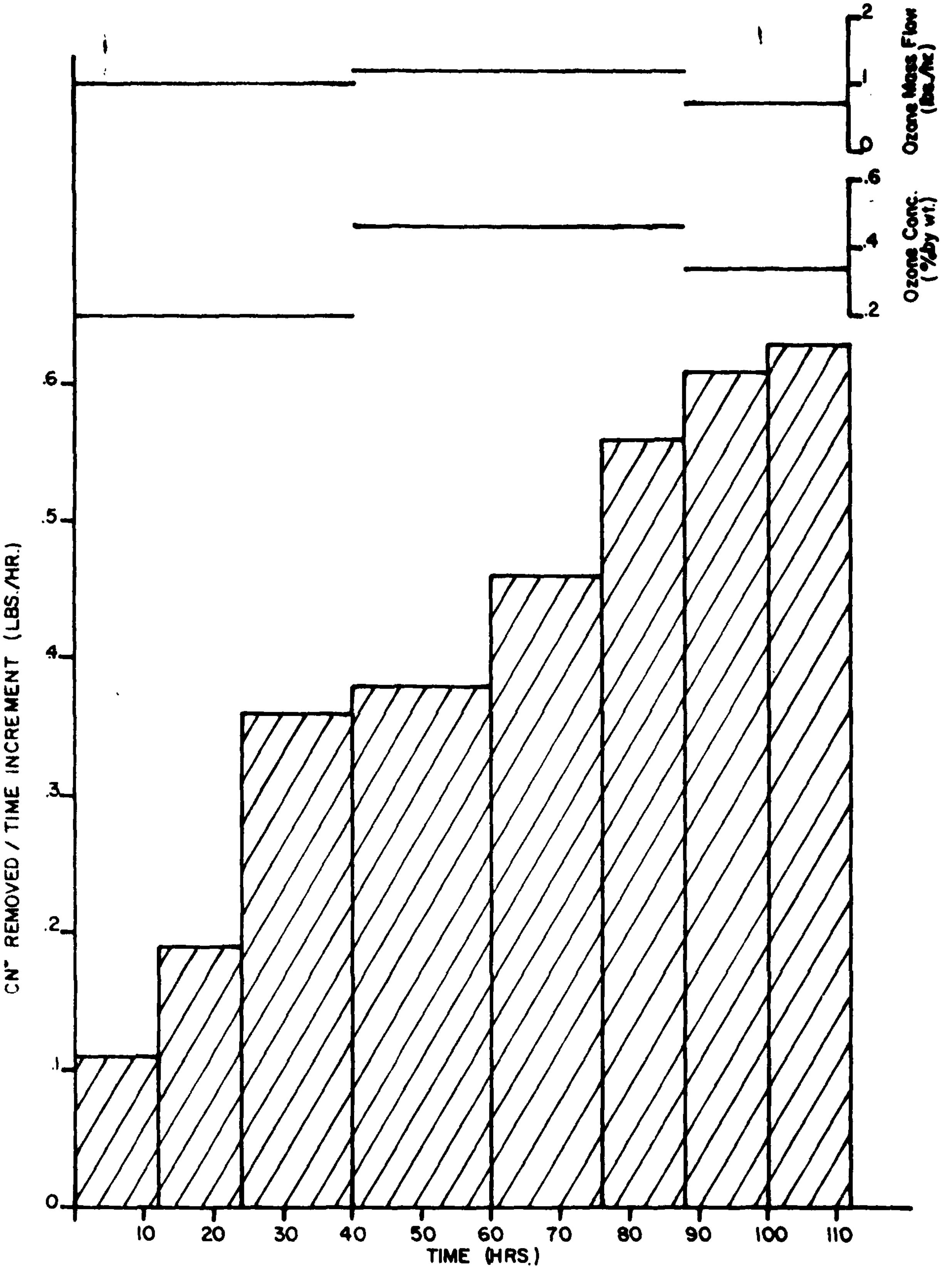

Figure 24 Cyanide removal rates during a batch test of reactor I.

