STUDIES ON THE "HYDROLYTICALLY-ASSISTED" EXTENDED AERATION PROCESS TREATMENT OF WASTES CONTAINING CYANIDES

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Dedicated to my beloved parents

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CHAPTER I

INTRODUCTION

Cyanides are among the most toxic compounds occurring in industrial discharges, and the disposal of wastes containing cyanides has been a problem for many years. Many industries are located in cities, and their wastes are usually discharged into municipal sewers and are a source of upset to the treatment process. If wastes pass into the plant effluent in any measurable amount, they can cause serious hazard to the aquatic life of the receiving streams.

Cyanide wastes can be treated by any of the techniques which destroy or render harmless their cyanide content. The most popular means of disposal of cyanide wastes at the present time are chemical methods; these include direct oxidation with chlorine to cyanates, acidification and stripping as HCN, and precipitation as insoluble iron cyanides. Acidification and volatilization of HCN gas into the atmosphere has been widely used in the past, but this method creates an obvious problem of atmospheric pollution. Disposal of wastes by oxidation is also wasteful of resources, because of the high chlorine doses required for oxidation of cyanide. Furthermore, most of the chemical methods are relatively expensive and often require further disposal of the products or are difficult to control and lack the desired efficiency. Therefore, it is easy to understand why the industries and all of those concerned with good management of the

country's water resources are very much interested in improved methods of disposal of cyanide wastes. This interest has led to the investigation of the use of biological processes to degrade the cyanide along with the organic substrate in the waste. However, it was generally felt that due to the toxicity of cyanides, particularly its effect on cytochrome oxidase, that the biological treatment of waste containing cyanide would be extremely difficult under acclimated conditions, and shock loading of cyanide to sewage treatment plants would lead to loss of viability of biological solids. Nearly twenty years ago, however, it was found that gradually acclimated activated sludge was able to degrade moderate concentrations of cyanide with a high removal efficiency. More recent work has shown that reasonably high concentrations of cyanide can be degraded biologically.

Various types of biological treatment processes can be generally classified into fluidized bed systems and fixed bed systems. An example of the former is activated sludge, and an example of the latter is percolating filtration. The activated sludge process has become one of the most widely used secondary treatments for waste effluents because of its versatility in regard to operational control. However, the problem with biological treatment, particularly the activated sludge process, is disposal of excess biological sludge. A fairly recent modification, the extended aeration activated sludge process, accomplishes both sludge disposal and wastewater purification by returning all sludge to the aeration tank, but the process has been used only for small wastewater flows during the first twenty years of its existence. The basic theory of the extended aeration process is total oxidation of the organic matter to CO_2 and H_2O. Many studies have been conducted on the

process; many researchers argue against the validity of the concept of total oxidation. However, after the long-term investigation conducted at Oklahoma State University, much of the controversy has been resolved and the results augur well for the concept. Also, a modification, termed the "hydrolytically-assisted" extended aeration process, has been proposed for engineering control of the biological solids concentration in the process. It has been operated successfully in laboratory-scale pilot plant investigations.

In the present investigation, there are two phases, both of which involve the biodegradation of cyanide. The first phase of the investigation was conducted to test the operational feasibility of using the "hydrolytic-assist" extended aeration process for a waste containing cyanide. The object of this study was to determine if the system could treat such a waste with good nitrification but without excessive build-up of sludge or accumulation of cyanide in the sludge. The aim of the second phase of the investigation was to determine the amount and the rate of cyanide degradation and COD removal efficiency by combined biological removal and physical stripping in batch systems.

CHAPTER II

LITERATURE REVIEW

It is well known that cyanides are highly toxic to mammals and fish. The minimum lethal dose for an average-size man has been established at 180-200 milligrams of 95-100 percent sodium cyanide (1). However, the dangerous or maximum tolerable concentrations of cyanides in water are not well defined. The United State Public Health Service has set 0.2 mg/l cyanide (CN^-) as the maximum allowable limit in potable water supply, and some states consider free cyanide (as CN^-) in excess of 0.025 mg/l to be unsafe for fish. Unfortunately, many industrial processes such as the electroplating of steel, carbonization of coal, cyanide hardening of ferrous metal, chemical manufacturing, petroleum, coke, and other important industries produce cyanides as by products, and large quantities must be disposed of (2)(3)(4). Wastewater from electroplating always carries a relatively small volume of spent plating solution but contains a high concentration of metallic salts (heavy metal ions contents, such as zinc, cadmium, copper, silver, nickel, and chromium). These heavy metal ions tend to form complex cyanides when combined with cyanide ion (4). Complex cyanides were found to be even more toxic to aquatic life than CN^- (5). Moreover, industrial effluents are not the only sources of cyanide found in the environment. Many plants, including some of agricultural importance--for example, cassava, flax, sorghum, alfalfa, peaches, almonds, and beans-- are cyanogenic,

releasing cyanide into the soil (6). Some West African cassava flour contains significant quantities of HCN (5 mg/l). In many areas of Nigeria, cassava flour forms a staple part of the diet. It has been estimated that in certain parts of Nigeria, human daily consumption of cyanide may reach 35 mg, which is equivalent to about one-half of the lethal dose of HCN when taken at one time. This is probably the reason for the widespread and chronic neurological disorders found in those areas (7).

Methods of Cyanide Waste Treatment

The above observations leave no doubt about the justification for the control of cyanides in effluents and the establishment of concentration limits in receiving waters. During the last thirty years, a large number of papers concerning cyanide waste detoxification have been published, and these may be classified broadly by procedures as follows:

Physical Methods

Dilution Treatment. Barnes (8) cites the discharge of a large quantity of cyanide and metals into the Cleveland sewers has little deleterious effect on the performance of the sewage treatment plant because of high dilution. However, Dodge and Reams (9) concluded that dilution alone will be forbidden increasingly by pollution control authorities as a primary method of treatment in this country.

Air Stripping

Scott (10) and Saito, et al. (11) described two different processes for the removal of cyanide. One process involved the acidification to pH 2 to 4, heating to 210°F (99°C), and the other process involved the release of HCN as an aerosol from a rotating spray nozzle with a pressure of 5-15 kg/cm^2. The liquid pH was adjusted to about pH 8.

Ion Exchange

The ion exchange process has been investigated for cyanide reduction by Tallmadge (12) and Walker (13). Double resin beds must be used; however, regenerated solutions are not sufficiently concentrated for direct reuse in plating baths. Therefore, further treatment would be required to either destroy the cyanide or concentrate it for reuse. It should be pointed out that ion exchange is not a means of disposing of wastes, but only a means of concentrating wastes, and would be of use only where water is difficult to obtain or where recycling of water is desirable. Consequently, the concentrated cyanide needs to be treated by other processes.

Electrolyte Removal

Silman (14), Kuhn (15), and Leclerc (16) studied the electrolytic removal of cyanide. Amai (17) reported that cyanide concentrations of 25,000 to 500,000 mg/l could be reduced to 500 to 1000 mg/l using electrolytic oxidation. For complete removal of cyanide residue, hypochlorite oxidation was exmployed. A single-step packed cell was described, wherein particles in the packing acted as individual cells

and increased the effective area of electrolytic reaction so that oxidation and reduction reactions could occur and effect removal of cyanide and heavy metals (18).

Chemical Treatment

Ozonation

Eiring (19) reported the use of ozone to break the stable metal-cyanide complexes at high pH values, thereby permitting the metal to precipitate as hydroxide. Lead and zinc in addition to arsenic were removed, provided cyanide destruction took place in the presence of calcium. Ferricyanides were stable to ozone. Fridmen, et al. (20) tested the synergism between ozone and hypochlorite, and concluded that hypochlorite should come after ozone oxidation.

Chemical Oxidation

Alkali-chlorination has become the most widely used procedure for the treatment of cyanide wastes. The chemistry includes oxidation of the cyanide to cyanate and, if required, further oxidation and/or hydrolysis of the cyanate to CO_2 and N_2. Silman (14) and Wierzbiki, et al. (21) concluded that chlorine was the best oxidant for cyanide oxidation with the optimum dose at 115-120 percent of theory. Zumbrunn and Malafosse (22) reported that final treatment cyanide concentrations less than 0.1 mg/l were possible with several suitable oxidants selected for the particular wastewater. Henry and Borglin (23) examined a wide variety of chemical oxidants and concluded that H_2O_2 was best for mildly alkaline cyanide wastes, while persulfates were

best for strong alkaline or strong cyanide wastes.

Miscellaneous Chemical Treatments

Hydrolysis (24). Volitalization of HCN from acidified solution (25) and formation of complex iron cyanides (9) are chemical treatment procedures which have been studied and used commercially on cyanide wastes. However, because of the high investment and operating cost and incomplete destruction of the cyanide, none of the above has gained wide commercial acceptance to date.

Bio-destruction of Cyanide Wastes

Physical and chemical treatments of cyanide waste have some disadvantages, such as

1) high installation costs
2) continued expenditure for chemicals and labor
3) creation of product (cyanates, HCN, or iron cyanides) that must be disposef of, and
4) they require a large amount of chemicals which could otherwise be put to more useful purposes than getting rid of a waste material.

These disadvantages have led to the investigation of methods other than the physical and chemical processes. Biological treatment which was considered impractical or impossible in the past simply because many scientists believed that cyanide would be toxic to certain enzymatic reactions, especially the oxidation of cytochromes (respiratory pigments), has now been found feasible. Since World War II, biological

treatment has received much investigative attention, and has been applied increasingly to treatment of cyanides.

Ridenour, et al. (26) reported work on the effects of cyanide on activated sludge. Pettet and Mills (27) investigated the treatment of cyanide on percolating filters. Gurnham (4) and Pettet, et al. (2) examined the appliction of biological filtration process for cyanide waste treatment. Nesbitt, et al. (28) have worked on the aerobic metabolism of KCN by activated sludge. Ludzack and Shaffer (29) also investigated activated sludge treatment of cyanide, cyanate, and thiocyanate. Howe, et al. (31) reported reduction of cyanides with the aid of digested sludge for both aerobic and anaerobic methods. Luczack, et al. examined the effective treatment of organic cyanides by activated sludge and anaerobic digestion methods. Mikami and Misono (33) examined the effect of heavy metals, Cr, Ni, Cu) on an activated sludge process treating cyanide waste. Howe (34) in another report on the treatment of toxic waste degradation and disposal discussed cyanide degradation by the biological process. Shimizu, et al. (35) investigated cyanide degradation reaction by Fusarium solani. Atkinson (36) reported on bacterial cyanide detoxification by B. stearothermophilus, and Knowles (37) discussed the microbial response to cyanide.

In the following paragraphs, a brief discussion of a few outstanding achievements on the biological degradation of cyanide wastes will be presented.

Biological Degradation in Lagoons

The degradation of cyanide in a two-stage sludge lagooning system

was investigated by Howe (38). It was found that humus-like and lignin-like material and the sulfide content in cyanide-containing sludge played an important role in the degradation of cyanide (31). According to the data collected by the author, it appeared that the more humus-like material present in the sludge containing cyanide, the better was cyanide degradation in the lagoon. Residence time was 180 days in the first lagoon, which removed cyanide with an efficiency of 75-93 percent, and residence time was 240 days in the second lagoon, which attained an efficiency of 78-88 percent. After a total of 360 days of operation, there was no overflow from the second-stage lagoon.

Biological Degradation by Digested Sludge, Adsorption, Complexation, Clarification, and Biological Oxidation in Sequences

Howe, et al. (31) developed a method utilizing digested sludge (both aerobic and anaerobic) for cyanide waste degradation by direct adsorption and complexing reactions. The process involved adding suitable amounts of digested sludge for the amount of cyanide present in the waste. Subsequently, a digested sludge-CN complex was formed, depending on the pH, NH_4OH, other organic chemicals and catalysts added. Also, one must determine the reaction time required for the optimum complexation. The mixed liquor can then be clarified, and the cyanide still remaining in the clarified liquor is mixed with a proper amount of digester supernatant and then aerated, again clarified, and finally the supernatant is biologically filtered. The first digested sludge-CN complex (removed by settling or flotation) and the final sludge are both pumped to a sealed long-term lagoon for degradation and natural

dewatering for at least six months. It was reported that about 200,000 lbs of cyanide have been decomposed or converted into non-toxic matter by this process at one treatment plant alone.

Anaerobic Degradation by Two-stage Digestion

Anaerobic degradation of cyanide wastes by two-stage high rate digestion was also investigated by Howe (30). This process employed a ten-day residence time for the first stage, was constantly heated (100-115^{o}F) and agitated. The cyanide concentration was increased slowly from 1 to 100 ppm until the first-stage began to overflow to an unheated second-stage digester. Some of the sludge from the second-stage digester was returned to the first-stage digester or withdrawn for further disposal. An overall daily cyanide degradation efficiency of 65 percent was reported.

Biological Degradation by Aerobic Contact Process

Howe, et al. (30) used digested sludge to condition a waste containing a high cyanide concentration (1000-35,000 mg/l) and then permitted the cyanide-digested sludge mixture to be decomposed aerobically through continuous contact with acclimated activated sludge. After 24 hours of oxidation, a cyanide reduction of 70-98 percent was attained--depending on the concentration of cyanide in the mixture and the flow rate.

Aerobic Degradation by Biological Filtration Process

Pettet, et al. (27) examined the effect of cyanide on a trickling filter. It was found that 2 mg/l of cyanide interfered with the functioning of the filter. However, after proper acclimation, the filter was capable of treating cyanide at concentrations up to 100 mg/l and a 99 percent efficiency of cyanide destruction was attained. Gurnham (4) reported that the filter destruction of cyanide is dependent on a suitable period of acclimatization. By slowly and steadily increasing cyanide concentration in the raw feed, the tolerance of the trickling filter to cyanide could be built up to concentrations as high as 200 mg/l. However, BOD removal was appreciably decreased at this high concentration. If the cyanide concentration concentration was maintained below 100 mg/l, an 80 percent cyanide destruction could be accomplished.

Winter (39) seeded laboratory-scale trickling filters with two cyanide-utilizing actinomycetes and fed the filters with KCN and cyanide plating wastes. Over 90 percent of the cyanide was degraded when the feed was held at 25 mg/l KCN for several weeks, but with an influent concentration of 45-137 mg/l KCN, the efficiency of degradation was only 63 percent. Feeding $Cu(CN)_2$ or a 4-1 mixture of $Cu(CN)_2$-$Zn(CN)_2$ at up to 18 mg/l of metal resulted in a 70-90 percent degradation of cyanide. When "grab samples" of cyanide plating wastes containing 0-50 mg/l Ni, Zn, Cu, Fe, Cr, and Al (7-35 mg/l of cyanide, total) were fed to the filter, cyanide degradation decreased to almost zero; however, it gradually recovered when refed KCN. Adjusting the grab samples to pH 6.5 gave an efficiency of cyanide decomposition of only about 40 percent,

but when complex metal cyanide plating wastes were fed, the efficiency was 95-100 percent (at pH 8 and 20-25 ppm of cyanide).

Aerobic Degradation by Activated Sludge Process

Nesbitt, et al. (28) studied the degradation of cyanide in activated sludge systems. They gradually acclimatized settled primary sludge to cyanide, and then fed the systems with 60 or 120 mg cyanide every day for several months. Cyanide served as the only source of carbon and nitrogen, and was completely metabolized. There was no loss of suspended solids; about 98 percent of the cyanide-carbon was converted to CO_2, and 75-90 percent of the cyanide-nitrogen was converted to ammonia, nitrate, and nitrite.

Ludzack and Schaffer (29) investigated the activated sludge treatment of cyanide, cyanate, and thiocyanide. Proper acclimation of the activated sludge to cyanide, maintenance of proper temperatures, and the addition of dextrose as a supplementary source of energy were considered important to the effective degradation of cyanide. According to their report, treatment was less effective when the CN^- concentration exceeded 60 mg/l. In another report, Ludzack and his co-workers (40) discussed the effective treatment or organic cyanides by activated sludge. They indicated that at certain concentrations, organic cyanides could be degraded successfully with CN^- acclimated activated sludge.

The effect of heavy metal ions on cyanide waste treatment in an activated sludge system was studied by Mikami and Misono (33), who observed total degradation of a concentration of 100-150 ppm cyanide. Eighty-five to 95 percent of the cyanide-nitrogen was found in the

effluent stream as NH_3, NO_2^-, and NO_3^-. By addition of Cr^{+6} or Cu^{+2}, the oxidation of NH_3 (to NO_2 and NO_3) was obstructed, resulting in the accumulation of NH_3 in the effluent. Biological treatment was possible only when the sludge was acclimated gradually from low metal concentration and the CN^- loading was controlled according to the concentration of the metal. The maximum allowable concentrations of Cr^{+6} and Cu^{+2} for biological treatment of cyanide waste were 20-30 mg/l and 5-10 mg/l, respectively. Ni^{+2} formed a complex compound when mixed with CN^- at a neutral pH. This complex could not be decomposed by microorganisms. The analysis of the total CN^- indicated that almost all of the inflowing cyanide (as NiCN complex) was recovered in the effluent.

Fundamental Biochemical Mechanism for Biological Detoxication of Cyanide

Cyanide is generally thought of as an inhibitor of cytochrome oxidase. In fact, cyanide inhibits a wide range of enzymes, many of which are hemeproteins or other metal-containing oxidases or oxygenases (37). Dixon and Webb (41) reported many cyanide-inhibiting enzymes. According to Knowles (39),

> . . . cyanide is a very reactive molecule, and it is not surprising that it is catholic in its inhibiting tastes. It forms stable complexes with many metals, reacts with keto groups to form cyanohydrins, and reduces thiol groups (p. 703).

It was also reported that at concentrations of about 10^{-4}M or lower, cyanide is highly inhibitory to cytochrome oxidase but has no effect on other enzymes which require at least 10^{-2}M cyanide for significant inhibition (37). However, there are some exceptions to this generalization.

A large variety of microorganisms have been shown to metabolize

cyanides (34). These include Gram-negative pseudomonas, Bacterium thiocyanoxidans, yeasts, fungi, cyanophyceae, chlorophyceae, Zooglea ramigera-like Gram-negative rods. Gram-positive bacteria, Bacillus megatherium, Flavobacterium devoraus, Propionibacterium freudenreichii, Propionibacterium shemanii, Bacillus subtilis, Escherichia coli, Lactobacillus arabinosus, Actino mycetaceae, Arthrobacters, etc. How do these microorganisms manage to adapt to growth in the presence of cyanide? According to Knowles (37), microorganisms can either produce cyanide-resistant enzymes or induce enzymes for cyanide degradation.

There have been several studies on cyanide-resistant respiration (43)(44)(45). However, there has been very little research on the adaptation of other cyanide-sensitive enzymes to cyanide resistance. Since many microorganisms are resistant, or can induce resistance (39)(44)(46), there is little wonder that cyanide-acclimated sewage systems have been reported to convert cyanide to CO_2 and ammonia, nitrite, or nitrate (2)(27)(28)(29)(30)(33)(39).

Ludzack, et al. (48) investigated the biodegradation of six different organic cyanides. They concluded that nitriles were biologically hydrolyzed, leading to the formation of end products such as organic acids and NH_3. The pathway may be as follows:

$$RCN + H_2O \xrightarrow{\text{enzyme}} RCO\ NH_2$$

$$RCONH_2 + H_2O \xrightarrow{\text{enzyme}} RCOOH + NH_3$$

or

$$RCN + 2H_2 \xrightarrow{\text{enzyme}} RCOOH + NH_3$$

Later, in another report, Ludzack, et al. (29) postulated that adding supplementary dextrose in the feed as an additional energy source could hasten the biodegradation of cyanide and cyanate. The suggested pathways are as follows:

For cyanate:

$$HCNO + H_2O \xrightarrow{enzyme} CO_2 + NH_3$$

$$NH_3 + 2O_2 \xrightarrow{enzyme} HNO_3 + H_2O$$

For thiocyanate:

$$HCNS + 2H_2O \xrightarrow{enzyme} CO_2 + H_2S + NH_3$$

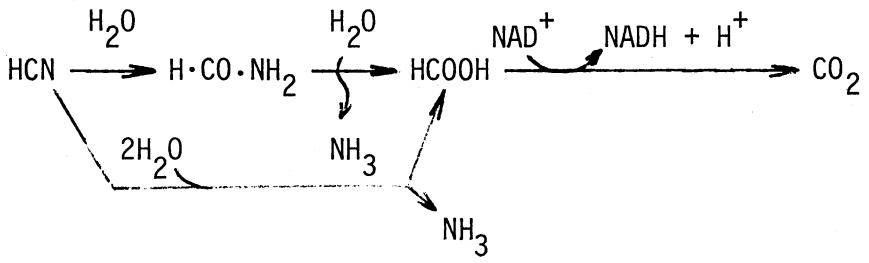
$$H_2S + 2O_2 \xrightarrow{enzyme} H_2SO_4$$

$$NH_3 + 2O_2 \xrightarrow{enzyme} HNO_3 + H_2O$$

It has also been reported (47) that the chemical reaction of cyanide with aldehyde and ketones may result in the formation of hydroxynitrile, which can be further converted to a hydroxy acid upon hydrolysis.

In a recent report, Knowles (37) suggested two biological methods, the complex method and the simple method, for detoxifying cyanide. The former method of detoxifying cyanide is by conversion to β-cyanoalanine or other products reported to be intermediates. Intermediates are then converted to ammonia and CO_2. The simple method of detoxifying cyanide is its conversion to formate and then to CO_2. Conversion to formate could be direct (by a nitrilase) or via formanide (by cyanide

hydratase and formanidase)



In either case, when cyanide is degraded biologically, its nitrogen and carbon are released for biological metabolism. In addition to nutrients, other conditions such as pH, temperature, oxygen availability, microbial population, minerals, and time are all essential for biodestruction of cyanide. Some advantages which accrue for the use of biological processes for cyanide degradation are as follows: practically no additional cost is involved when a biological treatment plant is available to an industry for handling a cyanide load. Even when a biological process is built specifically for cyanide removal, it is less costly than a chemical process. However, there would appear to be several disadvantages and reasons for caution in regard to the use of a biological process for cyanide degradation which should be recognized. When cyanide wastes also contain heavy metal wastes in appreciable concentrations, it is necessary to remove the heavy metal ions so that the biological treatment process will not be inhibited or interrupted. Additional costs of treatment will be incurred. Also, since any biological process can sometimes be upset without the presence of a toxic substance such as cyanide, and the recovery from an upset may require somewhat more time because of the presence of cyanide, some sort of standby facility such as a lagoon seems desirable. Also for successful

treatment, biological processes should be subjected to as much or more operational control than chemical treatment processes. The determination of the types of control and applicable process modifications are in need of evaluation and greater understanding on the part of the engineering chemist and biologist is needed.

The Extended Aeration Process

The extended aeration process (or total oxidation process) is one of the modifications of the activated sludge which is worth considering from an economic point of view if it can attain complete mineralization of organic wastes and obviate the need for separate sludge digestion facilities.

Many of the previous investigators in this laboratory who employed the extended aeration process in their research described it in sufficient detail in the literature review in their theses (49)(50)(51)(52)(53)(54). Thus, in this thesis, only a brief discussion of the literature need be made.

