GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

REVISED

Date: 12/18/79

Project Title: Study of the Treatment of Wastewaters Containing Aqueous Film Forming Foam (AFFF)

Project No: E-20-A02 (Formerly E-20-647)

Project Director(s): Dr. Edward S.K. Chian; Dr. M.T. Suidan, Dr. W.H. Cross

Sponsor: U.S. Army Medical Research & Development Command

Agreement Period: From ~~2/22/82~~ 10/1/79 4/30/82 Until ~~9/30/80~~ 5/31/82

Type Agreement: Contract No. DAMD17-78-C-8072

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$49,986

Reports Required: Quarterly Technical Progress Reports, Annual Progress Report
Final Report

Sponsor Contact Person (s):

Technical Matters

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Contractual Matters
(thru OCA)

Dennis H. Hunt, Contracting Officer's Representative
Department of the Army
U.S. Army Medical Research & Dev. Comm
Fort Detrick, Frederick, MD 21701

Defense Priority Rating: DO-C9(e)

Assigned to: Civil Engineering (School/Laboratory)

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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 11/20/84

Project No. E-20-A02 (Formerly E-20-647) School/~~Lab~~ E-20-A02

Includes Subproject No.(s)

Project Director(s) Edward Chian GTRI / ~~GIT~~

Sponsor U. S. Army Medical Research & Development Command

Title Study of the Treatment of Wastwaters Containing Aqueous Film Forming Foam (AFFF).

Effective Completion Date: 4/30/82 (Performance) 4/30/82 (Reports)

Grant/Contract Closeout Actions Remaining:

NOTE: Deliverables transferred to follow on project E-20-A03

- [X] None
- [ ] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
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ANAEROBIC-ACTIVATED CARBON FILTER FOR THE TREATMENT OF AQUEOUS FILM FORMING FOAM (AFFF) WASTEWATER

QUARTERLY PROGRESS REPORT
January, 1980

by

Makram T. Suidan, Edward S. K. Chian
and
Wendall H. Cross

Supported by

U.S. Navy Civil Engineering Laboratory
Port Hueneme, California 93043
U.S. Army Medical Research and Development Command
Fort Detrick
Federick, Maryland 21701
Contract No. DAMD 17-78-C-8072

Contract Monitors

D. B. Chan, Ph.D., USNCEL
B. Peterman, USAMBRDL

Introduction

The present research effort is directed towards an examination of the effectiveness of a two stage anaerobic filter in the treatment of wastewaters emanating from fire fighting training exercises at miliary installations. In addition to fuel oil and gasoline, combustion products and suspended solids, these wastewaters also contain the constituents present in the fire fighting agent used. Such agents, commonly referred to as Aqueous Film Forming Foam (AFFF) contain various glycols and surfactants in addition to various fluorocarbon compounds.

The environmental impact of the production of AFFF wastewaters may be subdivided into:

(a) The organic constituents present in AFFF have been reported to resist biodegradation in conventional biological process as well as contributing to operational problems and the eventual failure of biological treatment processes that receive AFFF as well as other domestic or industrial wastewaters (Chan, 1978).

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Chian (1978) examined the potential of several physicochemical processes in the treatment of AFFF wastewaters. Reverse osmosis and adsorption onto activated carbon were found to be two possible treatment alternatives that resulted in good treatment efficiencies. However, with the exception of reverse osmosis where resource recovery may render the process economical, Chian (1978) concluded that these processes were both too expensive for the treatment of AFFF wastewaters.

The anaerobic filter has recently gained popularity in the treatment of industrial and municipal wastewaters. Chan et al.(1978) investigated the stability of the anaerobic filter to shock loads of various industrial chemicals including phenol, catechol, resorcinol, nitrobenzene and cyanide. In all instances, Chan et al.(1978) reported the filter to withstand shock concentrations of these industrial chemicals. Friedman (1980) and Ragan (1980) reported very encouraging results on the treatment of pharmaceutical and chemical wastewaters, while Suidan et al. (1979a,b) demonstrated that the anaerobic environment is very amenable to the treatment of phenols bearing wastewaters.

In the present investigation, a two stage anaerobic filter has been selected for the treatment of a synthetic AFFF wastewater. The first stage filter is packed with Raschig rings for a support medium while in the second filter fluidized granular activated carbon is employed as a microbial attachment as well as a concentration polarization and toxicity reducing medium. The advantages anticipated from this reactor configuration arise from the combination of the energy efficient anaerobic filter with the long retention of adsorbable organic matter as provided by the activated carbon medium.

Experimental Apparatus

The experimental apparatus used in this study is shown in Figure 1. One such unit is currently in operation and four additional identical units are in the final phase of construction and testing. Each unit consists of the following:

a. Feed Pumps: The AFFF is diluted with distilled water to any desired concentration in a 20-ℓ concentrate reservoir (see Figure 1). This diluted substrate is fed into the reactor feed using a positive displacement FMI pump. Model RP G-20(Fluid Metering Incorporated, Oyster Bay, N.Y.) having a maximum flow rate of 5.4 ml/min and a maximum operating pressure of 50 psi. No other nutrients are added to this reservoir in order to prevent any biodegradation within the reservoir and the feed lines.

Dilution water containing the phosphate buffer and ammonium nutrients necessary for active biodegradation are pumped from another 55-ℓ reservoir using a positive displacement pump Model RP G150 (Fluid Metering Incorporated, Oyster Bay, N.Y.). This pump has a maximum flow rate setting of 96 ml/min and a maximum operating pressure of 20 psi. The flow from the two reservoirs is mixed in a tee connection prior to entry into the first-stage roughing anaerobic filter.

b. Roughing Anaerobic Filter

This roughing unit has a water jacketed plexiglas column having the following features

i. inner column (10.1 cm in internal diameter by 182 cm long) which will serve as the actual roughing anaerobic filter chamber.

ii. a water jacket (15.25 cm in internal diamter by 170 cm long) to allow the unit to be operated at a constant and controllable temperature bath (Model T31, HAAKE, Inc., Werk Karlsruhe, West Germany) through the jacket.

