EFFECT OF SODIUM CUPROCYANIDE ON TRICKLING FILTER OPERATION

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Richard Winthrop Bradt, Jr.

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This is to certify that the

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Major professor

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By

RICHARD WINTHROP BRADT, JR.

A THESIS

Submitted to the College of Engineering
Michigan State University of Agriculture and
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the requirements for the degree of

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ABSTRACT

Considerable interest has developed during recent years in the biological oxidation of industrial wastes. Work has been done on trickling filters concerning the effects and the ultimate destruction of simple and complex cyanides common to metal finishing wastes. Little data has been compiled, however, on the effects and the ultimate fate of the heavy metals associated with these complex cyanides. This investigation was primarily concerned with establishing a material balance on the copper in sodium cuprocyanide [$Na_2Cu(CN)_3$] during its passage through a trickling filter.

Four small single-pass trickling filters, each three inches in diameter and two feet deep, were operated for three to four months. The feed was settled sanitary sewage, alone or with sodium cuprocyanide and caustic added to simulate electroplating wastes. The effluent from each trickling filter flowed into a separate settling tank. Analyses were made on both influent and effluent liquors for BOD, cyanide, and copper. Sludge samples from the final settling tanks were dewatered and analyzed for residual copper. These data were then compiled to illustrate the change in concentration of copper in the effluent liquor with respect to influent concentration and time.

The influents were fed to the trickling filters at a rate of 14 to 18 cubic feet per square foot per day. The BOD reduction averaged 80% on sewage alone with an organic loading of 127 pounds of BOD per 1000 square feet per day. At this organic loading, the sodium cuprocyanide concentration was gradually increased from 0 to 7.6 mg/L $(CN)^-$. The BOD reduction temporarily decreased to 37%, and then recovered to 55%, remaining constant to the end of the run.

Only traces of cyanide were found in the effluent at the low concentrations of sodium cuprocyanide initially present in the influent. The cyanide concentration in the effluent ultimately reached and remained at 2 to 2.5 mg/L $(CN)^-$, when the influent concentration reached 7.6 mg/L $(CN)^-$.

At an influent concentration of 7.6 mg/L $(CN)^-$, equivalent to 5.0 mg/L Cu, 80% of the copper passed through the trickling filters. This is far in excess of that associated with the cyanide remaining in the effluent. Sludge analyses indicated that high concentrations of copper appeared in the sludge. Upon reaching maximum influent cyanide concentration approximately 0.30% Cu was found in the dried sludge, and at the completion of the run approximately 1.50% Cu was present.

The filter growth showed no apparent visual changes attributable to the copper at any time during the experimental run. Although no samples of the filter slime were taken, it may be concluded that the concentration of copper in the slime is approximately equal to that in the sludge collected in the settling tanks. This appears to be a reasonable conclusion based on the continuous sloughing observed throughout the entire experimental run.

APPROVED: ______________________
Major Professor

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INTRODUCTION

INTRODUCTION

The discharge of cyanides and cyanide wastes directly into streams and municipal sewerage systems is a matter of grave concern. Only low concentrations can be permitted, owing to the toxic nature of these wastes.

The toxic effects of cyanide on human and animal life, even in extremely low concentrations, are well known. The heavy metals often associated with cyanides, particularly in electroplating wastes, are also toxic. Copper has been found to be toxic to fish in concentrations as low as one milligram per liter. Possibly more important than these direct toxic effects are the effects on microorganisms in streams and sewerage systems.

Sudden shock loads of cyanides can seriously inhibit the biological activity in a secondary treatment plant, allowing a heavy organic waste load to reach the river or stream. Similarly, in a stream, heavy metal salts and cyanides may immobilize the bacteria, retarding "self-purification" of the stream, and allowing it to become so polluted that it creates a public nuisance and health hazard. Such waters are often incapable of retreatment for human consumption by conventional means.

Recent studies have demonstrated that trickling filters may be a means of destroying cyanides alone or in the presence of sanitary sewage. These investigations (23) have established the method as yielding a 97 to 99.9% destruction of cyanide in solutions containing sodium, potassium, cadmium, and copper. Less is known about the toxic effects of metals present in complex cyanides during this type of treatment.

The present investigation is concerned with establishing a material balance on the copper in sodium cuprocyanide $[Na_2Cu(CN)_3]$ during its passage through a trickling filter.

SURVEY OF PREVIOUS WORK

SURVEY OF PREVIOUS WORK

Early interest in the effects of simple and complex cyanides on biological sewage treatment arose during the period of World War II, with expansion of the metal finishing and electroplating industry. Plants using cyanides had been able, previously, to dispose of wastes to normal watersheds or municipal systems, because adequate dilutions were obtained in most cases, and stream pollution was not of great public concern. Rapid expansion of these industries during World War II focused attention on this problem and hastened the definition of allowable limits for discharge of cyanide-bearing wastes to streams and municipal sewage treatment plants.

There are two predominant methods of aerobic biological treatment of sewage: The activated sludge process and the trickling filter. Both methods employ a zoogleal mass of microorganisms which oxidizes the organic matter. In the activated sludge process, a liquid suspension of the organisms is maintained in an aeration tank; while in the trickling filter the mass is supported on a stone or other filter medium.

The earliest reported work concerned the activated sludge process. In 1936, Wooldridge and Standfast (31) reported that 200 mg/L of cyanide or the vapors from solid potassium cyanide completely inhibited bacterial action.

In 1946, Nolte and Bandt (20) operated a modified method, known as the Madgeburg process, with butyrates or m-cresol as the organic substrate. They reported that the bacteria were inhibited by shock doses of 5 mg/L KCN, but subsequently recovered. At 62 mg/L, after acclimatization, the effluent was found to be free from cyanides and butyrates. When normal activated sludge was supplied in the recycle, 330 mg/L KCN did not interfere with oxidation of the butyrates. Similar results were reported using m-cresol as the organic substrate.

In 1947, Lockett and Griffiths (18) reported 5 mg/L HCN as being definitely inhibitory to activated sludge, and found acclimatization extremely difficult and only partially successful. They were able to acclimate activated sludge to 1 mg/L HCN and concluded that, in low concentrations, cyanide is inhibitory rather than lethal to bacterial life.

In 1949, Coburn (6) found that 5 mg/L HCN resulted in partial inhibition of activated sludge and that 20 mg/L HCN caused complete inhibition. The sludge subsequently recovered when the cyanide was withheld for a period.

The earliest reported work on the trickling filter process is that of Pettet and Thomas (24) in 1948. They noted that the BOD of the filter effluent was not affected by less than 1 mg/L HCN in the feed. Increasing the cyanide to 2 mg/L HCN had little effect on BOD but nitrate formation was somewhat retarded. The increase to 4 mg/L HCN in the feed resulted in an increased BOD in the effluent, and nitrification was more markedly retarded. Similar results were found at 10 mg/L HCN. These effects disappeared after the filter had been in contact with stable concentrations for a period of time, and the cyanides were destroyed to a considerable degree.

When the cyanide was increased to 30 mg/L HCN, nitrification was completely stopped. About two months were required for acclimatization at this concentration. Total nitrogen in the effluent was then found to be greater than in the control, presumably due to conversion of cyanide nitrogen.

In 1951, the Water Pollution Research Board (Great Britain) began a series of experiments which have continued to the present time. An initial objective was to determine the effects of simple and complex cyanides on trickling filters. Findings were reported in 1951 (8) from a series of small scale trickling filters operating on KCN and a number of the complex metal cyanides. The report indicated 1 mg/L HCN had no effect on effluent BOD, but the permanganate oxygen demand rose above that of settled sewage for a period of seven days. Upon an increase to 2 mg/L HCN, the effluent BOD increased, while the permanganate oxygen demand remained stable.

Some retardation of nitrification was observed and the filter returned to normal in about two weeks. Only traces of HCN, no more than 0.01 mg/L, appeared in the effluent from all the filters except those operating on potassium ferrocyanide. In the latter case, 0.2 to 0.3 mg/L HCN was consistently reported.

In 1952, the Water Pollution Research Board (9) reported findings based upon a continuation of the same series of experiments. They concluded that the complex cyanides of cadmium, zinc, and copper were similar to KCN in their effects on effluent quality, and that nearly complete destruction of cyanide was possible in concentrations up to 100 mg/L HCN. At 200 mg/L HCN, 80% destruction was not uncommon. At 100 mg/L HCN, from 50 to 100% of the nitrogen from the cyanide could be accounted for in the effluent as ammonia plus nitrite plus nitrate. Ferrocyanide, apart from the fact that nitrification was much diminished at concentrations above 40 mg/L HCN, differed completely in behavior from the other cyanides. It had no discernible effect on effluent BOD, and from 30 to 80% of the cyanide passed through the filter unchanged. The effect of nickelocyanide was intermediate between that of ferrocyanide and that of the less stable complexes.

In 1953, the Water Pollution Research Board (10) continued this series of studies with the revised objective of developing a suitable means of biologically treating cyanide-bearing wastes. Results reported at this time indicated that simple and complex cyanides could be nearly completely destroyed in a trickling filter operating in the absence of organic nutrient. Complete destruction continued even at a concentration of 160 mg/L HCN. The treatment of cuprocyanide and nickelocyanide was less successful, and only 20 to 30% of the cyanide in the ferrocyanide was destroyed.