In the early 1950s, Porges, et al, and Hoover, et al. (55)(56)(57)(58) were the first group of researchers to test the concept of total oxidation of biological sludge. They employed skimmed milk wastes, and their results suggested that when a long detention time (18-24 hours) was employed and a proper food-to-microorganisms ratio was adopted, an activated sludge system could maintain a balance between synthesis and oxidation producing no excess sludge and discharge an effluent practically free of organic matter. These conclusions caused a considerable amount of research to be undertaken on the process, but most of the results of the researchers led to a conclusion that total oxidation was

theoretically impossible because of the synthesis of inert materials, e.g., nonbiodegradable extracellular polysaccharides (59)(60)(61)(62). They indicated that those biologically inert organic solids will gradually accumulate and that biological solids will escape with the effluent from the settling tank; therefore, drastic reduction in purification efficiency would take place. Thus, it was concluded that if no sludge was wasted, the extended aeration process could not perform successfully.

Later, in 1962, McCarthy and Broderson (63) suggested in their report that solids accumulation must be considered in the design of extended aeration systems and facilities for disposal of excess sludge are necessary. In the same year, Washington and Symons (64) in their studies on volatile solids accumulation in extended aeration systems concluded that there would be a continuous buildup of biologically inactive mass which was mainly extracellular polysaccharides. In 1965, Ludzack concluded from his studies on the extended aeration process, using a feed of weak sewage supplemented with fish meal operated at low loadings (long aeration periods and high mixed liquor suspended solids), that incomplete aerobic digestion of solids produced high solids carryover in the effluents. Periodic withdrawals of unit solids for ultimate disposal reduced effluent solids carryover.

Sawyer (66) presented some guidelines for the best results in using the extended aeration process. These were as follows: an aeration time of 24 hours, loading of 15 lbs BOD/day/1000 ft^3, and 5000-8000 mg/l biological solids concentration. In the mid 1960s, Gaudy and his coworkers started long-term systematic experiments in an attempt to show conclusively whether such a system could work. In one of the studies (67), an

extended aeration pilot plant was operated for two years. Their results indicated that such a system can be operated with good biochemical efficiency without continual solids accumulation or sludge wasting. They found that there were periods of solids accumulation and periods of solids de-accumulation, but no steady state of biological solids level. They concluded that the fluctuation in the concentration of biological solids was due to natural biological (ecological) regulation, i.e., the complex and dynamic ecosystem found in the heterogeneous population was capable of altering predominance ratio in order to allow for specific assimilation of virtually all cellular constituents. In another experiment (68) to determine the response of the extended aeration process to shock loading, it was shown that an extended aeration system could withstand as much as a five-fold increase in concentration of inflowing COD without significant loss of COD removal efficiency.

From the observation of these researchers, it became evident that the biological solids in the extended aeration system would not increase indefinitely, but the prediction of irregular cycles of solids accumulation and de-accumulation remained impossible. It was also found at times that the level of solids concentration in the mixed liquor was so high as to make the separation of solids difficult. Therefore, it was necessary to seek some sort of engineering assist to the process for the control of solids. Thus, in subsequent studies, Gaudy and his coworkers decided to initiate the procedure of withdrawing some of the sludge periodically and breaking down the macromolecules by chemical hydrolysis and recycling the liquefied cells along with the intact sludge. This process was termed the "hydrolytic-assist" (69). They concluded that an extended aeration process assisted by chemical

hydrolysis to aid the autodigestive process could be operated successfully for concurrent treatment of the organic waste and for sludge disposal. Thus, "the hydrolytic-assist makes it possible for the system to do chemically what is difficult to do biologically, and to do biologically what is difficult to do chemically." Later, Yang and Gaudy (70)(71) presented further proof in favor of the operational feasibility of the hydrolytic-assist extended aeration process through long-term pilot plant studies. They concluded that the hydrolytic-assist process made the system independent of the natural periods of accumulation and de-accumulation of biological solids, and they found that the system had a good ability to take shock loading. Of special importance, it was found that the hydrolytic-assist would not impair the production of a highly nitrified effluent and that the effluent was as nitrified as that from the normal extended aeration process. Other pertinent investigation conducted by Obayashi and Gaudy (73) were batch experiments using microbial polysaccharides produced by five microorganisms. The results provided direct evidence that extracellular polysaccharides serve as an excellent carbon source for growth of microorganisms; thus, they cannot be classified as biologically inert material, as reported by McKinney, et al. (59)(60)(61)(62).

Further studies were conducted by Saidi (1970), Murthy (1974), Roach (1976), and Reddy (1976) concerning the operational stability of the modified extended aeration process at higher organic loadings. Saidi (50) reported that the hydrolytic assist system functioned very stably at loadings of 500-1000 mg/l, and gave a highly nitrified effluent at a loading of 1000 mg/l. The investigation conducted by Murthy (51) showed that nitrified effluent could be obtained at a higher

organic loading of 1500 mg/l, but nitrification in the system eventually ceased at an organic loading of 2000 mg/l, essentially all of the NH_3 in the feed appearing in the effluent. Roach (52) reported from his investigation that the extended aeration system can accept a five-fold (1000 -6000 glucose and hydrolysate) organic shock loading without showing apparent upset in purification efficiency. However, he also concluded that increases in hydrolysate concentration in the feed of 2800 mg/l caused a high degree of leakage of filtrate COD. The waste used in nearly all of the studies above was synthetic waste consisting of a buffer salt medium using glucose as the carbon source, and ammonium ion as a source of nitrogen.

Reddy (49) conducted an investigation to test the ability of the hydrolytically assisted extended aeration to treat a waste containing a high ash content at an organic loading of 2000 mg/l COD. The unit employed for this investigation was already in operation--it had been used to treat, successfully, the same waste at lower loadings of 500 mg/l and 1000 mg/l COD (73). The results of this investigation indicated that the process can treat a waste of high ash content efficiently at organic loading of 2000 mg/l. It was shown that volatile solids content of the aeration solids as low as 40 percent does not affect the purification efficiency. Manikam took over the operation of the unit, and studies were designed to verify the previous result and obtain more definitive characterization of the sludge and performance of the system. It was definitely shown that high ash content would not hamper successful operation of this sytem. These results have been recently reported (73).

In a study aimed at improvement of the aerobic sludge digestion

process efficiency (74), Singh and Patterson indicated that acid hydrolysis plus autoclaving at pH 1 solubilized approximately 65 percent of the original volatile suspended solids. He also reported that uptake of soluble organics measured as COD in the aerobic digester was extremely rapid, with the rate of uptake being proportional to the substrate added. Their report provided additional proof that the extended aeration process is a biologically sound one and has much to recommend its use on a wide variety of wastes other than municipal or sanitary effluents. It has the obvious advantage of concurrent waste treatment and sludge disposal as well as nitrification capability, and is not easily upset by quantitative shock loading. The hydrolytic assist provides a way to gain engineering control over autodigestion of the sludge.

In considering use of the process for various industrial wastes, it was important to consider waste containing toxic components. Since various industrial wastes contain cyanide, a synthetic medium containing an easily metabolized carbon source (glucose), NH_3 as nitrogen source, and inorganic cyanide was employed in the present study. The aim was to determine if the waste could be successfully treated, nitrified, and all sludge recycled without excessive buildup. Since it was possible that cyanide could be taken up by the sludge but not metabolized, it could build up in the sludge. If so, it might be released upon hydrolysis. This could lead to two possibly harmful consequences. First, the cyanide might strip off as HCN in the hydrolysis unit, thus causing an air pollution hazard. Second, if this cyanide remained in the hydrolysate, it could add to the cyanide concentration in the aeration chamber or possibly escape in the effluent. Thus, it was important to determine the fate of cyanide in the bioreactor.

CHAPTER III

MATERIALS AND METHODS

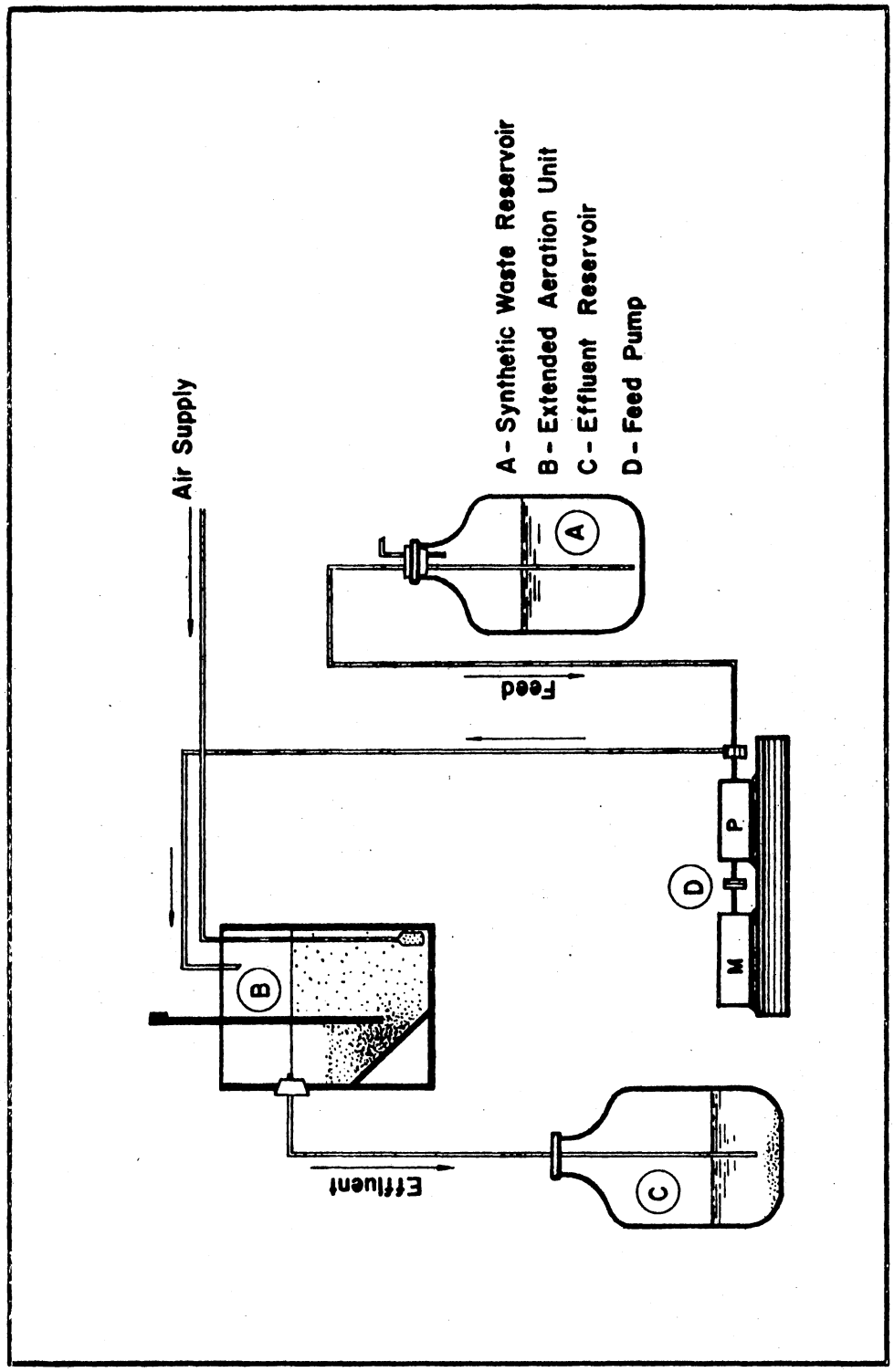
Studies on the "Hydrolytic-Assist" Extended Aeration Process for Wastes of Cyanide Content

To study whether the extended aeration process can be used to detoxify cyanide as well as remove organic matter, a bench-scale extended aeration pilot plant was operated.

Experimental Apparatus

The experimental apparatus used in these studies is shown in Figure 1. The plexiglass unit consisted of a 7.7-liter aeration tank and a 3.4-liter clarifier chamber (total volume of 11.1 liters). A movable baffle separated the two compartments and was set slightly above the bottom of the tank, leaving a small gap so that the mixed liquor could escape and settled sludge could return to the aeration chamber. The feed flow rate was 12 liters/day. The pump used for feeding was manufactured by the Milton Roy Company (Model 4-c-48R). Dual feed lines were maintained, and each of the feed lines was cleaned alternately by pumping a 1-percent solution of Clorox in distilled water. Thus, one of the lines was being disinfected while the other was being used. This procedure was adequate to prevent growth in the feed line. The

Figure 1. Schematic Flow Diagram of a Laboratory-Scale Continuous Flow Extended Aeration System


A - Synthetic Waste Reservoir
B - Extended Aeration Unit
C - Effluent Reservoir
D - Feed Pump
Air Supply
Feed
Effluent
A
B
C
D
P
M

temperature was monitored throughout the study. The pH of the system was 7.0 $\pm$ 0.1 and was adjusted as needed by adding a few drops of 10 Normal potassium hydroxide solution.

Feed Preparation

Glucose was used as carbon and energy source in these studies. The synthetic wastewater fed to the aeration tank was designed to have a chemical oxygen demand (COD) of 500 mg/l. Other required nutrients contained in the feed are shown in Table I. Cyanide at a fixed concentration (10, 15, 20) was added in stages, as described later. As part of the operational routine for the unit, 900 ml of sludge was withdrawn from the clarifier once every week. The withdrawn sludge was hydrolyzed (acidified to pH 1 with concentrated H_2SO_4, autoclaved for five hours at 15 psi, 120^{o}C, and then neutralized to pH 7 with 10 Normal KOH). Then it was divided into seven equal portions and frozen for later feeding at a rate of one portion per day along with the synthetic waste. The chemical oxygen demand (COD) of the combined feed was determined. Figure 2 is a flow diagram showing the incorporation of this "hydrolytic-assist" to the extended aeration process.

Experimental Procedure

Every other day the stock solution of the hydrolyzed sludge was thawed and checked for neutral pH. The feed at a concentration of 550 mg/l COD was prepared and adjusted to exactly pH 7.0. To the feed bottle which had been cleaned with chromic acid cleaning solution and rinsed thoroughly with tap water, the concentrated feed and hydrolyzed sludge were added and made up to volume (24 liters) with tap water.

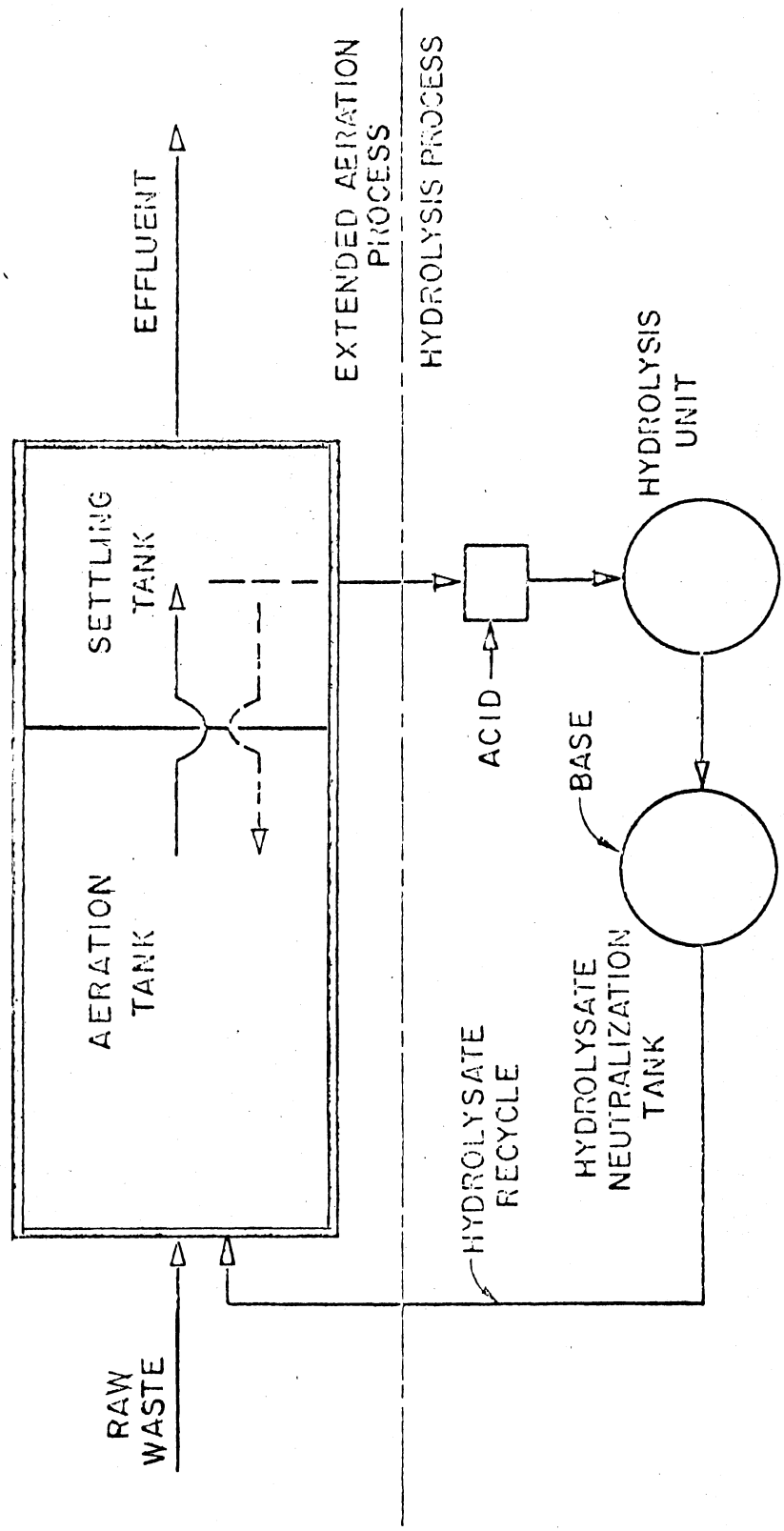
TABLE I

COMPOSITION OF FEED FOR 500 mg/l GLUCOSE SUBSTRATE

Glucose	500 mg/l
$(NH_4)_2SO_4$	250 mg/l
$MgSO_4 \cdot 7H_2O$	50 mg/l
$FeCl_3$	0.25 mg/l
CaCl	3.75 mg/l
$MnSO_4H_2O$	5 mg/l
Phosphate buffer, 10 M (pH 7.2)	5 ml/l
CN^-	10 mg/l 15 mg/l 20 mg/l
Tap water	to volume

Also, at this time the baffle in the unit was removed in order to allow complete mixing of all of the biomass in the reactor system. The pH of the system was checked and samples of the mixed liquor were taken for analysis. The baffle was re-inserted after 15 minutes. The flow rate was checked daily at regular intervals. The concentration of cyanide in the sludge was determined by the distillation procedure (preliminary sample treatment, as outlined in Standard Methods); therefore, 500 ml of sludge was taken from the unit once a week for this purpose. However, after day 410 of operation, the method of cyanide determination

Figure 2. Flow Diagram Showing the Incorporation of the "Hydrolytic-Assist" Into the Extended Aeration Activated Sludge Process


EFFLUENT
EXTENDED AERATION PROCESS
HYDROLYSIS PROCESS
SETTLING TANK
AERATION TANK
HYDROLYSIS UNIT
ACID
BASE
HYDROLYSATE RECYCLE
HYDROLYSATE NEUTRALIZATION TANK
RAW WASTE

was made by using a cyanide-ion-selective electrode. Thus, only 30-50 ml was taken from the unit every week for the purpose of cyanide determination.

The following parameters were monitored during the study period:

A) Feed (including hydrolysate mixed liquor)

a) unfiltered sample

COD

CN^-

b) filtered sample

NH_3-N

NO_3^--N

B) Mixed liquor

suspended solids

cyanide concentration in the sludge

C) Effluent

a) supernatant

COD

suspended solids

CN^-

b) filtrate

COD

NH_3-N

NO_3^--N

Batch Experiments

In order to assess the amount and rate of stripping of cyanide due to aeration, batch experiments were conducted. Also cyanide

disappearance by combined biological removal and physical stripping was determined by running batch systems at different concentrations of cyanide, aeration rate, and pH values. In all of these studies, the effect of stripping alone was studied by running dual systems--one with no biological solids added (to assess stripping alone), and one system which was seeded.

Experimental Apparatus

The aeration vessels used in these studies consisted of 20-inch high, 4-inch diameter glass jars with rounded bottoms. The aeration volume was three liters. A constant compressed air flow was supplied during the various batch experiments. A Gelman model airflow meter was employed to control airflow rate. The experimental apparatus is shown in Figure 3.

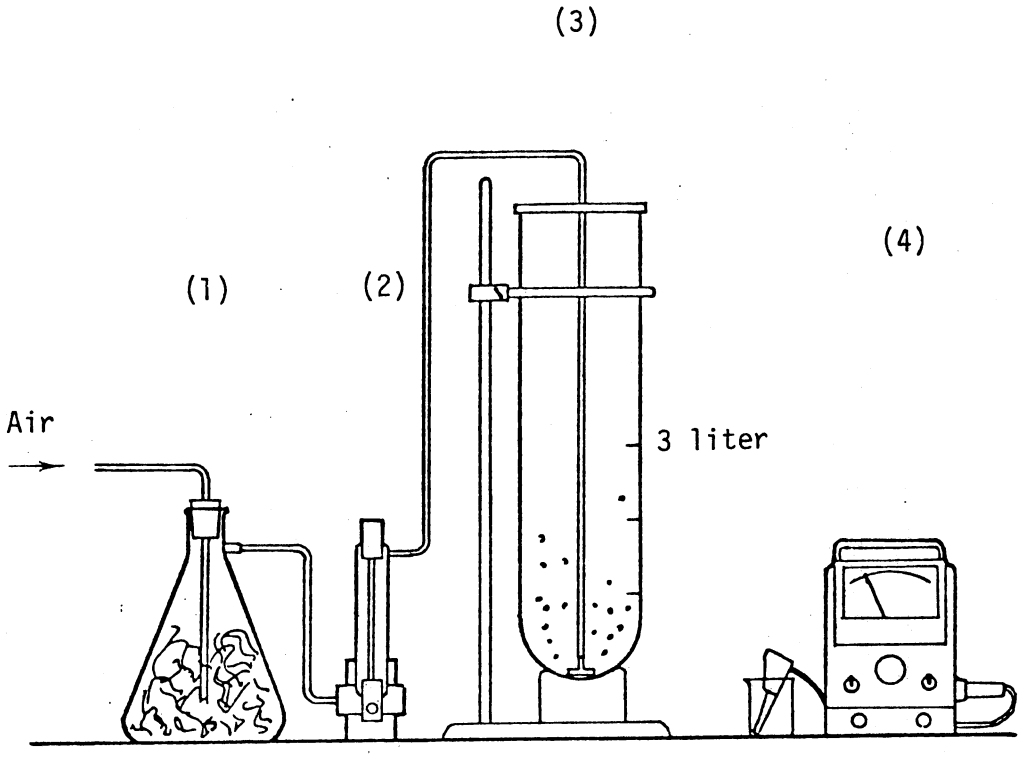
Experimental Procedure

Batch activated sludges were developed using cells taken from the continuous flow extended aeration pilot plant. The batch systems were started on July 28, 1976.