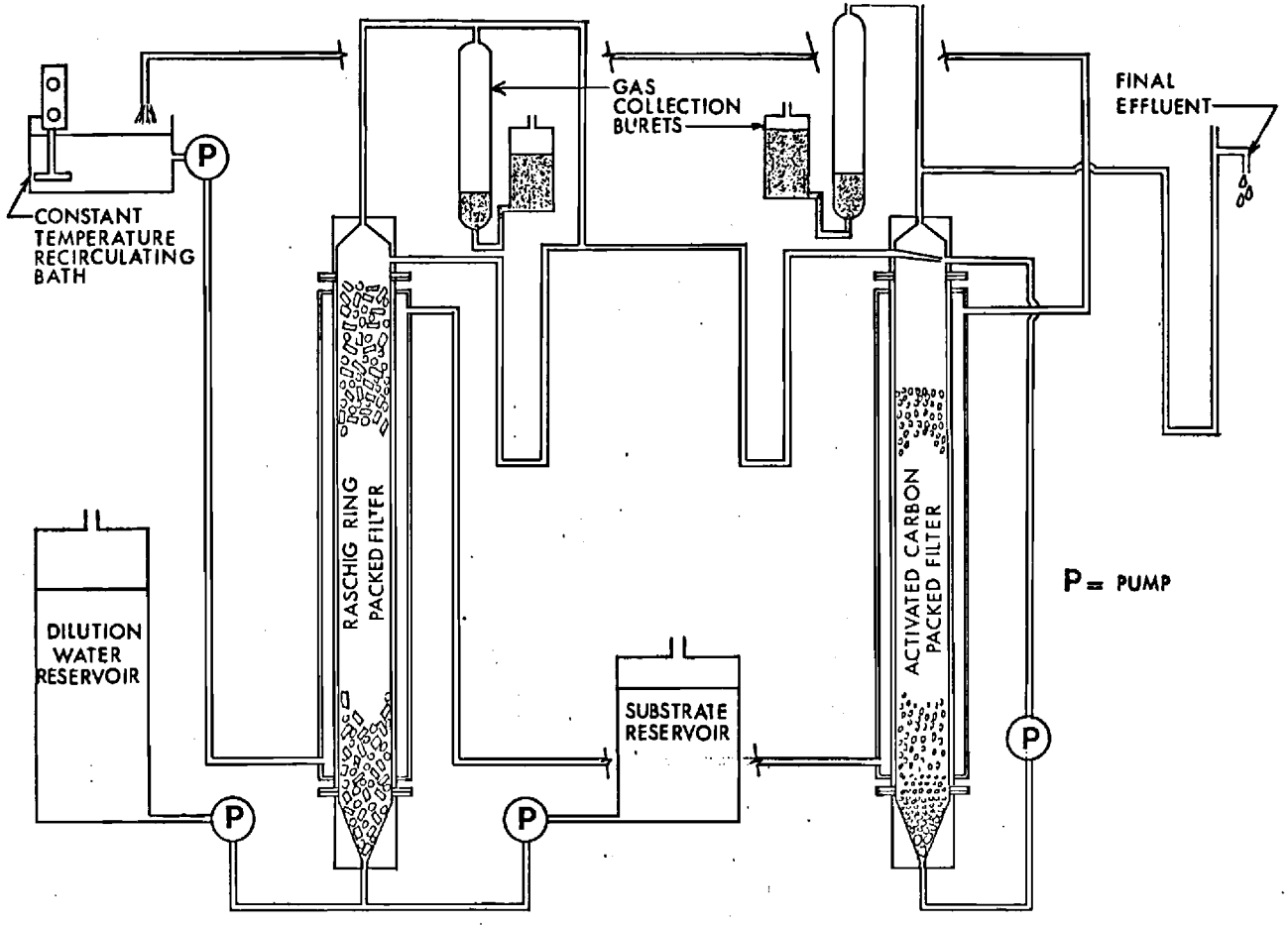

FIGURE 1. APPARATUS FOR THE TREATMENT OF SYNTHETIC PHENOLIC WATER

iii. influent header is constructed using a plexiglass column section and plates and its inner structure, which is 20 cm long, is tapered into an inverted conical shape in order to allow for better distribution of the influent flow. This unit is equipped with a perforated plate to allow for the introduction of the mixed feed solution.

iv. effluent structure: a conical shaped structure used to minimize the trapped gas volume and is equipped with fittings for connection to the gas collection system, connection to the effluent structure from this unit and a sampling port.

v. gas collection system consisting of two 4.5-ℓ gas burets, two leveling bottles and sampling ports to allow for monitoring of both the quantity and composition of the gaseous products produced and for the release of the excess gas produced.

vi. each of the new four units is equipped with a 1/2 HP centrifugal pump (Teel Pump, Dayton Electric Manufacturing Company, Chicago, Ill.). The purpose of this pump is to recirculate the aqueous contents of the filter.

c. Anaerobic Activated Carbon Filter

This unit is identical in structure to the first roughing unit except that it is equipped with a 1/3 HP centrifugal pump in the operating unit and a 1/2 HP centrifugal pump in the new four units (Teel Pump, Dayton Electric Manufacturing Company, Chicago, Ill.). The purpose of this pump is to recirculate the aqueous contents of the carbon filled filter and maintain this carbon fluidized in order to minimize gas trapping onto the carbon.

Filter Packings and Start Up of the Currently Operating System

The roughing anaerobic filter was packed with 1.27 cm (0.5 inch) raschig rings to a depth of 193 cm (6.33 ft). The packed column has a porosity of 58.33 percent and a specific surface area of 337.18 m^2/m^3 (102.65 ft^2/ft^3).

Because of its relatively high porosity and surface area, this packing is ideal for the roughing filter where a high growth rate and sludge accumulation are anticipated.

The anaerobic activated carbon filter was packed in an identical manner in a depth of 128 cm (4.20 ft) and backwashed down to a depth of 100 cm (3.28 ft) in order to eliminate carbon fines. The activated carbon used in this study is Calgon FMC 6 x 16 U.S. Mesh Size with an average particle size of 2.27 mm. However, after backwashing, a larger average particle size was retained in the filter.

The two columns were seeded with an anaerobic sludge obtained from the underflow of an anaerobic digester at the Atlanta Clayton Sewage Treatment Plant.

The dilution water reservoir is filled to capacity with dechlorinated and deaerated tap water to which nutrients and a phosphate buffer are added. In addition to serving as a nutrient, the phosphate mixture is designed to provide a buffer to the waste at the desired operating pH. The levels of addition of the phosphate, ammonium and other nutrients is higher than what is estimated to be needed for the successful operating of the system and the optimum value of these variables will be investigated later. The flow rate of the dilution water was set at 9.00 ml/min while the concentrate flow rate was set at 1.0 ml/min such that the feed concentration to the first column will be only 10 percent of the stock concentrate. The selection of the operating concentrations will be discussed later. The flow rate of 10 ml/min is selected in order to provide an empty bed contact time of 24 hours in each of the reactors.

The recirculation pump on the anaerobic activated carbon filter will be set to give an expanded bed height of 138 cm (4.25 ft) which translates to an expansion of 38 percent. However, provisions are available to vary

this expansion from zero to 83 percent by the readjustment of two valves that were incorporated in the design of the recirculation loop.

Synthetic Feed Substrate

The synthetic feed substrate to the currently operating two stage anaerobic filter was prepared in two separate solutions. The AFFF Ansul was selected as the first AFFF concentrate to be studied. A solution of AFFF and distilled water was prepared in 20ℓ batches and fed to the anaerobic filter.

