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OZONE OXIDATION OF CONCENTRATED CYANIDE WASTEWATER FROM ELECTROPLATING OPERATIONS AT TINKER AIR FORCE BASE

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A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirement for the

degree of

DOCTOR OF PHILOSOPHY

BY

HERBERT MICHAEL SCHORNICK

Norman, Oklahoma

1979

OZONE OXIDATION OF CONCENTRATED CYANIDE WASTEWATER FROM ELECTROPLATING OPERATIONS AT TINKER AIR FORCE BASE

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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 (1,2). 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 (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 (TAFB) in Oklahoma City. A full scale demonstration plant utilizing chemical oxidation with ozone was designed and constructed at TAFB to treat 3,000 gallons per month of primarily nickel strip wastes with total cyanide concentrations of up to 50,000 mg/l. It was to operate 24 hours a day five days per week at a flow of 6.25 gph. 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 of 1976 Leale E. Streebin 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 Schornick and Streebin 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 system is presented in Figure 1. The ozone contact 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 with three 25 HP screw type compressors, each having a capacity of 100 scfm at 100 psig. 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

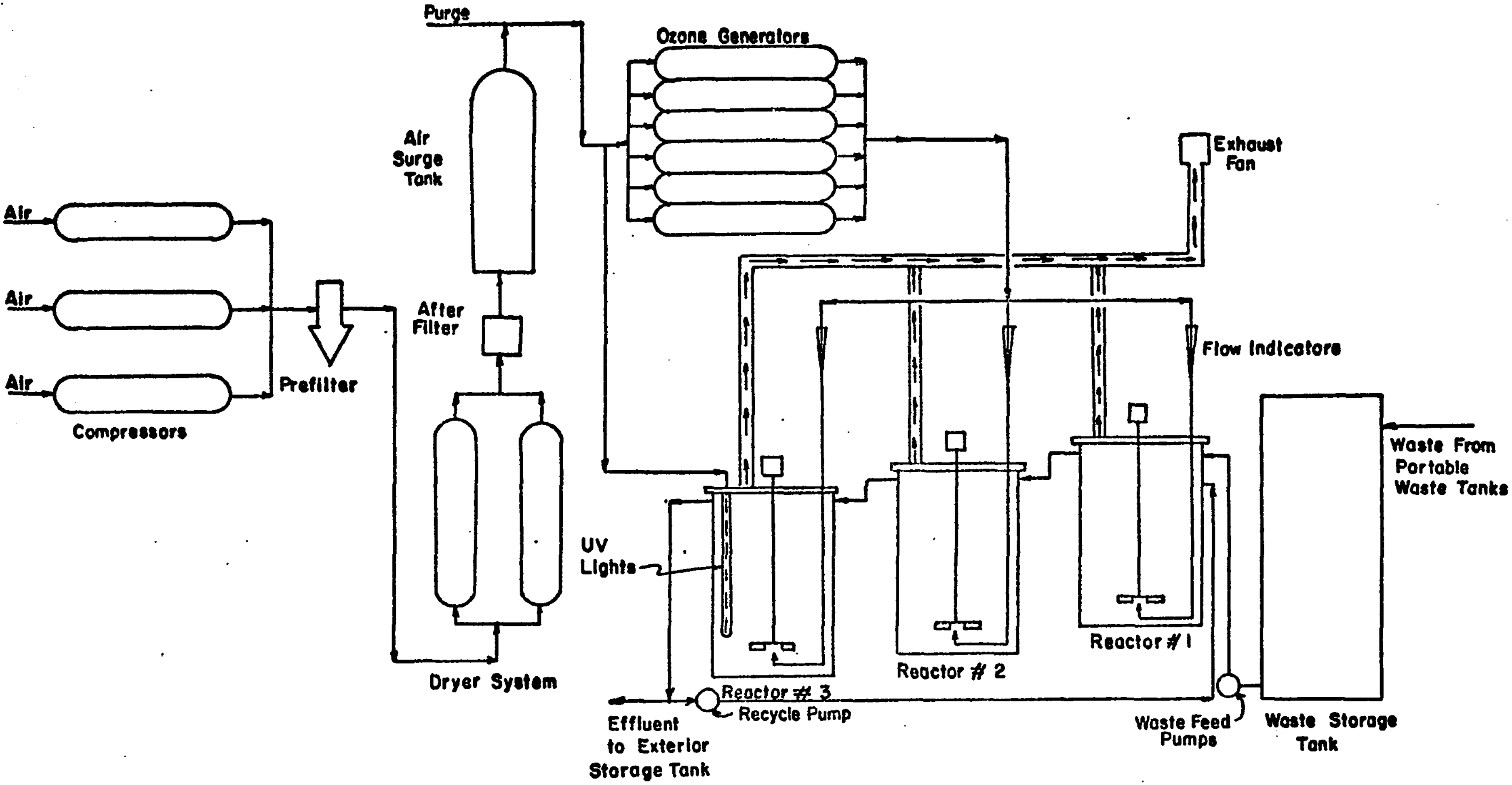

Figure I: Flow Diagram For Cyanide Treatment Plant.

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.

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% 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 fiberglass storage tank. From the storage tank the waste is 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 in diameter and at the 44 inch operating depth hold 400 gallons 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 mixer with 11 inch, 6 bladed impeller. Design air flow rates to reactor 1, 2, and 3 are 112 scfm, 35 scfm and 19 scfm at 12 psig, respectively.

Gas escaping from the liquid surfaces in the reactors is collected in a PVC ventilation system and exhausted to the atmosphere by an electric powered polypropylene fan.

Reactor 3 is equipped with two ultraviolet lamps placed in corex glasswells. The U.V. lights are 42 inches 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 diamotic state (O_2). Ozone's principle 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 (4). Ozonation is an excellent process for quick action in 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 (4).

Ozonation has several advantages over other oxidation processes. According to Rosen (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, there is some evidence that the lysing reaction occurs between nascent ozone and the microorganisms. Other advantages are high residual dissolved oxygen concentration in the effluent and the oxidized products produced by ozonation are less toxic than chlorinated or unoxidized products (6,7,5). 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 (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, 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 ozone dosage required to meet 200 fecal coliforms/100 ml ranged from 6 to 14 mg/l (8). Data show that during this investigation, f_2 viruses were completely destroyed by ozone after a contact period of approximately 5 minutes.

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 is a strongly endothermic reaction which is, therefore, accompanied by 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 (7). The factors that affect 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 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 (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 combines with oxygen, ozone, and water in the corona to produce nitric acids, which can damage the ozonator and further reduce ozone yield.

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 production ozone "Y" and the useful life of the generator. The ozone yield per area of electrode surface under optimum condition is calculated as follows (6):

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

V = Voltage across the discharge gap (peak volts).

f = Frequency of the applied voltage.

ε = Dielectric constant.

d = Thickness of the dielectric.

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 Systems

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 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, hydrastatic injectors, vortex propellers, air dispersing impellers, liquid-circulating impellers and packed beds or columns (10,11,12). 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 (6):

1. The purpose of the system--disinfection, BOD or COD reduction, etc.
2. Relative rates of possible competitive reactions--chemical oxidation, lysing bacteria, decomposition of ozone in aqueous solutions, etc.
3. Mass transfer rates for ozone from gas to wastewater.
4. Characteristics of the wastewater--total SS, organic loading, pH, temperature, etc.
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 is 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 (13).

Nebel et.al., 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 (8).

Bowers reported on three types of dispersion methods--gas injection systems, turbine mixers, pourous 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 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 installation.
Kerag	Emulsion Turbine	5	27	Introduced 1955 as pilot plant 3/4 mgd scale. Ozone losses 25%, no return on power expenditure.
Torricelli	Diffuser with recycle	0.25	8.5	Introduced 1951 as ½ mgd pilot plant. 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., studied several techniques for dissolving and dispersing ozone in water (14). They stated that systems with circulating water was the most efficient among those examined, which include: 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 was approximately two minutes. The injection depth was at least 4 to 5m. Pore openings of the diffusers range from 50 to 100 microns. The diffuser capacity ranged from 20 to 50 m^3 air/h/m^2 porous surface. Countercurrent injection appeared to be more effective than cocurrent injection. Ozone losses for countercurrent injection ranged from about 10 to 15%.

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 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 varies from 2 to 8.3 percent.

The Kerag System involves the ozone injection through a propeller set up just under the surface of the water to be treated. The system affects instant action of the concentrated ozonated air bubbles with the water rather than the delayed action of a residual ozone concentration. The loss of ozone ranges from 20 to 30 percent. The method can be adapted to preozonation.

The helix-propeller is immersed at one third of the vessel's depth and a vortex is created by rotating the propeller at an appropriate velocity. The movement imparted to the liquid enables a direct dissolution of the ozone by swirling of the ozonated air at 0.5 bar 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 will cause a loss of the dissolving action, so a sudden release of concentrated ozonated air will occur.

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

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

Studies were also performed using an air dispersing impeller. The injection was performed into the water flowing through baffled chambers. The average residence time in each chamber was two minutes. The impeller was placed five meters under the water level in the ozonation compartment. The total ozone loss from this system was between 10 and 15 percent. The advantage of the process is its relatively low energy consumption.

A liquid-circulating aeration turbine was another method investigated (14). The turbine consists of a water circulating mill-wheel that sucks and mixes the ozonated air into the circulated water. The device permits normal operation ranging from 50 to 170 percent of its total capacity of operation. 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 are maintained in the water.

1.3 Gas Transfer

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

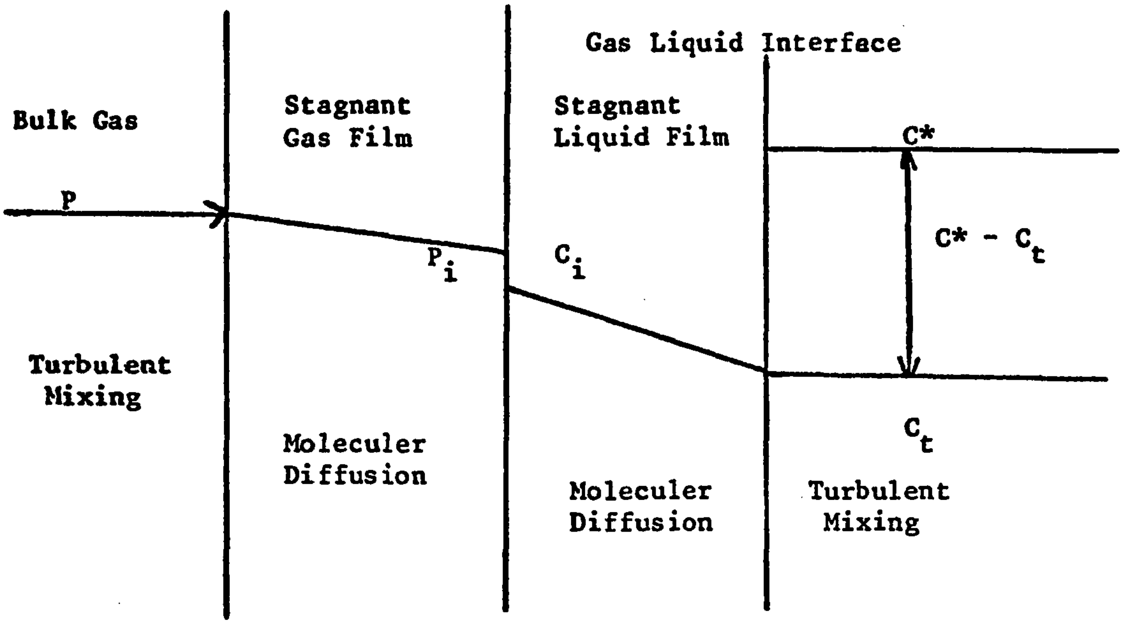

FIGURE 2: FILM THEORY MODEL

Ozone molecules are transferred to a liquid when the concentration in the liquid (C_t) is less than the concentration in equilibrium with the partial pressure in the gas (C*). 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.

$$N = K_La\ V\ (C^*-C_t) = K_Ga\ V\ (\overline{P} - P^*) \qquad (2)$$

$$N = K_LA\ (C^*-C_t) = K_GA\ (\overline{P} - P^*) \qquad (3)$$

where

N = rate at which ozone is transferred between phases, lb mole/hr

K_La, K_Ga = overall volumetric mass transfer coefficient, liquid- and gas-phase basis respectively.

V = volume of the system.

A = area across which diffusion is taking place.

C_t = concentration of ozone in the liquid phase.

$\overline{P}$ = partial pressure of ozone in the gas phase.

C^* = equilibrium concentration corresponding to the partial pressure of ozone in the gas phase.

$\overline{P}^*$ = equilibrium partial pressure corresponding to the concentration of ozone in the liquid phase.

If one studies the components of the mass transfer rate equations. the parameters which all reactors are designed to attain to a greater or lesser degree are apparent. For optimum reactions or transfer rates a large interfacial surface area to gas-volume ratio, which maximizes the diffusion area, must be developed. This can be done by generating many small bubbles. In non-agitated vessels the transfer rate is a function of the reactor depth and for agitated vessels 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 (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 area must constantly be created against the force of the interfacial tension. Bubbles are continually coalescing--and being redispersed. In most gas dispersion operations, bubbles rise through the liquid pool and escape from the surface, and must be replaced by new ones.

In this dynamic situation the volume of gas held up in the liquid pool is also a variable, depending on 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 a porous ceramic or metal plate. In some systems the gas flow provides sufficient mixing and 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 imperical equations apply for dispersion in pure liquids by a six-bladed turbine impeller. The average bubble diameter $\overline{D}_s$ in millimeters is given by

$$D_s = \frac{4.15(\sigma g_c)^{0.6}}{(Pg_c/V)^{0.4}\rho_L^{\,0.2}} \quad Z^{\frac{1}{2}} + 0.9 \qquad (4)$$

Where Pg_c/V is the power input per unit volume of ungassed liquid. The interfacial area a', in mm^{-1}, is given by

$$a' = \frac{1.44(Pg_c/V)^{0.4}\rho L^{0.2}}{(\sigma g_c)^{0.6}} \left(\frac{\overline{V}s}{U_t}\right)^{\frac{1}{2}} \qquad (5)$$

Where $V\overline{s}$ = superficial gas velocity

U_t = bubble rise velocity

Combining Eqs. (4) and (5) leads to the following equation for Z:

$$Z = \frac{\bar{V}s\ Z^{\frac{1}{2}}}{U_t} + 0.0216\ \frac{(Pg_c/V)^{0.4}\ \rho_L^{\ 0.2}}{(\sigma g_c)^{0.6}}\ \left(\frac{\bar{V}s}{U_t}\right)^{\frac{1}{2}} \qquad (6)$$

In the above equations all quantities involving the dimension of length are in millimeters.

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 with the Froude number to give:

$$N_Q,g = \frac{q_g}{n\ D_a^{\ 3}} = 0.194\ N_{Fr}^{\ 0.75} \qquad (7)$$

Where $N_{FR} = \frac{n^2 Da}{g}$. For Eq (7) to apply, N_{Fr} must be between 0.1 and 2.0.

The power required by a turbine impeller dispersing a gas is less then that indicated by:

$$P = \frac{K_T\ n^3\ Da^5 \rho}{g_c} \qquad (8)$$

which is the equation for power required in a well baffled tank at Reynolds numbers larger than 10,000. At high gas flow rates the power is about half that required with ungassed liquid. 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

$$N_p,g = \frac{P_g \, g_c}{n^3 \, Da^5 \rho_L} = 1.36 \, N_{Fr}^{-0.56} \qquad (9)$$

Equations (4) through (9) provide a basis for design of turbine agitated vessels for gas dispersion.

2. OZONATION OF CYANIDE WASTES

Tyler R. G. (16), et al, 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 while the pH ran from 9.25 to 10.16. The studies were small scale using a laboratory mode ozone generator. Ranges in ozone applied/CN^- removed ratios by weight of 1.40/1 to 1.96/1 were reported. The authors found most of the CN^- was oxidized rapidly as indicated in typical test results shown in Table 2.

Table 2: Relationship of Ozone Used to Cyanide Oxidized (Quantity = 1500 ml at 46 ppm CN^-) (16)

Application Time (minutes)	CN^- (p.p.m.)	pH	O_3 Used (grams)	
0	46.0	10.16	0	
5	7.0	8.2	0.0738	
8	2.8	7.5	0.118	Ozone appeared in air exhaust
10	1.15	7.47	0.148	
15	0.92	7.40	0.222	

The authors speculated the change in reaction speed at the appearance of ozone in the exhaust air indicated the point at which oxidation of the cyanate began. They postulated the following equations to describe the ozone/CN^- oxidation process:

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

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

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

The following conclusions were summarized:

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

Khandelwol, Bardunn, and Grove (17) investigated rates of oxidation of cyanide solutions by ozonized oxygen. The reaction rate constant more than doubled when copper (11) ions were added as a catalyst. Further increases in copper (11) concentration did not markedly affect the reaction rate. Also, the rate was found not to be affected by copper sulfate, nitrate, acetate, sulfide, or by temperatures from 13° to 30°C. The following rate equation was given to quantify the ozonation of cyanide based on cyanide disappearance:

$$\frac{-d\ CN^-}{do} = K\left[CN^-\right]^{1/3}$$

where CN^- = concentration

o = reaction time

K = reaction rate constant

During the lab tests the concentration of the ozone in the gas phase 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 KCN^- and initially contained 100 ppm CN^-.

Selm (18) reported the oxidation of simple cyanides by ozone was rapid and complete with mass transfer controlling the absorption. Based on the laboratory pilot studies he recommended the use of packed towers to provide adequate mass transfer time and surface. Also, the destruction of cyanates and cyanide complexes were slower than the cyanide oxidation with these substances being destroyed if sufficient contact time is provided for the reactions to take place. A pH of at least 9.0 was recommended for the treatment process. The chemistry of ozonation of cyanides and cyanates was reviewed. The author indicated ozonation of cyanides involves two separate steps, oxidation of cyanide to cyanate and then destruction of the cyanate by either oxidation or hydrolysis. He concluded, the mechanisms of destruction of the cyanate ion were not well understood and the predominate mechanism could not be identified. He found that contrary to past reports, ozone could oxidize ferrocyanides. It was found ozone oxidizes ferrocyanides first to ferricyanides and then to ferric hydroxide sols. The author performed laboratory scale investigations of ozonation of the free CN^- ion using a borosilicate glass column 4 inches in diameter packed with 1/4-inch ceramic Intalox saddles. The author felt the countercurrent absorption tower would provide more intimate contact and better mass transfer than stirred batch reactors. The airstream ozone concentration was 1.78% by weight for all tests. The results indicated that ozone concentration of CN^- in feed solutions varied from 44.5 p.p.m. to 82.5 p.p.m. would react on the basis of 0.33 moles of ozone per mole of cyanide. The author could not explain variations in cyanide removals at various waste feed rates.

Disadvantages of chemical oxidation using chlorine were listed:

1. Chlorine must be used in considerable excess, 8 lbs. of chlorine per lb. of cyanide.
2. Excess chlorine may have a 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 oxident than chlorine.

Studies on the oxidation with ozone of cyanides and cyanates were conducted at the chemical laboratory of the VODGEO Institution to determine the possibility of using ozonization for the purification of effluents containing cyanide compounts (19). These studies showed that cyanide is oxidized easily with ozone at a constant rate at concentrations of 3-4 mg/l. The process is independent of the pH within the 10.5 to 12 range. Oxidation of cyanate is much slower and the maximum rate is at pH 12. Oxidation of cyanates beings when a concentration of cyanides decreases to 3 to 4 mg/l. Complexed zinc cyanides are oxidized similarly to simple soluble cyanides. Complex copper cyanides are oxidized more easily, despite their higher stability. The high oxidation rate is apparently due to secondary oxidation of cyanide by Cu^{2+}. A similar phenomenon is observed in oxonization 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. Ozonization as a purification method is simple, easily controlled, and lends itself to full automation. The purified effluent does not become contaminated with the reagents used as in the case, e.g., with hypochlorite (19).

Tests carried out in France on an effluent from a large metal finishing factory showed that 25 mg/l of cyanide could be destroyed by 80 to 90 mg/l of ozone (20). The test results show that total destruction of cyanide is easily obtained and that the process is economical compared with other processes. Further, it was determined that the specific dose of ozone diminished when the concentration of cyanide increased and when the concentration of ozone in the air increased. Also, the loss of ozone from the reactor decreased with an increased concentration of ozone in the air stream. It is generally assumed that 1 1/2 parts of ozone is required for each part cyanide (20).

Garrison R. L., Mauk C. E., Prengle H. W. (21), with Houston Research Incorporated, performed lab scale tests and prototype scale tests on ozonation of actual Air Force cyanide wastes. The wastes studied could be classified generally as plating wastes and photographic wastes. More specifically, 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 studied a batch reactor with a 5.85 liter capacity was used. The reactor was provided with a variable speed mixer so that power input could be varied through the range of 1 to 30 horsepower per 1000 gallons of solution. An ozone generator could provide an ozone concentration of 0.5% to 10% by weight in the feed to the reactor. The ozone cyanide treatment characteristics were generally studied by diluting the actual wastes to different values and adding ozone at different concentrations and feed rates to study the relationships.