During the period 0-102 days, the batch system was operated by daily wasting one-third of the mixed liquor and removing another one-third of the supernatant after 30 minutes' settling. Then the synthetic waste and tap water were added to bring the volume to three liters. Since it was found that the solids concentration in the batch reactor at balanced operation was only about 600 mg/l, the operation of the batch system was changed as follows in order to obtain higher solids concentration: The batch system was run with no wastage of

Figure 3. Batch Treatability Study Apparatus

(1) cotton filter
(2) airflow regulator
(3) batch aeration tube
(4) dissolved oxygen probe


(3)
(1)
(2)
(4)
Air
3 liter

mixed liquor, but all supernatant was wasted after the 30-minute settling period. The pH value of the mixed liquor was maintained at 7.0 by adding 10 Normal KOH whenever it was needed. Daily, samples were taken before and after feeding. The COD and MLSS were determined to assess the performance characteristics of the system. The composition of the feed is shown in Table I. When the biological solids concentration and COD values were shown to be approximately the same each day, the following experiments were run in the batch system:

Batch Experiments on Stripping (no cells added)

1) Stripping tests with heavy metals added ($CuSO_4 \cdot 5H_2O$).
2) Stripping tests with and without addition of heavy metals at pH = 6 and pH = 4.
3) Stripping tests at various pH values (pH = 12, 10, 7, 6, 4).

Batch Experiments on Joint Stripping and Metabolism

1) Comparison of removal of cyanide in batch systems with solids concentration = 600 mg/l and without presence of biomass at an airflow rate of 3100 cc/min, COD = 500 mg/l, CN^- = 20 mg/l.
2) Comparison of removal of cyanide in the batch system with (solids concentration = 1600 mg/l) and without presence of biomass at airflow rate of 2500 cc/min, COD = 500 mg/l (glucose), CN^- = 20 mg/l.
3) Comparison of removal of cyanide in batch systems with and without presence of biomass at airflow rate = 1000 cc/min, COD = 500 mg/l (glucose), CN^- = 20 mg/l.
4) Comparison of removal of cyanide in batch systems with and without presence of biomass at five different conditions for COD = 500 mg/l (glucose), airflow rate = 500 cc/min, CN^- = 20

mg/l, Cu^{+2} = 1 mg/l. The first condition includes cells, CN^-, Cu^{+2}, and COD; the second condition includes cells, CN^-, and COD; the third condition includes cells and COD; the fourth condition includes CN^-, CU^{+2}, and COD; the fifth condition includes CN^-, and COD.

5) Comparison of removal of cyanide in the batch systems with and without presence of biomass at three different conditions for COD = 1000 mg/l (glucose), airflow rate = 500 cc/min, CN^- = 20 mg/l. The first condition includes cells, CN^-, and COD; the second condition includes cells and COD; the third condition includes CN^- and COD.

Growth Study

Two growth studies, with and without presence of heavy metals, were performed. The inocula for this study were taken from the extended aeration pilot plant and were grown in 250 ml-Erlenmeyer flasks with glucose concentration ranging from 100-1000 mg/l as the limiting nutrient; 20 mg/l CN^- was added to all of the flasks. Composition of the feed is shown in Table II. Initial inoculum concentration was the same in all flasks with an initial optical density of approximately 0.0605 (percent transmission = 87). The total volume of the reaction fluid per flask in these experiments was 40 ml. These flasks were placed on an oscillating shaker (Eberbach), which was adjusted to 100 oscillations/min. The growth curve was obtained by measuring the optical density at regular intervals. The final suspended solids and substrate concentrations were measured, which allowed determination of the cell yield, Y_t. The μ_{max} and k_s were calculated by using the data

obtained from the growth study experiment.

TABLE II

COMPOSITION OF GROWTH MEDIUM PER 600 mg/l GLUCOSE

Constituents	Amount
Glucose	600 mg/l
Ammonium sulfate $(NH_4)_2\ SO_4$	300 mg/l
Magnesium sulfate, $MgSO_4 \cdot 7H_2O$	60 mg/l
Ferric chloride, $FeCl_4 \cdot 6H_2O$	0.30 mg/l
Manganous sulfate, $MnSO_4 \cdot H_2O$	6.0 mg/l
Calcium chloride, $CaCl_2$	4.5 mg/l
1.0 M phosphate buffer solution, pH 7.0	6 ml/l
CN^-	20 mg/l
Cu^{+2}	0.02 mg/l
Tap water	to volume

Experiment for Stripping of Cyanide in the Extended Aeration Pilot Plant. Since cyanide is strippable, the purpose of this study was to find the amount of cyanide stripped by aeration in the extended aeration system without biological activity. Only cyanide determinations were made in this experiment.

Pulse Shock Loading to a Continuous Fed Reactor With and Without Biological Activity. In this experiment, cyanide was injected directly

to the aeration tank of the extended aeration unit in an amount needed to yield 50 mg/l. The slug dose experiment was conducted under two different conditions; first with active biomass, and then without active biomass. All other experimental conditions were exactly the same in both cases.

For the experiment involving biological activity, the following analyses were made:

A) Feed (including hydrolyzed sludge)
   a) unfiltered samples
      cyanide determination
      COD
B) Mixed liquor
   a) unfiltered samples
      suspended solids
      cyanide determination (both mixed liquor and sludge)
   b) filtrate
      COD
      NO_3^--N
      NH_3-N
   c) dissolved oxygen
C) Effluent
   a) unfiltered samples
      suspended solids
      cyanide determination
   b) filtered samples
      COD
      NO_3^- -N

NH_3-N

For the experiment without biological activity (stripping) in the extended aeration unit, only cyanide determination was done.

Analytical Methods

Chemical oxygen demand (COD) suspended solids concentration employing membrane filter technique (Millipore Corp., Bedford, Mass., HA 045 μm), NO_3-N (Brucine Method), dissolved oxygen measurement (Weston & Stack, Inc., Model 330), and cyanide determination (Titration Method and Cyanide-ion-selective Electrode Method) were run in accordance with the recommendation set forth in Standard Methods for the Treatment of Waste and Wastewater (5). NH_3-N was measured by the method of Ecker and Lockhard; pH was determined regularly, using a digital pH meter (Orion Research, Model 701).

CHAPTER IV

RESULTS AND DISCUSSION

Results of this investigation will be presented in two parts. Part A deals with the operational performance of a continuous flow "hydrolytically-assisted" extended aeration activated sludge pilot plant under the following conditions: 1) steady organic loading with various steady concentrations of cyanide (10, 15, and 20 mg/l added in stages); 2) steady organic loading with pulse loadings of cyanide, and 3) stripping of cyanide in the extended aeration pilot plant in the absence of biological activity.

The second part deals with the presentation of results on the removal of cyanide in batch systems, with and without biological activity at various pH values, aeration rates, and organic loadings. Results of batch growth studies will also be presented and discussed in part B.

Part A

Operational Performance of a "Hydrolytically-assisted" Extended Aeration Process on Waste Containing Cyanide

The unit employed for this investigation was placed in operation by M. Saleh, one of the author's co-research workers. The feed for the unit consisted of 500 mg/l COD (glucose) along with cyanide concentration of 10 mg/l. The unit was operated for a total of 500 days; the author started collecting operational data beginning on day 50. Figures 4, 5, 6, 7

Figure 4. Performance Data of an Extended Aeration Pilot Plant With "Hydrolytic-Assist" From Day 50 to Day 180 of Operation

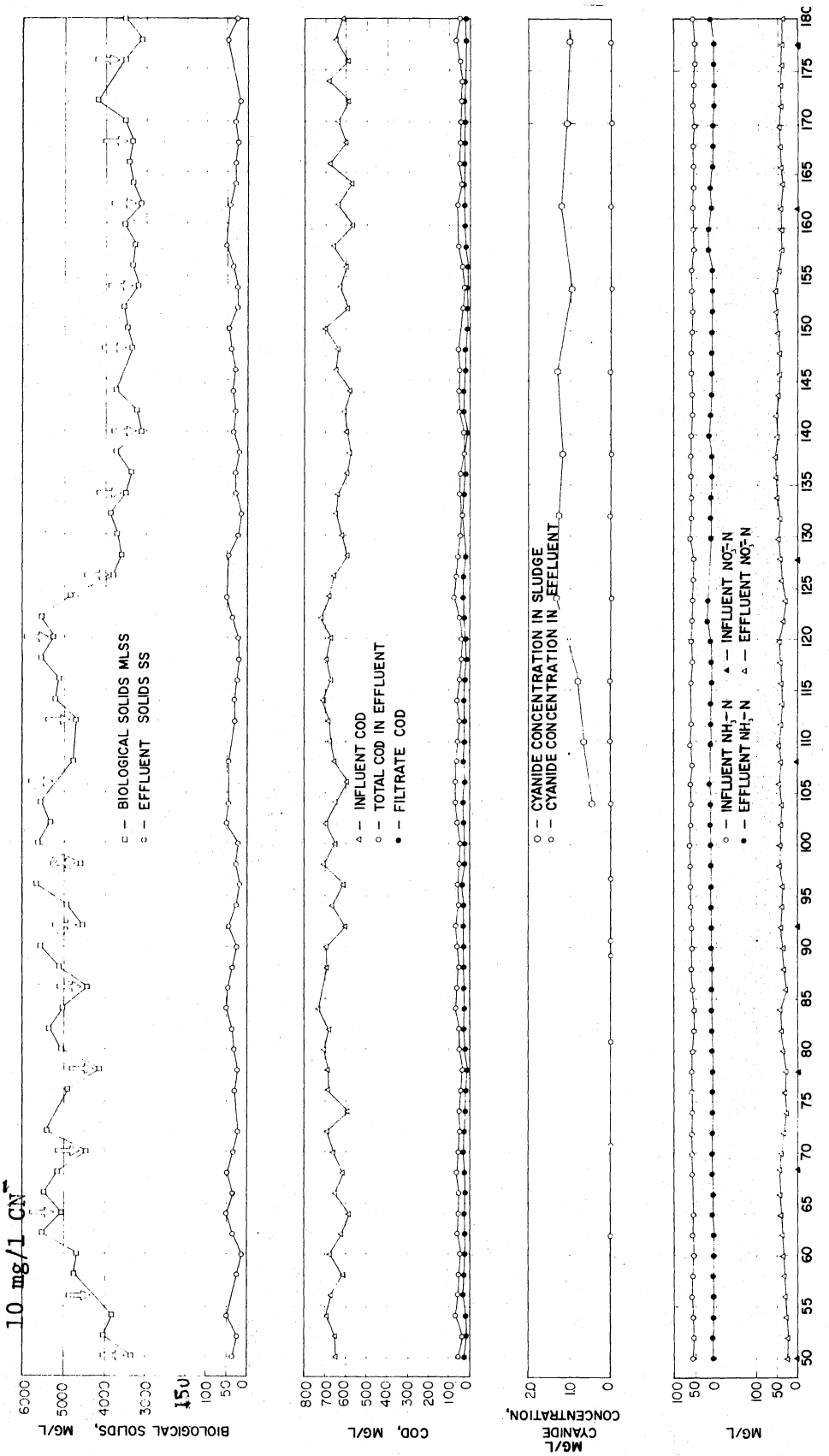

10 mg/l CN
□ – BIOLOGICAL SOLIDS MLSS
○ – EFFLUENT SOLIDS SS
BIOLOGICAL SOLIDS, MG/L
△ – INFLUENT COD
○ – TOTAL COD IN EFFLUENT
● – FILTRATE COD
COD, MG/L
○ – CYANIDE CONCENTRATION IN SLUDGE
○ – CYANIDE CONCENTRATION IN EFFLUENT
MG/L CYANIDE CONCENTRATION,
○ – INFLUENT NH3-N
▲ – INFLUENT NO3-N
● – EFFLUENT NH3-N
△ – EFFLUENT NO3-N
MG/L

Figure 5. Performance Data of an Extended Aeration Pilot Plant With "Hydrolytic-Assist" From Day 180 to Day 321 of Operation

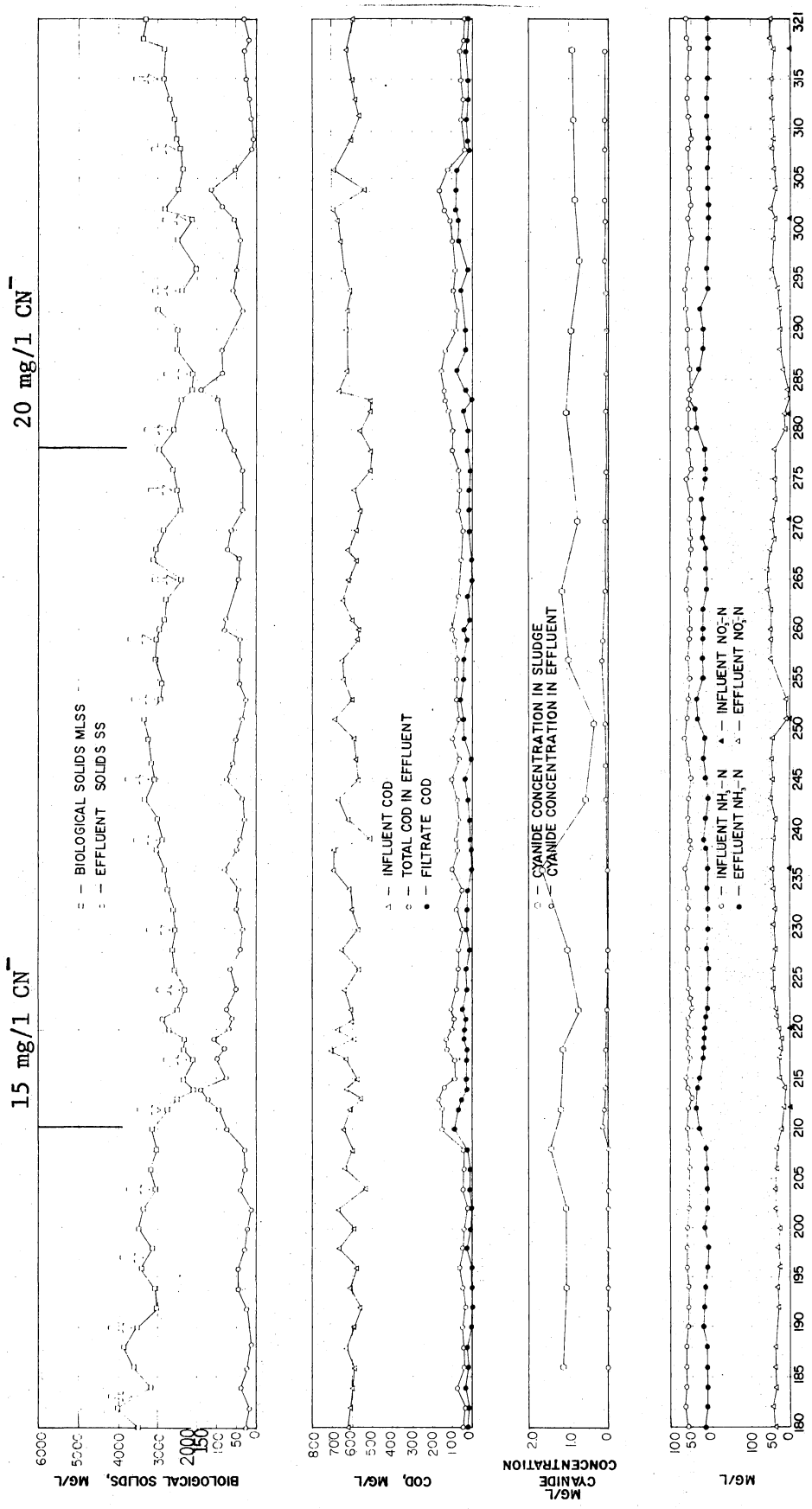

15 mg/1 CN⁻
20 mg/1 CN⁻
BIOLOGICAL SOLIDS, MG/L
BIOLOGICAL SOLIDS MLSS
EFFLUENT SOLIDS SS
COD, MG/L
INFLUENT COD
TOTAL COD IN EFFLUENT
FILTRATE COD
MG/L
CYANIDE CONCENTRATION
CYANIDE CONCENTRATION IN SLUDGE
CYANIDE CONCENTRATION IN EFFLUENT
MG/L
INFLUENT NH_3-N
EFFLUENT NH_3-N
INFLUENT NO_2^--N
EFFLUENT NO_2^--N

Figure 6. Performance Data of an Extended Aeration Pilot Plant With "Hydrolytic-Assist" From Day 321 to Day 461 of Operation

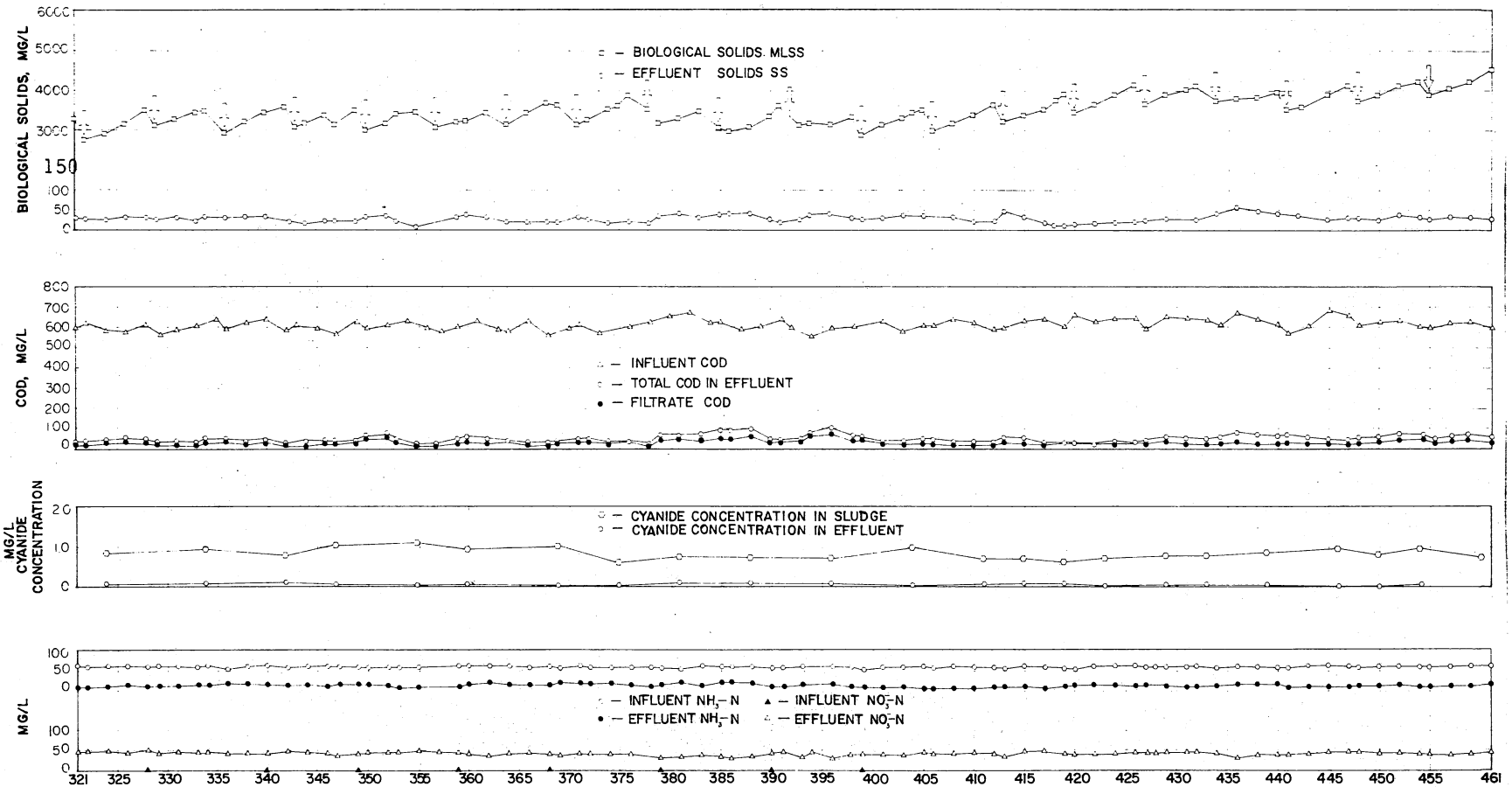
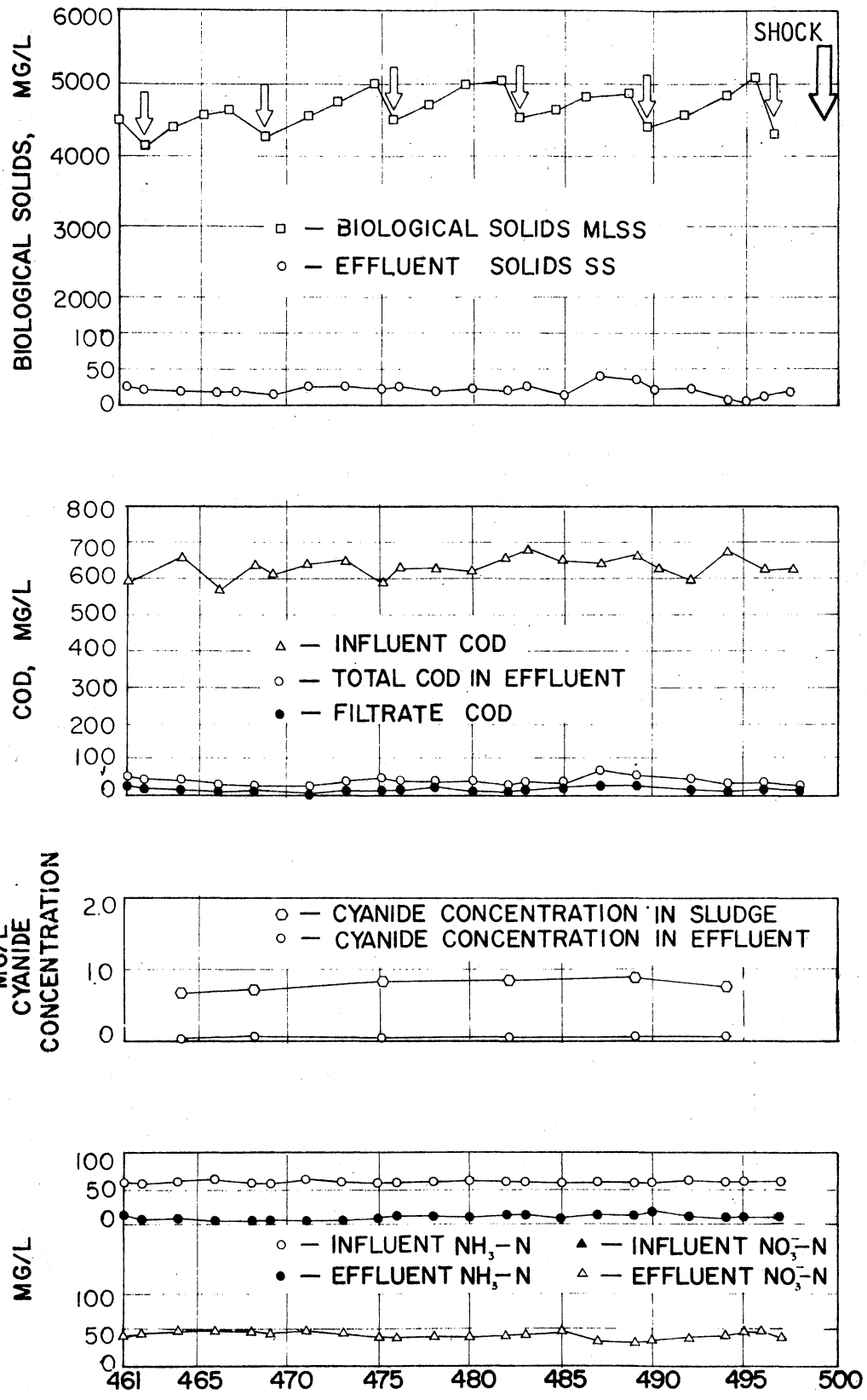

BIOLOGICAL SOLIDS, MG/L
6000
5000
4000
3000
150
100
50
0
□ — BIOLOGICAL SOLIDS MLSS
○ — EFFLUENT SOLIDS SS
COD, MG/L
800
700
600
500
400
300
200
100
0
△ — INFLUENT COD
○ — TOTAL COD IN EFFLUENT
● — FILTRATE COD
MG/L CYANIDE CONCENTRATION
2.0
1.0
0
□ — CYANIDE CONCENTRATION IN SLUDGE
○ — CYANIDE CONCENTRATION IN EFFLUENT
MG/L
100
50
0
100
50
0
○ — INFLUENT NH3—N
▲ — INFLUENT NO3—N
● — EFFLUENT NH3—N
△ — EFFLUENT NO3—N
321 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 461

Figure 7. Performance Data of an Extended Aeration Pilot Plant With "Hydrolytic-Assist" From Day 461 to Day 500 of Operation


BIOLOGICAL SOLIDS, MG/L
6000
5000
4000
3000
2000
100
50
0
SHOCK
— BIOLOGICAL SOLIDS MLSS
— EFFLUENT SOLIDS SS
COD, MG/L
800
700
600
500
400
300
200
100
0
— INFLUENT COD
— TOTAL COD IN EFFLUENT
— FILTRATE COD
MG/L CYANIDE CONCENTRATION
2.0
1.0
0
— CYANIDE CONCENTRATION IN SLUDGE
— CYANIDE CONCENTRATION IN EFFLUENT
MG/L
100
50
0
100
50
0
— INFLUENT NH3–N
— EFFLUENT NH3–N
— INFLUENT NO3–N
— EFFLUENT NO3–N
461
465
470
475
480
485
490
495
500

show the daily performance of the system. In the first stage, from day 50 to day 209, cyanide was added at a concentration of 10 mg/l; in the second stage, from day 210 to day 277, cyanide was added at a concentration of 15 mg/l; in the third stage, from day 280 to the end of the operation (day 500), cyanide was added at a concentration of 20 mg/l. Shown in these figures are MLSS concentration, effluent solids concentration, cyanide concentration in the sludge and effluent; COD, NH_3-N and NO_3^--N in the effluent and influent. The arrows along the plot of suspended solids indicate the days of withdrawal of 900 ml of mixed liquor for hydrolysis and subsequent recycling of equal fractional portions for succeeding feeding days between the next withdrawal. The influent COD plotted in these four figures is the COD including the hydrolyzed sludge; however, the hydrolysate portion is considered simply as a portion of the return sludge.

