190/6-1-84 OS ①

DR# 0032-9

Energy

FOSSIL

DOE/PC/30233-T4
(DE84008300)

TREATMENT OF COKE-OVEN WASTEWATER WITH THE POWDERED ACTIVATED CARBON-CONTACT STABILIZATION ACTIVATED SLUDGE PROCESS

Final Report

By
Makram T. Suidan
Mark A. Deady
Chai-Sung Gee

November 1983

Work Performed Under Contract No. FG22-80PC30233

University of Illinois at Urbana-Champaign
Urbana, Illinois

Technical Information Center
Office of Scientific and Technical Information
United States Department of Energy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A07
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts (ERA); Government Reports Announcements* and Index (*GRA* and I); *Scientific and Technical Abstract Reports (STAR);* and publication NTIS-PR-360 available from NTIS at the above address.

DOE/PC/30233-T4
(DE84008300)
Distribution Category UC-90i

FINAL REPORT

TREATMENT OF COKE-OVEN WASTEWATER WITH THE POWDERED ACTIVATED CARBON-CONTACT STABILIZATION ACTIVATED SLUDGE PROCESS

Makram T. Suidan
Mark A. Deady
Chai-Sung Gee

Department of Civil Engineering
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

November 1983

PREPARED FOR THE
UNITED STATES DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
UNDER GRANT NUMBER DE-FG22-80PC30233

ABSTRACT

The objective of the study was to determine optimum parameters for the operation of an innovative process train used in the treatment of coke-oven wastewater. The treatment process train consisted of a contact-stabilization activated sludge system with powdered activated carbon (PAC) addition, followed by activated sludge nitrification, followed by denitrification in an anoxic filter. The control and operating parameters evaluated during the study were: (a) the average mixed-liquor PAC concentration maintained in the contact-stabilization system, (b) the solids retention time practiced in the contact-stabilization system, and (c) the hydraulic detention time maintained in the contact aeration tank.

Three identical treatment process trains were constructed and employed in this study. The coke-oven wastewater used for this investigation was fed to the treatment units at 30 percent strength. At that dilution, the wastewater had average concentrations of chemical oxygen demand, dissolved organic carbon, ammonia-nitrogen, cyanide and thiocyanate of 1,240, 365, 995, 630 and 345, respectively.

The first part of the study was devoted to determining the interactions between the mixed liquor PAC concentration and the solids retention time in the contact-stabilization tanks. To achieve this end, average mixed liquor PAC concentrations of 0, 980 and 1,960 mg/ℓ were maintained in the contact-stabilization system, while the performance of the system at contact-stabilization solids retention times of 10, 20 and 30 day was evaluated at each carbon level. The general finding of this part of the study was that optimum overall system performance is attainable when the highest sludge age (30 day) and highest mixed liquor PAC concentration were practiced.

During the second phase of the study, all three systems were operated at a 30 day solids retention time while different detention times of 1, 2/3 and 1/3 day were evaluated in the contact tank. PAC addition rates were maintained at the former levels and, consequently, reduced contact times entailed higher mixed liquor carbon concentrations. Once again, the system receiving the highest PAC addition rate of PAC exhibited the best overall performance. This system exhibited no deterioration in process performance as a result of decreased contact detention time.

ACKNOWLEDGMENTS

The authors wish to acknowledge the numerous helpful suggestions offered by Dr. John T. Pfeffer during the conduct of the study. Particular thanks are also due to Mr. Michael A. Rataj, Gerald L. Siekerka, and Dr. Massoud Pirbazari for their active contributions to the various phases of the study. Special thanks are due to Ms. Connie B. Cassida for the long hours spent in the preparation of the final report.

This research was supported by the U.S. Department of Energy Pittsburgh Energy Technology Center under Grant Number DE-FG22-80PC30233. Special thanks are due to Mr. Charles J. Drummond, the technical project officer, for his active interest in the project and his many helpful suggestions and ideas.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

Chapter Page

Table of Contents (Continued)

Chapter Page

Table of Contents (Continued)

LIST OF TABLES

List of Tables (Continued)

LIST OF FIGURES

List of Figures (Continued)

List of Figures (Continued)

I - INTRODUCTION

The conversion of coal to synthetic fuels has been regarded as a promising technology for the production of the gaseous and liquid fuels needed to supplement dwindling reserves of petroleum and natural gas. Several coal conversion technologies have been proposed, tested and demonstrated to varying degrees. These processes differ in the size, degree of dryness and type of coal utilized, the operating temperature of the process, stream and feed gas requirements, and the mode of transport and mixing of the reactor contents. The wastewaters generated from coal conversion processes may exhibit significant differences in the individual strengths of the various constituents, however, these wastewaters invariably have the same constituent compounds.

The objective of this research project was to determine the effectiveness of an innovative process stream in the treatment of coal conversion wastewater. The treatment system consisted in series of a contact-stabilization activated sludge process, a nitrification activated sludge process, and an anoxic denitrification columnar reactor. Provisions for powdered activated carbon addition to the contact aeration tank were also made. Several process variables and their effects on treatment efficiency were studied. These variables were: (a) the mixed liquor powdered activated carbon concentration in the contact-stabilization system; (b) the fresh powdered activated carbon addition rate; (c) the solids retention time or sludge age maintained in the contact-stabilization system; and (d) the detention time in the contact aeration tank. The coal conversion wastewater used in the study was a coke-oven battery waste characterized by exceedingly high levels of cyanide, thiocyanate, and ammonia, and rather low levels of phenols.

II - REVIEW OF THE LITERATURE

A. Introduction

The aqueous by-products of coal conversion processes refer to the condensables present in the raw gas stream. These condensables are generally tars, light oils, water and other volatile materials removed from the coal during the carbonization process. The gas stream is washed with a spray of recycle gas liquor to condense wastes, light oil, tar, and to remove entrained dust.

Coal conversion wastewaters have been characterized by their alarmingly high concentrations of phenols (200-6,000 mg/l) and ammonia (2,500-11,000 mg/l), as well as the presence of appreciable concentrations of biologically inhibitory agents such as thiocyanate (21-200 mg/l) and cyanide (0.1-50 mg/l) (11,33,61). Singer et al. (61) subdivided the organic constituents of coal conversion processes into six distinct groups (a) monohydric phenols, (b) dihydric phenols, (c) polycyclic hydroxy compounds, (d) monocyclic N-aromatics, (e) polycyclic N-aromatics, and (f) aliphatic acids. Phenol represents the major oxygen demanding organic compound, accounting for 28 to 46 percent of the chemical oxygen demand (COD) of coal gasification wastewater (61).

Coal gasification is a relatively new technology in the United States and knowledge of the fate of the various organic and inorganic constituents present in the wastewater is limited to results of bench scale treatability studies. Due to the similarity between coking and coal gasification wastewaters, however, much of the coke plant wastewater treatment technology should be applicable to the treatment of coal gasification wastewater (46).

B. Current Practice in the Treatment of Coal Conversion Wastewater

A number of processes are available for the treatment of phenol and ammonia bearing coal conversion wastewaters. Solvent extraction of phenolics, ammonia stripping, incineration, adsorption, biological oxidation, chemical oxidation, distillation, reverse osmosis, and deep well injection have been suggested as the feasible alternatives for the total or partial treatment of coal conversion wastewater. The most widely used treatment scheme for coking wastewaters consists of ammonia removal followed by biological dephenolization (14). Many of the aforementioned treatment schemes are either limited in use or are less economical than biological treatment. Because of this, ammonia stripping and biological treatment will be the focus of this section.

1. Ammonia Removal

The high concentration of ammonia in coal conversion wastewaters is a result of the high partial pressure of carbon dioxide in the product gases and the high solubility of ammonia in water. Ammonia is commonly removed from coal conversion wastewaters by steam stripping. The fraction of total ammonia that can be stripped without pH adjustment is called "free ammonia" and is defined: $(\text{alkalinity-NH}_3)/\text{NH}_4^+$ where concentrations are expressed as equivalents per liter (30).

The removal of ammonia from coal conversion wastewater by stripping is usually necessary prior to biological treatment. Ammonia concentrations of 3,200-4,000 mg/l were found to be inhibitory to the activated sludge process for carbonaceous biological oxidation (30). Luthy et al. (33) reported that ammonia stripping may be utilized to reduce the total ammonia concentrations present in coal gasification wastewaters from 5,150 mg/l down to 330-580 mg/l.

Biological oxidation followed ammonia stripping and resulted in further ammonia reductions of 58 to 91 percent. Stamoudis and Luthy (63) treated wastes from two high BTU coal gasification pilot plants; one was of the HYGAS steam-oxygen type while the other was a slagging fixed-bed gasifier. The ammonia levels were reduced via stripping from 3,700 mg/l to 148 mg/l and from 5,200 mg/l to 471 mg/l, respectively. Subsequent biological oxidation nitrified 32 percent of the residual ammonia in the full strength HYGAS waste and 89 percent of the residual ammonia present in the slagging, fixed-bed gasifier wastewater when that waste was treated at 33 percent strength.

2. Removal of Phenols

Due to the high concentration of phenolic compounds present in some coal conversion wastewaters, recovery of phenol by solvent extraction may be economically feasible. The phenol recovered may be sold as a commodity or used as a fuel. The phenol removed would also reduce the organic loading to a biological treatment facility, thus lowering the cost of biological oxidation. Shock loads may also be reduced as a result of solvent extraction of the wastewater.

Luthy (30) and Luthy et al. (34) found that the organic matter remaining in coal gasification wastewater after solvent extraction was no more refractory to biological oxidation than what is present in the raw ammonia stripped wastewater. Furthermore, the presence of phenol and other organic acids may interfere with the ammonia stripping process (15).

The prevalent process for phenol recovery in the United States is continuous countercurrent liquid-liquid extraction. The phenols are recovered by mixing the waste with solvent. The solvent extracts the phenols and some of the other organic compounds. The wastewater-solvent mixture is separated and the solvent is distilled, which releases the phenolics for recovery while the solvent is recycled back to the extraction steps. Commonly used organic solvents are di-isopropyl ether (DIPE) in the phenosolvan process, toluene, n-butyl acetate (NBA) and methylisobutyl ketone (MIBK). Luthy et al. (34) reported reductions in TOC, COD, and BOD of 82, 88, and 89 percent, respectively, for MIBK solvent extracted Grand Forks Energy Technology Center slagging fixed-bed gasifier condensate using a five-step batch extraction sequence with clean solvent at each step and a 15:1 water to solvent ratio per step.

3. Biological Oxidation

The activated sludge process is the most widely used technology for the treatment of coal conversion wastewaters. This treatment process generally results in good reductions in COD and thiocyanate and very low effluent levels of phenols. However, long hydraulic detention times are usually necessary for adequate treatment and a considerable portion of the influent COD persists in the effluent.

Combined treatment of coke plant ammonia still wastewater and domestic sewage has been in practice since the advent of the activated sludge process. Mohlman (39) concluded that combined influent phenol concentrations of 30 to 40 mg/l were acceptable for the activated sludge process. Rudolfs (53) found that biological treatment of coke plant wastes with dilution factors of about 200 in a municipal activated sludge plant resulted in satisfactory removals of phenols and thiocyanate. Two cooperative studies between Gary (Indiana) Sewage Commission and the United States Steel Company have been reported (37,40). Mathews (37) reported that with a dilution factor of 40 to 1 and an influent phenol concentration of about 20 ppm, the plant effluent contained only a few ppb of phenols. In a subsequent study, Muller (40) found that for a nine hour hydraulic detention time in the aeration basin and a one percent contribution of ammonia still liquor to the influent wastewater, the removal of phenols was essentially complete.

Kostenbader and Flecksteiner (27) conducted a treatability study on weak ammonia liquor (WAL) produced at the Bethlehem Steel Plant using the activated sludge process. A full scale activated sludge plant received an average of 112,000 gpd of WAL at an average hydraulic detention time of 2-3 days. The average phenol load to the plant was 1,300 lb/day. The phenol concentration in the clarifier effluent remainded under 0.1 mg/l and BOD removal efficiency ranged from 85 to 95 percent during 2.5 years of operation. The thiocyanate oxidation efficiency ranged from 20 to 99 percent and averaged 70 percent during the same period of operation.

Barker and Thompson (5) reported on a one year pilot plant study on the biological removal of carbon and nitrogen compounds from coke plant wastes. The pilot plant consisted of two completely mixed activated sludge units in series. The first tank was used for organic carbon removal while the second unit was devoted to nitrification. A one day hydraulic detention time was used for each unit and the flow rate to the system was set at 1 gpm. The treatment system was operated for 40 days. During this period the influent COD, phenol and thiocyanate concentrations were 3,000 mg/l, 570 mg/l and 310 mg/l, respectively, with resulting removal efficiencies of 76, 99, and 10 percent, respectively. The second stage nitrification tank was fed a mixture of diluted first stage effluent and a supplemental ammonia solution.

Under these conditions 75 to 90 percent of the ammonia was nitrified. System upsets and the short term of operation of the process prevented the development of cultures capable of effective cyanide and thiocyanate oxidation.

Ganczarczyk and Elion (14) reported on the extended aeration activated sludge treatment of a coke plant effluent at Dominion Foundries and Steel Limited (DOFASCO) in Hamilton, Ontario. After equilization and stripping the wastewater was fed to a single-stage activated sludge treatment plant. Phenol removal averaged 99 percent for influent phenol concentrations ranging between 2.9 and 288 mg/l and an aeration detention time of 13.8 hours. The activated sludge system was operated at a sludge age of 41.4 days with solids wastage being totally over the effluent weir. Upon doubling the aeration detention time the phenol removal efficiency increased to 99.3 percent with the sludge age remaining essentially constant at 41.3 days. Thiocyanate removal was roughly 50 percent. In spite of the high sludge age and elevated reactor temperature nitrification did not occur.

Adams et al. (3) conducted laboratory studies on the biological treatment of two coke plant wastes. The wastewater from plant A contained average BOD, ammonia, phenol, and cyanide concentrations of 4,140 mg/l, 143 mg/l, 1,160 mg/l and 4.5 mg/l, respectively. Three identical activated sludge units were operated on plant A wastewaters using detention times of 6.6 days, 2.6 days and 1.8 days, respectively. The mixed liquor was maintained at roughly 2,500 mg/l in each of the three aeration tanks. Removal efficiencies for BOD, ammonia, phenol, and cyanide were 96.7, -3.5, 85.7 and 82.6 percent, respectively for the 6.6 day hydraulic detention time unit. The 2.6 day hydraulic detention time unit yielded removal efficiencies for the above parameters of 97.6, 10.5, 84.6 and 79.8 percent, respectively, while a detention time of 1.8 days resulted in removal efficiencies of 88.9, 21.7, 76.8 and 70.9 percent, respectively. The wastewater from plant B contained average BOD, ammonia, phenol and cyanide concentrations of 2,050 mg/l, 110 mg/l, 430 mg/l and 3 mg/l, respectively. This wastewater was treated in two activated sludge units using hydraulic detention times of 4.1 and 2.2 days and a mixed liquor concentration of 2,400 mg/l was maintained in each unit. Removal efficiencies for BOD, ammonia, phenol, and cyanide for the plant operated at a 4.1 day hydraulic detention time were 96.5, -101.8, >99.9 and 80.3 percent, respectively. Slightly lower removal efficiencies were observed for the plant operated at a hydraulic detention time of 2.2 days. Removal efficiencies for BOD, ammonia, phenol and cyanide in this plant were 93.7, -60.0, 99.9, and 78.7 percent, respectively. The increase in ammonia concentrations after treatment can be attributed to the ammonia formed as an end product of the oxidation of thiocyanate and cyanide.

Luthy and Jones (31) reported on the biological oxidation of an undiluted coke plant effluent. The COD, phenol, ammonia, cyanide, and thiocyanate content of the waste ranged from 3,880-4,600 mg/l, 750-1,010 mg/l, 35-92 mg/l, 3.2-4.4 mg/l, and 280-554 mg/l, respectively. Seven identical reactors were operated at sludge ages ranging from 10 to 40 days and hydraulic detention times of 2.7 to 9.2 days. Phenol removal efficiencies were consistently greater than 99 percent for all systems while thiocyanate removal efficiencies ranged from 90 to 99 percent. Cyanide, on the other hand, was only slightly removed. Nitrification occurred only in the reactor operated at the extreme levels of a 40 day sludge age and a 9.2 day hydraulic retention time. The authors concluded that a well managed activated sludge treatment plant operated at a 40 day sludge age and a 9.2 day hydraulic detention time could treat an undiluted coke plant waste and produce an effluent that approaches best available technology (BAT).

Johnson et al. (22) and Neufeld et al. (42) conducted treatability studies on the condensate from a synthane coal gasification pilot plant processing Montana and Illinois coals at a rate of 40 lb/hr. Bench scale treatment tests consisting of oil and grease removal, ammonia, and hydrogen sulfide stripping, biological oxidation and adsorption with by-product recovery were performed. Oil and tar removal was achieved using alum dosages of 150 mg/l in the pH range of 2-5. Ammonia was effectively stripped to levels below 500 mg/l at a pH of 11. Bio-oxidation studies on full-strength stripped wastewater and stripped wastewater diluted to 15 percent of the original strength were performed. The authors found that dilution to 15 percent of original strength permitted the treatment of the synthane process wastewater using a hydraulic retention time of 1 day and a sludge age of 10 days. Under these operating conditions phenol, TOC, and COD removal efficiencies of 95, 70, and 70 percent were respectively obtained.

Reap et al. (50) reported on a similar study using the wastewater generated during coal liquifaction with the H-Coal Process. The unstripped wastewater was characterized by COD, phenol, ammonia and sulfide concentrations of 88,660, 6,800, 14,400 and 29,300 mg/l, respectively. After ammonia and hydrogen sulfide stripping, however, the COD of the waste fell to approximately 28,000 mg/l due to removal of the sulfide. The wastewater was subsequently diluted to 12.5 percent strength prior to treatment in an activated sludge type process using a hydraulic detention time of 4.5 days.

Luthy and Tallon (35) evaluated the biological treatability of HYGAS coal gasification process condensate at full strength and at 50 percent dilution. These authors concluded that pretreatment for reduction of alkalinity was necessary to prevent upward pH fluctuations due to carbon dioxide stripping during biological treatment. Ammonia stripping was also found to be necessary prior to biological oxidation. This study demonstrated that at detention times of 2 and 3 days and sludge ages ranging between 10 and 40 days, it was possible to remove 80 percent of the COD, 99 percent of the phenol and 85 percent of the thiocyanate using the 50 percent diluted waste. However, the full strength wastewater resisted biological treatment.

Sack (55) reported on the treatability with the activated sludge process of ammonia stripped wastewater generated from a low BTU, elevated pressure, fluidized-bed, Wellman-Galusha gasifier. The author stated that the wastewater was treatable at 38 percent strength using detention times of 0.9 and 1.45 days and sludge ages of 14 to 18 days. Sack (55) also observed that the addition of powdered activated carbon (PAC) at a level that results in a mixed liquor PAC concentration of 6,000 mg/l produced a 75 percent TOC removal. Only 55 percent TOC removal was obtained from a parallel reactor operated without PAC addition. The additional TOC removed by the PAC activated sludge process amounted to 1.01 g TOC/g of PAC added. This was a much higher removal level than attributable to adsorption as observed from adsorption isotherm studies. One possible explanation of this phenomenon is that the PAC served to sequester some inhibitory compounds thus stimulating the biological activity within the treatment process.

Luthy et al. (33) conducted activated sludge treatability studies on the effluent from a slagging fixed-bed coal gasification pilot plant operated by the Grand Forks Energy Technology Center of the Department of Energy. Their findings reinforced previous work in which ammonia-stripped wastewater was processed reliably at 33 percent strength. It should be pointed out, however, that even at this dilution the organic content of the waste, which averaged 8,380 mg/l COD, was reportedly the highest treated for this type of wastewater. In a continuing study, Luthy and coworkers (34) evaluated the treatability of the same wastewater after that water had been pretreated. Phenols were removed by solvent extraction with methylisobutyl ketone and the ammonia was steam stripped. The solvent extracted and ammonia stripped wastewater was treated with activated sludge and PAC-activated sludge using aeration times of 12.6 and 11.7 days and sludge ages of 30 and 20 days, respectively. This study revealed that the solvent extracted and ammonia-stripped wastewater did not require dilution prior to biological treatment. Also, solvent extraction resulted in lower COD, TOC and color for both of the systems.

The relatively unstable operation reported for activated sludge systems during the treatment of coal conversion wastewaters can be explained by the presence of certain organic and inorganic compounds in the wastewater. Thiocyanate, cyanide, ammonia and phenol are all usually found in coal conversion wastewater at various concentrations. All of these compounds exhibit toxic effects at certain concentrations and may cause severe inhibition of the activated sludge process. Thiocyanate, which is poorly degraded in aerobic biological treatment, exhibits a noticeable inhibitory effect on the aerobic degradation of phenol (69). While cyanide, thiocyanate and phenol have been observed to inhibit nitrification even at hydraulic detention times and sludge ages exceeding 6 days and 41 days, respectively (14,56).

Juntgen and Klein (23) presented data on the coinhibition of phenol, thiocyanate and ammonia during the aerobic treatment of coke oven and coal gasification wastewaters. Phenol degradation was inhibited by concentrations of ammonia, thiocyanate and sulfide in excess of 1,700, 250, and 25 mg/l, respectively. Thiocyanate degradation was completely halted at ammonia, thiosulfate, and phenol levels of 1,000, 100, and 25 mg/l, respectively. Nitrification, on the other hand, was inhibited at levels of phenol, thiocyanate, and cyanide as low as 50, 10 and 10 mg/l, respectively.

The treatment of coal conversion wastewater with the extended aeration activated sludge process has, in general, proven to be an effective treatment process resulting in acceptable effluent concentrations of phenol, COD and organic carbon. Removal efficiencies of ammonia, cyanide and thiocyanate have not been satisfactory in most instances, however. Extremely long hydraulic detention times in aeration basins are a common feature of most of these systems as they seem to be required for stable operation of the reactors. Johnson et al. (22) and Neufeld et al. (42) utilized an aeration time of 1 day with resulting COD and TOC removal efficiencies of 70 percent, while Reap et al. (50) used hydraulic detention times exceeding 4 days for wastewater strengths of only 12.5 percent. Luthy and Tallon (35) employed aeration times of 2 and 3 days, while in subsequent studies, Luthy and coworkers (33,34) used aeration times of approximately 10 days. This apparent need for excessive aeration times to obtain acceptable effluent quality emphasizes the urgency for the development of a less energy intensive process for the purification of coal conversion wastewaters.

C. Activated Carbon in Aerobic Biological Treatment

Pure cultures may, in some instances, possess the potential for purifying wastewaters containing inhibitory compounds, such as phenols, at a faster rate than mixed cultures. However, the feasibility of such a treatment mode is unlikely. When faced with fluctuating concentrations of toxic and inhibitory substances, physical processes, such as activated carbon adsorption, may be assimilated into the biological system in order to stabilize the process and reduce the large volume of the aeration tank otherwise needed to dilute the fluctuations. This is especially true when the toxic or inhibitory agents have a strong affinity for the activated carbon surface.

In wastewater treatment, the adsorption stage has generally been regarded as a separate columnar phase of treatment designed to polish the effluent from the secondary biological processes. It was only recently that researchers have started appreciating the benefits realized from the combination of the two processes in one single reactor configuration. This has been accomplished through the addition of powdered activated carbon (PAC) to the activated sludge process (51). Zobell (70) and Heukelekian and Heller (19) noted that the presence of solid surfaces enhanced the physiological activity of bacteria, while King and Verma (25) also reported on the increased rate of degradation of organic matter in the presence of solid surfaces.

The addition of powdered activated carbon to activated sludge has been practiced for several years (1,57). Researchers have cited a number of benefits gained by the addition of PAC to the activated sludge system when the performance data are compared to those obtained from the activated sludge system alone. These benefits include an increase in the removal of soluble organics as well as an enhancement of process stability. DeWalle and Chian (9) summarized the benefits achieved through the addition of powdered activated carbon to the activated sludge process as being:

1. Increased stability against toxic organic shock loads;
2. Removal of color and odor;
3. Reduction of oxygen demand load on receiving water;
4. Lowered residual effluent toxicity to fish;
5. Reduction of foaming in aerator;

6. Increased stability against heavy metal shock loads;
7. Increased capacity of sludge dewatering units;
8. Increased capacity of secondary clarifiers; and
9. Reduction in effluent suspended solids.

As detailed above, the presence of PAC in activated sludge results in a number of distinct advantages. Generally, however, improving the effluent water quality beyond the capabilities of conventional biological treatment and enhancing the treatability of wastewaters that, otherwise, inhibit or toxify biological treatment systems are the primary objectives of the utilization of PAC in secondary biological treatment.

Nayor and Sylvester (41) subjected a continuous culture of E. coli to phenol pulse concentrations of 1 to 1,000 mg/l and monitored the transient behavior. No significant change in total organic carbon (TOC) or MLSS was noted for an impulse of 100 mg/l phenol, however, a noticeable decrease in MLSS and increase in TOC was observed for impulse concentrations of 500 and 1,000 mg/l. The same procedures were again repeated, however, in this instance, powdered activated carbon was added with the phenol. No enhancement of biological growth was observed, however, although a definite increase in the efficiency of the reactor in removing TOC was noted.

Sundstrom et al. (68) conducted experiments using PAC addition to activated sludge units that have been acclimated to glucose. When the glucose concentration of the influent was step changed from 750 to 1,500 mg/l and a carbon dose of 110 mg/l was applied, the steady state TOC concentration decreased from 65 to 12 mg/l. However, the continuous addition of carbon had no significant effect on the reactor performance. Impulses of phenol were also added to the reactors. When 500 mg/l and 1,000 mg/l impulses of phenol were added to the reactor, the TOC concentration increased and the MLSS concentration decreased. Simultaneous impulses of powdered activated carbon and phenol were also added to the reactors. When a 1,000 mg/l impulse of phenol and a 2,000 mg/l carbon impulse were introduced into the reactor, the TOC concentration increased from 35 mg/l to 60 mg/l. A similar experiment without carbon addition resulted in TOC concentration increases of 45 mg/l to 325 mg/l.

Adams (1) monitored the performance of a municipal wastewater plant that received 70 percent of its flow from an industrial textile dyeing and finishing mill. Powdered activated carbon was added at a concentration of 900 mg/l while the average influent BOD was 150 mg/l. The addition of PAC significantly stabilized the effluent quality and increased average BOD removals from 72 to 89 percent.

Ferguson, Keay, Merrill and Benedict (10) utilized the PAC biological contact stabilization process to determine the benefits of PAC addition to the biological process in terms of effluent quality and overall hydraulic retention time. A PAC concentration of 150 mg/l was sufficient to stabilize the biological process during toxic shock loadings of trichlorophenol. Heavy metal uptake was also noted in the presence of PAC. The addition of powdered activated carbon resulted in enhanced sludge settling properties and allowed for the operation of the system under reduced aeration detention times and lower sludge recycle ratios.

Grieves (17) reported on the results of a pilot plant study at the Amoco refinery in Texas City, Texas. The existing activated sludge plant was treating a waste having a phenol concentration of 3.95 mg/l and achieving a phenol removal efficiency of 99.5 percent or an effluent phenol concentration of 0.019 mg/l. The addition of only 25 and 50 mg/l powdered activated carbon resulted in a reduction of the effluent phenolics to 0.006 and 0.002 mg/l, respectively.

While the benefits realized from the addition of PAC to a biological process have been clearly demonstrated, the basic fundamentals of the physico-biological phenomenon remain somewhat controversial. Most data to date suggest that much more is involved than simple biological oxidation and physical adsorption. The activated carbon and biomass simultaneously physically and biologically remove degradable and adsorbable compounds. The two operations have been described as being synergistic (12).

Scaramelli and DiGiano (57) conducted a treatability study on a primary effluent from the municipal treatment plant at Amherst, Massachusetts using the PAC activated sludge process. The following conclusions were made: a) Biological growth was not enhanced by the addition of PAC and improved substrate removal was totally due to adsorption. b) There was no significant increase in oxygen uptake rates when PAC was added to the activated sludge system.

Hals and Benedek (18) explored the same topic, and arrived at a similar conclusion to that of Scaramelli and DiGiano (57). They postulated that the additional decrease in TOC was a result of physical adsorption onto the activated carbon surface. On the other hand, Kalinske (24) indicated that an increase in COD removal was a result of enhanced biological uptake in the presence of PAC. These conclusions were based on higher oxygen uptake rates and some increases in MLSS.

Robertaccio (52) investigated the treatment of three substrates; phenol, isopropyl alcohol and acetic acid with the PAC activated sludge process.

The selected substrates varied quite significantly with respect to adsorbability and biodegradability. It was found that the presence of PAC only slightly enhanced the removal of the relatively nonadsorbable acetic acid, whereas quite significant incremental reductions in phenol and isopropyl alcohol were observed. Again, using phenol as the substrate, Robertaccio (52) also concluded that the degree of enhancement in substrate removal is related to the carbon concentration in the system.

Koppe et al. (26) studies the fate of a slowly degradable substrate, pentaerythrital in the activated sludge process. Increased removal and a more rapid acclimation were observed when a single and initial dose of PAC was added to the system at a concentration of 30,000 mg/l.

These observations certainly reveal the complexity of this synergistic biological-physical process. Perhaps it is even more complex than it appears. Perotti et al. (49) postulate that there are four distinct processes occurring in the PAC activated sludge system that must be considered.

1. Adsorption on the surface of the activated carbon;
2. Biological adsorption and degradation - the spent carbon along with adsorbed pollutants settles with the sludge;
3. Activation of the carbon by biological action. The microorganisms present around the carbon desorb, degrade and digest the pollutants, thereby reactivating the surface sites for further adsorption; and
4. Improved solids settling in the final clarifier gives lower BOD and suspended solids in the effluent.

A review of the pertinent literature revealed that the activation of the carbon surface by biological action; otherwise known as biological regeneration, is still a somewhat controversial topic. Initial studies in this direction revealed that the presence of PAC in activated sludge enhanced the bio-oxidation activity. Further research was promulgated towards the investigation of the purification of the difficult to treat dye wastewater in a PAC activated sludge process. Enhanced activity, based on color reduction, was also evident.

DeWalle and Chian (9) used batch PAC activated sludge units and columns of activated carbon to investigate the biological regeneration of the carbon surface. The batch units resulted in an increase in the apparent maximum adsorptive capacity as the cell residence time was increased. They postulated that since the biomass concentration to PAC concentration ratio increases with increasing cell residence time, a more effective regeneration of the carbon surface can occur. The columns of activated carbon, on the other hand, showed a decrease in the maximum adsorptive capacity. It was concluded that biological processes are responsible for this phenomenon.

A study aimed at understanding the mechanisms of the PACT process was conducted by Shultz and Keinath (59). Activated sludge reactors with carbon addition and with phenol serving as the sole organic carbon source were used. Radiotracers of phenol were injected into the reactor vessels in order to monitor the fate of phenol in the treatment system. Several interesting conclusions were found. The authors concluded that PAC addition had no significant impact on the rate of $^{14}CO_2$ evolution of acclimated PACT and biomass cultures. All of the phenol initially adsorbed eventually desorbed from the PAC surface. Bioregeneration did occur in these systems. It was also concluded that the controlling mechanism for bioregeneration was desorption due to the fact that the phenol adsorption was completely reversible.

Studies on the adsorption-desorption characteristics of metabolic end products (MEP) excreted by the bacteria in the PACT culture were also conducted. These experiments supported the hypothesis that desorption is the principal mechanism of bioregeneration of PACT systems. The authors agreed that studies should be conducted on a nonreversible, biodegradable substrate to substantiate this hypothesis.

Perotti and Rodman (48) studied the catalytic effect of activated carbon on an aerobic bio-oxidation treatment process using phenol and glucose as substrates. As previous research had shown, the presence of activated carbon enhanced the aerobic activity and sustained a high bio-oxidation level. The following hypothesis was presented: The surface area of activated carbon, as much as 100 m^2/g, is composed of micropores with diameters on the order of 10-1,000 angstrom units. Bacterial cells characteristically have diameters larger than 1,000 angstrom units. Biological desorption, as a result of bacteria migration, is therefore, probably limited due to the size relationship. The microbes do, however, have the capability of producing digestive enzymes, approximately 10 angstrom units in diameter, which could diffuse through the porous carbon structure. By way of an enzyme-substrate complex, the substrate or organic material is desorbed and degraded bioligically.

III - MATERIALS AND METHODS

A. The Experimental Apparatus

Three identical treatment systems were constructed for the study. Each system consisted of a:

i. contact aeration tank,
ii. stabilization aeration tank,
iii. clarifier serving the contact-stabilization aeration tank,
iv. nitrification aeration tank,
v. clarifier serving the nitrification aeration tank,
vi. sump and overflow box, and
vii. denitrification contact column.

1. Aeration Tanks

The contact, stabilization, and nitrification aeration tanks were constructed using 0.25 inch (0.635 cm) thick Plexiglas plate. Each aeration tank was fabricated as a rectangular parallelepiped having a 12 inch (30.48 cm) per side square base and a height of 23 inch (58.42 cm) (see Figure 1). Two 0.25 inch (0.625 cm) Plexiglas plates were inserted in the parallelepiped in order to form an aeration volume having the shape of an inverted triangular prism. This particular shape was needed in order to maintain a reasonable depth of water within the tank when lower contact volumes were desired. An additional benefit of this shape was better mixing characteristics within the reactor. To allow for the attainment of different aeration volumes within the tank, each tank was fitted with five 1.0 inch (2.54 cm) NPT Swagelok tube fittings (Crawford Fitting Company, Solon, OH) at levels of 7, 9-7/8, 14, 17-1/8, and 19-3/4 inch (17.78, 25.08, 35.56, 43.50, 50.16 cm) from the bottom of the tank (see Figure 2). Each tank was also equipped with a 0.75 inch

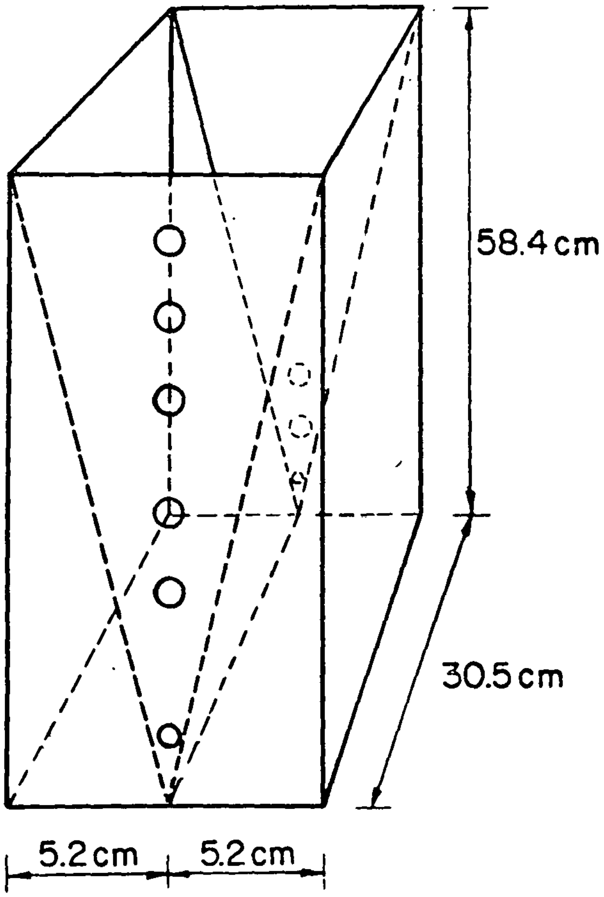
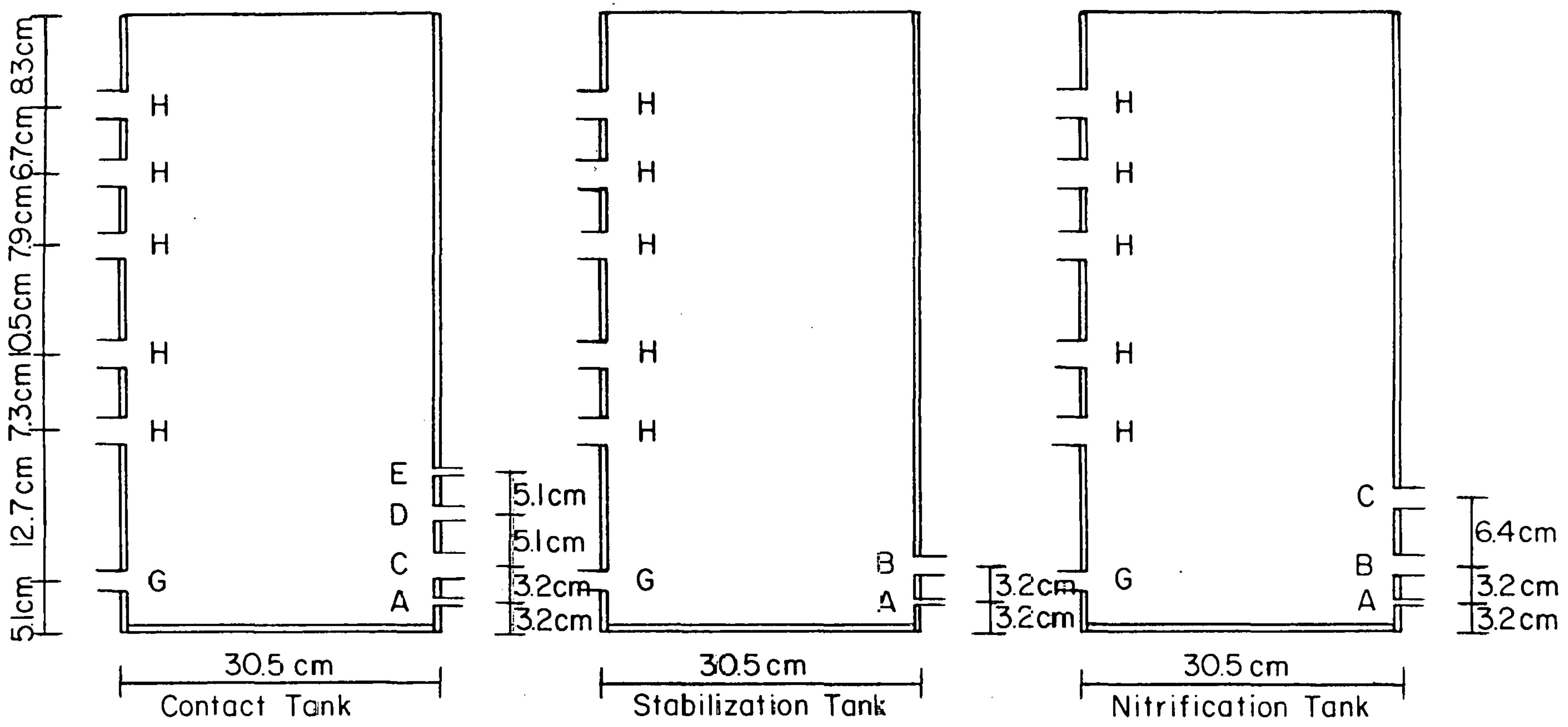


Figure 1. Schematic Diagram of Aeration Tank



A – 0.64 cm NPT Air Line Fitting
B – Sludge Inlet From Clarifier Underflow
C – Stabilized Sludge Return
D – Wastewater Feed Line
E – Powdered Activated Carbon Feed Line
F – Influent to Nitrification Tank
G – Drain Line
H – Effluent Line

Figure 2. Details and Port Positions of Aeration Tanks

(1.90 cm) NPT Swagelok tube fitting drain port located 2 inch (5.08 cm) from the base of the tank and a 0.25 inch (.64 cm) NPT Swagelok tube fitting located 1.25 inch (3.18 cm) from the bottom which served as an inlet port for a 5/16 inch (0.794 cm) OD plastic tube diffuser.