Results from several of the lab scale tests are depicted in Table 4. In test no. 2 full strength nickel-strip waste with 40,000 mg/l CN^- was ozonated for 12 hours to remove more than 99% of the CN^- at an ozone / CN^- ratio of 3.0. After 12 hours test No. 2 was continued for 14 additional hours with very little change in the CN^- concentration. Test No. 2 results are depicted in figure 3. Results on a diluted sample of the nickel strip waste is shown in figure 4. The authors indicate iron complexes present slowed the reaction rate. Similar results occurred for test No. 3 in Table 4 where the final CN^- concentration was 20 mg/l. In test No. 3, 8 more hours of ozonation at an elevated temperature of 150°F decreased the CN^- concentration further to 0.26 mg/l.

Table 3. Properties of Actual Air Force Cyanide Wastes (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	3.0	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

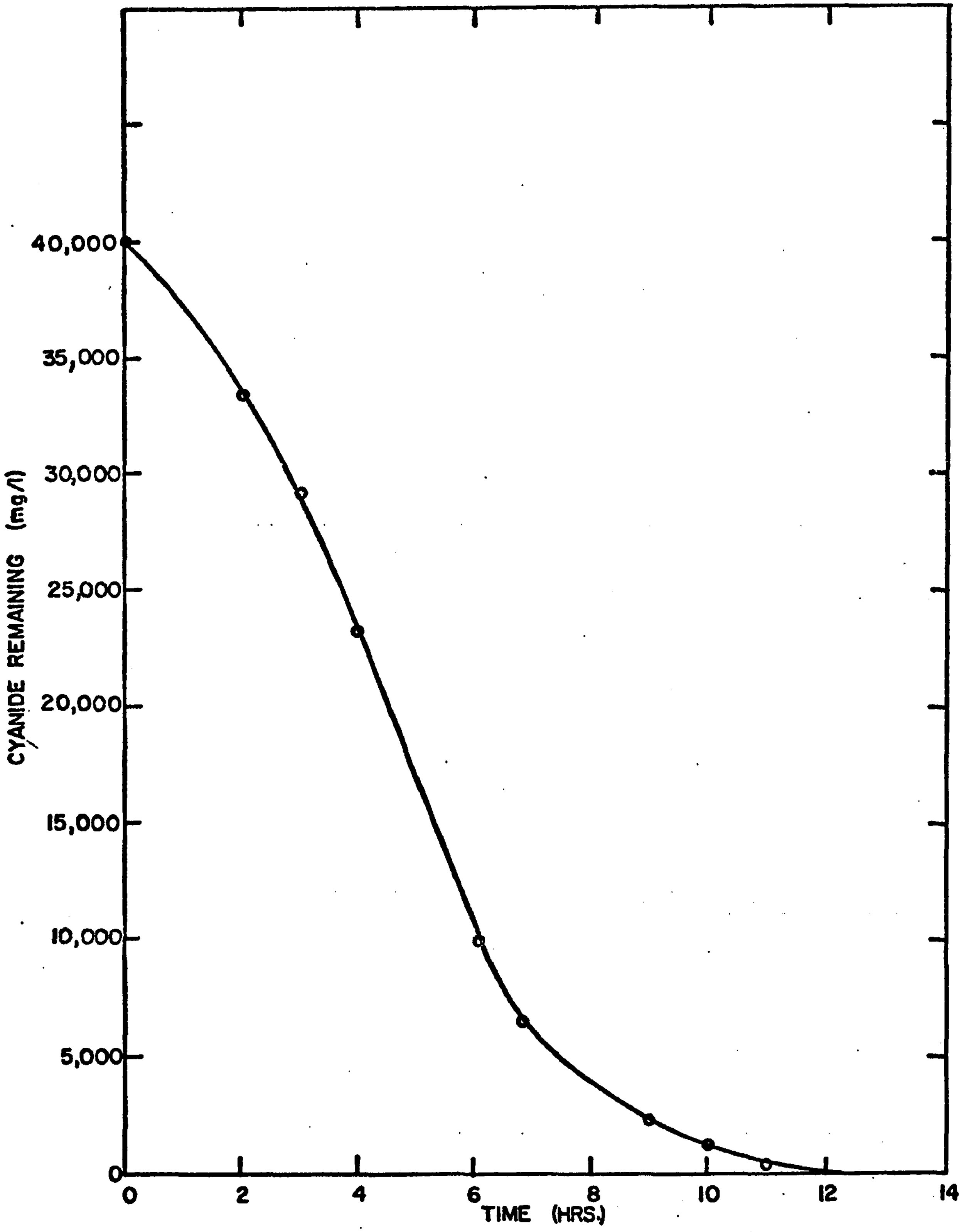

Figure 3: Ozonation of concentrated Nickel Strip Waste.

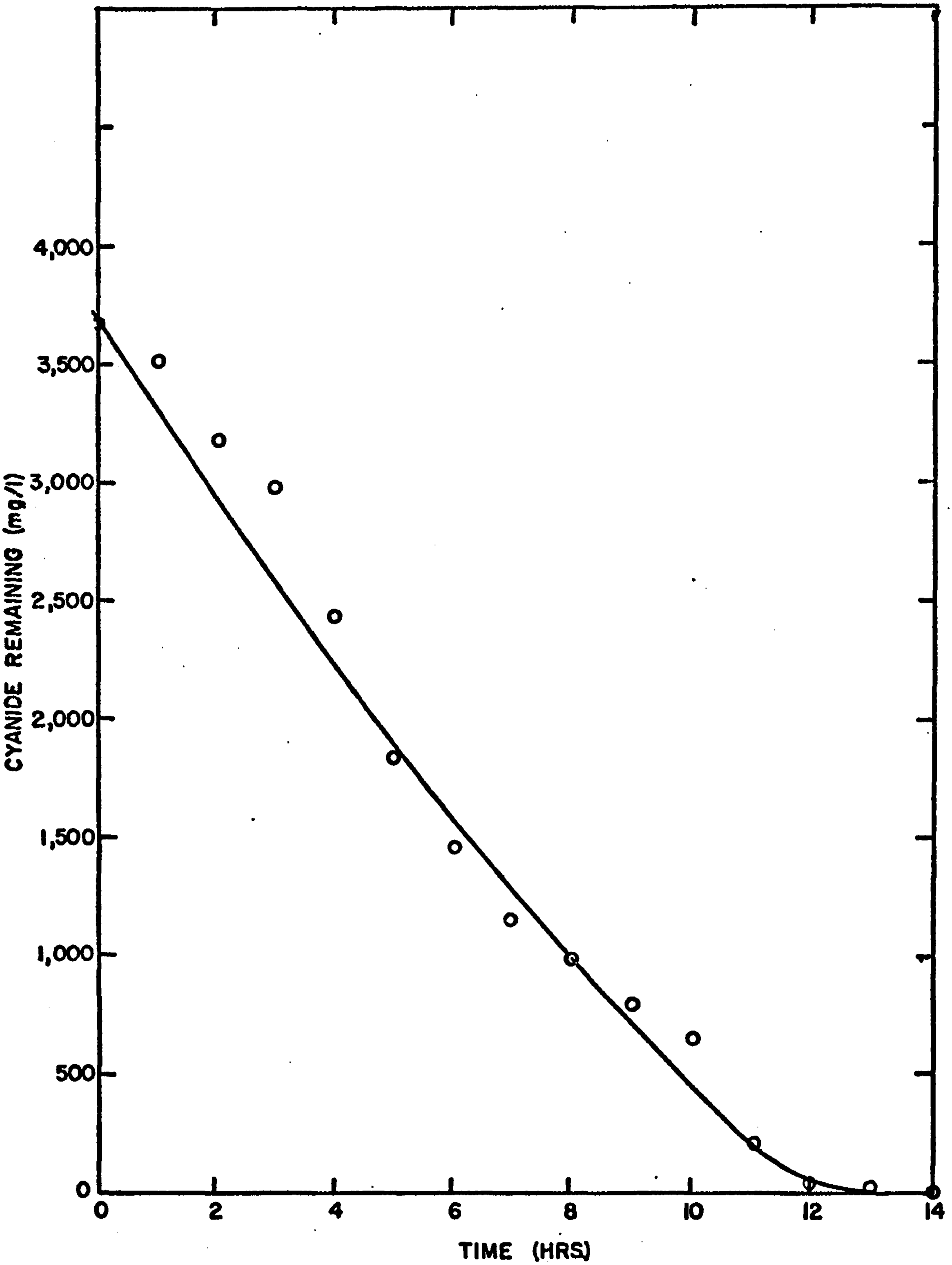

Figure 4: Ozonation of Medium Concentration Nickel Strip Waste

Test No. 5 depicts results obtained for full strength copper plating wastes. Again, for test No. 5, further ozonation did not decrease the CN^- concentration. This was explained to result from the presence of iron-CN^- complexes. Diluted copper plating wastewater was ozonated in test No. 6 for 2.5 hours resulting in more than 99% removal in CN^-. At this point in test No. 6 the reaction slowed and 16.5 additional hours of ozonation reduced the CN^- concentration to 4 mg/l. An additional 19 hours of ozonation in the presence of U.V. radiation reduced the CN^- concentration to 0.36 mg/l.

From Table 4 test No. 7 was performed on diluted photographic fixer wastes. The reaction was very slow and the ozone to CN^- ratio extremely high. This indicates the stability of the iron CN^- complexes. The same results occurred in test No. 8 for bleach cyanide wastewater.

Further tests on the bleach cyanide waste indicated U.V. radiation could speed the reaction rate. Test No. 9 in Table 4 is such an example where 3 U.V. bulbs at 4 watts each were used. The results indicate the removal still proceeded slowly but were much improved over previous results without U. V. radiation present.

Further continuous waste feed tests were performed using a three stage prototype system. Each reactor was 12 inches in diameter and 16.5 feet tall. Six 15 watt U. V.

lamps were mounted in each stage. Mixing was accomplished by six bladed disc impeller with constant 10 hp/1000 gallons power input maintained. The system was designed to treat 15 gpd of waste containing 4000 mg/l of CN^-. Tests were run on all wastes. Typical of results was the run performed using nickel strip waste diluted to 4000 mg/l. For the test 2.1 lbs. of ozone were added per day while 0.501 lbs. of CN^- were removed per day at equilibrium. This yielded an O_3/CN^- ratio of about 4.0. The discharge contained less than 0.1 mg/l CN^-.

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 to the liquid phase, but in reactions with dilute wastes the rate of oxidation of the waste is limited by the chemical reaction rate.

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

3. A pH of 7 was found to be optimum, resulting in the maximum reaction rate of ozone with iron cyanide.

4. No benefits occurred in the ozone/CN^- process by using either copper or silver catalysts.

Bollyky (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. First an alkaline cyanide waste stream flow of 6.75 gpm containing a maximum concentration of 60 mg/l cyanide. The acid waste stream contained no CN^- and had a waste flow of 16 gpm. The system consisted of an equalization tank, one ozone reactor tank for pretreatment of the alkaline cyanide waste. The discharge from this system is flash mixed with the acidic waste and settled before discharge. Porous diffusers were used in the ozone reactor tank for both dispersion and mixing of the ozone feed gas. No other form of mixing was provided. The ozone generator could produce 20 lb. oz/day. The plant was operated intermittently 16 hours/day for two weeks. Data from the first tests indicated the CN^- concentration could be reduced from around 15 mg/l to 0.08 mg/l in the CN^- treatment tank and required an ozone dosage of 1 to 1.5 moles of O_3/mole of CN^-. The following conclusions were summarized.

1. Optimum ozone dosage was 1 to 1.5 mole O_3/mole CN^-.
2. Optimum pH range was 7.0 to 9.5.
3. Ozone treatment was safe.
4. Ozone treatment rapidly and economically destroys copper and sodium cyanides.

Due to many operational problems the reliability of the report 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. The 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 (23), and Marechal (24) received patents in 1920 and 1905 respectively on processes utilizing ozone as an oxidant for purifying phenolic wastes.

Niegowski (25) reported in a paper on ozonation of phenolic 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. His results indicated 2 parts of ozone per part of phenol were required for total destruction of phenol in laboratory prepared solutions containing 100 mg/l phenol. The ozone air stream contained 1-2% O_3 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 ozone-phenol ratios for 99% removal of phenols as 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% reduction in C.O.D. showing the production of intermediate products. He reported on a toxicity study by the Academy of Natural Sciences (Philadelphia). Aquatic species including blue gills, diatoms and mayfly larvae were exposed to ozonated and untreated phenol solutions. The initial phenol content of 200 mg/l was ozonated to 0.1 mg/l. A phenol level of 2.7 mg/l was established as biologically safe for all the organisms.

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 (26) Niegowski investigated ozonation of phenols in petroleum wastewater. On a petroleum waste with 600 mg/l phenols at pH of 12 the ozone demand for complete phenol removal was less than one-half of the ozone demand at pH 7. Results of an oxidation of a refinery waste containing 11,600 mg/l phenol indicated an ozone/phenol ratio of only one reduced the phenol concentration by 99%. 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. Ozone added only oxygen to the water, B.O.D. and C.O.D. reductions accompanied phenol removal and the toxicity due to phenols was reduced in the same proportion as the removal of phenols.

Hall and Nellist (27) concluded ozonation of phenols in coke plant liquors was an efficient process for a range of concentrations from 100 mg/l to 2000 mg/l. Tests were run on spent liquors which besides phenol contained other chemicals which are oxidized by ozone such as thiosulphates and thiocyanates. Wastes from 13 coke plants having an average phenol concentration of 1030 mg/l (300 mg/l to 2000 mg/l) 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 waste. The initial pH of the liquors averaged 7.5 while the average final pH was 3.2 after phenol reduction. Further experiments indicated the ozone utilization efficiency could be increased by 25% if the original pH was raised to 10.0. Final pH in the latter tests averaged 7.8.

Labine (28) described a treatment plant for a refinery 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. Ozone then provided a polishing step and reduced the phenols 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 (29) carried out a series of detailed laboratory studies of 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

P_t = phenol concentration at time

R = ozone dose rate (moles of ozone added/initial f moles of phenol/minute

t = time (minutes

F = ozone gas flow rate (1/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 0.256. Eisenhauer concluded 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 (30) Eisenhauer showed 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 a pH of 11.06. Thus the reaction rate in ozonation of phenols more than doubled. The major change occurred between an initial pH of 9.14 where k = 0.307 and the pH of 11.06 (k=0.658). Further within the reaction temperature range of 20°-50°C over a range of ozone flow rates and concentrations, there was no significant effect of temperature on the rate of phenol ozonization.

Kroop (31) found ozone to effectively oxidize phenols at pH levels of 11.0 to 11.5. Batch and continuous pilot studies indicated 1.77 lb O_3/lb phenol and 2.66 lb O_3/lb respectively phenol were required to affect 99% phenol reduction. Initial phenol concentrations were between 2000 mg/l and 3000 mg/l in phenolic aircraft paint stripping wastewater from Vance AFB. In the continuous flow study 99% phenol reduction was accompanied by 65% COD reduction indicating the likely production of intermediate products. Kroop optimized the O_3 dose rate and pH, however, other optimization alternatives such as contact systems, temperature and U. V. radiation were not evaluated.

Pengle, Mauk and Payne (32) reported on UV/Ozone oxidation of five chlorinated compounds: Pentachlorophenol, O-dichlorobenzine, dichlorobutane choroform and polychlorinated biphenyls. Destruction of pentachlorophenol in the presence of O_3/UV proceeded more rapidly than with only ozone or only UV present. The authors compared the reaction to similar observances for phenol where they reported monitoring TOC indicated phenol is converted to CO_2 by ozone-UV at the stoichiometric rate at which ozone is added into the reactor. A refractory index (RFI) was defined which measures the difficulty at oxidation of a given compound by ozone.

$$RFI = \frac{B_c^o \, ty_2}{Ao}$$

$B_c^o = O_3$ supplied to $t_{1/2}$

$t_{1/2}$ = time for 1/2 conversion of Ao

Ao = initial amount of compound

Using the refractory index, a list was presented quantifying the RFI index for 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 (RFI = 1 to 100) with an RFI value of 1.6.

Bailey (33) reviewed past work on mechanisms of the ozone-phenol reaction. He concluded the most likely reaction pathway for ozonation of phenol was through 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 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 the authors. 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 new found 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 CN^- 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 found, 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

Table 6: System Deficiencies and Corrective Actions

Deficiencies	Corrective Measures	Adjustments in Operation	Results and Current Status
<u>Air Preparation System</u>			
Compressors: Frequent breakdown, Excessive oil carry over, High air discharge temp.	Complete 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 $-55^{\circ}F$ in air stream.

Table 6 (continued)

Deficiencies	Corrective Measures	Adjustments in Operation	Results and Current Status
<u>Ozone Generation System</u>			
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 230 v 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.
<u>Waste Handling Equipment</u>			
Magnetic drive transfer pump inoperable.	Replace with new pump.		Problem resolved.
Crystalization of sodium carbonate in piping system and metering pumps.	Repaired faulty room heaters.	Maintain ambient room temperature above 50°F	Problem resolved.

Table 6 (continued)

Deficiencies	Corrective Measures	Adjustments in Operation	Results and Current Status
Ozone Contact System			
Diffuser plugging and breakage.	Replaced with open gas discharge 1½ 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 U.V. 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.

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 compressor only when the required air flow rates exceeds 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 their operation. This installation was visited during the study to evaluate the performance of their equipment. Observations and conversations with the maintenance supervisor clearly reveal oil carry over from the compressors has been a big problem in their 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 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 preparatin 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% of the purported design.
2. Rectifier fuses protecting the solid state circuitry frequently blew.

The reduced power level of the ozone generator reduces the concentration of ozone in the air stream and limits 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. A more efficient SCR and diode design.
3. 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 would be accomplished by installing two Acme buck boost transformers in the ozpac module. Ozpac module no. 4 was selected for testing. Under the test pressure levels and air flow rates the maximum power ranges previously achieved for the ozpac was 20 to 22 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 v. transformer.
2. Main control box breaker after the 208 v. 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 Table 7 some work still remains in replacing one breaker.

With the buck booster transformers installed data was 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) coincides with the maximum system design flow rate. The lower flow rate is typical of a setting used at lower CN^- 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 some from one module to another. For example, at a system flow rate of 113 scfm the following variance was measured:

Power Settings (amps)

Ozpac 1	Ozpac 2	Ozpac 3	Ozpac 4	Ozpac 5	Ozpac 6	Total Amps	O_3 Concentration % of wt.
25	20	25	25	20	25	140	0.49
30	25	30	0	25	30	140	0.52

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, Ind. 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 problem.
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.

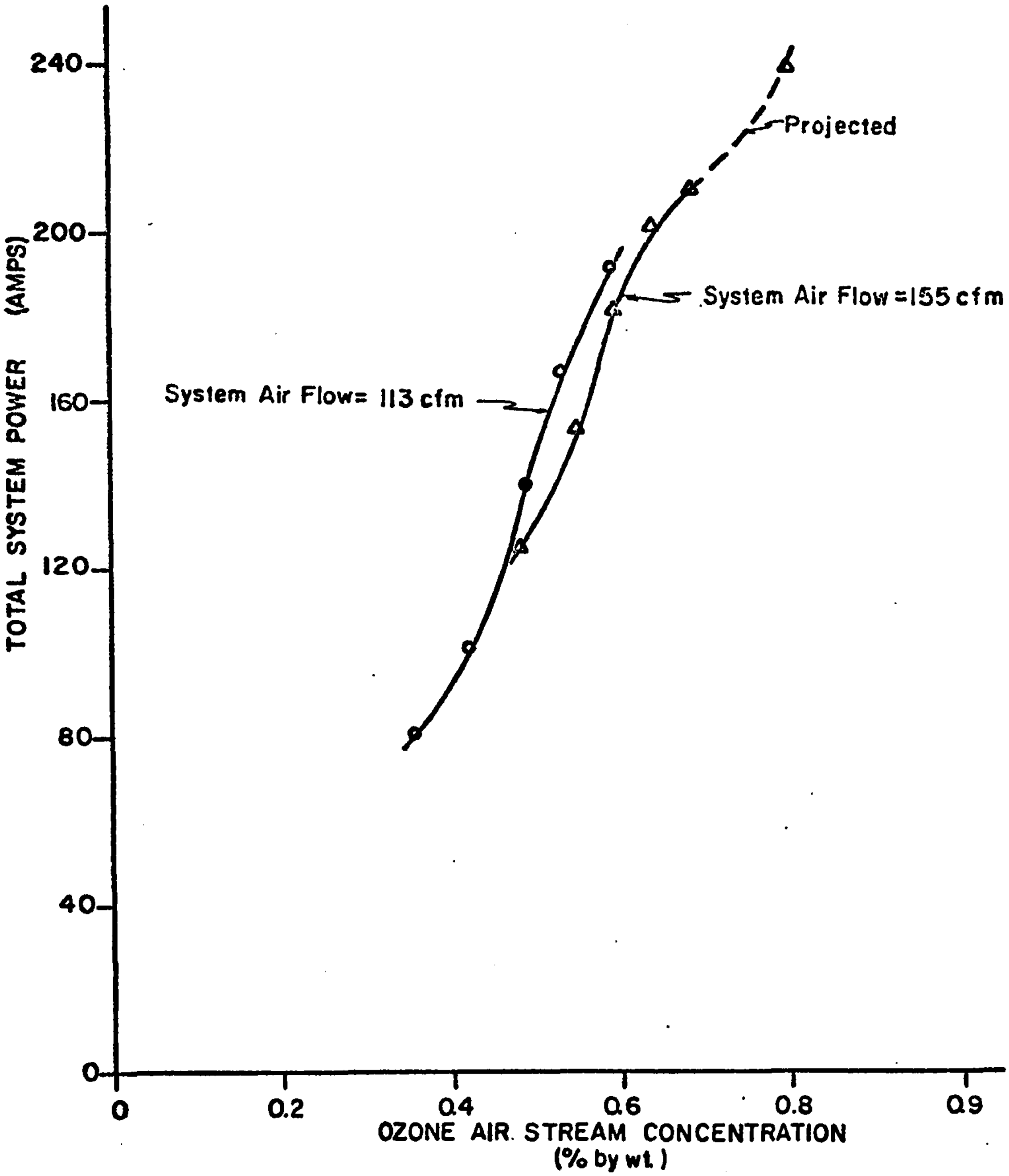

Figure 5: Ozone air stream concentration vs. total system power.