A proportion of each of the heavy metals was found in solution in the respective filter effluents. The concentration of iron corresponded well with that calculated from the observed cyanide as ferrocyanide or ferricyanide. The concentration of other metals in the effluents was more than equivalent to the cyanide present.

In 1954, the Water Pollution Research Board (11) attempted to isolate some of the microorganisms present in a cyanide-acclimated filter in order to determine the mechanisms involved in the destruction of cyanide, and to determine the depths at which destruction was essentially complete. A trickling filter was operated in conjunction with a commercial firm, on influent composed of mixed complex cyanides in water solution. Satisfactory treatment was obtained; in fact the average concentration of cyanide in the effluent was less than would have been expected had 100% of the cyanides of potassium, zinc, and copper, and 80% of the ferrocyanide been destroyed. About 50% of the cyanide nitrogen appeared in the effluent as ammonia plus nitrite plus nitrate.

In 1954, Daus (7) reported data from an experimental run using two trickling filters each six feet deep. The results were in general agreement with previous data indicating a noticeable decrease in BOD reduction when cyanide in the influent exceeded 1 mg/L $(CN)^-$. Additional data obtained by culture growth of bacteria extracted from the filters indicated that cyanide toxicity to microorganisms is a function of the nutrient medium supporting these organisms. The cyanide toxicity involves increased lag periods rather than decreased population levels. Cyanide exerts a bacteriostatic action.

In 1954, Southgate (29) published a survey of current technology of the treatment of waste water containing cyanides. He particularly stressed the recently reported work by the Water Pollution Research Laboratory.

Similar data was presented in 1954 by Pettet and Mills (25) of the Water Pollution Research Board in which they emphasized the development of commercially feasible biological methods for the treatment of cyanide-bearing wastes. They reported recent success in the treatment of cyanide-bearing wastes in the absence of organic nutrient. Also presented was data indicating the development of a "carry-over" resistance to cyanides of up to two weeks, suggesting the possible use of a trickling filter in the bio-oxidation of cyanides intermittently present in a waste disposal system.

In 1955, Gurnham (16) presented a paper at the 10th Purdue Industrial Wastes Conference which summarized earlier work of the Water Pollution Research Board. Data concerning the effects of cyanide-bearing wastes on sewers and sewage treatment processes agrees with that presented here. Particular emphasis was placed upon cyanide destruction on trickling filters and the imminent development of commercial plants utilizing biological techniques to treat metal-finishing wastes.

Additional data indicated that a considerable amount of cyanide was converted to ammonia in the top foot of a 4-foot filter. Nearly all of the cyanide was destroyed at the two-foot level. It was noted that the $(CN)^-$ ion rather than the complex metallocyanide is the inhibitory agent. This explains why the more stable complex cyanides have less effect on sewage purification in a trickling filter than the simple cyanides at equivalent concentrations.

In 1955, the Water Pollution Research Board (12) ran a series of tests utilizing a fifteen-foot filter in an attempt to obtain a greater area utilization and possibly to exceed the accepted application rate of 4.5 cubic feet per square foot per day. It was found that cyanide in concentration of up to 68 mg/L HCN and flows of 12.3 cubic feet per square foot per day could be easily tolerated and that nearly complete destruction took place in the top 6.5 feet of the filter. They subsequently observed that the greatest concentration of a cyanide-destroying bacteria occurred at a depth of 5.5 feet.

In 1956, the Water Pollution Research Board (13) continued previous tests on a fifteen-foot trickling filter. They concluded that a greater capacity could not be attained by increasing the cyanide concentration in the feed beyond 60 mg/L HCN. They reported that at this concentration essentially complete destruction of cyanide was attainable at a feed rate of 60 cubic feet per square foot per day. They also reported that greater volumetric efficiency was possible in filters containing specially graded support mediums. A four-foot filter, using No. 7 British Standard Screen to three-sixteenths inch graded gravel was reported as successfully treating at least 12 cubic feet per square foot per day at a concentration of 56 mg/L HCN. Essentially complete destruction was reported under these conditions. This filter also operated satisfactorily on an intermittent basis, i.e. eight hours on stream and sixteen hours off, suggesting its adaptability to a process operating on one shift per day.

In 1957, the Water Pollution Research Board (14) operated an experimental pilot scale filter four feet in diameter and six feet deep, containing 2.8 cubic yards of three-eighths inch gravel. The results indicated that at least 21.6 cubic feet per square foot per day of sodium cyanide solution containing 60 mg/L HCN or 19.4 cubic feet per square foot per day of sodium cyanide feed containing up to 90 mg/L HCN could be treated under industrial conditions yielding an effluent containing less than 1 mg/L HCN.

In 1958, Ware (30) of the Water Pollution Research Board reported that the biological destruction of cyanide is affected by temperature. There is little effect in the range of 10° to 35° Centigrade, but at higher or lower temperatures, biological activity is inhibited.

EXPERIMENTAL PROCEDURES

EXPERIMENTAL PROCEDURES

Four laboratory trickling filters were set up and operated for a period of three to four months, using a feed stock of settled domestic sewage with simulated electroplating waste added in controlled quantity. Feed rates were controlled in the range of 14 to 18 milliliters per minute, equivalent to 14 to 18 cubic feet per square foot per day. Periodic samples of influent and effluent liquor were analyzed for those variables necessary to develop satisfactory material balances and control data.

The trickling filter units (Figs. I, II) were glass cylinders so packed as to make an effective bed 24 inches high and 3 inches in diameter, having a cross sectional area of 0.049 square feet. The filter media used was 12 by 12 millimeter Pyrex Raschig rings. These filters were placed on small settling tanks having an overflow weir as illustrated. A sample tap was provided for effluent liquor samples. Sludge samples were taken by decanting the liquor and recovering the wet sludge. The overflow provided a continuous discharge of effluent from the tanks.

The basic feed stock was domestic sanitary sewage, free from industrial wastes, obtained from the primary settling tanks at the East Lansing municipal sewage treatment plant. This sewage was continuously pumped into a large storage tank with overflow weir, located inside the laboratory building. The holding tank served to equalize short time fluctuations in organic content and other variables of the sewage. The individual trickling filter feed tanks were filled daily from this storage tank.

The required amounts of sodium cuprocyanide stock solution were added to the feed stock in the individual supply tanks and thoroughly mixed. The standard stock solution was a specially prepared and analyzed solution of sodium cuprocyanide in demineralized water containing one part of sodium hydroxide per 7.5 parts of the complex cyanide, to stabilize pH and prevent the formation and loss of hydrogen cyanide gas.