The contact aeration tanks were also equipped with a 0.5 inch (1.27 cm) NPT Swagelok tube fitting for the raw wastewater influent line, a 0.25 inch (.635 cm) NPT Swagelok tube fitting for the powdered activated carbon feed line and a 1.0 inch (2.54 cm) NPT Swagelok tube fitting for the stabilized sludge return line. These three fittings were located at 4.5, 6.5, and 2.5 inch (11.43, 16.5, 6.35 cm) from the bottom, respectively. The stabilization and nitrification aeration tanks were provided with 0.75 inch (1.90 cm) NPT Swagelok tube fittings situated 2.5 inch (6.35 mm) from the bottom of the tank which functioned as sludge feed ports. The nitrification aeration tanks had an additional 0.75 inch (1.90 cm) Swagelok tube fitting positioned 5.0 inch (12.70 cm) from the bottom of the tank which served as the inlet port for the supernatant from the contact-stabilization clarifier (see Figure 2).

2. Clarifiers

Two identical clarifiers were constructed for use in each of the three experimental apparatuses; one served the contact-stabilization process while the other served the nitrification stage of the units. The main body of each clarifier was constructed of a 40.0 inch (1.016 m) long, 8 inch (20.32 cm) OD, 0.25 inch (6.35 mm) thick Plexiglas tube (see Figure 3). Mixed liquor was introduced into each clarifier through an 18 inch (45.72 cm) long, 2.25 inch (5.72 cm) OD, 0.125 inch (0.317 cm) thick Plexiglas tube supported in the center of the clarifier. An inverted cone structure was machined from eight 1 inch (2.54 cm) Plexiglas plates and placed on the base of each clarifier.

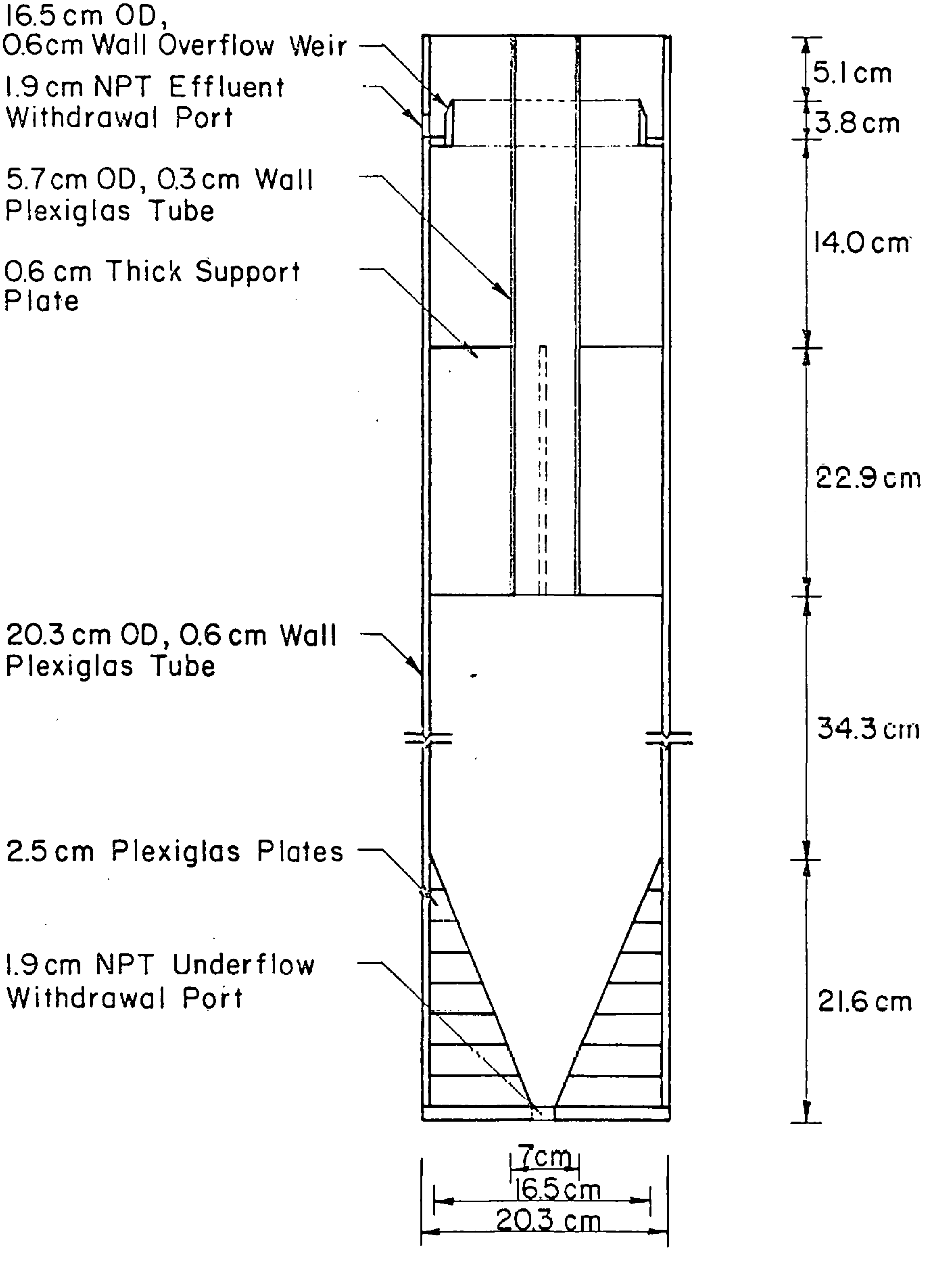


Figure 3. Schematic Diagram of Clarifier

The inner walls of the cone structure had a slope of 3.56:1. The inverted cone structure along with a mechanical sludge scraping device rotating at one revolution per minute provided the collection and concentration of biological sludge at the base of the clarifier prior to sludge recycle. The overflow weir structure was constructed of a 6.5 inch (16.51 cm) OD, 0.25 inch (6.35 mm) thick Plexiglas tube section 1.5 inch (3.81 cm) in length. The top part of the weir was bevelled to provide a sharp water contact. The inner wall of the clarifier tube and the outer wall of the weir tube were joined by a 0.25 inch thick Plexiglas plate to provide an effluent collection channel. The supernatant from the clarifier was withdrawn through a 0.75 inch (9.05 mm) NPT opening positioned flush with the effluent channel bottom while the concentrated biological sludge was withdrawn through another 0.75 inch (9.05 mm) NPT opening positioned at the center of the inverted cone structure at the base of the clarifier (see Figure 3).

3. Denitrification Feed Sumps

The effluent from every nitrification clarifier was collected in a sump with an overflow weir and the corresponding denitrification column was fed from this sump at a flow rate which was set lower than the clarifier effluent. The purpose of the sump was to ensure the maintenance of anoxic conditions in the denitrification column. The sump provided a water seal between the clarifier and the denitrification column. The sump also provided a reservoir volume of 4 ℓ of nitrified effluent (see Figure 4).

Each sump was constructed of 0.25 inch (6.35 cm) thick Plexiglas plate. The square base of the sump was 8.0 inch (20.32 cm) on the side while the height was 12.0 inch (30.48 cm). An 8.0 inch (20.32 cm) square 0.25 inch (6.35 mm) thick Plexiglas plate was used to divide each sump into two

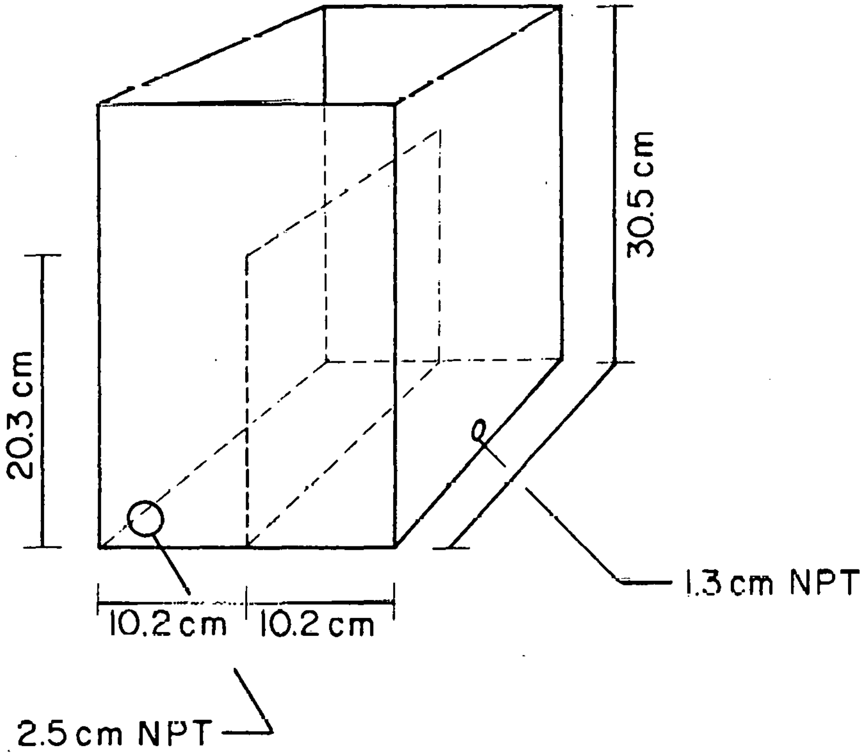


Figure 4. Schematic Diagram of Denitrification Sump and Overflow Structure

compartments. One compartment served to receive the nitrified effluent and a 0.5 inch (12.70 cm) NPT Swagelok tube fitting was placed at the outer wall of this compartment to provide the feed to the denitrification column. The other compartment served to receive the excess of nitrified effluent and a 1.0 inch (2.35 cm) NPT fitting was used to conduct this excess flow to a drain.

4. Denitrification Columns

Each denitrification filter consisted of a water jacketed column. The 48 inch (121.92 cm) inner tube was constructed using a 4.5 inch (11.43 cm) OD, 0.25 inch (6.35 mm) thick Plexiglas tube (see Figure 5). A 0.5 inch (1.27 cm) thick flange, 6.5 inch (16.51 cm) in diameter was attached to each end of the tube. These two flanges served to connect the main body of a column to the influent and effluent structures. A 45.0 inch (114.3 cm) long water jacket was constructed to surround the main body of the column using a 6.0 inch (15.24 cm) OD, 0.25 inch (6.35 mm) thick Plexiglas tube. The influent header (see Figure 5) was constructed using a 6.38 inch (16.19 cm) long inner tube section. An inverted cone structure, machined from ten 0.5 inch (1.27 cm) thick Plexiglas plates, was used to provide better distribution of the influent flow. A 0.5 inch (1.27 cm) thick flange, identical to the one attached to the inner tube provided the means for joining of the influent header to the main column. A similar header was used for the effluent structure of the column. The influent, effluent, and gas withdrawal ports were all 0.5 inch (1.27 cm) NPT Swagelok tube fittings. The gas collection system for each column consisted of a 6.5 ℓ gas buret, two leveling bottles and a sampling port. The gas burets were used for monitoring the volumetric gas production rate.

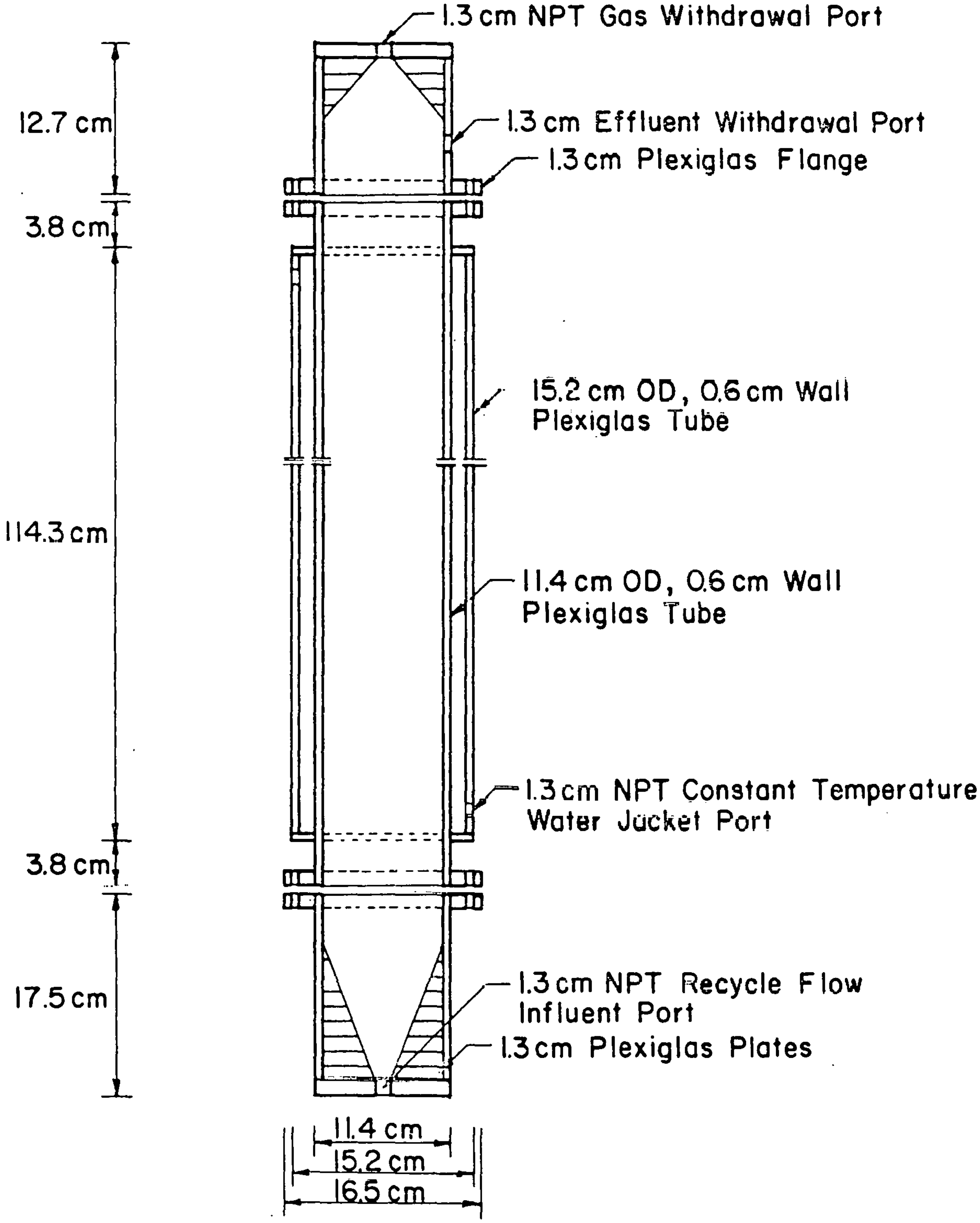


Figure 5. Schematic Diagram and Details of Denitrification Column

The biological support media consisted of 550 number 1 polypropylene intralox saddles (Norton Co., Rolling Meadows, IL). These saddles had a surface area of 21.38 ft^2 (1.99 m^2) yielding a specific surface area of 63 ft^2/ft^3 (206.7 m^2/m^3) excluding the column wall surface. The porosity of the packed bed was 0.92. The empty bed volume of the reactor was 648.7 in^3 (10.63 ℓ).

B. The Powdered Activated Carbon

Several powdered activated carbons were considered for use in this study. Four carbons were screened for their adsorptive capacities with the coke-oven wastewater. These were Nuchar SA-15, PX-21, Aqua-Nuchar, and Calgon RB Pulverized. Four identical isotherm experiments were conducted using each of the powdered activated carbons and 100% strength coke-oven waste. The COD isotherms are shown in Figure 6. As the data indicate the Amoco PX-21 carbon was superior. Unfortunately, this carbon is not commercially available, therefore, the Calgon RB Pulverized was selected for use in this study.

C. The Coke-Oven Wastewater

The coke-oven wastewater used in this study was obtained from a steel mill in batches of twelve 55-gallon drums. The first batch of wastewater was used to acclimate the systems while subsequent batches were used in operating the three experimental units during the data collection phase of the study. Analysis of these wastewaters revealed that the cyanide and thiocyanate concentrations were higher than what has been reported in the literature while the phenols were present at much lower levels. The characteristics of the three batches of the full strength coke-oven wastewater are shown in Table 1.

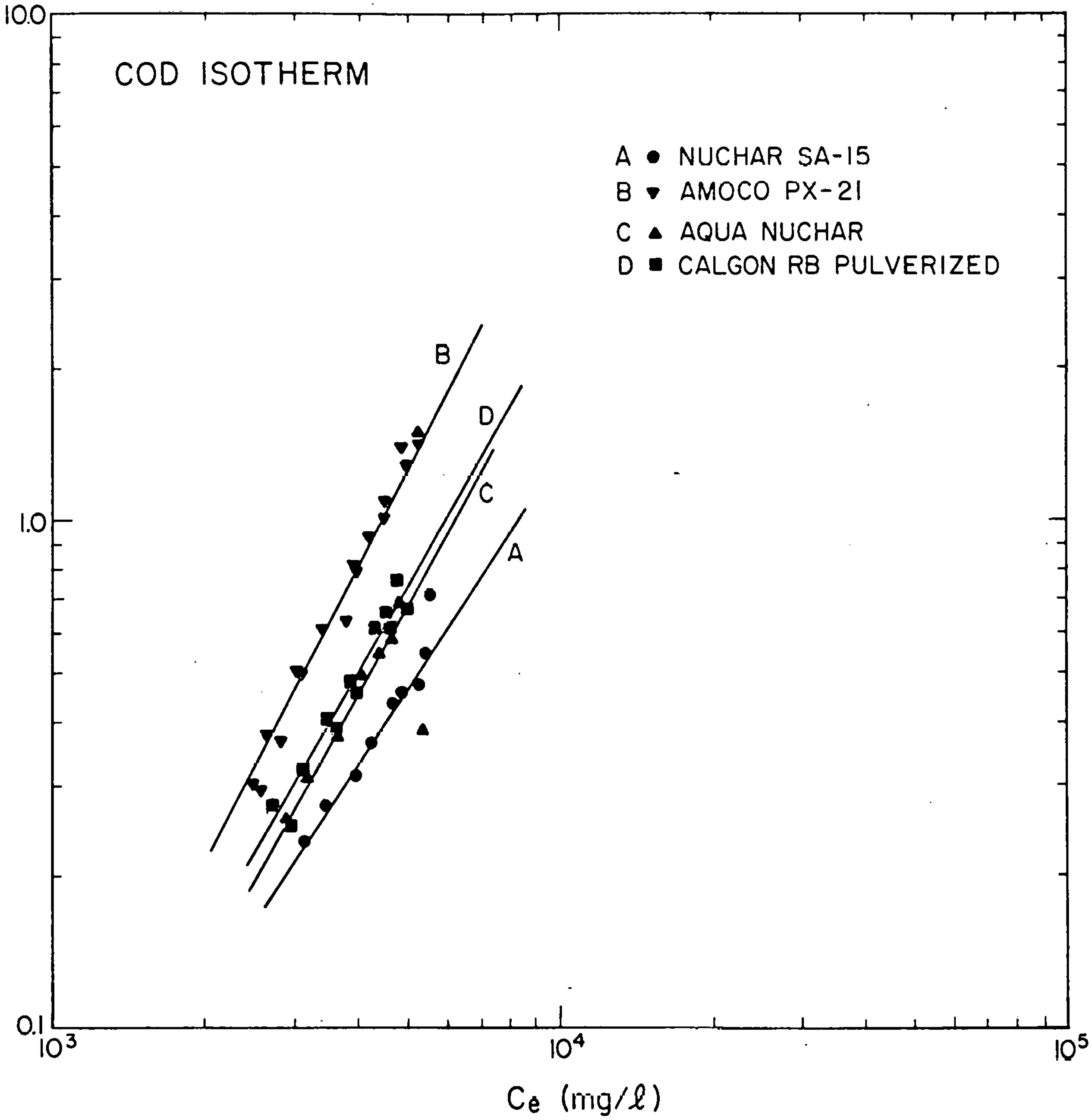


Figure 6. Adsorption Isotherms of Four Powdered Activated Carbons

Table 1

Characteristics of the Full-Strength Coke Oven Wastewaters

Parameter	Concentration Batch 1	Concentration Batch 2	Concentration Batch 3
pH	9.3	9.3	9.2
Alkalinity, mg/ℓ as $CaCO_3$	5,000-5,333	5,000-5,500	5,000-5,500
COD, mg/ℓ	5,500-5,835	5,050	3,960-5,025
DOC, mg/ℓ	1,700-1,800	1,270-1,554	1,035-1,250
Ammonia, mg/ℓ as N	3,720-3,850	5,020	3,155-3,825
Nitrate, mg/ℓ as N	<2	<2	<2
Nitrite, mg/ℓ as N	<2	<2	<2
Cyanide, mg/ℓ	800-1,000	2,660	2,170-2,150
Thiocyanate, mg/ℓ	800-1,000	1,727	1,400
Phenol, mg/ℓ	400	362	127
o-Cresol, mg/ℓ	41	38	7
m and p-Cresol, mg/ℓ	91	62	12
2,4-Dimethylphenol, mg/ℓ	--	0.6	1.7

D. System Operation

1. Operating Hydraulics

The various unit processes of each experimental apparatus were connected together as shown schematically in Figure 7. The feed wastewater was placed in a 50 ℓ polyethylene reservoir and fed to the contact aeration tank at the feed rate of 13.2 ℓ/day using a model 7565-10 console Masterflex drive and a 7015-00 pump head (Cole Parmer Instrument Co., Chicago, IL). A powdered activated carbon slurry in deionized water was prepared in a 10 ℓ glass reservoir and the suspension maintained using a Fisher Dyna-Mix Stirrer (Fisher Scientific Co., Chicago, IL). The contents of this reservoir were pumped into the contact tank at a rate of 2.3 ℓ/day using a 7543-02 low rpm fixed speed Masterflex drive and a 7016-20 pump head. The overflow from the contact aeration tank was gravity fed to the contact-stabilization clarifier through a 0.75 inch (19.05 mm) ID Tygon tube. The clarifier underflow was pumped to the stabilization tank using a model 7545-10 variable speed Masterflex drive and a 7018-00 pump head. The overflow from the stabilization tank was gravity fed to the contact aeration tank through a 0.75 inch (19.05 mm) ID Tygon tube. The supernatant from the contact-stabilization clarifier was fed to the nitrification aeration tank using a 0.5 inch (1.27 cm) ID Tygon tube, while the overflow from this aeration tank was fed to the nitrification clarifier through a 0.75 inch (19.05 mm) ID Tygon tube. Sludge return from the nitrification clarifier to the aeration tank was carried out using a model 7545-10 variable speed Masterflex drive and a 7018-00 pump head. Sodium carbonate was pumped from a reservoir to the nitrification aeration tank using a model 7565-10 console Masterflex drive and a 7013-00 pump head.

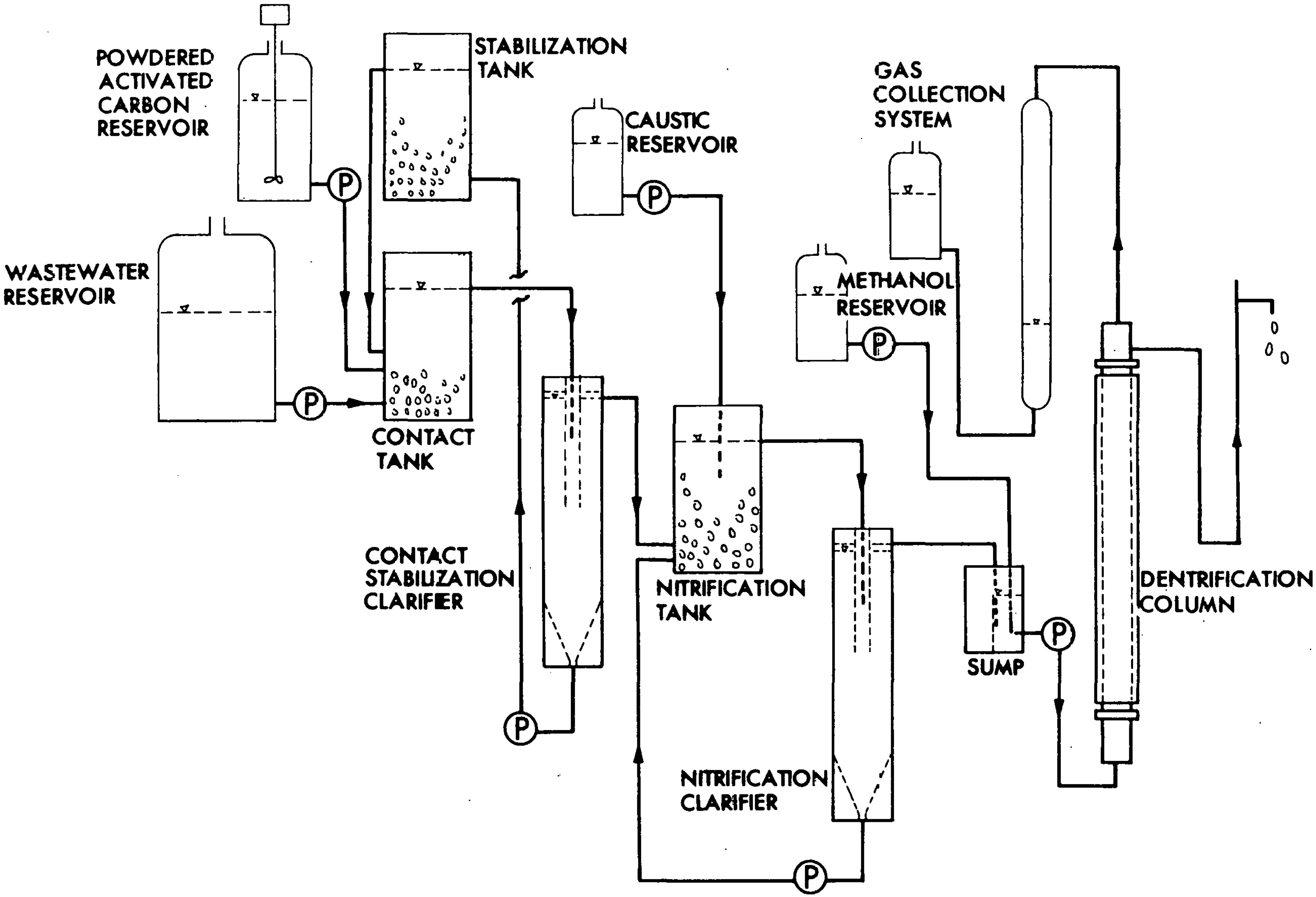


Figure 7. Schematic Diagram of Integrated Treatment System

The 4 N sodium carbonate solution was used to maintain the pH in the nitrification aeration tank at approximately 7.5. The supernatant from the nitrification clarifier was fed to the denitrification sump. A model 7543-02 fixed speed Masterflex drive and 7018-20 pump head were used to feed the denitrification column at a rate of 10.9 ℓ/day. Methanol was also pumped into the denitrification column using a 7543-02 fixed speed Masterflex drive and a 7013-20 pump head.

The air supply for all the aeration tanks was obtained from a central air compressor. Before introducing the air into the tanks, the air was humidified by bubbling through pressurized tanks containing water. This minimized water losses due to evaporation in the aeration tanks.

The unit processes, pumps, and reservoirs for every treatment apparatus were mounted on a unistrut structure in order to facilitate operation, maintenance, and level adjustment for gravity flow to occur.

2. Acclimation Phase

The first batch of coke-oven wastewater was used to acclimate the three treatment systems and to develop base-line conditions for the operation. The three aeration tanks and the denitrificiation column of each system were seeded with mixed liquor from the Champaign Sewage Treatment Plant. Powdered activated carbon (PAC) was also added to the contact and stabilization tanks. All three units were operated in an identical manner maintaining a 30 day solids retention time in the contact-stabilization system and a 40 day sludge age in the nitrification system. After several attempts to use a higher percent strength of wastewater, it was determined that the maximum wastewater feed strength for which stable operating conditions were attainable was

34 percent. After dilution with the PAC slurry the effective influent waste was 28.95 percent. The PAC slurry was fed to all systems at a strength of 193 mg/ℓ of the 28.95 percent strength wastewater.

During the period extending between days 268 and 300 of continuous operation, the three experimental systems were gradually acclimated to a new batch of wastewater. This acclimation phase was terminated on day 300. On day 300 the contents of all three contact aeration tanks were mixed together and distributed evenly between the three systems. This procedure was repeated for the stabilization and nitrification aeration tanks.

3. System Operation for the 10, 20, and 30 Day Sludge Age Studies

After the acclimation period, the contact-stabilization portion of each treatment system was operated at a 10 day sludge age. The nitrification portion of each system was maintained at a 40 day sludge age. The volume of each contact and stabilization aeration tank was fixed at 15.81 ℓ while the nitrification tank volume was maintained at 20.14 ℓ. The coke-oven wastewater was prepared for feeding into the systems at a strength of 35.5 percent. Concentrated hydrochloric acid was also added to lower the pH. This alleviated the problem of ammonia stripping occurring in the contact-stabilization portion of the treatment system. The feed reservoir was also supplemented with the nutrients $MgCl_2 \cdot 6H_2O$, $FeCl_3$ and KH_2PO_4 at concentrations of 10, 8, and 156 mg/ℓ, respectively. Powdered activated carbon slurries containing 0, 1,350, and 2,700 mg/ℓ were respectively fed to the contact aeration tank of each of the three systems at a flow rate of 2.3 ℓ/day. The diluted wastewater and PAC slurry flows resulted in a wastewater strength of 30.23 percent and PAC addition rates of 0, 200, and 400 mg/ℓ of combined feed, respectively. The mixed liquor powdered activated carbon (MLPAC) concentrations were 0, 980, and 1,960 mg/ℓ, respectively.

The resulting hydraulic retention time in the contact aeration tanks was 1.02 days, while the sludge return rate of the stabilization tanks was maintained at 8.93 ℓ/day thus resulting in a stabilization period of 1.77 days. The hydraulic detention time in the nitrification tank was set at 1.3 days, however, due to caustic addition for pH control, the effective detention time was 1.2 days. The solids retention times in the various systems was maintained by manual wasting twice daily. The mass of solids wasted was computed based on the measurement of the total suspended solids in the three aeration tanks and the two clarifier effluents.

The 10 day solids retention time study was ended on day 375 and all contact-stabilization systems were converted to a 20 day solids retention time operation. All operating procedures were identical to the 10 day sludge age studies except for carbon addition rate and sludge wasting. In order to maintain the same MLPAC concentrations in the contact-stabilization portion of the treatment system, the PAC slurry was reduced to 0, 675, and 1,350 mg/ℓ. This alteration in PAC slurry concentration changed the PAC addition rates to 0, 100, and 200 mg/ℓ of combined feed, respectively. The solids detention time in the nitrification aeration tank was maintained at 40 days. Sludge was wasted manually once per day. MLPAC concentrations were maintained at 0, 980, and 1,960 mg/ℓ. The 20 day solids retention time phase of operation was conducted from day 376 to day 466.

The next solids retention time studied was 30 days. Once again the only operating parameters changed were the PAC addition rates and the mass of sludge wasted. The same MLPAC concentrations of 0, 980, and 1,960 mg/ℓ were maintained by changing the PAC slurry concentrations to 0, 450, and

900 mg/ℓ, respectively. This change resulted in PAC addition rates of 0, 67, and 133 mg/ℓ, respectively. The nitrification tank solids detention time was maintained at 40 days. The appropriate volume of sludge was wasted from each system on a daily basis. The 30 day solids detention time operating phase was conducted between days 478 and 590.

4. Variable Contact Time System Operation

After the three solids detention time studies of the contact-stabilization portion of the treatment system were completed, the effect of hydraulic contact time was studied. Contact times of 1, 2/3, and 1/3 day were easily attainable with the variable levels in the contact aeration tank. The solids retention time for each of these contact times was maintained at 30 days. The operating procedure for the 1 day contact time was the 30 day solids retention time discussed earlier. Since we were only interested in the contact-stabilization portion of the treatment system, the nitrification and denitrification portions were dismantled when the 2/3 day hydraulic detention time study was under way. The contact tank volume was reduced from 15 ℓ to 10 ℓ resulting in a hydraulic detention time of approximately 2/3 of a day. Carbon addition rates of 0, 67, and 133 mg/ℓ were respectively maintained throughout the duration of the study. Sludge was also wasted in the usual manner. The 2/3 day contact time operating phase was carried out between days 603 and 680.

In order to facilitate a 1/3 day contact time, the contact tank volume was reduced from 10 ℓ to 5 ℓ. The carbon addition rates of 0, 67, and 133 mg/ℓ, were respectively maintained. This operating phase was conducted between days 681 and 726.

E. Sampling and Data Collection

Sample collection and analysis was done on a weekly basis for all phases of operation except for the 30 day sludge age study, where samples were collected every ten days. Equal volumes of influent were withdrawn from all feed reservoirs and combined. Contact clarifier effluent samples and nitrification clarifier effluent samples were withdrawn directly from the respective clarifier. Stabilization tank samples were withdrawn from the stabilization aeration tank. The final effluent from the denitrification column was collected from the effluent flow in order not to disturb the anoxic conditions within the column. All samples were centrifuged and then filtered through 0.45 μm membrane filter. The filtered samples were then stored in a refrigerator at 2°C. Solids samples were taken bi-weekly from the aeration tanks and clarifier effluents in order to control sludge age more accurately. These samples were also stored at 2°C.

The weekly or ten day samples were analyzed for chemical oxygen demand (COD), dissolved organic carbon (DOC), cyanide, thiocyanate, ammonia, nitrate, and nitrite. Total and volatile suspended solids (TSS and VSS) analyses were performed on the unfiltered samples bi-weekly. Gas composition was also performed once a week.

Upon completion of an operating phase, larger samples were taken for more complete analysis. In addition to the above analyses, organic nitrogen, oxygen uptake, and sludge settling rates were performed on the aeration tank samples. Color and GC analyses were performed on the filtered samples.

Daily data acquisition included flow rates, denitrification column gas production, and the pH in the aeration tanks.

F. Analytical Methods

1. pH. All pH measurements were made with a Beckman 3500 digital pH meter using a combination electrode.

2. Chemical Oxygen Demand. The COD of each samples was determined by the dichromate reflux method outlined in Section 508A of Standard Methods (62). Nitrite interference was eliminated by the addition of 20 g/ℓ of sulfamic acid to the standard dichromate solution.

3. Dissolved Organic Carbon. The DOC was determined with a carbon analyzer (Envirotech/Dohrmann Model DC-80). Samples were acidified to pH of 2 with phosphoric acid and purged with nitrogen gas to remove carbon dioxide.

4. Cyanide. The cyanide (CN^-) concentration of each sample was determined by the total cyanide after distillation method followed by titrimetric quantification as outlined in Sections 412A, B, and C of Standard Methods (62). Pretreatment of samples included precipitation of sulfide with $Cd(NO_3)_2 \cdot 4H_2O$ followed by lime addition for alkalinity removal. The pretreated sample was then filtered through 0.45 μm millipore membrane filter as described by Luthy et al. (29).

5. Thiocyanate. The thiocyanate (SCN^-) concentration of each sample was determined by the copper-pyridine colorimetric method adopted from Kruse and Mellon (71), Danchich and Boltz (72), and Standard Methods (62).

6. Ammonia. The ammonia concentration of each sample was determined by the distillation-titrimetric method outlined in Sections 417A and D of Standard Methods.

7. Nitrate. The nitrate (NO_3^-) concentration was determined by the chromatropic acid-colorimetric method outlined in Section 419E of Standard Methods (62). Samples were diluted with distilled water to eliminate color interference and to achieve a concentration in the 0 to 5 mg/ℓ range.