During operation of the ozone generation system it has been 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 kept between 85°F and 95°F.

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 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.

All cyanide analyses included the initial sample distillation procedure as outlined in Standard Methods. One hour of distillation was found to consistantly result in greater than 95% recovery of all cyanides. The major difficulties in performing the cyanide analyses were maintaining an

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

appropriate bubble rate during distillation and accurately standardizing the silver nitrate titrant. During the study some duplicate samples were analyzed by a certified independent laboratory for quality control of the analytical procedures.

The percent concentration of ozone in the air stream was determined by metering an air stream sample (50-70 ml/min) into a train of three bottles containing a 2% potassium iodide solution. The train insured 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 was recorded on special coding forms for easy key punching and eventual computer compilation and data analyses.

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, waste feed rates, etc. 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 mixer was mounted on reactor 1. The porous diffusers had been replaced with an open end pipe discharging 1.5 inches below the mixer impeller. One objective was to provide background information on operational performance of the 3 HP 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 cummulative length of run was 46 hours. Concentration of CN^- in reactor 1 versus time is plotted in Figure 6. During the first 20 hours of operation the average air flow to

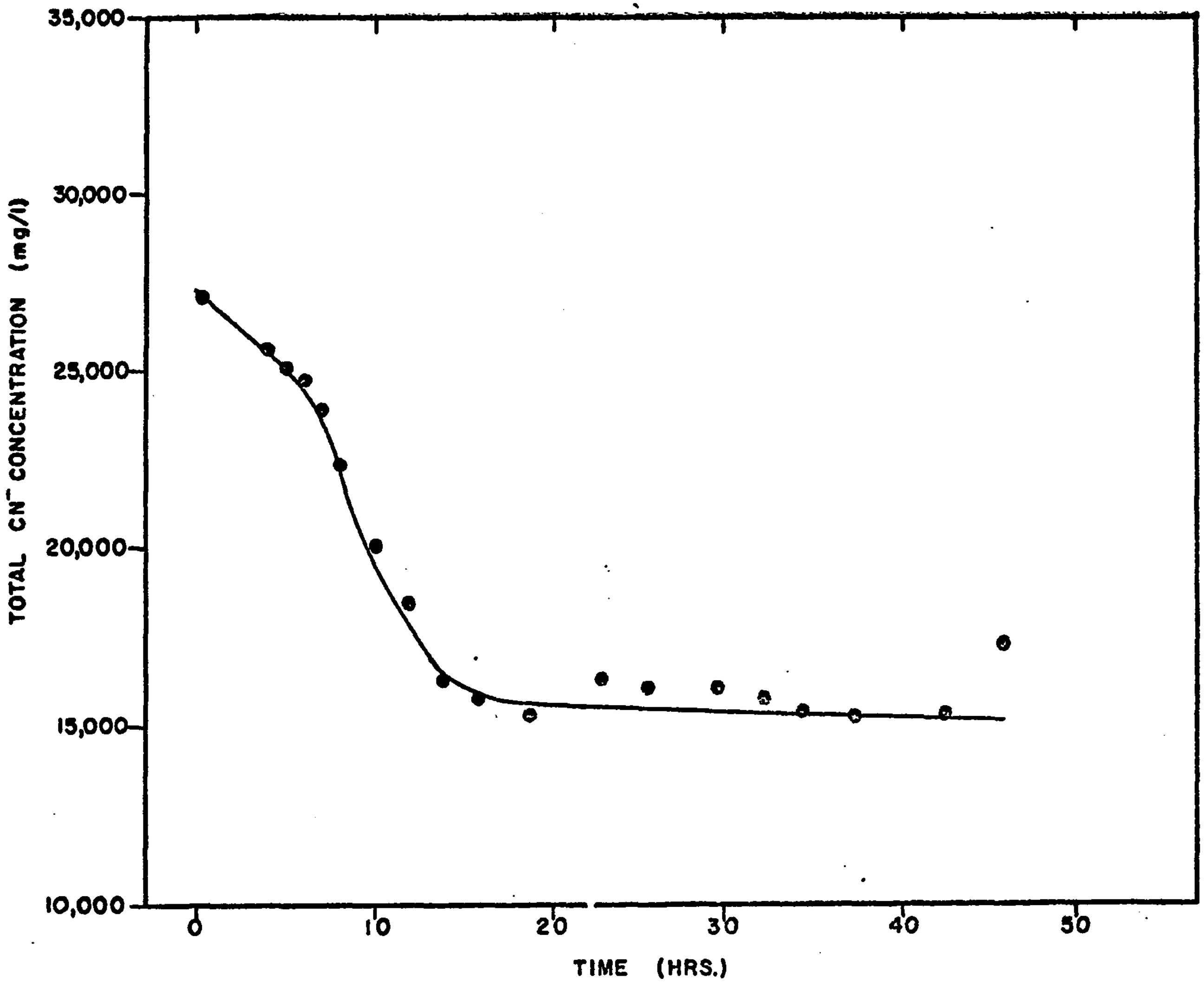

Figure 6: Batch Treatment of Waste in Reactor I.

reactor 1 was 68 scfm with a 0.85% ozone by weight concentration. This resulted in 38 lbs. of CN^- removed with the addition of 52 lbs. of ozone or a ratio of 1.4 lbs. O_3 added per lb. CN^- 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 and 0.60% O_3 by weight, respectively. During the final 29 hours essentially no cyanide was removed. The average temperature in the reactor was 62°F. 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 CN^- 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 are performed using the number of CN^- ions known (1) to complex with each metal to convert the metal concentration to the equivalent complexed metal CN^- concentration. The total CN^- 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 is 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 CN^- Complex Concentration

Metal	Concentration (mg/l)	No. CN^- ions complexed[1] with each metal	Calculated Conc. of complexed metal CN^- (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 waste in each of the three reactors being 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 below the mixer impellers. Also, the 3 HP mixer on reactor 1 had been replaced with the 7.5 HP variable speed mixer. The U.V. lamps in reactor 3 were operated continuously during this test. Reactor 1 was filled with untreated plating waste with a total CN^- concentration of 62,500 mg/l. The waste in reactor 2 and reactor 3 was a mixture of partially treated and untreated waste with total CN^- concentrations of 20,000 mg/l and 25,000 mg/l, respectively. At the beginning of the test the pH values for reactors 1, 2, and 3 were 13.3, 12.8, and 12.8, respectively. Changes in CN^- concentrations during the test are shown in Figures 7, 8, and 9.

The ozone concentration in the air stream and air flow rates to the reactors were significantly different for the first 40 hours compared to the rest of the testing period. The average ozone concentration in the air stream during the first 40 hours was 0.21% by weight and 0.41% 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, 31 scfm, and 17 scfm, respectively. These rates were decreased to averages of 53 scfm, 14 scfm, and 13 scfm, 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. Temperatures of the waste in reactors 1, 2, and 3 averaged $78^{o}F$, $80^{o}F$, and $118^{o}F$, respectively.

Inspection of the data indicates some initial scatter at the higher CN^- concentrations. These incidents are small in number compared to the total data. Obtaining a representative sample was more difficult at high CN^- concentrations due to the sample size limitation. Dilution techniques and other quality control methods, including having duplicate samples analyzed at an independent laboratory, were effective

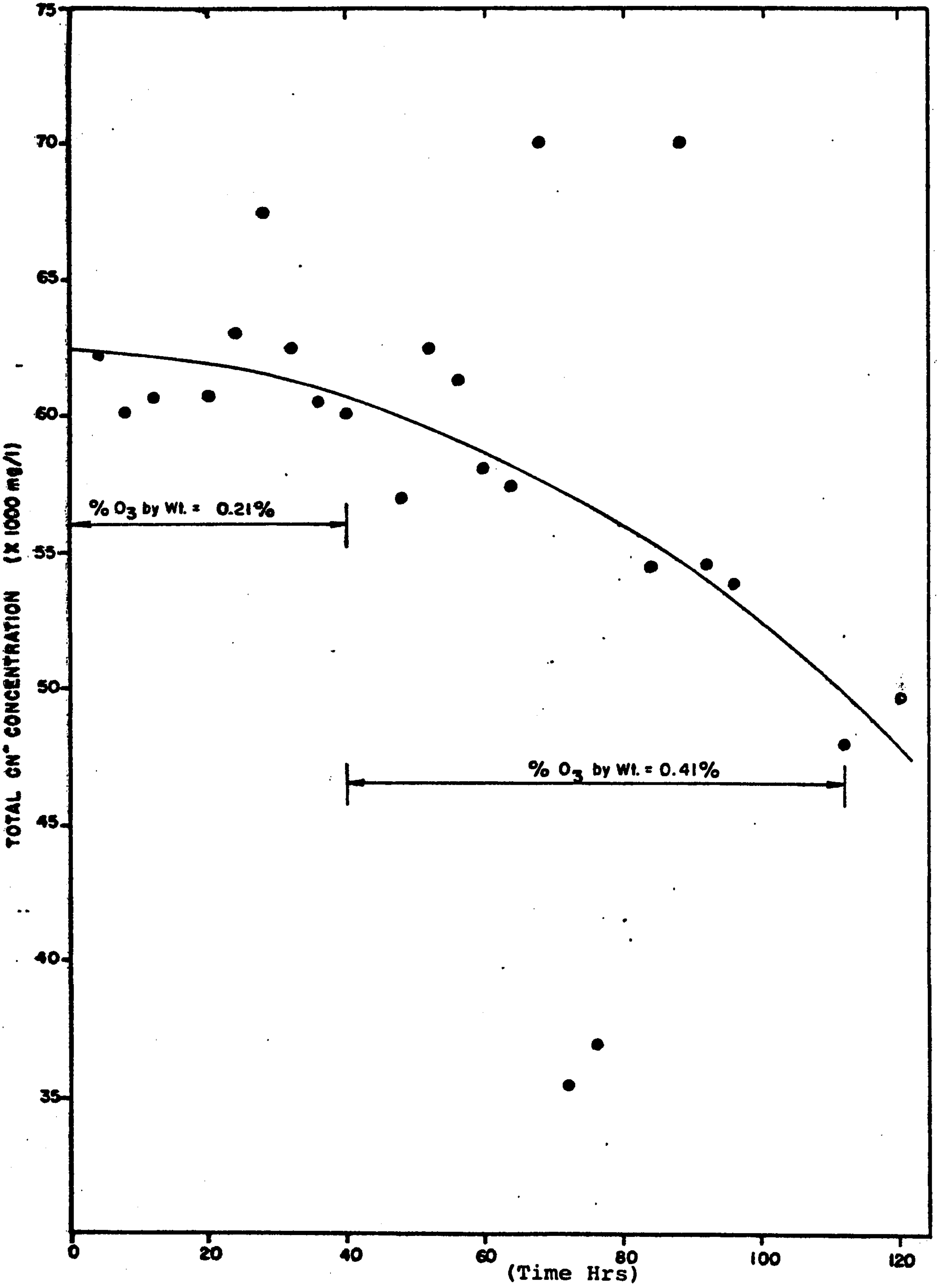

Figure 7: Batch Treatment of CN Waste in Reactor I.

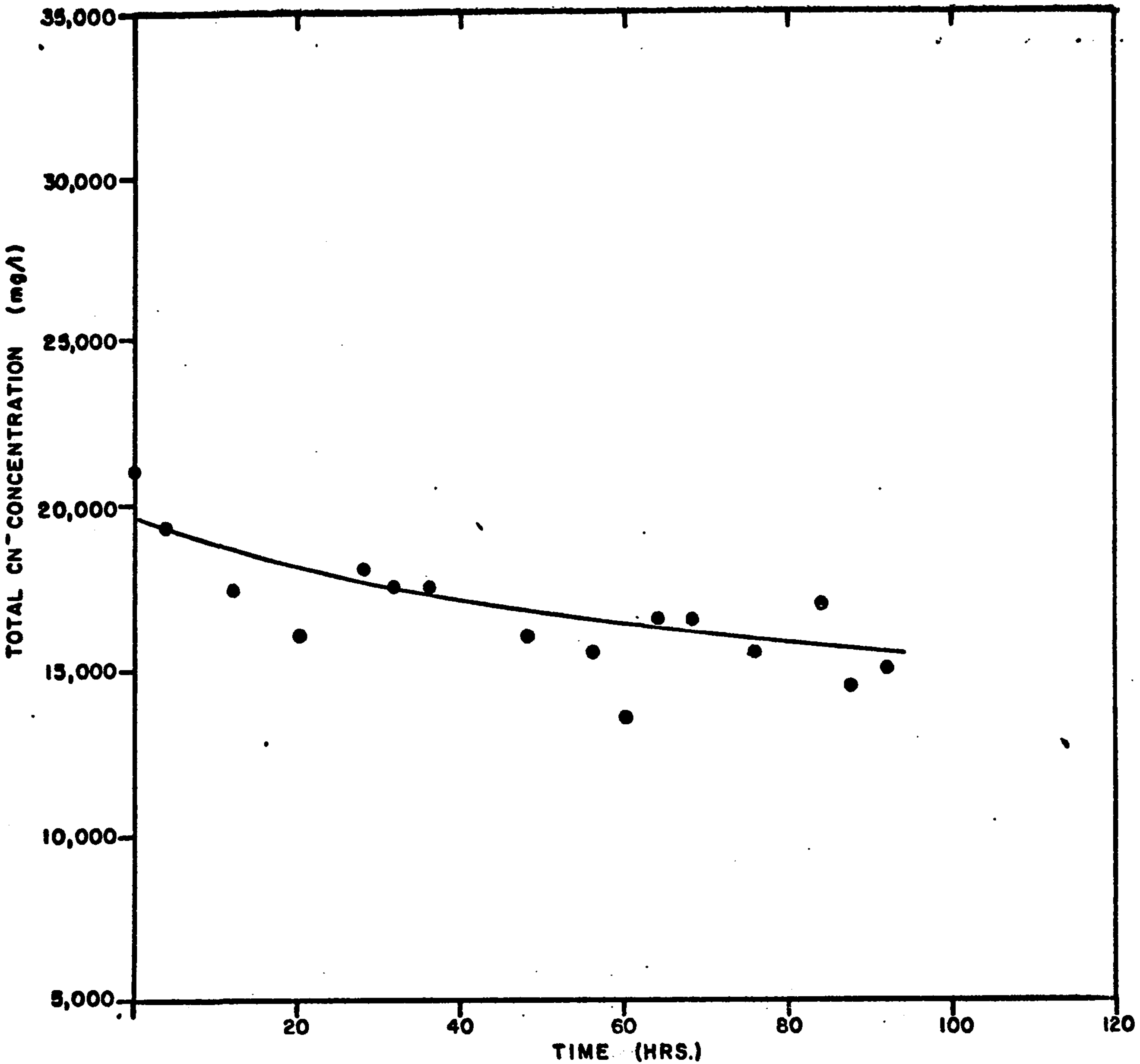

Figure 8: Batch Treatment of CN Waste in Reactor 2.

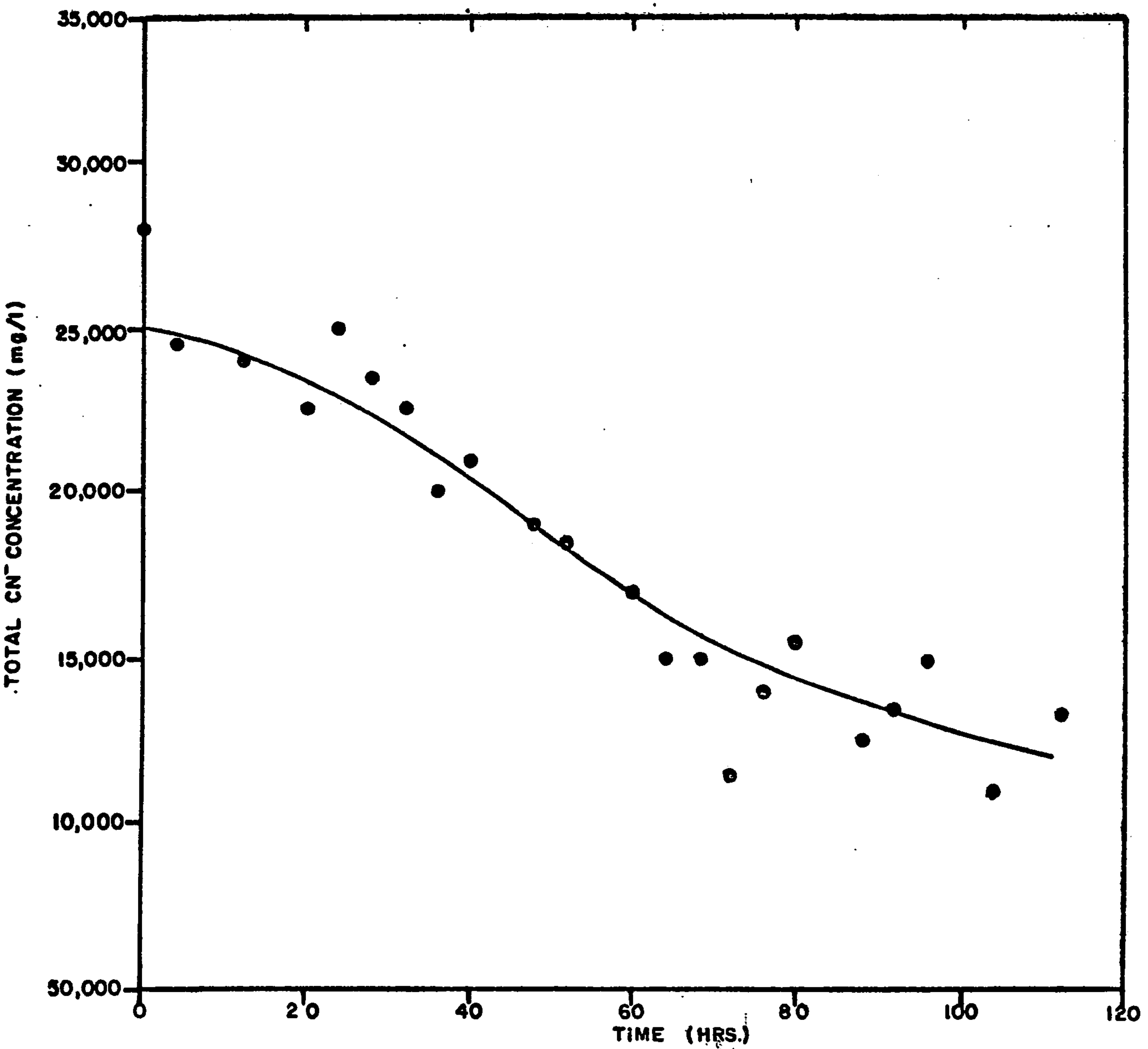

Figure 9: Batch Treatment of CN Waste in Reactor 3.

in minimizing the scatter. However, all data obtained in the study is 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 lbs. (1800 mg/l) of CN^- were removed (Figure 7). For the same period 42 lbs. of O_3 were added to reactor 1. The next 72 hours of operation resulted in 39 lbs. (12,000 mg/l) of CN^- removed in reactor 1 while adding 72 lbs. of ozone. 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. The final pH of reactor 1 was 13.4. 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 CN^- 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 uncomplexed form.