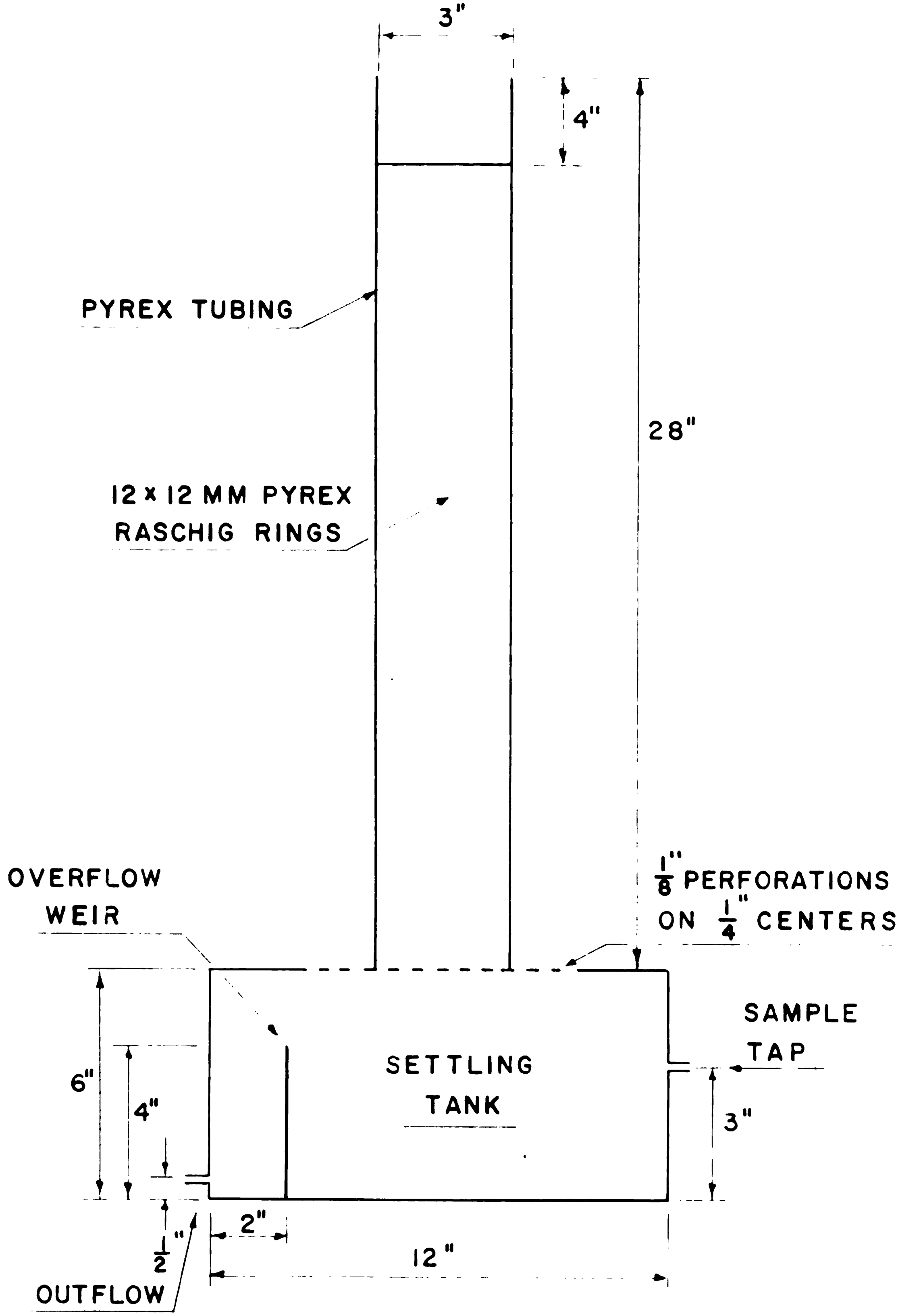


FIGURE 1

EXPERIMENTAL TRICKLING FILTER

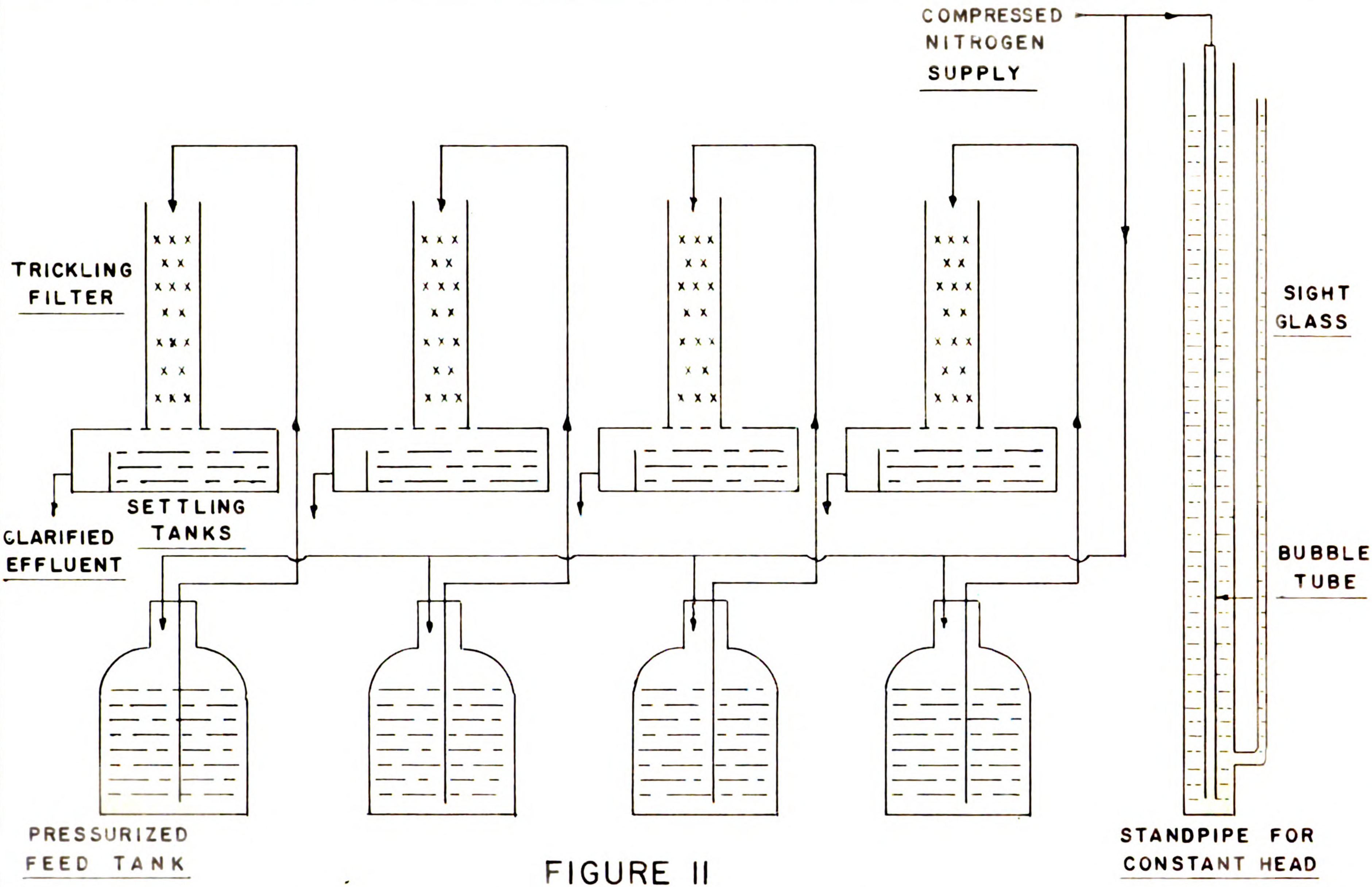


FIGURE II

FLOW DIAGRAM — TRICKLING FILTER

A constant flow of influent liquor to the filter was maintained by means of an atmosphere of nitrogen at a pressure of six feet of water. This pressure was controlled with a standpipe and bubbling tube. The flow was controlled with small glass nozzles located at each filter unit. Daily flow rate determinations were made by weighing the tared feed tanks before each refilling.

The filters were operated on settled sewage alone until a mature growth appeared on the filter media. Controlled amounts of cyanide stock solution were then added to give an initial concentration of 0.2 mg/L $(CN)^-$. This concentration was increased daily throughout the test period. Daily BOD determinations in duplicate were made on both influent and effluent samples, using the Winkler method with the Alsterberg azide (3) modification. Copper determinations were made frequently on effluent samples using the sodium diethyl-dithiocarbamate method (3, 22). Periodic cyanide determinations were made on effluent samples using the Leibig titration preceded by the Serfass (28) reflux procedure. The settled sludge samples were analyzed for copper by the method indicated above.

PRESENTATION OF RESULTS

PRESENTATION OF RESULTS

The four experimental trickling filters were initially packed with 3 by 3 millimeter glass Raschig rings. These proved undesirable as a support media, however, because as soon as a mature slime growth developed the void space became so restricted that ponding and localized clogging developed. Shortly thereafter, the growth became anaerobic and sloughed completely. Several attempts were made to operate these filters, with the same results.

The filters were then rebuilt using 12 by 12 millimeter glass Raschig rings to get a greater percent of voids and larger individual voids. The previously mentioned difficulties were eliminated for the most part and generally good operation resulted. After several weeks of operation on settled domestic sewage, excessive sloughing developed and BOD reduction became markedly depressed. As soon as the filter growth sloughed completely, a new growth appeared and performance quickly recovered to the level attained earlier.

At this time it was thought that the surface characteristics of the smooth glass rings might have been such as to provide poor anchorage between the filter growth and the support media, and that when the growth became sufficiently well developed it sloughed from the combination of weight and hydraulic action. An attempt was made to support this hypothesis and get better slime anchorage. The glass rings from one trickling filter were lightly etched with hydrofluoric acid. This filter was subsequently reactivated and although the sloughing was less pronounced than before, the improvement was not considered marked enough to support this hypothesis. This conclusion is supported by the data of Bryan (5), who reports development of good slime stability on smooth plastic surfaces.

At this point, siphons were added to the feed system to provide intermittent dosing of the filters. This modification markedly improved filter operation and the sloughing, while steady, never became excessive. The slime growth reached an equilibrium depth and good operations resulted.

During the start-up of Filter No. 3, and for a somewhat longer period on Filters 1, 2, and 4, the feed was settled domestic sewage. Trickling Filter No. 3 was acclimated to cyanide earlier than the other units since it was the first to have the mechanical improvements mentioned and subsequently developed a mature slime growth earlier. The influent feed rate was held relatively constant at 14 to 18 milliliters per minute, equivalent to 1400 to 1800 gallons per cubic yard per day. This is equivalent to most commercial high rate units operating at 20 to 25 million gallons per acre per day or 14 to 18 cubic feet per square foot per day.

The BOD of the influent throughout the entire experiment remained relatively constant at about 150 mg/L. During the periods when the filters were operating on domestic sewage alone, the mean effluent BOD was 30 mg/L (Fig. III). This represents a BOD reduction of 80% (Fig. IV), equivalent to most present day commercial filters operating at comparable feed rates.

Sodium cuprocyanide was added to the influent at a progressively increasing rate starting at an initial concentration of 0.2 mg/L $(CN)^-$ on one trickling filter (Fig. V). No marked change in BOD reduction was noted until the period from the 10th to the 14th days when the cyanide in the influent was increased from 2.5 mg/L to 6.0 mg/L $(CN)^-$. During this period the effluent BOD rose from 40 to 94 mg/L. Following this initial rise the effluent BOD fell gradually during the next 25 to 30 days to an average of about 68 mg/L and remained constant there throughout the remainder of the test. The BOD reduction during this period average 55% (Fig. VI). The cyanide concentration in the influent was increased until the 18th day, when it reached a maximum of 7.6 mg/L $(CN)^-$ and was held constant throughout the rest of the test.