It is important to note that cyanide determination was made by two different methods. From day 77 to day 410, cyanide concentration was determined by a titration method after distillation treatment of samples (as outlined in Standard Methods, 13th edition). The importance of the distillation procedure cannot be over-emphasized since this step not only eliminates interference, but also results in the conversion of the cyanide into simple NaCN, which may be readily measured by the titration method. The best sample volume for the distillation procedure was difficult to decide upon when the analyst was not familiar with the procedures and characteristics of the sample. However, after several trials, by gradually increasing the volume of the sample, the analyst became accustomed to the procedures and the properties of the sludge. It was then decided that 500 ml of sludge should be taken from the unit

every week for determination of cyanide.

After 410 days of operation, the method of cyanide determination was changed, using the cyanide-ion-selective electrode method according to the 14th edition of Standard Methods. Only a very small volume of the sample was needed for this method. Review of the MLSS data for the whole operational period suggests that the method of cyanide determination did influence the level of MLSS in the system. During the period when the distillation procedure was adopted for cyanide determination, the solids level in the reactor was about 3500 mg/l compared to the solids level of 5000 mg/l before and 4500 mg/l after this period. That is to say, the lower solids level in the system during this period may have been due to the indirect wastage of solids from the system to the extent of 500 ml per week. During the period before day 104, the solids level was higher because no sludge was withdrawn for analysis. During the period after 410 days of operation, the solids level was higher because a much smaller amount of MLSS (30-50 ml) was withdrawn for cyanide determination using the electrode method.

During the first stage of operation (day 50 to day 209), 10 mg/l of cyanide was added, and an excellent cyanide degradation efficiency was observed. There was no cyanide found in the effluent; COD removal was about 95 percent (average 25 mg/l of soluble COD in the effluent), and solids concentration in the effluent averaged 30 mg/l. Effluent NH_3-N was about 7 mg/l over the entire period. It is interesting to note that the NO_3^--N in the effluent increased from an average value of 30 mg/l to a level abovd 40 mg/l. Thus, very good nitrification was accomplished in the unit. During the study, a few analyses for NO_3^--N in the influent were made on the feed which contained the synthetic

waste plus a small amount of hydrolysate. It is seen that essentially no NO_3^--N was found in the feed.

The analyses for the presence of cyanide in the sludge during this period revealed that, on the average, only 1 mg/l of cyanide was present. This, along with the absence of an appreciable amount of cyanide in the effluent, indicates that cyanide might have been degraded to carbon and nitrogen. Also, from the data thus far presented, it cannot be said that the disappearance of CN^- was not due to stripping. This aspect is addressed later in this report.

Figure 5 shows the system performance during the second stage (day 210 to day 277). Cyanide was increased from 10 mg/l to 15 mg/l. A transition period was observed at the beginning of this stage. During the transition period, the effluent solids showed an increasing trend and reached a maximum value of 130 mg/l, and then started to decrease. A slight leakage of cyanide to the extent of 0.3 mg/l was observed during the first day after the step increases. After a few days, there was no detectible amount of cyanide in the effluent. COD removal efficiency decreased to 82 percent (90 mg/l of filtrate COD in the effluent) on the first day, but recovered 94 percent within five days. Nitrate concentration level in the effluent decreased from 40 mg/l to 12 mg/l in the days immediately following the step increase of cyanide, and returned to a steady level of 40 mg/l after 12 days. MLSS showed a decreasing trend during the first four days, then started to increase and reached an average level of 2700 mg/l when the new steady state was attained.

After recovering, the system seemed to undergo a secondary response (from day 233 to day 275), during which the appearance of the sludge became lighter in color and was less dense than it was formerly.

Microscopic examination revealed only a moderate amount of protozoan activity and a few filamentous organisms. The leakage of suspended solids in the effluent was due to dispersed bacterial growth and free swimming cells in the effluent. This indicated a change of predominance or secondary response occurring in the system, presumably due to the increase in cyanide.

The system performance during the third stage of operation started from day 278, when the cyanide concentration was increased from 15 mg/l to 20 mg/l (see Figures 5, 6, and 7). As before, there was a transition period. The transition period this time lasted for about four weeks. The efficiency of cyanide removal dropped very little--only 0.1 mg/l of cyanide was found in the effluent. However, COD removal efficiency decreased to an average value of 85.5 percent, and nitrification was very much hampered. NO_3^--N dropped to a level of 5 mg/l, while NH_3-N rose to about 50 mg/l in the effluent on the fifth day after the increase in CN^-. A maximum effluent solids concentration of 135 mg/l was found on the same day, and the MLSS concentration decreased to 2200 mg/l in the reactor. This whole transition period lasted for about four weeks, then rather suddenly, on day 308, the system came back to the "normal" condition.

As can be seen in Figures 5, 6, and 7, the performance of the unit after this four-week adjustment was excellent in terms of both COD and cyanide removal. An average value of only 0.06 mg/l cyanide was found in the effluent, and COD removal efficiency was 95 percent. Effluent NH_3-N was in the range of 3-12 mg/l, and effluent NO_3^--N averaged 44 mg/l throughout this stage.

It is observed that the overall performance of the "hydrolytically

assisted" extended aeration process for waste containing cyanide was exceptionally good. The percent efficiency of the system for COD removal and cyanide degradation remained nearly the same at different cyanide dosing levels, and there was no sign of accumulation of cyanide in the sludge. However, a three-to-four week transition period seems to be necessary for the biomass to acclimate to each new stage of higher cyanide loading. As an increased concentration of cyanide was applied, there was an immediate increase in COD in the effluent and a prompt decrease in nitrate. After a period of adjustment with increasing cyanide applied continuously, COD removal returned to normal and nitrate production also resumed. Therefore, it is evident that the tolerance of sludge to cyanide and efficiency of cyanide degradation needs a suitable period of acclimatization. In other words, shock loadings of cyanide were found to be metabolized by unacclimated sludges, but it took the system a few weeks to recover normal operation capability. The cyanide may have been bacteriostatic rather than bacteriocidal, and if one is treating CN^--containing wastes, cyanide concentration should be increased slowly and steadily over a considerable length of time, i.e., special operational care should be taken to avoid sudden surges in CN^- concentration.

It is true that a part of the cyanide will be removed by stripping in the aeration tank; however, according to Gurnham (4), this removal is too little and too late to benefit the microorganism. The transition periods between each stage where cyanide was added from 10 to 15 mg/l and from 15 to 20 mg/l, showed that the loss of cyanide due to aeration must be very little since even the slight increase of 5 mg/l cyanide in the system caused considerable stress to the biomass in the

reactor and was reflected in some deterioration in effluent quality. An aeration experiment on stripping of cyanide in the extended aeration pilot plant in the absence of biomass will be presented and discussed later.

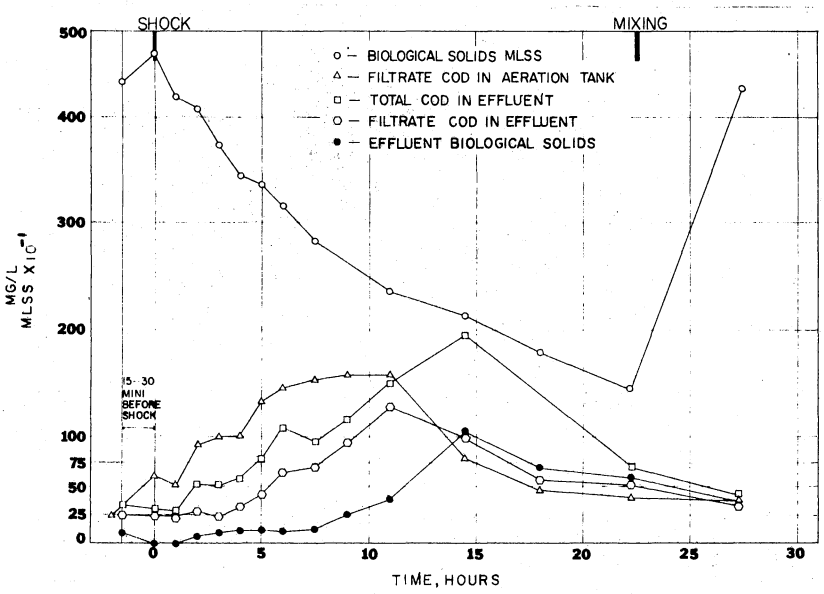
Response of a "Hydrolytically-assisted" Extended Aeration Process to a Pulse Shock Loading

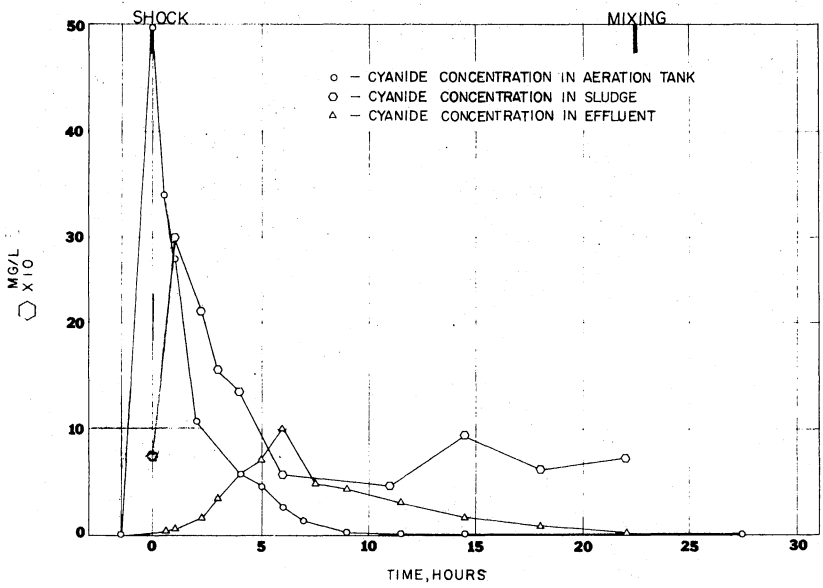
Figure 8 shows the biochemical response of the system after being slug dosed with cyanide directly to the aeration tank in an amount yielding 50 mg/l concentration of cyanide in the reactor. The system was also receiving 20 mg/l CN in the feed. In general, the system responded very well and recovered to normal condition rapidly. As shown in Figure 8, cyanide removal efficiency decreased in an increasing manner within the first six hours until it reached a peak value of 10 mg/l in the effluent. Twenty-two hours after the shock, only 0.20 mg/l cyanide was found in the effluent. The percentage of COD removal decreased to 74.5 percent at the 11th hour, then gradually recovered to 92.8 percent after 27 hours. Solids leakage reached a maximum of 108 mg/l at about 14 hours, then recovered to 40 mg/l after 27 hours.

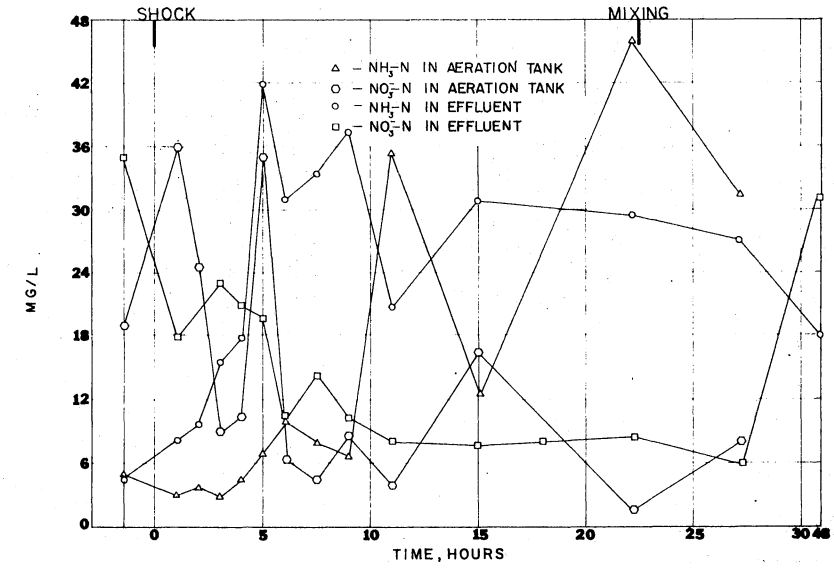
A serious leakage of NH_3-N in the effluent was observed, and a maximum value of 42 mg/l was detected at the fifth hour. Nitrification dropped rapidly and was low all through the period of intensive monitoring. The lowest level, 8 mg/l of NO_3^--N, was found at the 15th hour. After 48 hours, NO_3^--N level returned to 31 mg/l.

It is interesting to note that the MLSS concentration in the aeration tank decreased to 1500 mg/l at the 22nd hour. However, the MLSS did not come out in the effluent, since a portion of the sludge floated

Figure 8. Response of a "Hydrolytically-assisted" Extended Aeration Pilot Plant to a Pulse Shock Load of 50 mg/l of Cyanide


SHOCK
MIXING
o — BIOLOGICAL SOLIDS MLSS
Δ — FILTRATE COD IN AERATION TANK
□ — TOTAL COD IN EFFLUENT
○ — FILTRATE COD IN EFFLUENT
● — EFFLUENT BIOLOGICAL SOLIDS
15-30 MINI BEFORE SHOCK
MG/L MLSS X10⁻¹
500
400
300
200
100
75
50
25
0
0
5
10
15
20
25
30
TIME, HOURS


SHOCK
MIXING
o — CYANIDE CONCENTRATION IN AERATION TANK
○ — CYANIDE CONCENTRATION IN SLUDGE
Δ — CYANIDE CONCENTRATION IN EFFLUENT
MG/L X10
50
40
30
20
10
0
0
5
10
15
20
25
30
TIME, HOURS


SHOCK
MIXING
Δ — NH₃-N IN AERATION TANK
○ — NO₃-N IN AERATION TANK
○ — NH₃-N IN EFFLUENT
□ — NO₃-N IN EFFLUENT
MG/L
48
42
36
30
24
18
12
6
0
0
5
10
15
20
25
30
48
TIME, HOURS

in the clarifier as a thick layer under the screening device which had been placed near the effluent pipe. The baffle between the aeration and settling chambers was removed at the 22.5th hour in order to mix the whole system, and 4280 mg/l of MLSS was measured in the aeration tank after mixing. This is about the same level of MLSS as was present before the shock.

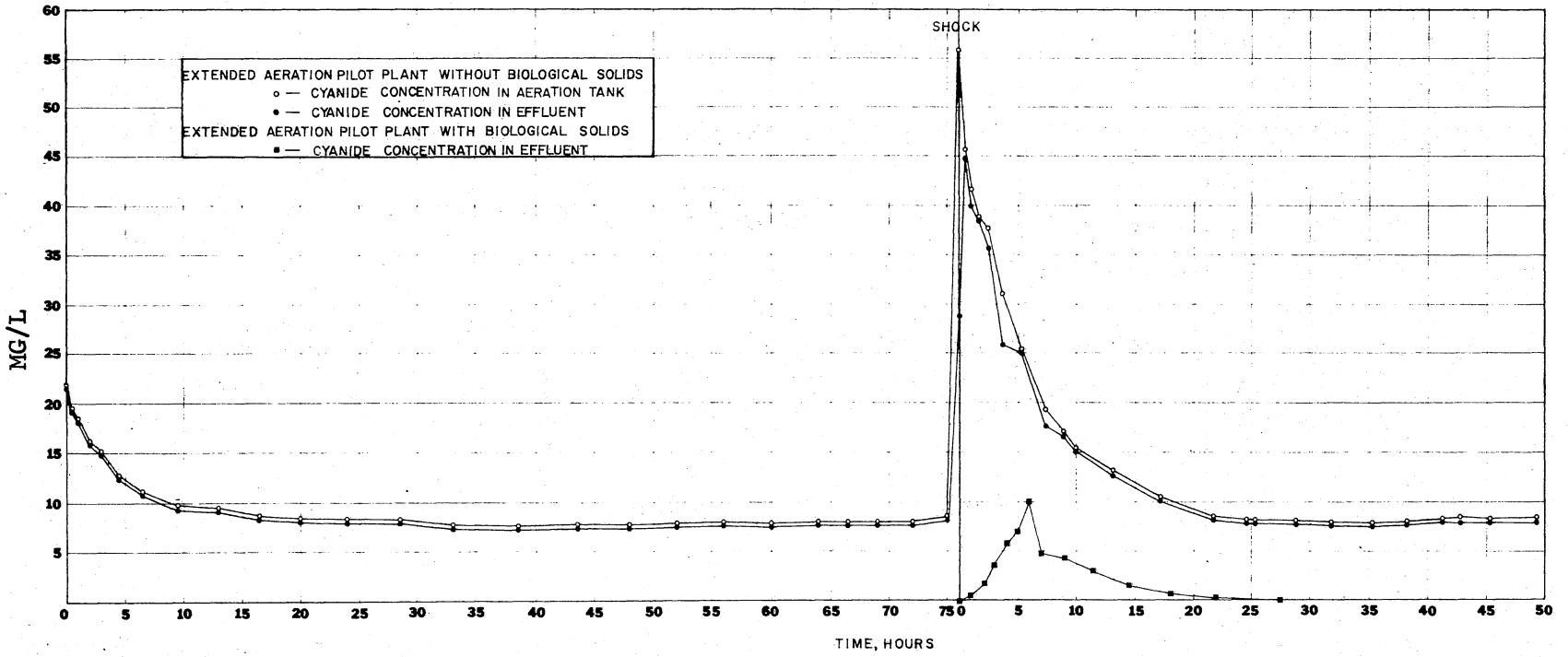
Examination of the sludge for cyanide content, as shown in the figure, reveals that cells accumulated cyanide rather than using it during the first few hours of operation. The internal cyanide storage in the cell reached a maximum concentration of 3 mg/l at the first hour. Also, one should remember that in addition to the slug dose of cyanide of concentration 50 mg/l, there was no cyanide in the incoming feed. The cyanide stored in the cells decreased rather rapidly.

Experiment on Stripping of Cyanide in the Extended Aeration Pilot Plant

It is known that cyanide can be stripped by aeration. Many early researchers encountered cyanide loss by volatilization in various biodegradation processes. Ludzack (29) cited the results from British research that an uninoculated filter resulted in 66 percent loss of feed cyanide with no evidence of biological action.

The extended aeration pilot plant employed for this experiment was the same one which was used for experiments reported earlier. The only difference in operation was that there were no biological solids in the unit during the current experiment. The results are shown in Figure 9. The figure shows that there is significant aeration loss of cyanide when fed with 20 mg/l of cyanide. As the system reached steady state, 60 percent cyanide added in the effluent was found stripped out by simple

Figure 9. Experimental Data for Stripping of Cyanide in the Extended Aeration Pilot Plant Without Biological Solids


EXTENDED AERATION PILOT PLANT WITHOUT BIOLOGICAL SOLIDS
o — CYANIDE CONCENTRATION IN AERATION TANK
• — CYANIDE CONCENTRATION IN EFFLUENT
EXTENDED AERATION PILOT PLANT WITH BIOLOGICAL SOLIDS
■ — CYANIDE CONCENTRATION IN EFFLUENT
SHOCK
MG/L
TIME, HOURS

aeration, i.e., 8 mg/l of cyanide was detected in the effluent. However, this does not mean that only 8 mg/l would have been biodegraded if the biomass were present in the system. It simply indicates how much cyanide could have been stripped out in the absence of biomass and biological activity. Furthermore, according to Ludzack (29), citation of results from the British researchers shows higher aeration solids decreased stripping rate of cyanide due to aeration. This is probably because of the solids hindering the contact between O_2 and cyanide ions. Therefore, if 4000 mg/l dead biological solids were placed into the system, the loss of cyanide due to aeration would be expected to be much smaller.

Further evidence of biodegradation of cyanide in the extended aeration system was obtained by applying a pulsing shock of cyanide to the system without biological activity. As seen in Figure 9, when addition of 50 mg/l cyanide was injected into the aeration tank, cyanide came out in the effluent along a normal dilute-out curve, while the system with biomass decomposed most of the slug dose of cyanide (see lower curve). The lower curve is replotted from Figure 8. The difference between aeration loss of cyanide and the amount of cyanide decomposed by the biomass is significant. Thus, it is ascertained that cyanide is biodegradable, and one can conclude without doubt that CN^- waste was biologically treated successfully by the hydrolytically-assisted extended aeration process.