From Figure 8 no significant change in removal rates is apparent for reactor 2 from the first 40 hour period to the second phase of the test. The concentration of CN^- in reactor 2 was reduced approximately 4000 mg/l or 13 lbs. of CN^- were removed during the first 90 hours of testing. For the 90 hour period 27 lbs. of ozone were added to the reactor to yield an O_3/CN^- removed ratio of 2.0. The final pH in reactor 2 was 12.7. 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 ultraviolet lamps were operated continuously during the entire test. For the first 40 hours, 15 lbs. of CN^- (4500 mg/l CN^-) were removed in reactor 3 with the addition of 7 lbs. of ozone. In the next 72 hours, 27 lbs. of CN^- (8000 mg/l CN^-) were removed while adding 17 lbs. of ozone. This yields 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. The final pH of the waste in reactor 3 was 10.2. Figure 9 shows the removal of CN^- 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 CN^- concentrations and second stage cyanate oxidation reactions by the ozone. It is also significant to recognize the substantially higher CN^- removal rates in reactor 3 than those of reactor 1 and 2 which indicate the benefits of ultraviolet radiation. It is further noted that the benefits from U.V. radiation were derived under conditions when the majority of the cyanide removed in reactor 3 was in the uncomplexed form. The increased reactor temperature was also likely beneficial by 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 the chief reaction species.[4,5,6]

4. SYSTEM BATCH OPERATION WITH CONTINUOUS RECYCLE FLOW

The system was operated during this test with no raw waste being introduced to the reactors but with flow from reactor 3 being continuously recycled back to reactor 1. Initial concentrations of CN^- 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 pH values in the reactors 1, 2, and 3 at the start were 13.0, 12.3, and 10.0, respectively. The average ozone concentration in the air stream was 0.52% by weight. Values of the average air flow rate to reactors 1, 2, and 3 were 85 scfm, 32 scfm, and 14 scfm, respectively. Throughout the test there was very little variation in the average ozone concentration and air flow rates. The U.V. lamps in reactor 3 were on for the entire test period. Average temperatures in reactors 1, 2, and 3 were 90°F, 87°F, and 115°F, respectively. Recycle flow from reactor 3 to reactor 1 averaged 5.6 gph. 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 CN^- was reduced by 156 lbs. which is equivalent to 72% of the CN^- present at the beginning of the test. A total of 323 lbs. 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 CN^- concentration occurred in reactor 1 during the test period. When the test was terminated, the concentration of CN^- in reactor 1 was 3100 mg/l. As noted 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 CN^- complexed with these metals was calculated to be 4460 mg/l. Thus, when unreacted ozone was detected in the off gas, the CN^- remaining in reactor 1 was in the complexed form. This illustrates how ozone alone is much less effective in

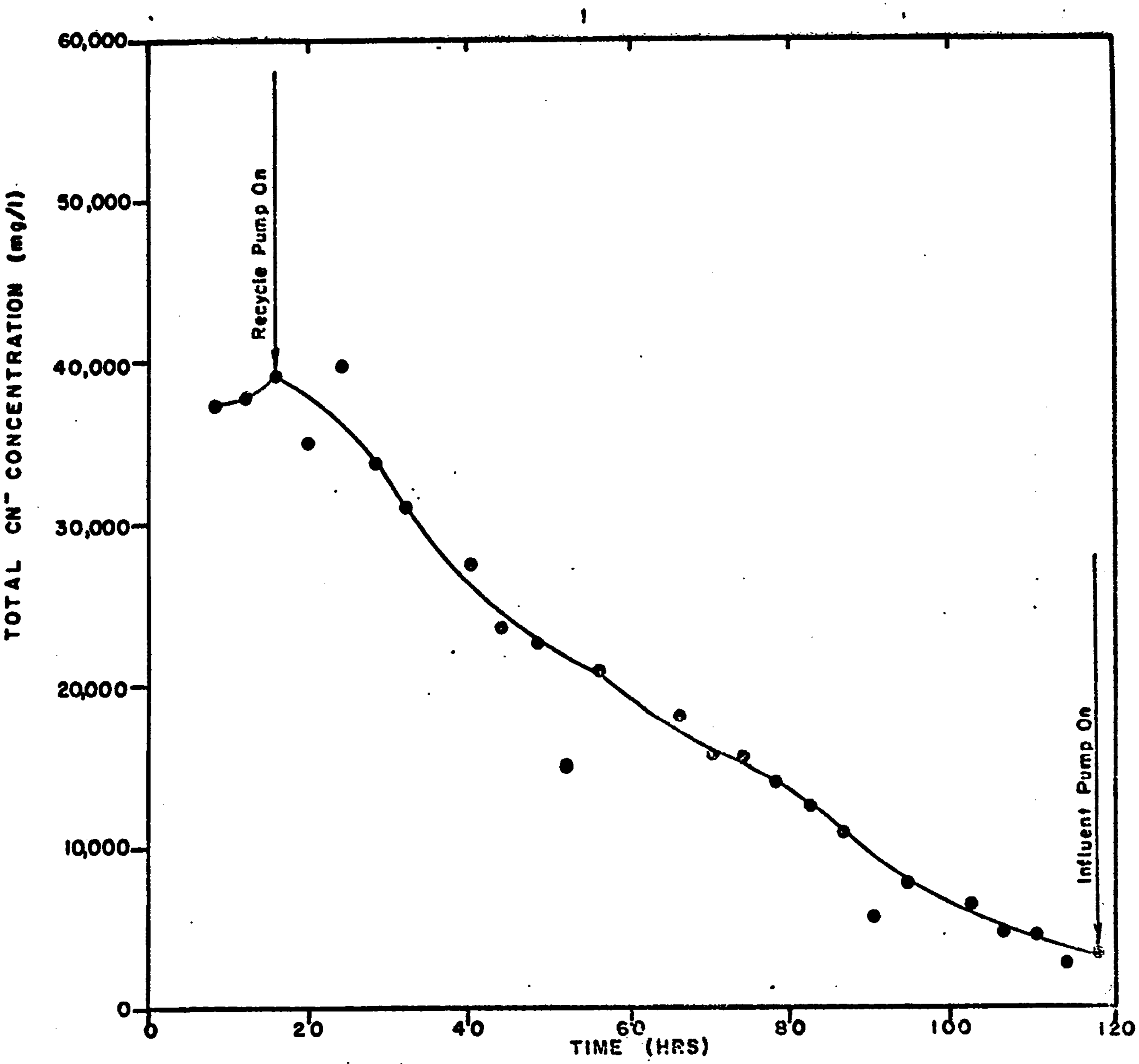

Figure 10: Batch Treatment of CN Waste in Reactor I With Continuous Recycle.

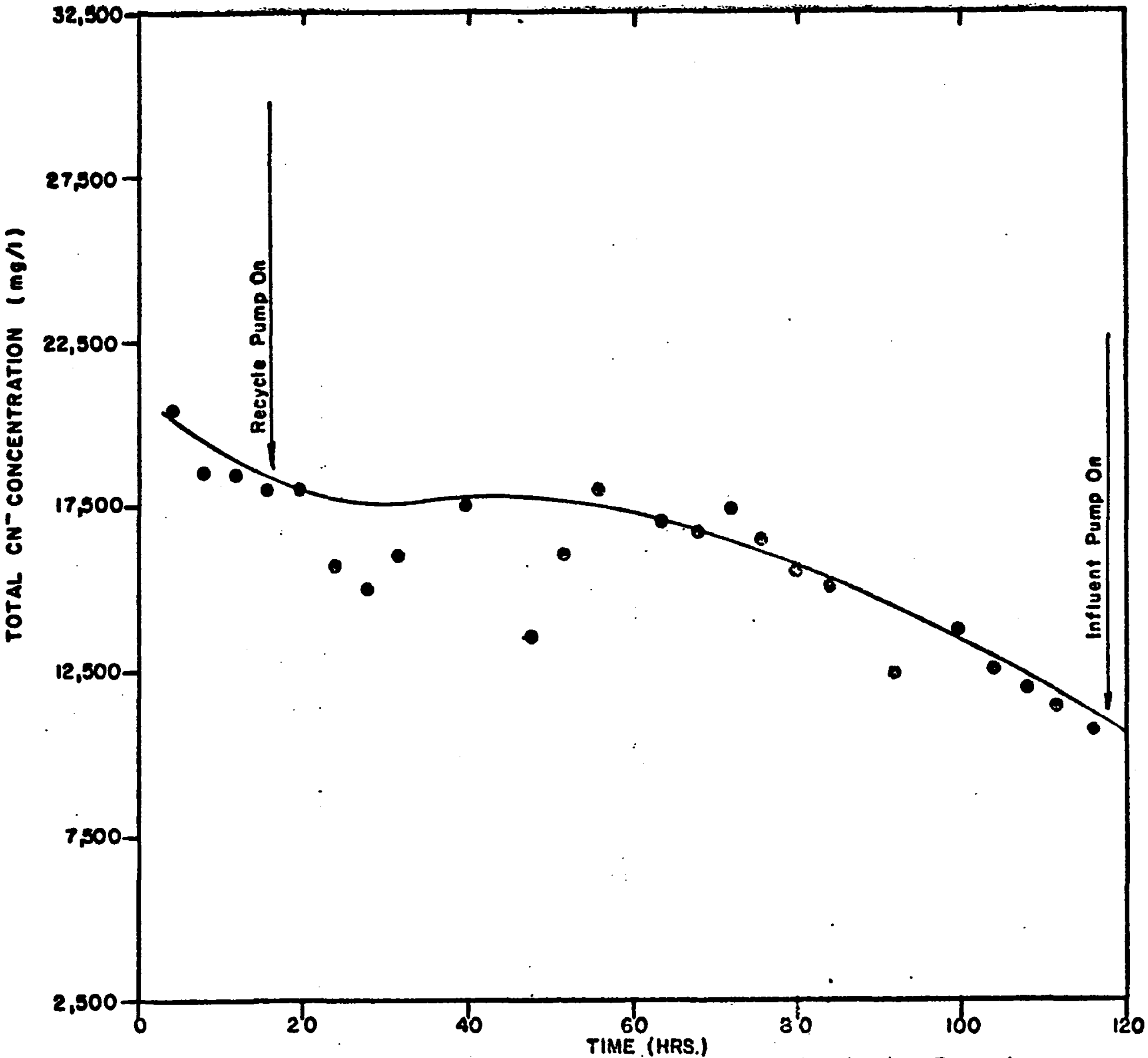

Figure 11: Batch Treatment of CN Waste in Reactor 2 With Continuous Recycle.

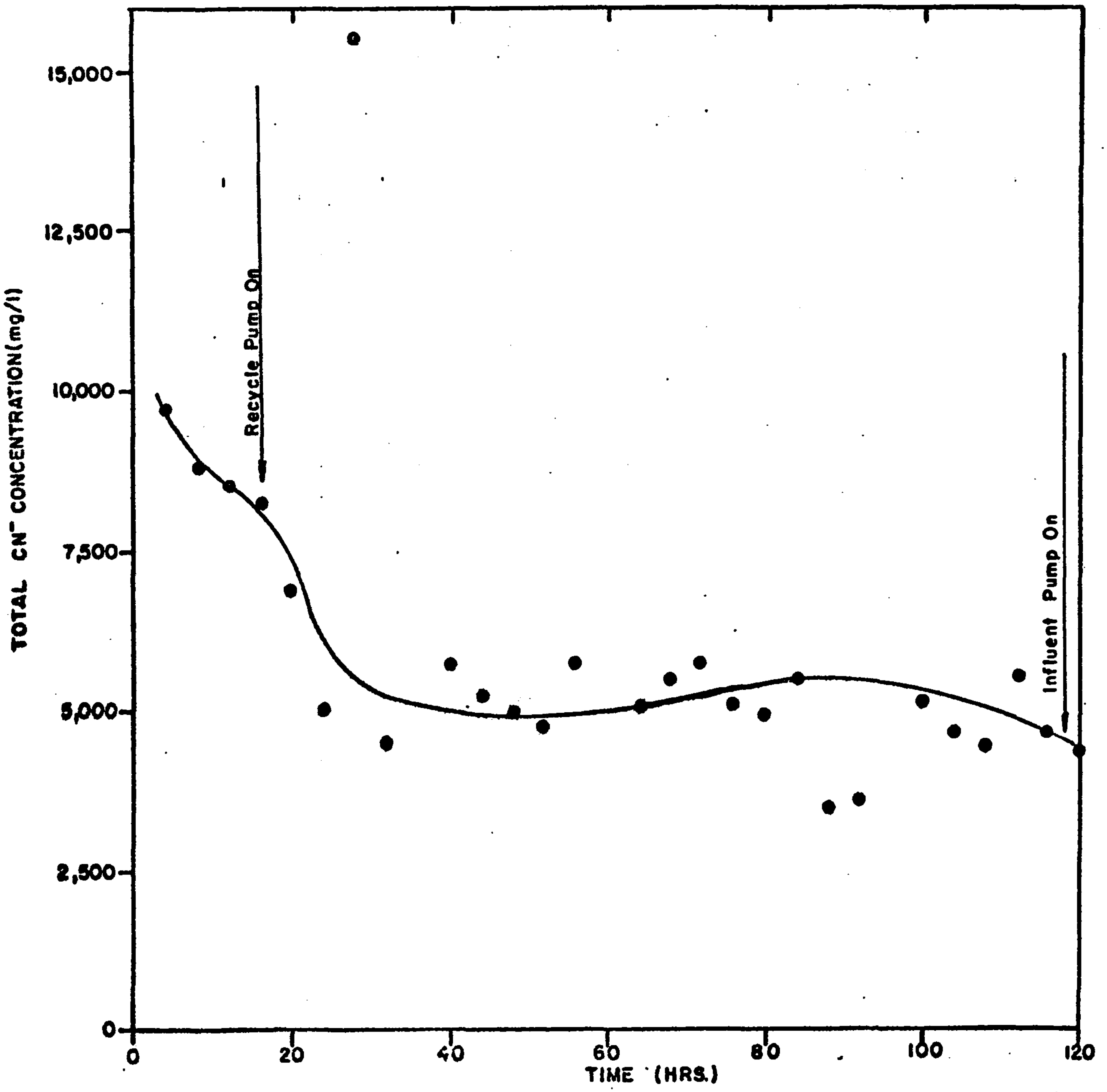

Figure 12: Batch Treatment of CN Waste in Reactor 3 With Continuous Recycle.

oxidizing complexed metal CN^- than free CN^-. Foaming in reactor 1 also increased substantially at the lower CN^- 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 lbs. of CN^- were removed in reactor 1 during the test period. This represents 57% of the total CN^- removed in the system (156 lbs.) and is 41% of the CN^- (218 lbs.) initially present in the system at the beginning of the test. A total of 210 lbs. of ozone were added to reactor 1. The O_3/CN^- removed by weight ratio was 2.4. The mixer speed during the test was 80 rpm. The final pH in reactor 1 was 9.7.

Mass balance computations indicate less CN^- was removed in reactor 2 than reactor 1. Total CN^- removed in reactor 2 was calculated to be 42 lbs. which accounts for 27% of the total CN^- removed, and is 19% of the initial CN^- in the system. During the test 78 lbs. 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 indicates efficient contact and transfer was occurring in reactor 2 during the test, and suggests 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 CN^- in reactor 2 at test termination was still considerably greater than the computed complexed CN^- concentration. The pH was 10.6 at the end of the test.

Figure 12 indicates a rapid decrease of CN^- concentration occurred in reactor 3 down to approximately 5000 mg/l. The reactor concentration then remained approximately constant for the remaining portion of the test period. The limiting concentration is approximately equal to the computed concentration of complexed CN^- (4460 mg/l) calculated from the metals analyses. Once the concentration in reactor 3 leveled off, all free cyanide entering reactor 3 was quickly oxidized. From the mass balance computations, 25 lbs. of CN^- were removed in reactor 3 during the test. The CN^- removed is 16% of the total CN^- removed during the test and 11% of the CN^- initially present in the system. The O_3/CN^- removed ratio of 1.4 for reactor 3 is less than those for either reactor 1 or reactor 2 but is greater than previous values for reactor 3 under batch conditions at higher CN^- concentrations. The high percentage of complexed CN^- present in reactor 3 accounts for the ratio increase. The final pH in reactor 3 was 9.8.

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 CN^- 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 CN^- 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 CN^- waste ran low and waste with lower CN^- concentration was added to the waste storage tank. The system began to approach equilibrium approximately 12 hours into the test. This discussion is limited to the first 50 or so hours when the incoming raw waste CN^- concentration was essentially constant.

Concentration of CN^- for each of the reactors and for the raw influent during the test are displayed in Figure 13. The average influent flow was 6.45 gph and average recycle flow was 5.61 gph. Ozone concentration was lower than previous output in other tests due to problems with ozone generators. Average air flows to reactors 1, 2, and 3 were 79 scfm, 26 scfm, and 14 scfm, respectively. Initial pH values in reactors 1, 2, and 3 were 10.2, 10.3, and 9.8, respectively. The U.V. lamps in reactor 3 were operated throughout the test period. Average temperatures of 90°F, 85°F, and 120°F were measured in reactors 1, 2, and 3, respectively.

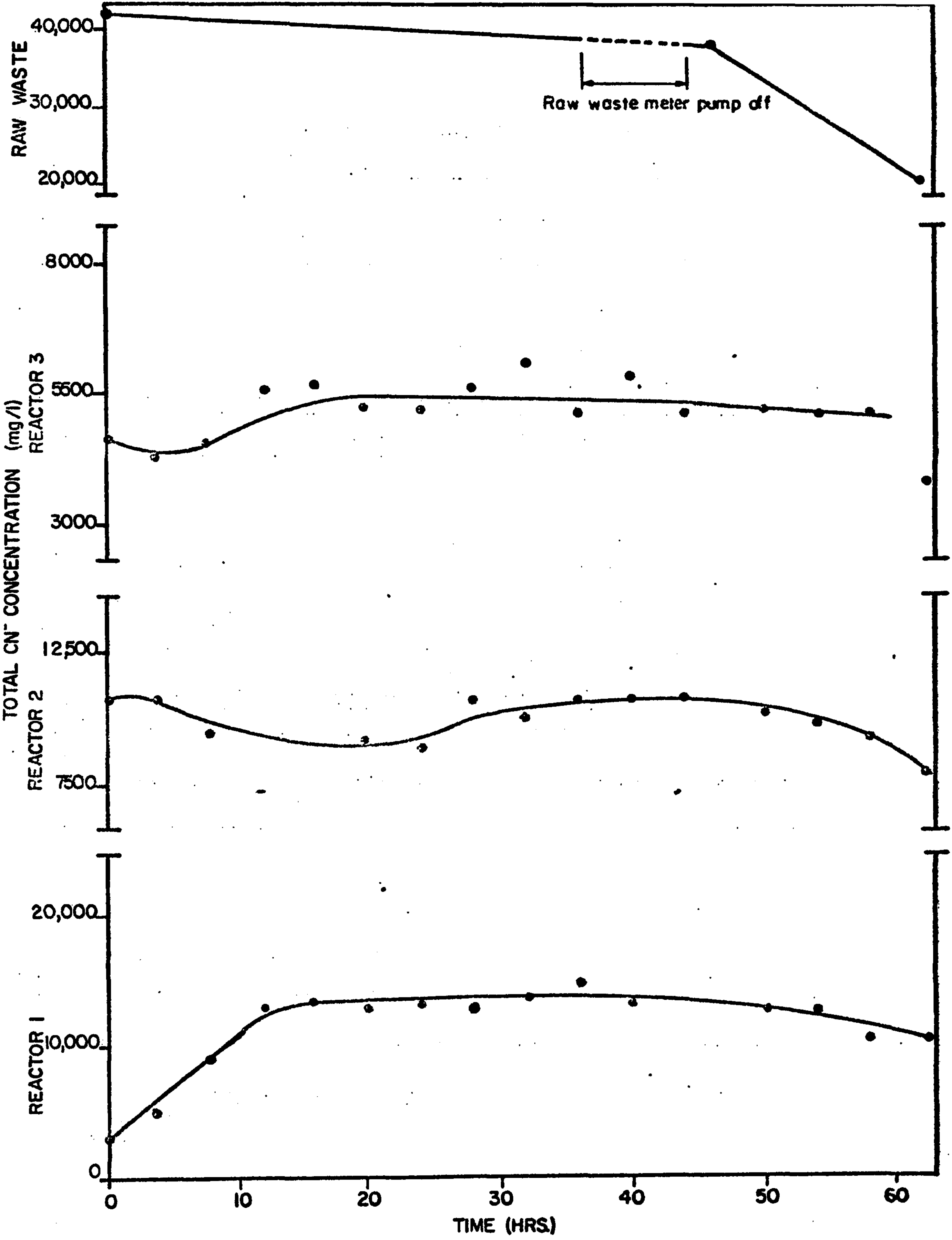

Figure 13: Treatment of CN waste with continuous Inflow and Recycle.

From Figure 13, after the beginning of the test the CN^- 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 hours as the influent CN^- 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 influent had an average concentration of 40,125 mg/l. A mass balance of total CN^- 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 CN^-. From the mass balance computations, reactor 1 was removing 1.1 lbs. of CN^- per 2.4 lbs. of CN^- added each hour or 46% of the incoming CN^-. Ozone was being added to reactor 1 at the rate of 1.3 lbs. per hour 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 will increase the ozone mass flow rate and improve the CN^- removal efficiency. The final pH was 10.3.

After the concentration of CN^- in reactor 1 leveled off the CN^- concentration in reactor 2 began to reach equilibrium. Reactor 2 was at equilibruim after approximately 36 hours with a CN^- concentration of approximately 11,000 mg/l. The inflow to reactor 2 was approximately 11.1 gph consisting of inflow to reactor 1 less evaporation losses. The inflow had a total CN^- concentration of 14,000 mg/l. This indicated 0.3 lbs. of CN^- per hour were removed for each 1.3 lbs. of CN^- added per hour or 23% of the incoming CN^- to reactor 2. Ozone was added at the rate of 0.43 lbs. per hour giving an O_3/CN^- removed ratio of 1.4. The CN^- concentration in reactor 2 eventually began to drop after 50 hours as the effects of decreasing waste strength began to be present. At the end of the test the pH was 9.9.

Reactor 3 was able to reach equilibruim during the test since the initial concentrations were already relatively close to equilibrium values. From Figure 13 the CN^- concentration in reactor 3 leveled off after 30 hours at approximately 5300 mg/l. The incoming waste had a concentration of 11,000 mg/l at a flow rate of 10.6 gph. Make up water at an average rate of 3.1 gph was being added to reactor 3 to account for evaporation losses in the system. Total outflow from reactor 3 was approximately 11.7 gph after subtracting reactor evaporation losses. Mass balance computations indicate 0.45 lbs. CN^- per hour was removed in reactor 3 with 0.97 lbs. of CN^- per hour added. Thus 46% of the CN^- entering reactor 3 was being removed. The O_3/CN^- removed ratio was 0.50 based on 0.22 lbs. of ozone added per hour. Again the advantages of the U.V. radiation are apparent from the high ozone utilization efficiency. The limiting concentration in reactor 3 was approximately equivalent to the complexed CN^- concentration calculated from the metals analyses. Reactor 3 had a final pH of 9.7.