This data appears to disagree with previously published data which states that a negligible interference with sewage purification occurs in an acclimated filter at cyanide concentrations of up to 50 mg/L HCN. It must be noted, however, that the other units were 4 feet deep and were operated at a feed rate of only 1.2 cubic feet per square foot per day. The rates used in the present work were

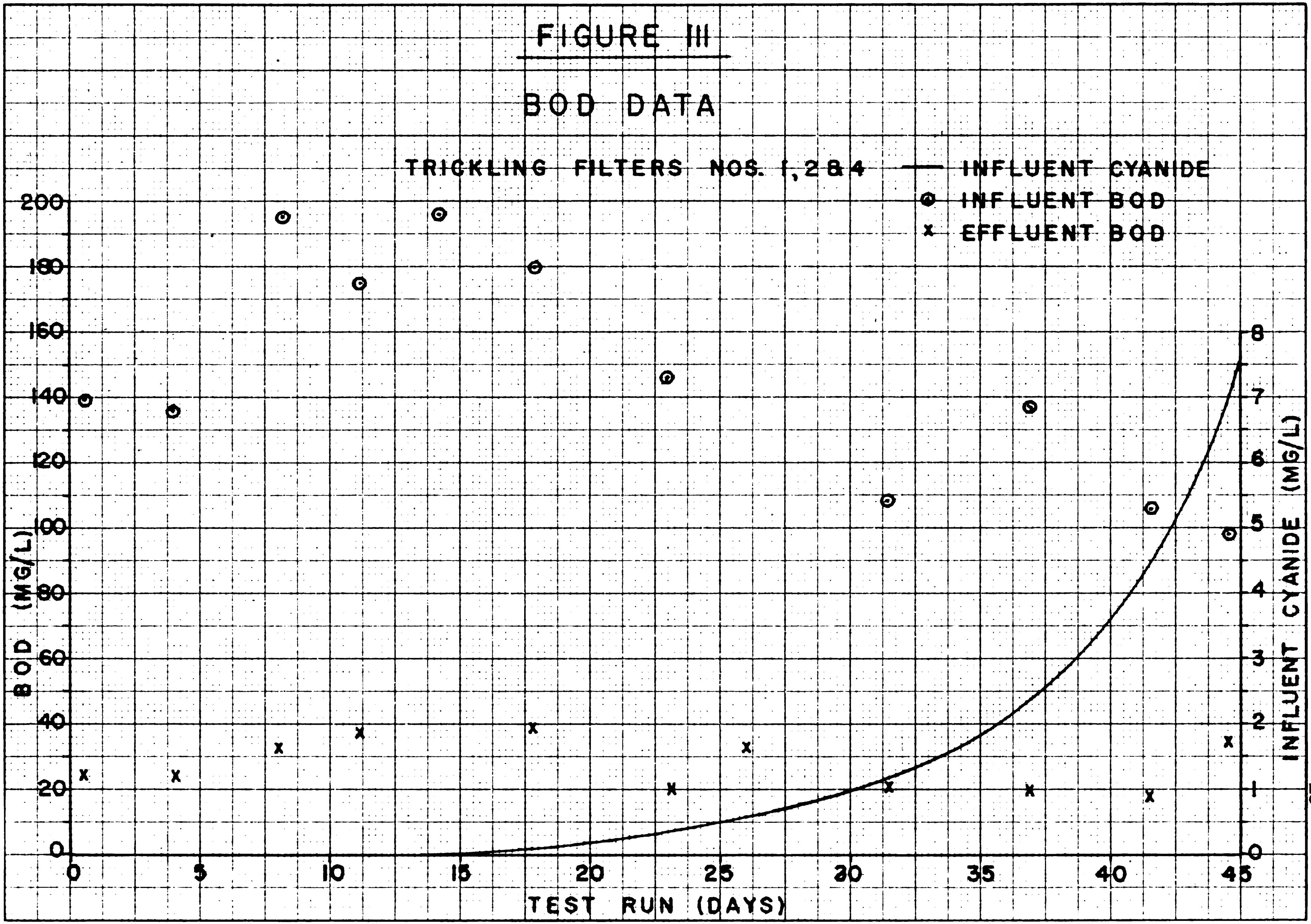


FIGURE III
BOD DATA
TRICKLING FILTERS NOS. 1, 2 & 4
INFLUENT CYANIDE
INFLUENT BOD
EFFLUENT BOD
BOD (MG/L)
INFLUENT CYANIDE (MG/L)
TEST RUN (DAYS)
0
20
40
60
80
100
120
140
160
180
200
1
2
3
4
5
6
7
8
5
10
15
20
25
30
35
40
45

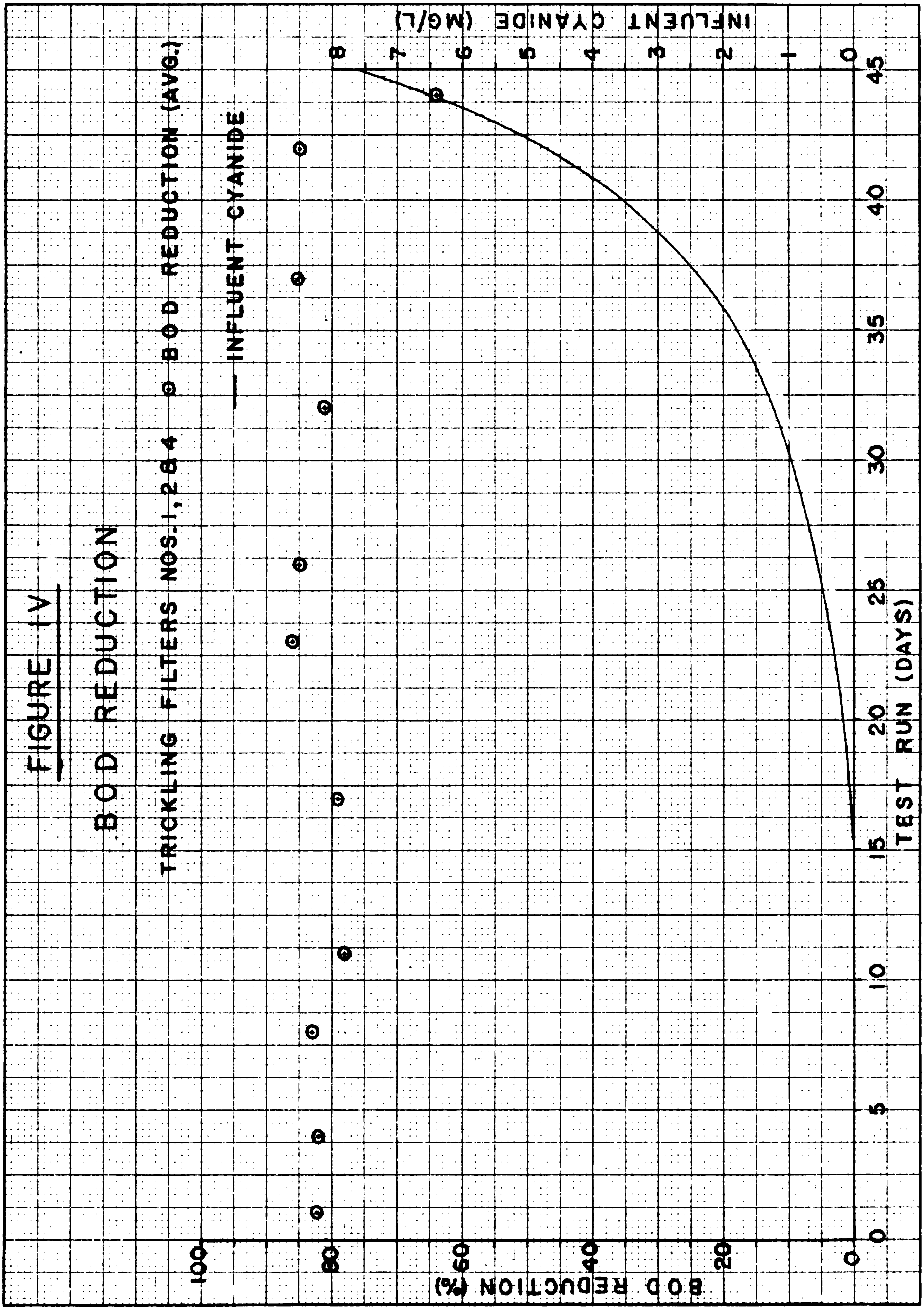


FIGURE IV

B O D REDUCTION

equivalent to 127 pounds of BOD per 1000 square feet per day and 6.7 pounds of $(CN)^-$ per 1000 square feet per day compared to 3.5 pounds of $(CN)^-$ per 1000 square feet per day in the earlier work. Reported on this basis the effect on sewage purification efficiency is not entirely unexpected.

Only traces of cyanide were detectable in the effluent during the early stages of the experimental run. After a period of operating at 7.6 mg/L $(CN)^-$ in the influent, the effluent contained from 2 to 2.5 mg/L $(CN)^-$. This represents a 60 to 75% reduction of cyanide at a loading of 6.7 pounds of cyanide as $(CN)^-$ per 1000 square feet per day. These high cyanide loadings suggest the possibility of development of a high efficiency trickling filter for industrial wastes, with increased depth and with a synthetic media having a high surface area and a high percentage of voids.