A dilution water solution was also fed to the columns from a separate 55ℓ reservoir. In addition to serving as a dilution water this solution also contained biological nutrients, ammonium chloride and a phosphate buffer. The concentration of the constituents of the growth nutrients in the dilution reservoir was maintained at the levels indicated in Table I. In addition to these nutrients, additional ammonium chloride and a phosphate buffer were added and their strengths are presented with the operating data in Table II.

Anaerobic Filter Acclimation

Phase 1 - After the two anaerobic filter columns were seeded, the AFFF concentrate was set at 2000 mg/l TOC and it was pumped into the first anaerobic filter at a flow rate of 2.06 ml/min. The dilution buffer and nutrient solution was pumped at a flow rate of 18.55 ml/min, thus resulting in a feed TOC of 1000 mg/l. At the specified flow rates, an empty bed contact time of 12 hours was provided in each filter. Initially, significant gas production and COD and TOC reductions were observed. However, following this brief period of approximately 3 weeks, a marked decrease in gas production and COD and TOC reduction was evident. It should be noted here that almost all of the observed reduction in COD and TOC during this period was due to adsorption onto the activated carbon surface.

Phase 2 - Because of the apparent slow acclimation of the process to the degradation of AFFF, it was decided to accelerate the acclimation process

TABLE I. Concentration of Nutrients in Buffer Solution

Compound	Concentration (mg/l)
$FeCl_3 \cdot H_2O$	4.83
$MnCl_2 \cdot 4H_2O$	0.71
$Zn\ Cl_2$	0.49
$CoCl_2 \cdot 6H_2O$	0.43
$Na_2B_4O_7 \cdot 10H_2O$	0.17
$Na_3C_6H_5O_7$ (sodium citrate)	26.33
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.31
KH_2PO_4	60.98
$NaH_2PO_4 \cdot H_2O$	37.09
$(NH_4)_2SO_4$	23.66
NH_4Cl	112.00
$CaCl_2 \cdot 2H_2O$	26.55
$MgCl_2 \cdot 6H_2O$	36.42
Vitamin Extract*	0.16 ml

*The Vitamin Extract was prepared by adding 10 grams of a multivitamin to 333 ml of 95% ethanol and 667 ml of distilled water. The solution was allowed to stir for 10-12 hours at 60°C, settled for 24 hours and decanted. The decanted solution was the vitamin extract.

TABLE II. Operating Conditions for Two-Stage Anaerobic Filter

Phase No.	Duration (days)	Empty Bed Contact Time (hours)	Flow Rate (ml/min)	Influent TOC Total (mg/l)	Influent TOC AFFF-TOC (mg/l)	Buffer Phosphate Content (m/l)	NH_4Cl Content (mg/l)
1	26	12/filter 24 total	20	1000	1000	-	153
2	24	24/filter 48 total	10	1133	333	0.1	306-1030
3	24	24/filter 48 total	10	733	333	0.06	611
4	12	24/filter 48 total	10	533	333	0.06	611-397
5	65 total 35 in operation	24/filter 48 total	10	867	667	0.06	680
6	13	24/filter 48 total	10	1200	1000	0.06	890
7	19	24/filter 48 total	10	1080	1000	0.03	840
8	Ongoing	24/filter 48 total	10	1000	1000	0.01	840

through the addition to the synthetic feed of 2000 mg/l of glucose. At the same time the TOC contribution of the AFFF was reduced to 333 mg/l. This resulted in a feed TOC of 1133 mg/l. It was felt that the addition of glucose will allow for the increase in the biomass strength within the filters and accelerate methane production. However, due to the readily degradable nature of the glucose, the pH in the effluent from the first anaerobic filter dropped to a value of around 5 thus warranting an increase in the buffer content of the dilution water from a value of 0.01 moles/l which prevailed in phase one to a new strength of 0.1 moles/l throughout the duration of this phase of the experiment. In addition, the ammonium chloride content of the buffer solution was increased to a value of 1.03 g/l in order to maintain a COD to nitrogen of 100:6. This ratio was maintained throughout the remainder of the study. The empty bed detention time in each of the two anaerobic filters was also increased to 24 hours for the remainder of the study in order to allow for more degradation to occur. Details of the operating conditions throughout this study are given in Table II.

A marked increase in growth was noticed following the increase in the NH_4Cl content of the feed. This is also obvious from Figure 2 and 3 where on day 31 of continuous operation gas production became evident at a daily rate of 1.03ℓ of methane from the first column and 0.47ℓ of methane from the second column. The total methane production rate from the treatment system which amounted to 1.5ℓ/day corresponds to an oxygen equivalent of 298 mg of COD per liter of feed solution. The feed COD during this phase of the experiment averaged at 2200 mg/l thus resulting in a production of methane gas equivalent to 13.6% of the feed substrate.

The reduction in COD across the treatment system was around 28% (see Figure 4) during this phase of the experiment which indicates that 14.4% of the COD fed into the system was either adsorbed onto the activated