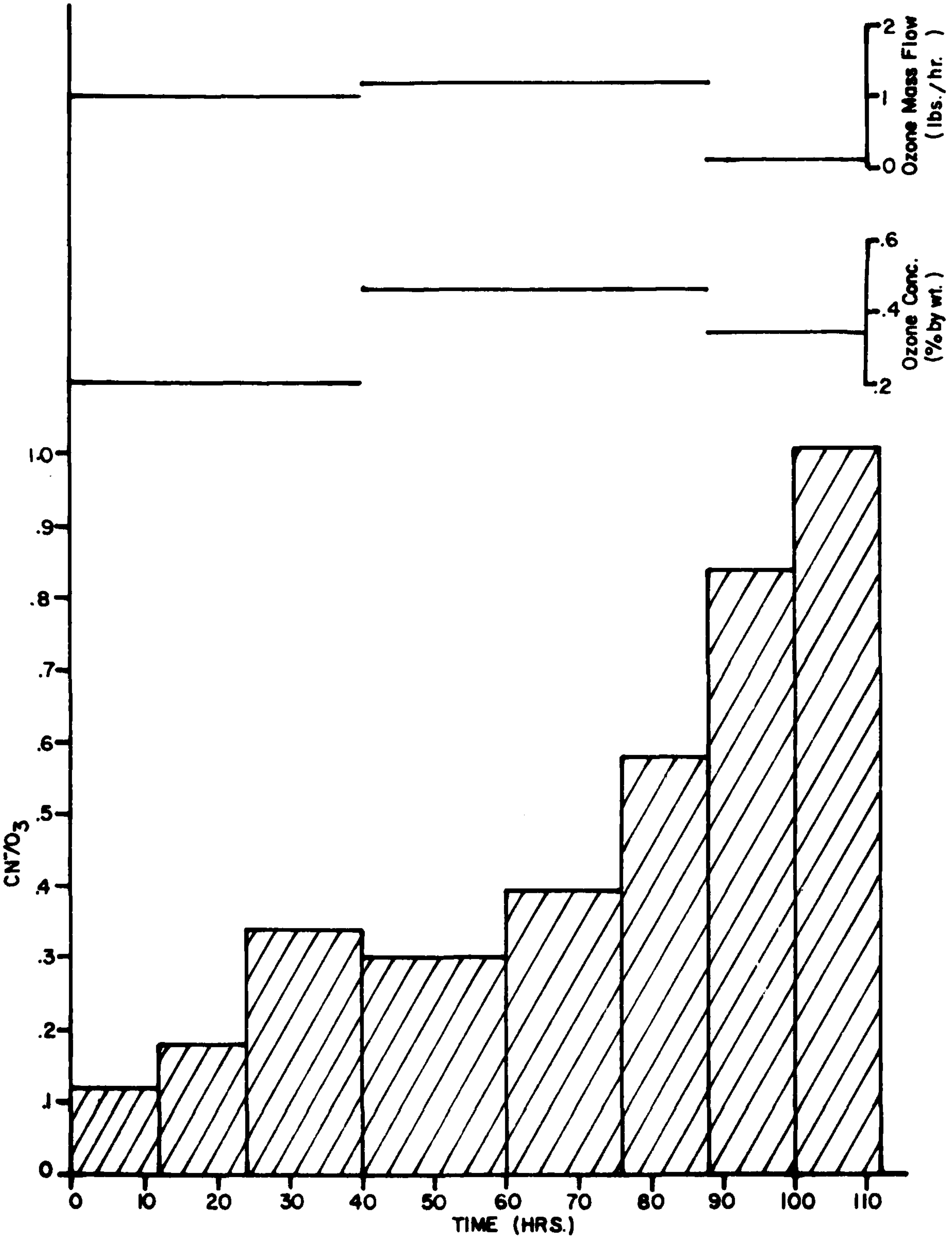

Figure 25 Values of the ratio CN^-/O_3 during a batch test of reactor I

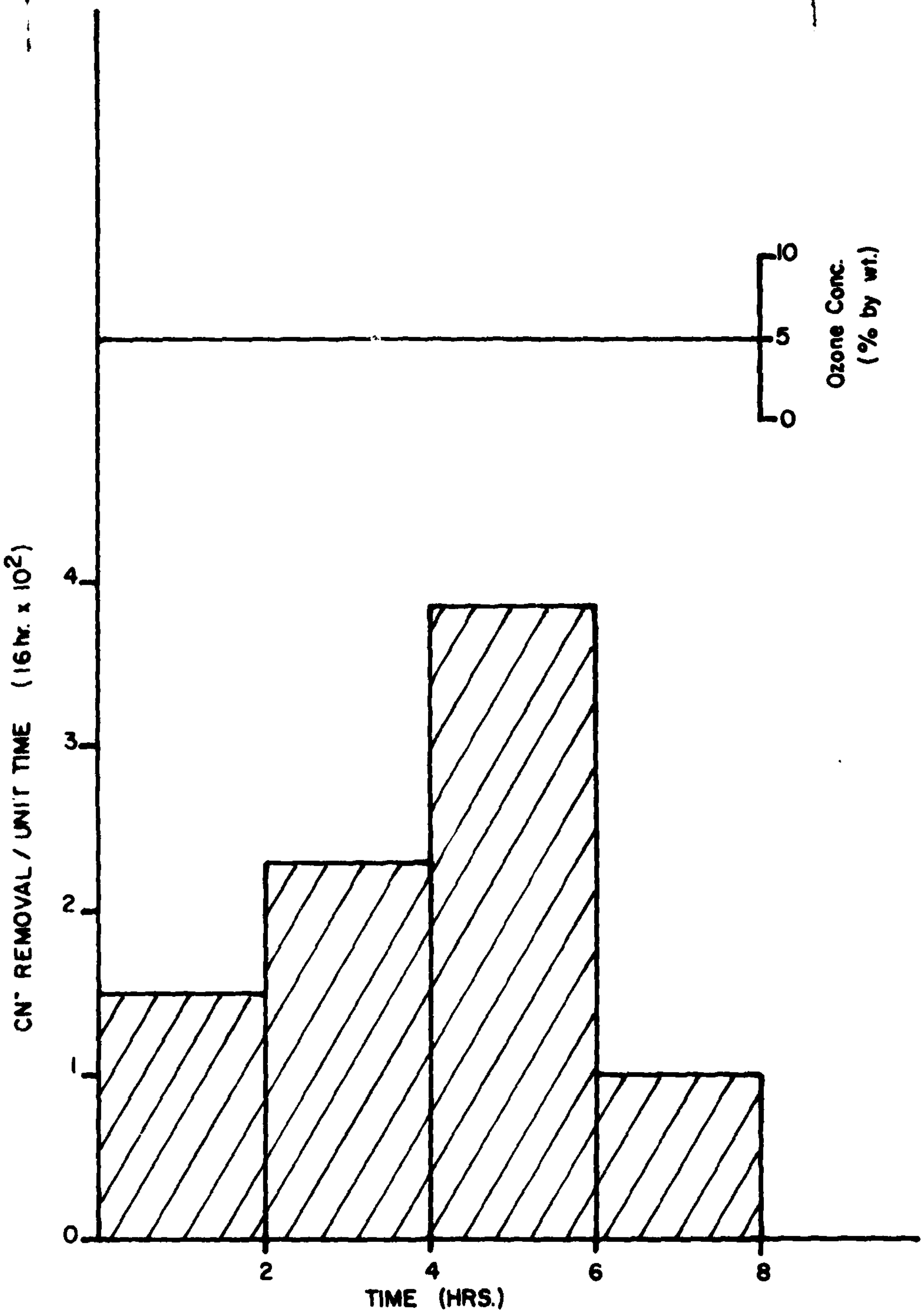

Figure 26 CN^- removal rates for Nickel Strip CN^- waste(3) ozone per hour. Also, ozone concentration in the air stream varied from 0.4 to 0.6 percent by weight. The cyanide loading rates were greatest for test no. 3 [2.4 lb/hr (1 kg/hr)]. This difference was not due to waste flow rate but to the equivalent cyanide concentration in the raw waste inflow which ranged from 11,000 mg/L to around 13,000 mg/L for test nos. 1 and 2 as compared to around 25,000 mg/L for test no. 3.

The cyanide removal efficiencies of tests nos. 1 and 2 averaged 91 percent and 93 percent, respectively, at equilibrium compared to 45 percent for test no. 3. The resulting reactor cyanide concentrations were around 1,000 mg/L for the first two tests compared to 14,000 mg/L for test no. 3.

However, since the ozone concentrations and ozone mass flow rates were comparable for all tests, the best measure of process efficiency is given by the CN^-/O_3 ratio shown in Table 16. For the first two tests this ratio averaged 0.32 and 0.83 for test no. 3.

For tests no. 1 and no. 2, analysis of the metals presented in the raw waste indicated approximately 2400 mg/L of cyanide would be in the complexed form. Thus the average reactor concentration of 975 mg/L was well below this concentration, indicating approximately 1425 mg/L (2400-975) of the complexed cyanide was being removed. Based on batch tests of the reactors with only complexed cyanide present at these concentrations, a range of 7 to 10 pounds of ozone per pound of complexed cyanide removed was required. The total ozone added from Table 16 averaged 1.8 pounds (0.8 kg) ozone/hour for tests nos. 1 and 2. Thus, assuming a requirement of 10 pounds ozone/pound of complexed cyanide removed, the complexed cyanide removed (1425 mg/L), based on the waste flow rate, has an ozone requirement of about 0.77 lb. O_3/hr. For the complexed cyanide removed in test no. 1 and no. 2 the process efficiency (CN^-/O_3) is then computed to have an average value of 0.10. For the free cyanide removed in test nos. 1 and 2, the process efficiency (CN^-/O_3) is computed to actually be 0.49 compared to the overall value of CN^-/O_3 equal to 0.32. This indicates the approximate effect that the complexed cyanide removed in test no. 1 and no. 2 had on the overall efficiency.

In comparison, for test no. 3, the concentration of complexed cyanide present was estimated to be 4500 mg/L from metals analysis. The reactor equilibrium concentration of 14,000 mg/L indicates no appreciable amount of complexed CN^- was being removed in this case. Thus the CN^-/O_3 value of 0.833 associated with test no. 3 represents a ratio related to free cyanide removal.