A mass balance of the system during equilibrium indicates 86% of the incoming CN^- was removed. Ozone at 0.36% by weight in the air stream was added at a rate of 1.93 lbs. per hour while CN^- was being removed at a rate of 1.85 lbs. per hour giving an overall O_3/CN^- removed ratio of approximately 1.0.

6. BATCH TREATMENT OF COMPLEXED CN^-

The previous tests indicate the reaction of ozone with CN^- slowed when the CN^- concentration approached levels equal to the complexed CN^- concentration calculated from the metals analyses. It was felt that treatment of the complexed CN^- needed further clarification. Following the previous test, CN^- concentrations in reactors 2 and 3 were reduced by ozonation to levels less than 5000 mg/l. Then a series of batch tests were performed on these two reactors to clarify the complexed CN^- 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. The initial CN^- concentrations in both reactors were below the levels of complexed CN^- calculated from the metals analyses. The test was continued for 20 hours. The U.V. lamps in reactor 3 were on throughout the test. Average

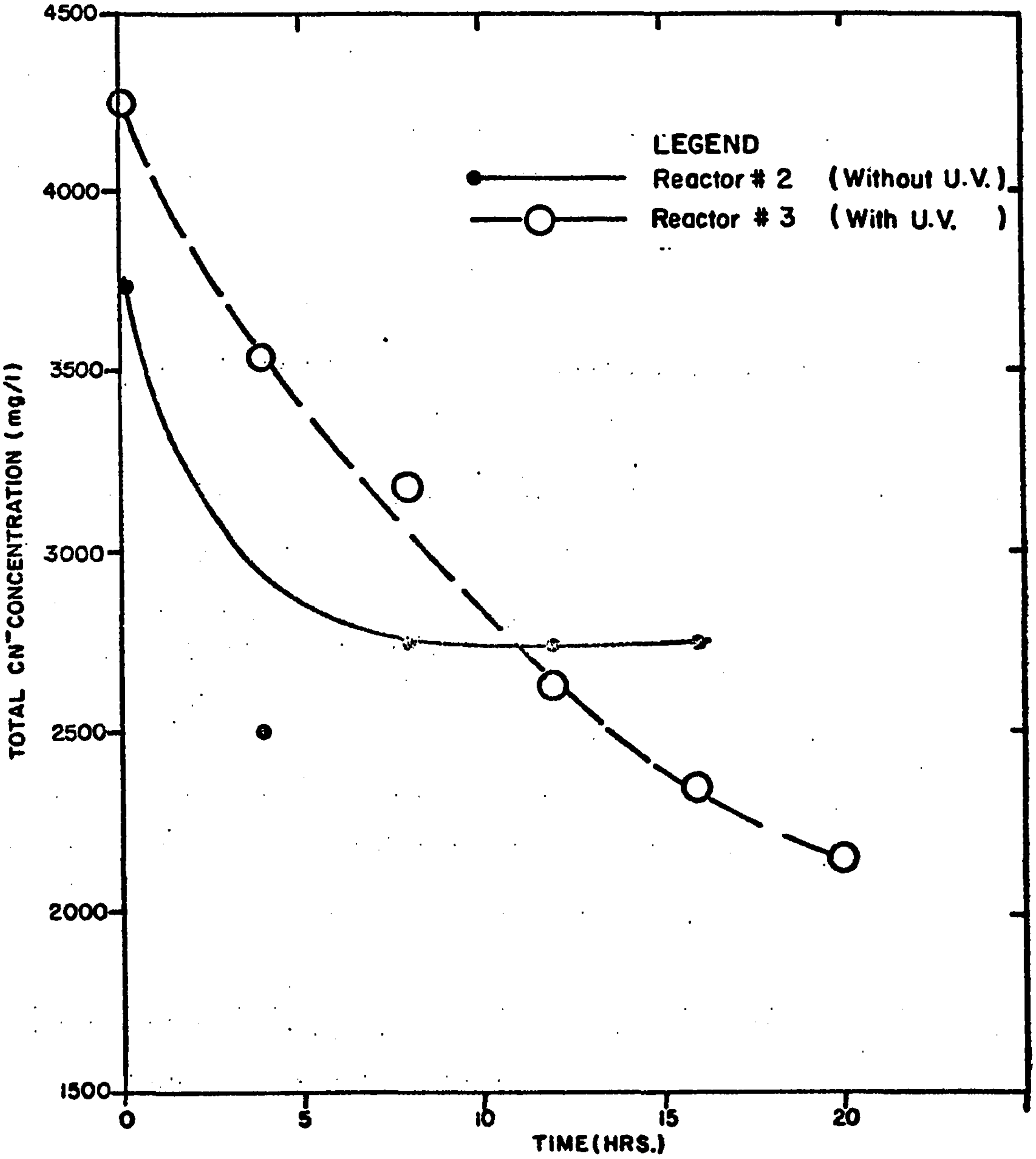

Figure 14: Ozonation of Complexed Metal Cyanide.

air flow rates and temperatures in reactors 2 and 3 were 14.8 scfm and 25.1 scfm, 95°F and 126°F, respectively. The initial pH was 10.2 for both reactors. The average ozone concentration in the air stream was 0.91% by weight. Mass balances performed on reactor 2 for the test indicated 3.3 lbs. of CN^- were removed and 10.2 lbs. of ozone were added. For reactor 3 it was calculated that 7.0 lbs. of CN^- were removed and 21.2 lbs. 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 CN^- 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 indicates the U.V. radiation was effective in breaking down the complexed metal CN^-. 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 CN^- 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 CN^- was apparently reaction rate limiting. Clearly U.V. radiation is every effective in increasing the destruction of cyanide complexed with metals.

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

At this point it was decided to investigate the effect that dilution and pH adjustment would have on the removal rates. It was felt that dilution of the waste would increase the penetration from the U.V. lamps. First, 75% of the waste in reactor 3 was discharged, then the reactor was refilled with tap water. After dilution the CN^- 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 and had an average ozone concentration of 0.92% by weight. The average temperature of the reactor was 120°F. The test was continued for 11 hours. The CN^- concentrations are presented in the first part of Figure 15. During the test 0.60 lbs. of CN^- were

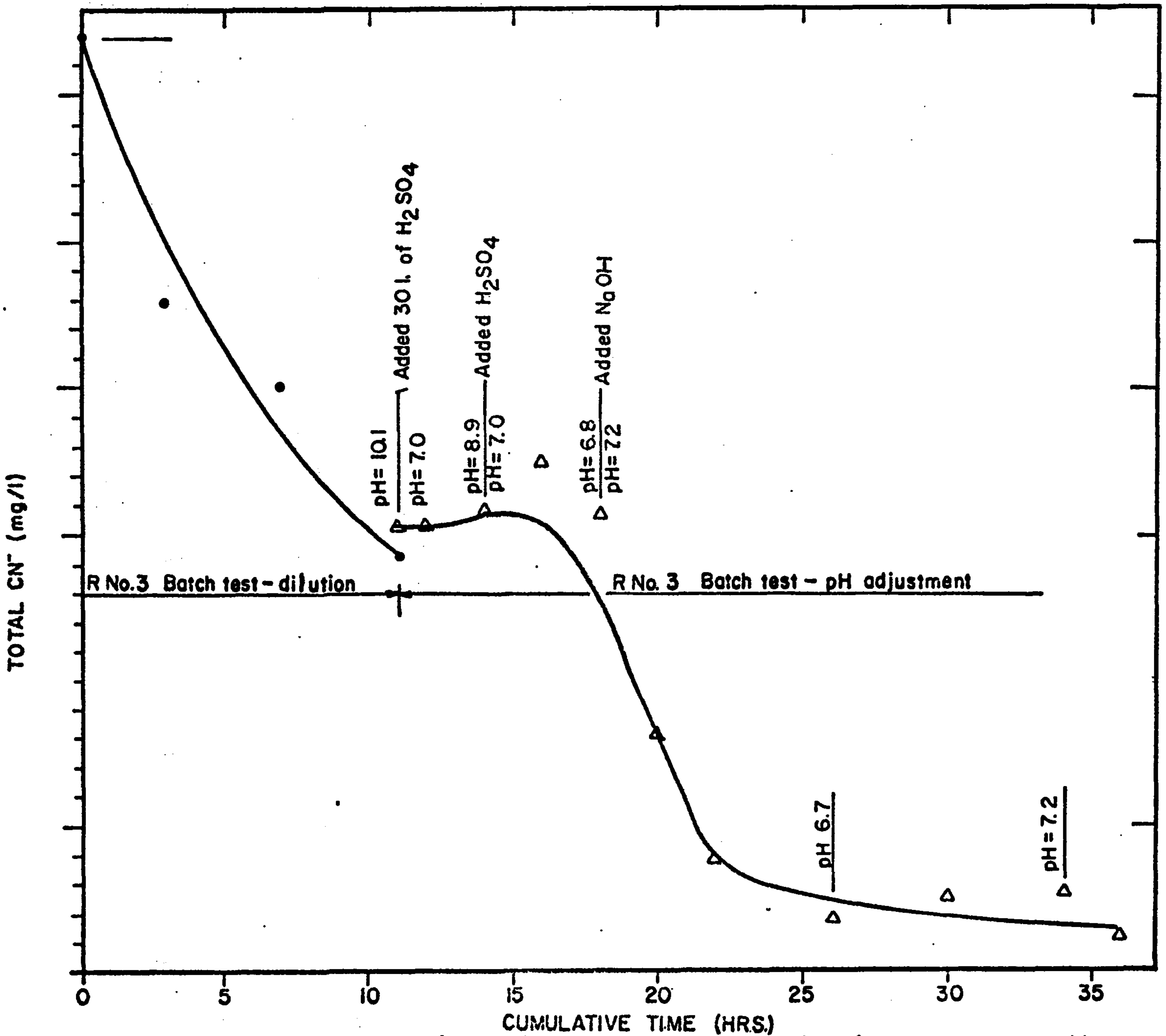

Figure 15: Effect of dilution and pH adjustment on ozonation of complex metal cyanide.

removed and 9.55 lbs. of ozone were added or a O_3/CN^- removed rate of 16. The removal rate for this test was 0.054 lbs. of CN^- per hour compared to 0.062 lbs. of CN^- per hour for the previous test without dilution. Thus dilution 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% 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 CN concentration was detected until after 9 hours of treatment. The concentration of CN^- 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 CN^- 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.

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 CN^- concentration was 81 mg/l. Air flow and ozone concentration averaged 20 scfm and 0.76% by weight, respectively, during the test. CN^- concentration versus cummulative test time is plotted in Figure 16.

The data shows the CN^- concentration initially decreased to 35 mg/l CN^- after four hours of treatment. This was followed by a period in which the CN^- 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. of ozone were added and 0.18 lbs. of CN^- was removed in reactor 3 giving a O_3/CN^- removed ratio of 122. The temperature in reactor 3 averaged 125°F. These results indicate certain metal CN^- complexes, primarily iron/CN^- complexes, are very resistant to treatment by ozone oxidation, even with U.V. radiation present.

7. CONTINUOUS SYSTEM OPERATION

The final system performance tests were made under conditions characterized by continuous raw waste feed to the system and discharge. No waste was recycled during this testing phase. Prior to the test, buck boost transformers were

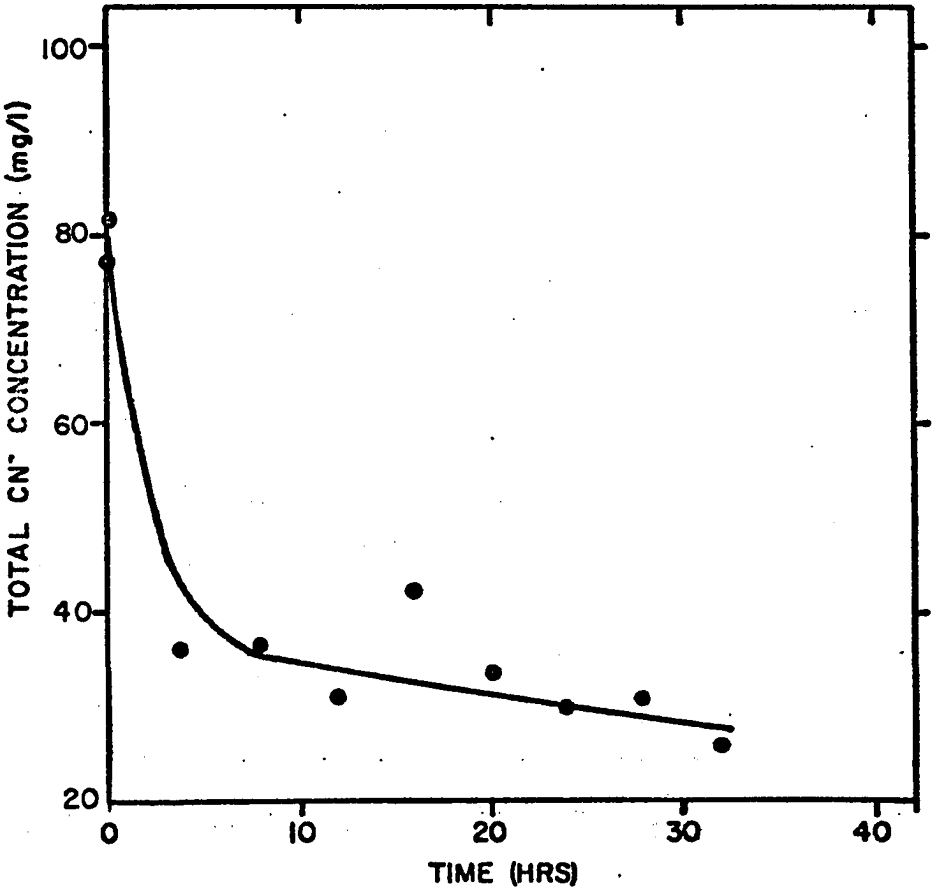

Figure 16: Batch treatment of reactor 3 at low CN⁻ concentration.

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 CN^- waste was obtained from the plating shop for the test. During the test the CN^- concentration of the incoming waste was virtually constant with an average total CN^- value of 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 CN^- 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. The average air flow rates to reactors 1, 2, and 3 were 73.7 scfm, 17.3 scfm, and 19.8 scfm, respectively. 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% by weight. The U.V. lamps in reactor 3 were on throughout the test period.

From Figure 17, the CN^- concentration in reactor 1 began to level off at approximately 1050 mg/l after 20 hours of continuous operation. Reactor 1 was removing 91% of the CN^- present in the incoming waste. From mass balance computations

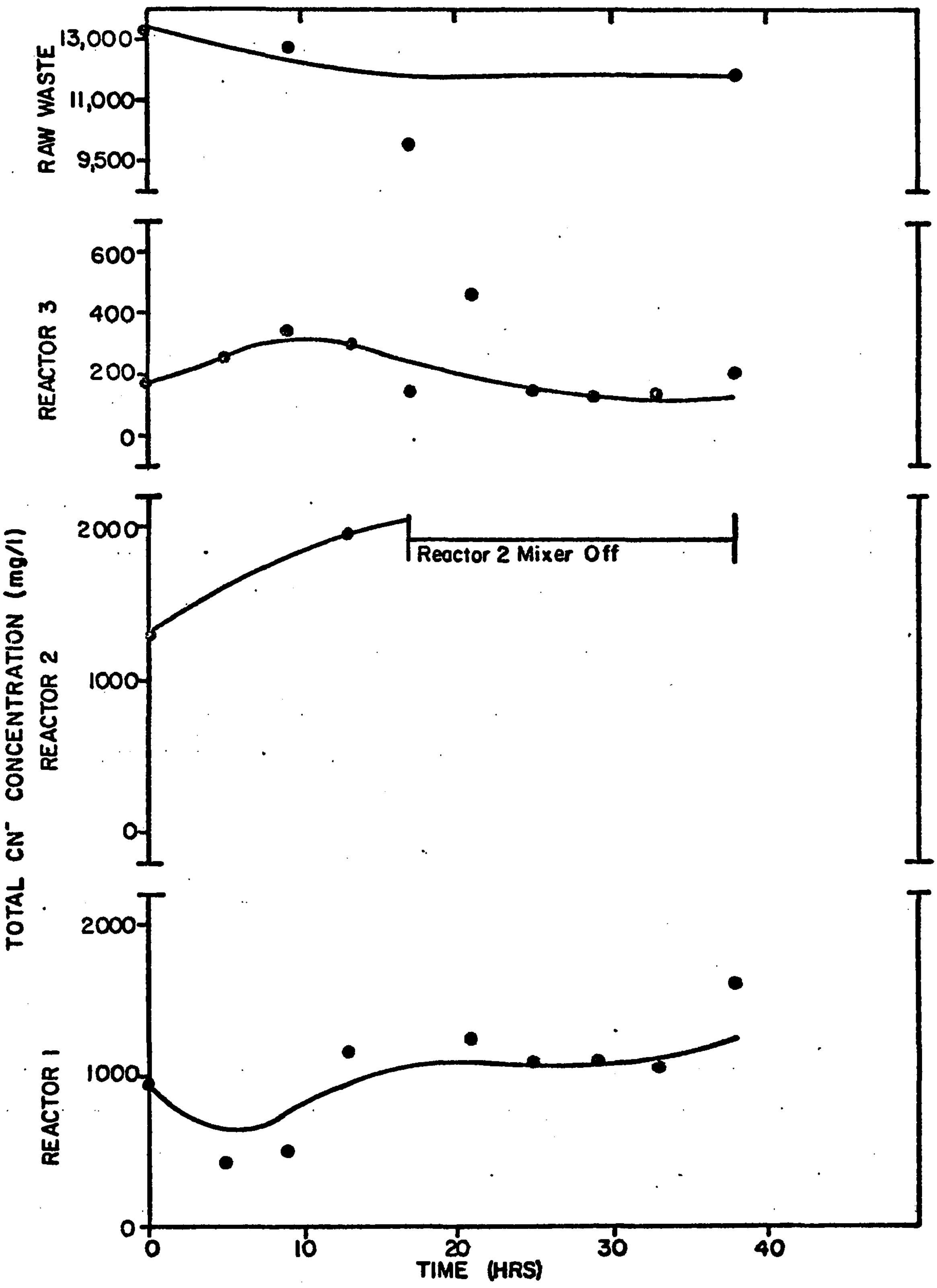

Figure 17: Treatment of CN^- waste with continuous inflow.

reactor 1 was removing 0.58 lbs. of CN^- per 2.0 lbs. of O_3 added each hour. This is equivalent to an O_3/CN^- removed rate of 3.4. An analysis of concentrations of metals in the raw waste entering reactor 1 was performed. The concentrations 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 CN^- complexed with the metals was calculated to be 2409 mg/l. These results indicate all free CN^- present in the raw waste was being removed in reactor 1. Further, reactor 1 was likely removing at least 50% of the CN^- present in complexed form. These observations and the relatively high O_3/CN^- removed ratio of 3.4 computed for reactor 1 indicates the process was radiation rate limiting. The average pH in reactor 1 was 10.5.

The CN^- concentration in reactor 2 had not reached equilibrium when the mixer motor burnt out. At this point air flow to reactor 2 was discontinued. The motor was replaced before the next test began.

From Figure 17 the CN^- concentration in reactor 3 reached equilibrium approximately 24 hours after the test began. The equilibruim concentration of CN^- in reactor 3 was 120 mg/l. The incoming waste had a CN^- concentration of approximately 1050 mg/l. Therefore, 89% of the CN^- entering reactor 3 was being removed and 8% of the CN^- present in the raw waste (12,110 mg/l) was oxidized in reactor 3. Mass balance computations indicate 0.53 lbs. of O_3 were added for each 0.05 lbs. of CN^-

added per hour or a O_3/CN^- removed ratio of 10.6. Again, it is observed that the complexed metal CN^- present in the waste are limiting the reaction rate in reactor 3. The average pH of the waste in reactor 3 was 10.3 during the test.

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. Air flows to reactors 1, 2 and 3 averaged 74.2 scfm, 15.6 scfm, and 19.2 scfm, respectively. The previous week's results indicated mass flow of ozone was not limiting the CN^- removal rate but rather the complexed metal CN^- 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% by weight. The U.V. lamps were operated continuously in reactor 3. Average temperatures in reactors 1, 2, and 3 were 89°F, 92°F, and 127°F, respectively.