8. Nitrite. The concentration of nitrite (NO_2^-) was determined by the colorimetric method described in Section 420 of Standard Methods (62). Once again samples were diluted with distilled water to eliminate color interference and to achieve concentrations in the proper range.

9. Suspended Solids. The total and volatile suspended solids content of each sample were determined by the procedure outlined in Sections 209G and D of Standard Methods (62).

10. Gas Analysis. The nitrogen content of the gas produced from each denitrification column was determined by means of gas chromatography using a Fisher gas partitioner (Model 1200, Fisher Scientific Co., Chicago, IL). Helium was the carrier gas and samples were collected in a 500 $\mu\ell$ gas tight syringe.

11. Color Analysis. A comparative color analysis was performed on the contact clarifier effluent and the nitrification clarifier effluent at the end of each study. The spectrophotometric method outlined in Section 408B of Standard Methods was used. A Beckman Acta^{TM} III scanning spectrometer and 10 ordinates were used.

12. Organic Nitrogen. The organic nitrogen content of the aeration tank samples was determined by the Kjeldahl method outlined in Section 421 of Standard Methods (62). Organic nitrogen was run on the total sample and the supernatant and the difference was the organic nitrogen of the solids.

13. Phenols. Phenol, o, m, and p-cresols concentrations were determined by gas chromatography. Acid fraction extraction followed by gas chromatographic separation using an 8 ft long 2 mm ID column packed with 10 percent SP 2100 on 80/100 Supelcoport.

14. Alkalinity. Alkalinity concentrations were determined by the method described in Section 403 of Standard Methods (62).

IV - RESULTS AND DISCUSSION

A. Phase One

During the first phase of the study, which extended between day 305 and day 375 of operation, the solids retention time in the contact-stabilization portion of each of the three treatment systems was maintained at 10 days. Solids samples were taken biweekly and sludge was wasted from the stabilization tank twice daily. The mixed liquor powdered activated carbon (MLPAC) concentration averaged over the contact and stabilization aeration tanks was maintained at 0, 980, and 1,960 mg/l for systems 1, 2, and 3, respectively. The solids retention time in the nitrification aeration tank was maintained at 40 days with daily sludge wastage.

1. Chemical Oxygen Demand and Dissolved Organic Carbon

The performance of the three treatment systems relative to reduction of chemical oxygen demand (COD) is shown in Figures 8-10, while the corresponding data relative to dissolved organic carbon (DOC) are shown in Figures 11-13. The data appearing for the period extending between day 305 and day 375 represent the 10 day sludge age study. The numerical values of these two parameters averaged over the last 42 days of operation are given in Tables 2 and 3. The effluent from the contact-stabilization portion of these two parameters averaged over the last 42 days of operation are given in Tables 2 and 3. The effluent from the contact-stabilization portion of the treatment system receiving no powdered activated carbon (PAC) was consistently lower in COD and DOC than the corresponding effluents from both systems receiving PAC. These results are surprising since the addition of PAC was anticipated to result in improved effluent quality. The poorer

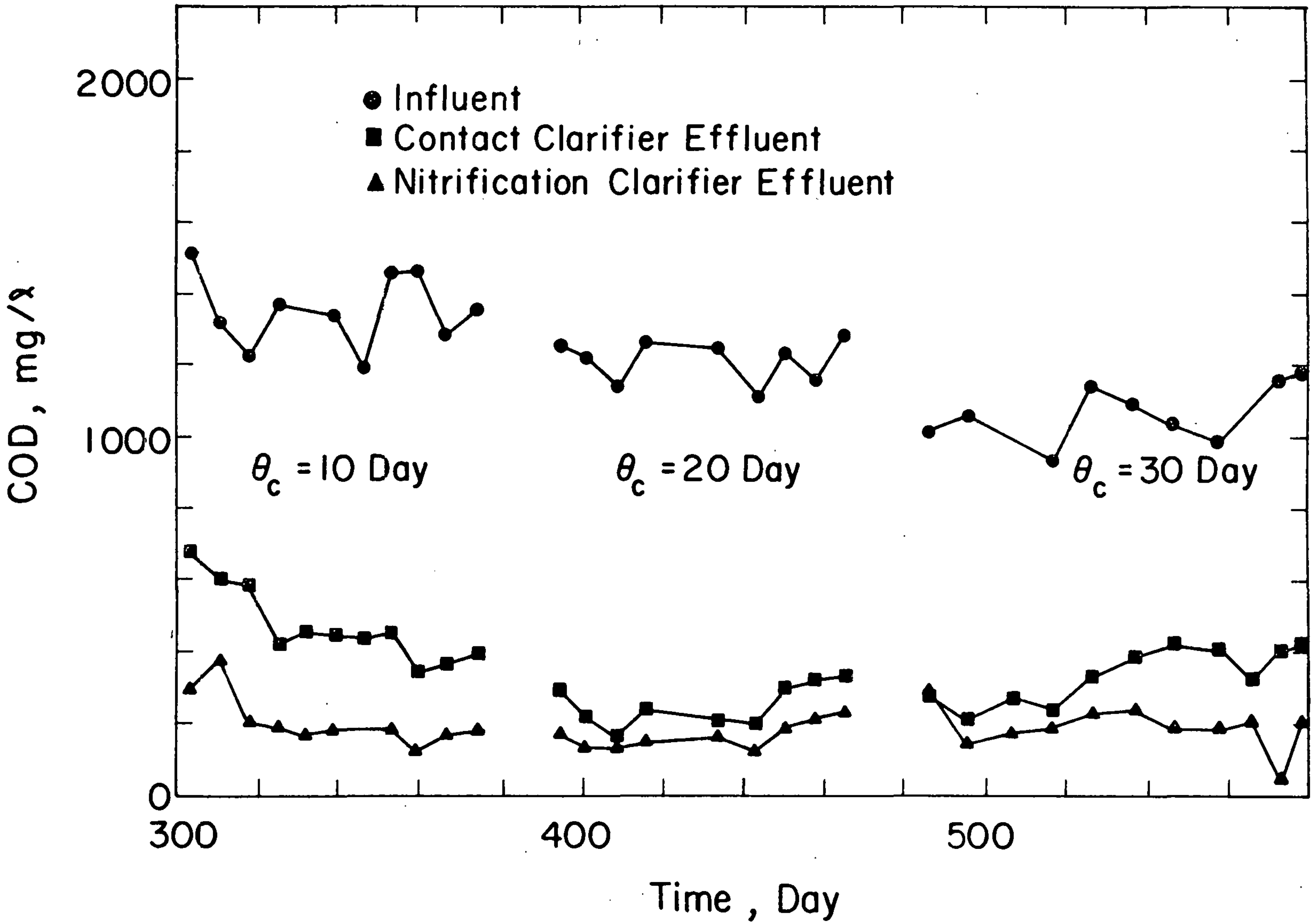


Figure 8. COD Reduction in 0 mg/ℓ MLPAC System

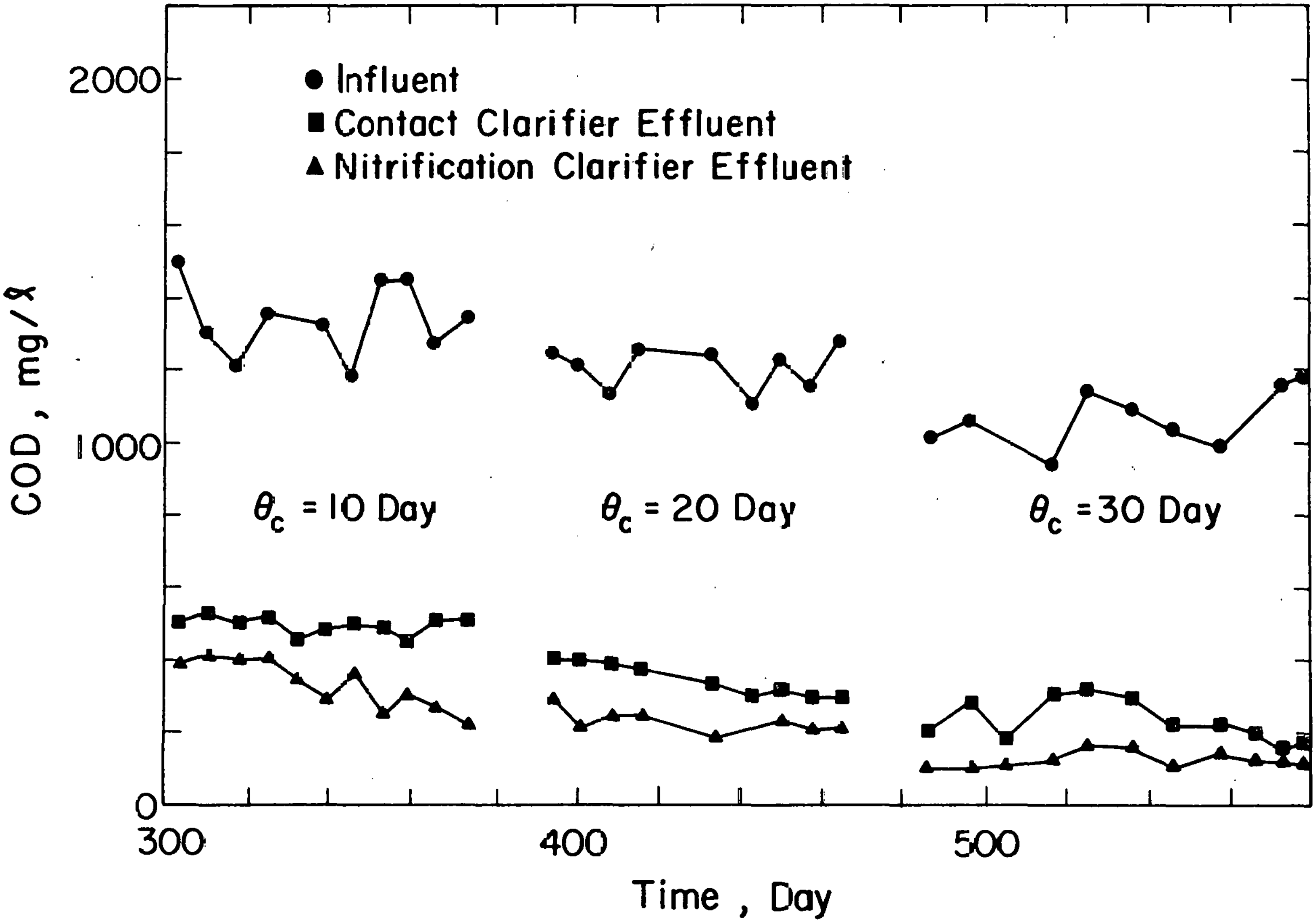


Figure 9. COD Reduction in 980 mg/ℓ MLPAC System

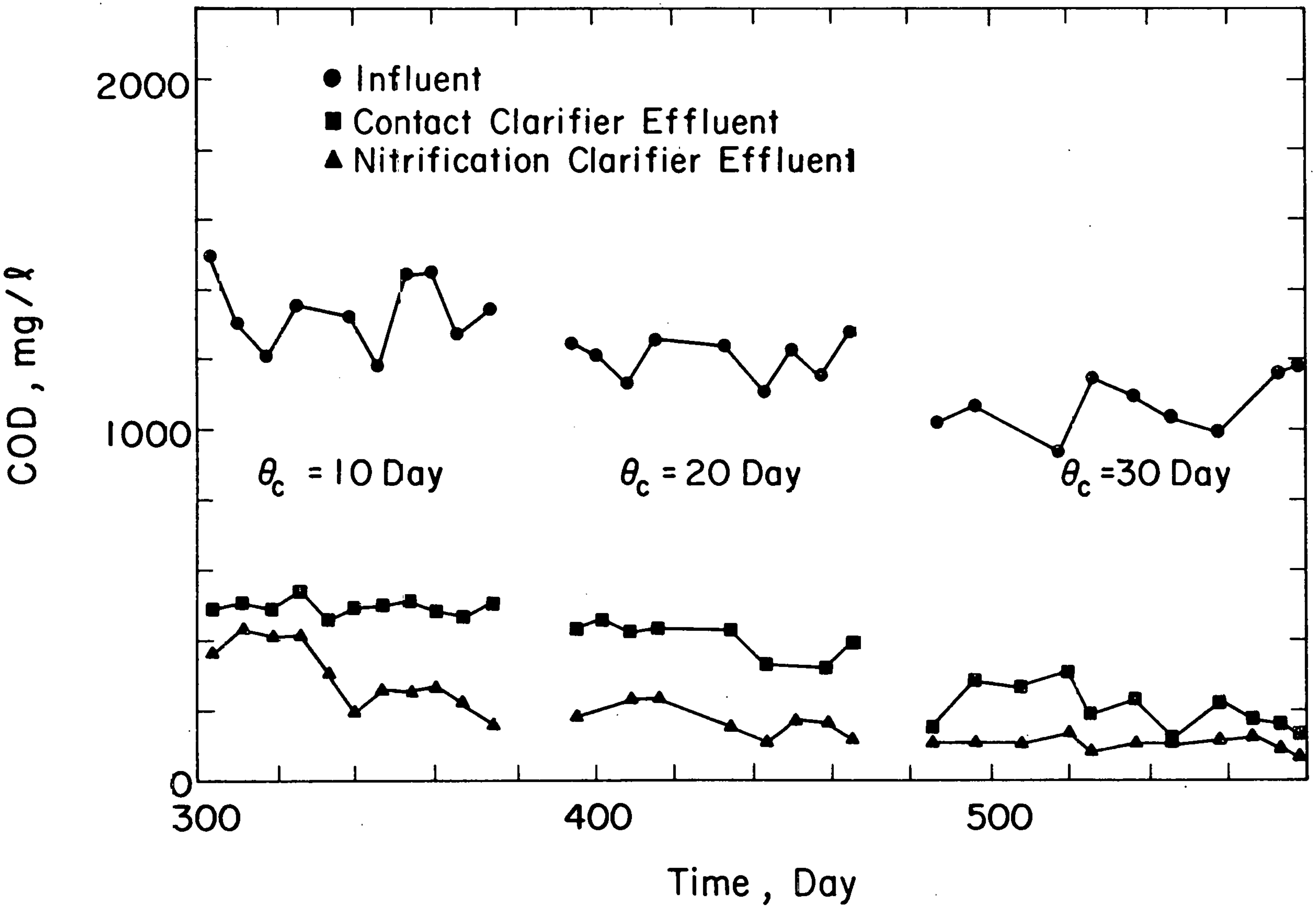


Figure 10. COD Reduction in 1960 mg/ℓ MLPAC System

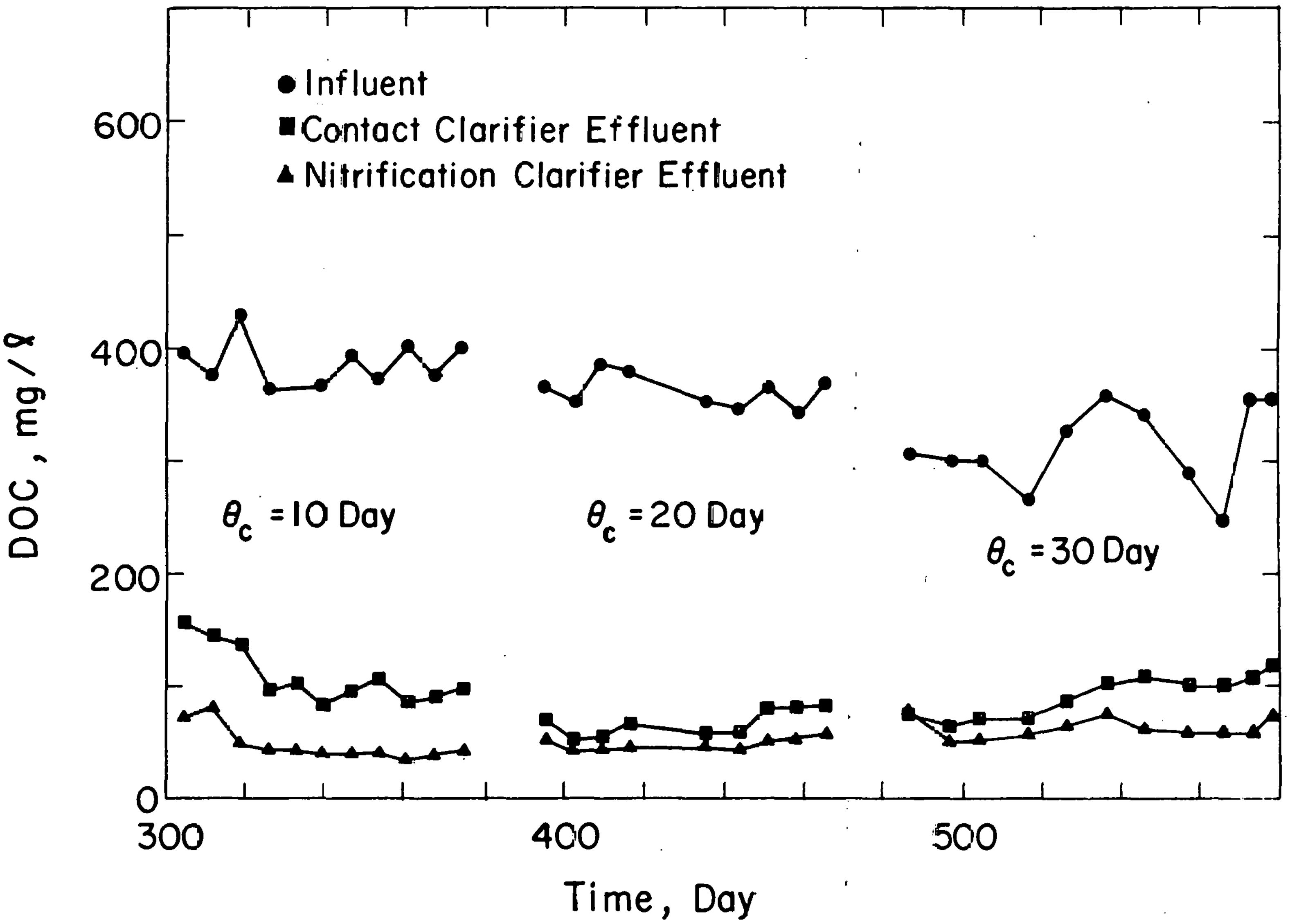


Figure 11. DOC Reduction in 0 mg/ℓ MLPAC System

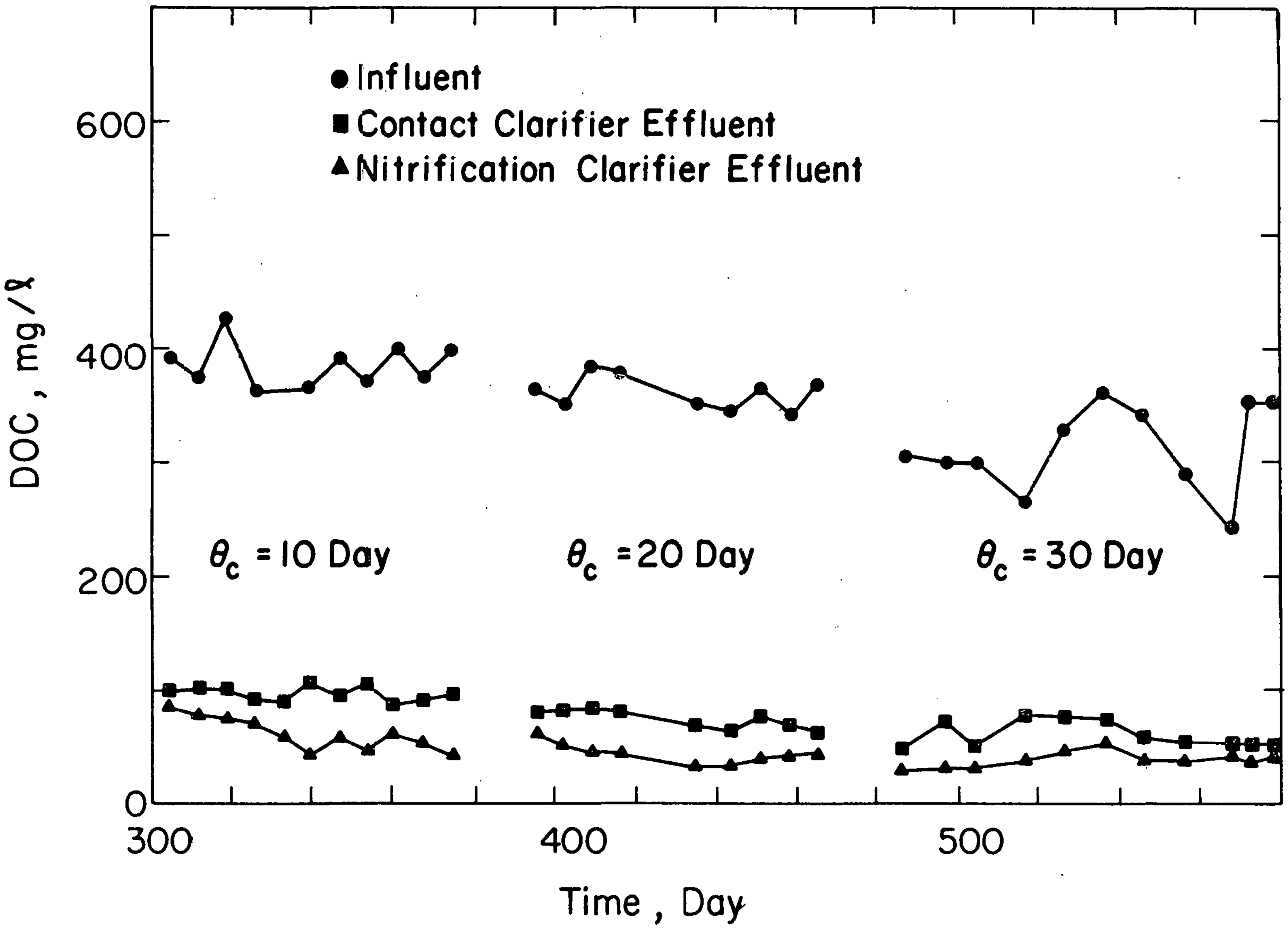


Figure 12. DOC Reduction in 980 mg/ℓ MLPAC System

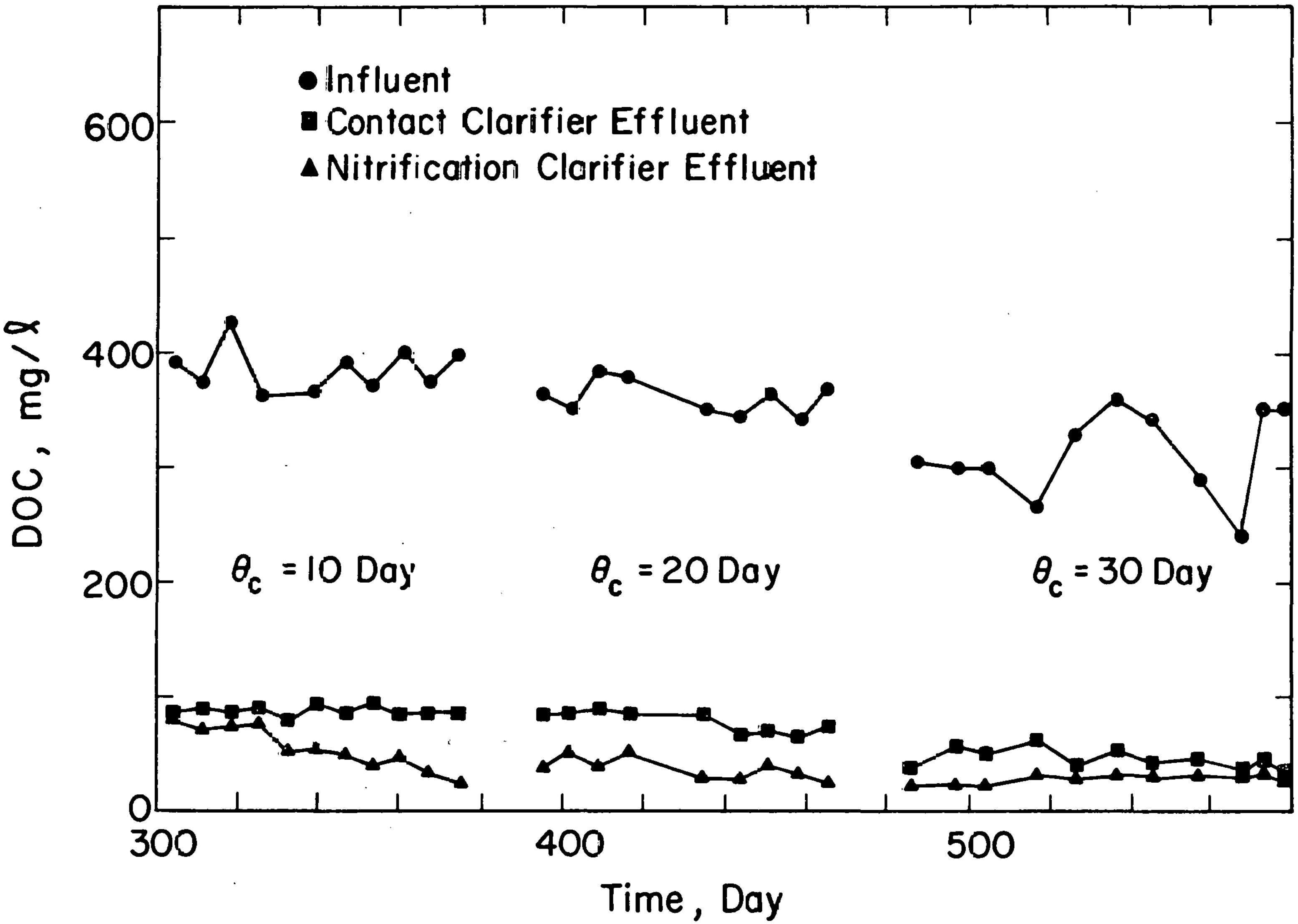


Figure 13. DOC Reduction in 1960 mg/ℓ MLPAC System

Table 2

Performance of Treatment System in Reducing COD

	0 mg/ℓ MLPAC System			980 mg/ℓ MLPAC System			1,960 mg/ℓ MLPAC System		
	θ_c = 10 Day COD(mg/ℓ)	θ_c = 20 Day COD(mg/ℓ)	θ_c = 30 Day COD(mg/ℓ)	θ_c = 10 Day COD(mg/ℓ)	θ_c = 20 Day COD(mg/ℓ)	θ_c = 30 Day COD(mg/ℓ)	θ_c = 10 Day COD(mg/ℓ)	θ_c = 20 Day COD(mg/ℓ)	θ_c = 30 Day COD(mg/ℓ)
Influent	1,350(103)	1,204(77)	1,165(12)	1,350(103)	1,204(77)	1,165(12)	1,350(103)	1,204(77)	1,165(12)
Contact Clarifier Effluent	406(55) *69.93%	304(63) 74.75%	415(15) 64.35%	495(20) 63.41%	306(10) 74.58%	165(15) 85.84%	500(19) 62.96%	356(33) 70.43%	152(14) 86.95%
Stabilization Tank	298(56) 77.93%	310(75) 74.25%	399(25) 65.75%	512(23) 62.07%	258(28) 77.74%	159(6) 86.35%	517(19) 61.70%	348(32) 71.10%	133(15) 88.58%
Nitrification Clarifier Effluent	199(70) 85.26%	205(63) 82.97%	177(46) 84.81%	278(65) 79.41%	188(69) 81.56%	120(6) 89.70%	233(57) 82.74%	148(36) 87.70%	77(14) 93.39%

( ) Quantity in parentheses represents standard deviation.

* Percent removal.

Table 3

Performance of Treatment Systems in Reducing DOC

	0 mg/ℓ MLPAC System			980 mg/ℓ MLPAC System			1,960 mg/ℓ MLPAC System		
	θ_c = 10 Day DOC(mg/ℓ)	θ_c = 20 Day DOC(mg/ℓ)	θ_c = 30 Day DOC(mg/ℓ)	θ_c = 10 Day DOC(mg/ℓ)	θ_c = 20 Day DOC(mg/ℓ)	θ_c = 30 Day DOC(mg/ℓ)	θ_c = 10 Day DOC(mg/ℓ)	θ_c = 20 Day DOC(mg/ℓ)	θ_c = 30 Day DOC(mg/ℓ)
Influent	385(15)	355(15)	353(2)	385(15)	355(15)	353(2)	385(15)	355(15)	353(2)
Contact Clarifier Effluent	90(13) *76.62%	77(12) 78.31%	111(8) 68.73%	97(8) 74.81%	68(7) 80.84%	49(1) 86.12%	89(5) 76.88%	69(5) 80.56%	40(7) 88.67%
Stabilization Tank	61(14) 84.16%	72(14) 79.72%	111(2) 68.73%	89(12) 76.81%	52(8) 85.35%	41(5) 88.38%	90(4) 76.62%	57(16) 83.94%	31(1) 91.22%
Nitrification Clarifier Effluent	40(4) 91.17%	55(11) 34.51%	62(10) 82.44%	53(13) 86.23%	41(7) 88.45%	40(4) 88.67%	41(12) 89.35%	32(11) 90.98%	29(3) 91.78%

( ) Quantity in parentheses represents standard deviation.

* Percent removal.

performance of the contact-stabilization portion of the two systems receiving PAC may be due to competition for substrate between the activated carbon and the biomass. This competition for substrate may result in lower biomass concentrations in the reactors and limited bioregeneration of the PAC in the stabilization tanks. This limited biological activity that was observed for the systems receiving PAC becomes evident when the performance of the stabilization tanks of the three systems is evaluated relative to DOC and COD removal as given in Tables 2 and 3. The stabilization tank of the 0 mg/l MLPAC system accounted for the removal of 0.96 and 0.26 gram per day of aqueous phase DOC and COD, respectively, whereas no net reduction in these parameters was observed in the stabilization tanks of the other two units.

The superior performance of the treatment system receiving no PAC was also reflected in the COD and DOC concentrations in the nitrification clarifier effluent. The reduced organic load on the nitrification aeration tank improved the organics removal performance of that portion of the treatment system. Again, the system receiving no PAC exhibited superior total COD and DOC reduction.

Upon closer examination of Figures 8-13 we find that the contact-clarifier effluents from the systems receiving PAC, although higher in COD and DOC concentrations, were somewhat more stable than the system receiving no PAC. The PAC addition to these systems appeared to provide more stable operation of the contact-stabilization units. Furthermore, PAC addition seemed to alleviate foaming in the aeration tanks. Foaming represented a severe problem in the aeration tanks of the unit receiving no PAC.

2. Ammonia, Cyanide, and Thiocyanate

The ammonia, cyanide, and thiocyanate profiles across the three treatment systems are shown in Figures 14-22. The data that pertain to this phase