Thus, for the tests a more realistic comparison of process efficiencies would be an average value of 0.49 for test no. 1 and no. 2 versus 0.833 for test no. 3. The differences can be directly related to the residual reactor cyanide concentrations. The CN^-/O_3 ratios fall within the ranges given for a batch test of reactor 2 (Figure 20) which varied from a maximum of 0.82 to a minimum of around 0.22. It was previously demonstrated for the batch test that the rate of cyanide removal was a function of the concentration of cyanide remaining in the reactor. Similarly, for equilibrium conditions of the continuous tests, the high CN^-/O_3 ratios (0.833) were associated with high cyanide concentrations in the incoming waste and in the reactor whereas the low CN^-/O_3 ratios (0.29 to .36) were associated with lower cyanide concentrations in the incoming waste and in the reactor.

These ranges for the CN^-/O_3 ratio can be used to evaluate the relative efficiency of the ozone/cyanide oxidation process. The magnitude of the

TABLE 16. CONTINUOUS SYSTEM OPERATION PARAMETERS AT EQUILIBRIUM

Test No.	Reactor No.	Equilibrium CN^- Conc. (mg/L)	CN^- Added to Reactor (lb/hr.)	Ozone Conc. (% by wt.)	Ozone Mass Flow (lb/hr.)	CN^-/O_3	CN^- Removal Rate (lb/hr.)	CN^- Removal Eff. (%)
1	1	1050	0.64	0.6	2.0	0.29	0.58	91
2	1	904	0.62	0.6	1.6	0.36	0.58	93
3	1	14,000	2.4	0.4	1.3	0.83	1.08	45

CN^-/O_3 parameter indicates, to a certain extent, the dependence of the efficiency on the reactor and incoming waste cyanide concentrations.

2.5 Effect of pH on Process Efficiency

For a batch test of reactor no. 3, Table 17 presents changes in pH compared to process efficiency as measured by the CN^-/O_3 parameter at different times. No pH adjustment was performed during this test. From Table 17, the pH gradually decreased during the first 60 hours of the test, then slightly increased. In comparison, the values for CN^-/O_3 ratio decreased from 2.10 to 1.92 during the first 20 hours of testing, increased to 2.54 after 60 hours, and decreased again to 1.97 at the completion of the test. For reactor pH values of 11.5 and 10.5, the associated CN^-/O_3 ratios were 1.92 and 2.45, respectively. The same observation was made for a pH of 10.4 and 10.5 where the CN^-/O_3 ratios were 1.97 and 2.45. Thus, for the pH range in Table 17, 10.2 to 12.3, no significant change in the process efficiency resulted. This indicates that within the pH range of 10.0 to 12.0 no pH control for the process is required.

TABLE 17. CHANGES IN REACTOR pH DURING SYSTEM BATCH TESTING

Test Time (hours)	CN^-/O_3	pH
0	0	12.8
4	2.10	12.3
20	1.52	11.6
32	1.92	11.5
40	2.45	10.5
60	2.54	10.2
80	2.20	N.D.
100	1.97	10.4

3. EVALUATION OF REACTION RATES

In subsections 2.1 and 2.2 data for batch tests of reactors 2 and 3 were presented and discussed. Reactor-cyanide concentrations were at the same levels for both reactors. Periods were identified during which the cyanide removal rates continually decreased as ozone mass-flow and ozone air-stream concentrations were kept constant. In both instances, this indicates that the reactions occurring during these periods were dependent on residual cyanide concentrations in reactors 2 and 3.

In addition, process efficiencies for the two batch tests were discussed and compared. Figure 23 graphically depicts the comparative efficiencies as measured by the CN^-/O_3 parameter. The process efficiency for reactor 3 greatly exceeded that of reactor 2 in all cases. As waste concentrations and characteristics were the same for both reactors, the increased efficiencies in reactor 3 resulted from UV radiation and associated elevated temperatures.

For the two batch tests, reaction rates were evaluated. The data used in these computations coincide with the test periods in which the removal rates were found to be dependent upon the residual cyanide concentration.

For a first order reaction, the rate of removal is directly proportional to the concentration of reactant remaining. Mathematically this is expressed as follows (Reference 40):

$$-\frac{dC}{dt} = kC$$

where

C = reactant concentration
k = rate constant for the reactor
t = time

k has the units of reciprocal time. This expression can be integrated to give the following relationship:

$$\ln \frac{C_o}{C} = kt$$

C_o = initial reactant concentration

For a first order reaction, a plot of $\ln(C_o/C)$ versus time yields a straight line, and the reaction rate constant, k, is determined by evaluating the slope of the line. Taking cyanide concentrations in the reactors to be reactant concentrations (C) in the above expresssions, the plots shown in Figures 27 and 28 were prepared from data observed in the batch tests of reactors 2 and 3, respectively. Again, only data in the regions where the removal rates were concentration dependent were used in the analysis.

The data in Figures 27 and 28 yielded straight line plots. The associated reaction rates (k) were 0.009 hr^{-1} and 0.003 hr^{-1} for the reactors with and without UV radiation, respectively. This strongly indicates improvements in process efficiency associated with the UV radiation and elevated temperatures. It also provides a method for modeling batch treatment operations under similar conditions. Further, based on the reaction rates, a constant can be computed which approximates the dependence of the ozone/cyanide oxidation process on the presence of UV radiation and elevated temperatures. To make this evaluation, the reactor temperature was assumed to be a direct measure of the combined effects produced by UV radiation and elevated temperatures. The Arrhenius equation gives an expression for reaction rate variation with temperature:

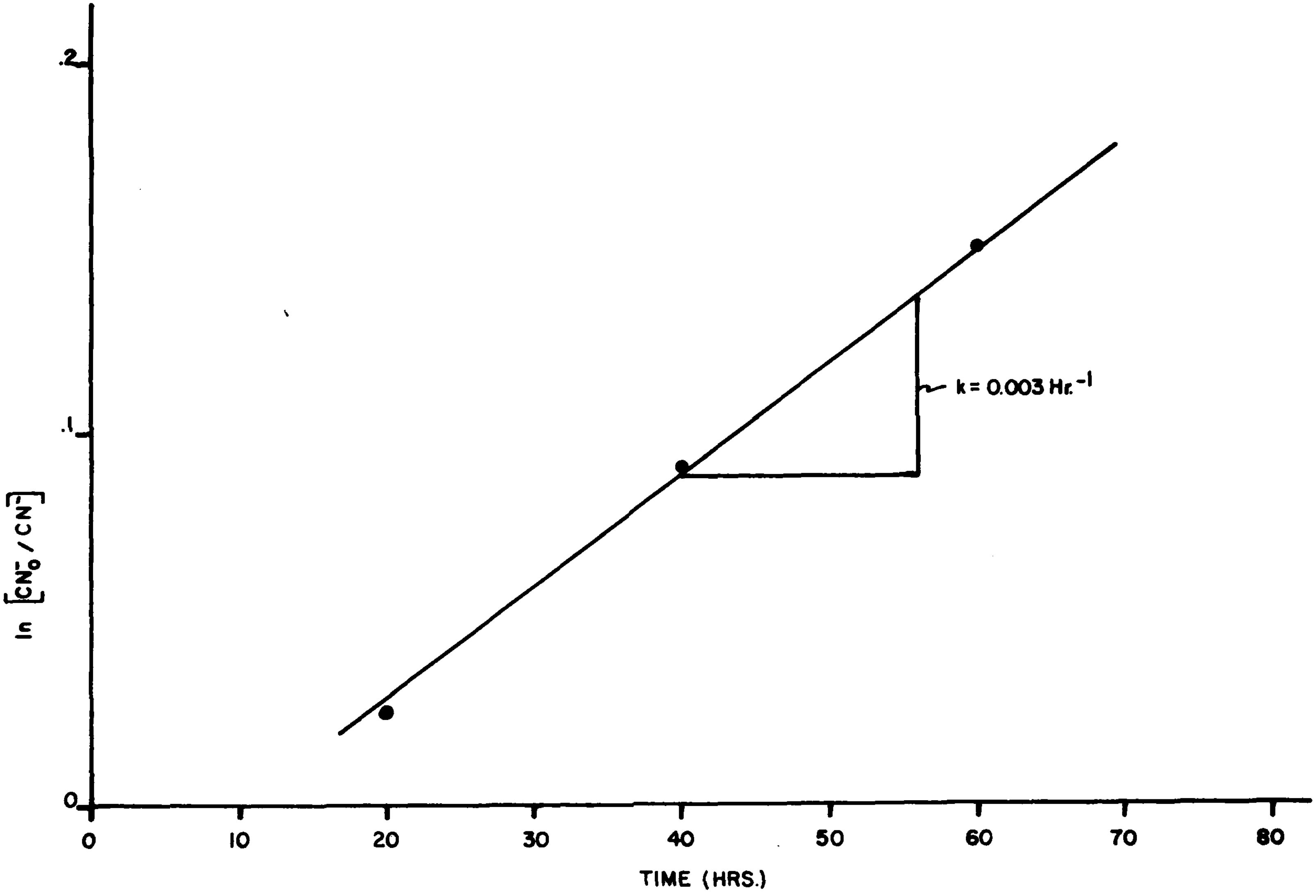

Figure 27 Reaction rate evaluation at high cyanide concentrations without U.V. radiation present

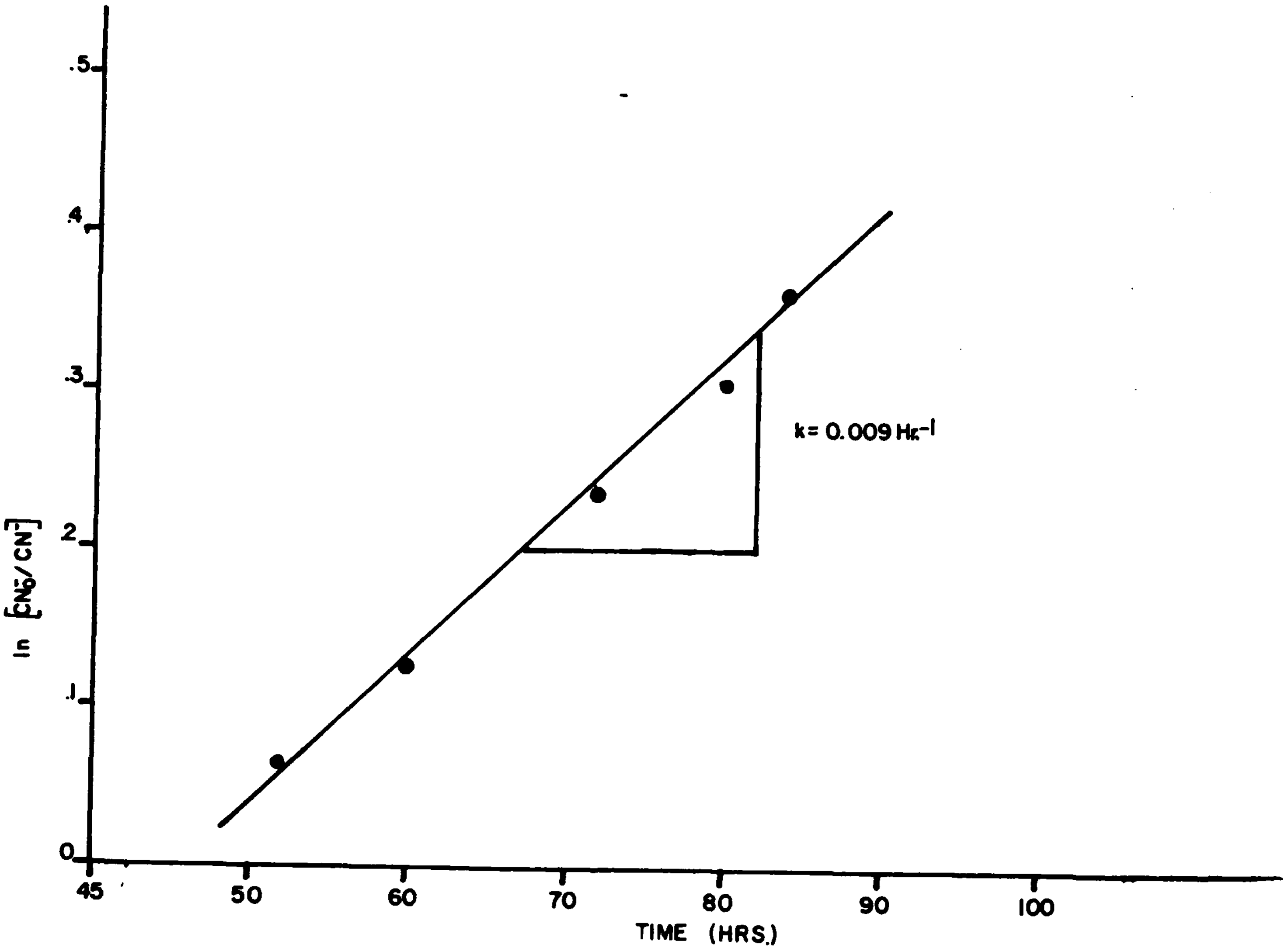

Figure 28 Reaction rate evaluation at high cyanide concentrations with U.V. radiation present

$$\ln \frac{k'}{k} = \theta\ (T' - T) \qquad (1)$$

where

k', k = reaction rates
T', T = temperatures
θ = constant

For the ozone/cyanide oxidation process it is assumed:

k' = Reaction rate determined with UV radiation and elevated temperatures.
k = Reaction rate determined without UV radiation and the associated elevated temperatures.

Equation 1 can be solved for the constant θ:

$$\theta = \ln(k'/k)/(T'-T) \qquad (2)$$

The parameters determined for the two batch process operations are:

$$k' = 0.009\ \text{hr}^{-1},\ T' = 49.5\ \text{C}° \ (121.2\ \text{F}°)$$

$$k = 0.003\ \text{hr}^{-1},\ T = 26.5\ \text{C}° \ (79.7°\text{F})$$

Substitution of the parameter values into equation 2 yields:

$$\theta = 0.0478$$

Therefore, the effect of UV radiation and elevated temperatures on the ozone cyanide oxidation rate is given by the following relationship:

$$k' = ke^{0.0478(T'-T)} \qquad (3)$$

In general, although temperature coefficients are called constants, they do vary over limited temperature ranges. An example is the BOD reaction rate coefficient which had been found to vary from 0.135 (temperature range from 40° to 20°C, 104°F to 68°F), down to 0.056 in the temperature range from 20° to 30°C (68°F-86°F)(Reference 39). Thus the application of the temperature coefficient computed for the ozone process should be limited to conditions close to those under which it was derived.