The primary objective of this investigation was to trace the copper in sodium cuprocyanide through a trickling filter and to determine its ultimate fate and its effect, if any, upon the filter itself. Figure VII and VIII show the concentration of copper in both influent and effluent liquors from all of the filter units. In Filter No. 3, the concentration of copper in the influent was increased rapidly to 5 mg/L and then held constant. The other units were fed settled domestic sewage for some time before copper was added to the influent. The concentration of copper was then increased gradually to 5 mg/L at the end of the test period. The effluent copper concentration increased with that of the influent and then remained quite constant at about 4 mg/L or 80% of the influent concentration. The occasional erratic results shown on Figure VII are attributed to the observed heavy sloughing of the filter at that time. No observable visual changes were noted during the period before and during the complex cyanide application.

Samples of the sludge removed from the trickling filter settling tanks at different times during the test run were analyzed for residual copper. Samples taken immediately as the influent copper concentration reached 5.0 mg/L indicated that copper was present in the sludge to the extent of 0.305 to 0.339 % Cu (dry basis). Toward

FIGURE VII

CYANIDE AND COPPER TEST DATA

TRICKLING FILTERS NOS. 1, 2 & 4

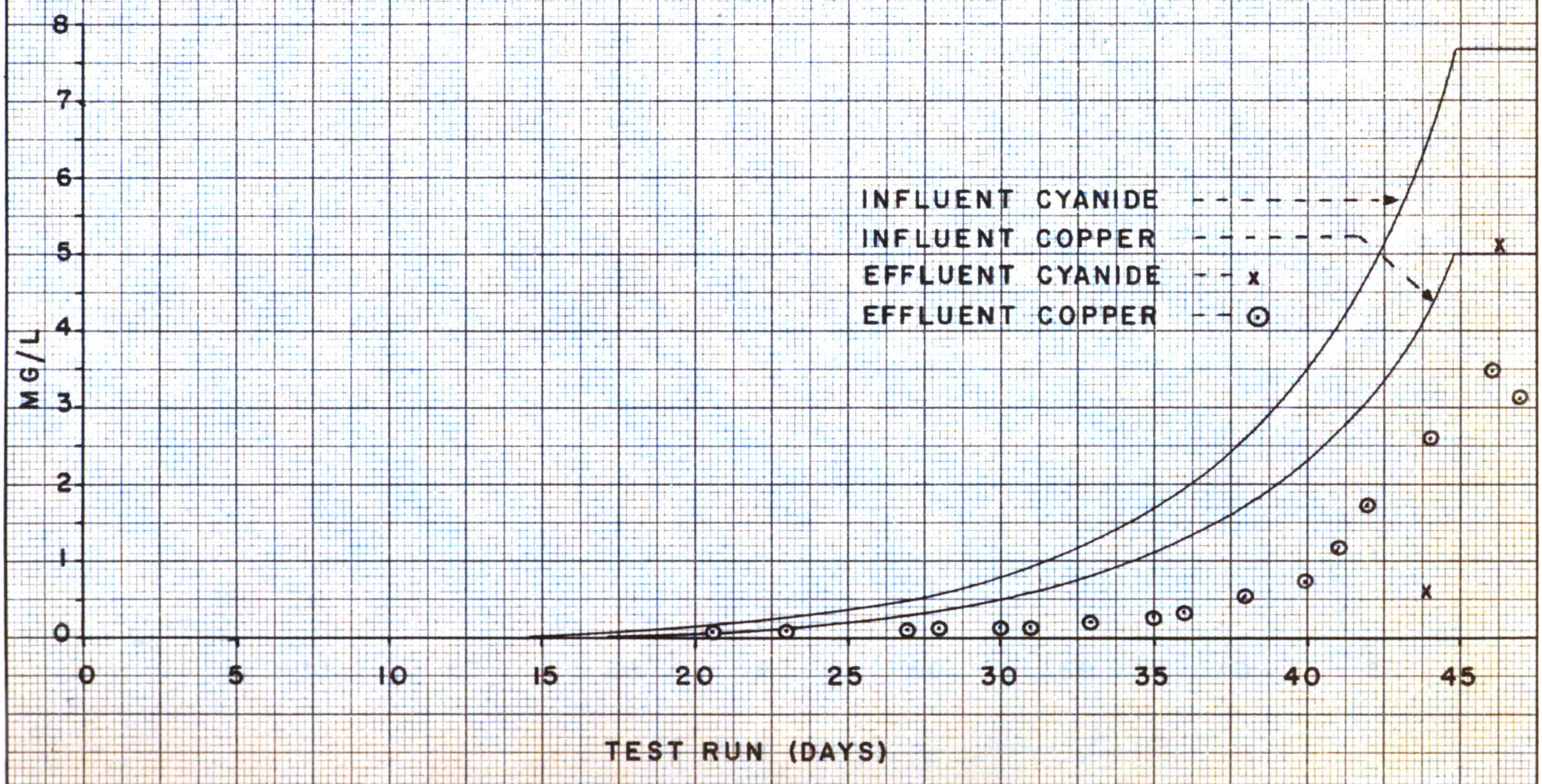
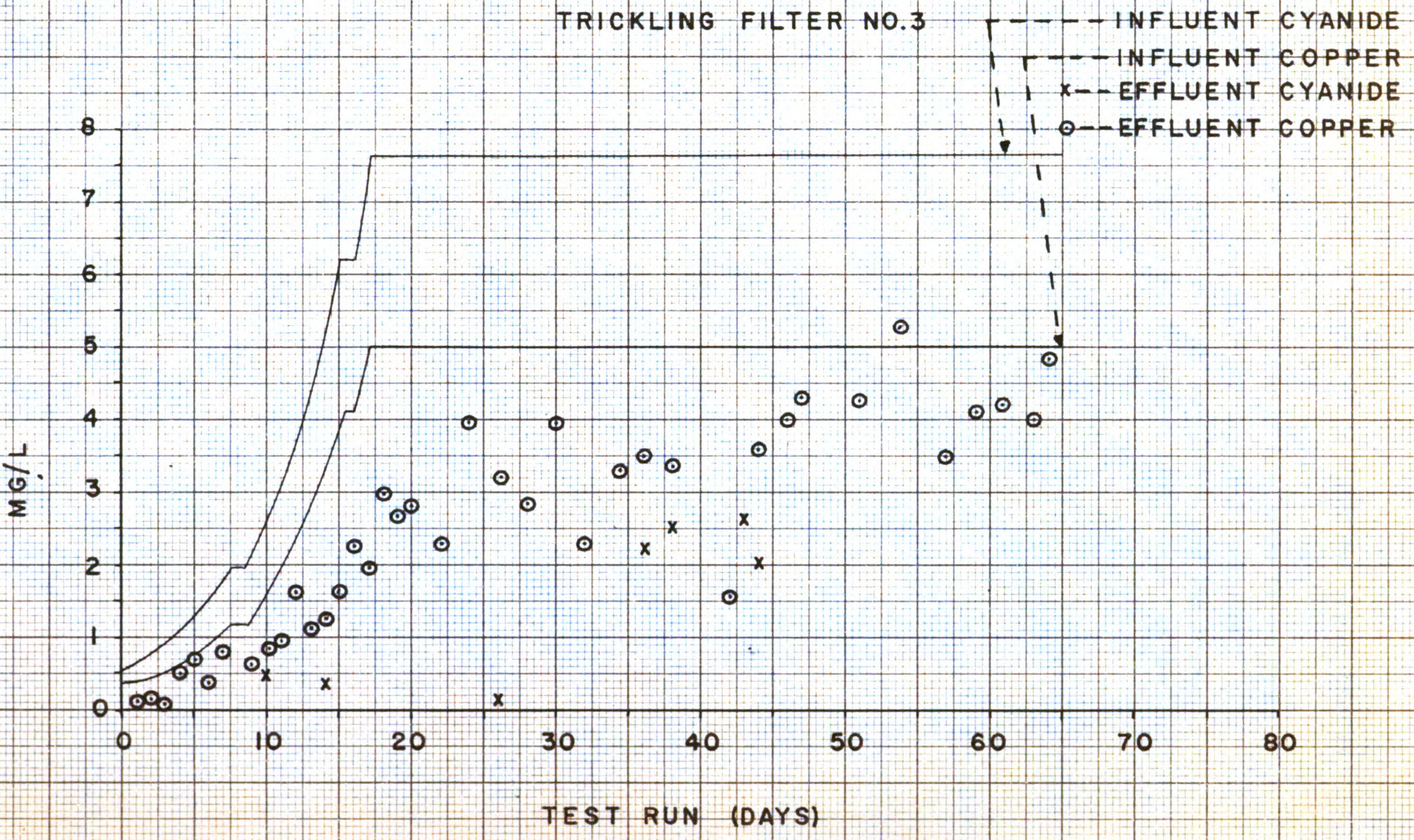


FIGURE VIII

CYANIDE AND COPPER TEST DATA

TRICKLING FILTER NO. 3



the end of the test period on Filter No. 3, additional sludge samples showed a copper concentration of 1.52 % Cu (dry basis).