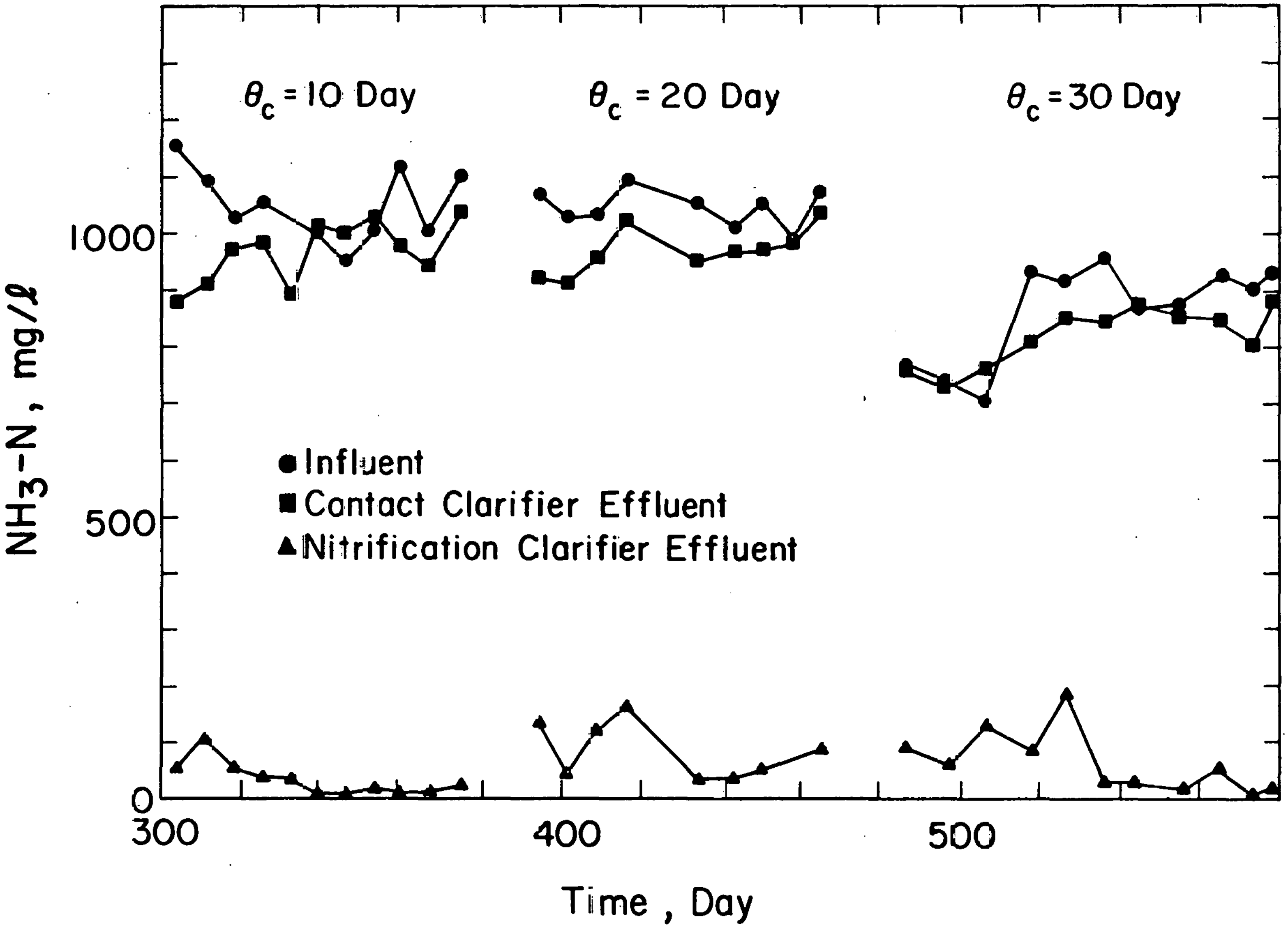


Figure 14. Ammonia-Nitrogen Reduction in 0 mg/ℓ MLPAC System

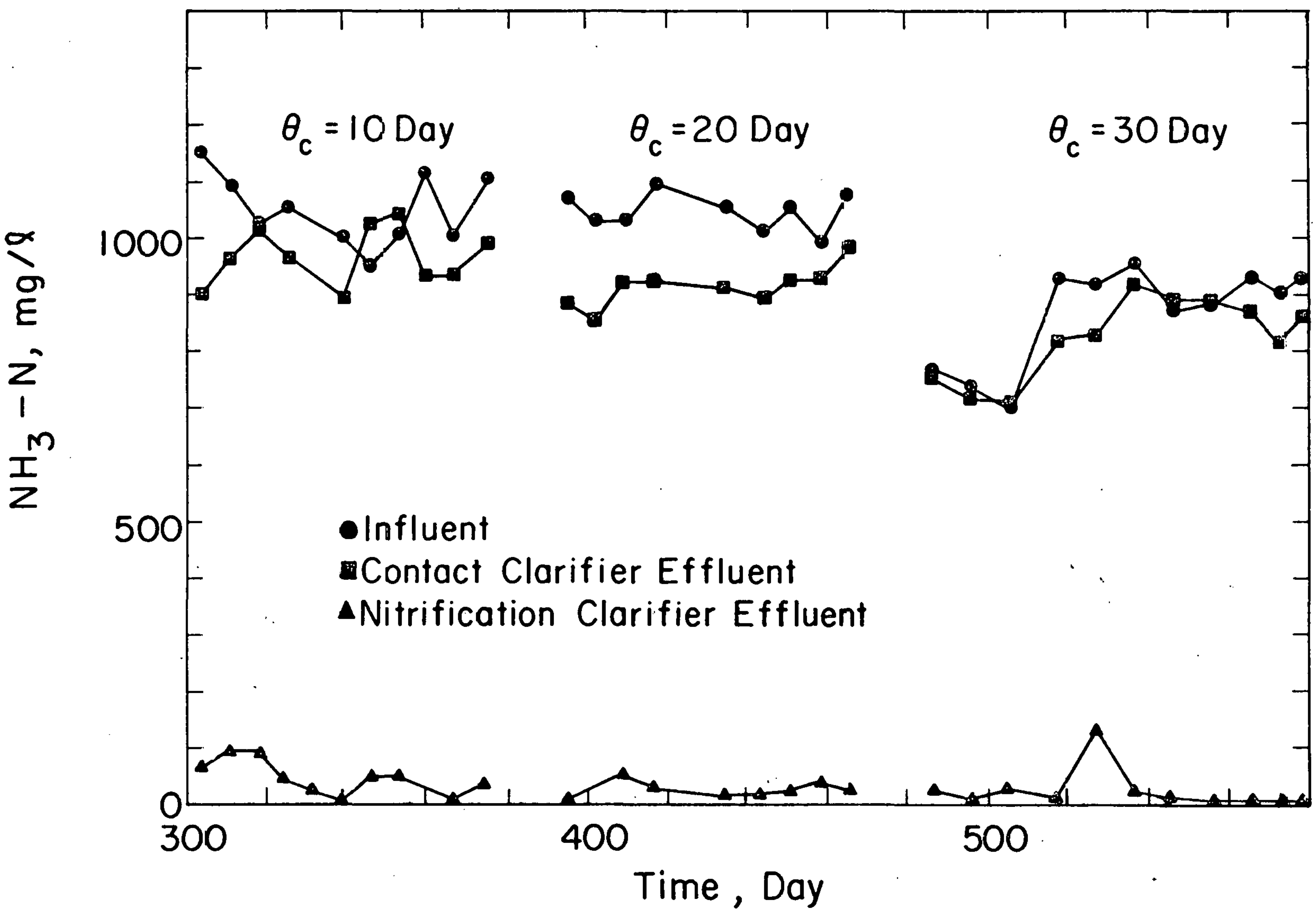


Figure 15. Ammonia-Nitrogen Reduction in 980 mg/ℓ MLPAC System

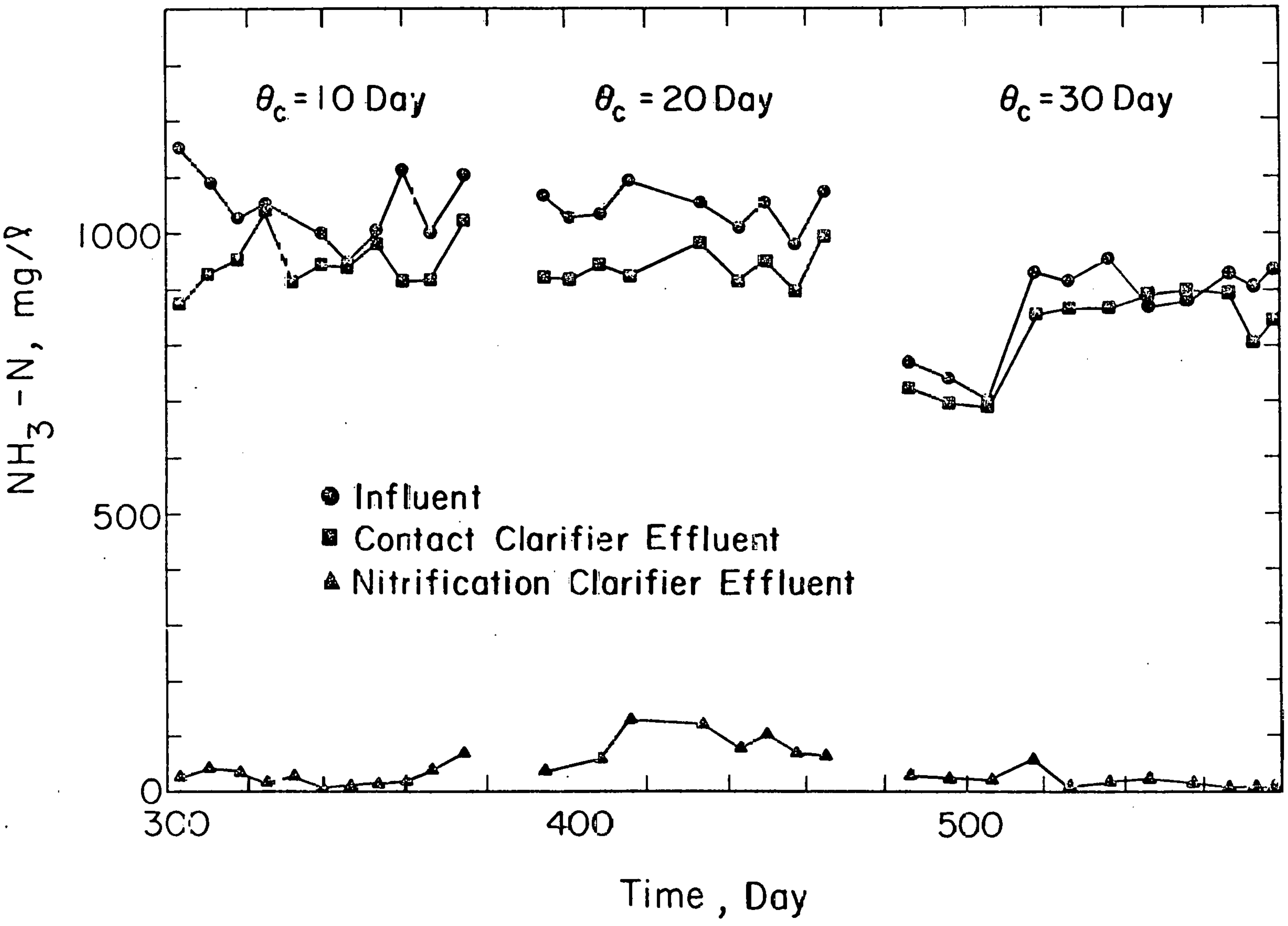


Figure 16. Ammonia-Nitrogen Reduction in 1960 mg/ℓ MLPAC System

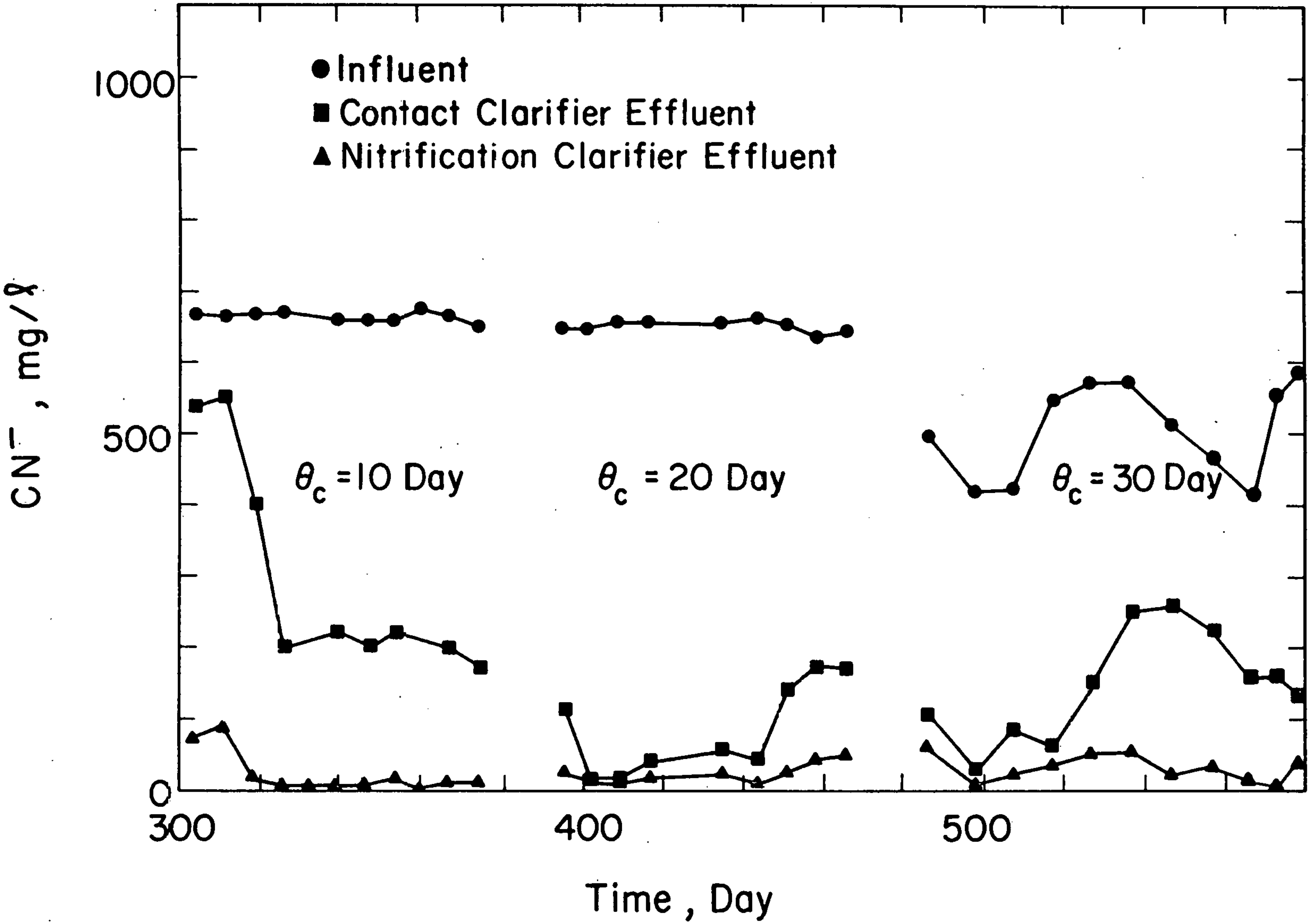


Figure 17. Cyanide Reduction in 0 mg/ℓ M_PAC System

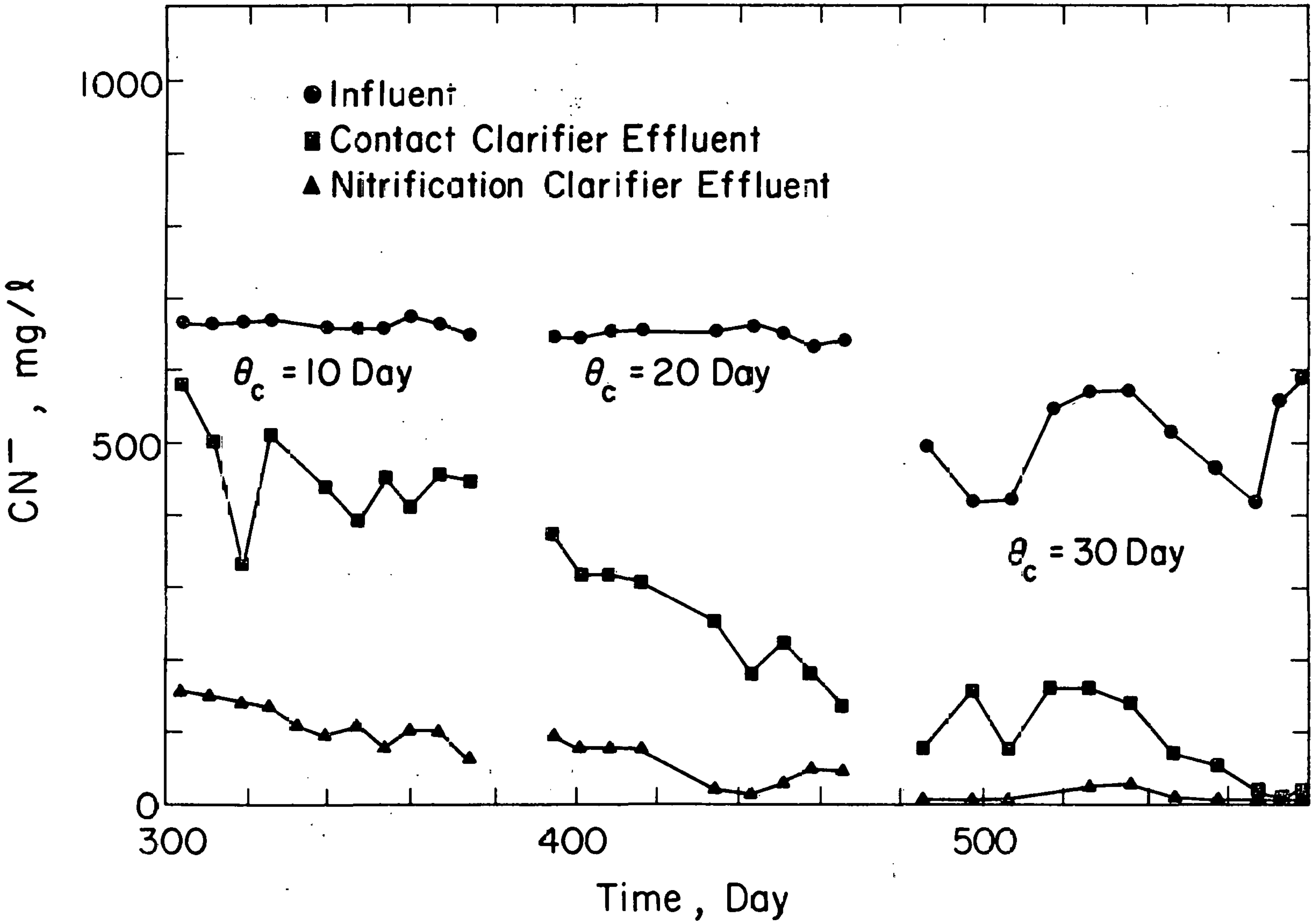


Figure 18. Cyanide Reduction in 980 mg/ℓ MLPAC System

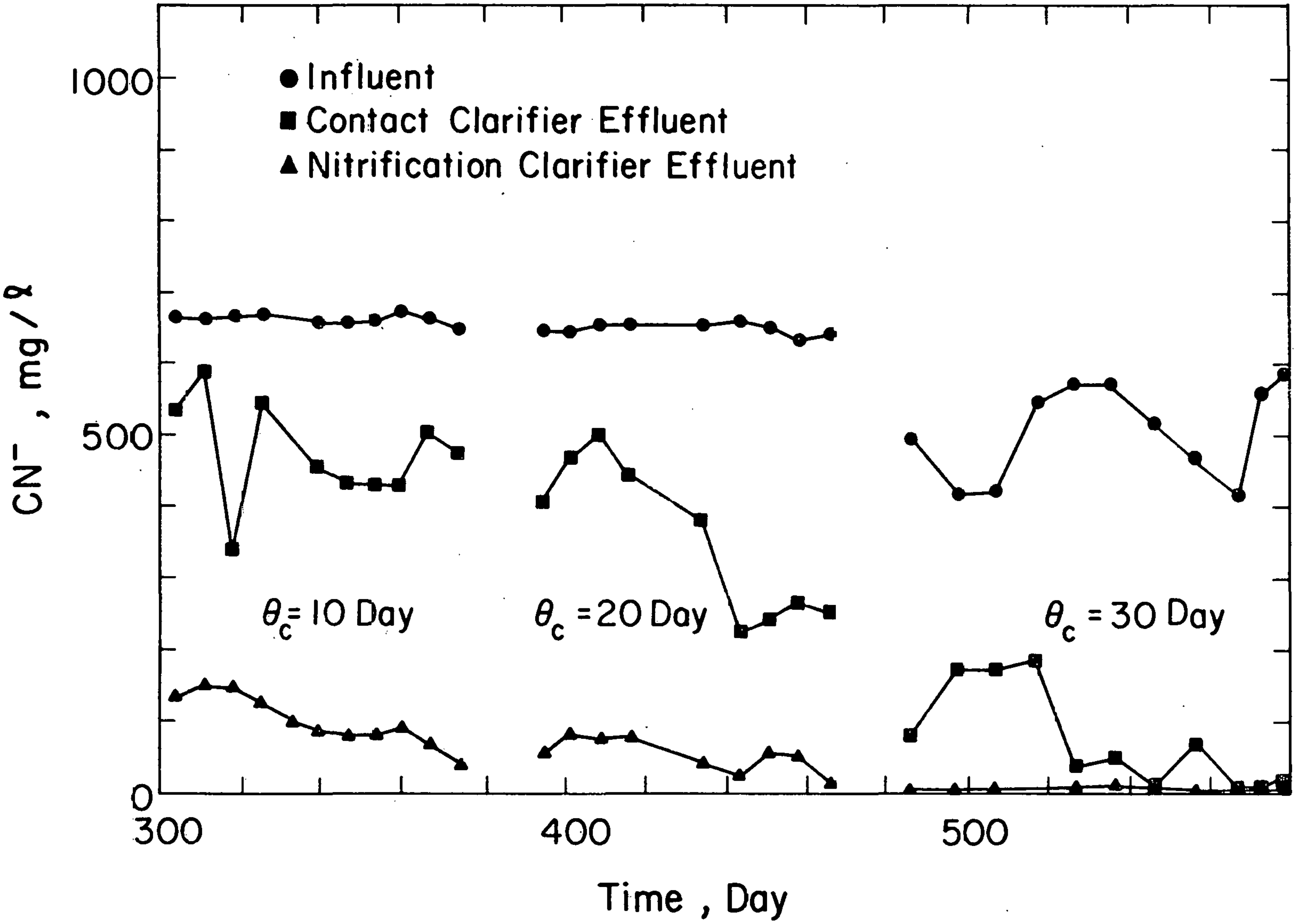


Figure 19. Cyanide Reduction in 1960 mg/ℓ MLPAC System

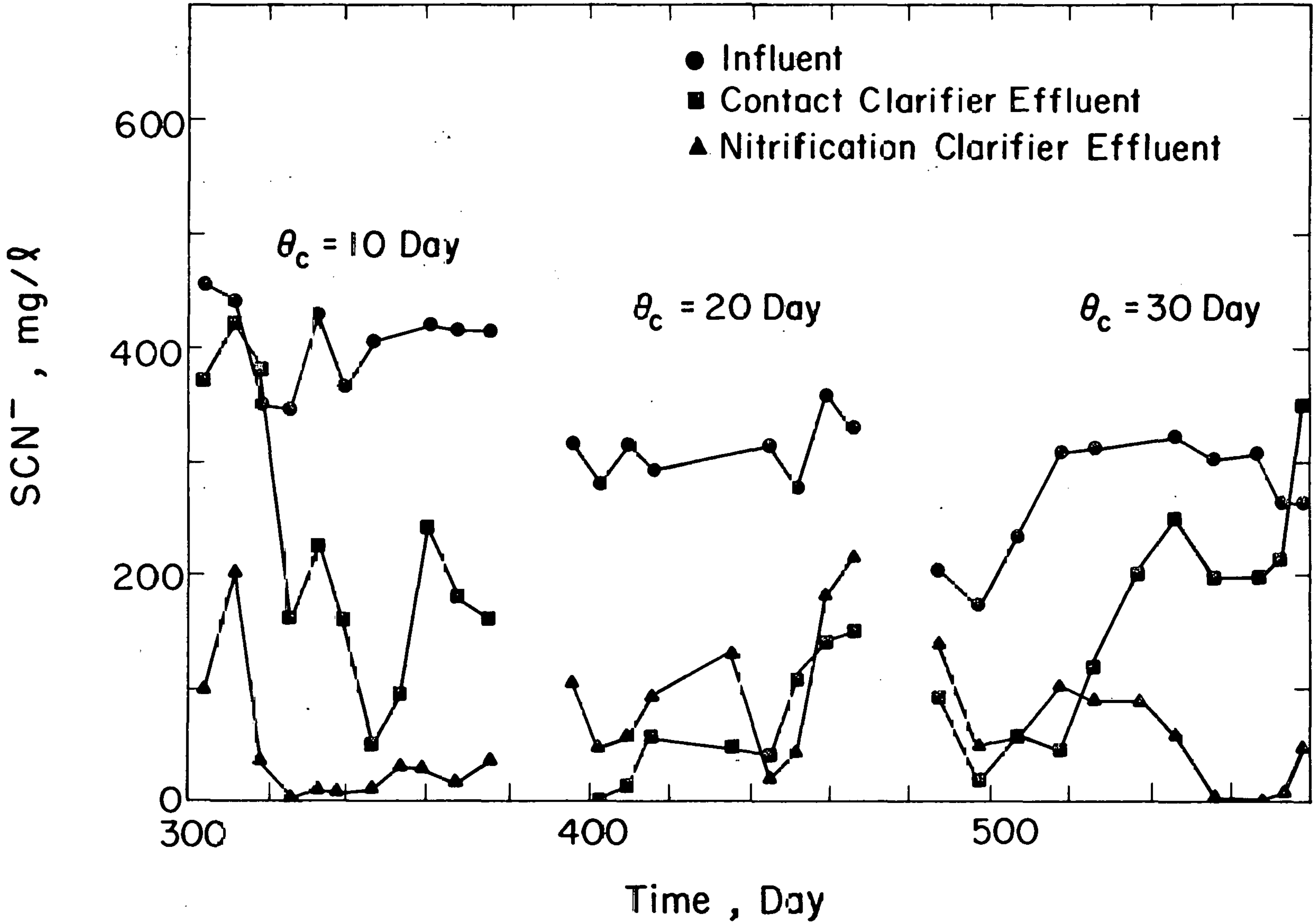


Figure 20. Thiocyanate Reduction in 0 mg/ℓ MLPAC System

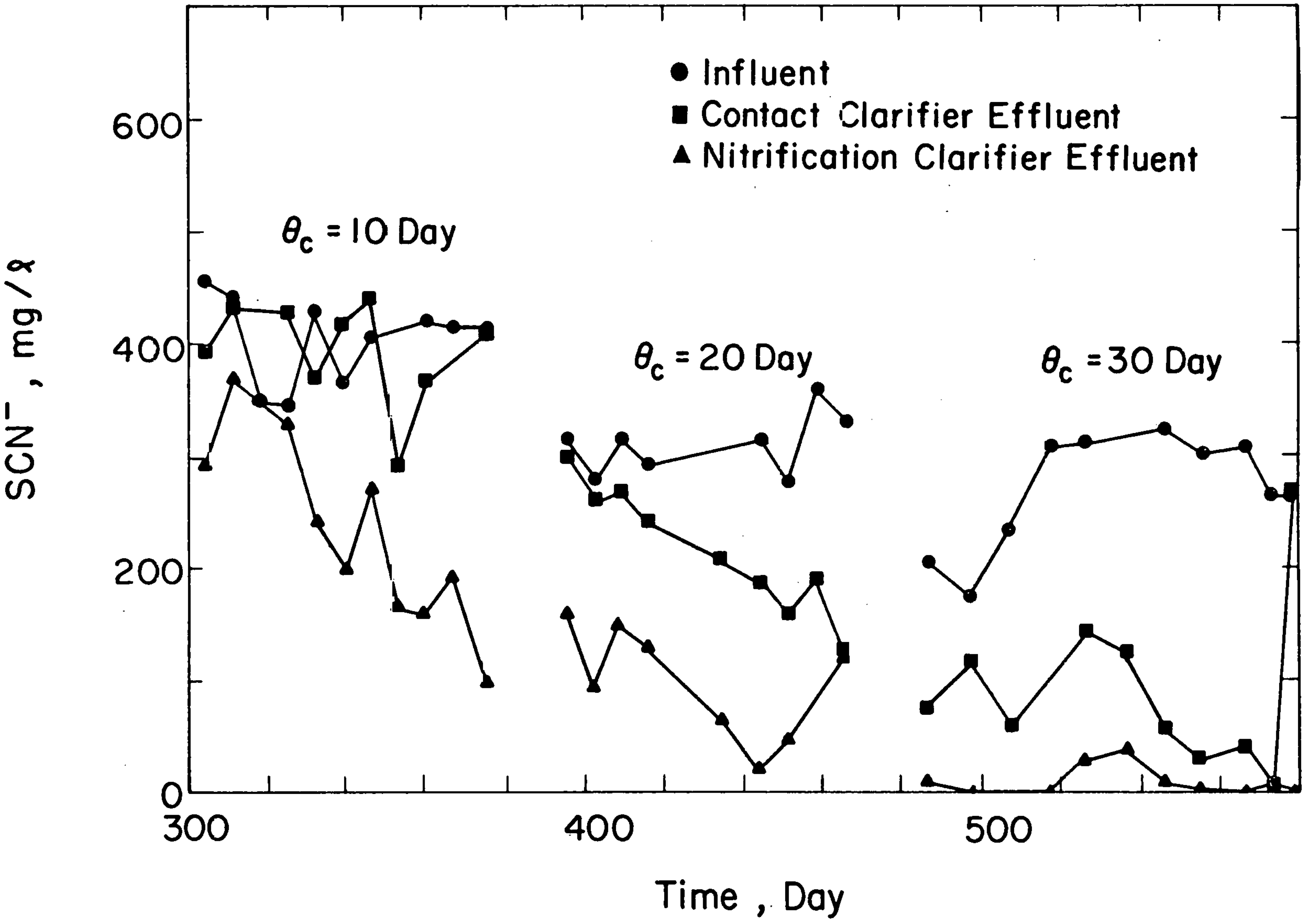


Figure 21. Thiocyanate Reduction in 980 mg/ℓ MLPAC System

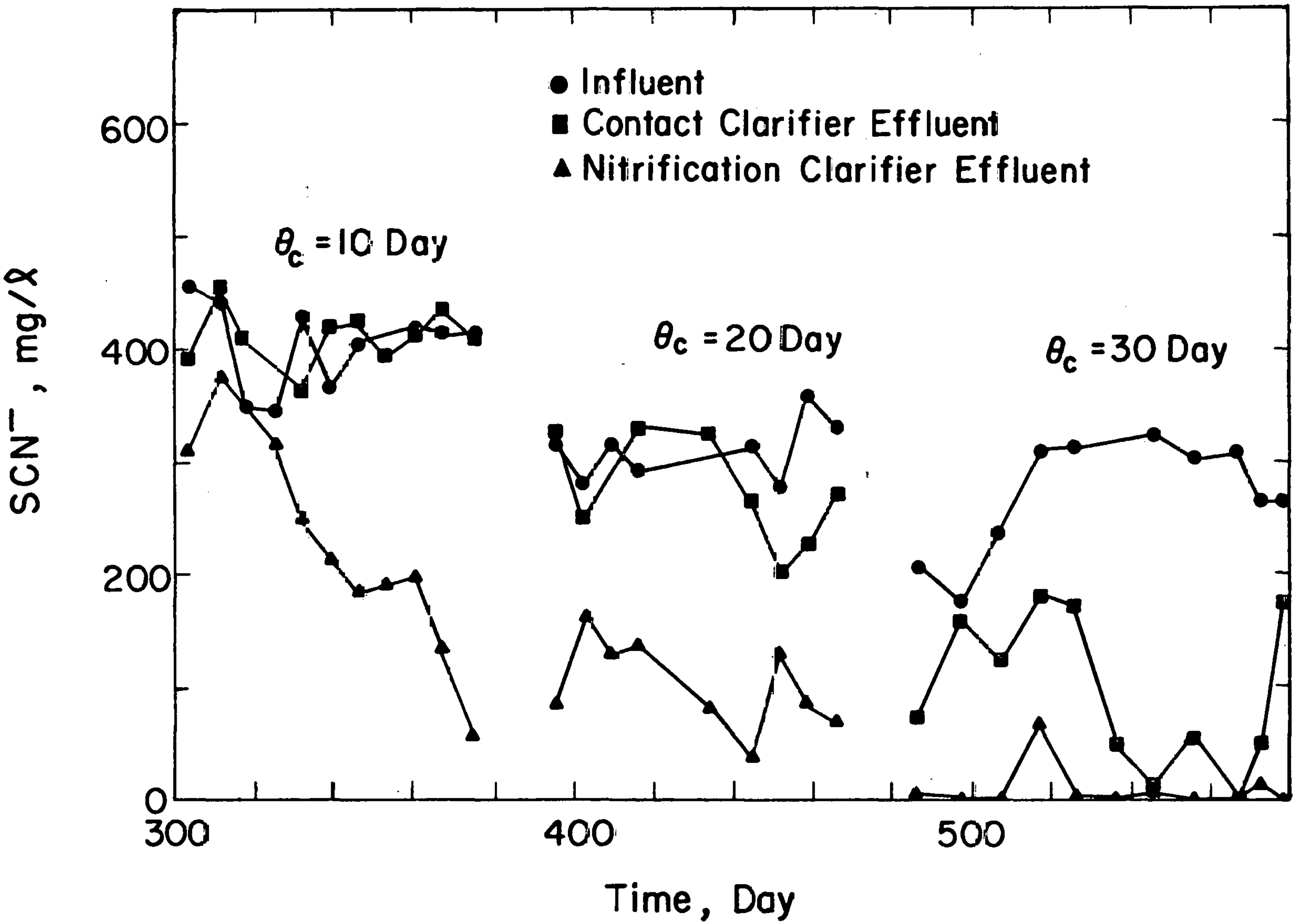


Figure 22. Thiocyanate Reduction in 1,960 mg/ℓ MLPAC System

of the study are given between day 305 and day 375 and the numerical values of these parameters averaged over the last 42 days of operations are shown in Tables 4-6. The fate of these three constituents are discussed simultaneously due to the fact that ammonia is released as a result of the oxidation of cyanide and thiocyanate.

The three treatment systems exhibited a slight decrease in ammonia in the contact-stabilization portion of the treatment systems. However, as shown in Table 7, the concentration of nitrite and nitrate nitrogen in the effluent from the contact-stabilization portion of the treatment systems was consistently lower than 10 mg/l, indicating that the reduction in ammonia was primarily due to ammonia utilization by synthesis and to a much lesser extent to stripping (the pH in the contact and stabilization aeration tanks was maintained between 7.6 and 8.4). The reduction in ammonia in the contact-stabilization portion of the 0 mg/l MLPAC system was slightly lower than the removals observed in the other two units. This difference may be due to the fact that reductions in cyanide and thiocyanate were much higher in the 0 mg/l MLPAC system, and consequently, ammonia released during the oxidation of these compounds contributed to an increase in the overall ammonia concentration.

When the principal nitrogen containing compounds are expressed in terms of their equivalent nitrogen concentration (Table 7), the 0 mg/l MLPAC system shows the highest reduction in total nitrogen when compared to the other systems. This may be attributed to the fact that more nitrogen was utilized for cell synthesis in the 0 mg/l PAC system since higher reductions in organic matter and no removal of organics by adsorption were possible in this system.

Table 4

Performance of Treatment Systems in Reducing NH_3-N

	0 mg/ℓ MLPAC System			980 mg/ℓ MLPAC System			1,960 mg/ℓ MLPAC System		
	θ_c = 10 Day NH_3-N(mg/ℓ)	θ_c = 20 Day NH_3-N(mg/ℓ)	θ_c = 30 Day NH_3-N(mg/ℓ)	θ_c = 10 Day NH_3-N(mg/ℓ)	θ_c = 20 Day NH_3-N(mg/ℓ)	θ_c = 30 Day NH_3-N(mg/ℓ)	θ_c = 10 Day NH_3-N(mg/ℓ)	θ_c = 20 Day NH_3-N(mg/ℓ)	θ_c = 30 Day NH_3-N(mg/ℓ)
Influent	1,035(63)	1,030(42)	920(20)	1,035(63)	1,030(42)	920(20)	1,035(63)	1,030(42)	920(20)
Contact Clarifier Effluent	1,006(39) * 2.80%	991(31) 3.79%	845(55) 8.15%	981(47) 5.22%	959(35) 6.89%	839(34) 8.80%	954(4[illegible]) 10.83%	937(37) 9.03%	829(32) 9.89%
Stabilization Tank	1,046(68) -1.06%	976(32) 5.24%	748(39) 18.70%	975(40) 5.31%	933(38) 9.42%	781(31) 15.11%	949(25) 8.31%	936(24) 9.13%	801(63) 12.93%
Nitrification Clarifier Effluent	14(5) 98.65%	57(2[illegible]) 94.46%	19(7) 97.93%	27(20) 97.39%	27(9) 97.34%	1(1) 99.89%	27(23) 97.39%	75(18) 92.72%	3(1) 99.67%

( ): Quantity in parentheses represents standard deviation.

* Percent removal.

Table 5

Performance of Treatment Systems in Reducing Cyanide

	0 mg/ℓ MLPAC System			980 mg/ℓ MLPAC System			1,960 mg/ℓ MLPAC System		
	θ_c = 10 Day CN$^-$(mg/ℓ)	θ_c = 20 Day CN$^-$(mg/ℓ)	θ_c = 30 Day CN$^-$(mg/ℓ)	θ_c = 10 Day CN$^-$(mg/ℓ)	θ_c = 20 Day CN$^-$(mg/ℓ)	θ_c = 30 Day CN$^-$(mg/ℓ)	θ_c = 10 Day CN$^-$(mg/ℓ)	θ_c = 20 Day CN$^-$(mg/ℓ)	θ_c = 30 Day CN$^-$(mg/ℓ)
Influent	658(32)	657(30)	574(23)	658(32)	657(30)	574(23)	658(32)	657(30)	574(23)
Contact Clarifier Effluent	204(66) *69.00%	166(20) 74.73%	146(22) 74.56%	428(32) 34.95%	179(46) 72.75%	8(5) 98.60%	450(41) 31.61%	255(13) 61.19%	9(8) 98.43%
Stabilization Tank	18(12) 97.26%	149(11) 77.32%	132(3) 77.00%	422(35) 35.87%	108(56) 83.56%	5(2) 99.13%	397(55) 39.67%	223(6) 66.06%	6(4) 99.13%
Nitrification Clarifier Effluent	14(8) 97.87%	41(12) 93.76%	22(19) 96.17%	89(22) 86.47%	42(11) 93.61%	6(1) 98.95%	69(25) 89.51%	28(17) 95.74%	6(1) 98.95%

( ) Quantity in parentheses represents standard deviation.

* Percent removal.

Table 6

Performance of Treatment Systems in Reducing Thiocyanate

	0 mg/ℓ MLPAC System			980 mg/ℓ MLPAC System			1,960 mg/ℓ MLPAC System		
	θ_c = 10 Day SCN^- (mg/ℓ)	θ_c = 20 Day SCN^- (mg/ℓ)	θ_c = 30 Day SCN^- (mg/ℓ)	θ_c = 10 Day SCN^- (mg/ℓ)	θ_c = 20 Day SCN^- (mg/ℓ)	θ_c = 30 Day SCN^- (mg/ℓ)	θ_c = 10 Day SCN^- (mg/ℓ)	θ_c = 20 Day SCN^- (mg/ℓ)	θ_c = 30 Day SCN^- (mg/ℓ)
Influent	412(6)	321(34)	306(3)	429(7)	321(34)	306(3)	428(7)	321(34)	306(3)
Contact Clarifier Effluent	183(52) *59.58%	109(42) 66.04%	187(17) 38.89%	409(35) 4.66%	166(29) 48.29%	36(7) 88.23%	425(15) 0.70%	242(34) 24.61%	39(30) 87.25%
Stabilization Tank	30(12) 92.72%	111(63) 65.42%	256(31) 16.34%	392(35) 8.62%	128(44) 60.12%	18(25) 94.12%	442(20) -3.27%	236(23) 26.48%	19(17) 93.79%
Nitrification Clarifier Effluent	18(11) 95.63%	116(99) 63.86%	3(3) 99.02%	190(57) 55.71%	65(52) 79.75%	3(3) 99.02%	148(59) 65.42%	81(39) 74.77%	7(9) 94.44%

( ) Quantity in parentheses represents standard deviation.

* Percent removal.

Table 7

Performance of Treatment Systems in Reducing Nitrogen Containing Compounds, θ_c = 10 Day

	0 mg/l MLPAC System						980 mg/l MLPAC System						1960 mg/l MLPAC System					
	NH_3-N mg/ℓ	CN-N mg/ℓ	SCN-N mg/ℓ	NO_3-N mg/ℓ	NO_2-N mg/ℓ	Total N mg/ℓ	NH_3-N mg/ℓ	CN-N mg/ℓ	SCN-N mg/ℓ	NO_3-N mg/ℓ	NO_2-N mg/ℓ	Total N mg/ℓ	NH_3-N mg/ℓ	CN-N mg/ℓ	SCN-N mg/ℓ	NO_3-N mg/ℓ	NO_2-N mg/ℓ	Total N mg/ℓ
Influent	1,035	354	99	-	-	1,488	1,035	354	104	-	-	1,493	1,035	354	103	-	-	1,492
Contact Clarifier Effluent	1,006	110	44	30	5	1,168	981	230	99	1	1	1,312	954	242	103	1	-	1,300
Stabilization Tank	1,046	10	7	7	45	1,115	975	227	95	2	7	1,306	949	214	107	1	2	1,273
Nitrification Clarifier Effluent	15	8	4	1,045	13	1,085	29	52	50	900	60	1,090	29	40	39	941	31	1,080

The removal of cyanide and thiocyanate in the contact-stabilization portion of the 0 mg/l MLPAC system was superior to the two units receiving PAC. The 0 mg/l MLPAC system was twice as effective in removing cyanide as either of the other two units. Very little thiocyanate reduction occurred in either of the 980 mg/l and 1,960 mg/l MLPAC systems, while roughly 55 percent removal of thiocyanate occurred in the contact-stabilization portion of the 0 mg/l MLPAC unit.

All three nitrification tanks resulted in ammonia removal efficiencies exceeding 97 percent. The nitrate-nitrogen concentration in the 0 mg/l MLPAC system was noticeably higher than the concentration in the other two units. The effluent from the nitrification clarifier in the no PAC system was consistently more fully nitrified.

Substantial reductions in cyanide and thiocyanate occurred in all of the nitrification aeration tanks. The systems receiving carbon exhibited additional reductions in cyanide by roughly 50 percent in the nitrification aeration tanks. Thiocyanate reduction in the two systems receiving PAC also occurred primarily in the nitrification aeration tanks. The 0 mg/l MLPAC system experienced the highest overall efficiencies with respect to both cyanide and thiocyanate reduction. An interesting observation from the systems receiving PAC was that the relatively high concentrations of both cyanide and thiocyanate did not seem to noticeably inhibit nitrification as has been frequently reported in the literature (23).