A reaction rate was also estimated for batch test when the majority of the reactor-waste was in the complexed form. This was done for reactor no. 3 which utilized UV radiation and elevated temperatures. The test evaluated had approximately the same system parameter conditions that existed in the previous tests for which reaction rates were determined. The rate value under these conditions was estimated to be 0.0032 hr^{-1}. This value can be compared to 0.009 hr^{-1}, the rate determined for reactor 3 at the high cyanide concentration level. The reaction rate decreased by a factor of 3.

SECTION VIII

OPERATION AND MAINTENANCE COSTS

A summary of the annual operation and maintenance costs are presented in Table 18. Costs were computed on data collected during the 24 hour/day operation of the system. Operation costs included an allowance for the number of operators the authors felt were necessary to run the system. Maintenance costs included those recurring annual expenses necessary to insure optimum system performance. Maintenance costs reflected annual expenditure estimates based on actual maintenance costs of the system during the project. The costs reflect the system as it is functioning presently. Power costs were based on 1979 commercial rates in Oklahoma City, Oklahoma. Average unit power costs for Tinker Air Force Base (1.5¢/KWh) were less than the commercial rates used in the calculations.

From Table 18 total annual O & M cost for the ozone-cyanide system was $49,850. Power costs were 28% of this total. Labor costs account for 50% of the total O & M costs.

Assuming the system removed 90 percent of the cyanide from the waste, and based on a design flow and cyanide concentration of 3000 gallons per month and 50,000 mg/L, respectively, the system would remove 13,500 pounds (6136 kg) of cyanide annually. The cost for treatment based on operation and maintenance would be $3.70 per pound of cyanide removed.

TABLE 18. OPERATION AND MAINTENANCE COSTS

Operation System Component	Annual Power Costs		Annual Maintenance ($/Yr)	Labor Costs ($/Yr)
	Kilowatt Hrs/Yr	Annual Cost ($/Yr) at 2¢/KWh		
Air Preparation System	233,000	5,000	4,000	
Ozone Generation System	281,000	6,000	2,000	
Ozone Contact System	119,000	2,000	3,000**	
Waste Handling Equipment	2,400	50	100	
Miscellaneous	34,000	700	2,000	
TOTALS		13,750	11,100	$25,000*

*Total cost represents 50% equivalent annual time obligation by one operator (at $8.00 per hour, 3120 total hours).

**Includes 2,500 $/yr for replacement of UV lamps.

SECTION IX

CHLORINE OXIDATION OF CYANIDE WASTEWATER AND COST COMPARISON WITH THE OZONE OXIDATION PROCESS

1. INTRODUCTION

The alkaline chlorination process oxidizes cyanide by the addition of chlorine. Chlorine has been the most widely used chemical oxidant in treating cyanide bearing industrial wastewater. In the alkaline chlorination process, the initial reaction forms cyanogen chloride (CNCl) which can be volatile and odorous. In the presence of caustic, the cyanogen chloride is transformed to sodium cyanate (NaCNO) and the reaction proceeds most efficiently at a pH above 8.5. Further addition of chlorine will oxidize the cyanate to carbon dioxide and nitrogen. The latter reaction is most efficient within a pH range of 6.5 to 6.8. However, a pH of around 8.5 is usually maintained to allow the other reactions to proceed simultaneously, to simplify the process, and to prevent formation of nitrogen trichloride (Reference 38). These reactions can be summarized as follows for simple cyanides:

$$NaCN + Cl_2 \rightleftharpoons CNCl + NaCl$$

$$CNCl + 2NaOH \rightleftharpoons NaCNO + 2H_2O + NaCl$$

$$2\ NaCNO + 4\ NaOH + 3\ Cl_2 \rightleftharpoons 2\ CO_2 + 6\ NaCl + N_2 + 2H_2O$$

In the process, excess chloride is used to complete the reaction. The overall reaction is completed with 7.35 parts of chlorine/part cyanide while theoretically the chlorine requirement is only 6.82 parts chlorine/part cyanide. The caustic soda requirement (NaOH) is about 6 parts NaOH/part CN removed. Interferences to this reaction result from the presence of other organic compounds, oxidizable metals and complexes. Complexed metal cyanides in the form of ferro- and ferri-cyanide are oxidized at a slow rate in this process.

Chlorine oxidation has several disadvantages. Chlorine residual and other chlorinated by-products can be more toxic and harmful than the original wastes treated. Large chlorine doses will cause extreme pH inbalance resulting in maintenance problems for the process pumps, concrete or steel structural work and is toxic to an aquatic environment. From the viewpoint of practical plant operation, the treatment process is subject to interruptions in the supply of the chlorine, caused for example by rail or trucking strikes. Further, the plant management looses a great deal of control over treatment costs by having to continuously purchase chlorine oxidant. As shipping and production costs continue to spiral, the latter point will become more important.

At Tinker Air Force Base, the alkaline chlorination process has long been used to treat the cyanide-bearing wastewaters from electroplating operations. Unable to obtain proper performance of the ozone oxidation system when initially constructed, the operators reverted back to the chlorine system and presently use this method to treat the cyanide wastewaters.

2. ALKALINE CHLORINATION SYSTEM AND PERFORMANCE AT TINKER AIR FORCE BASE

The chlorine system at Tinker Air Force Base is operated on a batch basis. Figure 29 presents a flow diagram showing the typical operation of the system. The system is simple and has no automated monitoring or control. Laboratory analysis determines amounts and times of the caustic soda addition. A one-ton cylinder of liquified chlorine is used for the oxidant supply. The chlorine is injected into the waste stream as the cyanide wastewater is circulated through a pump. The pump used, typically operates at 20-30 gpm. The chlorine cylinders are replaced manually, and treatment continues until the desired cyanide level is reached. If complete cyanide removal is achieved to below detection limits, the treated wastewater may be discharged to the sludge drying beds and subsequently trucked to a hazardous landfill along with some of the other plant residues. Otherwise, the wastewater is fed into the main plant process stream which averages about 1.5 mgd (94,635 liters/hr) for dilution. Generally, the residual cyanide concentration in the treated cyanide wastewater is a few thousand milligrams per liter or less before dilution by the main plant flow is permitted. As noted previously, the volume of cyanide wastewater averages approximately 36,000 gallons (136,260 liters) per year with initial cyanide concentrations ranging from 30,000 to 50,000 mg/L. From March 1978 to March 1979, 31,300 gallons (118,470 liters) of cyanide waste were treated at the facility.