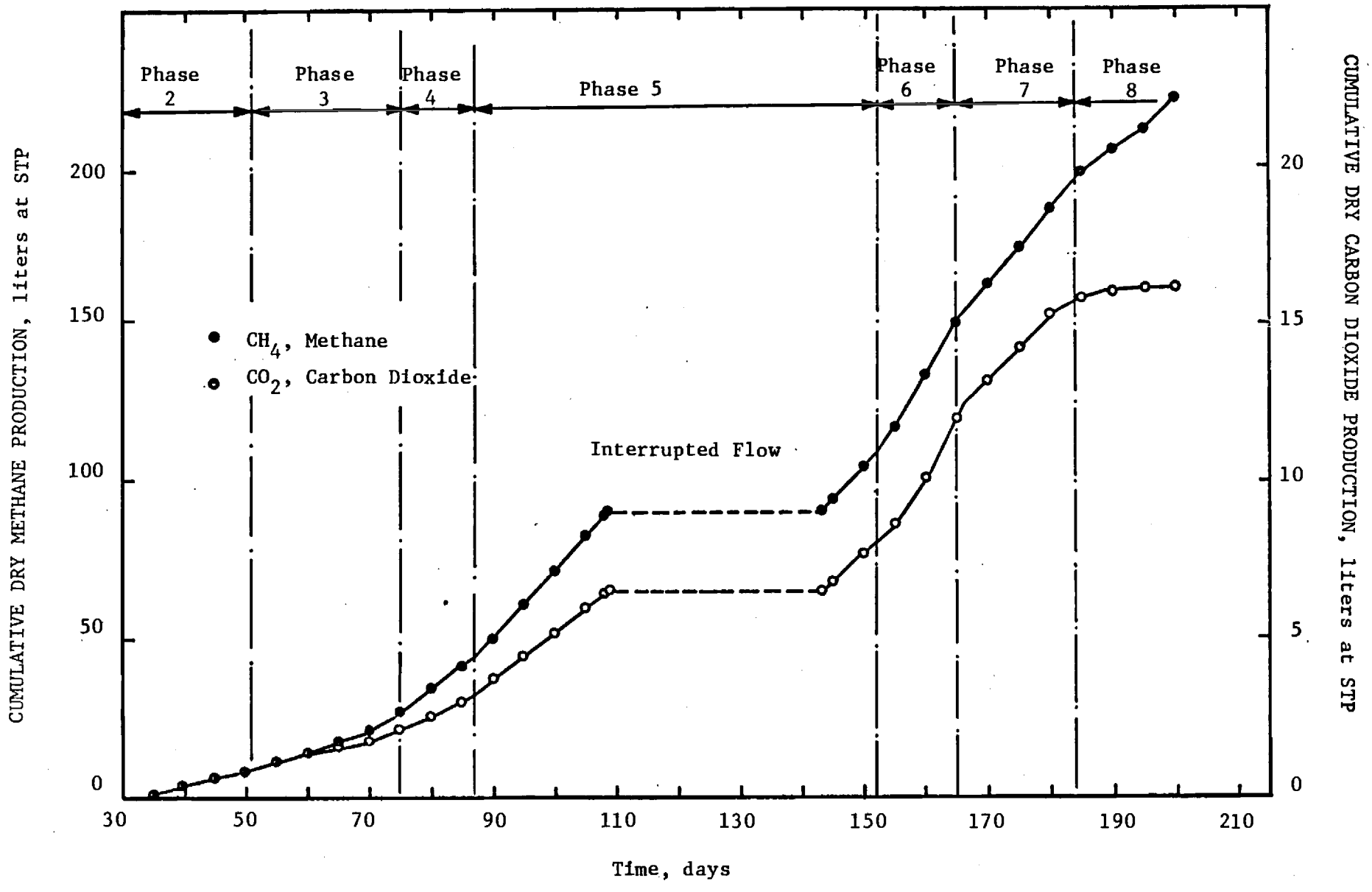

Figure 2. Methane adn Carbon Dioxide Production from the Second Stage Anaerobic Filter

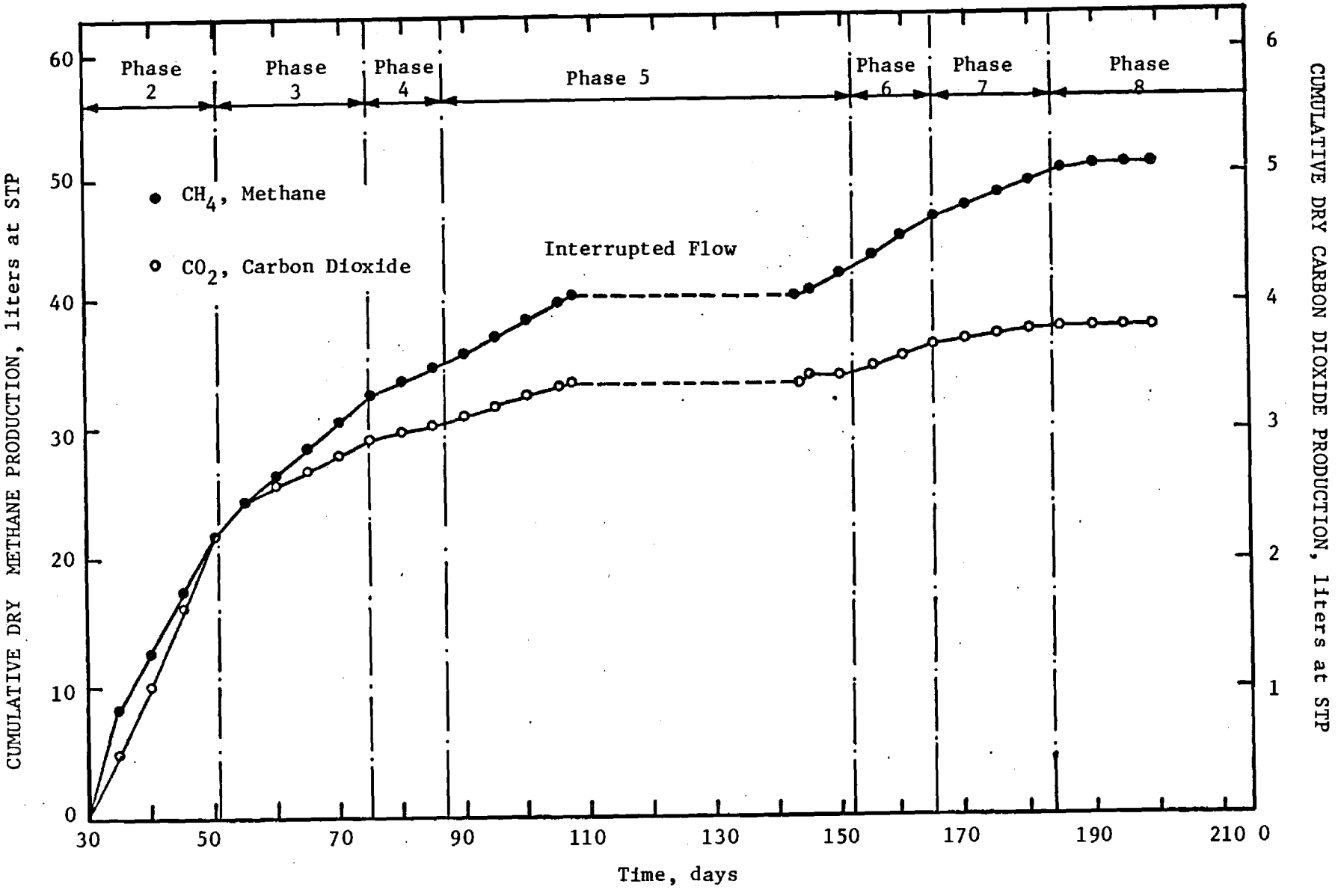

Figure 3. Methane and Carbon Dioxide Production from the First Stage Anaerobic Filter