3. Suspended Solids

The suspended solids profiles for the various aeration tanks and clarifier effluents are shown in Figures 23-25. The numerical values of the solids concentrations averaged over the final 42 days of operation are

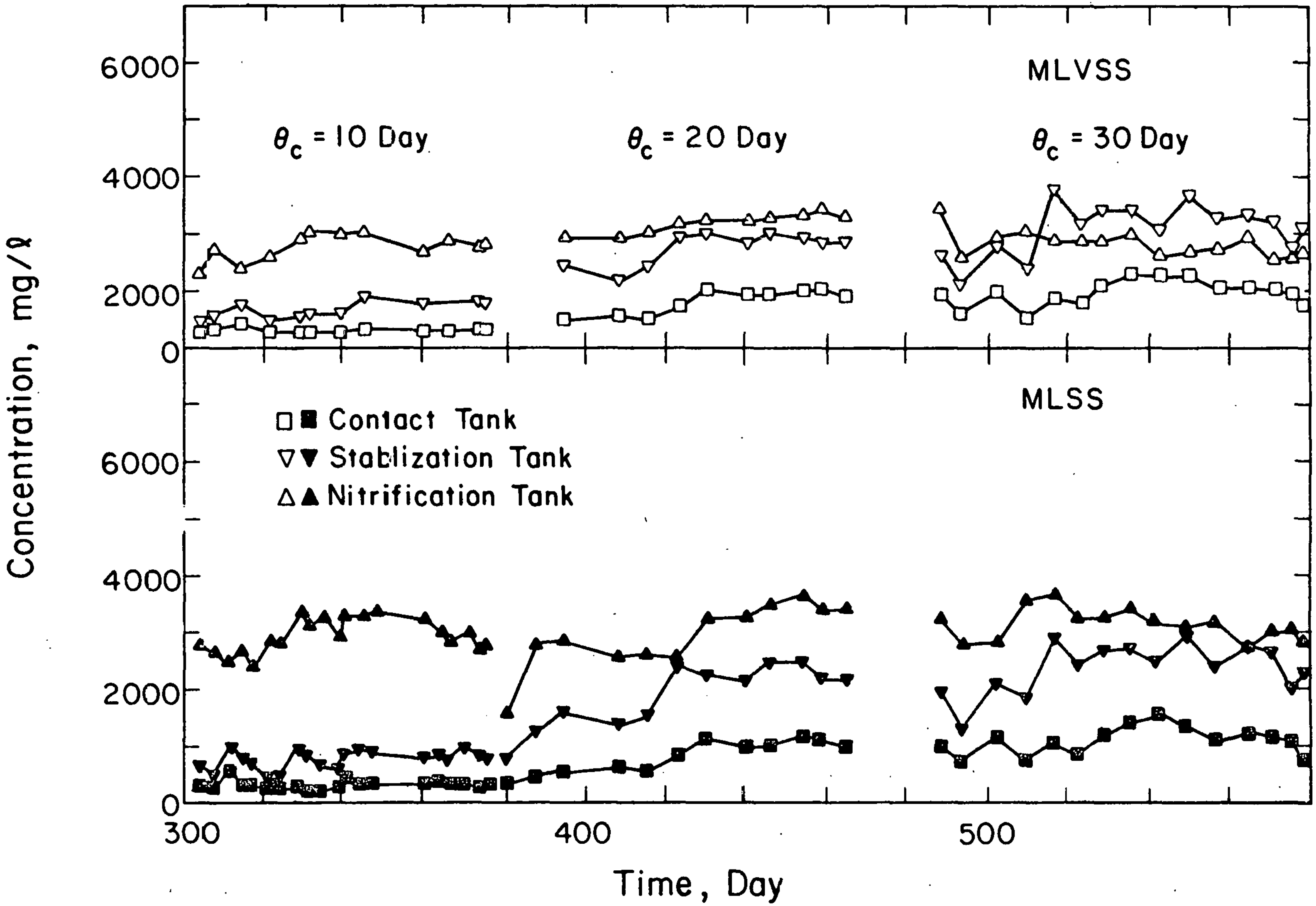


Figure 23. Total and Volatile Suspended Solids in 0 mg/ℓ MLPAC System Aeration Tanks

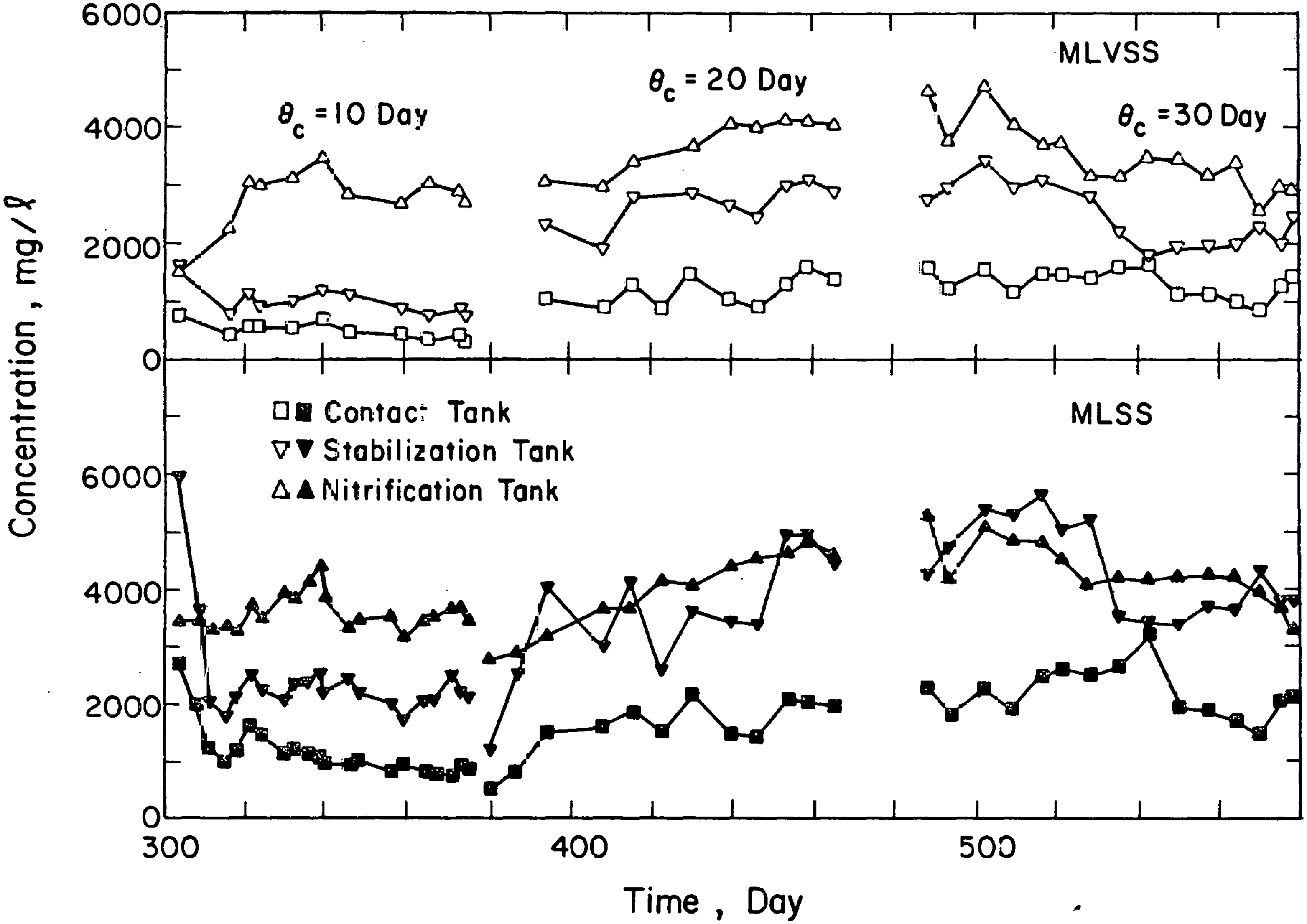


Figure 24. Total and Volatile Suspended Solids in 980 mg/ℓ MLPAC System Aeration Tanks

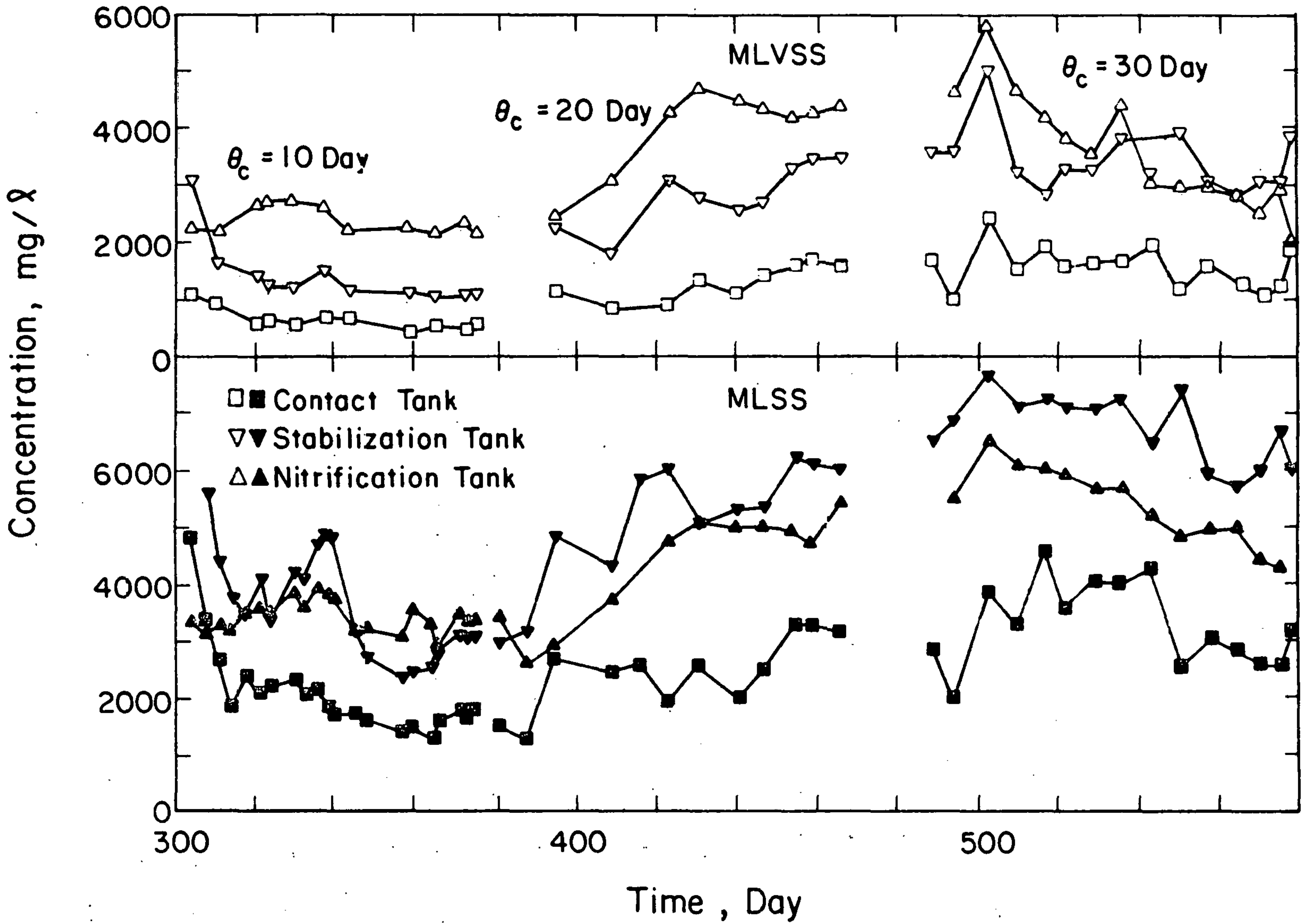


Figure 25. Total and Volatile Suspended Solids in 1,960 mg/ℓ MLPAC System Aeration Tanks

shown in Table 8. The powdered activated carbon concentration values were calculated using the feed levels, the solids concentration, and the hydraulic retention time data. In making these calculations it was assumed that the solids composition in the contact and stabilization tanks of every system was the same. Additionally, it was also assumed that the PAC fraction in the solids escaping clarification was the same as that in the mixed liquor. Consequently, it was estimated that appreciable concentrations of PAC persisted in the nitrification tanks of the two systems receiving PAC although no direct PAC addition to these tanks was practiced.

Upon examination of Figures 23-25, it becomes apparent that the solids concentrations in the contact and stabilization aeration tanks were fairly stable for all systems while the nitrification aeration tanks exhibited more variation in solids concentration. This can be explained by the sensitivity of the nitrifying organisms to pH. A slight variation in pH may cause a change in the biomass concentration. Furthermore, the nitrification tanks were operated using a very long sludge age of 40 days. Because of this extended sludge age, it is expected that stable operating conditions are only attainable after long feeding periods.

The yield coefficients for the various aeration tanks are shown in Table 9. These values were calculated from the total suspended solids present in each tank averaged over the final 42 days of operation of this phase of the study. The mass of total suspeneded solids in the contact and stabilization tanks were summed together and then divided by the sludge age in order to compute the mass of solids produced per day. The mass of COD consumed per day was then computed and the total solids yield, Y, was the ratio of mass of solids produced per day over the mass of COD reduced per day. This procedure was satisfactory for the 0 mg/l MLPAC system, but some

Table 8

Suspended Solids Concentration in Treatment Systems, θ_c = 10 Day

	0 mg/ℓ MLPAC System			980 mg/ℓ MLPAC System				1,960 mg/ℓ MLPAC System			
	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	PAC(mg/ℓ)	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	PAC(mg/ℓ)
Contact Tank	349(79)	326(27)	93.41	855(156)	442(130)	51.70	614	1,541(134)	474(81)	30.76	1,365
Stabilization Tank	931(128)	848(92)	91.08	1,874(562)	926(309)	49.41	1,346	2,887(553)	1,130(101)	39.14	2,557
Nitrification Tank	3,013(256)	1,723(313)	57.48	3,412(488)	2,892(253)	84.76	1,150	3,066(445)	2,260(340)	73.71	1,691
Contact Clarifier Effluent	41(25)	-	-	52(20)	-	-	37	62(25)	-	-	55
Nitrification Clarifier Effluent	52(20)	-	-	71(22)	-	-	24	80(27)	-	-	44

( ) Quantity in parentheses represents standard deviation.

Table 9

Total Solids Production from Treatment Systems

	0 mg/ℓ MLPAC System			980 mg/ℓ MLPAC System			1,960 mg/ℓ MLPAC System		
	θ_c = 10 Day Y gTSS/gCOD	θ_c = 20 Day Y gTSS/gCOD	θ_c = 30 Day Y gTSS/gCOD	θ_c = 10 Day Y gTSS/gCOD	θ_c = 20 Day Y gTSS/gCOD	θ_c = 30 Day Y gTSS/gCOD	θ_c = 10 Day Y gTSS/gCOD	θ_c = 20 Day Y gTSS/gCOD	θ_c = 30 Day Y gTSS/gCOD
Contact-stabilization aeration tanks	.271	.349	.174	.416	.626	.229	.591	.638	.324
Nitrification aeration tanks	.013	.026	.021	.013	.025	.024	.008	.026	.032

modifications in the calculations had to be exercised in applying this procedure to the systems receiving PAC. For the 980 mg/l MLPAC and the 1,960 mg/l MLPAC system the effect of carbon in the system had to be dealt with. Once again the total mass of solids in the contact and stabilization tanks was computed and this mass was divided by the sludge age. The mass of carbon introduced daily into the system was substracted from the total daily mass of solids produced in order to account for the carbon in the system. The yield obtained from this procedure was thought to be more usable in terms of system evaluation. A deficiency of this procedure, however, is the fact that the mass of PAC may increase upon addition to the system due to adsorption of organic matter. This is not believed to constitute a major discrepancy because the primary organic constituents of this wastewater, cyanide and thiocyanate, are nonadsorbable.

The yield in the nitrification aeration tanks was computed similarly except both COD reduction and ammonia conversion to nitrate had to be formulated. The COD in grams per day was computed similarly to the method used in the calculation on the contact-stabilization portion of the system while the ammonia reduction was calculated differently. The difference between the total nitrogen in the forms of ammonia-nitrogen, cyanide-nitrogen, and thiocyanate nitrogen entering into the nitrification tank and the total nitrogen out of the tank determined the total ammonia reduction across the system. All three forms of nitrogen had to be accounted for due to the production of ammonia by the oxidation of cyanide and thiocyanate. The total nitrogen removed in g/day was then multiplied by a conversion factor of 4.57 and added to the COD removed in g/day in order to represent the oxygen demand satisfied in the aeration tank. The effects of carbon carry over on the nitrification tank was also accounted for. The daily influx of PAC mass into the nitrification tank was substracted from the total solids produced per day.

The yields found in Table 9 indicate that the amount of solids produced increased with increasing carbon addition rates in the contact-stabilization portion of the treatment system. The amount of sludge handled and ultimately disposed of was greatest for the 1,960 mg/l MLPAC system. The nitrification cell yield values however, indicate that less sludge was produced from the systems receiving carbon. This difference in mass of solids produced is not as pronounced in the nitrification aeration tanks, as it was in the contact-stabilization tanks, however.

4. Denitrification of Nitrite and Nitrate

The performance of the denitrification columns is shown in Table 10. The concentrations of the nitrite-nitrogen and nitrate-nitrogen were altered from the nitrification clarifier concentrations due to dilution by the methanol fed into the denitrification column. As Table 10 indicates, greater than 97 percent of the nitrate-nitrogen and nitrite-nitrogen into the columns was converted to nitrogen gas for all three systems. The COD of the denitrification column effluents was consistently higher than the influent to these columns indicating that the rate of denitrification was most probably not limited by the availability of organic carbon.

5. Phenolic Compounds

The coke-oven wastewater employed in this study was characterized by a lower than usual content of phenolic compounds and considerably higher than expected concentrations of cyanide and thiocyanate. The data in Table 11 represent the steady-state fate of phenol, 0, m, and p-cresol, and 2,4-dimethyl phenol in the treatment systems. All three treatment systems

Table 10

Performance of the Denitrification Columns

	0 mg/ℓ MLPAC System									980 mg/ℓ MLPAC System									1,960 mg/ℓ MLPAC System								
	θ_c = 10 Day			θ_c = 20 Day			θ_c = 30 Day			θ_c = 10 Day			θ_c = 20 Day			θ_c = 30 Day			θ_c = 10 Day			θ_c = 20 Day			θ_c = 30 Day		
	NO_3-N	NO_2-N	Total	NO_3-N	NO_2-N	Total	NO_3-N	NO_2-N	Total	NO_3-N	NO_2-N	Total	NO_3-N	NO_2-N	Total	NO_3-N	NO_2-N	Tota	NO_3-N	NO_2-N	Total	NO_3-N	NO_2-N	Total	NO_3-N	NO_2-N	Total
*Nitrification Clarifier Effluent	923	15	938	480	366	846	817	40	857	795	52	847	644	271	915	825	0	825	866	28	894	835	9	844	829	0	829
Denitrification Column Effluent	24	3	27	9	106	115	0	0	0	8	4	12	17	106	123	0	0	0	14	6	20	7	2	9	0	0	0
Percent Removal		97.12			86.40			100.00			98.60			86.56			100.00			97.76			98.93			100.00	

*The concentrations of nitrite and nitrate-nitrogen are corrected for the dilution with methanol.

Table 11

Performance of Treatment System in Reducing Phenols, θ_c = 10 Days

		0 mg/ℓ MLPAC System			980 mg/ℓ MLPAC System			1,960 mg/ℓ MLPAC System		
Parameter	Influent	C-S Clarifier	Stab. Tank	Nit. Clarifier	C-S Clarifier	Stab. Tank	Nit. Clarifier	C-S Clarifier	Stab. Tank	Nit. Clarifier
Phenol (mg/ℓ)	45	4.75	< DL*	< DL	2.5	< DL	< DL	1.75	< DL	< DL
o-Cresol (mg/ℓ)	2.64	1.75	< DL	< DL	0.77	0.57	< DL	0.675	0.75	< DL
m & p-Cresol (mg/ℓ)	4.27	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
2,4-Dimethylphenol (mg/ℓ)	0.60	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL

---

* < DL = below detection limit

resulted in excellent removal efficiencies for the phenolic compounds, and no detectable concentration of any of these compounds was found in the effluents from the three nitrification tanks.

B. Phase Two

After the first phase of the study was completed the solids retention time in the contact-stabilization portion of each system was increased to 20 days. Solids samples were taken biweekly and sludge was wasted once per day. The average MLPAC concentration in the contact and stabilization aeration tanks was maintained at 0, 980, and 1,960 mg/l for systems 1, 2, and 3, respectively. The solids retention time in the nitrification aeration tanks was not altered, thus remaining at 40 days with daily sludge wastage.

1. Chemical Oxygen Demand and Dissolved Organic Carbon

The performance of the three treatment systems relative to reduction in COD is shown in Figures 8-10, while the corresponding data relative to DOC are shown in Figures 11-13. The data that describe this phase of the study appear between day 376 and day 466 in the pertinent figures. The numerical values of these two parameters averaged over the last 21 days of operation are shown in Tables 2 and 3. The effluents from the contact-stabilization portion of the 0 mg/l MLPAC and the 980 mg/l MLPAC systems exhibited relatively the same level of performance in terms of COD reduction, while the 1,960 mg/l MLPAC system resulted in slightly lower COD reduction. Some discrepancy occurs, however, when removal efficiencies in terms of DOC and COD are compared. The DOC data in Table 3 indicate that the 980 mg/l MLPAC and 1,960 mg/l MLPAC systems exhibited slightly better performance than the 0 mg/l MLPAC counterpart. All systems were very close in COD and DOC reduction and for all practical purposes achieved the same level of performance. When the 20 day sludge age data are compared with the results of the 10 day sludge age studies, it becomes apparent that the performance of all three systems relative to COD and DOC reduction had improved considerably with increased sludge age. The systems receiving carbon showed the most substantial increase in COD and DOC removal efficiencies.

The level of performance in reducing COD and DOC concentrations in the nitrification aeration tank was noticeably higher in the 1,960 mg/l MLPAC system as compared to the other two units. An additional 17 percent of the COD was removed in the 1,960 mg/l MLPAC system while only an additional 6-8 percent of the COD was removed in the nitrification aeration tanks of the other two systems. The same observation also applies to DOC reduction in the nitrification aeration tanks of the three systems. These results indicate that the performance of the overall treatment scheme of the 1,960 mg/l MLPAC system was superior over the 0 mg/l MLPAC and 980 mg/l MLPAC systems.

When the 20 day sludge age COD and DOC data for the nitrification portion of the systems are compared to the data from the 10 day sludge age, we find that the systems receiving carbon improved in COD and DOC reduction while the 0 mg/l MLPAC exhibited a deterioration in overall performance.

The systems receiving PAC experienced somewhat more stable operating characteristics when compared to the 0 mg/l MLPAC systems. The COD and DOC profiles for the systems receiving PAC did not fluctuate as much as those for the 0 mg/l system. This phenomena is evident in both the contact-stabilization and nitrification portions of the treatment scheme.

2. Ammonia, Cyanide, and Thiocyanate

The ammonia, cyanide, and thiocyanate profiles across the three treatment systems are shown in Figures 14-22 for the period extending between days 376 and 466 of operation. The numerical values of these parameters averaged over the last 21 days of operation are shown in Tables 4-6. Once again, a loss of nitrogen occurred in the contact-stabilization portion of each of the three treatment systems as pointed out in Table 12. Roughly the same amount of nitrogen loss was exhibited in all three treatment systems. This loss in nitrogen is approximately one and a half times the mass of nitrogen that was not accounted for in the liquid phase of the 10 day sludge age study. An increase in sludge age will usually result in decreased net synthesis and, consequently, less nitrogen utilization for growth. However, the yields for all three systems increased during this phase of the study suggesting that increased biomass synthesis may be responsible for the increased nitrogen loss (Table 9).

The amount of nitrification occurring in the contact and stabilization aeration tanks increased slightly during the 20 day sludge age phase of the study as compared to the degree of nitrification experienced during the previous phase of operation. The total nitrate-nitrogen and nitrite-nitrogen concentration in the contact clarifier effluent ranged from 12 mg/l for the 0 mg/l MLPAC system to 58 mg/l in the 1,960 mg/l MLPAC system. The majority of the oxidized nitrogen was found to be in the form of nitrite-nitrogen, however, thus suggesting inhibited nitrification.

The reduction in cyanide and thiocyanate in the contact-stabilization portion of the 0 mg/l MLPAC system remained greater than the reduction observed in the systems receiving activated carbon. The removal of cyanide

Table 12

Performance of Treatment Systems in Reducing Nitrogen Containing Compounds, θ_c = 20 Day

	0 mg/ℓ MLPAC System						980 mg/ℓ MLPAC System						1,950 mg/ℓ MLPAC System					
	NH_3-N mg/ℓ	CN-N mg/ℓ	SCN-N mg/ℓ	NO_3-N mg/ℓ	NO_2-N mg/ℓ	Total N mg/ℓ	NH_3-N mg/ℓ	CN-N mg/ℓ	SCN-N mg/ℓ	NO_3-N mg/ℓ	NO_2-N mg/ℓ	Total N mg/ℓ	NH_3-N mg/ℓ	CN-N mg/ℓ	SCN-N mg/ℓ	NO_3-N mg/ℓ	NO_2-N mg/ℓ	Total N mg/ℓ
Influent	1,030	354	77	-	-	1,461	1,030	354	77	-	-	1,461	1,030	354	77	-	-	1,461
Contact Clarifier Effluent	991	89	26	8	14	1,128	959	96	40	5	17	1,117	937	137	58	15	43	1,190
Stabilization Tank	976	80	27	21	65	1,169	933	58	31	14	48	1,084	936	120	57	24	64	1,201
Nitrification Clarifier Effluent	92	24	30	543	415	1,104	29	25	17	730	307	1,108	81	16	22	946	10	1,075

achieved in the 0 mg/l MLPAC system was 2 and 13 percent over the 980 mg/l MLPAC systems and 1,960 mg/l MLPAC system, respectively. All systems exhibited increased effectiveness in treating cyanide and thiocyanate when compared to the 10 day sludge age study. The systems receiving PAC experienced a two-fold increase in the cyanide removal efficiency. The thiocyanate removal efficiency, on the other hand, increased from 5 to 48 percent, and 1 to 25 percent for the 980 mg/l MLPAC and 1,960 mg/l MLPAC systems, respectively.

All three nitrification aeration tanks achieved ammonia removal efficiencies in excess of 92 percent. The 980 mg/l MLPAC system experienced the highest level of performance at 97 percent removal while the other two units achieved between 92 and 94 percent removal efficiencies. Once again, the two units that received PAC in the contact aeration tank operated at a somewhat more stable condition than the 0 mg/l MLPAC system. Upon examining Table 12 we find a considerable portion of the nitrified effluent is in the nitrite-nitrogen form in the 0 mg/l MLPAC and 980 mg/l MLPAC systems, while almost all the ammonia nitrogen in the 1,960 mg/l MLPAC system was converted to nitrate-nitrogen.

Substantial reduction of cyanide occurred in all three nitrification aeration tanks. The 1,960 mg/l MLPAC system exhibited the greatest additional reduction in cyanide concentration over what was oxidized in the contact-stabilization system, while the 0 mg/l and 980 mg/l MLPAC systems exhibited similar patterns of cyanide reduction. However, these removal levels were slightly less than those observed in the 1,960 mg/l MLPAC system. Thiocyanate removal varied quite extensively between the three systems. Virtually no thiocyanate reduction occurred in the 0 mg/l MLPAC system nitrification aeration tank, while the majority of thiocyanate reduction in the

1,960 mg/l MLPAC system occurred in the nitrification aeration tank. The 980 mg/l system experienced the greatest overall removal efficiency of thiocyanate.

When the cyanide and thiocyanate reduction profiles of the 20 day solids retention time studies are compared to the profiles obtained from the 10 day solids retention time studies, we find that all systems improved substantially in reducing these compounds in the contact-stabilization portion of the treatment systems. The reduction of cyanide and thiocyanate in the nitrification aeration tanks of the systems receiving carbon also improved with increasing sludge age, however, the 0 mg/l MLPAC system exhibited a deterioration in performance relative to reducing these parameters when the sludge age in the contact-stabilization units was increased to 20 days. An interesting phenomenon occurred in the systems receiving PAC with regards to thiocyanate and cyanide removal; the tank where the major reduction in these compounds occurred shifted from the nitrification aeration tank to the contact and stabilization tanks when the sludge age was increased to 20 days.

3. Suspended Solids

The suspended solids profiles obtained for the various aeration tanks during the 20 day sludge age study are shown in Figures 23-25 in the period between day 376 and day 466 of operation. The numerical values of these parameters averaged over the last 21 days of operation are shown in Table 13. It is apparent from Figures 24-26 that the solids concentrations in the contact and stabilization aeration tanks increased shortly after the solids retention time was increased. A new level of solids concentration was achieved and the systems remained at that new level. The contact-stabilization aeration tanks of the systems receiving PAC exhibited more

Table 13

Suspended Solids Concentration in Treatment Systems, θ_c = 20 Day

	0 mg/ℓ MLPAC System			980 mg/ℓ MLPAC System				1,960 mg/ℓ MLPAC System			
	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	PAC(mg/ℓ)	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	PAC(mg/ℓ)
Contact Tank	1,108(136)	981(128)	88.54	2,325(287)	1,459(181)	62.75	640	3,342(717)	1,736(532)	51.94	1,467
Stabilization Tank	2,321(485)	2,073(425)	89.31	4,791(1061)	3,111(647)	64.93	1,320	5,586(990)	3,342(678)	59.83	2,453
Nitrification Tank	3,548(337)	2,301(190)	64.85	4,593(368)	4,006(315)	87.22	862	5,014(315)	4,285(83)	85.46	560
Contact Clarifier Effluent	58(14)	50(17)	86.16	104(22)	86(23)	83.32	28	82(23)	63(18)	76.06	36
Nitrification Clarifier Effluent	59(14)	38(13)	63.47	102(29)	63(17)	61.84	-	83(32)	49(18)	59.18	-

( ) Quantity in parentheses represents standard deviation.

deviation from this level than the 0 mg/l MLPAC counterpart. The amount of solids escaping clarification increased with the decreased carbon addition rates. Insufficient information is available to explain this observation, however, a major effect of the increase in the solids escaping the contact-stabilization system is an increase in the level of PAC in the nitrification tanks of the systems receiving PAC.

When the solids profiles for the 10 and 20 day sludge age studies are compared, we find that the 0 mg/l MLPAC experienced more stable operating characteristics while the 980 mg/l MLPAC and 1,960 mg/l MLPAC systems deteriorated somewhat in reactor operating characteristics. When the 20 day sludge age was completed, however, these reactors exhibited a noticeable improvement in performance stability.

The cell yields for the 20 day solids retention time study are shown in Table 9. These values were calculated in the same manner as stated earlier for the 10 day sludge age study except, in this case, the ammonia oxidized in the contact-stabilization portion of the treatment systems was included in the oxygen demand balance because of the substantial conversion of ammonia that took place in these units during this phase of the study. Ammonia conversion was computed in terms of mass of nitrogen produced in the form of nitrate-nitrogen and nitrite-nitrogen. The cell yield in the contact and stabilization aeration tanks of the 0 mg/l MLPAC systems was roughly one half the cell yield obtained for the systems receiving PAC while the nitrification units of all three systems exhibited essentially identical cell yields. The increased solids handling needed for the systems operating at the 20 day sludge age may be a direct result of the increases in COD and ammonia reduction that were experienced during this phase.

4. Denitrification of Nitrate and Nitrite

The performance of the denitrification columns is shown in Table 10. The 0 mg/l MLPAC system and the 980 mg/l MLPAC system exhibited a substantial loss in denitrification efficiency while the 1,960 mg/l MLPAC system experienced relatively the same performance as was obtained during the 10 day sludge age study. Organic carbon limitation was not the cause for the deterioration in the 0 mg/l MLPAC and 980 mg/l MLPAC system due to the fact that the COD of the denitrification column effluent was consistently greater than the COD of the nitrification clarifier effluent. The most probable cause for the loss in reactor performance is the amount of nitrite-nitrogen entering the denitrification column. The nitrite-nitrogen concentration in the nitrification clarifier effluent increased in the 20 day solids retention time study due to incomplete nitrification of ammonia to nitrate. The biomass present in the denitrification column was previously acclimated to an influent of primarily nitrate-nitrogen. When the column was fed substantial concentrations of nitrite-nitrogen decreased conversion efficiencies resulted.

5. Phenolic Compounds

The fate of the various phenolic compounds across the treatment system is shown in Table 14. The increase in the influent concentration of phenols did not have any adverse effect on reactor performance. The level of phenolics present in all of the contact aeration tanks decreased sharply when compared to the 10 day sludge age study. The stabilization aeration tanks of these units on the other hand, contained barely detectable levels of phenols. Overall removal efficiency of the phenolic compounds increased

Table 14

Performance of Treatment System in Reducing Phenols, $\theta_c = 20$ days

Parameter	Influent	0 mg/ℓ MLPAC System			980 mg/ℓ MLPAC System			1,960 mg/ℓ MLPAC System		
		C-S Clarifier	Stab. Tank	Nit. Clarifier	C-S Clarifier	Stab. Tank	Nit. Clarifier	C-S Clarifier	Stab. Tank	Nit. Clarifier
Phenol (mg/ℓ)	71	0.05	0.05	< DL	0.09	0.02	< DL	0.11	0.10	< DL
o-Cresol (mg/ℓ)	3.02	0.13	0.12	< DL	0.19	0.14	< DL	0.01	< DL	< DL
m & p-Cresol (mg/ℓ)	5.30	0.30	0.02	< DL	0.05	< DL	< DL	0.07	0.02	< DL
2,4 Dimethylphenol (mg/ℓ)	0.56	0.01	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL

---

* < DL = below detection limit

with increasing sludge age. The results suggest that the role of carbon in the removal of phenol is less important than the diversity of culture obtained by increasing sludge age due to the fact that less fresh carbon was added to the systems when operating at a 20 day sludge age. Virtually complete phenol removal occurred across all the treatment systems. The concentrations of the various phenolic compounds were below detection limits in all three nitrification clarifier effluents.

C. Phase Three

Following the 20 day sludge age study the contact-stabilization units in each of the systems were converted to a 30 day solids retention time operation. Solid samples were taken biweekly and daily sludge wastage was practiced. Samples were taken every ten days instead of the weekly sampling that was practiced during the two other sludge age studies. The average MLPAC concentration in the contact and stabilization aeration tanks was maintained at 0, 980, and 1,960 mg/l for Systems 1, 2, and 3, respectively. The solids retention time in the nitrification aeration tank was maintained at 40 days with daily sludge wastage. All other operating conditions were maintained the same as during the two other sludge age studies.

1. Chemical Oxygen Demand and Dissolved Organic Carbon

The performance of the treatment systems relative to COD reduction is shown in Figures 8-10. The data pertinent to this phase of the study appear between day 487 and day 580 of operation. The corresponding DOC data are shown in Figures 11-13. The numerical values of these two parameters averaged over the final 20 days of operation are given in Tables 2 and 3.

The contact-stabilization portion of the 980 mg/l MLPAC system and the 1,960 mg/l MLPAC system achieved relatively the same level of performance in COD reduction. The 0 mg/l MLPAC system, on the other hand, experienced

COD removal efficiencies far below the values found for the systems receiving carbon. The steady-state COD in the contact clarifier effluent from the 0 mg/l MLPAC system was about 2.5 times greater than the corresponding concentration found in the contact clarifiers of the 980 mg/l MLPAC and 1,960 mg/l MLPAC systems. When the DOC effluent concentrations from the contact-stabilization portions of the three treatment systems are compared the same relationship holds. The COD and DOC concentrations in the stabilization aeration tank were found to be similar to the concentrations of these parameters present in the corresponding contact aeration tank for each of the three units.

A comparison between the 20 and 30 day sludge age studies revealed a substantial increase in the removal efficiency of COD and DOC in the contact-stabilization portion of the two units receiving PAC, while the 0 mg/l MLPAC system exhibited a decrease in the removal efficiency of these parameters when the sludge age was increased. Close examination of the COD and DOC concentration levels leaving the contact tank of the 0 mg/l MLPAC system reveals a slow but steady deterioration in effluent quality with time. This observation is reinforced by the fact that the solids concentration in the contact and stabilization tanks remained relatively the same instead of increasing in response to the increased sludge age. The cyanide and thiocyanate levels present in the contact-stabilization effluent from the 0 mg/l MLPAC system decreased in response to the increase in sludge age. These levels, however, were much higher than those obtained from the two systems receiving PAC during the 30 day sludge age study (Tables 5 and 6). The mechanism of cyanide and thiocyanate inhibition may be directly related to the sludge age of the reactor.

Another explanation for this may be due to the presence of another nondegradable but adsorbable toxin that tends to accumulate in the reactor when the sludge age is increased.

The 1,960 mg/l MLPAC system exhibited the highest level of removal in COD and DOC across the contact-stabilization portion of the treatment system. The COD removal efficiency for this unit was approximately 87 percent while the DOC removal efficiency was found to be almost 89 percent. The contact-stabilization portion of the 1,960 mg/l MLPAC system was found to be most effective in reducing organic matter when operated at a solids retention time of 30 days. In fact, this unit out performed all other combinations of sludge age and MLPAC concentrations tested.

Further COD and DOC reductions occurred in all three of the nitrification aeration tanks. The 0 mg/l MLPAC nitrification system experienced the highest additional removal of COD and DOC mass of the three units while the 1,960 mg/l MLPAC system resulted in the best overall effluent quality in terms of COD and DOC. Slightly over 93 percent total COD removal occurred in the entire treatment scheme of the 1,960 mg/l MLPAC system while 85 and 90 percent removal efficiencies were achieved in the 0 mg/l MLPAC and 980 mg/l MLPAC systems, respectively. All systems experienced improved COD and DOC removal in the nitrification aeration tanks.

The two systems receiving PAC exhibited more stability in COD and DOC reduction when compared to the 0 mg/l MLPAC system, although all systems showed a decrease in stability when compared to the 20 day sludge age study. The reason for this behavior may be due to the variability in the influent COD and DOC concentrations fed to the system during this phase of the study.