The plant chemist reports minimum requirements of 6 lbs. of chlorine and 6 to 10 lbs. of NaOH per lb. of cyanide removed. A batch treatment process from the plant laboratory logs is summarized in Table 19. From Table 19, 10,000 gallons (37,850 liters) of wastewater initially containing 31,400 mg/L cyanide were treated to a concentration of 1,200 mg/L which is equivalent to removing 96.2 percent of the initial cyanide in a 20 week period. The treatment required 8 tons (7,272 kg) of chlorine and 6.7 tons (6090 kg) of NaOH. This yielded ratios of 6.35 pounds of chlorine and 5.32 pounds of NaOH per pound of cyanide removed. When this level of treatment was reached, the operators discharged 5,000 gallons (18,925 liters) of the waste at 1,200 mg/L cyanide into the main plans flow for dilution. This example typically represents the cyanide treatment process at Tinker AFB. There were no data available to assess the complexed metal-cyanide treatment by the chlorine process in this or any other batch treatment information at Tinker AFB. Certainly, as with ozone, it is expected that the removal rates of the complexed cyanides greatly slowed for the chlorine process and likely much more so than for ozone which is more reactive and used in conjunction with UV radiation.

The process experiences operational difficulties, many of which result from the basic process disadvantages of the alkaline chlorination process described previously. One of the major problems is continuous pump wear and maintenance. The operators estimate that one pump system is replaced for every batch of waste treated. Another problem which occurs is the production of large volumes of sludge during the process. However, the author feels this is more related to periodic additions of permanganate from other waste sources

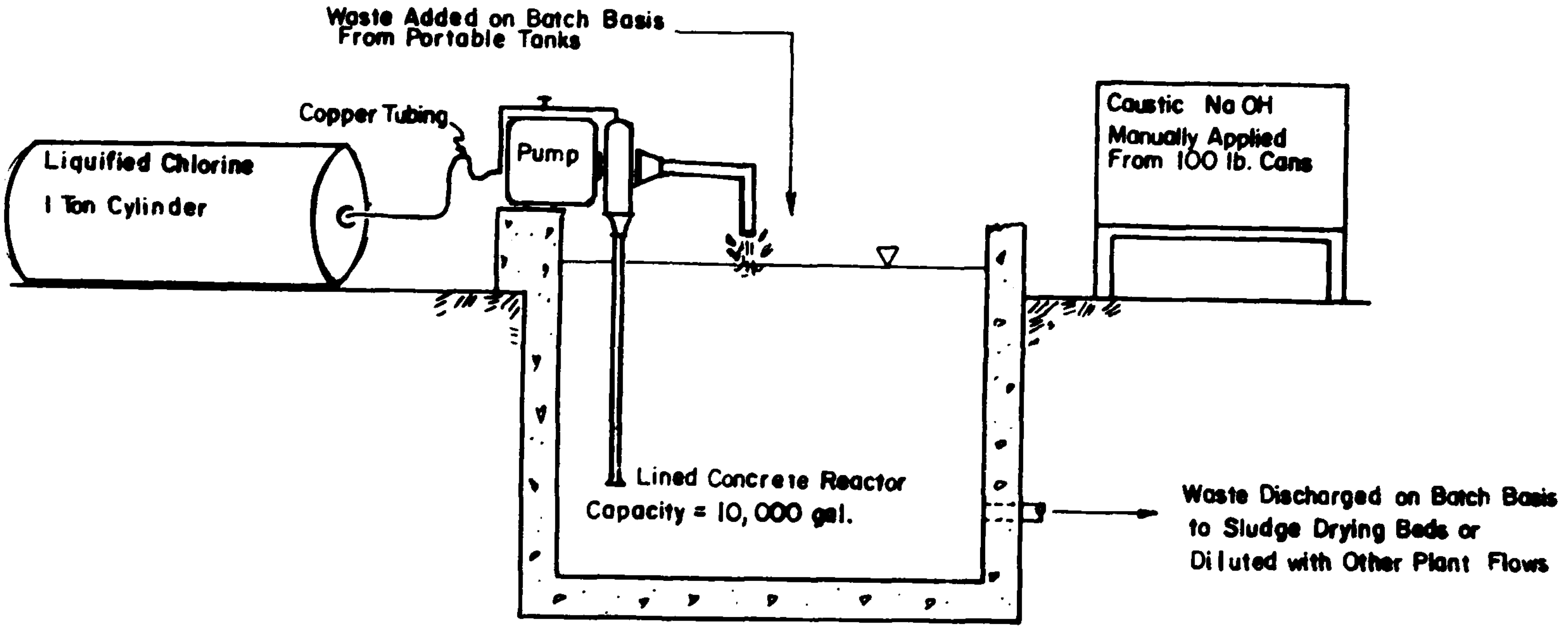

Figure 29 Alkaline Chlorination System at Tinker Air Force Base

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OPTIMIZATION AND TEST OF THE OZONE CYANIDE WASTE TREATMENT SYST--ETC(U)
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TABLE 19. TYPICAL BATCH TREATMENT RESULTS FOR CYANIDE WASTEWATER USING CHLORINE OXIDATION AT TINKER AIR FORCE BASE

Treatment Dates:	September 12, 1978 to January 29, 1979
Treatment Time:	139 days = 20 weeks
Volume Treated:	10,000 gallons (37,800 liters)
Initial Cyanide Concentration:	31,400 mg/L
Final Cyanide Concentration:	1,200 mg/L
Chlorine Added:	8 tons (7,272 kg)
Caustic Soda Added:	6.7 tons (6090 kg)

used by the operators as an oxidant supplement. Potassium permanganate when used as an oxidizing agent results in the production of manganese dioxide (Reference 39).

$$MnO_4^- + 3CN^- + H_2O \rightleftharpoons 2\ MnO_2 + 3CNO^- + 2OH^-$$

The formation of "dark brown" manganese sludge makes it undesirable as a treatment method. Kroop (Reference 31) found that oxidation of phenolic wastes with potassium permanganate produced significant quantities of sludge (up to 23,000 mg/L).

3. COMPARISON OF TREATMENT COSTS FOR OZONE OXIDATION VERSUS CHLORINE OXIDATION OF CYANIDE WASTES AT TINKER AFB

Based on data obtained during the study and information available on the chlorine system at Tinker AFB, a cost comparison can be made. The analysis is based on costs associated with each system in removing 90 percent of the cyanide from the waste with a design flow and cyanide concentration of 3,000 gallons (11,355 liters) per month and 50,000 mg/L respectively. This assumption was made in generating the cost data for ozone oxidation in Section VII, Table 20 summarizes the computed operation and maintenance costs for both systems. The total energy requirements are a great deal more for the ozone process (13,750 $/yr.) than for chlorine (1800 $/yr.). The high energy costs for the ozone process reflects the fact that the oxidant ozone is manufactured on site with the related energy cost accounting for 90 percent of the total energy consumption. The maintenance cost for the chlorine system is only 57 percent of the ozone system maintenance cost, reflecting primarily the greater quantity of equipment required for on site ozone production.

Alkaline chlorination at Tinker AFB requires the purchase of both the chlorine oxidant and NaOH caustic from private enterprise. Table 20 indicates that this cost amounted to 42,800 $/yr. in the analysis and represents 65 percent of the total O & M cost. The caustic soda is obtained locally; whereas the chlorine must be shipped from Wichita, Kansas. This emphasizes the dependence of the chlorine process on market and labor conditions. The significance of this dependence will increase in the future. Table 20 indicates that no cost for process chemicals is required for ozone. The cost for on-site production of ozone is reflected in all of the other O & M categories.