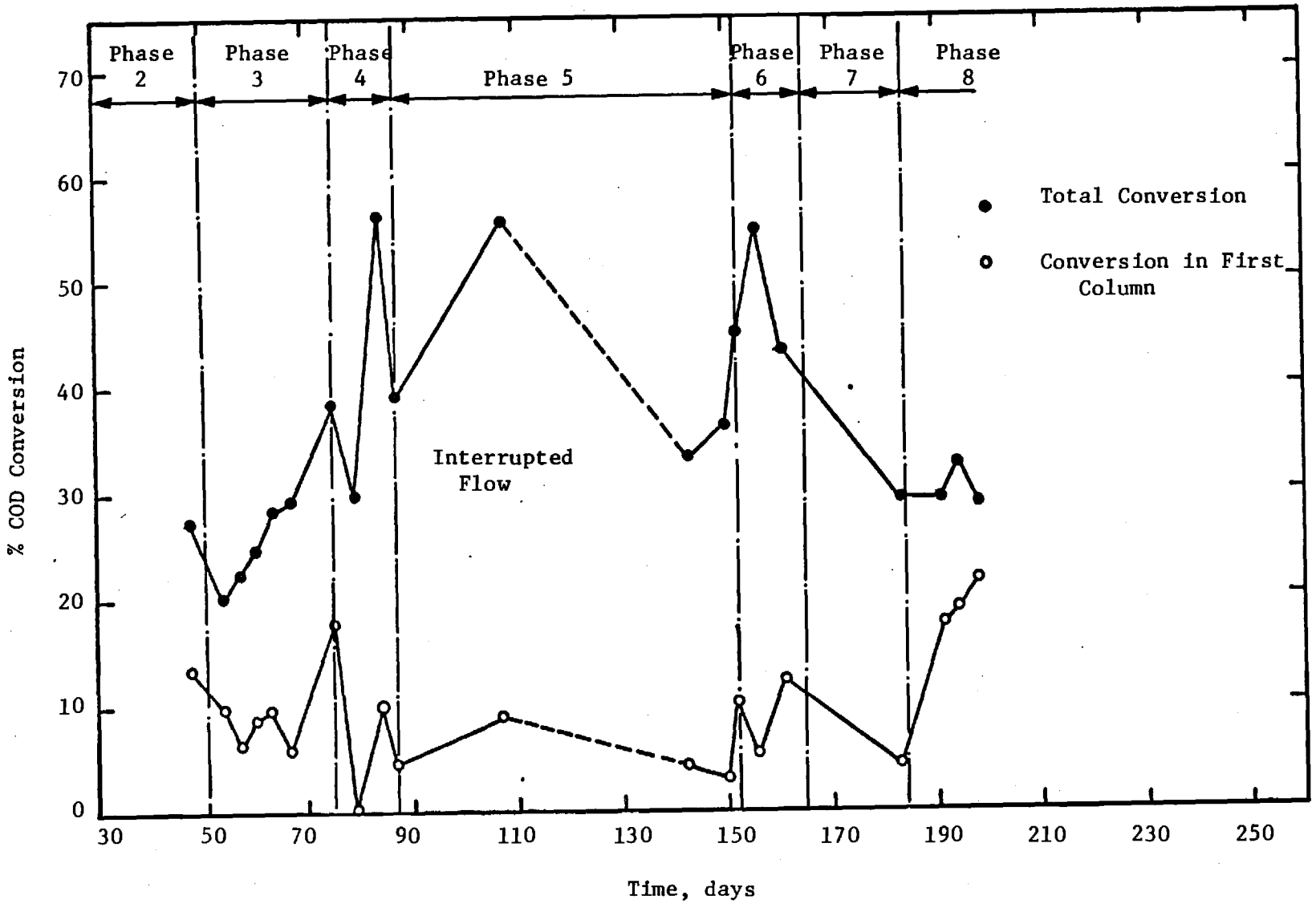

Figure 4. Chemical Oxygen Demand Conversion in Two Stage Anaeorbic Filter

carbon or converted to biomass. A 23% reduction in TOC was also recorded during this phase of the experiment (see Figure 5). The methane equivalent of the 2000 mg/l of glucose that was added translates to a maximum methane production rate of 10.8ℓ/day at STP. Consequently, only acclimation and not full glucose degradation was the objective of this phase of the experiment. Of interest, it is important to note that since methane production was observed from both columns, the reportedly sensitive methanogens were not inhibited by the constituents present in the AFFF concentrate.

Phases 3 and 4 - The acclimation protocol that was pursued from this point on was to gradually decrease the glucose in the feed from 2000 mg/l to 1000 mg/l and then to 500 mg/l while maintaining the AFFF TOC contribution in the feed at 333 mg/l. The objective of this reduction in the feed glucose concentration was to allow the microbial cultures in the anaerobic filters to be gradually exposed to AFFF as the predominant carbon source.

The decrease in the feed glucose concentration from 2000 down to 1000 mg/l resulted in an immediate reduction in the gas production from the first column (see Figure 2). Methane production from the first column during Phase 3 averaged at 0.40ℓ/day down from the previous production level of 1.03ℓ/day during Phase 2. Methane gas production from the second column, however, increased slightly over the production rate observed during Phase to a new level of 0.74ℓ/day. Inspite of the limited data, it may be inferred from these results that the reduction in the glucose substrate resulted in more inhibition to gas production due to the presence of AFFF in the first column where activated carbon adsorption was not available.

During the third phase of the experiment the first column resulted in average reductions in COD and TOC of 7.5% and 17%, respectively, while the reduction in these parameters throughout the system averaged at 28% and 43%, respectively.