This variability in wastewater characteristics may be attributed to the fact that the wastewater supply was about to be exhausted around that time and the bottom of the barrel samples exhibited increased fluctuations.

2. Ammonia, Cyanide, and Thiocyanate

The ammonia, cyanide, and thiocyanate profiles across the treatment systems are shown in Figures 14-22. The data pertaining to this phase of the study appear between day 487 and day 580 in these figures. The corresponding numerical values of these parameters averaged over the final 20 days of operation are reported in Tables 4-6.

As experienced during the 10 and 20 day sludge age studies, a loss of nitrogen occurred in the contact-stabilization portion of all the treatment systems when these units were operated at a 30 day solids retention time (Table 15). The system receiving no PAC exhibited the least amount of nitrogen loss while the 980 mg/l MLPAC and 1,960 mg/l MLPAC systems were similar to each other in nitrogen loss in the contact-stabilization portion of the treatment system.

The amount of ammonia oxidized in the contact-stabilization portion of the 980 mg/l MLPAC and 1,960 mg/l MLPAC systems increased sharply when the sludge age in these systems was increased to 30 days. The 0 mg/l MLPAC system, however, showed no change in cyanide reduction, while the thiocyanate reduction efficiency in this unit worsened when the sludge age was increased to 30 days. The concentration of cyanide and thiocyanate in the effluents from the contact clarifiers of the systems receiving carbon were consistently below 10 and 40 mg/l, respectively, during the 30 day sludge age study. These removal efficiencies of cyanide and thiocyanate seem to be higher than any reported in the literature for similar wastewaters.

Table 15

Performance of Treatment Systems in Reducing Nitrogen Containing Compounds, θ_c = 30 Day

	0 mg/ℓ MLPAC System						980 mg/ℓ MLPAC System						1,960 mg/ℓ MLPAC System					
	NH_3-N mg/ℓ	CN-N mg/ℓ	SCN-N mg/ℓ	NO_3-N mg/ℓ	NO_2-N mg/ℓ	Total N mg/ℓ	NH_3-N mg/ℓ	CN-N mg/ℓ	SCN-N mg/ℓ	NO_3-N mg/ℓ	NO_2-N mg/ℓ	Total N mg/ℓ	NH_3-N mg/ℓ	CN-N mg/ℓ	SCN-N mg/ℓ	NO_3-N mg/ℓ	NO_2-N mg/ℓ	Total N mg/ℓ
Influent	920	309	74	-	-	1,303	920	309	74	-	-	1,303	920	309	74	-	-	1,303
Contact Clarifier Effluent	845	79	45	43	92	1,104	839	4	9	65	22	939	829	5	9	37	61	941
Stabilization Tank	748	72	62	56	49	987	781	3	4	80	0	868	801	3	5	45	105	959
Nitrification Clarifier Effluent	21	13	1	925	45	1,005	1	3	1	934	0	939	3	3	2	938	0	946

The performance of the 980 mg/l MLPAC and 1,960 mg/l MLPAC contact-stabilization systems were virtually identical in removal of cyanide and thiocyanate.

All nitrification units consistently exhibited greater than 97 percent ammonia removal efficiencies. The 980 mg/l MLPAC system and the 1,960 mg/l MLPAC system achieved almost complete nitrification with only 1 mg/l and 3 mg/l of ammonia-nitrogen persisting in the respective nitrification clarifier effluents. The 0 mg/l MLPAC system, on the other hand, yielded effluent ammonia-nitrogen concentrations of approximately 20 mg/l. Complete oxidation of ammonia to nitrate occurred in the systems receiving activated carbon, where as roughly 45 mg/l of nitrite-nitrogen persisted in the nitrification tank of the 0 mg/l MLPAC system.

The concentration of cyanide in the nitrification aeration tank of the 980 mg/l MLPAC and 1,960 mg/l MLPAC systems was virtually the same as the concentration leaving the contact-stabilization units of these two systems. Thiocyanate, on the other hand, was further reduced in the nitrification aeration tanks of the systems receiving carbon. The concentration of cyanide and thiocyanate present in the effluents of all three nitrification clarifiers were very similar (Table 6). All units yielded effluent cyanide levels of below 22 mg/l while effluent thiocyanate concentrations were consistently below 10 mg/l.

The stability of performance of the nitrification aeration tank of the 1,960 mg/l MLPAC system in oxidizing ammonia was found to be superior, during the 30 day sludge age study, to the 0 mg/l MLPAC and 980 mg/l MLPAC systems. The 980 mg/l MLPAC system experienced an upset in pH early in the 30 day sludge age study, the effect of this was only temporary as the ammonia-nitrogen decreased to its previous level within the next 10 days. The

0 mg/l MLPAC system exhibited the least stability in terms of ammonia reduction. The same relationship applies to cyanide and thiocyanate removal efficiencies in the three systems as shown in Figures 17-22.

3. Suspended Solids

The suspended solids profiles of the contact-stabilization, and nitrification aeration tanks of the various units are shown in Figures 23-25. The numerical values of these parameters averaged over the final 20 days of operation are shown in Table 16. The contact aeration tanks of all three systems showed somewhat unstable operating conditions due to the fluctuations in influent DOC concentration. The effect of this fluctuation in influent composition was even more pronounced on the stabilization aeration tanks of the three systems. For the most part, stable solids concentrations in the contact and stabilization aeration tanks were achieved several weeks before the 30 day sludge age study was completed. The average solids concentration in the contact and stabilization aeration tanks of the 980 mg/l MLPAC system dropped slightly while the 0 mg/l MLPAC system and the 1,960 mg/l MLPAC system remained relatively the same when the sludge age was increased.

This lack of increase in the aeration tank solids when the sludge age was increased to 30 days was totally unexpected and could only be explained by assuming very high endogenous decay rates of the biomass. It is feasible that at a sludge age of 30 days, the net rate of microbial decay neutralized the biomass buildup effect of the increased solids retention time.

The solids yield data for the 30 day sludge age study are shown in Table 9. Nitrification occurring in the contact-stabilization and aeration tank was included in these calculations. A sharp decrease in solids yield

Table 16

Suspended Solids Concentration in Treatment Systems, θ_c = 30 Day

	0 mg/ℓ MLPAC System			980 mg/ℓ MLPAC System				1,960 mg/ℓ MLPAC System			
	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	PAC(mg/ℓ)	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	PAC(mg/ℓ)
Contact Tank	1,082(201)	957(156)	88.45	1,822(311)	1,120(246)	61.47	627	2,796(284)	1,339(334)	47.89	1,228
Stabilization Tank	2,430(343)	2,104(290)	86.58	3,878(293)	2,172(245)	56.01	1,333	6,131(432)	3,197(453)	52.14	2,692
Nitrification Tank	2,920(141)	1,662(135)	56.92	3,759(397)	2,939(332)	78.19	331	4,570(373)	2,765(214)	60.50	708
Contact Clarifier Effluent	55(15)	38(2)	69.10	83(11)	61(15)	73.41	27	74(21)	51(14)	68.83	23
Nitrification Clarifier Effluent	29(5)	12(2)	40.14	37(15)	20(6)	53.66	-	71(41)	36(20)	50.99	

( ) Quantity in parentheses represents standard deviation.

was exhibited for the contact-stabilization portion of all three treatment systems. These values were the lowest experienced for all three sludge ages studied. The solids yield from the nitrification aeration tanks of the 0 mg/l MLPAC and the 980 mg/l MLPAC systems remained relatively the same as the value reported for the 20 day sludge age. The solids yield of the 1,960 mg/l MLPAC system, on the other hand, exhibited a noticeable increase during the 30 day sludge age study. The solids yield data obtained during the 30 day sludge age study are very encouraging in that the lowest mass of sludge to be disposed of coincided with operating conditions that resulted in the best performance of all units. The amount of money saved by the lower cost of sludge disposal may offset the increased cost of aeration associated with the increased sludge age. Furthermore, the 30 day sludge age study corresponds to the smallest mass of fresh powdered activated carbon addition to the system. Thus additional savings are possible if this operating mode is practiced.

4. Denitrification of Nitrite and Nitrate

The performance of the denitrification columns for the 30 day solids retention time study are shown in Table 10. The denitrification columns of all three systems converted all of the incoming nitrate-nitrogen and nitrite-nitrogen to nitrogen gas. The incomplete denitrification experienced during the 20 day mean cell residence time study did not persist during the 30 day sludge age study. The absence or decreased level of nitrite-nitrogen in the denitrification column influent was most probably the reason for the complete denitrification observed during this phase of the study.

5. Phenolic Compounds

The fate of the various phenolic compounds across the treatment systems is not given here due to the fact that gas chromatographic analysis of the steady-state samples showed virtually no phenolic compounds in any of the treatment units. The influent concentration of the various phenolic compound was the same as that reported for the 20 day sludge age. The organic solvent with which the aqueous samples were extracted had to be concentrated to a great extent in order to obtain any response on the gas chromatograph. At such a concentration level, background noise and interference due to impurities and handling made it impossible to obtain any meaningful data. Therefore, for all practical purposes the removal of phenolic compounds was complete for all systems operated at a 30 day solids retention time.

D. Color and Foaming

At the end of each sludge age experiment color analysis was performed on the contact-stabilization clarifier effluent of each system as outlined in Section II. The results of this particular analysis are presented in Figure 26. The filtered contact clarifier effluent purity, in percent, is plotted versus the PAC addition rate. The parameter purity is a measure of clarity of a liquid with distilled water having a purity of 0 percent. The PAC addition rate varied with solids retention time in the contact-stabilization section in order to keep the MLPAC concentration of each system constant throughout the entire study. The PAC addition rates shown in Figure 26 represent the actual PAC mass fed to the contact tank when this mass is normalized to the combined flow of the coke-oven wastewater and the PAC slurry.

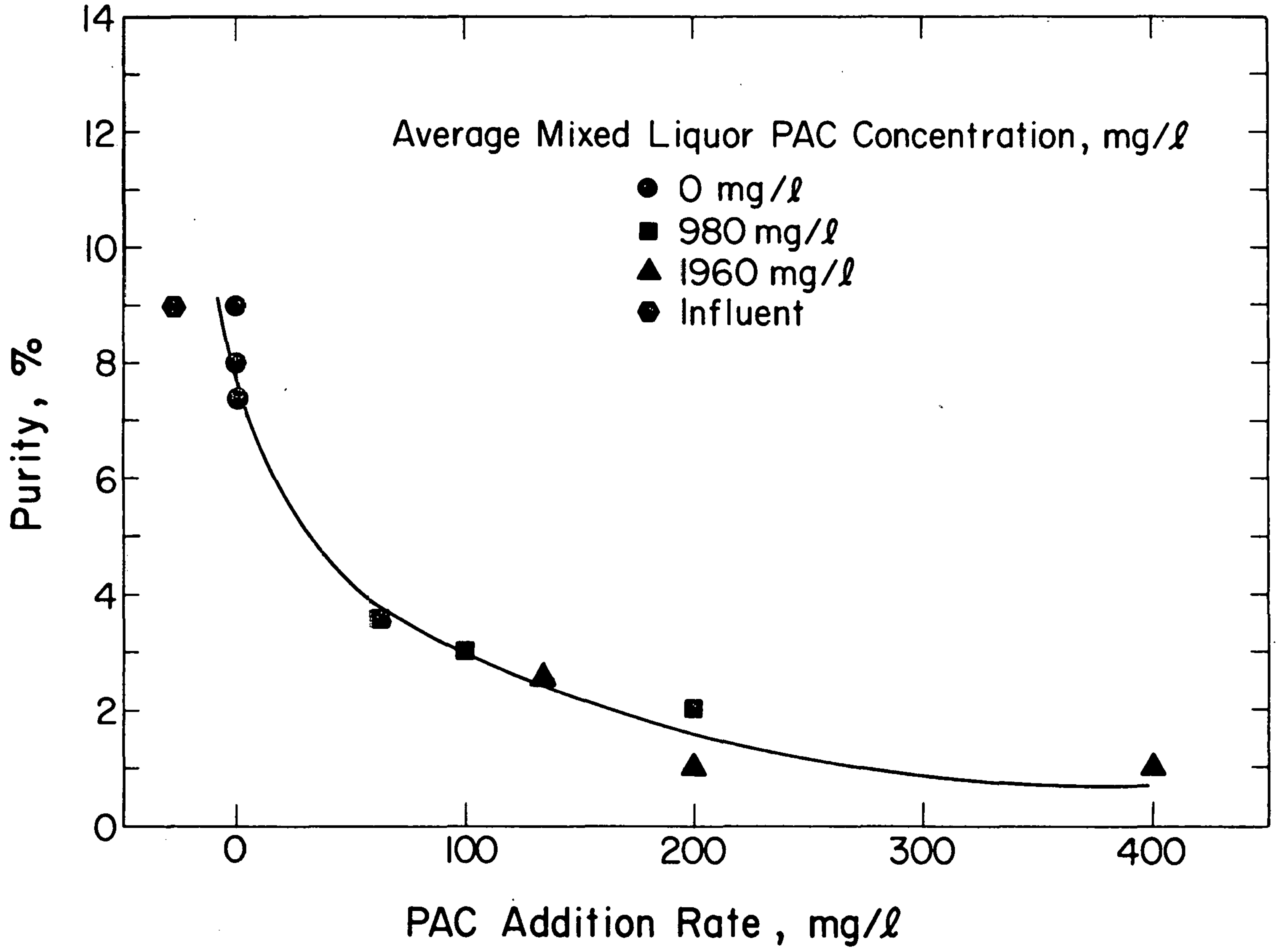


Figure 26. Effect of MLPAC Concentration and Fresh PAC Addition Rate on Contact Clarifier Effluent Purity

Close examination of the data in Figure 26 reveals that best effluent quality in terms of color removal corresponds to the highest addition rate of PAC. In fact, if the percent purity reduction is normalized to the PAC addition rate and the resulting data are plotted versus the contact-stabilization effluent purity, an almost linear relationship results. This observation suggests that color removal is virtually totally due to adsorption of color causing compounds onto the PAC. At this junction an important question arises as to whether it is more economical to add PAC to the biological system or whether color removal may be more economically achieved by passing the final effluent through a granular activated carbon adsorption column. If such an economic analysis is considered, other advantages attributable to PAC addition to the contact aeration tank must be considered. Some of these advantages pertain to improved COD, DOC, ammonia, cyanide and thiocyanate removal.

A severe foaming problem was encountered in all the aeration tanks of the 0 mg/l MLPAC system. The nitrification unit of this system exhibited a lesser degree of foaming than did the contact and stabilization aeration tanks. The 0 mg/l MLPAC unit exhibited the worst foaming problem during the 10 day sludge age operating period, while the problem was less severe as the sludge age of the contact-stabilization system was increased. Both systems receiving PAC exhibited minimal foam buildup regardless of the solids retention time maintained in the contact-stabilization units. No anti-foam agents were used to control foaming. The inverted triangular prism configuration of the aeration tank was observed to allow for the formation of a stable foam level at which foam breakup equalled foam formation.

E. Sludge Settleability Studies

Zone settling velocity determinations were performed on sludge samples obtained from all aeration tanks at the end of every sludge age experiment. For every sludge sample, the zone settling velocity of that sludge was determined for a minimum of three sludge suspended solids concentrations. These tests were performed in 1 liter graduated cylinders that were raked with a stirring device rotating at 1 rpm. The zone settling data are given in Tables 17-19.

The zone settling velocity data given in Tables 17-19 were plotted versus total suspended solids concentration using logarithmic scales. Analysis of the resulting curves revealed that for each of the MLPAC concentrations studied, the settleability of the suspended solids in the contact-stabilization aeration tanks deteriorated with increasing sludge age. This observation cannot be attributed to the fractional PAC content of sludge solids since the same observation held true for the 0 mg/l MLPAC system.

Another general observation was that PAC addition resulted in a marked increase in zone settling velocity when samples that were collected at one sludge age were compared. Furthermore, sludge samples obtained from the 1,960 mg/l MLPAC system did not settle faster than samples obtained from the 980 mg/l MLPAC system. This observation suggests that a moderate PAC content is sufficient to improve sludge settleability.

The zone settling velocity curves for all the nitrification tank sludges were very similar to one another. This is not surprising since all these systems were operated at one value of sludge age namely 40 day. It is important to note, however, that nitrification tank sludges were gelatinous in nature and they settled much slower than the granular sludge obtained from the contact and stabilization aeration tanks.

Table 17

Contact Aeration Tank Sludge Zone Settling Velocity Data

	θ_c = 10 Day			θ_c = 20 Day			θ_c = 30 Day		
Sample #	0 mg/ℓ MLPAC System	980 mg/ℓ MLPAC System	1,960 mg/ℓ MLPAC System	0 mg/ℓ MLPAC System	980 mg/ℓ MLPAC System	1,960 mg/ℓ MLPAC System	0 mg/ℓ MLPAC System	980 mg/ℓ MLPAC System	1,960 mg/ℓ MLPAC System
1	*(5,551;2.66)	(39,670;3.48)	(34,850;2.26)	(13,541;0.50)	(30,741;1.48)	(56,422;0.75)	(9,492;0.33)	(30,407;0.75)	(25,110;0.87)
2	(4,900;2.86)	(28,568;6.24)	(25,125;4.12)	(12,703;0.75)	(26,489;1.83)	(47,242;0.93)	(8,071;0.61)	(23,424;1.05)	(20,496;1.27)
3	(4,142;3.57)	(19,687;10.62)	(16,700;7.06)	(10,777;1.16)	(20,294;2.60)	(36,761;1.25)	(5,551;0.86)	(19,076;1.46)	(17,263;1.85)
4	(2,678;5.02)	(12,685;14.22)		(8,994;1.38)	(17,319;3.08)	(28,682;2.39)	(5,483;1.51)	(16,407;1.88)	(14,589;2.16)
5				(6,729;1.86)	(15,319;3.72)	(24,765;3.57)	(4,754;1.78)	(13,025;2.36)	(12,737;2.81)
6				(5,703;2.48)	(12,199;4.94)	(16,466;4.8[illegible])	(3,965;2.42)	(10,449;3.46)	(10,008;3.60)
7				(4,237;3.60)	(9,941;7.00)	(13,831;7.34)	(2,803;4.40)	(7,699;5.27)	(7,551;5.80)
8				(2,924;5.58)	(6,886;10.66)	(9,225;10.08)	(2,054;5.88)	(4,949;8.41)	(5,224;9.26)

---

*(;) The pair of numbers between parentheses represent the total suspended solids concentration expressed in mg/ℓ, and the corresponding zone settling velocity expressed in m/h.

Table 18

Stabilization Aeration Tank Sludge Zone Settling Velocity Data

Sample #	θ_c = 10 Day 0 mg/ℓ MLPAC System	 980 mg/ℓ MLPAC System	 1,960 mg/ℓ MLPAC System	θ_c = 20 Day 0 mg/ℓ MLPAC System	 980 mg/ℓ MLPAC System	 1,960 mg/ℓ MLPAC System	θ_c = 30 Day 0 mg/ℓ MLPAC System	 980 mg/ℓ MLPAC System	 1,960 mg/ℓ MLPAC System
1	*(6,907;1.14)	(45,062;2.23)	(51,407;0.84)	(10,017;0.77)	(39,647;0.58)	(50,972;0.37)	(9,068;0.21)	(26,805;0.63)	(29,504;0.65)
2	(5,172;1.74)	(32,820;3.60)	(33,568;1.74)	(8,165;1.06)	(32,889;0.76)	(43,244;0.65)	(7,754;0.48)	(21,386;0.95)	(25,008;0.99)
3	(3,486;3.07)	(22,640;6.45)	(22,218;3.71)	(7,011;1.22)	(26,895;1.12)	(35,174;1.11)	(6,220;1.13)	(17,331;1.52)	(20,975;1.42)
4	(1,743;6.14)	(13,045;9.88)	(13,637;6.48)	(5,922;1.65)	(22,964;1.57)	(29,873;1.27)	(5,263;1.28)	(14,068;2.02)	(17,136;1.77)
5				(5,025;2.02)	(19,199;2.14)	(25,381;1.73)	(4,373;1.96)	(11,771;2.41)	(15,347;2.30)
6				(4,059;3.17)	(15,113;2.67)	(19,670;2.78)	(3,559;2.34)	(8,949;3.79)	(12,212;3.14)
7				(3,085;3.50)	(13,786;4.75)	(13,320;3.50)	(2,703;4.33)	(6,339;5.62)	(9,220;5.00)
8				(2,475;4.04)	(9,195;7.56)	(8,880;7.16)	(1,890;7.44)	(4,360;8.22)	(6,678;7.07)

---

*(;) The pair of numbers between parentheses represent the total suspended solids concentration expressed in mg/ℓ, and the corresponding zone settling velocity expressed in m/h.

Table 19

Nitrification Aeration Tank Sludge Zone Settling Velocity Data

Sample #	θ_c = 10 Day			θ_c = 20 Day			θ_c = 30 Day		
	0 mg/ℓ MLPAC System	980 mg/ℓ MLPAC System	1,960 mg/ℓ MLPAC System	0 mg/ℓ MLPAC System	980 mg/ℓ MLPAC System	1,960 mg/ℓ MLPAC System	0 mg/ℓ MLPAC System	980 mg/ℓ MLPAC System	1,960 mg/ℓ 1,960 System
1	*(18,407;0.30)	(23,396;0.47)	(30,933;0.27)	(13,996;0.24)	(15,816;0.54)	(15,506;0.19)	(10,971;0.22)	(21,550;0.17)	(15,907;0.53)
2	(13,256;0.59)	(20,424;1.12)	(27,623;0.67)	(11,032;0.39)	(12,765;0.95)	(11,517;0.39)	(9,377;0.38)	(18,231;0.40)	(13,030;0.92)
3	(7,937;1.71)	(11,453;2.38)	(15,535;1.28)	(9,291;0.60)	(10,899;1.20)	(9,870;0.53)	(7,545;0.72)	(15,739;0.69)	(11,227;1.20)
4	(3,766;4.75)	(5,877;6.57)	(10,136;2.68)	(7,838;0.94)	(9,142;1.73)	(8,818;0.80)	(5,631;0.92)	(12,697;1.13)	(9,356;1.54)
5		(3,438;9.26)	(5,697;5.30)	(6,068;1.23)	(8,366;2.11)	(7,360;0.90)	(5,487;1.34)	(10,310;1.76)	(7,268;2.07)
6				(5,013;1.77)	(6,292;4.01)	(5,036;1.19)	(4,513;1.98)	(8,286;3.04)	(6,166;3.12)
7				(3,919;2.75)	(4,773;8.10)	(4,542;2.39)	(3,437;3.29)	(4,998;5.06)	(4,678;4.54)
8				(2,695;4.80)	(3,430;9.80)	(2,950;4.55)	(2,352;4.90)	(3,225;6.85)	(3,218;6.28)

---

*(;) The pair of numbers between parentheses represent the total suspended solids concentration expressed in mg/ℓ, and the corresponding zone settling velocity expressed in m/h.

F. Contact Aeration Detention Time Studies

After the 30 day solids retention time study was completed, the effect of varying the contact aeration detention time on the performance of the contact-stabilization portion of the treatment system was studied. The contact-stabilization data generated from the 30 day sludge age study were used to represent the performance of the system when a 1 day contact period was used. Two other contact detention times of 2/3 day and 1/3 day were also studied. To maintain these new contact detention times, the contact aeration volume was simply reduced from 15.81 liters to 10 liters yielding a contact aeration detention time of approximately 16 hours. The 8 hour contact aeration detention time was achieved by further reducing the liquid volume of the contact tank to 5 liters. The sludge age throughout the duration of this study was maintained at 30 days. Solids wastage was practiced once daily. The PAC carbon addition rates were 0, 67, and 133 mg/l for systems 1, 2, and 3, respectively. These carbon addition rates were the same as those employed in the 30 day sludge age, one day contact aeration time study. The MLPAC concentrations in the aeration tanks increased from the levels used during the 1 day contact aeration detention time study due to the changes in the volume of the contact tank. The steady-state MLPAC concentrations are given in Tables 20-22.

The nitrification units of the three systems were disconnected once the 2/3 day contact aeration time study was underway. The objective of this study was to determine the effect of the contact aeration time on the performance of the contact-stabilization portion of the treatment system.

Table 20

Suspended Solids Concentration in Treatment Systems, $\theta_c = 30$ Day, $\theta = 1$ Day

	0 mg/ℓ PAC System			67 mg/ℓ PAC System				133 mg/ℓ PAC System			
	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	PAC(mg/ℓ)	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	PAC(mg/ℓ)
Contact Tank	1,082(208)	957(156)	88.45	1,822(371)	1,120(246)	61.47	622	2,796(284)	1,339(334)	47.89	1,228
Stabilization Tank	2,433(343)	2,104(240)	86.58	3,878(293)	2,172(245)	56.01	1,333	6,131(432)	3,197(453)	52.14	2,692
Contact Clarifier Effluent	29(5)	12(2)	40.14	37.15	20(6)	53.66		71(41)	36(20)	50.99	

( ) Quantity in parentheses represents standard deviation.

Table 21

Suspended Solids Concentration in Treatment Systems, θ_c = 30 Day, θ = 2/3 Day

	0 mg/ℓ PAC System			67 mg/ℓ PAC System				133 mg/ℓ PAC System			
	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	PAC(mg/ℓ)	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	PAC(mg/ℓ)
Contact Tank	1,527(79)	1,420(69)	92.99	2,863(588)	2,325(472)	81.21	915	3,963(298)	2,555(114)	64.47	1,564
Stabilization Tank	2,148(401)	1,962(348)	91.34	4,335(522)	2,868(195)	66.16	1,385	7,444(910)	5,194(170)	69.77	2,938
Contact Clarifier Effluent	62(15)	61(17)	98.38	37(7)	33(5)	89.19		76(35)	63(28)	82.89	

( ) Quantity in parentheses represents standard deviation.

Table 22

Suspended Solids Concentration in Treatment Systems, θ_c = 30 Day, θ = [illegible]/3 Day

	0 mg/ℓ PAC System			67 mg/ℓ PAC System				133 mg/ℓ PAC System			
	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	PAC(mg/ℓ)	TSS(mg/ℓ)	VSS(mg/ℓ)	% VSS	PAC(mg/ℓ)
Contact Tank	1,533(162)	1,408(157)	91.85	2,912(359)	2,220(141)	76.24	964	4,592(970)	3,037(1156)	66.14	2,036
Stabilization Tank	2,848(102)	2,580(86)	90.59	5,010(641)	3,689(44)	73.63	1,659	7,407(1359)	4,931(242)	66.57	3,284
Contact Clarifier Effluent	43(13)	37(10)	86.05	59(5)	45(3)	76.27		79(3)	72(7)	91.14	

( ) Quantity in parentheses represents standard deviation.

1. Chemical Oxygen Demand and Dissolved Organic Carbon

The performance data of the three treatment systems relative to COD and DOC reduction are shown in Figures 27-32. The numerical values of these parameters averaged over several weeks of stable operating conditions are given in Table 23.

When the contact aeration detention time was reduced from 1 day to 2/3 day the 0 mg/l PAC system showed a considerable reduction in COD and DOC removal efficiency. The COD of the influent increased significantly when the contact aeration time was changed due to an error in wastewater dilution. The effect of this shock load was most pronounced on the 0 mg/l PAC system. The contact clarifier effluent COD and DOC concentrations from this system increased sharply when the shock load was introduced. When the error in wastewater dilution was corrected, however, the performance of the 0 mg/l PAC system improved. The final level of system performance, however, was considerably poorer than that found when the system was operated at the 1 day contact detention time. The systems receiving PAC, on the other hand, experienced only slight decreases in COD and DOC reduction as a result of the shock loading period. After the feed wastewater strength was corrected, both systems recovered rapidly and finally settled at COD and DOC removal efficiencies that were only slightly lower than the corresponding removal efficiencies obtained during the 1 day contact aeration time study. The 67 mg/l PAC and 133 mg/l systems were found to handle the shock loading condition and the change in the contact detention time more effectively than the system receiving no PAC.

When the detention time in the contact aeration tank was further reduced to 1/3 day the systems receiving PAC exhibited only slight decreases

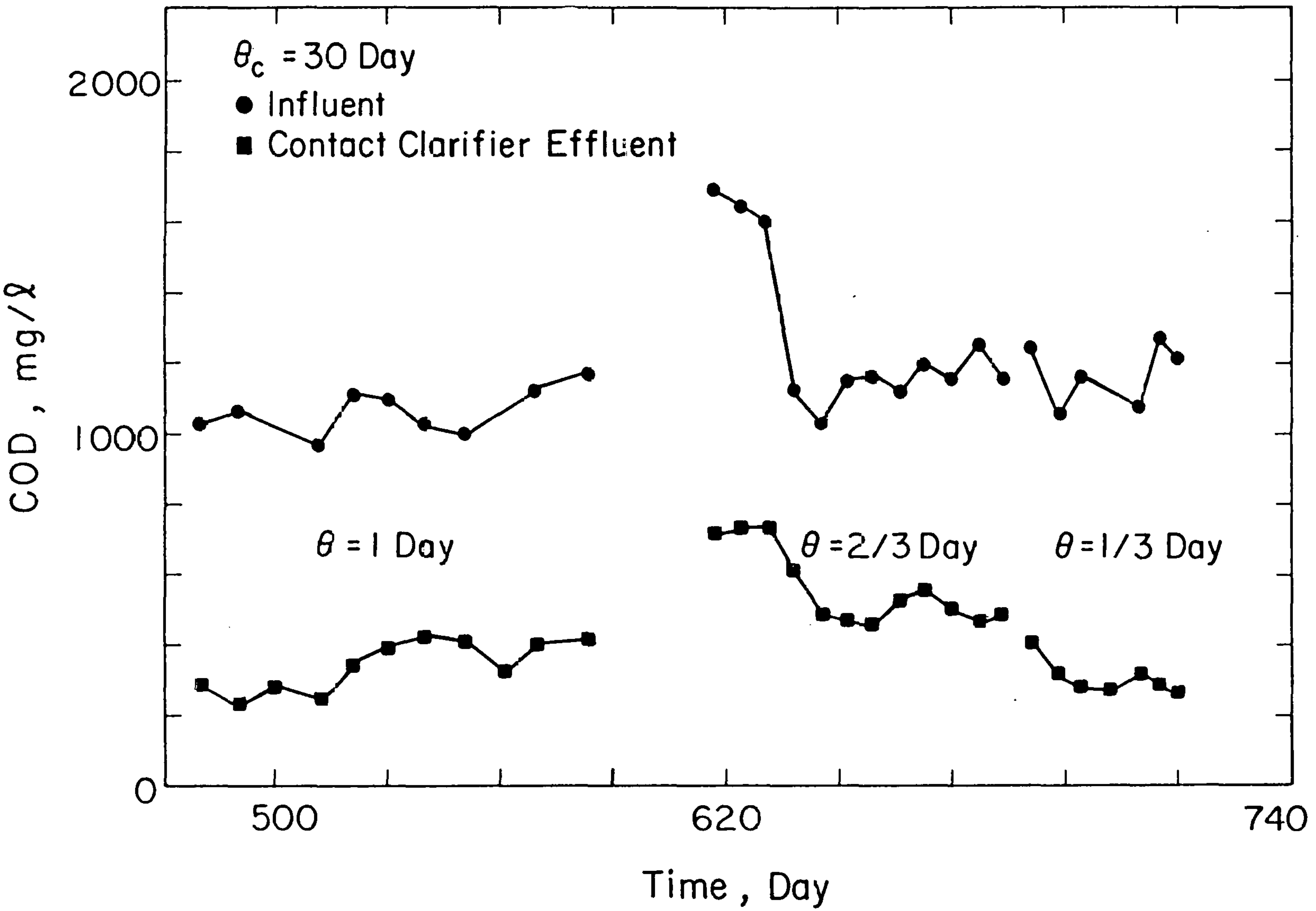


Figure 27. Effect of Contact Detention Time on COD Recuction in 0 mg/ℓ PAC System

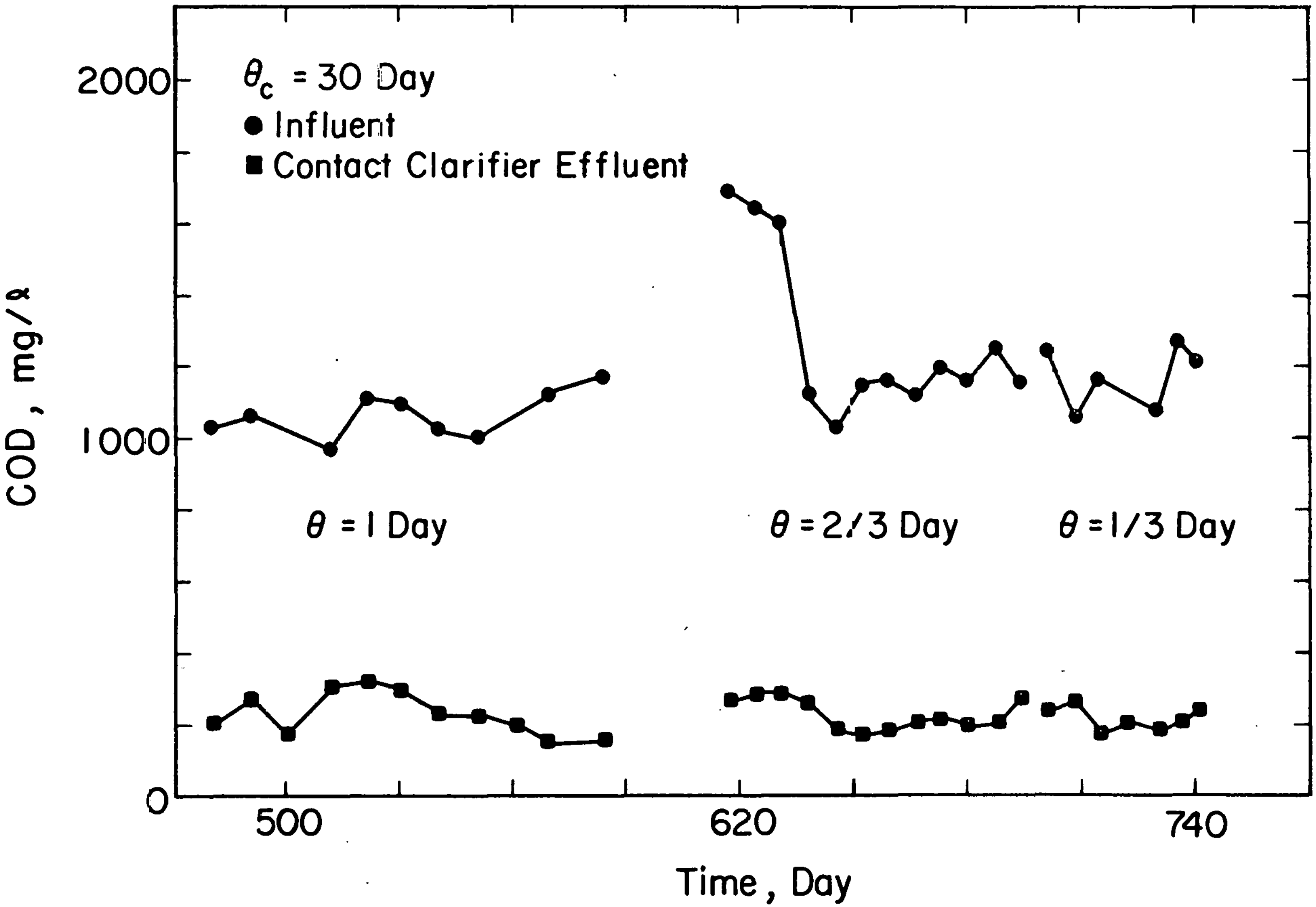


Figure 28. Effect of Contact Detention Time on COD Reduction in 67 mg/ℓ PAC System

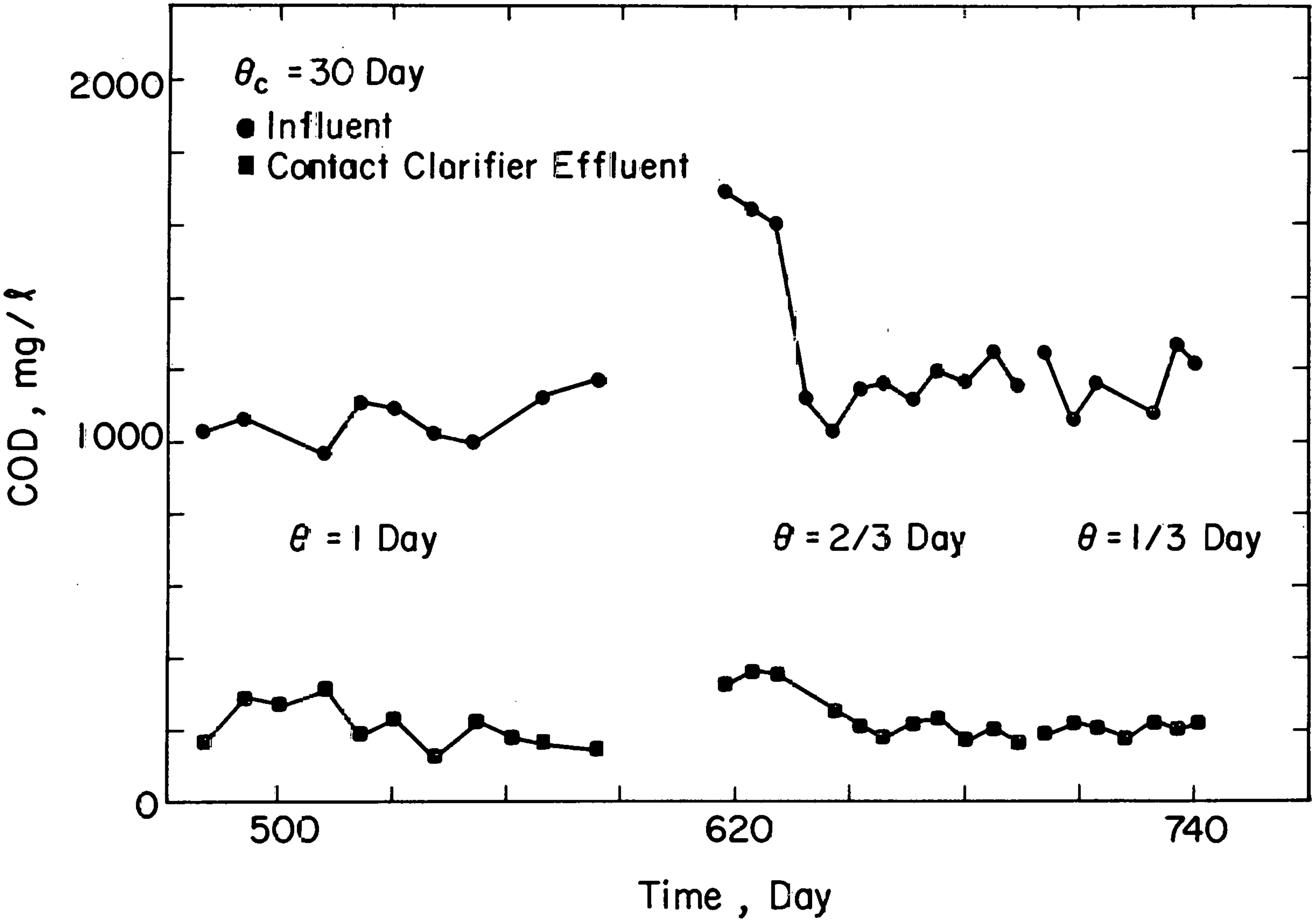


Figure 29. Effect of Contact Detention Time on COD Reduction in 133 mg/ℓ PAC System