Part B

This section deals with presentation of results based on various types of batch experiments.

Air Dispersion Test

A preliminary experiment for testing the effect of mode of dispersion of air bubbles in the batch systems was conducted. In this experiment, two 3-liter aeration vessels were filled at 300 mg/l of cyanide (no buffer added). In one of them, one air diffuser stone was used and the other was fitted with two diffusers. Both systems were aerated for 12 hours at the same aeration rate of 3100 cc/min. At the end of 12 hours, the reaction vessel with one air diffuser had a 250 mg/l cyanide residue while the other had a residual of 200 mg/l of cyanide. These data showed that when stripping off a cyanide from solution, the greater the number of air diffusers, the faster was the stripping rate of cyanide, probably because of the greater number and dispersion of air bubbles. Hence, it was determined that it would be important to use the same number of air diffusers in the following comparative batch experiments.

Studies on Stripping of Cyanide in Batch Systems (no cells added). This study consisted of three major experiments, and the results are shown in Figures 10, 11, and 12. The purpose of this study was to examine the physical stripping characteristics of cyanide at different pH values and the effect of heavy metal, copper ion (Cu^{+2}) on the stripping of cyanide.

Figure 10 shows the results of stripping tests at pH values of 12, 10, 6, and 4. Since the simple alkali cyanide, such as KCN, readily changed to HCN in acid conditions, there is little wonder that the stripping rate of pH = 4 was the most rapid. In aqueous solutions of the simple alkali cyanide, the ratio of cyanide present as HCN to total

Figure 10. Experimental Data for Stripping of Cyanide in Batch Systems at Different pH Values

○ = cyanide solution at pH = 12
□ = cyanide solution at pH = 10
△ = cyanide solution at pH = 6
⬡ = cyanide solution at pH = 4

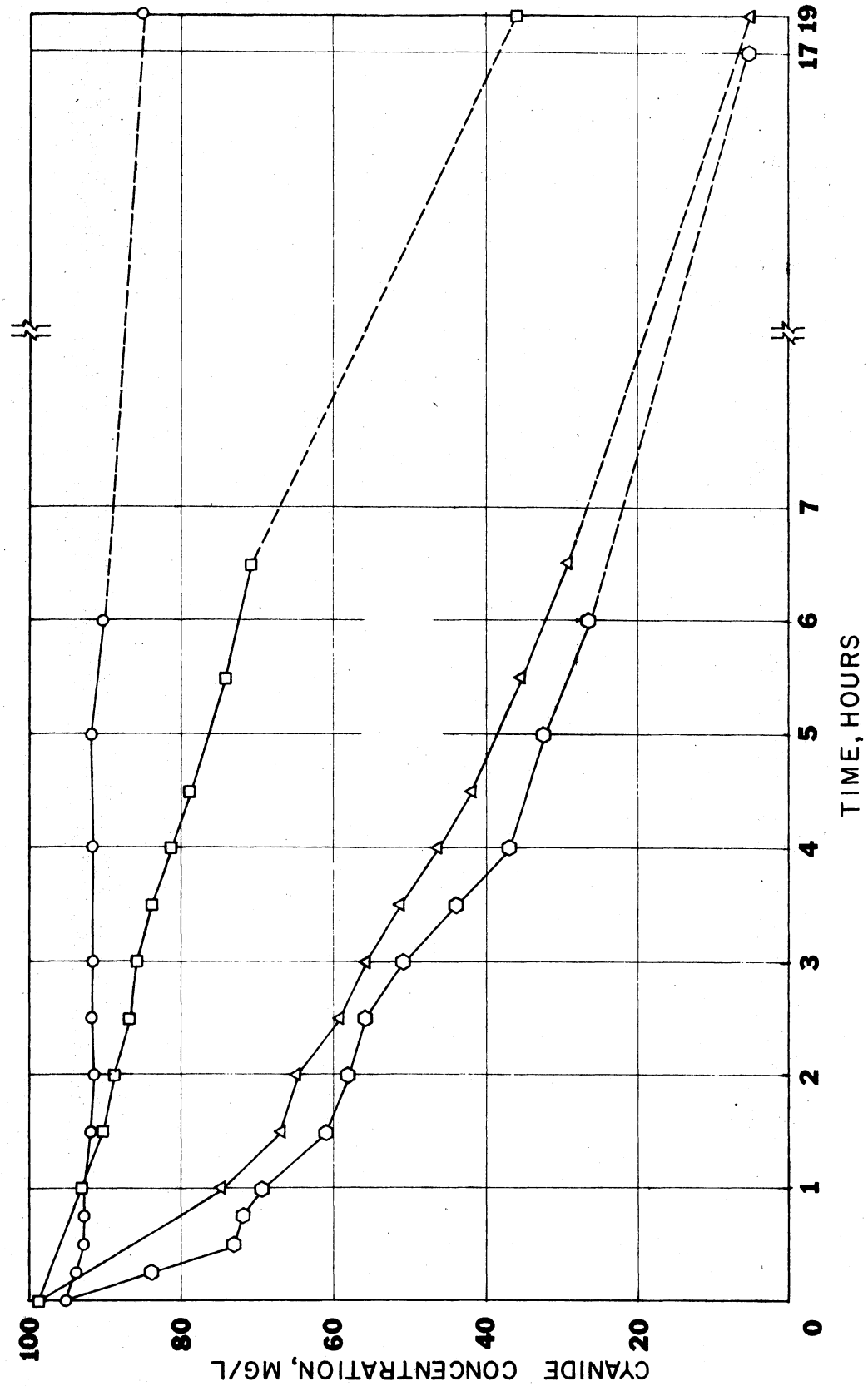

CYANIDE CONCENTRATION, MG/L
100
80
60
40
20
0
TIME, HOURS
1
2
3
4
5
6
7
17
19

Figure 11. Experimental Data for Stripping of Cyanide in Batch Systems With Different Concentrations of Copper Ions

□ = 300 mg/l CN^- + 146.6 mg/l Cu^{+2} (without buffer)
○ = 300 mg/l CN^- + 146.6 mg/l Cu^{+2} (with buffer, pH = 7.3)
△ = 300 mg/l CN^- + 219.9 mg/l Cu^{+2} (with buffer, pH = 7.3)
◇ = 300 mg/l CN^- + 293.9 mg/l Cu^{+2} (with buffer, pH = 7.3)

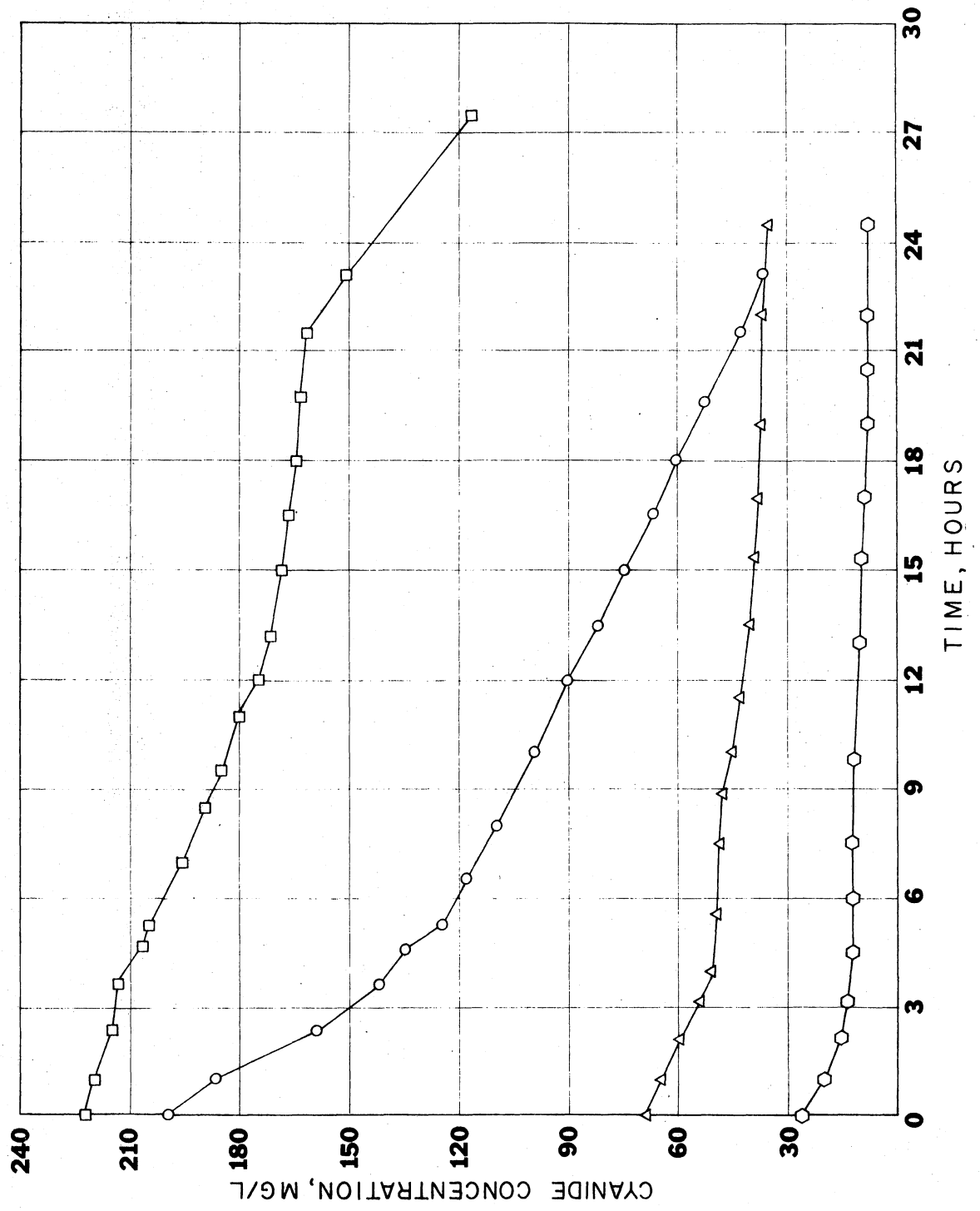

CYANIDE CONCENTRATION, MG/L
240
210
180
150
120
90
60
30
0
3
6
9
12
15
18
21
24
27
30
TIME, HOURS

Figure 12. Experimental Data for Stripping of Cyanide in Batch Systems Without Addition of Copper Ions at Different pH Values

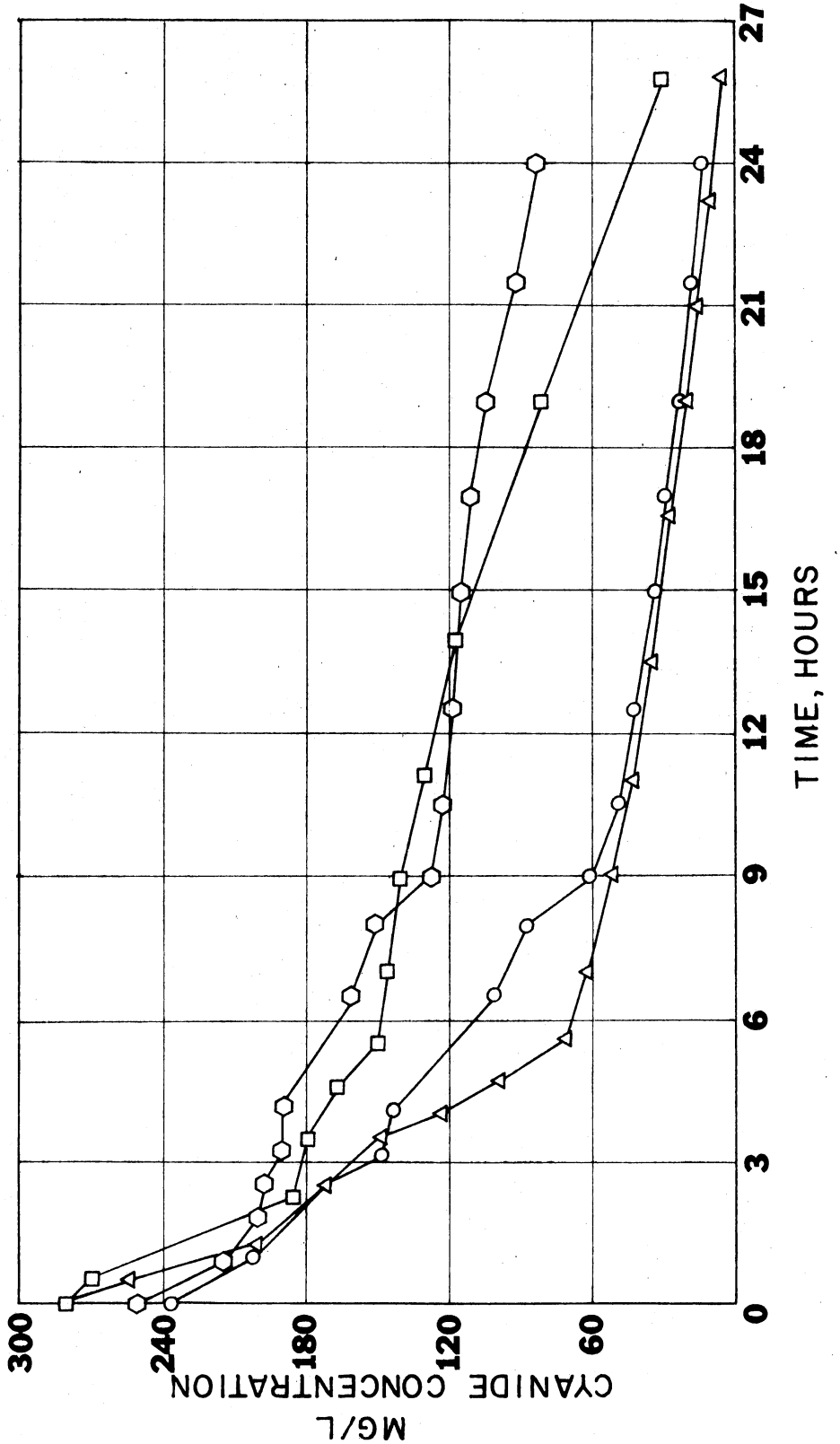
CN^- = 300 mg/l, Cu^{+2} = 73.7 mg/l

↻ = cyanide solution with copper ions at pH = 6

□ = cyanide solution without copper ions at pH = 6

○ = cyanide solution with copper ions at pH = 4

△ = cyanide solution without copper ions at pH = 4


CYANIDE CONCENTRATION
MG/L
300
240
180
120
60
0
3
6
9
12
15
18
21
24
27
TIME, HOURS

cyanide is very much dependent on the pH values.

The cyanide stripping tests described below were carried out in order to determine the effect of each of the following four conditions:

1) copper with buffer added

2) copper without buffer

3) and 4) various concentrations of Cu^{+2} with buffer added.

The results are shown in Figures 11 and 12.

According to Ford and Smith (75), the addition of Cu^{+2} ions to a cyanide solution would result in the formation of 2 $CuCN \cdot Cu(CN)_2$, which is very stable and would exert stronger resistance to formation of HCN. Also, they state that the degree of dissociation of the metal-locyanide complexes to cyanide ion increases with decreased concentrations of metal ions and decreased pH.

The method used here for determination of cyanide can detect only free cyanide ion present in the system. The metallocyanides will not be detected by the method used, regardless of the concentration. Hence, it is apparent that the results in Figure 11 cannot be compared directly but we can come to some reasonable conclusions based on the slope of the curves. The stripping rate of cyanide in the solution with pH controlled at 7.3 was faster than that without buffer (pH = 10.8-9.6). Also, it may be concluded that the more Cu^{+2} added, the more stable will be the cyanide in solution; i.e., the stripping of cyanide will be less. Figure 12 shows the significant effect of pH in the metallocyanide solutions. The stripping rate of cyanide at pH = 4 was faster than that at pH = 6, even when Cu^{+2} (75 mg/l) was added, and the stripping rate was higher in the solution without Cu^{+2} than in the solution with Cu^{+2} = pH 4.

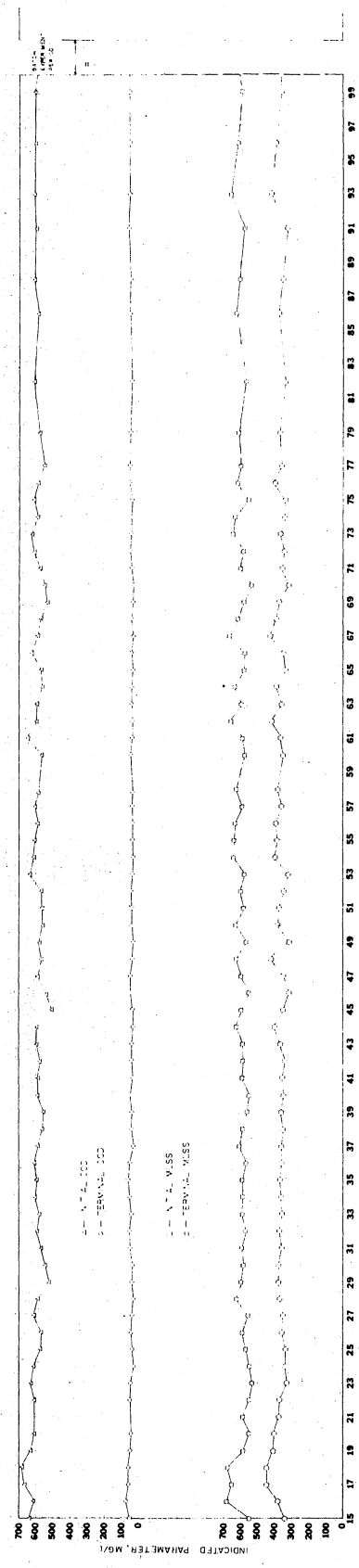
Studies to Test the Effectiveness of Cyanide Degradation in Activated Sludge Batch Systems

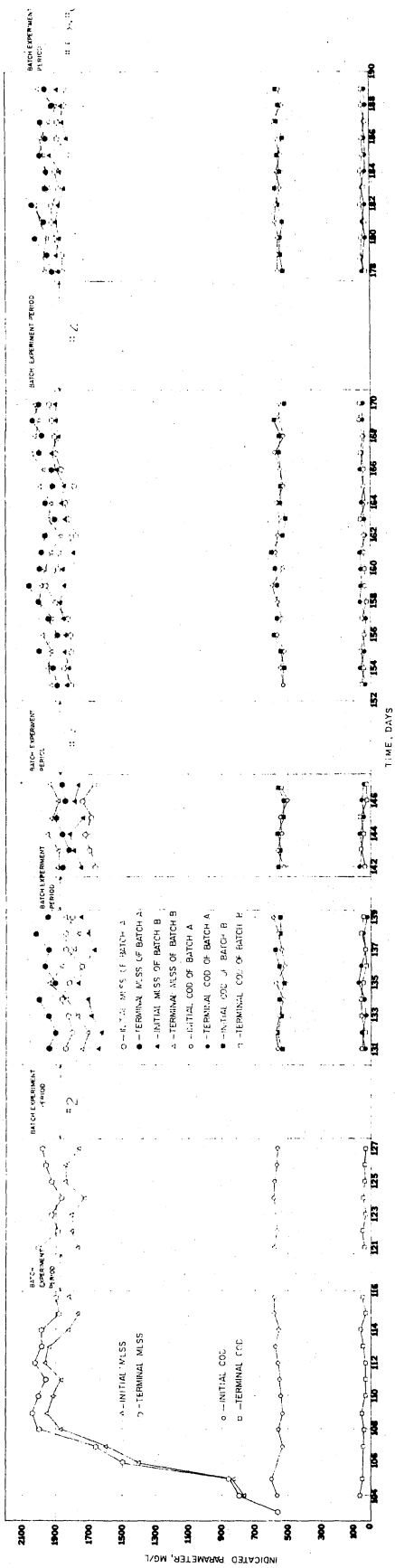
Development of Sludge Used in the Experiments. A batch activated sludge system was started on July 28, 1976 (day zero, Figure 13), using a small microbial population from the continuous flow "hydrolytically-assisted" extended aeration system. Daily values of COD and MLSS in the batch system were measured before and after feeding to ascertain if the terminal solids level (MLSS before feeding) and COD, i.e., COD_e, were nearly constant and if an acclimated microbial population had been developed for use in the batch experiments to test for substrate and cyanide removal and the rate of cyanide degradation. Daily performance data prior to each set of batch experiments are shown in Figure 13. The data shown in the figure indicate that fairly constant biological solids production and COD_e were attained; i.e., the system had reached a balanced condition prior to using the cells for the batch experiments.

The time when the six sets of batch experiments were run are marked on the performance chart. Before the first set of batch experiments on joint stripping and metabolism were conducted, the system was run by daily wasting one-third of the MLSS and removing another one-third of the supernatant after 30 minutes' settling (day 15-day 102). However, after the first batch experiment (shown in Figure 14), it was found that substrate removal and cyanide degradation were not very significant during the test with solids level of only 600 mg/l obtained by this mode of operation of the batch unit.

In order to have higher solids concentration in the batch unit during steady state conditions, the mode of operation was changed.