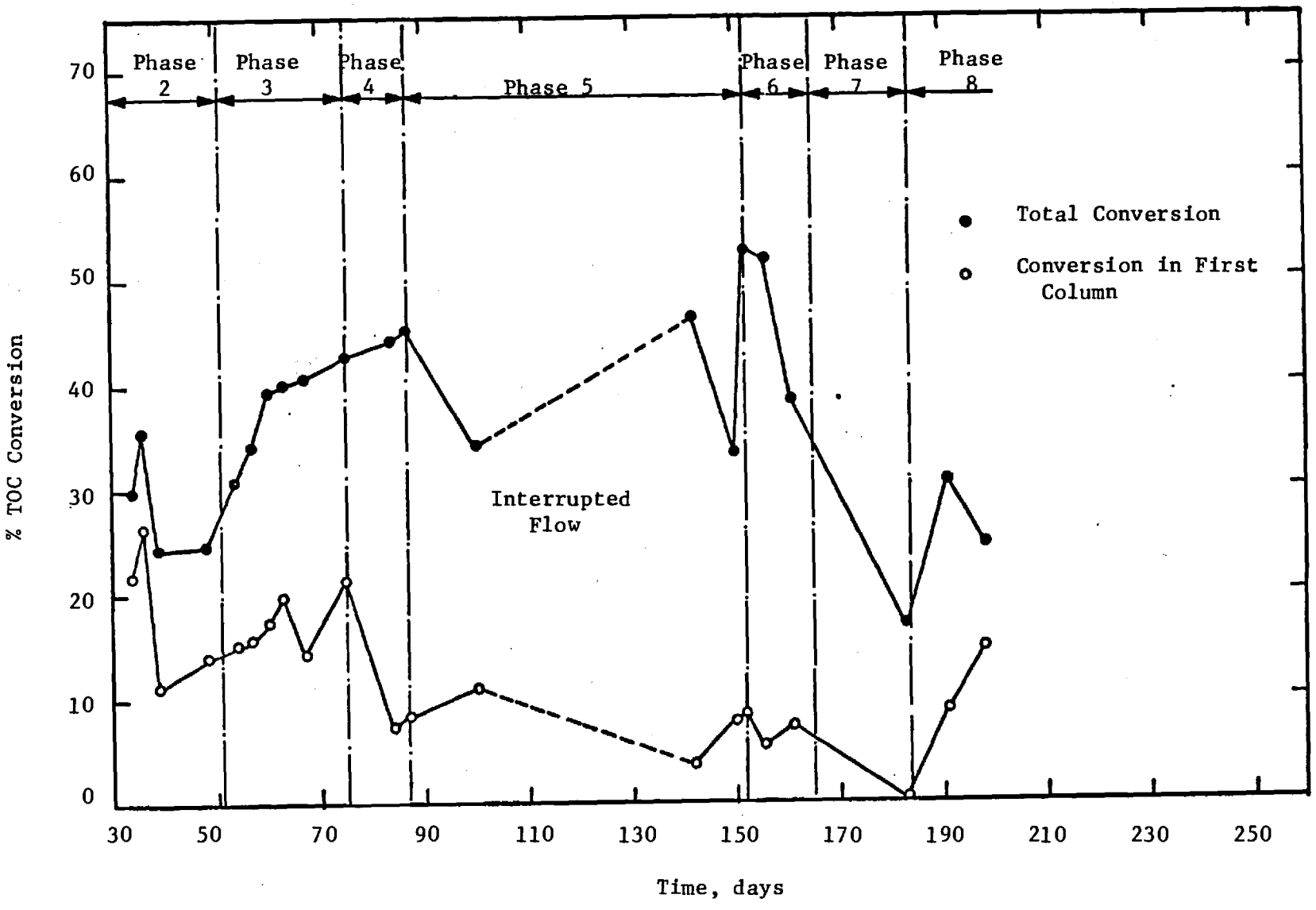

Figure 5. Total Organic Carbon Conversion in Two-Stage Anaerobic Filter

The response of the treatment system to a further reduction in the glucose content of the feed down to 500 mg/l was exhibited by a further decrease in methane production from the first column and an increase in the production of methane from the second column. Methane production from the first column during the fourth phase averaged at 0.21ℓ/day while the rate of formation of methane from the second column averaged around 1.46ℓ/day for the same period. This results in a total methane production rate of 1.67 ℓ/day which corresponds to glucose equivalent of 4.46 grams/day or 310 mg/l of feed substrate. The average COD and TOC conversions across the treatment system attained during phase 4 were 41.7% and 44.5%, respectively.

Phases 5 and 6 - During these phases of the acclimation stage of this experiment the contribution of AFFF to the feed TOC was successively raised to 667 mg/l during phase 5 and later to 1000 mg/l during phase 6 while the concentration of glucose in the synthetic substrate was maintained at 500 mg/l. After 13 days of continuous operation into phase 5, the seal on the centrifugal recirculation pump of the anaerobic-activated carbon filter broke and the whole system was shut down for a period of 30 days. After this shutdown period pumping resumed and the response of the system, as depicted from the gas production data in Figures 2 and 3, was identical to that observed prior to breakdown. During the period of shutdown, the second column was exposed to a severe oxygen contamination and apparently this contamination did not retard gas production as measured after resumption of operations thus indicating the anaerobic-activated carbon filter to be a very resistant system to shock effects both in terms of absence of nutrients and exposure to oxygen for a period of 30 days.

The response of the first column to an increase in AFFF in the feed was a slight increase in gas production from a previous level of 0.21ℓ/day during phase 4 to a new level of 0.26ℓ/day of methane. Gas production from the

second column, on the other hand, increased more markedly from a previous level of 1.46ℓ/day of methane. The net methane production from the system which averaged at 2.44ℓ/day at STP during phase 5 corresponds to 6.52 g of glucose per day while the total glucose fed to the system was 7.2 g/day. Consequently, the increased methane production may be attributed partly to increased glucose degradation or a partial degradation of some of the organic constituents of AFFF.

During phase 6 of the experiment both anaerobic columns responded to a further increase in AFFF in the feed by immediate increases in the methane production rate. Methane production from the first column averaged at 0.31ℓ/day while the second column contributed a daily production of that gas of 3.4ℓ. Thus the net methane production rate from the system increased to 3.71ℓ/day which corresponds to 9.91 g of glucose per day. Since the methane production rate from the system exceeded that rate that may be anticipated if all the feed glucose was converted to methane, it may be concluded that the anaerobic filter was actually degrading some of the organic constituents of AFFF.

Phase 7 - During the seventh phase of this experiment which lasted for a period of 19 days, the glucose content in the feed substrate was decreased to 200 mg/l while the TOC contribution of the AFFF constituents was maintained at 1000 mg/l. The immediate response of the system was a decrease in gas production from both anaerobic filters. Methane production from the first stage filter averaged at 0.2ℓ/day which the production rate of methane from the second column was 2.37ℓ/day. The net gas production of 2.57ℓ/day corresponds to 6.86 g of glucose per day which is appreciably greater than the 2.88 g of glucose fed to the system daily thus indicating an appreciable increase in the degradation of some of the organic constituents of AFFF.

Phase 8 - During the last phase of the experiment the glucose content of the feed substrate was eliminated thus reducing the organic carbon content of the feed to 1000 mg/l of TOC totally attributed to AFFF. Methane production was observed to decrease from both anaerobic filters as a result of the elimination of glucose from the feed. However, after 7 days of operation methane production started increasing until it reached a present level of 2.0 /day from the second column. No gas production is currently observed from the first column.

The two-stage anaerobic filter system will continue to be fed AFFF at a level of 1000 mg/l of TOC until steady state conditions are attained. It is anticipated that after the acclimation period, both gas production and COD and TOC reduction will continue to increase until an acceptable limit of both is attained.

Future Work

Four more two-stage anaerobic filter systems are currently in the final phase of construction. These units will be acclimated in a manner similar to the one used in the first column system and then operated at two feed TOC levels of AFFF using two Aqueous Film Foam Forming agents.

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EW-A62 Cross

ANAEROBIC-ACTIVATED CARBON FILTER FOR THE TREATMENT OF AQUEOUS FILM FORMING FOAM (AFFF) WASTEWATER

Period covered: Mar '80

QUARTERLY PROGRESS REPORT
April, 1980

by

Makram T. Suidan, Edward S. K. Chian
and
Wendall H. Cross

Supported by

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For the purposes of the present research, five two-stage anaerobic filter treatment systems were constructed. The first column of one unit was packed with Raschig rings while all other columns were packed with granular activated carbon. The granular activated carbon packed columns are fluidized by effluent recycle and the use of activated carbon is believed to result in concentration polarization and toxicity reduction in addition to providing a microbial attachment surface.

Experimental Apparatus

Two types of experimental systems were employed in this study. One anaerobic filter system was constructed with Raschig rings serving as a contact medium in the first column while the second column which was equipped with effluent recycle was packed with granular activated carbon (Figure 1). Four additional units were constructed in a similar manner, however, in this instance both columns of every reactor system were equipped with effluent recycle and both were packed with granular activated carbon (Figure 2.).