From Figure 18 the concentration of CN^- in reactor 1 remained fairly constant throughout the test. The average CN^- concentration in reactor 1 was 904 mg/l. Reactor 1 was removing 93% of the incoming CN^-. Ozone was being added at a rate of 1.6 lbs. per hour and CN^- removed at a rate of 0.58 lbs. per hour or an O_3/CN^- removed ratio of 2.8. Although the rate is

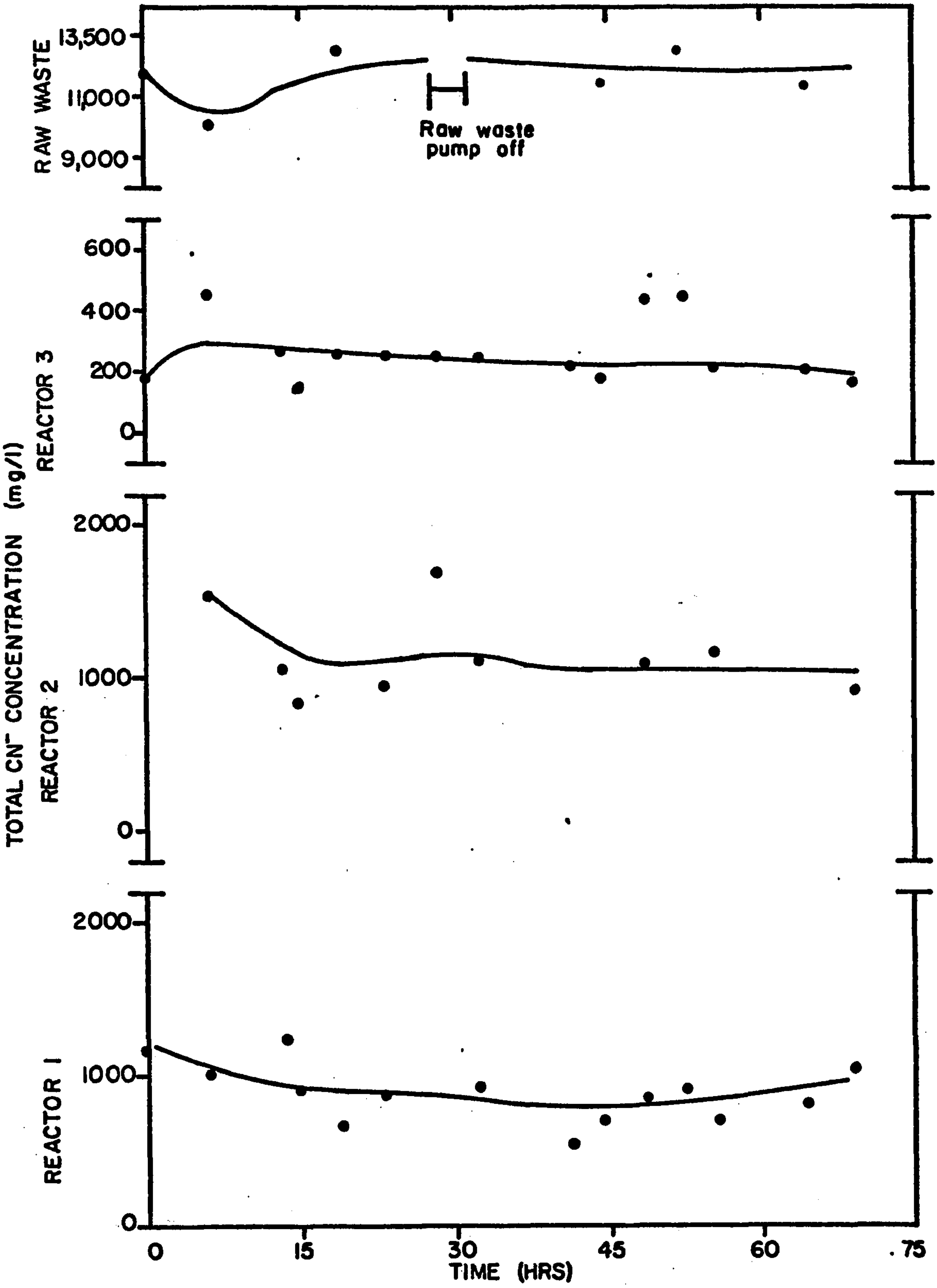

Figure 18: Treatment of CN⁻ waste with continuous inflow.

relatively high it is still less than the previous test rate of 3.4 for reactor 1. This further illustrates the influence of the complexed metal CN^- 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. The average pH in reactor 1 was 10.3.

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

In contrast to reactor 2, the complexed CN^- was more effectively removed in reactor 3 as evidenced in Figure 18. The CN^- 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. per hour and CN^- removed at a rate of 0.05 lbs. 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. U.V. radiation was very effective in increasing the removal rates in reactor 3 when comparison with reactor 2 is made. The pH in reactor 3 averaged 10.4 during the test.

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

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% on a dry weight basis consisted of Fe, Zn, Ni, Cd, Co, and Cu. Relative contributions for the metals were 3.45% Fe, 0.975% Zn, 10.75% Ni, 6.57% Cd, 0.0158% Co and 2.475% Cu.

SECTION VII

EVALUATION OF CYANIDE TREATABILITY

1. INTRODUCTION

In ozone oxidation of cyanide waste, several factors were found to influence the overall efficiency of the system during the study. Many of these previously identified include, for example, ozone mass flow rate, ozone air stream concentration, U.V. 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 measure of the effects of U.V. 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 have been prepared depicting the results in terms of parameters which reflect process efficiency. One of the parameters used is the change in reactor cyanide per incremental time period (CN^- removed/unit time as lbs. 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 the quantity of ozone added to the system per unit time (CN^- removed/unit time//O_3 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 CN^- concentrations studied, the bar graph was found by the author to be a good method

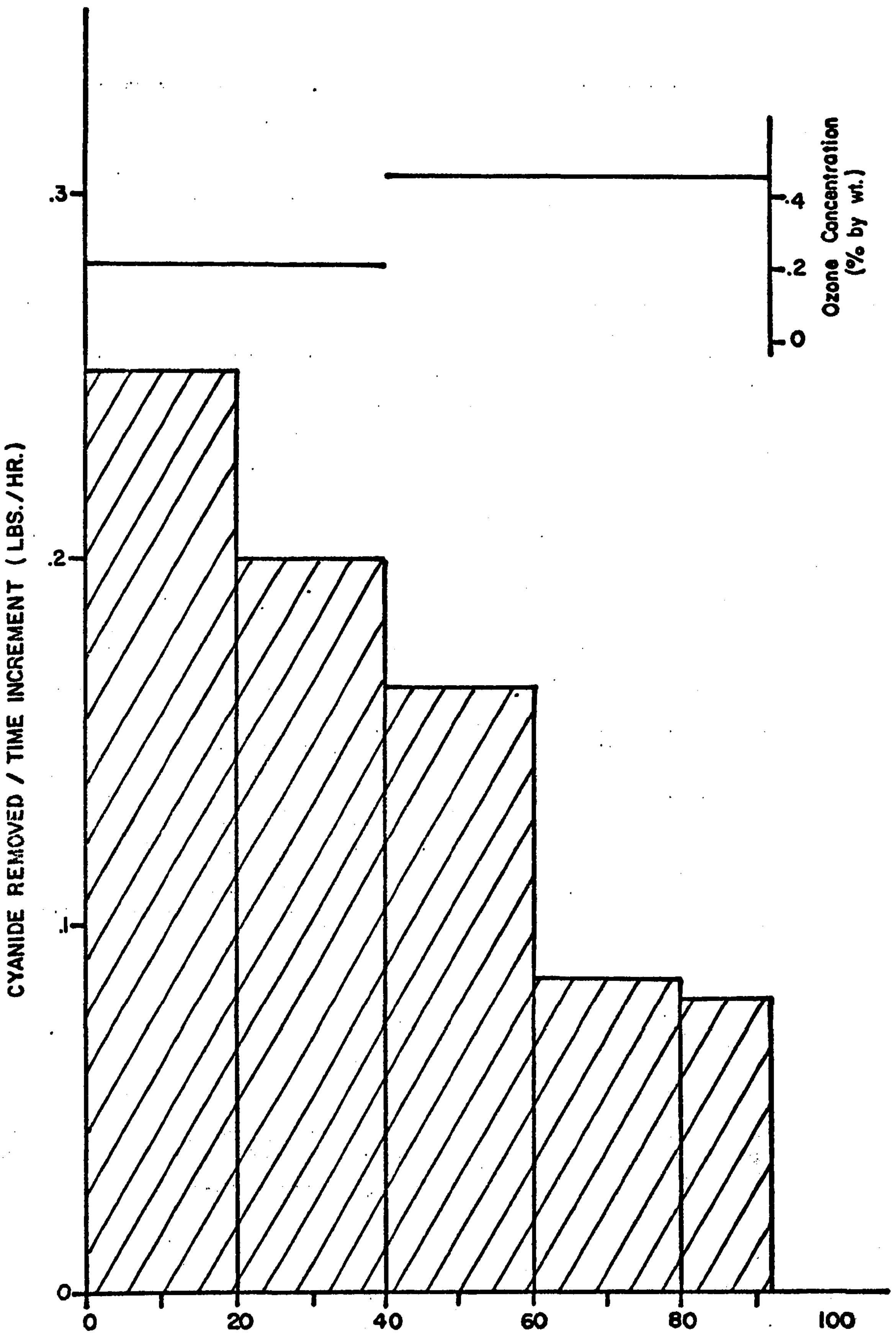

Figure 19: Cyanide removal rates during a batch test of reactor 2.

to illustrate the changes in the system efficiency parameters and is used for this purpose throughout the section.

During the first incremental test period the figure shows cyanide was being removed at a rate of around 0.25 lbs/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 and was then increased to a second constant plateau for the remainder of the test period. It can be observed the removal rates continue to follow a decreasing pattern with constant and increasing ozone concentrations. Thus, the rate of cyanide removal is seen, in this case, to depend on the concentration of cyanide remaining in the reactor.

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 the process efficiency as measured by the parameter CN^-/O_3 did not decrease at this time even though the CN^- removal rates had decreased. This suggests optimizing the process in terms of ozone utilization efficiency

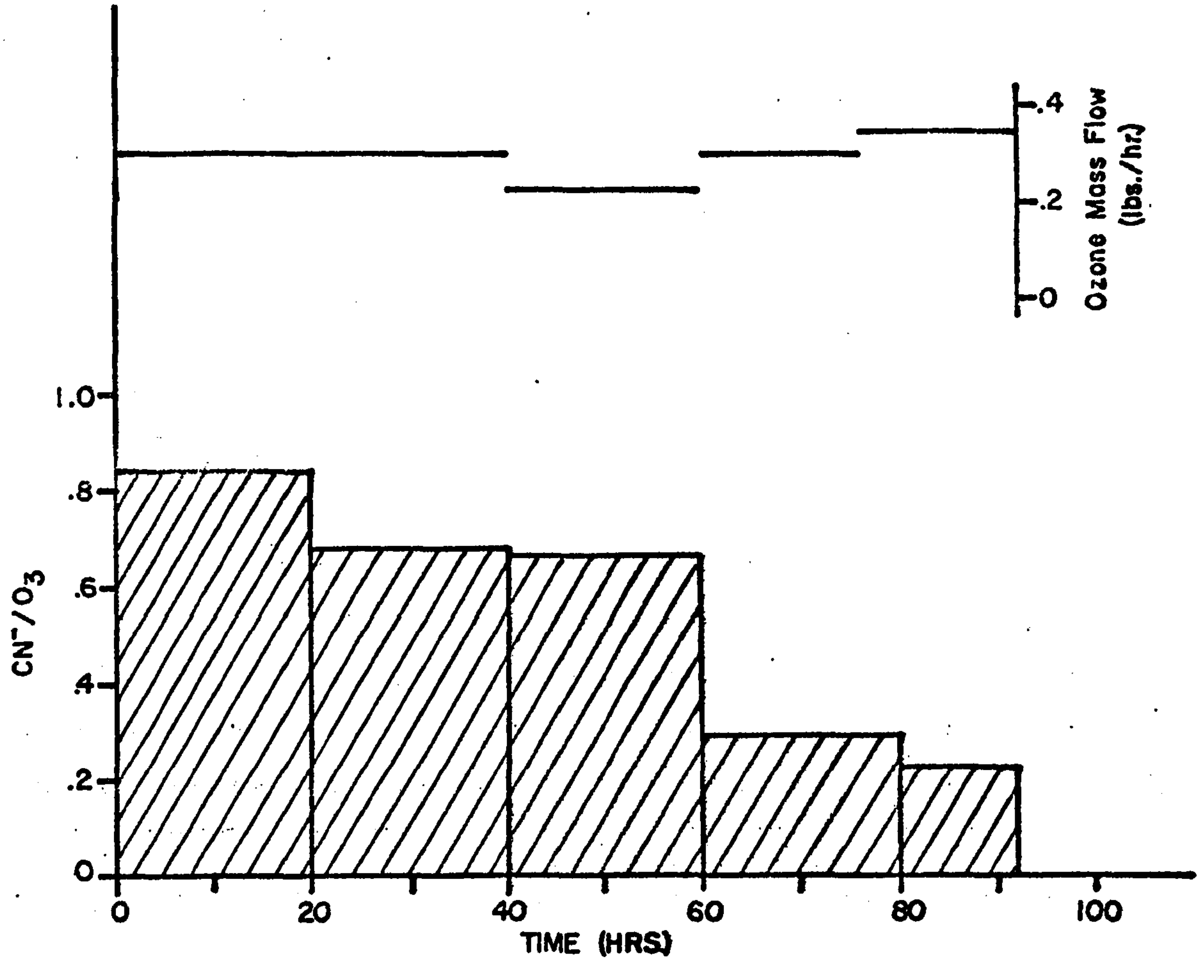

Figure 20: Changes in process efficiency at high reactor CN^- concentrations.

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 U.V. Radiation Present

The graph, Figure 21, presents the variation in cyanide removal rates which occurred during a batch test of reactor 3. Cyanide concentration varied from 25,000 to 12,000 mg/l. This reactor contains U.V. lamps in contrast to reactor 1 and 2. The initial CN^- 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 follow the same type of declining curve as observed for the previous 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 the CN^- concentration remaining in the reactor. For reactor 2 and 3 the reactor CN^- 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. Observe

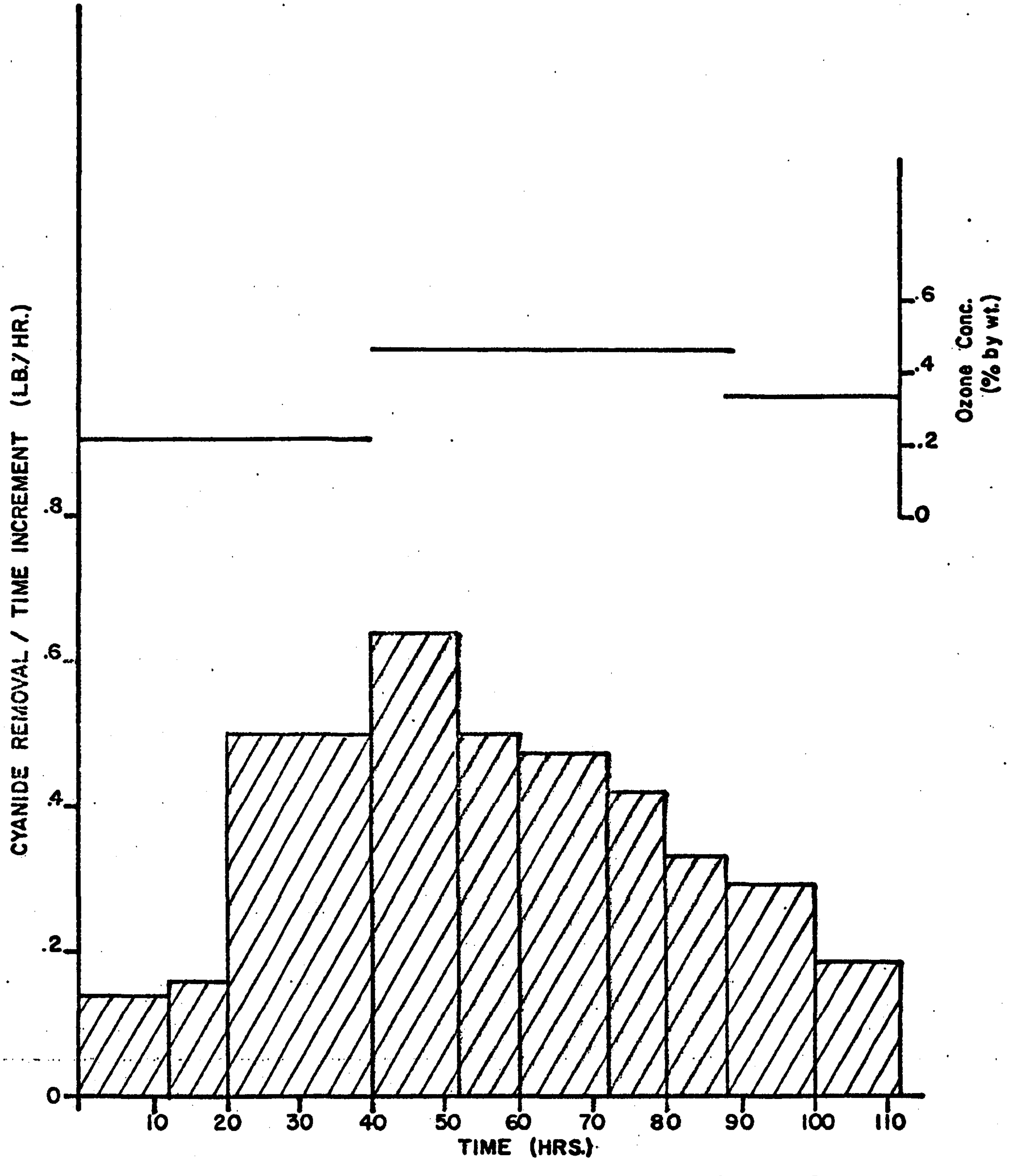

Figure 21: Cyanide removal rates during a batch test of reactor 3.

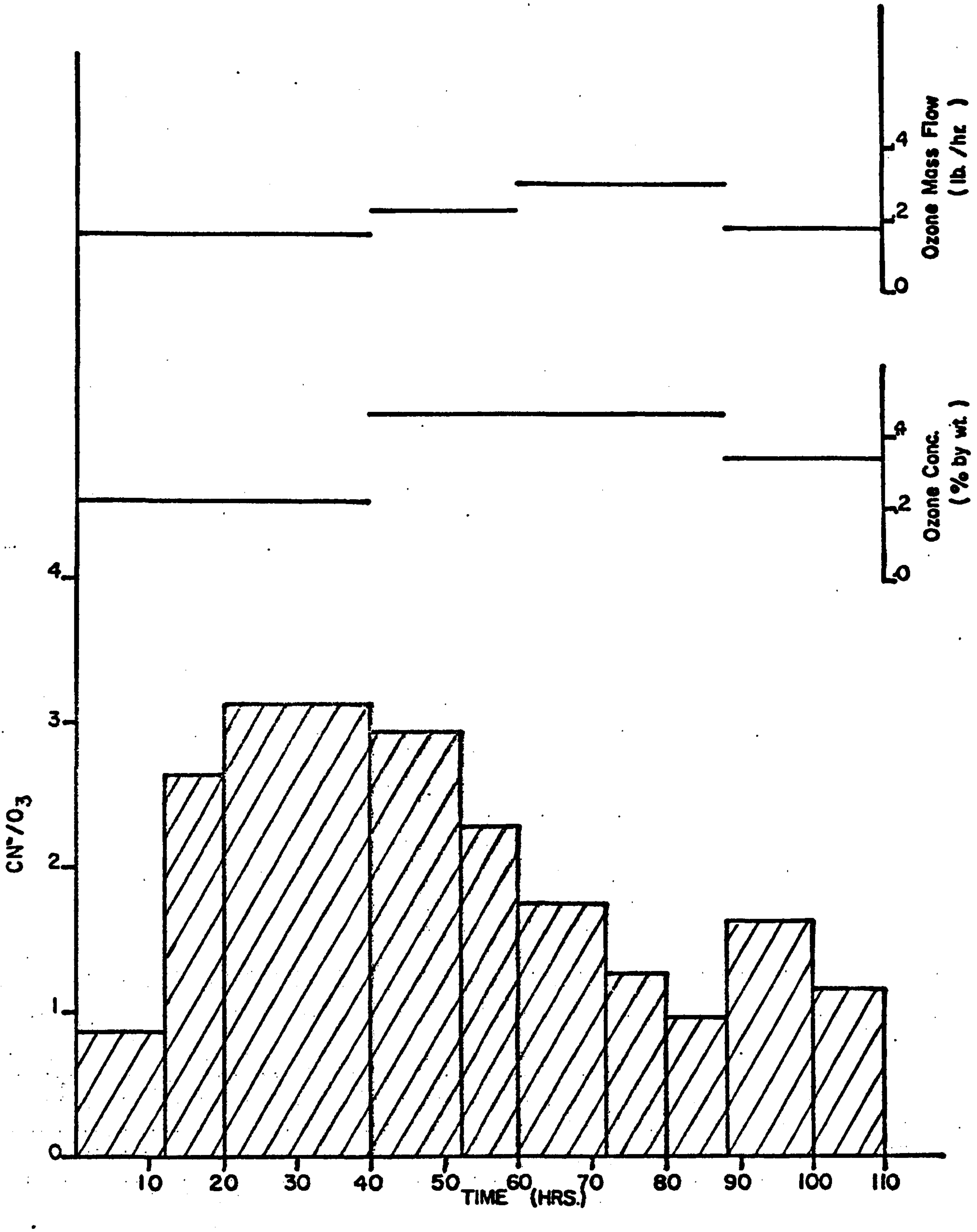

Figure 22: Value of the ratio CN^-/O_3 during a batch test of reactor 3.

that 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% to 0.46% by weight. At 0.46% ozone, the process efficiency continued to decrease until about 90 hours into the test. At this point the process efficiency was increased by decreasing the ozone concentration to 0.34% 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 reactor 3 and 2 are superimposed in Figure 23. The ozone concentrations were the same during both tests. Also, reactor CN^- concentrations were both high, in the 20,000 mg/l range initially. Examination of the initial 12 hours indicates the reactor process efficiencies were the same. Then reactor 3 takes a significant jump. This indicates the elevated temperatures resulting from the U.V. radiation likely play a significant role in the ozone cyanide process efficiency. The reactor temperatures at the point were 26°C and 52°C for reactor 2 and 3, respectively. Figure 23 further illustrates the process efficiencies in reactor 3