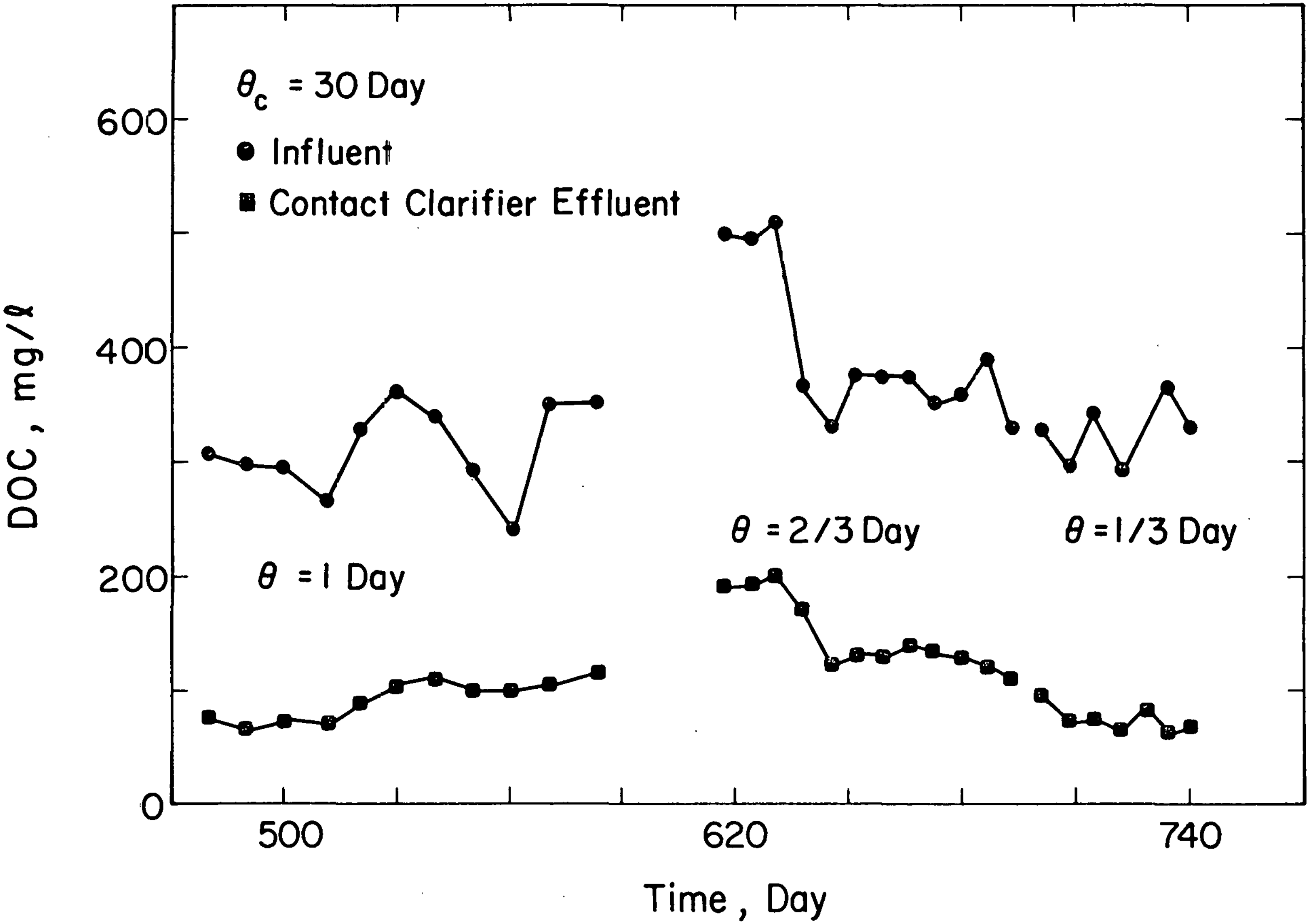


Figure 30. Effect of Contact Detention Time on DOC Reduction in 0 mg/ℓ PAC System

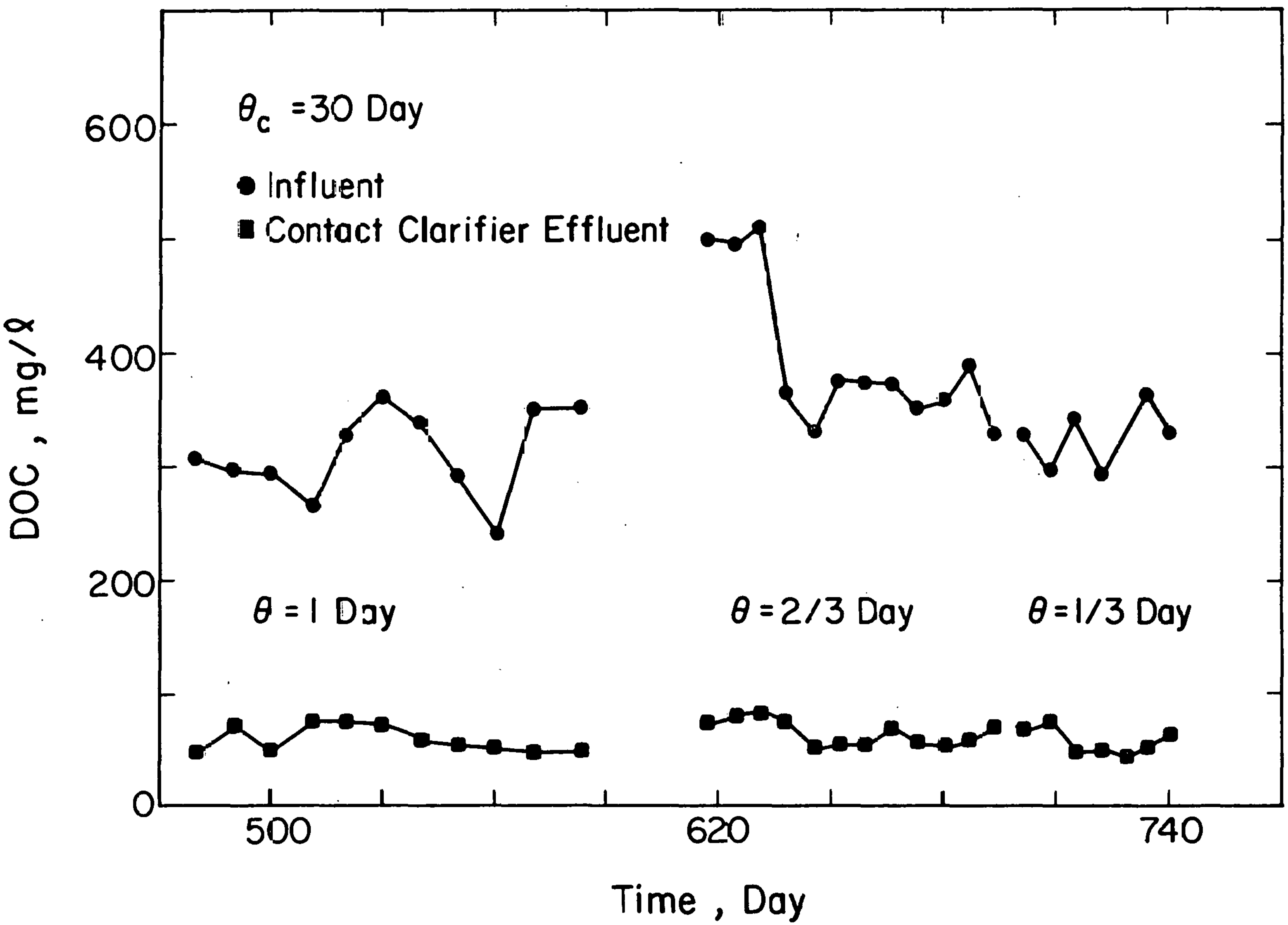


Figure 31. Effect of Contact Detention Time on DOC Reduction in 67 mg/ℓ PAC System

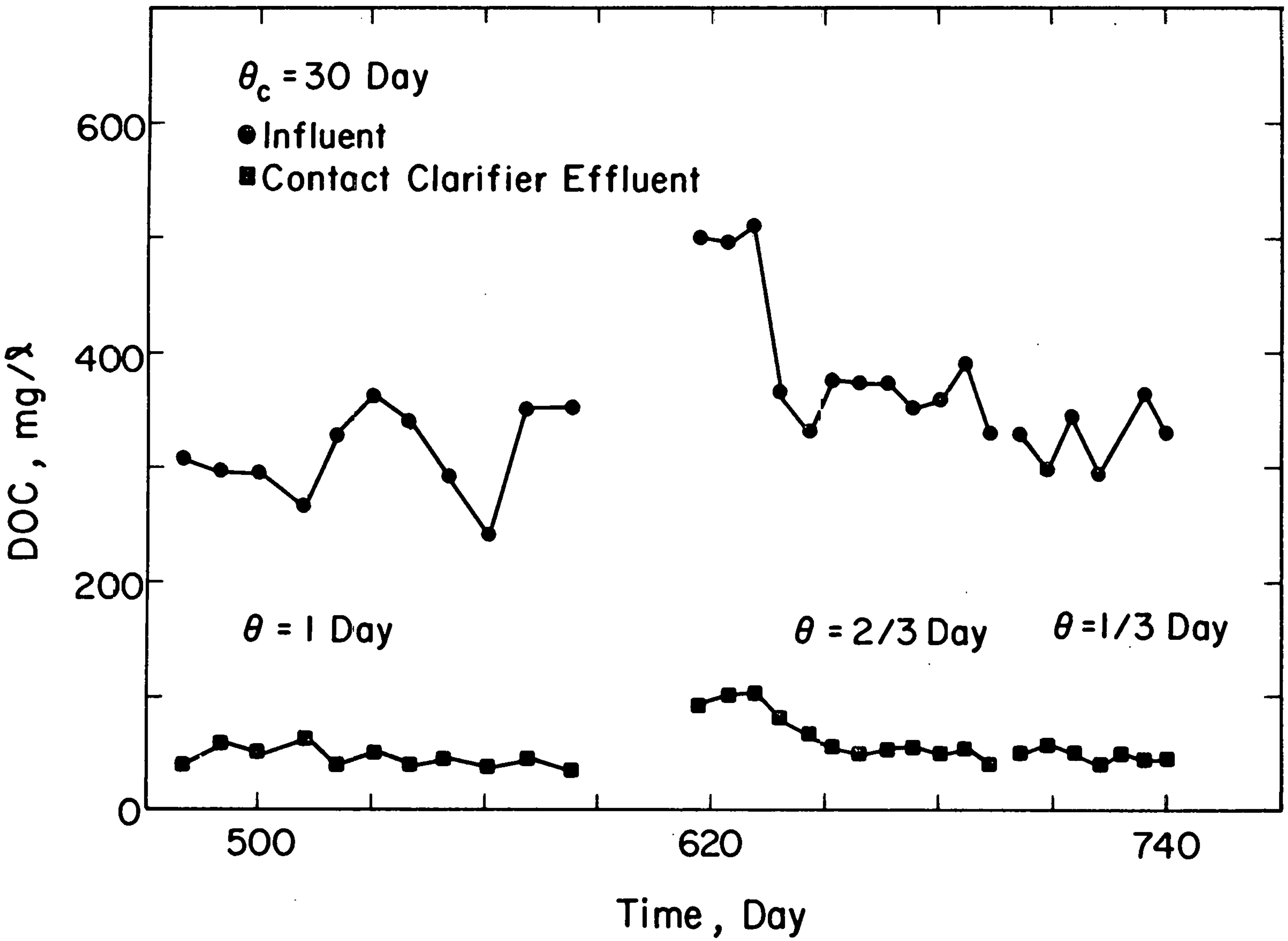


Figure 32. Effect of Contact Detention Time on DOC Reduction in 133 mg/ℓ PAC System

Table 23

Effect of Contact Detention Time on COD and DOC Reduction, θ_c = [illegible] Day

	0 mg/ℓ PAC System						57 mg/ℓ PAC System						133 mg/ℓ PAC System					
	θ = 1 Day		θ = 2/3 Day		θ = 1/3 Day		θ = 1 Day		θ = 2/3 Day		θ = 1/3 Day		θ = 1 Day		θ = 2/3 Day		θ = 1/3 Day	
	COD mg/ℓ	DOC mg/ℓ	COD mg/ℓ	DOC mg/ℓ	COD mg/ℓ	DOC mg/ℓ	COD mg/ℓ	DOC mg/ℓ	COD mg/ℓ	DOC mg/ℓ	COD mg/ℓ	DOC mg/ℓ	COD mg/ℓ	DOC mg/ℓ	COD mg/ℓ	DOC mg/ℓ	COD mg/ℓ	DOC mg/ℓ
Influent	1,165(12)	353(2)	1,175(47)	363(21)	1,189(100)	329(37)	1,165(12)	353(2)	1,175(47)	363(21)	1,189(100)	329(37)	1,165(12)	353(2)	1,175(47)	363(21)	1,189(100)	329(37)
Contact Clarifier Effluent	415(15) 64.35%*	111(8) 68.73%	502(37) 57.28%	126(11) 65.29%	291(27) 75.52%	71(11) 78.42%	165(15) 85.84%	49(1) 86.12%	215(30) 81.70%	61(7) 83.20%	207(29) 82.59%	54(11) 83.54	152(14) 86.95%	40(7) 88.67%	193(28) 83.57%	51(5) 85.95%	212(7) 82.17%	47(3) 85.71%
Stabilization Tank	399(25) 65.75%	111(8) 68.73%	480(27) 59.15%	127(13) 64.67%	246(13) 79.31%	57(2) 82.67%	159(6) 86.35%	41(5) 88.38%	185(26) 84.25%	50(4) 86.22%	143(21) 87.97%	40(3) 87.84%	133(15) 88.58%	31(1) 91.22%	167(28) 85.79%	34(4) 90.63%	128(11) 89.23%	29(2) 91.18%

( ) Quantity in parentheses represents standard deviation.

* Percent removal.

in their COD and DOC removal efficiencies. The 0 mg/l PAC system, on the other hand, showed a surprising increase in its ability to reduce COD and DOC. The performance of this system in terms of COD and DOC reduction was the highest found for the three 0 mg/l PAC contact detention times studied. Unfortunately, due to time limitation and to the exhaustion of the coke-oven wastewater supply, the study was terminated at the conclusion of the 8 hour contact detention time study experiments. No definite reasons for the sudden improvement in the performance of the 0 mg/l PAC system are available at present. However, close examination of the operating data seems to suggest the possibility of microbial stimulation during the shock loading period.

The COD and DOC removal efficiencies exhibited by the 67 mg/l and 133 mg/l PAC systems were substantially higher than the corresponding removal efficiencies obtained from the system receiving no PAC. The operating characteristics of the PAC receiving systems were also more stable than those observed for the 0 mg/l PAC unit.

2. Ammonia, Cyanide, and Thiocyanate

The ammonia, cyanide, and thiocyanate profiles across the three treatment systems obtained during the contact aeration time studies are shown in Figures 33-41. The net degree of ammonia reduction obtained in the three systems were minimal as is obvious from Figures 33-35. The numerical values of the cyanide and thiocyanate concentrations entering and leaving the treatment systems were averaged over periods of stable operation and are given in Table 24.

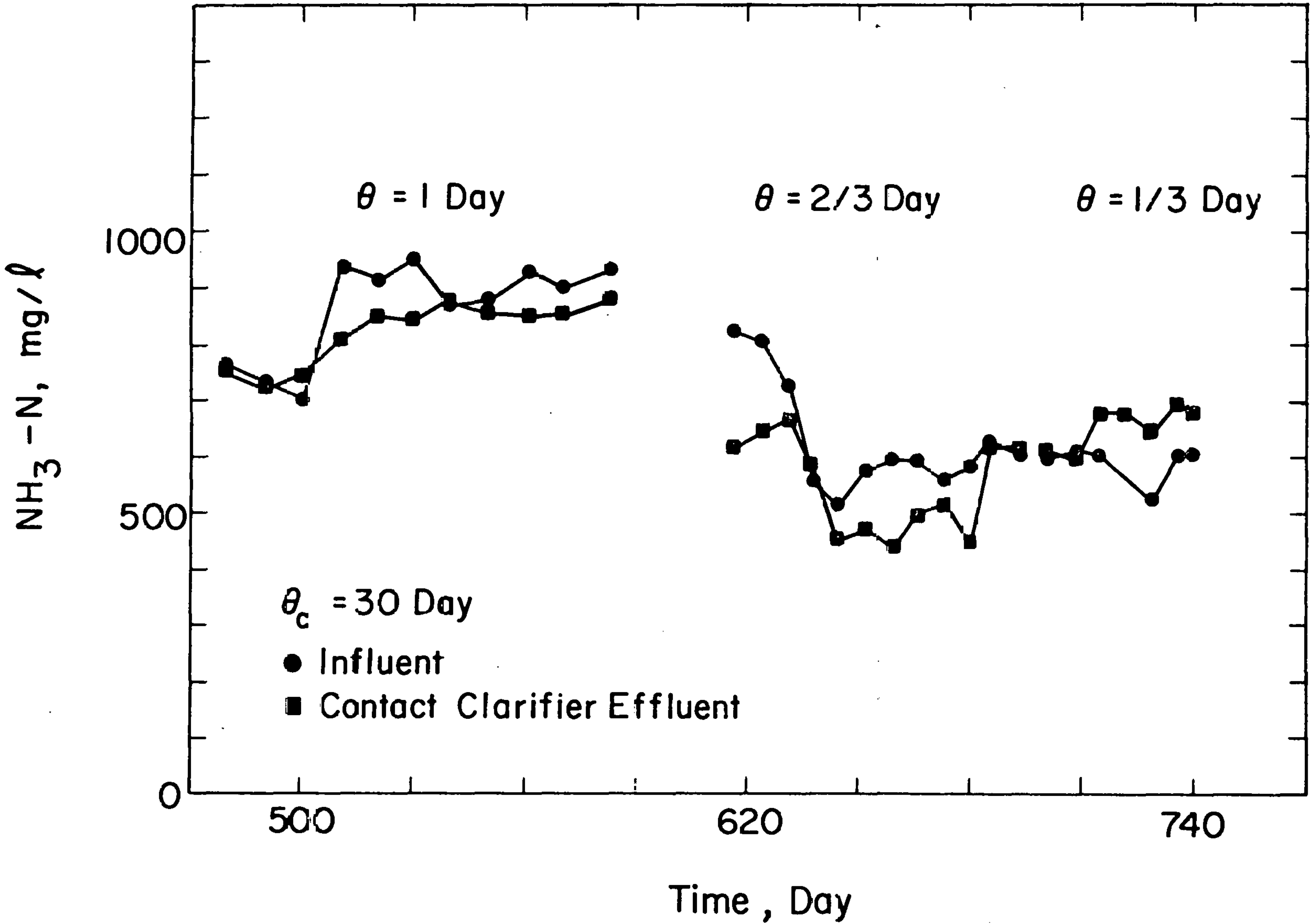


Figure 33. Effect of Contact Detention Time on Ammonia Reduction in 0 mg/ℓ PAC System

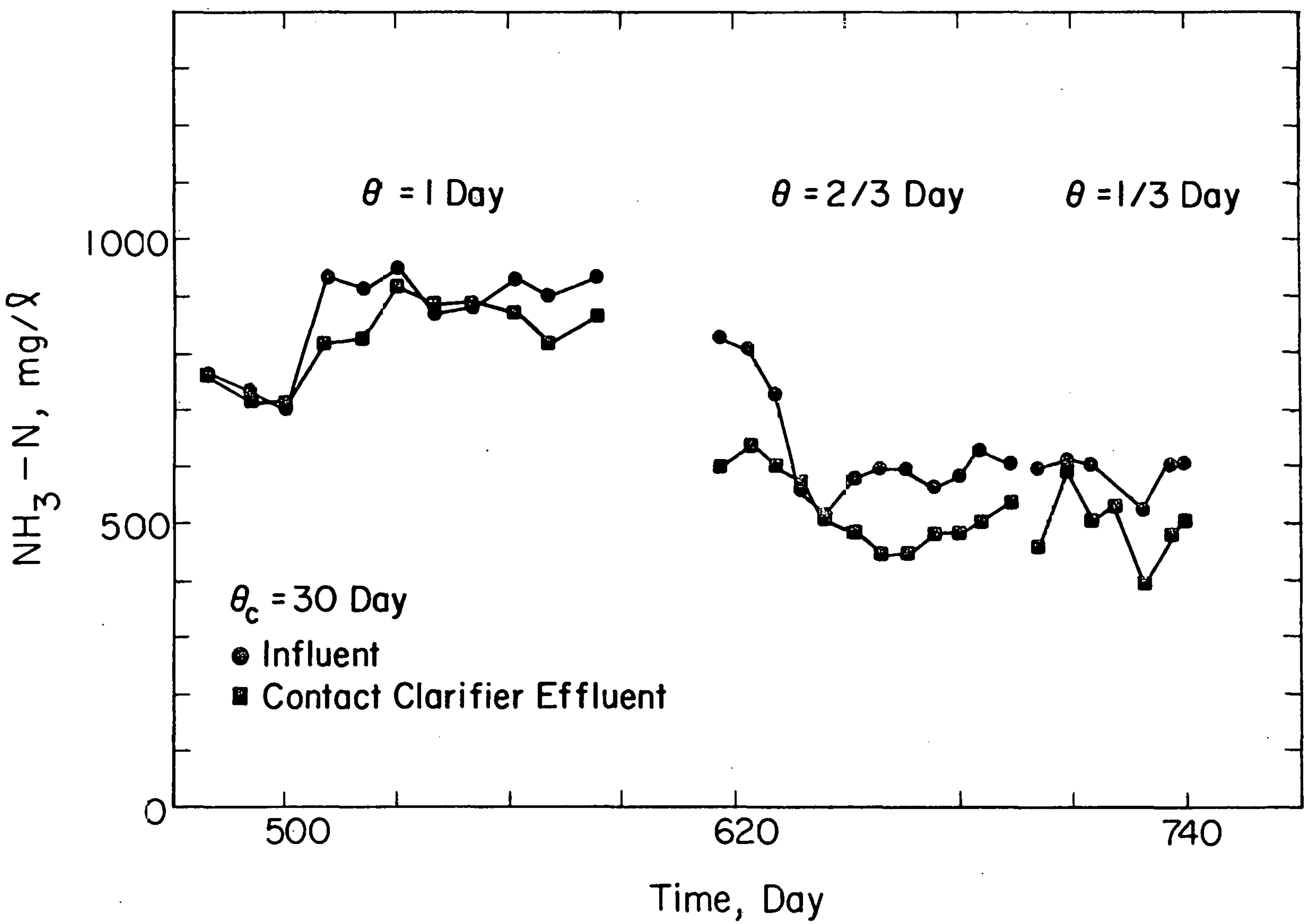


Figure 34. Effect of Contact Detention Time on Ammonia Reduction in 67 mg/ℓ PAC System

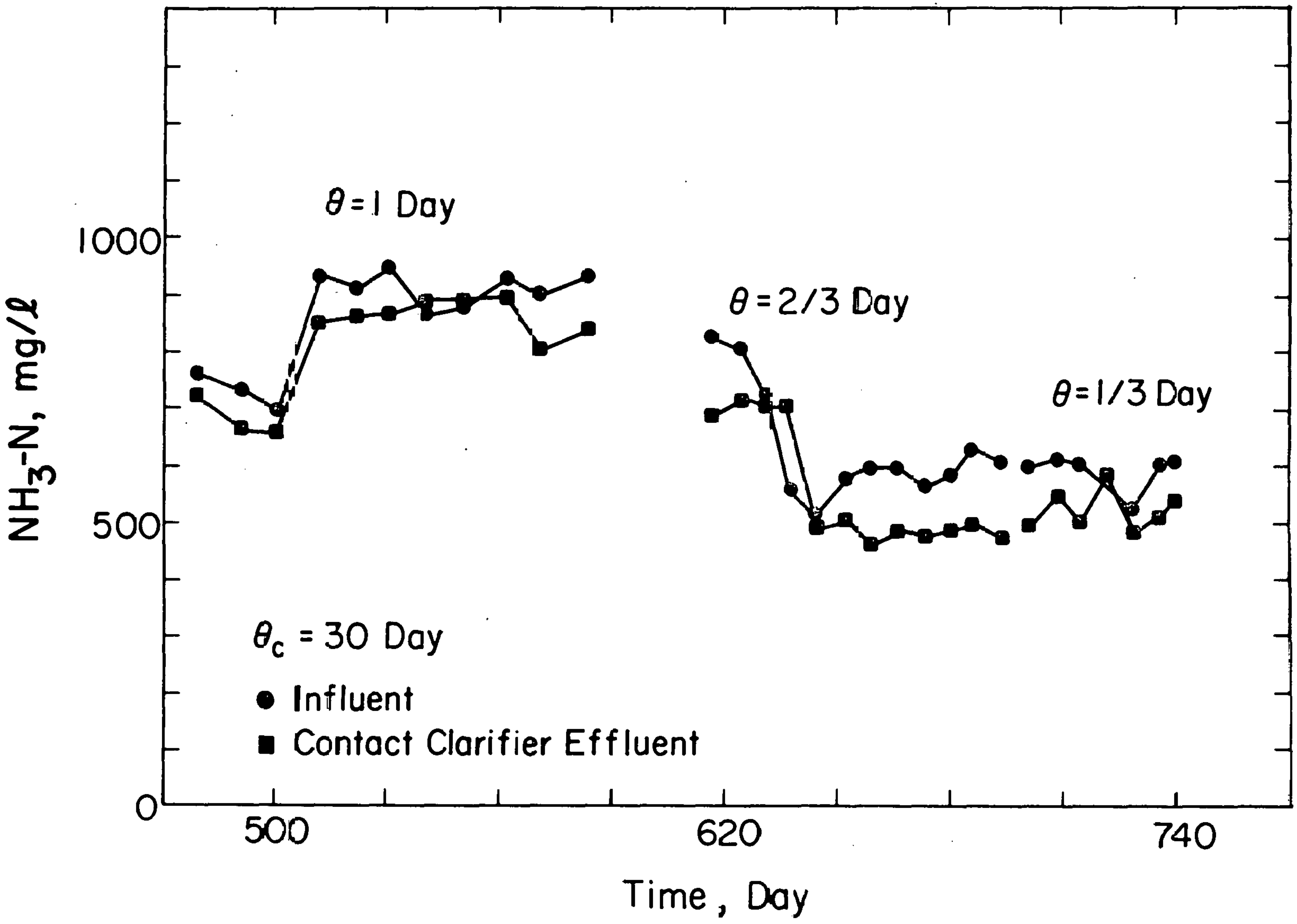


Figure 35. Effect of Contact Detention Time on Ammonia Reduction in 133 mg/ℓ PAC System

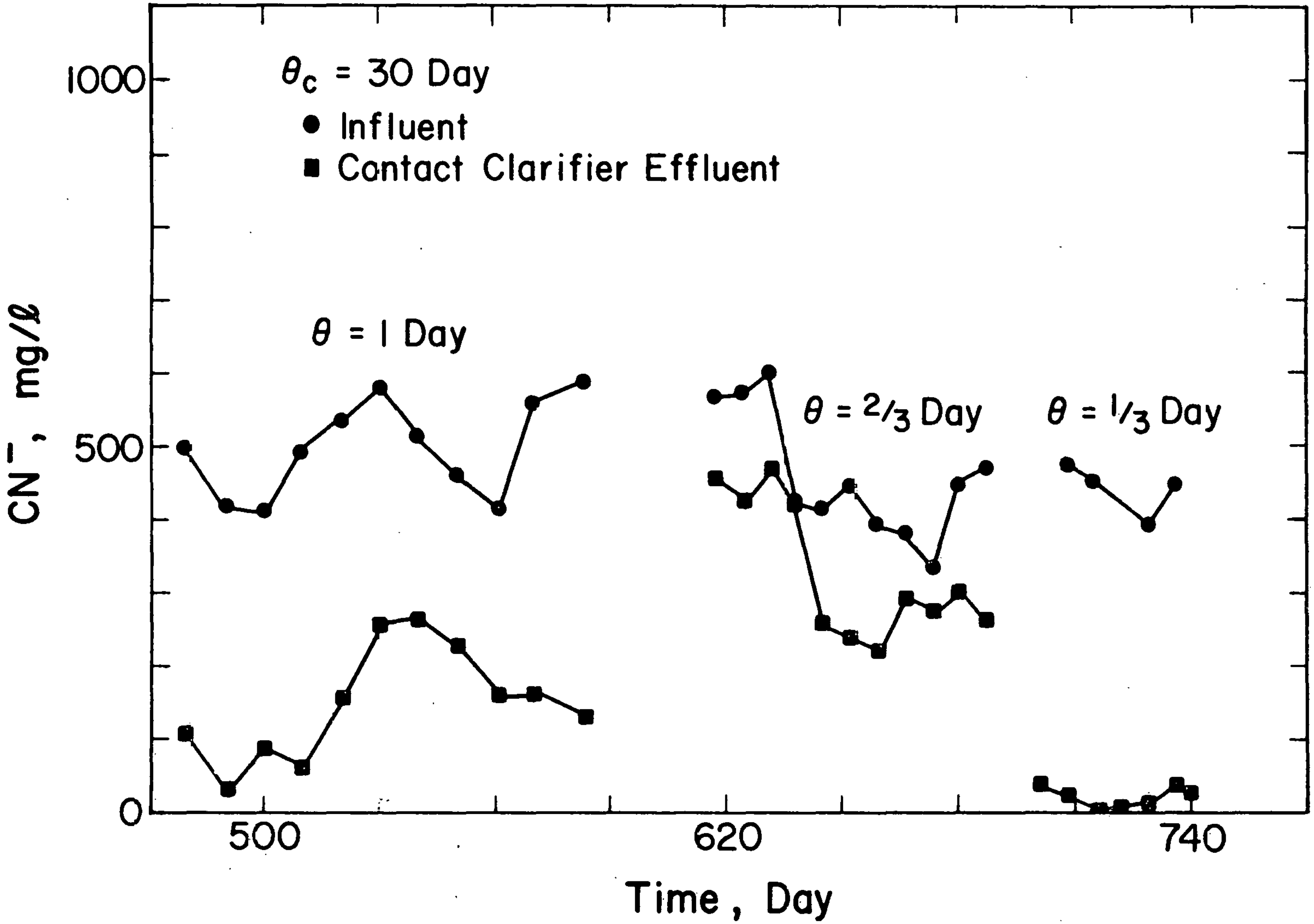


Figure 36. Effect of Contact Detention Time on Cyanide Reduction in 0 mg/ℓ PAC System

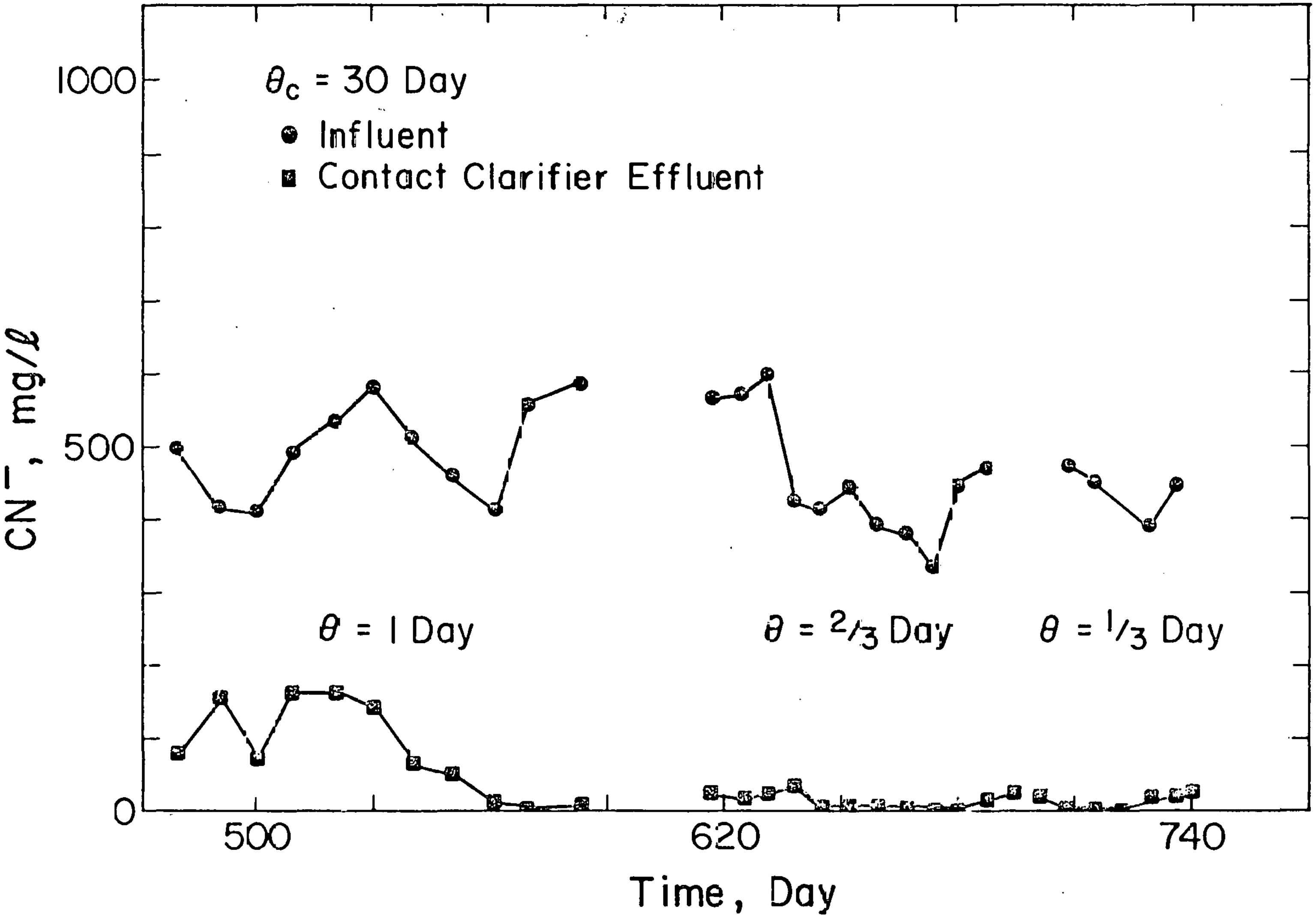


Figure 37. Effect of Contact Detention Time on Cyanide Reduction in 67 mg/ℓ PAC System