Figure 13. Performance Data of the Batch Activated Sludge Unit From Day 15 (August 11, 1976) to Day 190 of Operation


INDICATED PARAMETER, MG/L
TIME, DAYS

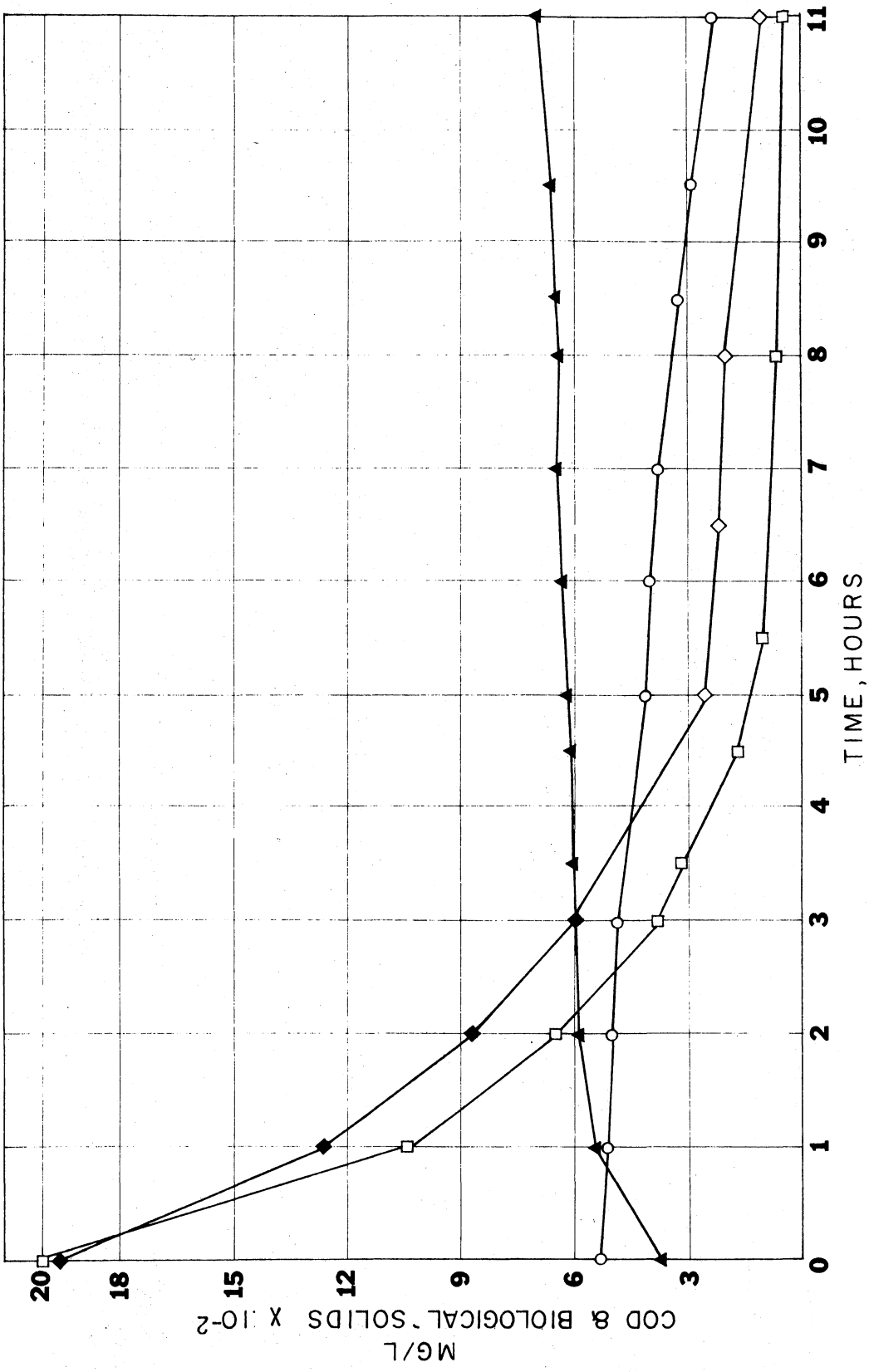

INDICATED PARAMETER, MG/L
TIME, DAYS

Instead of wasting one-third of the MLSS, all solids were retained in the system. However, after the second set of batch experiments (shown in Figure 15) it was found that besides comparison of removal of cyanide in batch systems with and without the presence of biomass, an additional control was needed for the observation of substrate removal efficiency at the same organic loading but without addition of cyanide. Therefore, in order to obtain sludge for this control system, the sludge in the batch system was divided equally into two batches and both were operated with no wastage of MLSS to obtain higher solids level for subsequent batch experiments. Thus, both systems were the same, each receiving glucose plus 20 mg/l Cn^- (day 28-day 190). However, after the system reached a balanced condition, an average solids concentration varying from 1800 to 2100 mg/l proved to be too high to observe the growth of biomass; therefore, each of the batch systems was diluted before each batch experiment (beginning with experiment 2) according to the previous day's MLSS concentration in order to maintain a solids level in the range of 1500-1800 mg/l. This permitted better observation of the growth of solids.

Batch Experiments. The results of the first batch experiment are shown in Figure 14. The initial COD was 500 mg/l and cyanide concentration was 20 mg/l for both batch systems, with and without biomass. The airflow rate was 3100 cc/min in both systems. The difference in cyanide reduction in the systems was not very great; also, COD removal in the system with biomass was not rapid. The poor performance was probably due to the low solids concentration and the high airflow rate which caused most of the cyanide to be stripped out. Therefore, it was

Figure 14. Batch Experiment #1. Comparison of Removal of Cyanide in the Batch Systems, With and Without Biological Solids, at an Airflow Rate of 3100 cc/min

▲ = biological solids
○ = COD in the system with biological solids
◆ = cyanide reduction in the system without biological solids
□ = cyanide degradation in the system with biological solids

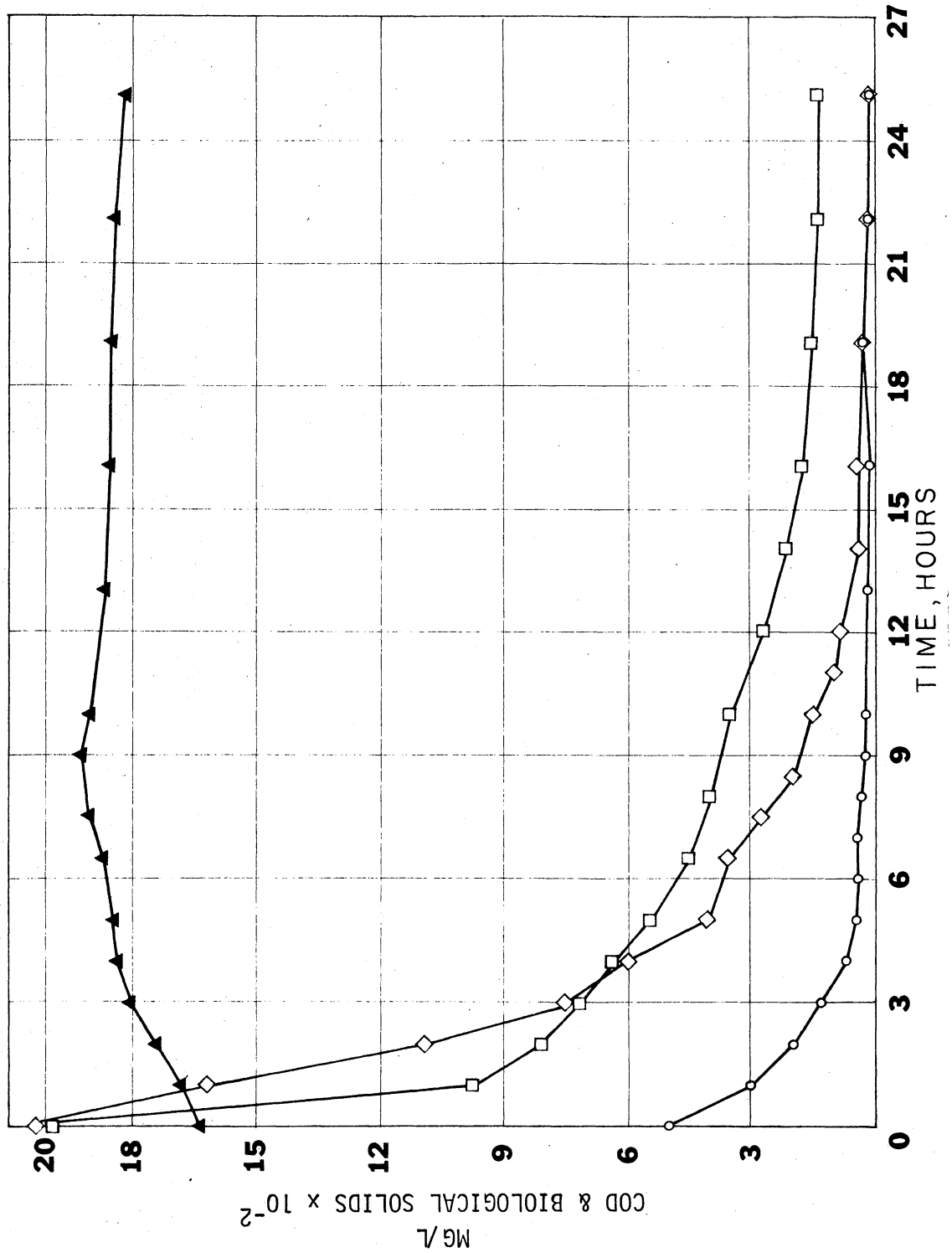

MG/L
COD & BIOLOGICAL SOLIDS X 10-2
20
18
15
12
9
6
3
0
1
2
3
4
5
6
7
8
9
10
11
TIME, HOURS

decided to change the operation of the batch system as mentioned before, and wastage of MLSS was stopped in order to obtain a higher solids concentration.

The second batch experiment was thus conducted after a balanced higher level solids concentration ranging from 1700-2000 mg/l was attained. The results of the second experiment are shown in Figure 15. The initial COD and cyanide concentrations were the same as in the previous experiment. The airflow rate was lowered to 2500 cc/min to reduce the stripping loss of cyanide. The results show that this batch with a higher solids concentration removed cyanide at a faster rate than that in the stripping system for the first two hours, and good COD removal efficiency (90 percent) was achieved within five hours. The cell yield was about 0.4 after 24 hours; however, the stripping system shows a better cyanide reduction after the third hour. This result could have been due to the fact that the airflow rate of 2500 cc/min was still too high for the 3-liter aeration volume. The higher the airflow rate, the better the mixing between O_2 and cyanide ions, favoring the stripping of cyanide while the 1800 mg/l of solids might hinder the contact between O_2 and cyanide ions. Thus, it was decided that in succeeding experiments, the airflow rate needed to be further reduced. In addition to reducing the airflow rate, it was decided to add another control system for the biomass, i.e., a system without addition of cyanide on the day of the experiment. Then, as mentioned before, the sludge in the batch system was divided equally into two batches and these were fed and operated in the same way; i.e., no wastage of MLSS. After these systems reached a steady condition with respect to biological solids (1700-2000 mg/l), the third batch

Figure 15. Batch Experiment #2. Comparison of Removal of Cyanide in the Batch Systems, With and Without Biological Solids, at an Airflow Rate of 2500 cc/min

▲ = biological solids
○ = COD in the system with biological solids
◇ = cyanide reduction in the system without biological solids
□ = cyanide degradation in the system with biological solids


MG/L
COD & BIOLOGICAL SOLIDS x 10⁻²
20
18
15
12
9
6
3
0
3
6
9
12
15
18
21
24
27
TIME, HOURS

experiment was started.

The results of this experiment are shown in Figure 16. The initial COD and cyanide concentrations were 500 mg/l and 20 mg/l, respectively. The airflow rate was lowered to 1000 cc/min to minimize the aeration loss of cyanide. The COD removal curves show the effect of cyanide on substrate removal. As indicated in the figure, at the first hour, the substrate removal efficiency was about 70 percent in the batch without addition of cyanide, while only about 30 percent in the batch to which cyanide was added. To attain a substrate removal efficiency of 83 percent, it took only three hours for the batch without cyanide while it took 15 hours for the batch to which cyanide had been added. This phenomenon can be attributed to the inhibitory action of cyanide on the cells; the mode of the inhibition is not known. All of the cells may have been partially hampered in removing substrate or some cells may have been killed, thus reducing the effective population available for substrate removal.

In the fourth set of batch experiments, five batches were run under the following conditions:

System 1 - biological control batch systems containing cells and glucose.

System 2 - stripping control batch system A, containing cyanide and glucose--no cells.

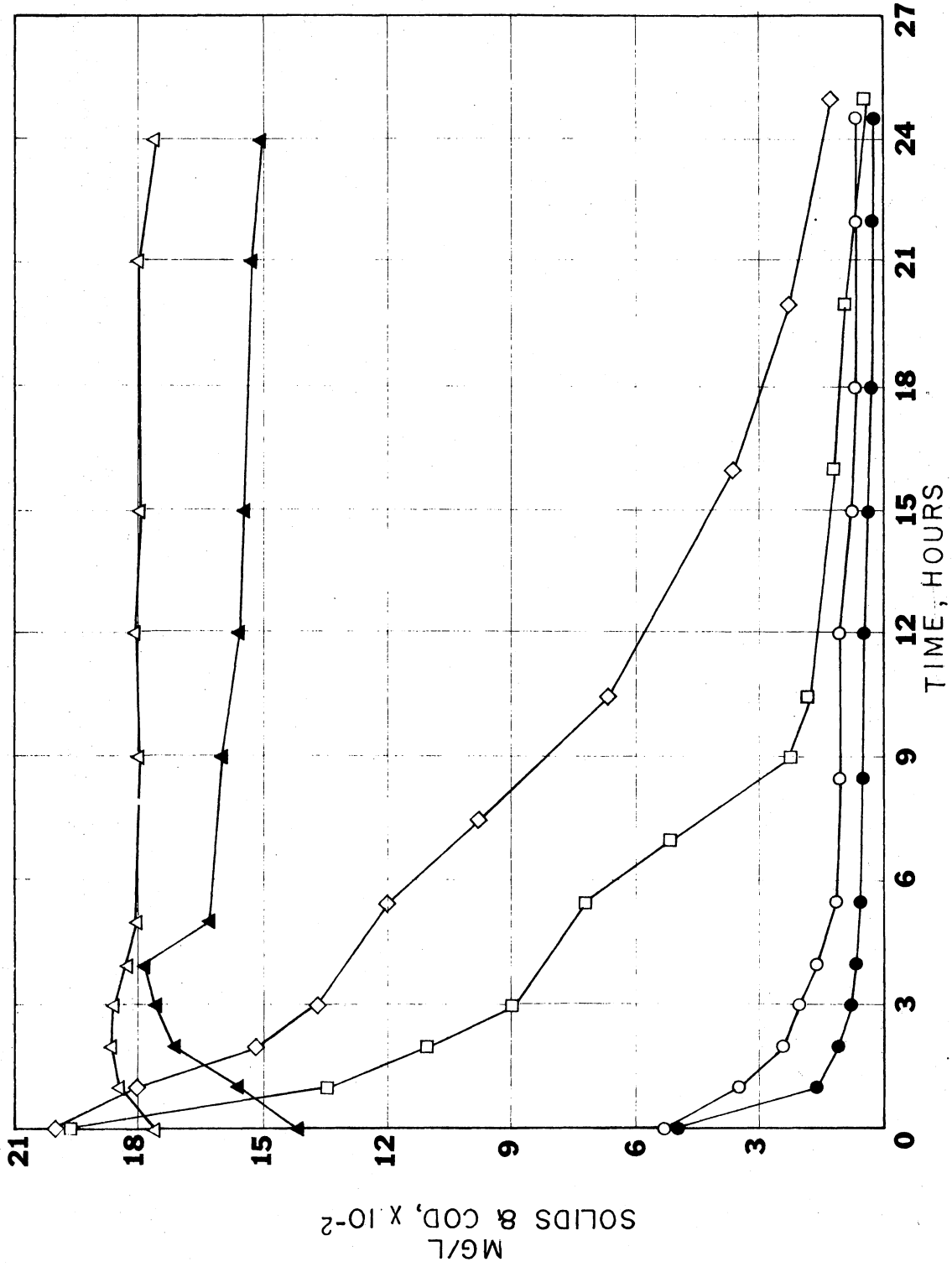
System 3 - stripping control batch system B, containing cyanide, copper, and glucose--no cells.

System 4 - biological batch system containing cyanide and glucose.

System 5 - biological batch system containing cyanide, copper, and glucose.

Figure 16. Batch Experiment #3. Comparison of Removal of Cyanide in the Batch Systems, With and Without Biological Solids, at an Airflow Rate of 1000 cc/min

△ = biological solids in the system without presence of cyanide
▲ = biological solids in the system with presence of cyanide
○ = COD in the system with presence of cyanide
● = COD in the system without presence of cyanide
◇ = cyanide reduction in the system without biological solids
□ = cyanide degradation in the system with biological solids


MG/L
SOLIDS & COD, X 10-2
21
18
15
12
9
6
3
0
3
6
9
12
15
18
21
24
27
TIME, HOURS

The results of batch experiment 4 are shown in Figure 17. The initial COD and cyanide concentrations are the same as in the previous three experiments, but airflow rate was lowered to 500 cc/min. It is known that formation of 2 $CuCN \cdot Cu(CN)_2$ ties up the CN^-, retarding stripping; therefore, it was thought the addition of Cu^{+2} ions might reduce the aerator loss of cyanide. Hence, 1 mg/l Cu^{+2} was added to systems 1 and 4, with and without biological solids. However, the cyanide solution with Cu^{+2} ions interfered with the cyanide determination even after EDTA procedures were included (Standard Methods, 14th edition), which were supposed to help overcome interference due to heavy metals. The cyanide reduction curves for these two batch systems are therefore omitted.

The airflow rate of 500 cc/min reduced the aeration loss of cyanide to a minimum, as shown in Figure 17. The difference of cyanide reduction rate between the batches, with and without biomass, became more significant; therefore, cyanide removal due to the sludge is definitely shown. The COD removal curves give information about the effect of Cu^{+2} and CN^- ions. The control batch system without addition of Cu^{+2} or CN^- shows the best efficiency--92 percent COD removal at four hours, while the other two systems (CN^-, Cu^{+2}, and CN^- added, respectively) reach only 74 percent and 60.4 percent, respectively.

Figures 18 and 19 show results of batch experiments run on successive days. In both experiments, stripping control systems were run. In experiment 5 (Figure 18), CN^- was withheld from one of the duplicate batch systems. In experiment 6 (Figure 19), this system received the dose of CN^- but CN^- was withheld for the system which had received the CN^- dosage in experiment 5.

Figure 17. Batch Experiment #4. Comparison of Removal of Cyanide in Batch Systems, With and Without Biological Solids, at Five Different Conditions for COD = 500 ppm (Glucose). Airflow Rate = 500 cc/min, CN^- = 20 ppm, Cu^{+2} = 1 ppm

System 1 - biological control batch system containing cells and glucose
System 2 - stripping control batch system A, containing cyanide, copper, and glucose--no cells
System 3 - stripping control batch system B, containing cyanide and glucose--no cells, copper ion
System 4 - biological batch system containing cyanide and glucose
System 5 - biological batch system containing cyanide, copper, and glucose

△ = biological solids in the system without the presence of either cyanide or copper ions (System 1)
◬ = biological solids in the system with the presence of cyanide (20 ppm) and copper ions (System 5)
▲ = biological solids (1 ppm) in the system with the presence of cyanide ions (System 4)
● = COD in the system without the presence of either cyanide or copper ions (System 1)
◐ = COD in the system with the presence of cyanide ions (System 4)
○ = COD in the system with the preence of cyanide (20 ppm) and copper (1 ppm) ions System 5
◇ = cyanide reduction in the system without biological solids (System 2)
□ = cyanide degradation in the system with biological solids

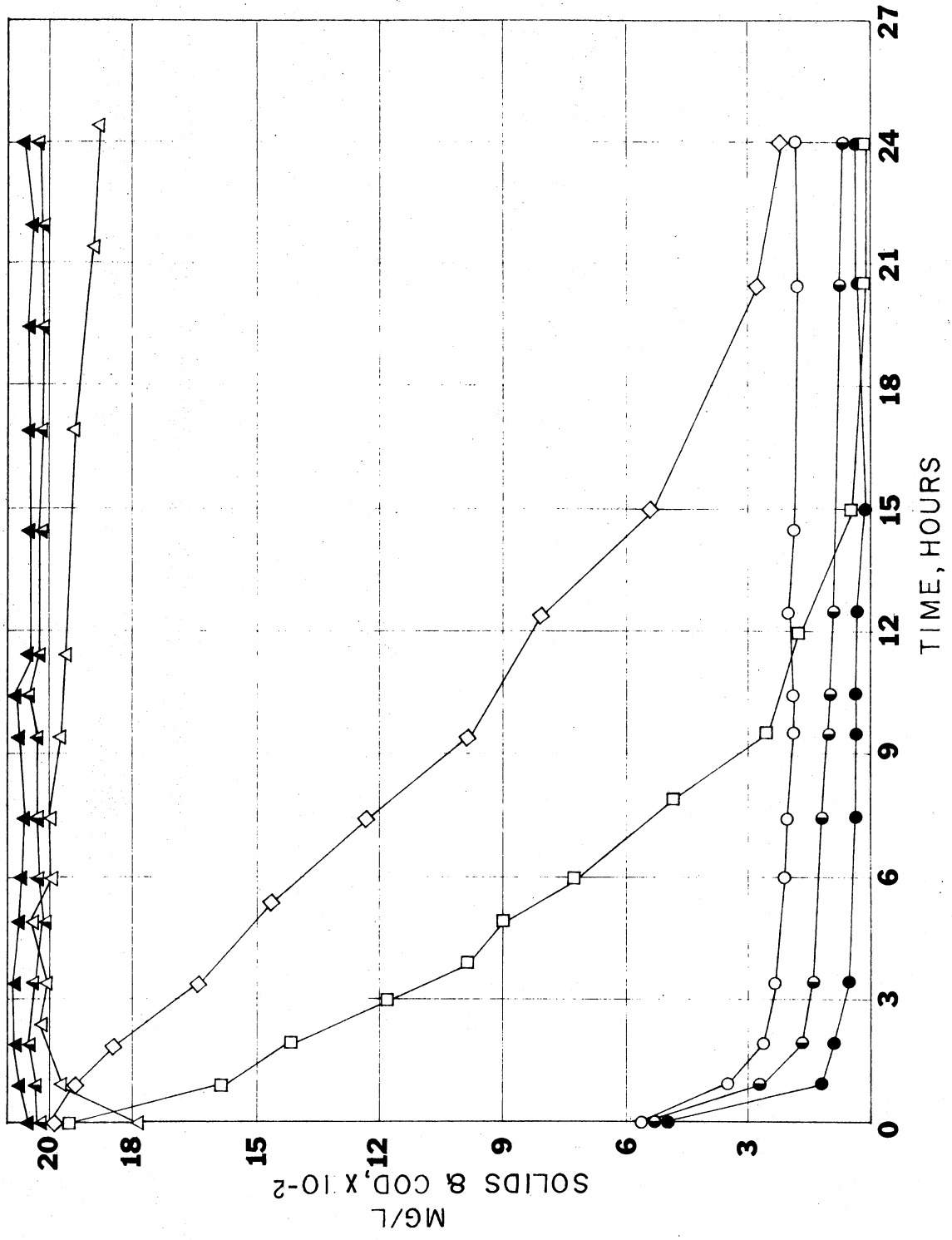

MG/L
SOLIDS & COD, X 10-2
20
18
15
12
9
6
3
0
3
6
9
12
15
18
21
24
27
TIME, HOURS

Figure 18. Batch Experiment #5. Comparison of Removal of Cyanide in the Batch Systems, With and Without Biological Solids, at Three Different Conditions for COD = 1000 ppm (Glucose), Airflow Rate = 500 cc/min, CN^- = 20 ppm. The First Condition Includes Cells, CN^- and COD; the Second Condition Includes Cells and COD; the Third Condition Includes CN^- and COD

▲ = biological solids in the system with presence of cyanide
△ = biological solids in the system without presence of cyanide (control unit)
○ = COD in the system with presence of cyanide
● = COD in the system without presence of cyanide (control unit)
◇ = cyanide reduction in the system without biological solids
□ = cyanide degradation in the system with biological solids
⬡ = cyanide concentration in the sludge
⊠ = DO in the sytem without biological solids
• = DO in the system without presence of cyanide (control unit)
◡ = DO in the system with presence of cyanide