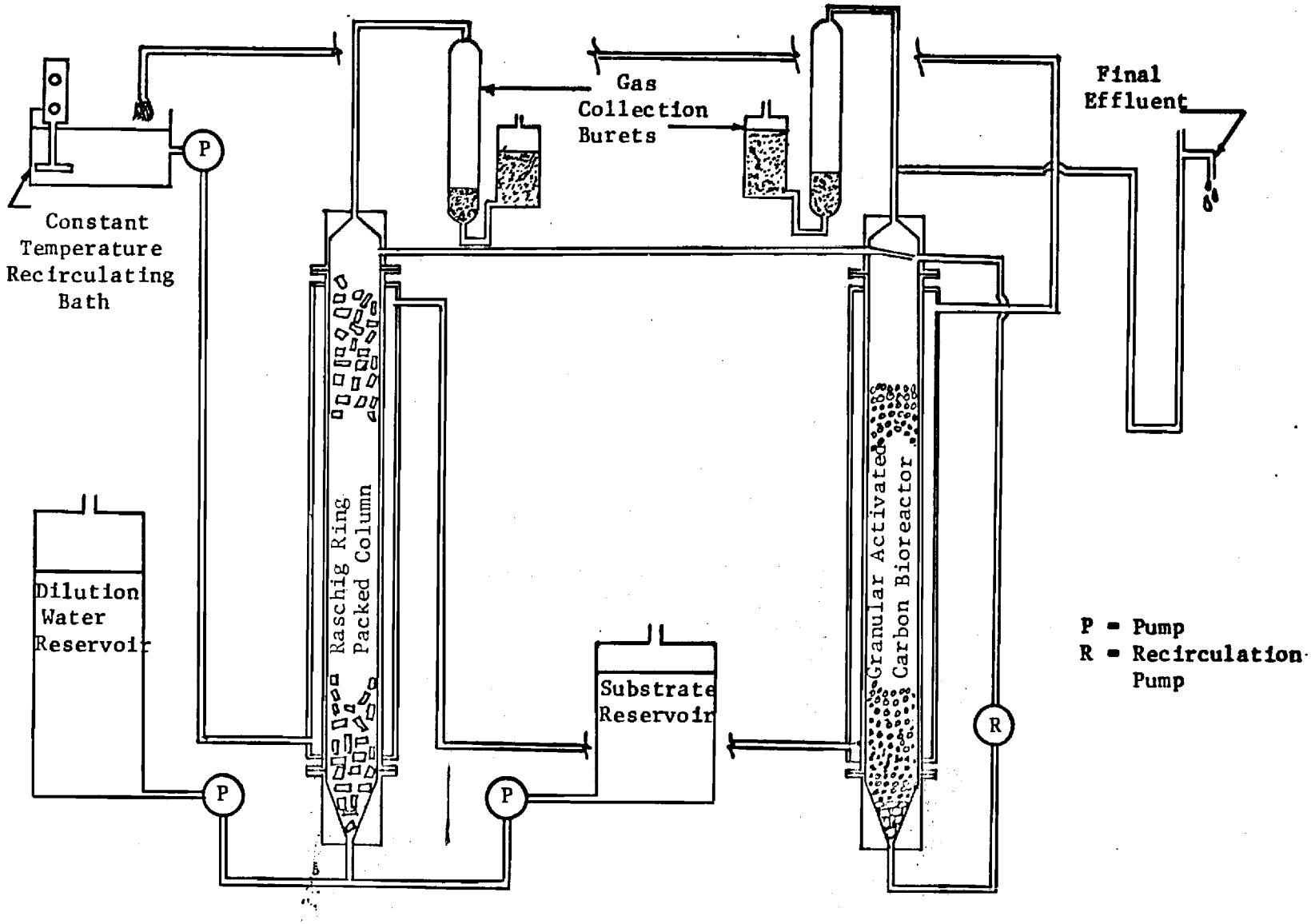

Figure 1. Schemetic Diagram of Raschig Ring - Granular Activated Carbon Packed Two-Stage Anaerobic Bioreactor