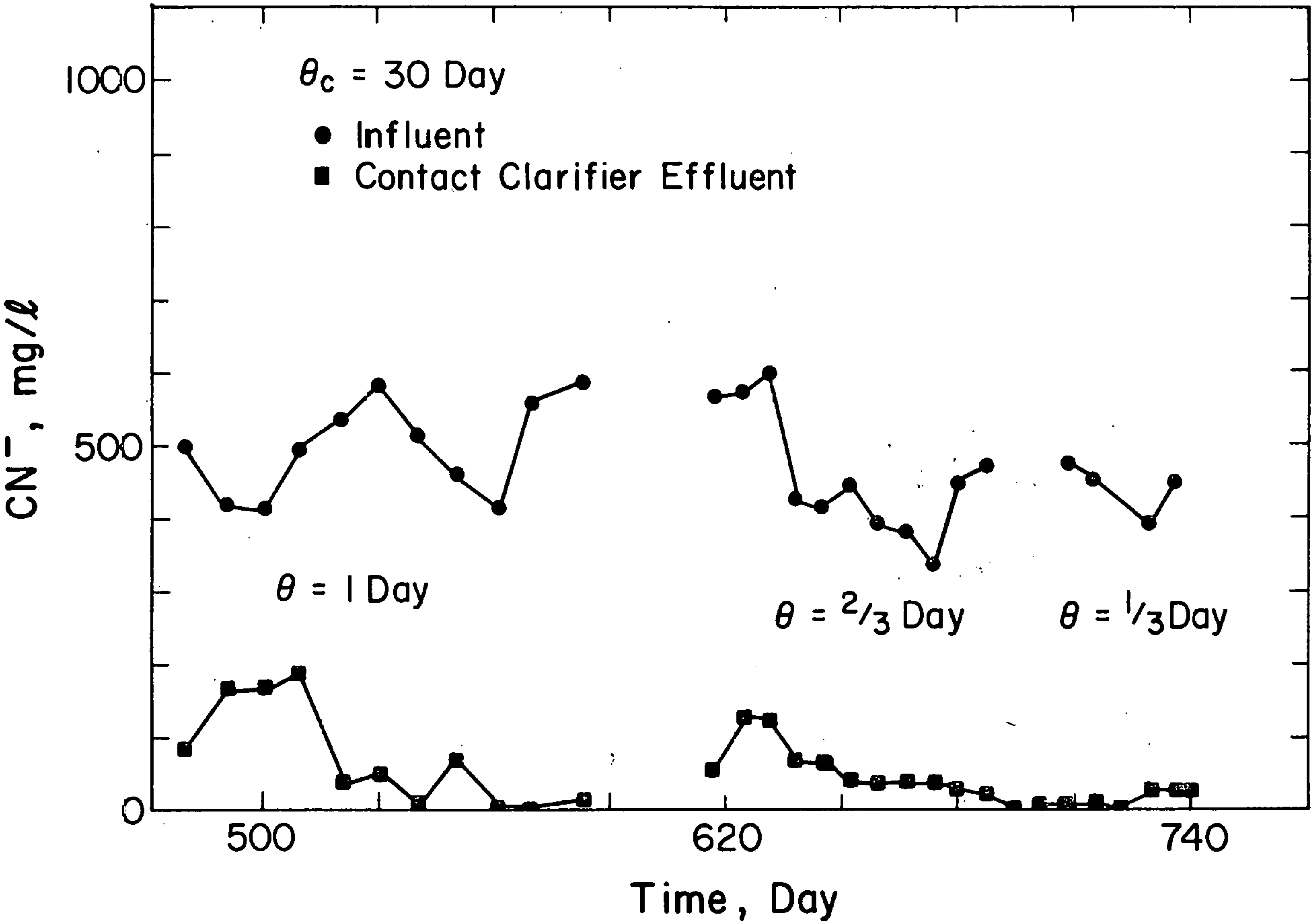


Figure 38. Effect of Contact Detention Time on Cyanide Reduction in 133 mg/ℓ PAC System

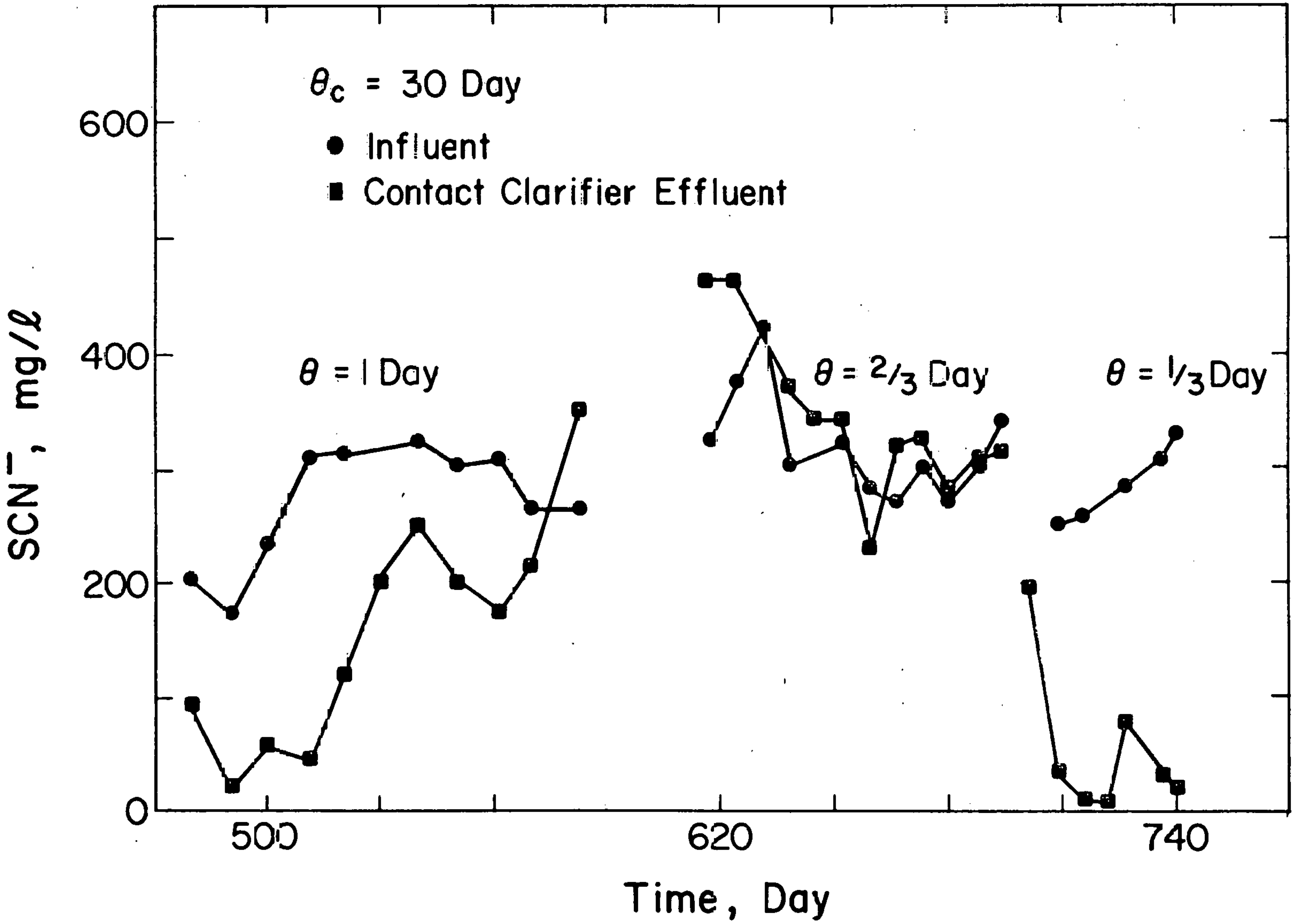


Figure 39. Effect of Contact Detention Time on Thiocyanate Reduction in 0 mg/ℓ PAC System

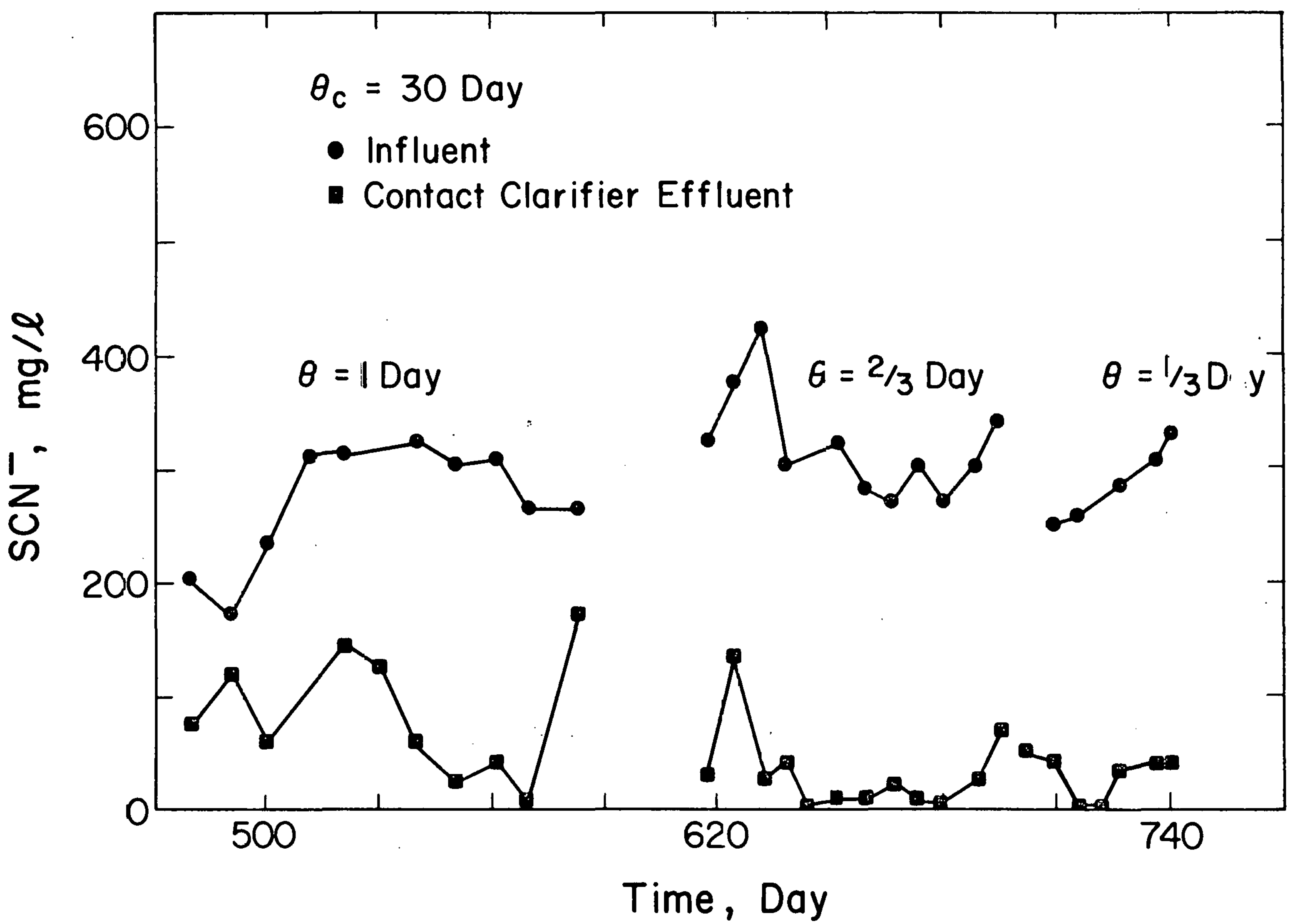


Figure 40. Effect of Contact Detention Time on Thiocyanate Reduction in 67 mg/ℓ PAC System

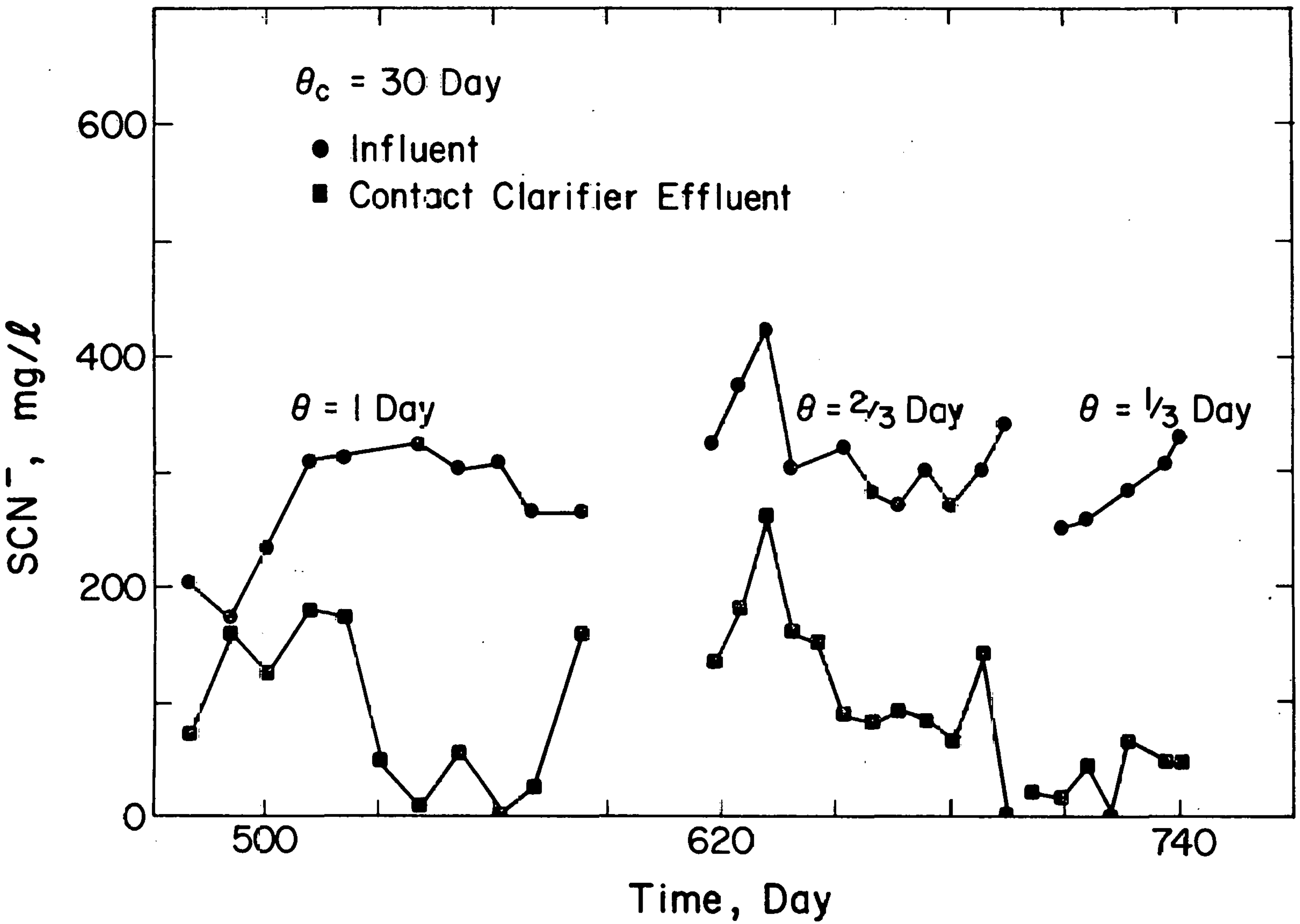


Figure 41. Effect of Contact Detention Time on Thiocyanate Reduction in 133 mg/ℓ PAC System

Table 24

Effect of Contact Detention Time on Cyanide and Thiocyanate Reduction, θ_c = 30 Day

	0 mg/ℓ PAC System						67 mg/ℓ PAC System						133 mg/ℓ PAC System					
	θ = 1 Day		θ = 2/3 Day		θ = 1/3 Day		θ = 1 Day		θ = 2/3 Day		θ = 1/3 Day		θ = 1 Day		θ = 2/3 Day		θ = 1/3 Day	
	CN^- mg/ℓ	SCN^- mg/ℓ	CN^- mg/ℓ	SCN^- mg/ℓ	CN^- mg/ℓ	SCN^- mg/ℓ	CN^- mg/ℓ	SCN^- mg/ℓ	CN^- mg/ℓ	SCN^- mg/ℓ	CN^- mg/ℓ	SCN^- mg/ℓ	CN^- mg/ℓ	SCN^- mg/ℓ	CN^- mg/ℓ	SCN^- mg/ℓ	CN^- mg/ℓ	SCN^- mg/ℓ
Influent	574(23)	306(3)	405(52)	296(27)	421(46)	308(23)	574(23)	306(3)	405(52)	296(27)	421(46)	308(23)	574(23)	306(3)	405(52)	296(27)	421(46)	308(23)
Contact Clarifier Effluent	146(22) 74.56%	187(17) 38.89%	269(31) 33.58%	297(36) -0.34%	19(13) 95.48%	43(30) 86.04%	8(5) 98.60%	36(7) 88.23%	11(8) 97.28%	24(24) 91.89%	18(9) 95.72%	40(6) 87.01%	9(8) 98.43%	39(30) 87.25%	28(13) 93.09%	77(46) 73.99%	23(12) 94.54%	52(9) 83.12
Stabilizer Tank	132(3) 77.00%	256(31) 16.34%	221(70) 45.43%	309(14) -4.39%	6(6) 98.56%	6(4) 98.05%	5(2) 99.13%	18(25) 94.12%	5(1) 98.76%	4(3) 98.65%	3(1) 99.29%	4(4) 98.70%	6(4) 99.13%	19(11) 93.79%	5(1) 98.76%	3(3) 98.99%	4(2) 99.05%	7(9) 97.73

( ) Quantity in parentheses represents standard deviation.

* Percent removal.

The effect of decreasing the contact detention time on the reduction of cyanide and thiocyanate is similar to the effects observed on the COD and DOC reduction efficiencies. The 0 mg/l PAC system experienced a substantial decrease in the cyanide removal efficiency when the contact time was decreased to 16 hours. The effect of the shock load period on the cyanide removal efficiency of the 0 mg/l PAC system was very pronounced. The concentration of cyanide in the effluent from that system increased almost instantaneously to approximately the feed levels. However, when the influent concentration of cyanide was lowered, the system began to recover. The effects of both the shock load and change in contact detention time were even more severe when evaluated in terms of thiocyanate reduction. There was virtually no thiocyanate oxidation in the 0 mg/l PAC system during the whole duration of the 16 hour contact detention time study. The systems exhibited only mild decreases in their cyanide and thiocyanate removal efficiency when the contact detention time was reduced from 1 day down to 2/3 day.

Further reduction in the contact detention time to 1/3 day seemed to have little effect on the removal efficiency of cyanide and thiocyanate in the 67 mg/l PAC and 133 mg/l PAC systems. However, the improved performance of the 0 mg/l PAC system that was observed when the contact aeration detention time was reduced to 1/3 day is not explainable.

3. Suspended Solids

The concentrations of suspended solids maintained in the aeration tanks were averaged over several weeks of stable operating conditions for the 1, 2/3, and 1/3 day contact aeration time. These averaged values are given in Tables 20-22. An increase in solids concentration was observed in the contact aeration tanks of all systems when the contact aeration detention time was decreased. This increased concentration of suspended solids is a direct result of the decrease in the total aeration volume of each system. Suspended solids were regularly monitored in order to permit strict sludge age control.

V - SUMMARY AND CONCLUSIONS

Coal conversion wastewaters have traditionally been treated using the extended aeration activated sludge process. This treatment process is usually very energy intensive due to the use of lengthy aeration detention times and excessively long solids retention times. The powdered activated carbon contact-stabilization process was proposed as an alternative treatment system designed to reduce the total aeration detention time and result in better effluent quality.

Three identical treatment process trains were constructed. Each system consisted of a contact aeration tank that received the coke-oven wastewater flow, a powdered activated carbon (PAC) slurry, and the return sludge from the stabilization tank. The effluent from the contact tank was clarified in a settling tank. The underflow from the settling tank was returned to the stabilization tank while the clarified effluent was gravity fed to a nitrification activated sludge system. The nitrified effluent was subsequently fed to an anoxic methanol-fed denitrification column.

The effectiveness of the three systems in treating coke-oven wastewater was evaluated using 30 percent strength wastewater. At that dilution, the average concentrations of chemical oxygen demand (COD), dissolved organic carbon (DOC), ammonia-nitrogen, cyanide and thiocyanate were 1,240, 365. 995, 630, and 345 mg/l, respectively.

During the first period of study the three treatment systems were acclimated to the coke-oven wastewater. These units were subsequently used to determine the effect on treatment efficiency of the solids retention time and the mixed liquor powdered activated carbon (MLPAC) concentration maintained in the contact stabilization portion of each system.

During this evaluation hydraulic detention times in the contact, stabilization, and nitrification aeration tanks were maintained constant at 1.02, 1.77 and 1.2 days, respectively. The hydraulic detention time in the stabilization tank was computed using the sludge return flow rate. MLPAC levels of 0, 980 and 1,960 mg/l were maintained in the contact-stabilization portion of the respective units throughout this part of the study, while solids retention times of 10, 20 and 30 days were tested in each of the units. The nitrification systems were all maintained at 40 day solids retention times.

The system receiving no PAC exhibited its best performance at the 10 day solids retention time, while its poorest performance was obtained during the 30 day solids retention time study. This phenomenon suggested that some inhibitory and poorly or nondegradable material present in the wastewater must have accumulated in the contact-stabilization system. Consequently, increased solids retention time resulted in a buildup of concentration of the toxin, and hence poorer performance resulted. The performance of the 1,960 mg/l MLPAC system, on the other hand, improved markedly with increasing solids retention time. This observation suggests that the toxin discussed earlier must be adsorbable on PAC and thus improved performance was possible when the solids retention time was increased.

In summary, the best overall treatment efficiency was obtained from the 1,960 mg/l MLPAC system when this unit was operated at the 30 day solids retention time. The performance of this unit was judged superior in terms of COD, DOC, ammonia, cyanide and thiocyanate removal efficiency, as well as with respect to system or performance stability. It is interesting to note that the fresh PAC addition rate to this system that was needed to maintain a MLPAC concentration of 1,960 during the 30 day solids retention time study was less than the rates required when lower solids retention times were maintained in this system. This observation suggests that as long as a minimum PAC addition level which sufficiently adsorbed the toxins was employed, the benefits reaped from increased sludge age outweighed those associated with the availability of higher adsorptive capacities.

During the latter part of the project period, the effect of the detention time maintained in the contact aeration tank on the performance of the contact-stabilization system was evaluated. Contact detention times of 1 day, 2/3 day and 1/3 day were tested while the solids retention times in the three systems were maintained at 30 days. Reducing the hydraulic detention time in the contact aeration tanks from 1 day to 2/3 and 1/3 day did not adversely affect the performance of the two contact-stabilization systems receiving PAC. However, this reduced contact aeration volume appeared to induce increased instability in the performance of the unit receiving no PAC. It is significant that reducing the contact retention time to 1/3 the original value did not significantly change the performance of the systems. Optimization of this section of the system will result in the biggest advantage of this process since the contact aeration tank handles a larger flow volume than the stabilization aeration tank. Further reduction in the contact detention time may be possible since there was no real change in effluent quality when the detention time was reduced to 1/3 day.

REFERENCES

1. Adams, A. D., "Improving Activated Sludge Treatment with Powdered Activated Carbon," Proceedings of the 28th Purdue Industrial Waste Conference, Vol. 28 (1973).

2. Adams, C. E., "Treatment of High Strength Phenolic and Ammonia Wastestream by Single and Multistage Activated Sludge Processes," Proceedings of the 29th Purdue Industrial Waste Conference, Ann Arbor Science Publishing Co., Ann Arbor, Mich., pp. 617-630 (1974).

3. Adams, C. E., Stein, R. M., and Eckenfelder, W. W. Jr., "Treatment of Two Coke Plant Wastewaters to Meet Effluent Guideline Criteria," Proceedings of the 29th Purdue Industrial Waste Conference, Ann Arbor Science Publishing Co., Ann Arbor, Mich., pp. 864-880 (1974).

4. Anthonisen, A. C., Loehr, R. C., Prakasam, T.B.S., and Srinath, E.G., "Inhibition of Nitrification by Ammonia and Nitrous Acid," Journal of the Water Pollution Control Federation, Vol. 48, No. 5 (May 1976).

5. Barker, J. E. and Thompson, R. J., "Biological Removal of Carbon and Nitrogen Compounds from Coke Plant Wastes," EPA Report #EPA-22-73-167, (April 1973).

6. Benefield, L. D. and Randall, C. W., "Design Procedure for a Contact Stabilization Activated Sludge Process," Journal of the Water Pollution Control Federation, Vol. 48, No. 1 (January 1976).

7. Catchpole, J. R. and Cooper, R. L., "The Biological Treatment of Carbonization Effluents-III, New Advances in the Biochemical Oxidation of Liquid Wastes," Water Research, Vol. 6, pp. 1459-1474 (1972), Great Britain.

8. Cooke, R. and Graham, P. W., "Biological Purification of the Effluent from a Lurgi Plant Gasifying Bituminous Coals," International Journal of Air and Water Pollution, Vol. 2, No. 3 (1965).

9. DeWalle, F. B. and Chian, E.S.K., "Biological Regeneration of Powdered Activated Carbon Added to Activated Sludge Units," Water Research, Vol. II, p. 439 (1977).

10. Ferguson, J. F., Keay, G.F.P., Merrill, M. S., and Benedict, A. H., "Powdered Activated Carbon Biological Treatment: Low Detention Time Process," Proceedings, Purdue Industrial Waste Conference, Vol. 31 (1976).

11. Forney, A. J., Haynes, W. P., Gasior, S. F., Johnson, G. E., and Strakey, J. P., "Analysis of Tars, Chars and Water in Effluents from the Synthane Process," U.S. Bureau of Mines Technical Progress Report 76, Pittsburgh, Energy Technology Center, Pittsburgh, Penn. (1977).

12. Frohlich, G. and Vollstedt, T. J., "Performance of a Biophysical Treatment Process on a High-Strength Industrial Waste," 31st Purdue Industrial Waste Conference, Purdue University (May 1976).

13. Ganczarczyk, J. J., "Second-Stage Activated Sludge Treatment of Coke-Plant Effluents," Water Research, Vol. 13, No. 4, pp. 337-342 (April 1979).

14. Ganczarczyk, J. and Elion, D., "Extended Aeration of Coke-Plant Effluents," Proceedings of the 33rd Purdue Industrial Waste Conference, Ann Arbor Science Publishers Inc., Ann Arbor, Mich. (May 9-11, 1978).

15. Goldstein, D. J. and Yung, D., "Water Conservation and Pollution Control in Coal Conversion Processes," EPA-600/7-77-065 (June 1977).

16. Grieves, C. G., Crame, L. W., Venardos, D. G., and Ying, W., "Powdered Versus Granular Carbon for Oil Refinery Wastewater Treatment," Journal of Water Pollution Control Federation, Vol. 52, No. 3 (March 1980).

17. Grieves, C. G., Stenstrom, M. K., Walk, J. D., and Grutsch, J. F., "Effluent Quality Improvement by Powdered Activated Carbon in Refinery Activated Sludge Processes," Paper Presented at API Refining Department, 42nd Midyear Meeting, Chicago, Ill. (May 1977).

18. Hals, O. and Benedek, A., "Simultaneous Biological Treatment and Activated Carbon Adsorption," Paper Presented at the 46th Annual Conference, Water Pollution Control Federation, Cleveland, Ohio (1973).

19. Heukelekian, H. and Heller, A., "Relation Between Food Concentration and Surface for Bacterial Growth," Journal Bacteria, Vol. 40, p. 547 (1940).

20. Hockenbury, M. R. and Grady, C.P.L., Jr., "Inhibition of Nitrification Effects of Selected Organic Compounds," Journal of Water Pollution Control Federation, Vol. 49, p. 708 (1977).

21. Hutton, W. C. and LaRocca, S. A., "Biological Treatment of Concentrated Ammonia Wastewaters," Journal Water Pollution Control Federation, Vol. 47, No. 5 (May 1975).

22. Johnson, G. E., Neufeld, R. D., Drummond, C. J., Strakey, J. P., Haynes, W. P., Mack, J. D., and Valiknac, T. J., "Treatability Studies of Condensate Water from Coal Gasification," Pittsburgh Energy Technology Center Report No. PERC/RI-77/13 (November 1977).

23. Juntgen, H. and Klein, J., "Purification of Wastewater from Coking and Coal Gasification Plants Using Activated Carbon," Energy Sources, Vol. 2, No. 4 (1977).

24. Kalinske, A. A., "Enhancement of Biological Oxidation of Organic Wastes Using Activated Carbon in Microbial Suspensions," Water Sewage Works, 115 (1972).

25. King, D. L. and Verma, R. D., "The Role of Particulate Substrates in Biotic Degradation," Proceedings, Purdue Industrial Waste Conference, Vol. 23 (1968).

26. Koppe, P., Sebesta, G., and Harkelmann, H., "The Biochemical Oxidation of a Slowly Degradable Substance in the Presence of Activated Carbon: Biocarbon Unit," Gesundheits Ingenieur, Vol. 95, p. 247 (1974).

27. Kostenbader, P. D. and Flecksteiner, J. W., "Biological Oxidation of Coke Plant Work Ammonia Liquor," Journal Water Pollution Control Federation, Vol. 41, No. 2, Part 1 (February 1969).

28. Lamb, J. C., III, Singer, P. C., Rader, R. D., Reckhow, D. A., and Speitel, G. E., "Characterization and Biological Treatability of Coal Conversion Wastewaters," Proceedings of the 34th Purdue Industrial Waste Conference, pp. 63-72 (1979).

29. Luthy, R. G., "Manual of Methods; Preservation and Analysis of Coal Gasification Wastewaters," Report to Department of Energy, FE-2496-16 (1978).

30. Luthy, R. G., "Treatment of Coal Coking and Coal Gasification Wastewaters," Journal of the Water Pollution Control Federation, Vol. 53, No. 3, pp. 325-339 (1981).

31. Luthy, R. G. and Jones, L. D., "Biological Oxidation of Coke Plant Effluent," Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers, Vol. 106, No. EE4 (August 1980).

32. Luthy, R. G., Bruce, S. G., Jr., Walters, R. W., and Nakles, D. V., "Cyanide and Thiocyanate in Coal Gasification Wastewaters," Journal of the Water Pollution Control Federation, Vol. 51, No. 9 (September 1979).

33. Luthy, R. G., Sekel, D. J., and Tallon, J. T., "Biological Treatment of Synthetic Fuel Wastewater," Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers, Vol. 106, No. EE5 (June 1980).

34. Luthy, R. G., Stamoudis, V. C., Campbell, J. R., and Harrison, W., "Removal of Contaminants from Coal Conversion Condensates," Journal of the Water Pollution Control Federation, Vol. 55, No. 2, (February 1983).

35. Luthy, R. G. and Tallon, J. T., "Biological Treatment of Hygas Coal Gasification Wastewater," NTIS FE-2496-43, Department of Civil Engineering, Carnegie-Mellon University forthe Department of Energy, (December 1978).

36. Luthy, R. G. and Tallon, J. T., "Biological Treatment of a Coal Gasification Process Wastewater," Water Research, Vol. 14, pp. 1269-1282, Pergamon Press, Great Britain (1980).

37. Mathews, W. W., Sewage and Industrial Wastes, Vol. 24, No. 2, pp. 164-180 (1952).

38. Methods for Chemical Analysis of Water and Wastes, EPA (1974).

39. Mohlman, F. W., "Sewage Treatment with Ammonia Liquor," American Journal of Public Health, Vol. 19, No. 1, pp. 145-154 (1929).

40. Muller, J. M. and Conventry, F. L., "Disposal of Coke Plant Waste in the Sanitary Water System," Blast Furnace and Steel Plant, Vol. 56, No. 5, pp. 400-406 (May 1968).

41. Nayor and Sylvester, "Control of Phenol in Biological Reactors of Powdered Activated Carbon," Water Research, Vol. 13 (1979).

42. Neufeld, R. D., Drummond, C. J., and Johnson, G. E., "Biokinetics of Activated Sludge Treatment of Synthane Fluidized Bed Gasification Wastewaters," Paper Presented at the 175th National ACS Meeting, Anaheim, Calif. (March 1978).

43. Nutt, S. G., Melcer, H., and Pries, J. H., "Two-Stage Biological Fluidized Bed Treatment of Coke Plant Wastewater for Nitrogen Control," Paper Presented at the 54th Annual WPCF Conference, Detroit, Mich., Session #37 (October 8, 1981).

44. Olthoff, M., "Nitrification of Coke Oven Wastewater with High Ammonia Concentration," Proceedings of the 34th Purdue Industrial Waste Conference, Ann Arbor Science Publishing Co., Ann Arbor, Mich., pp. 22-35 (1979).

45. Olthoff, M., Pearson, E. F., Mancuso, N., and Wittmann, I. E., "Biological Treatment of Coke-Oven Wastewater Including Provisions for Nitrification," Iron and Steel Engineer (June 1980).

46. Parsons, W. A. and Nolde, W., "Applicability of Coke Plant Water Treatment Technology to Coal Gasification," Proceedings, Environmental Aspects of Fuel Conversion Technology III, Hollywood, Florida (September 1977).

47. Paulk, C. M., Jr., "The Role of Powdered Activated Carbon in Bio-Oxidation of Phenol-Mixed Liquor Carbon Concentration and Sludge Age Interaction," Special Research Problem, School of Engineering, Georgia Institute of Technology, Atlanta, Georgia (December 1979).

48. Perrotti, A. E. and Rodman, C. A., "Factors Involved with Biological Regeneration of Activated Carbon," AIChE Symposium Series, Vol. 70, No. 144, p. 316 (1974).

49. Perrotti, A. E., Rodman, C. A., and Shunney, E. L., "Biological Regeneration of Activated Carbon," Carbon Adsorption Handbook, ed. by P. N. Cheremisinoff and F. Ellerbusch, Ann Arbor Science Publishing Inc., (1978).

50. Reap, E. J., Davis, G. M., Duffy, M. J., and Koon, J. H., "Wastewater Characteristics and Treatment Technology for the Liquefaction of Coal Using H-Coal Process," Proceedings of the 32nd Purdue Industrial Waste Conference, Ann Arbor Science Publishers Inc., Ann Arbor, Mich. (1977).

51. Robertaccio, F. L., Hutton, D. G., Grulich, G., and Goltzer, H. L., "Treatment of Organic Chemical Plant Wastewater with the Dupont Pact Process," AIChE Symposium Series No. 125, Vol. 65 (1972).

52. Robertaccio, F. L., "Powdered Activated Carbon Addition to Biological Reactors," Ph.D. Thesis, University of Delaware, Newark, Delaware (June 1976).

53. Rudolfs, Willem, Industrial Wastes, Reinhold Publishing Corporation, New York (1953).

54. Rudolfs, W. and Trubnick, E. H., "Activated Carbon in Sewage Treatment," Journal Sewage Works, Vol. 7, p. 852 (1955).

55. Sack, W. A., "Biological Treatability of Gasifier Wastewater," NTIS METC/CR-79/24, U.S. Department of Energy, Morgantown Energy Technology Center (June 1979).

56. Sack, W. A. and Bokey, W. R., "Biological Treatment of Coal Gasification Wastewater," Proceedings of Purdue Industrial Waste Conference, Vol. 33 (1978).

57. Scaramelli, A. B. and DiGiano, F. A., "Upgrading the Activated Sludge System by Addition of Powdered Activated Carbon," Water Sewage Works, Vol. 120, p. 90 (1970).

58. Schora, F. C. and Fleming, D. K., "Effluent Considerations in Coal Gasification," Proceedings, Environmental Aspects of Fuel Conversion Technology, II, Hollywood, Florida (December 1975).

59. Schultz, J. R. and Keinath, T. M., "PACT Process Mechanisms," Paper Presented at the 55th Annual Conference of the Water Pollution Control Federation, St. Louis, Miss. (October 4, 1982).

60. Siekerka, G. L., "Anaerobic Activated Carbon and Nitrification System for the Treatment of the Constituents in Coal Gasification Wastewater," M.S. Thesis, University of Illinois at Urbana-Champaign (1982).

61. Singer, P. C., Pfaender, F. K., Chinchilli, J., and Lamb, J. C., III, "Composition and Biodegradability of Organics in Coal Conversion Wastewaters," Paper Presented at the 3rd Symposium on Environmental Aspects of Fuel Conversion Technology (1977).

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

63. Stamoudis, V. S. and Luthy, R. G., "Determination of Biological Removal of Organic Constituents in Quench Waters from High-BTU Coal Gasification Pilot Plants," Water Research, Vol. 14, pp. 1143-1156, Pergamon Press, Ltd. (1980).

64. Strubler, C. E., "Treatment of Coal Gasification Wastewater with Anaerobic Filters Followed by Activated Sludge," M.S. Thesis, University of Illinois at Urbana-Champaign (1983).

65. Suidan, M. T., Pirbazari, M., Gee, C. S., and Deady, M. S., "Treatment of Coal Conversion Wastewater with the Powdered Activated Carbon-Contact Stabilization Activated Sludge Process," First Semiannual Technical Progress Report, for the Period August 1, 1980 - January 31, 1981, Department of Energy No. DOE/PC/30233-T1 (1981).

66. Suidan, M. T., Gee, C. S., Deady, M. A., and Pirbazari, M., "Treatment of Coal Conversion Water with the Powdered Activated Carbon-Contact Stabilization Activated Sludge Process," First Annual Technical Progress Report for the Period February 1, 1981 - July 31, 1981, Department of Energy Report No. DOE/PC/30233-T2 (1981).

67. Suidan, M. T., Gee, C. S., and Deady, M. A., "Treatment of Coal Conversion Water with the Powdered Activated Carbon-Contact Stabilization Activated Sludge Process," Third Semiannual Technical Progress Report for the Period August 1, 1981 - January 31, 1982, Department of Energy Report No. DOC/PC/30233-T3 (1982).

68. Sundstrom, D. W., Klei, H. E., Tsui, T., and Nayar, S., "Response of Biological Reactors to the Addition of Powdered Activated Carbon," Water Research, Vol. 13, pp. 1225-1231 (1979).

69. Valiknac, T. J. and Neufeld, R. D., "Thiocyanate Toxic Inhibition of Phenol Bio-oxidation," Proceedings of the 33rd Purdue Industrial Waste Conference, May 9-11, 1978, Ann Arbor Science Publishers Inc., Ann Arbor, Mich. (1979).

70. Zobell, C. E., "The Influences of Solid Surfaces Upon the Physiological Activities of Bacteria in Sea Water," Journal Bacteria, Vol. 33, No. 86 (1937).

71. Kruse, J. M. and Mellon, M. G., Analytical Chemistry, Vol. 35, No. 3, p. 446 (1953).

72. Danchick, R. S. and Boltz, D. F., Analytical Chemistry, Vol. 40, No. 14, p. 2215 (1968).

☆U.S. GOVERNMENT PRINTING OFFICE: 1983-746-081/2573