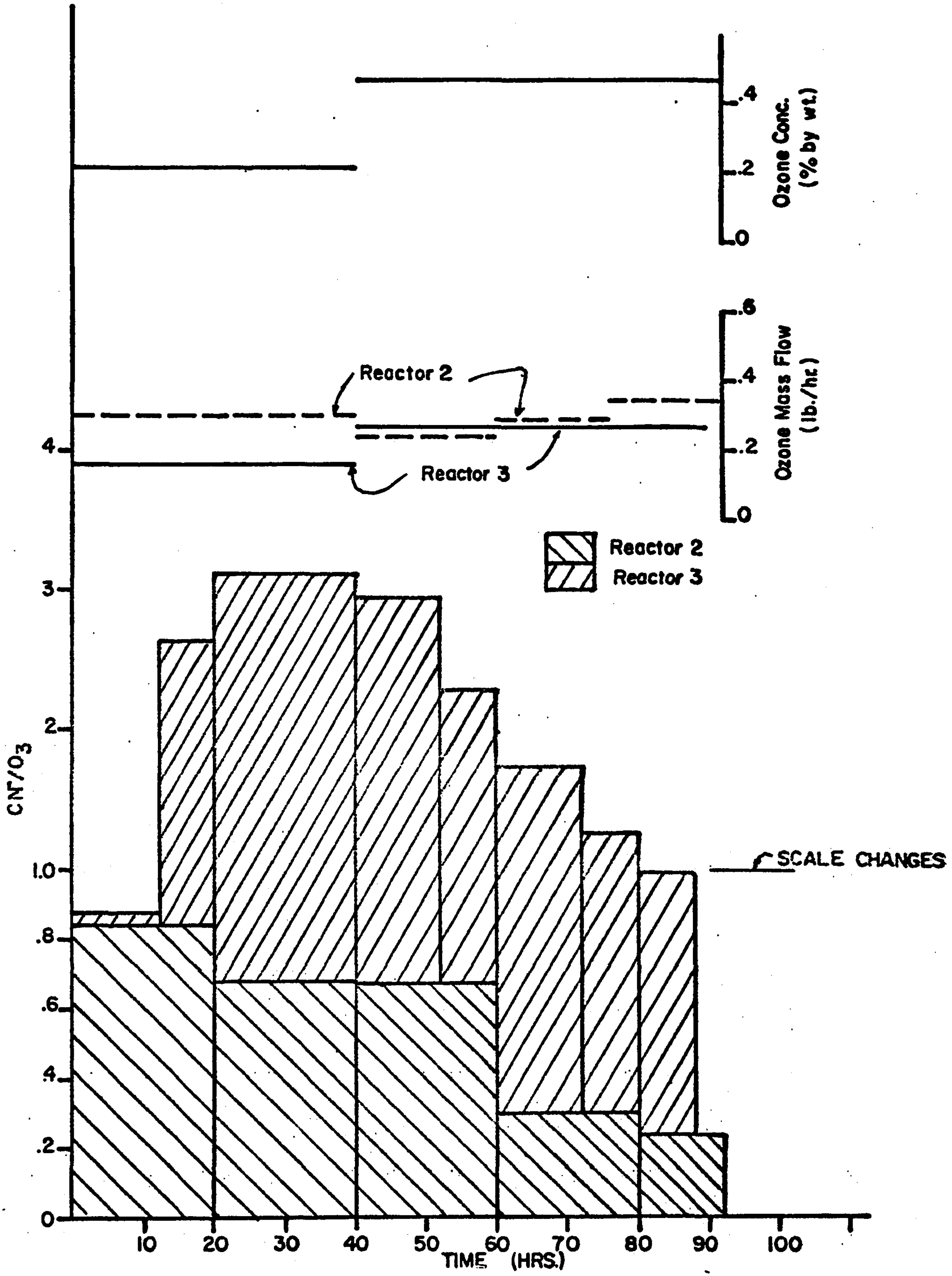

Figure 23: Comparison of CN⁻O$_3$ for reactors 2&3.

are significantly greater than reactor 2 during the remainder of the test period. As the reactor test conditions are the same, it is concluded that U.V., radiation and 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 CN^- Removal Rates at High CN^- Concentrations

During the study it was observed that an initial period of relatively slow removal rates occurred for some of the CN^- waste treated, followed by gradually increasing rates. This was especially true for raw untreated wastes. These periods are of significant duration to warrant their 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 and had a total CN^- concentration of 63,000 mg/l CN^-. 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 the rates continuously increased during the 100 hour plus batch test. Figure 25 shows the associated process efficiencies during the test. The process efficiencies also increased proportionately. Further, the reactor pH did not change during the test period

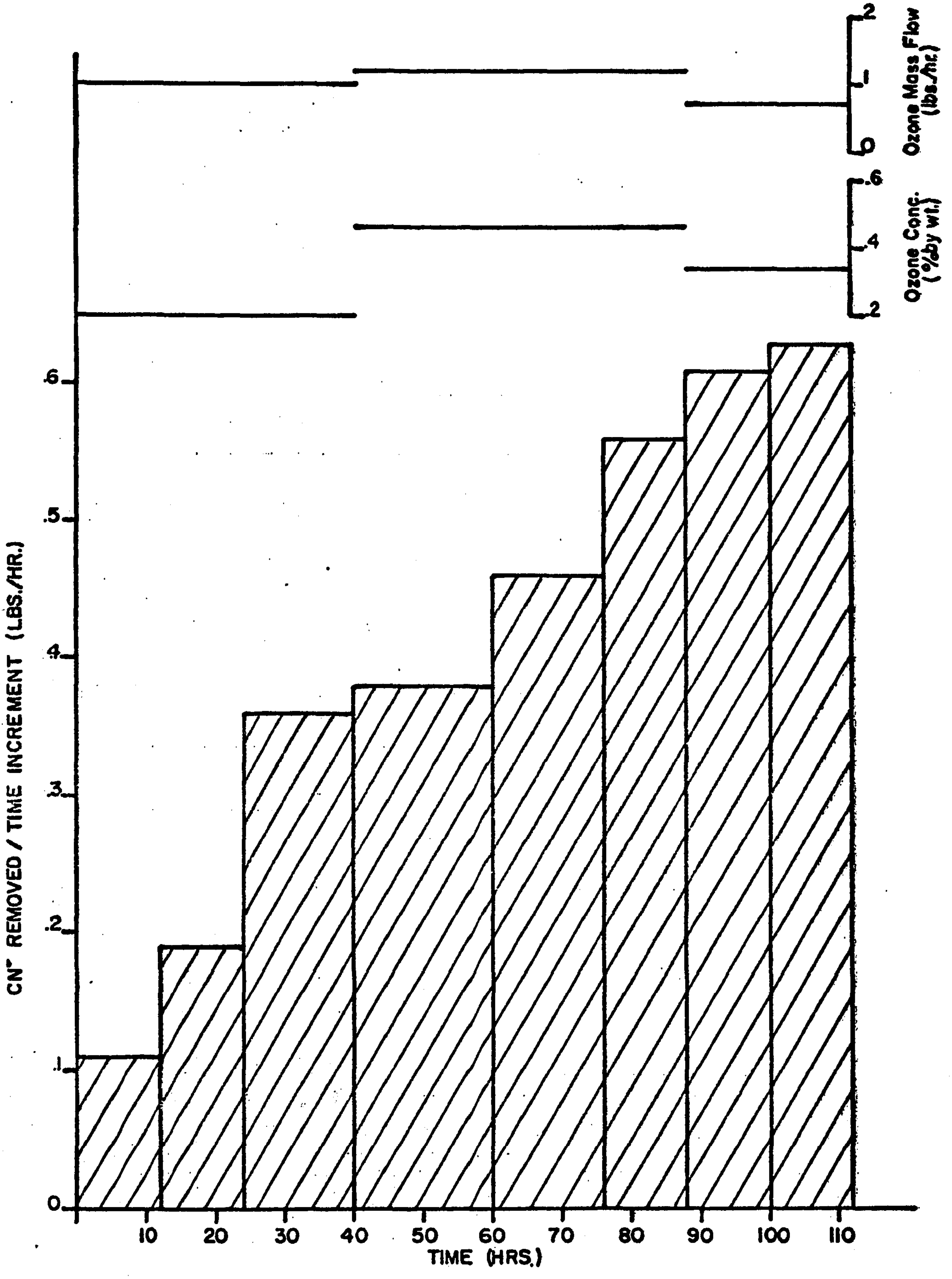

Figure 24: Cyanide removal rates during a batch test of reactor I.

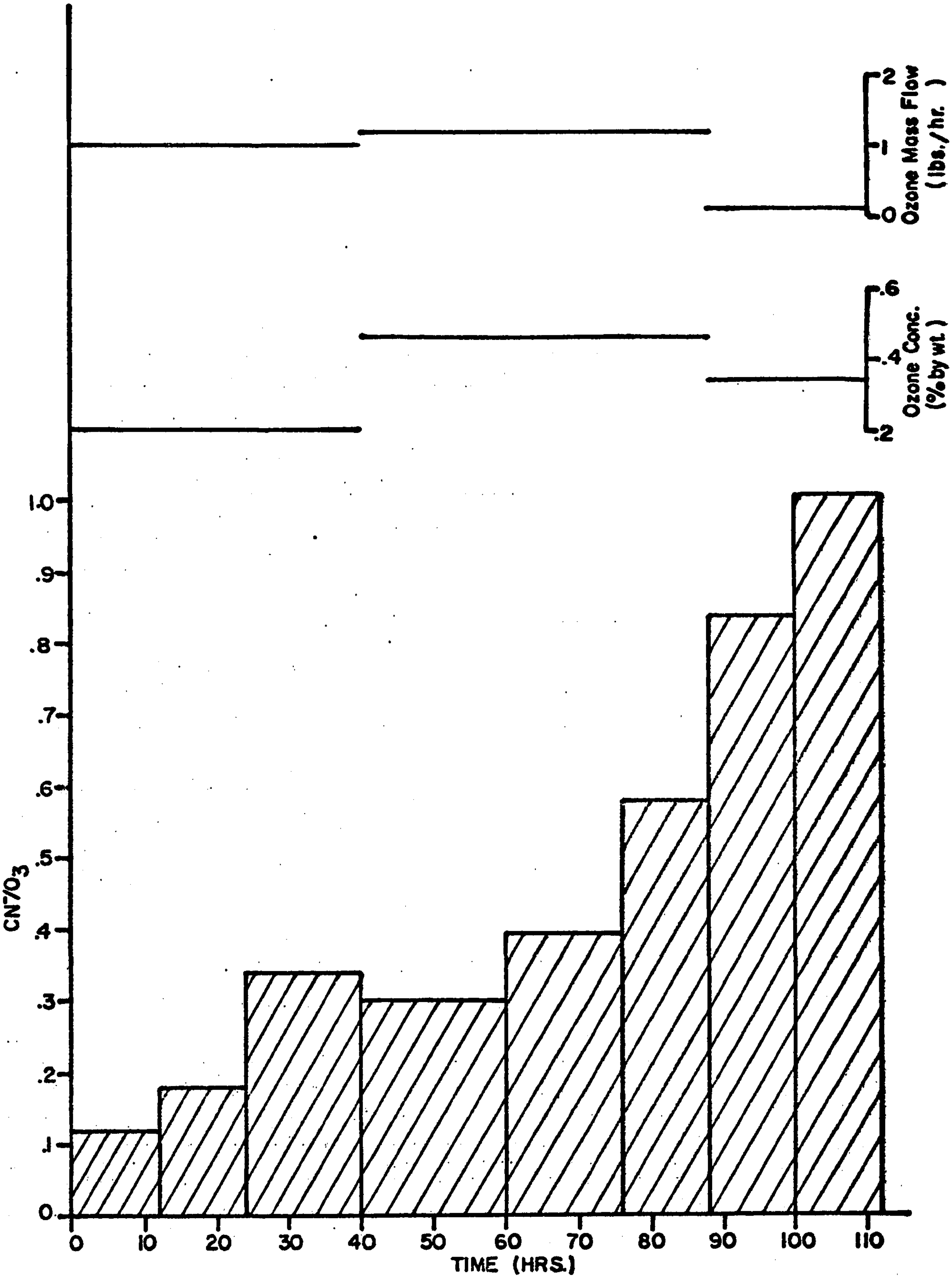

Figure 25: Values of the ratio CN^-/O_3 during a batch test of reactor I.

and appears therefore unrelated to the cyanide removal rate pattern. Based on these observations, most likely a secondary carbon source was present in the waste and was preferentially oxidized by the ozone.

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

These observations indicate 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

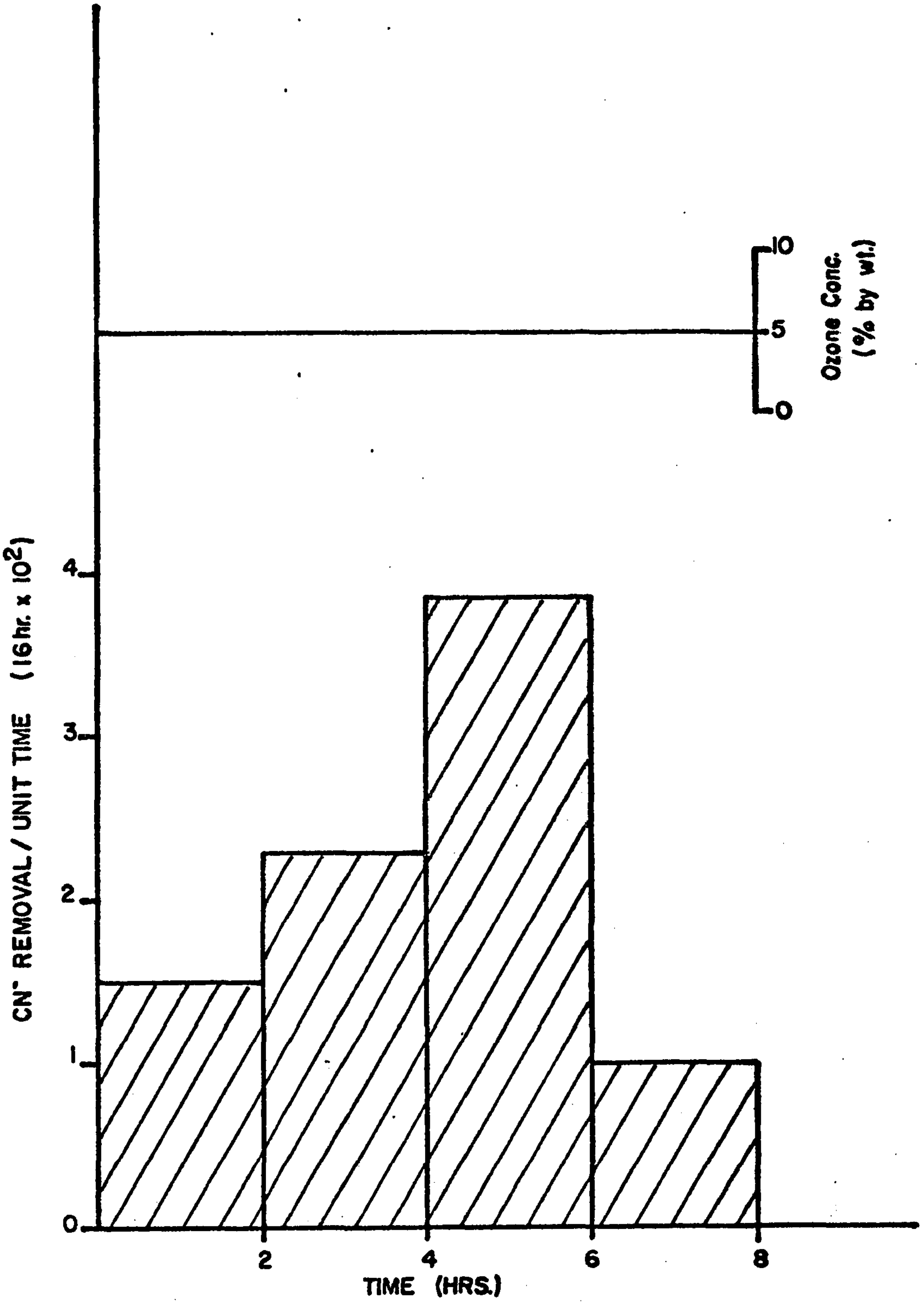

Figure 26: CN⁻ removal rates for Nickel Strip CN⁻ waste.(3)

are shown in Table 10. The ozone mass flow rates for the three tests are comparable with a variance from 1.3 to 2.0 lb. of O_3 per hour. Also, ozone concentration in the air stream varied from 0.4 to 0.6% by weight. The CN^- loading rates are greatest for test no. 3 at 2.4 lb/hr. This difference was not due to waste flow rate but was related to the equivalent CN^- concentration in the raw waste inflow which ranged from 11,000 mg/l to around 13,000 mg/l for test no. 1 and 2 compared to around 25,000 mg/l for test no. 3.

The cyanide removal efficiencies of test no. 1 and 2 averaged 91% and 93%, respectively, at equilibrium compared to 45% for test no. 3. The resulting reactor CN^- 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 10. For the first two tests this ratio averaged 0.32 compared to a CN^-/O_3 ratio of 0.83 for test no. 3.

For tests no. 1 and no. 2, analysis of the metals present in the raw waste indicated approximately 2400 mg/l of CN^- 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

Table 10: Continuous System Operation Parameters at Equilibrium

Test No.	Reactor No.	Equilibrium CN^- Conc. (mg/1)	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

the reactors with only complexed cyanide present at these concentrations, a range of 7 to 10 lb. O_3 per lb. of complexed cyanide removed was required. The total ozone added from Table 10 average 1.8 lb. O_3/hr. for tests no. 1 and 2. Thus, assuming a requirement of 10 lb. O_3/lb. of complexed CN^- removed, the 1425 mg/l of complexed CN^- removed, 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 no. 1 and no. 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 the complexed CN^- removed in test no. 1 and no. 2 had on the overall efficiency.

In comparison, for test no. 3, the concentration of complexed CN^- 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 concentrations of CN^- remaining in the reactors. 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 the equilibrium conditions of the continuous tests, it is found the high CN^-/O_3 ratios (0.833) are associated with high CN^- concentrations in the incoming waste and in the reactor whereas the low CN^-/O_3 ratios (0.29 to .36) are associated with lower CN^- concentrations in the incoming waste and in the reactor.

It appears 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 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 11 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 11, it is observed that the pH gradually decreased during the first 60 hours of the test, then slightly increased. In comparison, the values for CN^-/O_3 ratio decrease from 2.10 to 1.92 for the first 20 hours of testing, increase to 2.54 after 60 hours, and then decrease 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 are 1.92 and 2.45, respectively. The same observation is made for a pH of 10.4 and 10.5 where the CN^-/O_3 ratios are 1.97 and 2.45. Thus, for the pH range in Table 11, 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 11: Changes in Reactor pH During System Batch Testing

Test Time (hrs.)	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 CN^- 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 the reactions during these periods were dependent on the cyanide concentrations remaining in reactor 2 and 3.

In addition, process efficiencies for the two batch tests were also discussed and compared. Figure 23 graphically depicts the comparitive efficiencies as measured by the CN^-/O_3 parameter. The process efficiency for reactor 3 greatly exceeded the process efficiency for reactor 2 in all cases. As waste concentrations and characteristics were the same for both reactors it was concluded the increased efficiencies in reactor 3 result from U.V. radiation and associated elevated temperatures.

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

For a first order reaction the rate of removal is directly proportional to the concentration of reactent remaining.

Mathematically this is expressed as follows[39]:

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

where C = reactent 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 reactent concentration

For a first order reaction a plot of $\ln(C_o/C)$ versus time will yield a straight line. The reaction rate constant k is then determined by evaluating the slope of the line. Taking cyanide concentrations in the reactors to be reactent concentrations (C) in the above expressions, 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 it was known the removal rates were concentration dependent was used in the analysis.

The data in Figures 27 and 28 yield straight line plots. The associated reaction rates (k) are 0.009 hr^{-1} and 0.003 hr^{-1} for the reactors with and without U.V. radiation, respectively.