No samples of the filter slime itself were taken for analysis; however the rate of sloughing suggested that no appreciable accumulation of copper would be found and that all of the copper would ultimately be found in the filter effluent, either in the liquid or the sludge.

SUMMARY

SUMMARY

This investigation was primarily concerned with establishing a material balance on the copper in sodium cuprocyanide [$Na_2Cu(CN)_3$] during its passage through a trickling filter. Data was also taken on BOD and cyanide reduction for comparison with results reported earlier by the Water Pollution Research Board of Great Britain. General agreement was found between the results of this investigation and those of the earlier work with few exceptions.

Four small scale trickling filters were operated for three to four months on a feed made up of settled domestic sewage and sodium cuprocyanide. Numerous analyses were made of both influents and effluents for BOD, copper, and cyanide. Sludge samples from the final settling tanks were dewatered and analyzed for residual copper. This data was then compiled to illustrate graphically changes in the concentration of copper in the effluent liquor with respect to influent concentration and time.

During the initial start-up of the trickling filters, considerable difficulty was encountered with ponding and localized clogging and the subsequent development of anaerobic conditions. Mass sloughing soon developed and the filters became biologically inactive until new biological growth developed.

This condition was substantially corrected by replacing the support media with larger Raschig rings having a greater percent of voids and larger individual voids. Further improvement was effected by incorporating intermittent siphons into the feed system to provide intermittent dosing of the filter units. The problems were attributed to the restrictively small void spaces together with heavy continuous hydraulic action.

Settled domestic sewage, alone or with simulated electroplating wastes, was fed to the single pass trickling filters at 14 to 18 cubic feet per square foot per day. The BOD reduction averaged 80% on sewage alone at an application rate of 127 pounds of BOD per 1000 square feet per day. The reduction decreased to 55% in the presence of 7.6 mg/L $(CN)^-$ at an application rate of 6.7 pounds of cyanide per 1000 square feet per day.

Only traces of cyanide were present in the effluent at the initial low concentration of sodium cuprocyanide added to the influent liquor. The cyanide concentration in the effluent ultimately reached and remained at 2 to 2.5 mg/L $(CN)^-$ when the influent concentration reached 7.6 mg/L $(CN)^-$.

Earlier investigations carried out by the Water Pollution Research Board of Great Britain found little or no lasting effect on BOD reduction until cyanide concentrations far in excess of those encountered in this work were reached. Some initial retardation of sewage purification was reported, but it disappeared within two to six weeks of operation. Similar initial retardation of BOD reduction was found in this investigation but full recovery was never experienced. This can probably be attributed to the higher organic loading (127 pounds BOD per 1000 square feet per day) and the shallow (2 feet) packed bed depths used in this investigation.

The Water Pollution Research Board also reported nearly complete (97 to 99.9%) destruction of cyanides on a 4 foot deep filter at application rates of up to 1.2 cubic feet per square foot per day sanitary sewage containing 150 mg/L HCN. Application rates of up to 60 cubic feet per square foot per day at 60 mg/L HCN were reported in the absence of organic nutrient on a fifteen foot trickling filter. They also reported that the greatest concentration of cyanide-consuming bacteria occurred at the 5.5 foot level in this latter work. It may be concluded that the reduced cyanide destruction experienced here is the combined result of the high application rate (14 to 18 cubic feet per square foot per day), the high organic loading (127 pounds of BOD per 1000 square feet per day), and, the reduced packed bed depths.

About 80% of the copper passed through the trickling filter at an influent concentration of 5 mg/L. This is far in excess of that associated with the undestroyed cyanide in the effluent, and is in general agreement with the earlier findings of the Water Pollution Research Board. Sludge analyses indicated high concentrations of copper at different times during the run. Immediately after acclimatization there was 0.305% to 0.339% Cu (dry basis) present and at the termination of the run there was 1.52% Cu (dry basis).

The filter growth showed no apparent visual effects of the copper at any time; however, it must be assumed that the copper not appearing in the effluent was retained for some time in the filter slime. An equilibrium must exist between the old and new growth such that the copper reaches a maximum concentration in the slime after a moderate period of operation. Since no actual slime analyses were made in the investigation, we can only presume that the copper concentration is approximately equal to that in the sludge. This seems a reasonable conclusion based on the continuous sloughing noted throughout the course of this work.

CONCLUSIONS

CONCLUSIONS

1. An 80% reduction of BOD was noted while operating on settled domestic sewage at 14 to 18 cubic feet per square foot per day. This indicates an excellent efficiency for high surface area synthetic filter media.

2. The BOD reduction decreased to 55% while operating on an influent containing sodium cuprocyanide equivalent to 7.6 mg/L $(CN)^-$.

3. The cyanide in sodium cuprocyanide was 60 to 75% destroyed at an application rate of 6.7 pounds of cyanide per 1000 square feet per day using an influent containing 7.6 mg/L $(CN)^-$.

4. Of the copper in sodium cuprocyanide 80% passed through the trickling filter and appeared in the effluent while operating on an influent containing sodium cuprocyanide equivalent to 5.0 mg/L Cu.

5. The sludge initially contained about 0.30% Cu (dry basis); this increased to about 1.52% Cu (dry basis) at the end of the run.

6. The copper had no discernible effect on the filter slime, and it was concluded from the uniform continuous sloughing that the copper concentration in the slime closely approximated that of the sludge discharged from the trickling filter.

SUGGESTIONS FOR FURTHER WORK

SUGGESTIONS FOR FURTHER WORK

It is recommended that future investigators study the practicability of using some of the newer synthetic trickling filter packings, particularly those of the plastic honeycomb type (5), in view of the high cyanide loading rates found allowable in this investigation. These media have a high percent of voids and large individual void spaces, in addition to a high surface area per cubic foot. It is expected that this would completely eliminate the clogging and resultant sloughing experienced in this work.

A further recommendation is to investigate the relationship between influent feed rates and packed bed depths with respect to cyanide destruction. This might prove particularly worthwhile on the type of media mentioned above, since it could well lead to extremely high filtration rates on relatively economical units.

Further work is desirable in obtaining slime samples at varying depths within a filter and analyzing for copper or the other heavy metals involved. Continuous sloughing precluded any marked copper accumulation in the slime during this work. However, less frequent sloughing and resulting heavier growth might well be expected using a media with larger void spaces.

Similar data to that reported in this investigation is probably desirable for other heavy metal cyanide complexes common to the plating industry. It is suggested however, that this be done on modified trickling filters using greater packed depths and an improved packing media as suggested above.

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APPENDIX

Page

TABLE I

TRICKLING FILTER NO. 1

DATE (1956)	INFLUENT (mg/L) BOD	CYANIDE	COPPER	FEED RATE (gal/yd^3 per day)	BOD	EFFLUENT (mg/L) CYANIDE	COPPER
Oct. 15	-	0.00	0.00	703	-	-	-
16	-	0.00	0.00	1237	-	-	-
17	137	0.00	0.00	2354	27	-	-
18	-	0.00	0.00	1550	-	-	-
19	-	0.00	0.00	1480	-	-	-
20	-	0.00	0.00	1990	-	-	-
21	134	0.01	0.01	1917	34	0.00	-
22	-	0.01	0.01	1359	-	-	0.01
23	-	0.01	0.01	1577	-	-	-
24	-	0.02	0.01	1553	-	-	-
25	195	0.02	0.01	1795	42	-	0.01
26	-	0.03	0.02	1407	-	-	-
27	-	0.03	0.02	1786	-	-	0.05
28	174	0.04	0.03	1456	37	-	-
29	-	0.04	0.03	1456	-	-	0.04
30	-	0.05	0.03	1529	-	-	-
31	195	0.06	0.04	1262	-	-	0.04
Nov. 1	-	0.06	0.04	-	-	-	-
2	-	0.08	0.05	1238	-	-	-
3	-	0.09	0.06	-	-	-	-
4	180	0.10	0.07	1941	31	-	0.04
5	-	0.12	0.08	2038	-	-	-
6	-	0.14	0.09	1844	-	-	0.07
7	147	0.18	0.12	1674	20	-	0.03
8	-	0.21	0.14	1844	-	-	0.11
9	-	0.26	0.17	1504	-	-	-
10	216	0.31	0.20	1456	44	-	0.08
11	-	0.37	0.24	1820	-	-	-
12	-	0.44	0.29	1430	-	-	0.04
13	-	0.53	0.36	1529	-	-	-
14	-	0.63	0.41	1893	-	-	0.14
15	108	0.76	0.50	1334	24	-	0.14
16	-	0.96	0.60	1432	-	-	-
17	-	1.10	0.72	1786	-	-	-
18	-	1.32	0.86	-	-	-	-
19	-	1.32	0.86	1868	-	-	0.32
20	137	1.56	1.02	1456	21	0.00	0.27
21	-	1.86	1.21	-	-	-	-
22	-	2.20	1.43	1692	-	-	0.43
23	-	2.62	1.71	1286	-	-	-

TABLE I (continued)