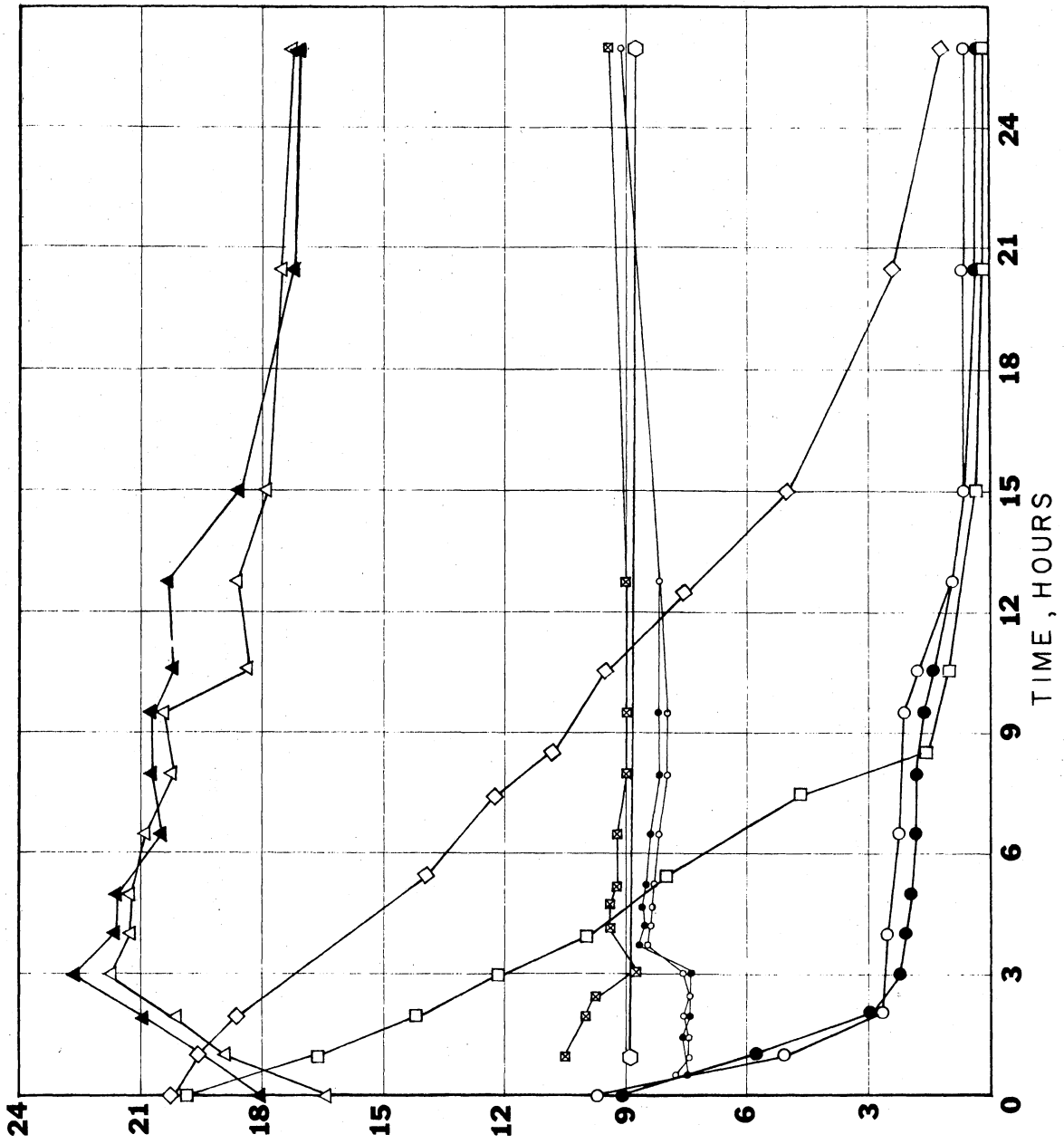
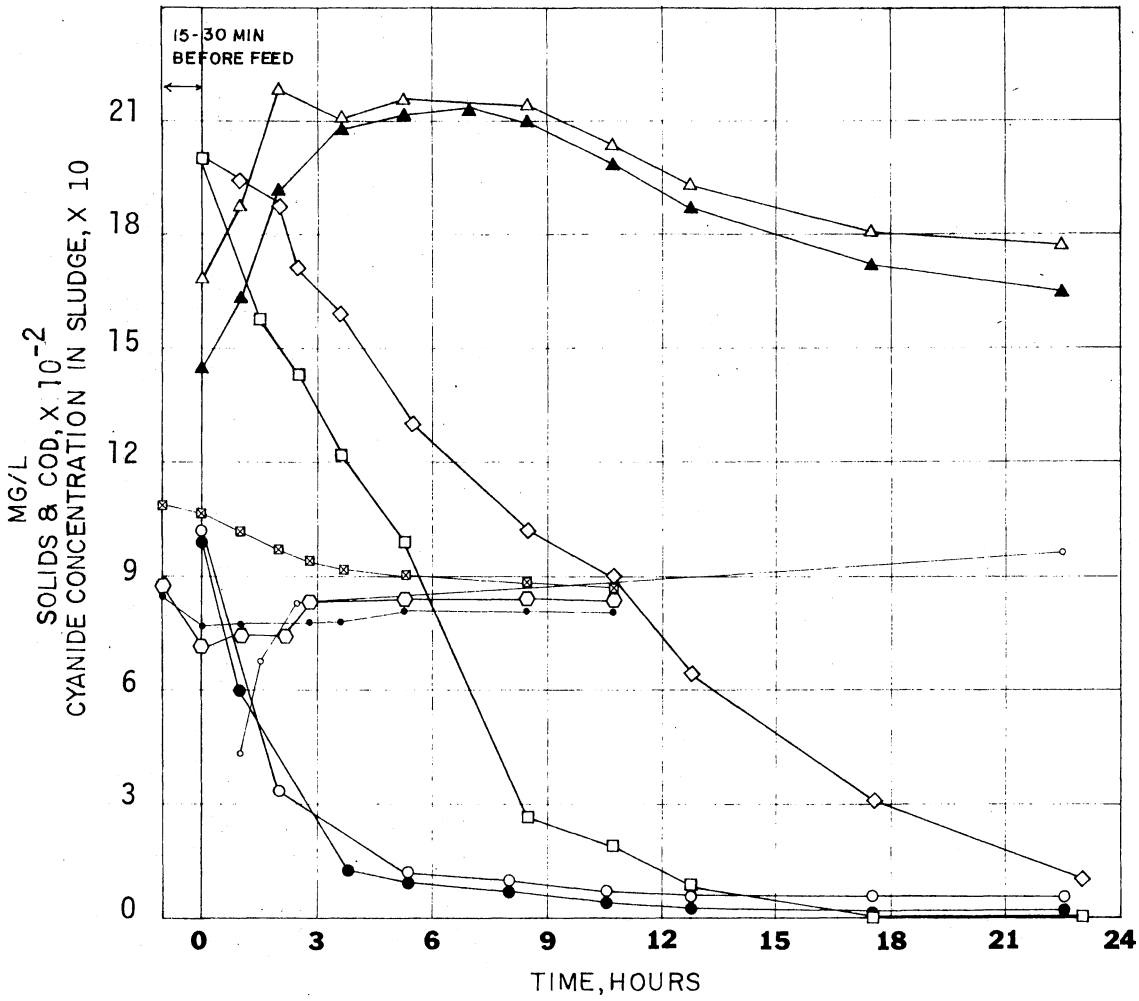

MG/L
SOLIDS & COD, × 10⁻²
CYANIDE CONCENTRATION IN SLUDGE, X 10
0
3
6
9
12
15
18
21
24
TIME, HOURS

Figure 19. Batch Experiment #6. Comparison of Removal of Cyanide in the Batch Systems, With and Without Biological Solids, at Three Different Concentrations for COD = 1000 ppm (Glucose), Airflow Rate = 500 cc/min, CN^- = 20 ppm. The First Condition Includes Cells, CN^-, and COD: the Second Condition Includes Cells and COD; the Third Condition Includes CN^- and COD

△ = biological solids in the system without presence of cyanide (control unit)
▲ = biological solids in the system with presence of cyanide
● = COD in the system without presence of cyanide (control unit)
○ = COD in the system with presence of cyanide
◇ = cyanide reduction in the system without biological solids
□ = cyanide degradation in the system with biological solids
› = cyanide concentration in the sludge
⊠ = DO in the system without presence of biological solids
• = DO in the system without presence of cyanide (control unit)
⬡ = DO in the system with presence of cyanide


15-30 MIN
BEFORE FEED
MG/L
SOLIDS & COD, X 10^{-2}
CYANIDE CONCENTRATION IN SLUDGE, X 10
0
3
6
9
12
15
18
21
24
TIME, HOURS

From Figure 18 it is seen that the unit which received glucose and cyanide maintained a cyanide level of about 0.9 mg/l in the cells. This is approximately the CN^- level found in the sludge of the continuous flow unit. Cellular CN^- was not run on the unit which received no CN^-. However, on the next day (Figure 19, experiment 6) when this sludge was the one dosed with CN^-, the CN^- concentration in the early hours of the experiment was much lower than 0.9 mg/l. Furthermore, it is seen that the CN^- level built up during the day to the 0.9 level. Thus, it appears that when CN^- is withheld for a short period, the residual cellular CN^- is metabolized or released into solution. Since only trace amounts of CN^- were found in the effluent for the continuous flow unit whereas approximately 1 mg/l was found in the sludge, it would appear that the cellular CN^- was biologically degraded in the pilot plant.

In these two experiments, DO was measured at regular intervals. The results provide assurance that the systems were in no way limited by low dissolved oxygen concentrations at this air flow rate, 500 cc/min, and rather high initial substrate concentration of 1000 mg/l glucose compared to the 500 mg/l feed concentration used in the earlier experiments. It is also interesting to note that the time for substrate removal was more or less the same at 500 mg/l COD level as it was at the higher organic loading, and the rate of change in CN^- degradation was approximately the same.

Growth Study

It was important to assess the effect the presence of CN^- had on the growth characteristics of the cells. However, since cyanide is

strippable, a simple shaker test was conducted prior to the growth study in order to determine the stripping rate of cyanide during the studies. The results of the test are shown in Figure 20. The experiment conditions were the same as those in the growth studies. Total volumes of 40 ml cyanide solution with and without buffer were placed into 250-ml Erlenmeyer flasks, then the flasks were put on an oscillating shaker (Eberbach) which was adjusted to 100 osc/min. The initial concentration of cyanide in solutions without buffer was 350 mg/l, and it required 23 hours to strip off all cyanide from the flasks. The initial concentration of cyanide in solutions with buffer was 250 mg/l (pH = 7.6), and all of the cyanide was stripped off in six hours in the flasks. Thus, if there is a lag period in growth of the cells, cyanide might be removed before growth is started.

Figures 21, 22, and 23 show the results of the growth studies with and without the presence of heavy metals. There was no lag period observed for the cells. The plotting of straight-line relationships of Monod's equation yielded a maximum specific growth rate, μ_{max} = 0.0625 hr^{-1}, a saturation constant, K_s = 31.3 mg/l, Y = 0.44 for the batch without the presence of heavy metals, and a μ_{max} = 0.078 hr^{-1}, K_s = 97.3 mg/l, Y = 0.53 for the batch with the presence of heavy metals. The results of the growth study show the inhibitory effect of cyanide ions on the growth of the cells. The maximum growth rate of cyanide utilizing cells is much lower (5 to 10 times) than values usually obtained for cells grown in the same medium without CN present.

Figure 20. Experimental Data for Stripping of Cyanide on the Shaker Test

○ = cyanide solution without buffer (pH = 10.8)
◇ = cyanide solution with buffer (pH = 7.6)

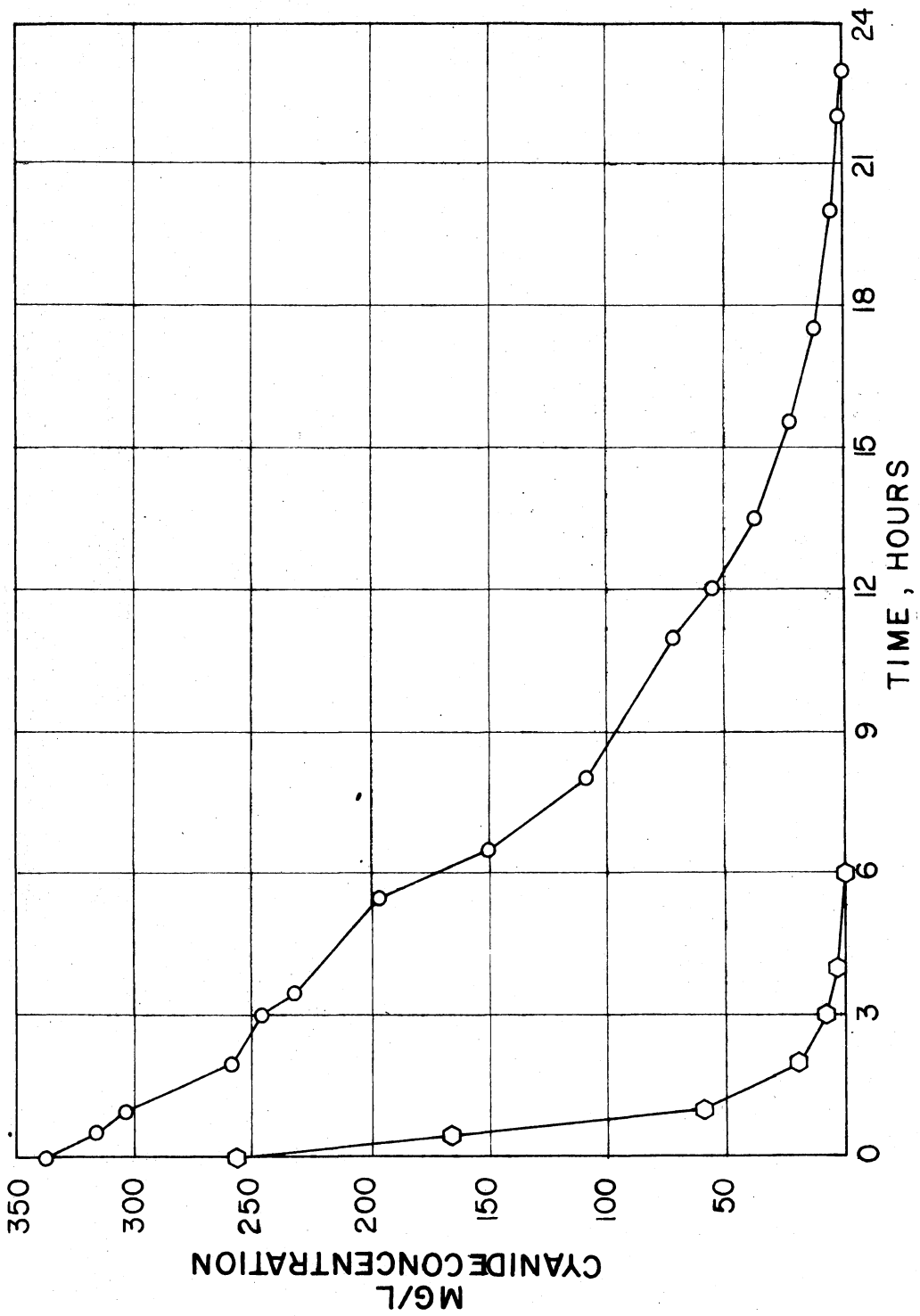

MG/L
CYANIDE CONCENTRATION
350
300
250
200
150
100
50
0
3
6
9
12
15
18
21
24
TIME, HOURS

Figure 21 (left). Growth Study With Presence of Cyanide.

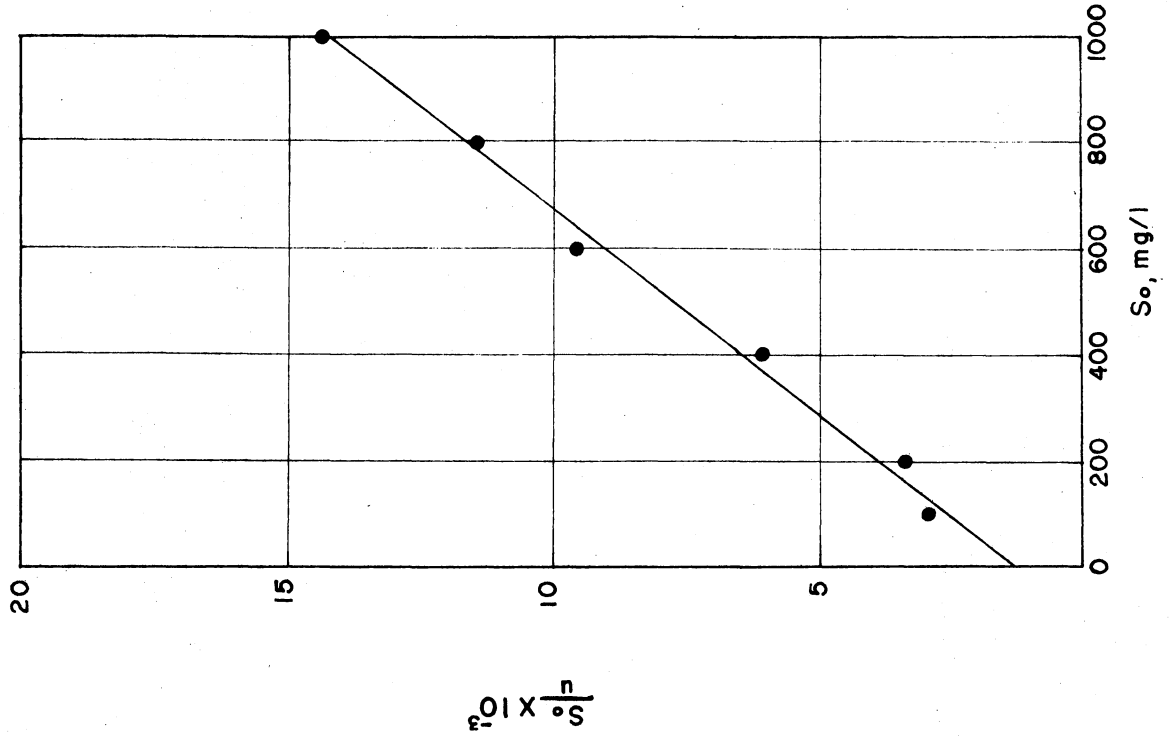
μ_{max} = 0.063
K_s = 31.2
Y = 0.44

The μ_{max} and K_s values are obtained from the plot of S_o/μ vs. $1/S_o$

Figure 21 (right). Growth Study With Presence of Both Copper and Cyanide Ions (Cu^{+2} : CN^- = 1 : 100)

μ_{max} = 0.078
K_s = 97.3
Y = 0.53

The μ_{max} and K_s values are obtained from the plot of S_o/μ vs. $1/S_o$


$\frac{S_o}{u} \times 10^{-3}$
20
15
10
5
0
200
400
600
800
1000
S_o, mg/l

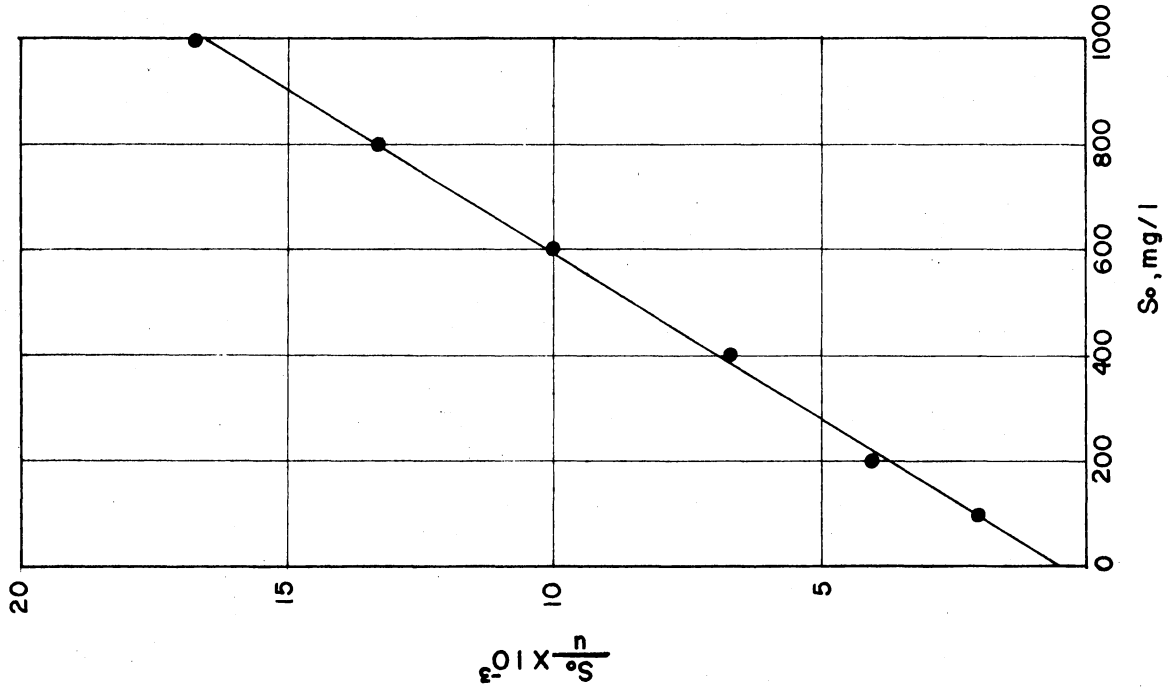

$\frac{S_o}{u} \times 10^{-3}$
20
15
10
5
0
200
400
600
800
1000
S_o, mg/l

Figure 22. Growth Study With Presence of Cyanide Ions (20 ppm) at Various Initial Substrate Concentrations