TABLE 20. OPERATION AND MAINTENANCE COSTS FOR THE OZONE PROCESS AND CHLORINE PROCESS

	Annual O & M Costs $/Yr.				
Process	On-Site Energy	System Maintenance	Process Chemicals	Personnel	Total O & M
Ozone	13,750	11,000	0	25,000	49,850
Chlorine	1,800	6,300	42,800	12,700	63,600

The analysis also indicates the chlorine system is less labor intensive than the ozone system. Personnel costs for the ozone system represent 50 percent of the total cost of operation and maintenance of the process. The ozone labor costs will decrease as the reliability of the equipment and operator experience increases. By comparison, labor costs for alkaline chlorination amount to only 20 percent of the process O & M costs. This has long been noted as one of the major advantages of the chlorine oxidation process.

Comparison of total O & M costs for the two systems indicates the ozone process to be the most cost effective presently at 49,850 $/yr. versus 63,600 $/yr. for the chlorine process. The costs are equivalent to $3.70/pound of cyanide removed and $4.71/pound of cyanide removed for the ozone and chlorine processes, respectively. The major cost category for the chlorine system is for chemicals (67 percent of total) and will only increase in the future. On the other hand, the major cost category for ozone process is for labor, 50 percent of the total, and will likely decrease as much experience with the system is gained. Energy and maintenance costs will likely increase proportionately for both systems. In light of these observations, the ozone oxidation process is currently the more cost effective system.

SECTION X

SUMMARY OF RESULTS

1. OVERALL PROJECT GOAL ACCOMPLISHED

A full-scale ozone/cyanide system was operated and tested. Concentrated nickel strip waste from electroplating operations at Tinker AFB was the actual waste source. The system was renovated from a completely inoperable state to one of satisfactory performance. Modifications in the design were made and implemented in the system. Previously unavailable data on equipment and process performance for a full-scale ozone cyanide system were obtained and documented. The process was compared to the alkaline chlorination system currently being used for cyanide waste treatment at Tinker AFB.

2. EQUIPMENT PERFORMANCE AND RELIABILITY

The overall performance of the equipment is good with a few minor problems still persisting in the air preparation system and the ozone generators. Small amounts of oil carry-over still occur in the air preparation system but are much less than observed at the start of the project. The reduction is due to improved equipment maintenance and operation procedures. Also, a second prefilter has helped to reduce oil carry-over. Elimination of oil carry-over can be accomplished by replacing the present screw-type compressors with oil-free compressors.

During the project, significant progress was made in improving the performance of the ozone generators. The most significant improvement occurred by stepping-up the primary voltage and increasing the power output capabilities of the ozone generators. Secondary problems with overloading breakers resulted from this modification, but the breakers were resized and replaced as required. A secondary benefit of boosting the input voltage was more efficient operation of the circuitry system resulting in a great reduction in the frequency of the rectifier fuse failures.

All other components of the system which originally performed inadequately have been modified or repaired. These include modifying the diffusers in the contact system to an open-end-pipe discharge below the impellers, replacing the mixer on reactor 1 with a more efficient, variable speed mixer, modifying the reactor ventilation system to remove all toxic gases, renovating all monitoring equipment, and repairing all other ancillary equipment.

The project has proven that the equipment is reliable if proper maintenance and operation procedures are followed. This fact is documented by two months of uninterrupted, continuous operation of the compressors, filters and dryers. The original operational problems associated with the compressors, such as frequent broken belts, were eliminated with proper maintenance. The dryers continuously maintained a dewpoint of -58°C (-72.4°F), well below the design level of -40°C (-40°F) during system operation. The dryers are virtually trouble free with only periodic maintenance, such as cleaning the valves, required. The reliability of the ozone generators was good with the exception of frequent failures of the rectifier fuses. This problem was greatly reduced by boosting the primary input voltage and changing the operation procedures. After modifying the contact-ventilation and monitoring system, the dependability of these units was satisfactory. Throughout the project the UV lamps were dependable. The corex tubes housing the UV lamps required cleaning once a week (a process taking approximately one hour to complete). A new design for tube removal is desirable to facilitate cleaning. The metering pumps required periodic cleaning, but did not interfere with the overall system performance. These pumps were recently replaced with a more reliable diaphragm system.

In summary, with proper attention the equipment will perform satisfactorily. The process requires approximately 50 percent obligation by one operator to successfully operate the system. This operator must be given the required back-up in terms of maintenance personnel and budget to insure optimum performance. Further, the ozone cyanide system cannot be intermittently started and stopped during the course of a week. Instead, optimum performance will result by continuously operating the system 24 hours a day throughout the week with shut-downs recommended only for weekends and maintenance.

3. PROCESS PERFORMANCE AND CYANIDE TREATABILITY

For plating wastes with high concentrations of cyanide, efficient ozonation of the free cyanide occurs in all reactors at air-stream ozone concentrations of 0.4 percent to 0.6 percent by weight. The quantity of ozone applied can limit the cyanide removal rates. At the design flows (approximately 6.25 gph) the system was found capable of removing 85 percent to 99 percent of the total cyanide from the waste on a continuous basis. These removal efficiencies correspond to a total cyanide concentration range of 44,000 mg/L to 13,000 mg/L encountered during the project. Improvements in the ozone generators will improve the treatment efficiency of the system.

The removal efficiency of batch and continuous operation was limited by the amount of complexed metal cyanide present. The phenomena is likely controlled by the rate at which the complexes are broken down. The presence of UV radiation was shown to greatly speed the destruction of the metal complexes. Neither dilution nor decreasing the pH of the waste increased the complexed metal cyanide removal rates. The quantity of metal cyanide will control the ultimate efficiency of the process.

There are several operation parameters which play a role in the process performance. A graphical method was presented for evaluating the effects of various parameters. A process efficiency parameter (CN^-/O_3) was found to be very useful in the system analysis. Using these procedures, it was determined:

A. At cyanide concentrations as high as/20,000 mg/L, the related analysis of batch-test data showed that the cyanide removal rates were dependent on the residual reactor cyanide concentration. This occurred with and without UV radiation present.

B. At high cyanide concentrations, UV radiation and elevated temperatures increased the process efficiency by a factor of 4 to 5 measured by the CN^-/O_3 parameter.

C. A method of optimizing the system performance and ozone utilization efficiency was established by simultaneously monitoring the cyanide removal rates and the CN^-/O_3 parameter. The ozone mass flow and concentration are then incrementally adjusted to maintain the process efficiency and cyanide removal rate at the maximum levels.

D. The presence of other oxidizable material in raw cyanide plating wastes resulted in slow cyanide removal rates initially. The other organic sources present are preferentially oxidized by ozone. The initially slow reaction rates cause a significant impact on the process efficiency. This has not been considered adequately in the ozone cyanide system design.

E. Values of the efficiency parameter CN^-/O_3 during continuous operations were compared to results in batch operations. The magnitudes provide a measure of the relative dependence of the continuous process on raw waste and reactor cyanide concentrations. This provides a tool for system optimization.