	24	-	2.90	1.89	-	-	-	-
	25	106	3.22	2.10	1698	11	-	0.84
	26	-	3.80	2.48	1795	-	-	-
	27	-	4.58	2.99	1698	-	-	1.68
	28	98	5.50	3.59	1359	44	-	-
	29	-	6.60	4.30	1698	-	-	2.69
	30	-	7.05	4.04	-	-	-	-
Dec.	1	143	7.65	5.00	1650	54	-	3.06
	2	-	7.65	5.00	1698	-	-	4.29

TABLE II

TRICKLING FILTER NO. 2

DATE (1956)	INFLUENT (mg/L) BOD	CYANIDE	COPPER	FEED RATE (gal/yd^3 per day)	EFFLUENT (mg/L) BOD	CYANIDE	COPPER
Oct. 15	-	0.00	0.00	1043	-	-	-
16	-	0.00	0.00	1650	-	-	-
17	137	0.00	0.00	1529	26	-	-
18	-	0.00	0.00	1334	-	-	-
19	-	0.00	0.00	1238	-	-	-
20	-	0.00	0.00	1601	-	-	-
21	134	0.01	0.01	1504	28	-	-
22	-	0.01	0.01	1359	-	-	0.01
23	-	0.01	0.01	1189	-	-	0.03
24	-	0.02	0.01	1189	-	-	-
25	195	0.02	0.02	1189	33	-	0.00
26	-	0.03	0.02	8492	-	-	-
27	-	0.03	0.02	1310	-	-	0.12
28	174	0.04	0.03	1577	42	-	0.00
29	-	0.04	0.03	1431	-	-	0.03
30	-	0.05	0.03	1553	-	-	-
31	195	0.06	0.04	1359	-	-	0.01
Nov. 1	-	0.06	0.04	-	-	-	-
2	-	0.08	0.05	1334	-	-	0.13
3	-	0.09	0.06	1504	-	-	-
4	180	0.10	0.07	995	29	-	0.14
5	-	0.12	0.09	1334	-	-	-
6	-	0.14	0.09	1456	-	-	0.05
7	147	0.18	0.12	1334	23	-	-
8	-	0.21	0.14	1650	-	-	0.05
9	-	0.26	0.17	1310	-	-	-
10	216	0.31	0.20	1553	27	-	0.06
11	-	0.37	0.24	1868	-	-	-
12	-	0.44	0.29	1237	-	-	0.05
13	-	0.53	0.36	1334	-	-	-
14	-	0.63	0.41	1601	-	-	0.20
15	108	0.76	0.50	1383	19	-	0.03
16	-	0.96	0.60	1577	-	-	-
17	-	1.10	0.72	1407	-	-	-
18	-	1.32	0.86	-	-	-	-
19	-	1.32	0.86	2111	-	-	0.14
20	137	1.56	1.02	1007	22	0.00	0.36
21	-	1.86	1.21	849	-	-	-
22	-	2.20	1.43	-	-	-	0.48
23	-	2.62	1.71	801	-	-	-

TABLE II (continued)

	24	-	2.90	1.89	-	-	-	-
	25	106	3.22	2.10	1553	16	0.60	0.39
	26	-	3.80	2.48	1213	-	-	-
	27	-	4.58	2.99	1383	-	-	1.92
	28	98	5.50	3.59	1359	29	-	-
	29	-	6.60	4.30	1771	-	-	2.45
	30	-	7.05	4.64	1553	-	-	-
Dec.	1	143	7.65	5.00	1650	54	-	3.65
	2	-	7.65	5.00	1698	-	6.00	2.73

TABLE III

TRICKLING FILTER NO. 3

DATE (1956)	INFLUENT (mg/L) BOD	CYANIDE	COPPER	FEED RATE (gal/yd^3 per day)	EFFLUENT (mg/L) BOD	CYANIDE	COPPER
Oct. 1	-	0.63	0.41	1553	-	-	0.11
2	-	0.75	0.48	1601	-	-	0.17
2	-	0.90	0.59	1698	-	-	0.14
3	77	1.09	0.77	1698	27	-	0.59
4	-	1.31	0.86	1674	-	-	0.71
5	-	1.58	1.03	1456	-	-	0.41
6	-	1.87	1.22	1456	-	-	0.85
7	-	-	-	-	-	-	-
8	-	2.12	1.38	1262	-	-	0.69
9	136	2.55	1.66	1189	39	0.50	0.88
10	-	3.06	2.00	1674	-	-	1.01
11	-	3.65	2.38	1529	-	-	1.73
12	-	4.42	2.88	1674	-	-	1.17
13	208	5.18	3.38	1917	94	0.40	1.29
14	-	6.20	4.05	1795	-	-	1.67
15	-	6.20	4.05	1189	-	-	2.29
16	-	7.47	4.88	1868	-	-	2.01
17	158	7.65	5.00	1747	76	0.00	3.01
18	-	7.65	5.00	1553	-	-	2.77
19	-	7.65	5.00	1359	-	-	2.89
20	-	7.65	5.00	1795	-	-	-
21	148	7.65	5.00	1844	77	-	2.37
22	-	7.65	5.00	1456	-	-	-
23	-	7.65	5.00	1359	-	0.00	3.99
24	-	7.65	5.00	1601	-	-	-
25	197	7.65	5.00	1723	70	0.20	3.25
26	-	7.65	5.00	1359	-	-	-
27	-	7.65	5.00	1359	-	-	2.85
28	182	7.65	5.00	1601	80	0.00	-
29	-	7.65	5.00	1335	-	-	3.99
30	-	7.65	5.00	1383	-	-	-
31	192	7.65	5.00	1626	72	0.00	2.37
Nov. 1	-	7.65	5.00	-	-	-	-
2	-	7.65	5.00	1577	-	-	3.35
3	-	7.65	5.00	2087	-	-	-
4	140	7.65	5.00	1504	60	2.33	3.55
5	-	7.65	5.00	2087	-	-	-
6	-	7.65	5.00	1650	-	2.50	3.39
7	144	7.65	5.00	1407	61	-	-
8	-	7.65	5.00	1674	-	-	3.01
9	-	7.65	5.00	1237	-	-	-

TABLE III (continued)

	10	216	7.65	5.00	1237	-	-	1.53
	11	-	7.65	5.00	1310	-	2.67	-
	12	-	7.65	5.00	1480	-	2.00	3.61
	13	-	7.65	5.00	1786	-	-	-
	14	-	7.65	5.00	1893	-	-	3.99
	15	108	7.65	5.00	1383	-	-	4.33
	16	-	7.65	5.00	1577	-	-	-
	17	-	7.65	5.00	1407	-	-	-
	18	-	7.65	5.00	-	-	-	-
	19	-	7.65	5.00	2111	-	-	4.29
	20	170	7.65	5.00	1007	65	0.00	-
	21	-	7.65	5.00	1560	-	-	-
	22	-	7.65	5.00	1490	-	-	5.33
	23	-	7.65	5.00	-	-	-	-
	24	-	7.65	5.00	-	-	-	-
	25	90	7.65	5.00	1553	50	-	3.49
	26	-	7.65	5.00	1213	-	-	-
	27	-	7.65	5.00	1626	-	-	4.13
	28	102	7.65	5.00	1359	71	-	-
	29	-	7.65	5.00	1771	-	-	4.25
	30	-	7.65	5.00	1553	-	-	-
Dec.	1	143	7.65	5.00	1650	76	-	4.03
	2	-	7.65	5.00	1698	-	-	4.89

TABLE IV

TRICKLING FILTER NO. 4

DATE (1956)	INFLUENT (mg/L) BOD	CYANIDE	COPPER	FEED RATE (gal/yd^3 per day)	EFFLUENT (mg/L) BOD	CYANIDE	COPPER
Oct. 15	-	0.00	0.00	1189	-	-	-
16	-	0.00	0.00	1844	-	-	-
17	137	0.00	0.00	1723	23	0.00	-
18	-	0.00	0.00	1577	-	-	-
19	-	0.00	0.00	1067	-	-	-
20	-	0.00	0.00	1990	-	-	-
21	134	0.01	0.01	1844	11	-	0.00
22	-	0.01	0.01	1577	-	-	-
23	-	0.01	0.01	1456	-	-	-
24	-	0.02	0.01	1504	-	-	0.00
25	195	0.02	0.02	1650	24	-	0.00
26	-	0.03	0.02	1213	-	-	-
27	-	0.03	0.02	1480	-	-	-
28	174	0.04	0.03	1844	33	-	-
29	-	0.04	0.03	1577	-	-	-
30	-	0.05	0.03	1601	-	-	-
31	195	0.06	0.04	1202	-	-	0.02
Nov. 1	-	0.06	0.04	-	-	-	-
2	-	0.08	0.05	1237	-	-	0.03
3	-	0.09	0.06	2135	-	-	-
4	180	0.10	0.07	1553	55	-	0.04
5	-	0.12	0.08	2184	-	-	-
6	0	0.14	0.09	1893	-	0.00	0.04
7	147	0.18	0.12	1723	16	-	-
8	-	0.21	0.14	1965	-	-	0.06
9	-	0.26	0.17	1577	-	-	-
10	216	0.31	0.20	1795	30	-	0.09
11	-	0.37	0.24	1456	-	-	-
12	-	0.44	0.29	1893	-	0.00	0.08
13	-	0.53	0.36	1116	-	-	-
14	-	0.63	0.41	1965	-	-	0.12
15	108	0.76	0.50	1310	22	-	0.19
16	-	0.96	0.60	1407	-	-	-
17	-	1.10	0.72	1286	-	-	-
18	-	1.32	0.86	-	-	-	-
19	-	1.32	0.86	1698	-	-	0.14
20	137	1.56	1.02	1140	18	0.00	0.22
21	-	1.86	1.21	970	-	-	-
22	-	2.20	1.43	-	-	-	0.51
23	-	2.62	1.71	825	-	-	-