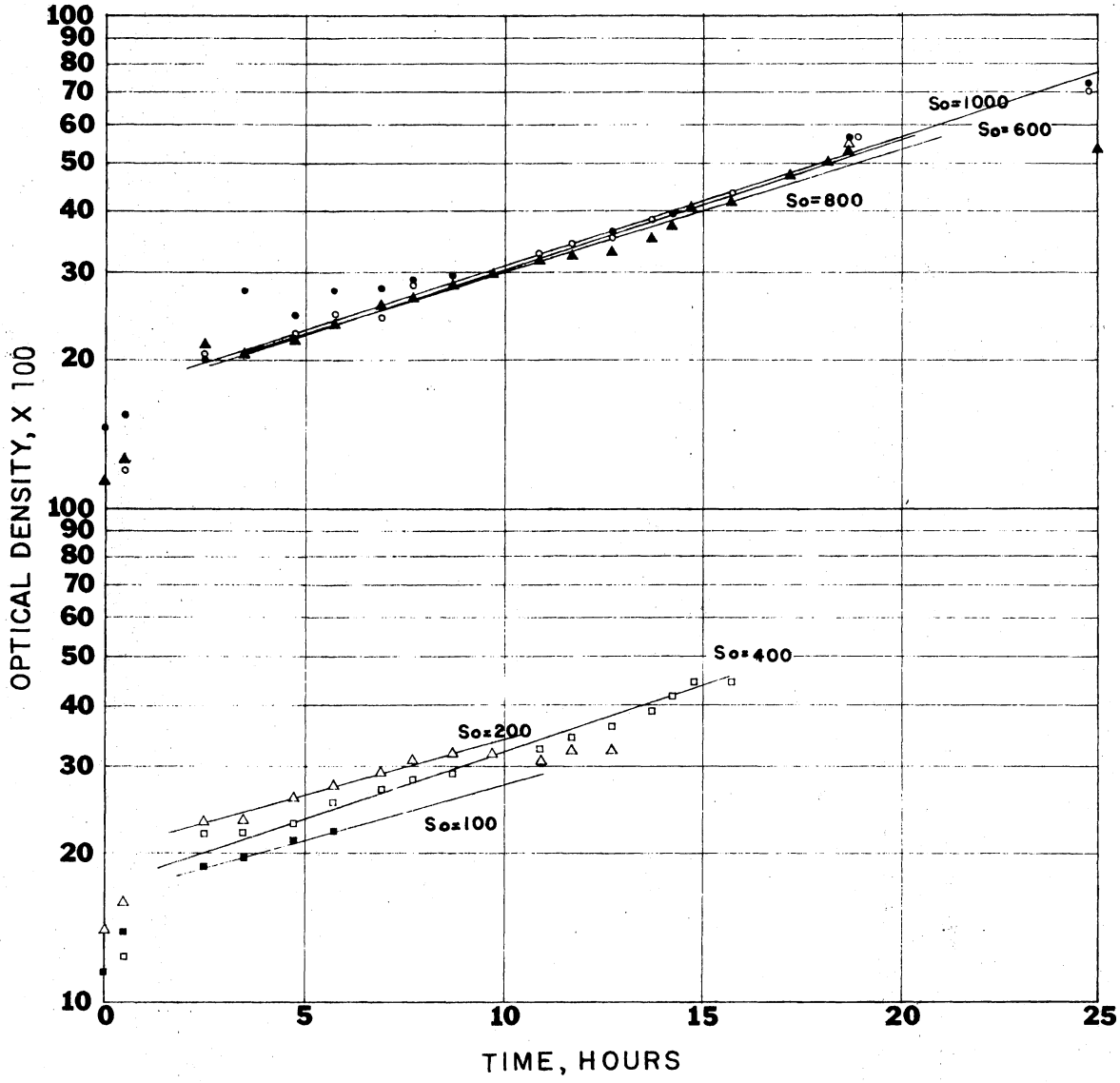
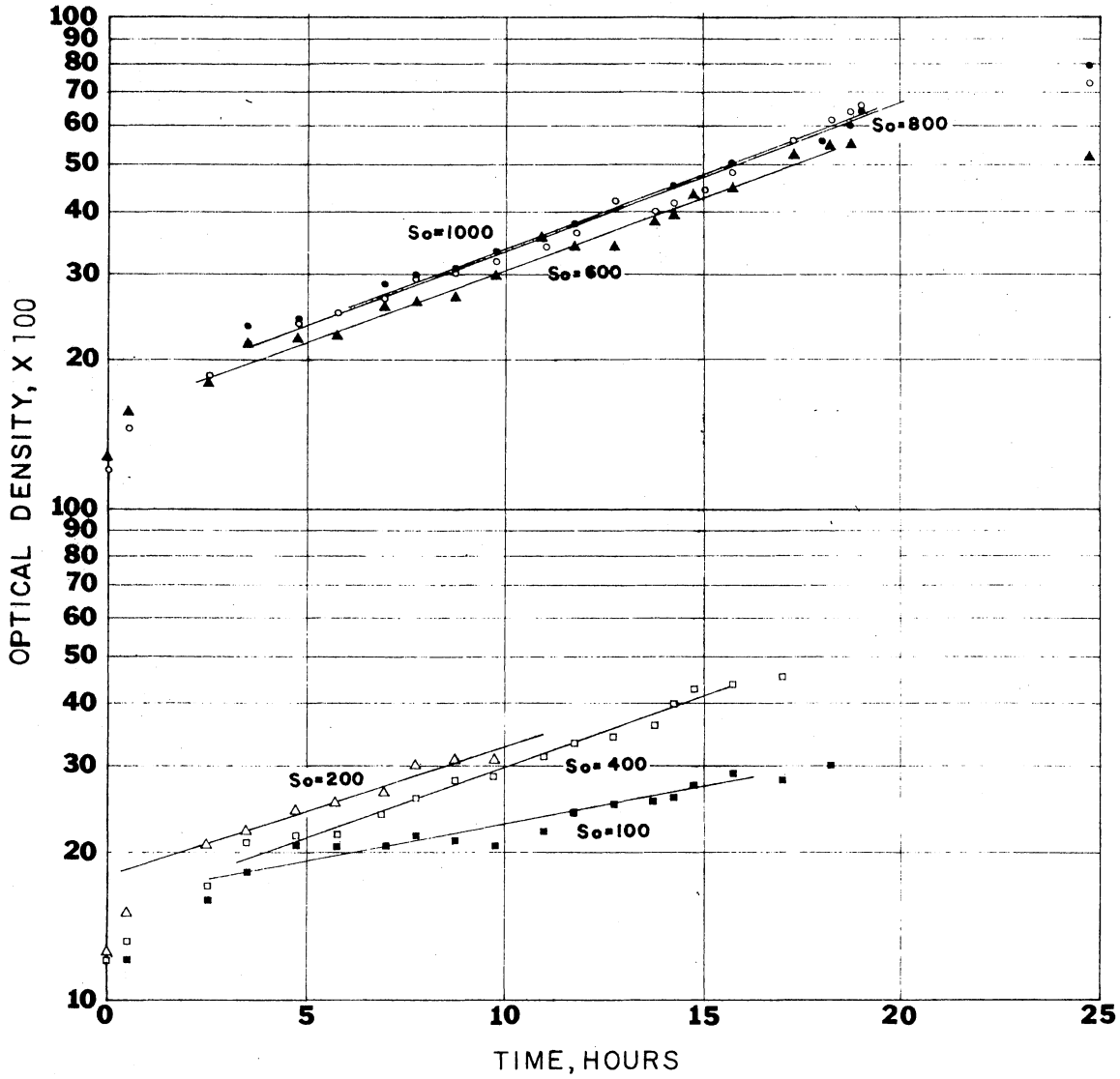

OPTICAL DENSITY, X 100
TIME, HOURS
So=1000
So=600
So=800
So=400
So=200
So=100

Figure 23. Growth Study With Presence of Both Copper and Cyanide Ions at Various (CN^-:Cu^{+2} = 1:100) Initial Substrate Concentrations


OPTICAL DENSITY, X 100
TIME, HOURS
So=1000
So=800
So=600
So=200
So=400
So=100
100
90
80
70
60
50
40
30
20
10
0
5
10
15
20
25

CHAPTER IV

CONCLUSIONS

Results of the investigation on the "hydrolytically-assisted" extended aeration process have led to the following conclusions:

1) The "hydrolytic-assist" extended aeration process will treat effectively a waste having a cyanide concentration of 20 mg/l. The system with 20 mg/l CN can be expected to produce an effluent of a quality comparable to that obtained without cyanide in the waste.

2) An acclimation period was required for each step increase of cyanide, and this affected the biodegradation performance. A three- to four-weeks' transition period was required.

3) Large increases in cyanide concentration in the feed tended to result in disruption of the system for a while, as manifested by the leakage of filtrate COD, NH_3-N, and cyanide in the effluent during the transition period. However, the system is capable of rapid recovery from a severe pulse shock of 50 mg/l of cyanide concentration.

4) With high biological solids concentration in the system, the loss of cyanide due to stripping can be minimized, thus reducing hazard to plant personnel.

5) Presence of cyanide in the sludge indicates that cyanide is taken up by the cells and then biodegraded. The amount of cyanide in the sludge will vary, but in these studies it was at an average level of 1 mg/l.

The following conclusions are made from the results of the investigation on the batch experiments:

1) Cyanide is degraded effectively by an acclimated activated sludge. However, the presence of cyanide does inhibit the performance of COD removal in the system even after prolonged acclimation.

2) The yield of cyanide acclimated sludge on glucose was in a normal range, $\pm$ 0.4, but the maximum growth rate was less than 0.1 hr^{-1}. This suggests that in cells which develop a tolerance and/or can break down CN^-, its presence none-the-less, most probably can be suspected to cause permanent interference with key pathways which control the rate of synthesis.

CHAPTER VI

SUGGESTIONS FOR FUTURE STUDY

Based on the findings of this study, the following suggestions are made for future investigation on the "hydrolytic-assist" extended aeration process for wastes containing cyanide:

1) Study the stability of the "hydrolytic-assist" extended aeration process for treatment of waste of higher cyanide content at organic loadings higher than 500 mg/l COD.

2) Since today most of the cyanide wastes originate in the electroplating and metal-treating industries which produce complex heavy metal cyanides, investigation of the biological treatability of complex cyanides in the hydrolytically-assisted extended aeration process is warranted.

3) Investigate the complex reactions and interactions among physiology, morphology, and biochemical aspects for a heterogeneous microbial population growing in the transition period. That is to say, attempt to isolate individual species from the system and study their growth singly and in mixture in cyanide-containing media.

4) Further studies of the extended aeration process with continuous external recycle of sludge instead of internal recycle by employing separate aeration and settling tanks.

5) More intense investigation of biological mechanisms of resistance to and detoxication of cyanides should be undertaken in both heterogeneous and pure culture systems.

BIBLIOGRAPHY

1. Manufacturing Chemists Association, "Sodium Cyanide, 'Chemical Safety Data Sheet SD-30,'" p. 15.

2. Pettet, A. E., and Wave, G. C., "Disposal of Cyanide Waste Water." Chem. Ind., 1232-1238 (1955).

3. Smith, Stuart E., Plating and Cyanide Wastes." Journal Water Pollution Control Federation, 44, 6, 1100-1104 (1972).

4. Gurnham, C. F., "Cyanide Destruction on Trickling Filters." Proceedings, 10th Industrial Waste Conference, Purdue University, p. 187 (1955).

5. Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 14th Edition: New York (1975).

6. Eyjolfsson, R.,"Recent Advances in the Chemistry of Cyanogenic Glycosides." Fortschr. Chem. Org. Naturst, 28, 74-108 (1970).

7. Conn, E. E., "Biosenthysis of Cyanogenic Glycosides." Biochemical Society Symposium, The Biochemical Society, London, Vol. 38, 277-502 (1973).

8. Barnes, G. E., "The Economics of Electroplating Wastes Disposal." Plating, 55, 727 (1968).

9. Dodge, B. F., and Reams, D. C., American Electroplaters' Society Research Report Serial No. 14, "Disposal of Plating Room Wastes, II. A Critical Review" (1949).

10. Scott, L. F., "Converting Cyanide Wastes Into Sodium Cyanide." U. S. Patent 31592,586 (1971).

11. Saito, T., et al, "Aeration of Cyanide Waste. II. Treatment of Cyanide Waste Using Newly Developed Aeration Apparatus." Osaka Kagyo Gijutsu Shikenij's Kiko (JAP.) 20-23 (1969); Water Pollution Abs. (G. B.),45, 1988 (1970).

12. Tallmadge, J. A., "Ion Exchange Treatment of Mixed Electroplating Wastes." Ind. and Engr. Chemistry, 6, 4, 419 (1967).

13. Walker, C. A., and Zabban, W., American Electroplating Society Research Serial No. 25, "Disposal of Plating Room Wastes. V. Treatment of Cyanide Waste Solutions by Ion Exchange." (1953).

14. Silman, H., "Treatment of Rinse Water From Electro-Chemical Processes." Metal Finishing, 69, 6-62 (1971).

15. Kuhn, A. T., "Electrolytic Decomposition of Cyanides, Phenols, and Thiocyanides in Effluent Stream." Literature Review, J. Appl. Chem. Biotechnol., 21, 2-29 (1971).

16. Leclerc, G., "Effluents From Surface Treatments; Problems and Solutions." Galoano (Fr.), 40, 39; Chem. Abs., 75, 9690 (1971).

17. Imai, Y., "Electrolytic Decomposition of Concentrated Cyanide Wastes." Kogyo Yosui (Jap.) (1970), Chem. Abs., 75, 9690 (1971).

18. Anon., "Electrolysis Speeds up Waste Treatment." Envir. Sci. and Technol., 4, 201 (1970).

19. Eiring, L. V., "Kinetics and Mechanism of Ozone Oxidation of Cyanide-Containing Waste Water." Tset Metally. Mosc. (USSR) 42, 12-73 (1969)., Water Pollution Abs. (G. B.), 43, 1989 (1970).

20. Fridman, I. D., et al., "Removal of Toxic Cyanide From Waste Water of Gold Extracting Mills." Sb. Mosc. Inst. Stali Splavor (USSR), 55, 106 (1969), Water Pollution Abs. (G. B.) 43, 1208 (1970).

21. Weirgbiki, T., et al., "Removal of Cyanides and Some Metal Ions From Waste Water Electrochemical Metal-Working." Caj. Woda. Tech. Sanit. (Pol.), 45, 101 (1971)., Chem. Abs., 75, 9689 (1971).

22. Zumbrunn, J. P., and Malafosse, J., "Elimination of Cyanides in the Waste Waters of the Metalurgical Industry." Intl. Congress on Ind. Waste Water, Stockholm, Sweden (1970), Water Pollution Abs. 2, 5, 71-5TF, 1068 (1971).

23. Henry, C., and Borglin, J. C., "Decyaniding With Peroxidized Products. Theory and Practice of Purification of Waste Water Containing Cyanide Compounds From the Mineral and Organic Industries." (EBE - DEAU (Fr.) 24, 331 (1971), Chem. Abs., 75, 1211 (1971).

24. Anon., "Solved With Simplicity." Chemical Week, p. 57, Nov. 21, (1953).

25. Dodge, B. F., and Zabgan, W., "American Disposal of Plating Room Wastes. IV. Batch Volatization of Hydrogen Cyanide." Plating, 38, 561 (1951).

26. Ridenour, G. M., Preliminary Report on Effect of Cyanide Case Hardening, Copper and Zinc Plating Wastes on Activated Sludge Treatment. Sewage Works Journal, 16, 774 (1944).

27. Pettet, A. E., and Mills, E. V., "Biological Treatment of Cyanides With and Without Sewage." J. Appl. Chem., 4, 434-444 (1959).

28. Nesbitt, J. B., "Aerobic Metabolism of KCN." Proceedings, 14th Industrial Waste Conference, Purdue University, 518 (1959).

29. Ludzack, F. J., and Schaffer, R. E., "Activated Sludge Treatment of Cyanide, Cyanate, and Thiocyanete." Proceedings, 14th Industrial Waste Conference, Purdue University, 547 (1959).

30. Howe, R. H. L., U. S. Patent #3,145,166, Disposal of Toxic Chemical Wastes Having a High Concentration of Cyanide Iron.

31. Howe, R. H. L., and Pardiso, S. M., "Chemical Properties of Digested Sludge and Their Useful Application in Waste Treatment." Proceedings, 17th Industrial Waste Conference, Purdue University, 258 (1962).

32. Ludzack, F. J., "Experimental Treatment of Organic Cyanides by Conventional Sewage Disposal Processes." Proceedings, 15th Industrial Waste Conference, Purdue University, 434 (1960).

33. Mikami, E., and Misono, T., "Microbial Purification of Some Specific Industrial Wastes. (XI). Effect of Heavy Metal Ions on Cyanide Waste Treatment and Control of the Treatment With Cyano-Sensor." J. Ferment. Technol., 46, No. 12, 1056-1066 (1968).

34. Howe, R. H. L., "Toxic Wastes Degradation and Disposal Process." Biochem., 37 (1969).

35. Shimizu, T., et al., "Microbial Treatment of Industrial Wastes Containing Cyanide. V. Kinetic Studies on Cyanide Degradation Reaction by Fusarium solani. Chem. Abs., 72, 311 (1970).

36. Atkinson, A., "Bacterial Cyanide Detoxification." Biotech. and Bioeng., XVII, 457-460 (1975).

37. Knowles, C. J., "Microorganisms and Cyanide." Bacteriological Review, 40, 642-680 (1976).

38. Howe, R. H. L., "Bio-destruction of Cyanide Wastes - Advantages and Disadvantabes." Int. J. Air Water Pollution, 9, 463-478 (1965).

39. Winter, J. A., "The Use of a Specific Actinomycate to Degrade Cyanide Waste." Proceedings, 18th Industrial Waste Conference, Purdue University, 703-716 (1963).

40. Ludzack, F. J., and Schaffer, R. B., "Experimental Treatment of Organic Cyanides by Conventional Sewage Disposal Processes." Proceedings, 14th Industrial Waste Conference, Purdue University, 54 (1959).

41. Dixon, D. M., and Webb E. C., The Enzymes. (2nd Ed.), New York: Academic Press, Inc., 338 (1964).

42. Hendrickson, H. R., and Conn, E. E., "Cyanide Metabolism in Higher Plants. IR. Purification and Properties of the B-Cyanoalanine Synthase of Blue Lupine. J. Biol. Chem., 244, 2632-2640 (1969).

43. Lambowitz, A. M., and Slayman, C. W., "Cyanide-Resistant Respiration in Neurospord crassa." J. Bacteriol., 108, 1087-1096 (1971).

44. Skowronski, B., and Strobel, G. A., "Cyanide Resistance and Cyanide Utilization by a Strain of Bacillus pumilus." Can. J. Microbiol., 15, 95-98 (1969).

45. Weston, J. A., Collins, P. A., and Knowles, C. J., "The Respiratory System of the Marine bacterium Beneckea natriegens. II. Terminal Branching of Respiration to Oxygen and Resistance to Inhibition by Cyanide." Biochim. Biophys. Acta, 368, 148-157 (1974).

46. Ware, G. C., and Painter, H. A., "Bacterial Utilization of Cyanide." Nature, 175, 900 (1955).

47. Howe, R. H. L., "Recent Advances in Cyanide Waste Reduction Practice." Proceedings, 18th Industrial Waste Conference, Purdue University, 690-705 (1963).

48. Ludzack, F. J., et al., "Biochemical Oxidation of Some Commercially Important Organic Cyanides. I. River Water Oxidation." Proceedings, 13th Industrial Waste Conference, Purdue University, 29 (1958).

49. Reddy, P. S., "Studies on Total Oxidation Process With Internal and External Sludge Recycle." Master's Thesis, Oklahoma State University (1976).

50. Saidi, H., "Studies on the Hydrolytically-assisted Extended Aeration Process and on Pre-hydrolysis of Sludge in Aerobic Digestion Processes." Master's Thesis, Oklahoma State University (1974).

51. Murthy, K. S., "Operational Performance and Nitrifying Characteristics of a Hydrolytically-assisted Extended Aeration Process at High Organic Loadings." Master's Thesis, Oklahoma State University (1974).

52. Roach, L. W., "Studies on Response of a Hydrolytically-assisted Extended Aeration Activated Sludge System and a Completely Mixed Once-through System to Various Types of Step and Cyclic Shock Loads." Master's Thesis, Oklahoma State University (1975).

53. Yang, P. Y., "Studies on Extended Aeration Activated Sludge and a Modification of the Process Employing Chemical Hydrolysis of Portions of the Return Sludge." PhD Thesis, Oklahoma State University (1972).

54. Scott, David, "Studies on the Performance of the Hydrolytically-assisted Extended Aeration Process as a Means of Treating Soluble Organic Waste Materials." PhD Thesis, Oklahoma State University (1973).

55. Porges, N., Pepinsky, J. B., Handler, N. V., and Hoover, S. R., "Biochemical Oxidation of Daily Wastes. I. Methods of Study." Sewage and Industrial Wastes, 22, 318-325 (1950).

56. Porges, N., Jasewicz, L., and Hoover, S. R., "Measurement of Carbon Dioxide Evolution From Activated Sludge." Sewage and Industrial Wastes, 24, 1091-1097 (1952).

57. Hoover, S. R., Jasewicz, L., Pepinsky, J. B., and Porges, N., "Assimilation of Dairy Wastes by Activated Sludge." Sewage and Industrial Wastes, 23, 167-173 (1951).

58. Porges, N., Jasewicz, L., and Hoover, S. R., "Aerobic Treatment of Dairy Wastes." J. Appl. Microbiol., 1, 262-270 (1953).

59. Kountz, R. R., and Fourney. C. Jr., "Metabolic Energy Balance in a Total Oxidation Activated Sludge System." Sewage and Industrial Wastes, 31, 819-826 (1959).

60. Symons, J. M., and McKinney, R. E., "The Biochemistry of Nitrogen in the Synthesis of Activated Sludge." Sewage and Industrial Wastes, 30, 874-890 (1958).

61. Busch, A. W., and Myrick, N., "Food-Population Equilibria in Bench-scale Bio-oxidation Units." J. Water Pollution Control Federation, 32, 949-959 (1959).

62. Washington, D. R., Hetling, L. J., and Rao, S. S., "Long-term Adaptation of Activated Sludge Organisms to Accumulated Sludge Mass." Proceedings, 19th Industrial Waste Conference, Purdue University, 655-666 (1964).

63. McCarty, P. L., and Brodersen, C. F., "Theory of Extended Aeration Activated Sludge." J. Water Pollution Control Federation, 34, 1095-1102 (1962).

64. Washington, D. R., and Symons, J. M., "Volatile Sludge Accumulation in Activated Sludge Systems." J. Water Pollution Control Federation, 34, Part 2, 767-789 (1962).

65. Ludzack, F. J., "Observations on Bench-scale Extended Aeration Sewage Treatment." J. Water Pollution Control Federation, 37, 1092 (1965).

66. Sawyer, C. N., "Milestones in the Development of the Activated Sludge Process." J. Water Pollution Control Federation, 37, 151-162 (1965).

67. Gaudy, A. F. Jr., Ramanathan, M., Yang, P. Y., and DeGeare, T. V., "Studies on the Operational Stability of the Extended Aeration Process." J. Water Pollution Control Federation, 42, 165-179 (1970).

68. Ramanathan, M., Gaudy, A. F. Jr., and Ragthaidee, W., "Response of Extended Aeration Activated Sludge to Quantitative Shock Loads." Proceedings, 19th Oklahoma Industrial Waste Conference, Oklahoma State University, Stillwater (1968).

69. Gaudy, A. F. Jr., Yang, P. Y., and Obayashi, A. W., "Studies on the Total Oxidation of Activated Sludge With and Without Hydrolytic Pre-treatment." J. Water Pollution Control Federation, 43, 40-54 (1971).

70. Yang, P. Y., and Gaudy, A. F. Jr., "Control of Biological Solids Concentration in the Extended Aeration Process." Proceedings, 28th Industrial Waste Conference, Purdue University (1973).

71. Yang, P. Y., and Gaudy, A. F. Jr., "Nitrogen Metabolism in Extended Aeration Processes Operated With and Without Hydrolytic Pre-treatment of Portaions of the Sludge." Biotechnology and Bioengineering, XVI, 1-20 (1974).

72. Obayashi, A. W., and Gaudy, A. F. Jr., "Aerobic Digestion of Extracellular Microbial Polysaccharides." J. Water Pollution Control Federation, 45, 1584-1594 (1973).

73. Gaudy, A. F. Jr., Manickam, T. S., Saidi, H., and Reddy, M. P., "Biological Treatment of Waste With High Ash Content Using a Hydrolytically-assisted Extended Aeration Process." Biotechnology and Bioengineering, XVI, 704-721 (1976).

74. Singh, T., and Patterson, J. W., "Improvement of the Aerobic Sludge Digestion Process Efficiency." J. Water Pollution Control Federation, 46, 1, 102-112 (1974).

75. Ford-Smith, M. H., and Phil, M. A. D., The Chemistry of Complex Cyanide. London: Her Majesty's Stationery Office, 1964.

VITA - 2

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