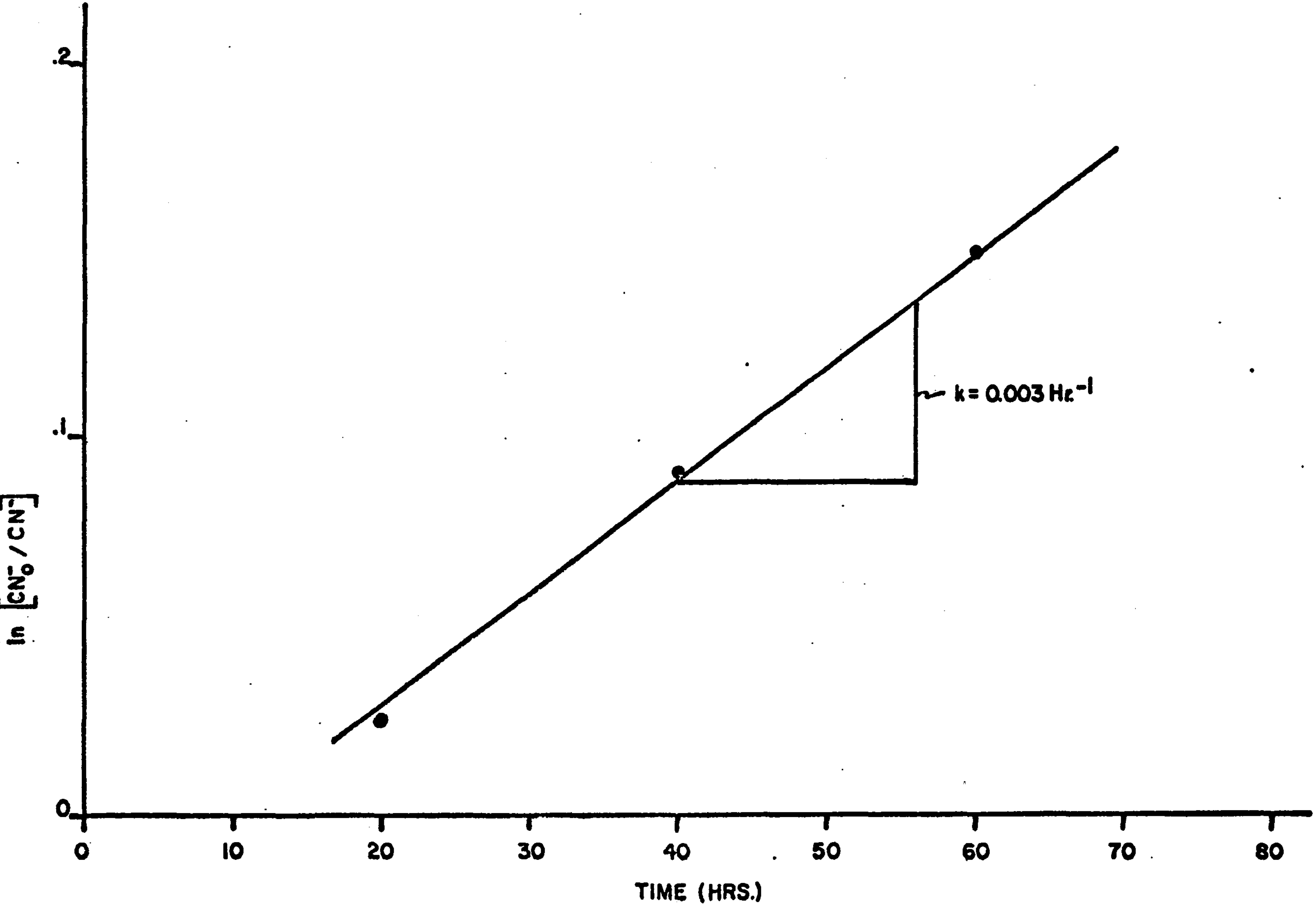

Figure 27: Reaction rate evaluation at high cyanide concentrations without U.V radiation present.

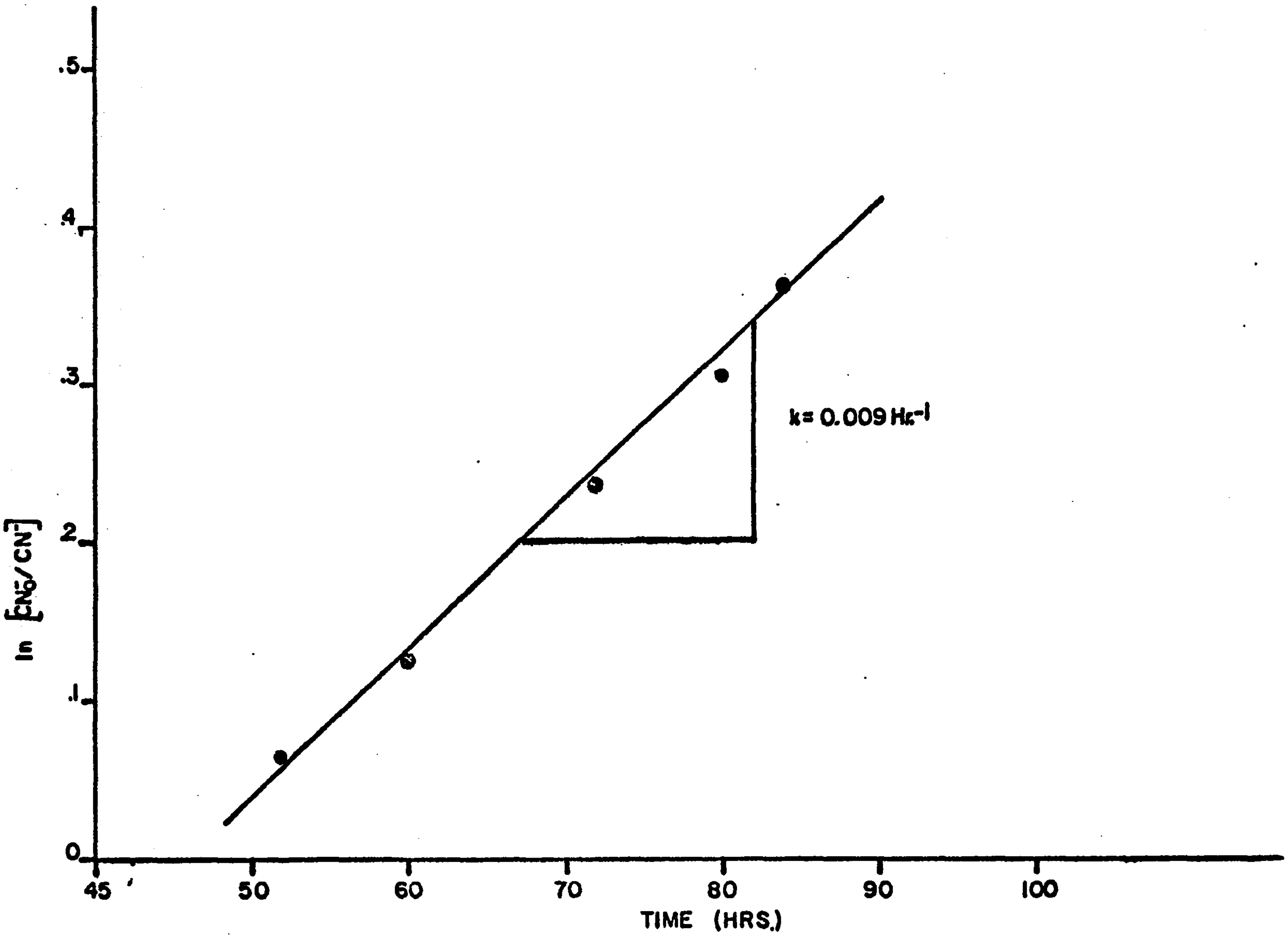

Figure 28: Reaction rate evaluation at high cyanide concentrations with U.V. radiation present.

This strongly indicates improvements in process efficiency associated with the U.V. 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 U.V. radiation and elevated temperatures. To make this evaluation, the reactor temperature is assumed to be a direct measure of the combined effects produced by U.V. radiation and elevated temperatures. The Arrhenius equation gives an expression for reaction rate variation with temperature:

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

where k', k = reaction rates

T', T = temperatures

θ = constant

For the ozone cyanide oxidation process it is assumed:

k' = reaction rate determined with U.V. radiation and elevated temperatures present.

k = reaction rate determined without U.V. radiation and the associated elevated temperatures.

Equation 1 can be solved for the constant θ :

$$\theta = \ln(k'/k)/(T'-T) \qquad \text{eq. 2}$$

The parameters determined for the two batch process operations are:

$$k' = 0.009\ \text{hr}^{-1},\ T' = 49.5\ \text{C}^{\circ}\ (121.2\ \text{F}^{\circ})$$
$$k = 0.003\ \text{hr}^{-1},\ T = 26.5\ \text{C}^{\circ}\ (79.7\ \text{F}^{\circ})$$

Substitution of the parameter values into equation 2 yields:

$$\Theta = 0.0478$$

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

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

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

A reaction rate was also estimated for conditions during a batch test when the majority of the reactor waste present was in the complexed form. This was done for reactor no. 3 which has U.V. radiation and elevated temperatures. The test evaluated had approximately the same system parameter conditions as 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 CN^- concentration level. The reaction rate is seen to decrease approximately by a factor of 3.

SECTION VIII

OPERATION AND MAINTENANCE COSTS

A summary of the annual operation and maintenance costs are presented in Table 12. Costs were computed based upon data collected during 24 hour/day operation of the system. Operation costs include an allowance for operators the authors feel are necessary to run the system. Maintenance costs include items which will be reoccurring annual expenses to insure optimum system performance. The maintenance costs reflect 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 are based on 1979 commercial rates in Oklahoma City, Oklahoma. Average unit power costs for Tinker Air Force Base (1.5¢/KWh) are less than the commercial rates used in the calculations.

From Table 12 total annual O & M cost for the ozone-cyanide system is $50,000. Power costs are 28% of this total. Labor costs account for 50% of the total O & M costs.

Assuming the system removed 90% of the CN^- from the waste, then based on a design flow and CN^- concentration of 3000 gallons per month and 50,000 mg/l, respectively, the

Table 12. 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		14,000	11,000	25,000*

*Cost represents 50% time obligation by one operator.

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

system would removed 13,500 lbs. of CN^- annually. The cost for treatment based on operation and maintenance would be \$3.70/lb. CN^- removed.

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 prevent formation of nitrogen trichloride (37). 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 Cl_2/part CN while theoretically the chlorine requirement is only 6.82 parts Cl_2/part CN. The caustic 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 fervo-and ferricyanide 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, Oklahoma City, 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 addition which is typically NaOH. 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 about 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

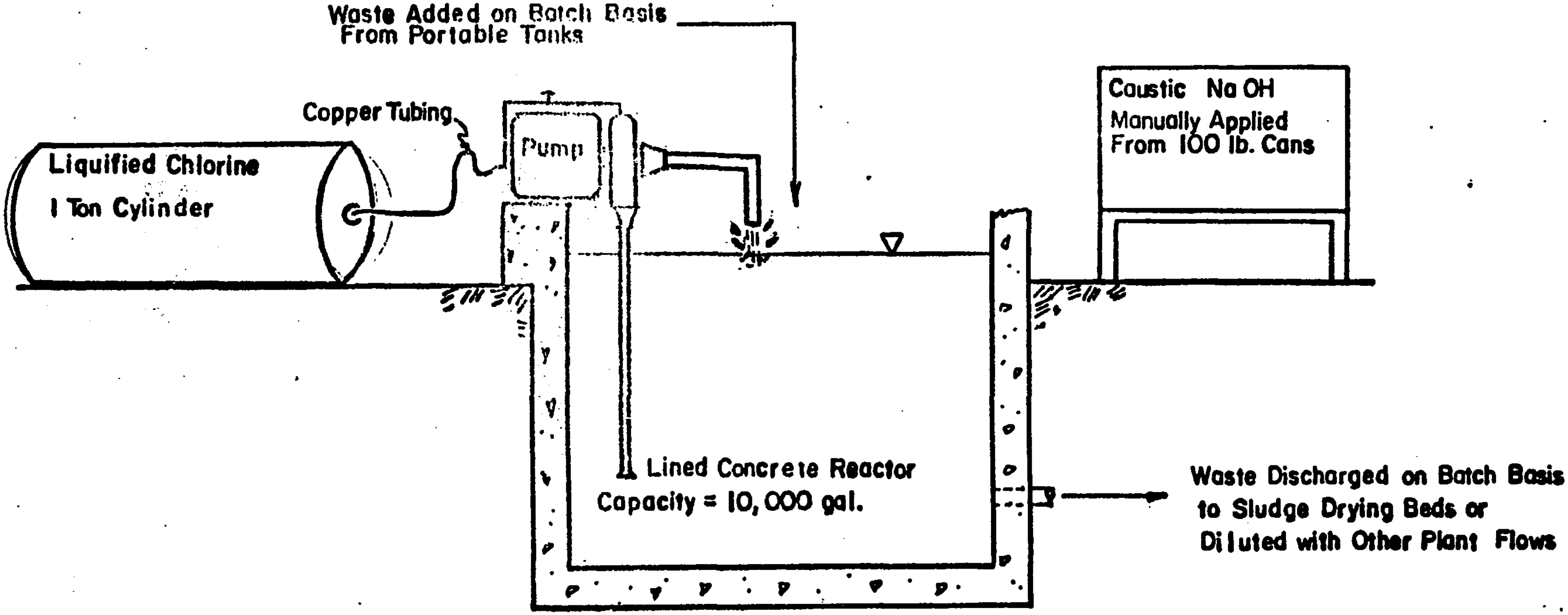

Figure 29: Alkaline Chlorination System at Tinker Air Force Base.

residues. Otherwise the wastewater is fed into the main plant process stream which averages about 1.5 mgd for dillution. Generally, the residual CN^- concentration in the treated CN^- wastewater is on the order of a few thousand milligrams per liter or less before dilution into the main plant flow is permitted. As noted previously the volume of CN^- wastewater averages approximately 36,000 gallons per year with initial CN^- concentrations from 30,000 to 50,000 mg/l. From March 1978 to March 1979, 31,300 gallons of CN^- 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. An actual batch treatment process from the plant laboratory logs is summarized in Table 13. From Table 13, 10,000 gallons of wastewater initially containing 31,400 mg/l CN^- was treated to a concentration of 1,200 mg/l which is equivalent to removing 96.2% of the initial CN^- in a 20 week period. The treatment required 8 tons of chlorine and 6.7 tons of NaOH. This yielded ratios of 6.35 lbs. of chlorine and 5.32 lbs. of NaOH per lb. of CN^- removed. When this level of treatment was reached the operators discharged 5,000 gallons of the waste at 1,200 mg/l CN^- into the main plant flow for dilution. This example typically represents the CN^- treatment process at T.A.F.B. There was no data available to assess the complexed metal-CN^- treatment by the

Table 13: Typical Batch Treatment Results for CN^- 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
Initial CN^- Conc.:	31,400 mg/l
Final CN^- Conc.:	1,200 mg/l
Chlorine Added: (CL_2)	8 tons
Caustic Added:	6.7 tons

chlorine process in this or any other batch treatment information at T.A.F.B. Certainly as with ozone, it is expected the removal rates at complexed CN^- concentrations greatly slowed for the chlorine process and likely much more so than for ozone which is more reactive and used in conjunction with U.V. 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 one pump system is replaced for every batch of waste treated. Another problem which occurs is production of large sludge volumes during the process. However, the author feels this is more related to periodic additions of permanganate from other waste sources used by the operators as an oxidant supplement. Potassium permanganate when used as an oxidizing agent results in the production of manganese dioxide (38).

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

The formation of "dark brown" manganese sludge makes it undesirable as a treatment method. Kroop (31) found oxidation of phenolic waste 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 CN^- WASTES AT T.A.F.B.

Based on data obtained during the study and information available on the chlorine system at T.A.F.B., a cost comparison can be made. The analysis is based on costs associated with each system in removing 90% of the CN^- from the waste with a design flow and CN^- concentration of 3,000 gallons per month and 50,000 mg/l respectively. This assumption was made in generating the cost data for ozone oxidation in Section VII. Table 14 summarizes the computed operation and maintenance costs for both systems. The total energy requirements are a great deal more for the ozone process at 13,800 $/yr. than for chlorine at 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% of the total energy consumption. The maintenance cost for the chlorine system is only 57% of the ozone system maintenance cost, reflecting primarily the greater quantity of equipment required for on site ozone production.

Alkaline chlorination at T.A.F.B. requires the purchase of both the chlorine oxidant and NaOH caustic from private enterprise. Table 14 indicates this cost amounted to 42,800 $/yr. in the analysis and represents 65% of the total O & M cost. The caustic is obtained locally whereas the chlorine must be shipped from Wichita, Kansas. This emphasizes the

Table 14: 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	13,800	11,100	0	25,000	50,000
Chlorine	1,800	6,300	42,800	12,700	63,600

dependence of the chlorine process on market and labor conditions. The significance of this dependence will increase in the future. Table 15 indicates 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.

The analysis indicates the chlorine system is less labor intensive than the ozone system. Personnel costs for the ozone system represent 50% of the total cost of operation and maintenance of the process. The ozone labor cost will decrease as the reliability of the equipment and operator experience increases. By comparison, labor costs for alkaline chlorination amount to only 20% 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 50,000 \$/yr versus 63,600 \$/yr. for the chlorine process. The costs are equivalent to \$3.70/lb. CN^- removed and \$4.71/lb. CN^- removed for the ozone and chlorine processes, respectively. It is noted that the major cost category for the chlorine system is for chemicals (67% of total) and will only increase in the future. On the other hand, the major cost category for ozone process is for labor, 50% 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 T.A.F.B. 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 was obtained and documented. The process was compared to the alkaline chlorination system currently being used for cyanide waste treatment at T.A.F.B.

2. EQUIPMENT PERFORMANCE AND RELIABILITY

The overall performance of the equipment is good with some 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 is much less than observed at the start of the project. The reduction is primarily due to much 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, much 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 making this modification but the breakers were resized and replaced as the problem arose. A secondary benefit of boosting the input voltage appears to be a 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 open end pipe discharge below the impellers, replacing a mixer on reactor 1 with a more efficient and flexible system, modifying the reactor ventilation system to remove all toxic gasses, renovating all monitoring equipment and repairing all other ancillary equipment.

The project has established that the equipment is reliable if proper maintenance and operation procedures are followed. This is documented by two months of uninterrupted continuous operation of the compressors, filters and dryers. The original operation problems associated with the compressors such as frequent broken belts were eliminated with proper maintenance. The dryers continuously maintained a dewpoint of -58°C, well below the design level of -40°C during system operation. The dryers are virtually trouble free with only periodic maintenance required such as cleaning the valves. 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 very satisfactory. Throughout the project the U.V. lamps were dependable. The corex tubes housing the U.V. lamps require cleaning once a week, a process taking approximately 1 hour to complete. A new design for tube removal is desirable to facilitate cleaning. The metering pumps require periodic cleaning but did not interfere with the overall system performance. These pumps were recently replaced with a more reliable diaphram system.

In summary, with proper attention the equipment will perform satisfactorily. The process requires approximately 50% 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 is not one which should be intermittently started and stopped during the course of a week. Instead, optimum performance will result by continously 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 the plating waste with high concentrations of cyanide, efficient ozonation of the free cyanide present occurs in all reactors at air stream ozone concentrations of 0.4% to 0.6% by weight. The quantity of ozone applied can limit the CN^- removal rates. At the design flows (approximately 6.25 gph) the system was found to be capable of removing 85% to 99% 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 likely is controlled by the rate at which the complexes are broken down. The presence of U.V. radiation was shown to greatly speed the destruction of the metal complexes. It was found that neither dilution nor decreasing the pH of waste increased the complex 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 the cyanide removal rates to be dependent on the concentration of cyanide remaining in the reactor. This occurred with and without U.V. radiation present.

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

C. A method of optimizing the system performance and ozone utilization efficiency was established by simultaneously monitoring the cyanide removal rates and 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 results 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 operation 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 effect 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 U.V. radiation/elevated temperatures, respectively. This indicates a more efficient process occurs with U.V. radiation and elevated temperatures. With mostly complexed CN^- present the reaction rate was estimated to be 0.003 hr^{-1} with U.V. radiation present under similar conditions.

H. The reactor temperature was taken as a measure of the combined presence of U.V. 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 with a computer program. This 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% and 50% of the total, respectively.

J. The alkaline chlorination process is currently used for cyanide treatment at T.A.F.B. The system performance and operation costs were evaluated from plant operational logs and other sources. Several problems exist in the system and were noted. The operation and maintenance costs for the alkaline chlorination system were determined to be 4.71 \$/lb. CN^- removed presently. This compares to 3.70 \$/lb. CN^- removed for the ozone process. Chemical costs (chlorine and caustic) account for 67% 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 T.A.F.B. 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. INDUSTIRAL WASTE MANAGEMENT AT T.A.F.B.

About 1.5 mgd of primarily industrial wastes are being treated at the Tinker Air Force Base Industrial Waste Treatment complex. The main system consists of 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. Chrome wastes, for example, are reduced with SO_2 and discharged to the sludge drying beds. Also, the cyanide plating wastes are presently being treated by the chlorine oxidation process described in this paper. Once the CN^- 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 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 NPDES discharge permit requirements for several toxic substances. The ozone cyanide system could improve the overall plants operation by more efficiently treating the CN^- waste before discharge to the main plant stream.

2. OZONE-CYANIDE SYSTEM IMPLEMENTATION AT T.A.F.B.

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 process, ozonation was 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 T.A.F.B. An implementation program should be formulated to prevent the reoccurrence 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 reestablished for the program to be successful. This would require demonstration runs on actual waste 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 found to be 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 T.A.F.B. 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 T.A.F.B.

is currently being 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 sky rocket.

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

Other organic wastes present at T.A.F.B. are likely to be amenable to ozone oxidation also. 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, U.V. radiation and others. Based on favorable results obtained in this study, it has been recommended U.V. radiation be added to one or both of the reactors which are without it presently. With U.V. radiation present, the process efficiency greatly increases. However, with U.V. present, a significant increase in reactor temperature also occurs.

A study is recommended which would demonstrate the relative importance of reactor temperature versus U.V. radiation. This would be very beneficial in optimizing the process from a practical standpoint. If the main benefit results from a temperature increase then a cheaper and more maintenance free heat source other than U.V. radiation could be employed. The result would be a significant decrease in annual operation costs associated with U.V. lamp replacement.

Another area of interest not covered completely in the present study is evaluation of other organics present in the cyanide wastewater. Some project data has 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.

SECTION XII

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