TABLE IV (continued)

24	-	2.90	1.89	-	-	-	-
25	106	3.22	2.10	1650	23	0.52	0.62
26	-	3.80	2.48	-	-	-	-
27	-	4.59	2.99	1237	-	-	1.45
28	98	5.50	3.59	1359	32	-	-
29	-	6.60	4.30	1723	-	-	2.53
30	-	7.05	4.64	1698	-	-	-
Dec. 1	143	7.65	5.00	1140	52	-	3.47
2	-	7.65	5.00	1407	-	4.00	2.29

ANALYTICAL METHODS

ANALYTICAL METHODS

Routine daily analyses of biochemical oxygen demand (BOD) were performed following the methods outlined in Standard Methods (3) using the Alsterberg (sodium azide) modification. Three dilutions were made using dilution water seeded with 3 ml. of aged, settled sewage per liter. The results reported are the averages of all individual dilutions that showed a 40 to 90% depletion of initial dissolved oxygen.

Several common methods based on titration and colorimetry are available for the analysis of cyanides. Many of these, however, are difficult to apply to the routine laboratory analysis of samples containing sewage and industrial wastes. Three of these methods (19) have been found to be the most effective on industrial wastes containing domestic sewage. Two of these: The benzidine-pyridine method of Aldridge (1, 2) as modified by Nusbaum and Skupeko (21) and the pyridine-pyrazolone method of Epstein (15), while satisfactory, require fresh reagents daily to insure reliable results. Since only occasional determinations were to be made, these methods were not seriously considered.

The modified Leibig titration using the p-dimethyl-amino benzalrhodanine indicator of Ryan and Culshaw (27) and outlined by Ruchhoft (26) was decided upon as being the most adaptable to this project. This method has been established by Serfass (28) to be preferable to the colorimetric techniques in the anticipated range of 1 mg/L or greater. The titration was preceded by the reflux distillation technique of Serfass. This method of isolation has been found to yield high recoveries of HCN on simple and most complex cyanides. Sewage and river water samples containing low concentrations of interfering compounds have consistently yielded cyanide recoveries of 95% using the reflux distillation for isolation. Some complex salts including those of copper require a second hour of distillation for their recovery (19).

Another isolation procedure, Kruse and Mellon (17), is available for separation of the cyanides from certain organic compounds which can destroy the cyanides during distillation. This technique utilizes solvent extraction with 2,2,4-trimethylpentane (iso-pentane), hexane, or chloroform (preference in the order named). It has been very successful in removing organic material without lowering cyanide recovery.

This extraction technique was not employed in this research since the required analyses were to be made on stock solutions containing no organic matter and on trickling filter effluents which ultimately proved to be low in organic compounds. The possibility of interference with cyanide recovery from the low concentration of organic matter present in the trickling filter effluents was neglected since this data was to be used only as a measure of filter performance. Prior data of Daus (7) and Ludzack (19) have established the normal range of cyanide to be expected in the filter effluent under comparable conditions.

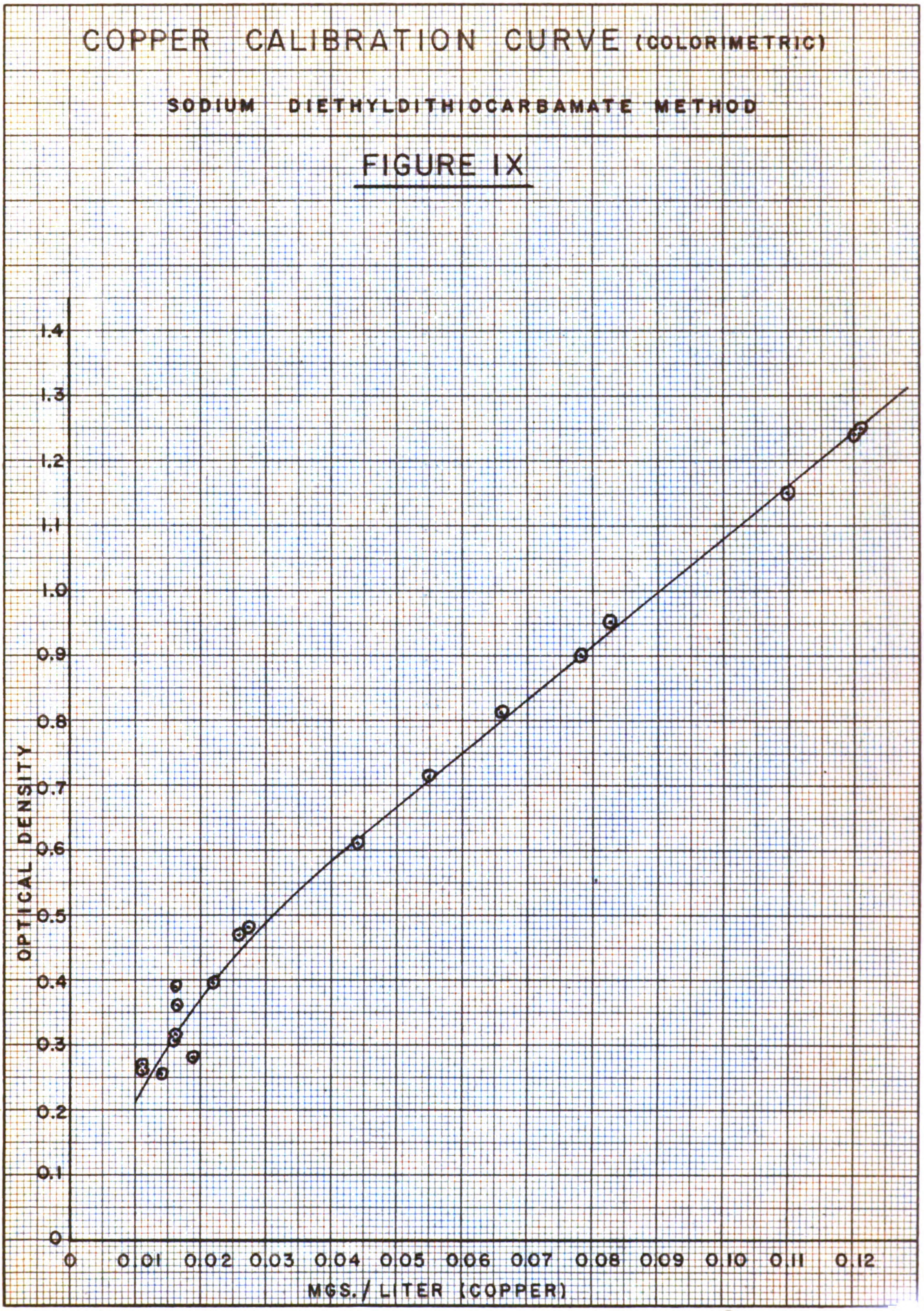
The copper determinations were made using the well established colorimetric method as outlined in Standard Methods (3) and Procedures for Analyzing Metal Finishing Wastes (22). The sample is treated with hot concentrated acids to remove organic matter and the copper is extracted with mercaptobenzothiazole and chloroform. Sodium diethyl dithiocarbamate is added to the chloroform extract to produce a strongly colored orange-yellow complex which is measured on a colorimeter or filter photometer. Figure IX shows that this method yields excellent results in the absence of bismuth, mercury, silver, and lead. There is at least a 98% recovery with a standard deviation of plus or minus 1 to 4% in the presence of small concentrations of other metallic ions.

The liquid samples for copper analysis were treated as above: however, the sludge required additional pretreatment. Sludge samples were dewatered in a suction filter, and then treated with acid as above. A second sample was weighed, dried to constant weight in oven, and reweighed to provide a correction for entrained liquid. Liquid removed in the filter was analyzed for copper and a true dry sludge analysis calculated.

TABLE V

COPPER CALIBRATION DATA

Sample No.	mg of Cu per liter	Optical Density
1	0.0110	0.260
2	0.0140	0.255
3	0.0160	0.390
4	0.0166	0.360
5	0.0221	0.395
6	0.0260	0.470
7	0.0276	0.480
8	0.0310	0.510
9	0.0442	0.610
10	0.0450	0.630
11	0.0552	0.715
12	0.0650	0.790
13	0.0662	0.810
14	0.0780	0.900
15	0.0828	0.950
16	0.0840	0.950
17	0.1100	1.060
18	0.1104	1.150
19	0.1200	1.240
20	0.1214	1.250
21	0.1370	1.380
22	0.1546	1.500
23	0.1656	1.650


COPPER CALIBRATION CURVE (COLORIMETRIC)
SODIUM DIETHYLDITHIOCARBAMATE METHOD
FIGURE IX
OPTICAL DENSITY
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
0.11
0.12
MGS./ LITER (COPPER)