F. For high cyanide concentrations, variation in pH in the range from 10 to 12 did not affect the efficiency of the ozone cyanide system. Thus, pH control of the waste is not recommended.

G. Reaction rates for the high concentration cyanide waste were determined. These rates were established from test data in which the cyanide removal rates were known to be dependent on the cyanide concentration remaining. The data plots indicated the reaction was first order. Reaction rates were .009 hr^{-1} and .003 hr^{-1} for the process with and without UV radiation/elevated temperatures, respectively. This indicates a more efficient process occurs with UV radiation and elevated temperatures. With mostly complexed cyanide present the reaction rate was estimated to be 0.003 hr^{-1} with UV radiation present under similar conditions.

H. The reactor temperature was taken as a measure of the combined presence of UV radiation and elevated temperatures. This enabled the derivation of a constant to predict the resulting change in the reaction rates:

$$k' = ke^{0.0478(T'-T)}$$

I. Equipment operational data such as power required and time of operation were collected throughout the study and compiled by computer. These data provided a basis for a detailed analysis of the operation and maintenance costs for the ozone cyanide process. The cost was determined to be 3.70 $/lb. of cyanide removed presently. Power and labor costs account for 28 percent and 50 percent of the total, respectively.

J. The alkaline chlorination process is currently used for cyanide treatment at Tinker AFB. The system performance and operation costs were evaluated from plant operational logs and other sources. Several problems existed in the system and were noted. The operation and maintenance costs for the alkaline chlorination system were 4.71 $/pound of cyanide removed. This compares to 3.70 $/pound of cyanide removed for the ozone process.

Chemical costs (chlorine and caustic soda) account for 67 percent of the total for the alkaline chlorination system. The dependence of the chlorine system on an outside oxidant source is considered a major disadvantage since Tinker AFB has no control on the supply and cost. Ozone, on the other hand, is produced on site. Ozone was found to be the most cost effective of the two systems.

SECTION XI

RECOMMENDED FUTURE STUDIES

1. INDUSTRIAL WASTE MANAGEMENT AT TINKER AFB

About 1.5 mgd (94,625 liters/hr) of primarily industrial wastes are being treated at the Tinker AFB Industrial Waste Treatment complex. The main system consists of chromium reduction, hydroxide precipitation, biological stabilization by trickling filters with clarification followed by a chlorine oxidation polishing step with settling. Discharge is to a small stream which ultimately flows into the North Canadian River.

Sludges from the main plant system are dewatered via a vacuum filtration system. The cake is hauled off for disposal in a hazardous waste landfill in Kansas.

There are several secondary industrial waste treatment systems at the site for those wastes too toxic for biological treatment directly. Concentrated chromium wastes, for example, are reduced with SO2 and discharged to the sludge drying beds. Also, the cyanide-bearing plating wastes are presently treated by the chlorine oxidation process described in this paper. Once the cyanide concentration is reduced to lower limits, the waste is metered into the main waste stream for further dilution and pH adjustment.

Another concentrated waste which is managed at the industrial waste treatment plant is phenolic cleaning solution. This waste contains 100,000 mg/L to 150,000 mg/L of phenols and amounts to about 10,000 gallons (37,850 liters) per year of waste. Two options are utilized for management of the phenolic waste consisting of direct feed to the main plant flow for dilution or direct disposal of the waste in a hazardous waste facility.

All sludges from the sludge drying beds are transported to a hazardous waste site for disposal.

Presently the main industrial waste treatment plant is falling short of complying with the National Pollution Discharge (NPDES) discharge permit requirements for several toxic substances. The ozone cyanide system could improve the overall plant's operation by more efficiently treating the cyanide waste before discharging to the main plant stream.

2. OZONE-CYANIDE SYSTEM IMPLEMENTATION AT TINKER AFB

The project findings show ozone oxidation of cyanide wastewater is a viable alternative. Compared to the operation and maintenance cost for the present alkaline chlorination processes, ozonation is more cost effective. The capital expenditures for the ozone plant have already been incurred. Therefore, it is recommended that a change-over from the alkaline chlorination system to the ozone system be done in the near future at Tinker AFB. An implementation program should be formulated to prevent the recurrence of a plant shut-down as happened when the ozone system was first installed.

A main goal of the proposed implementation system would be to train the existing operator staff in the proper operation and maintenance of the ozone system. Operator confidence in the process would have to be re-established for the program to be successful. This would require demonstration runs on actual wastewaters with operator participation to help establish the system capabilities. The original operations manual has already been rewritten and details the recommended changes in maintenance and operation required in the present study. A one-year operation assistance period would provide sufficient time to carry out implementation of the ozone system for continuous treatment of the cyanide wastes.

3. OZONE OXIDATION OF OTHER ORGANIC WASTES

There are other industrial type wastes at Tinker AFB which could be treated via ozone oxidation. Of specific interest is the phenolic wastes. A significant quantity of concentrated phenolic wastes (100,000 mg/L) at Tinker AFB are currently disposed of by transporting to a hazardous waste landfill in Kansas. Besides being very costly, this method is subject to interruption by any of several occurrences. Truck strikes and road conditions are potential threats. The status of the hazardous landfill in terms of the upcoming environmental regulations should be established. As energy supplies decrease, transportation costs associated with landfilling will skyrocket.

The literature review presented in this paper indicates that ozone oxidation of phenolic wastewaters is a very feasible alternative treatment method. A study on the treatability of the concentrated phenolic waste of Tinker AFB would establish the capabilities for this site specific waste. The ozone system presently at Tinker AFB could be immediately used for the treatability study with virtually no modification required. A series of batch tests would provide base data, followed by continuous inflow plant operation. A side benefit of the study would be to provide additional training of the base staff in operation of the ozone system.

Other organic wastes present at Tinker AFB are also amenable to ozone oxidation. The treatability of these organics by ozone oxidation could easily be investigated as outlined for the phenolic waste above.

4. FURTHER OPTIMIZATION OF THE OZONE CYANIDE SYSTEM

The present study has demonstrated the importance of various system parameters such as ozone mass-flow rate, ozone concentrations, UV radiation and others. Based on favorable results obtained in this study, it has been recommended that UV radiation be added to one or both of the reactors which are without it presently. With UV radiation present, the process efficiency greatly increases. However, a significant increase in reactor temperature also occurs.

A study is recommended which would demonstrate the relative importance of reactor temperature versus UV radiation. This would be very beneficial in optimizing the process from a practical standpoint. If the main benefit results from operating at a higher temperature, a less expensive, maintenance-free, heat source other than UV radiation could be employed. The result would be a significant decrease in annual operation costs associated with UV lamp replacement.

Another area of interest, not covered completely in the present study, is evaluation of other organics present in the cyanide wastewater. Project data have indicated the likely presence of other compounds more preferentially oxidized by ozone. This was indicated by slow cyanide removal rates which occurred initially for raw wastewater and later significantly increased. A study to quantify the amounts of extraneous organics initially present and their subsequent oxidation would provide beneficial information relative to the overall process. A simple method would involve monitoring total organic carbon through a series of batch tests.

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