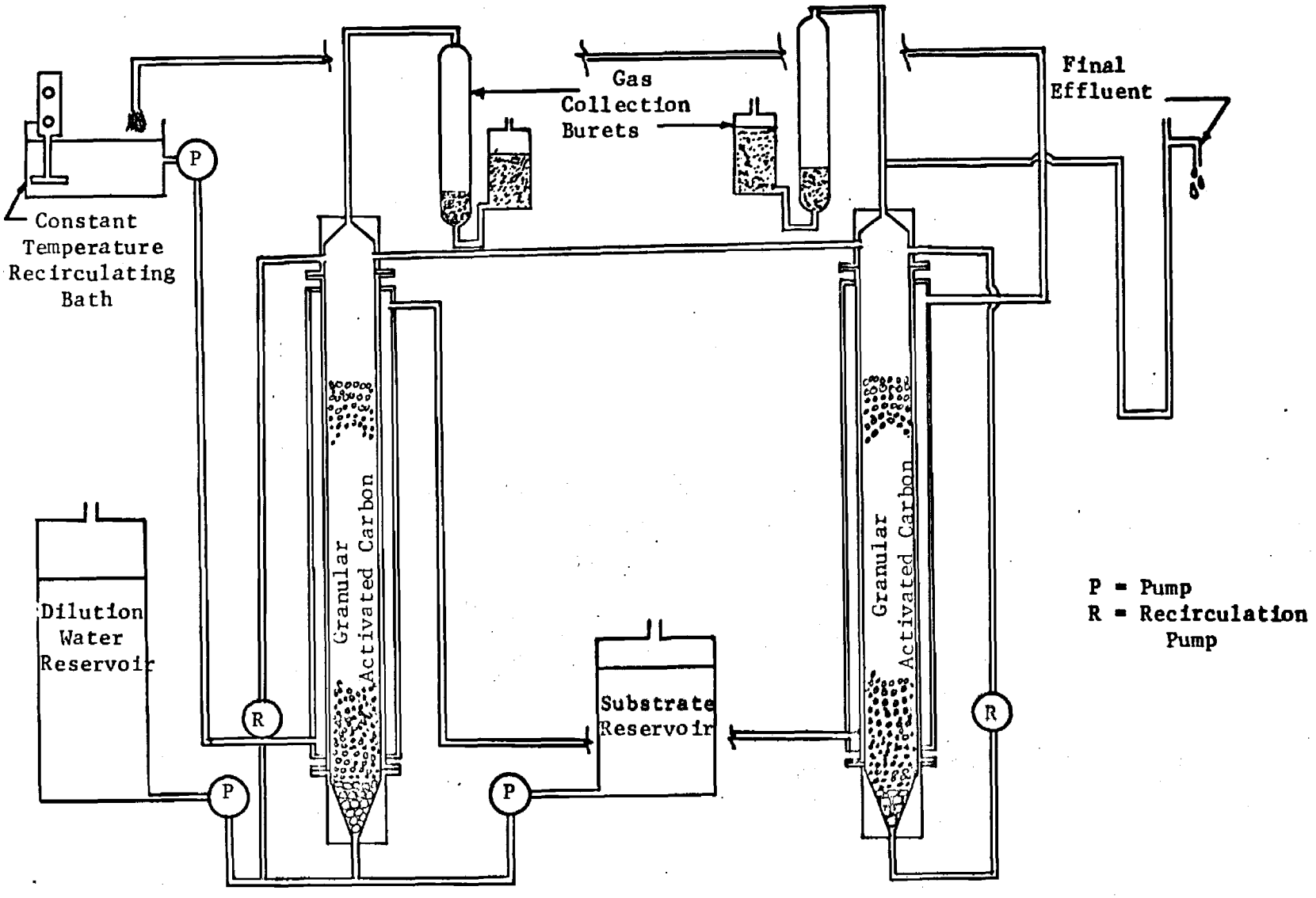

Figure 2. Schematic Diagram of Fluidized Granular Activated Carbon Packed Two Stage Anaerobic Bioreactor

Feed Pumps. The AFFF is diluted with distilled water to any desired concentration in a 20-ℓ concentrate reservoir (Figures 1 & 2). This diluted substrate is fed into the reactor feed using a positive displacement FMI pump, Model RP G-20 (Fluid Metering Incorporated, Oyster Bay, N.Y.) having a maximum flow rate of 5.4 ml/min and a maximum operating pressure of 50 psi. No other nutrients are added to this reservoir in order to prevent any biodegradation within the reservoir and the feed lines.

Dilution water containing the phosphate buffer and ammonium nutrients necessary for active biodegradation are pumped from another 55-ℓ reservoir using a positive displacement pump Model RP G150 (Fluid Metering Incorporated, Oyster Bay, N.Y.). This pump has a maximum flow rate setting of 96 ml/min and a maximum operating pressure of 20 psi. The flow from the two reservoirs is mixed in a tee connection prior to entry into the first-stage anaerobic filter.

Raschig Ring Packed Anaerobic Filter. This filter consists of a water jacketed plexiglas column having the following features:

i. inner column (10.1 cm in internal diameter by 182 cm long) which will serve as the actual roughing anaerobic filter chamber.

ii. a water jacket (15.25 cm in internal diameter by 170 cm long) to allow the unit to be operated at a constant and controllable temperature through the circulation of water from a constant temperature bath (Model T31, HAAKE, Inc., Werk Karlsruhe, West Germany) through the jacket.

iii. influent header is constructed using a plexiglas column section and plates and its inner structure, which is 20-cm long, is tapered into an inverted conical shape in order to allow for better distribution of the influent flow. This unit is equipped with a perforated plate to allow for the introduction of the mixed feed solution.

iv. effluent structure: a conical shaped structure used to minimize the trapped gas volume and is equipped with fittings for connection to the gas collection system, connection to the effluent structure from this unit and a sampling port.

v. gas collection system consisting of two 4.5-ℓ gas burets, two leveling bottles and sampling ports to allow for monitoring of both the quantity and composition of the gaseous products produced and for the release of the excess gas produced.

Granular Activated Carbon Packed Filters. This unit is identical in structure to the roughing unit except that it is equipped with a 1/3 HP centrifugal pump in the operating unit and a 1/2 HP centrifugal pump in the new four units (Teel Pump, Dayton Electric Manufacturing Company, Chicago, Ill.). The purpose of this pump is to recirculate the aqueous contents of the carbon filled filter and maintain this carbon fluidized in order to minimize gas trapping onto the carbon. Details of the recirculation system are presented in Figure 3.

Filter Packings and Start Up of the Currently Operating System

The roughing anaerobic filter was packed with 1.27 cm (0.5 inch) raschig rings to a depth of 193 cm (6.33 ft). The packed column has a porosity of 58.33 percent and a specific surface area of 337.18 m^2/m^3 (102.65 ft^2/ft^3). Because of its relatively high porosity and surface area, this packing is ideal for the roughing filter where a high growth rate and sludge accumulation are anticipated.

The anaerobic activated carbon filter was packed in an identical manner in a depth of 128 cm (4.20 ft) and backwashed down to a depth of 100 cm (3.28 ft) in order to eliminate carbon fines. The activated carbon used in

this study is Calgon FMC 6 x 16 U.S. Mesh Size with an average particle size of 2.27 mm. However, after backwashing, a larger average particle size was retained in the filter. The new filter columns were each packed with 2.5 Kg of Calgon FMC 6 x 16 U.S. Mesh Size granular activated carbon and backwashed to a depth of 115 cm.

All columns were seeded with an anaerobic sludge obtained from the underflow of an anaerobic digester at the Atlanta Clayton Sewage Treatment Plant.

The dilution water reservoir is filled to capacity with dechlorinated and deaerated tap water to which nutrients and a phosphate buffer are added. In addition to serving as a nutrient, the phosphate mixture is designed to provide a buffer to the waste at the desired operating pH. The levels of addition of the phosphate, ammonium and other nutrients is higher than what is estimated to be needed for the successful operation of the system. The concentration of the various nutrients in the dilution water reservoir are given in Table I. The flow rate of the dilution water was set at 9.00 ml/min while the concentrate flow rate was set at 1.0 ml/min such that the feed concentration to the first column will be only 10 percent of the stock concentrate. The selection of the operating concentrations will be discussed later. The flow rate of 10 ml/min is selected in order to provide an empty bed contact time of 24 hours in each of the reactors.

The recirculation flow rate on the anaerobic granular activated carbon packed filters is adjustable through the control of the bypass flow (Figure 3). This rate can be varied in order to determine the minimum recirculation flow rate that would allow for economic and efficient operation of the system.

TABLE I. Concentration of Nutrients in Buffer Solution

Compound	Concentration (mg/l)
$FeCl_3 \cdot H_2O$	4.83
$MnCl_2 \cdot 4H_2O$	0.71
$Zn\ Cl_2$	0.49
$CoCl_2 \cdot 6H_2O$	0.43
$Na_2B_4O_7 \cdot 10H_2O$	0.17
$Na_3C_6H_5O_7$ (sodium citrate)	26.33
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.31
KH_2PO_4	60.98
$NaH_2PO_4 \cdot H_2O$	37.09
$(NH_4)_2SO_4$	23.66
NH_4Cl	112.00
$CaCl_2 \cdot 2H_2O$	26.55
$MgCl_2 \cdot 6H_2O$	36.42
Vitamin Extract*	0.16 ml

*The Vitamin Extract was prepared by adding 10 grams of a multivitamin to 333 ml of 95% ethanol and 667 ml of distilled water. The solution was allowed to stir for 10-12 hours at 60°C, settled for 24 hours and decanted. The decanted solution was the vitamin extract.

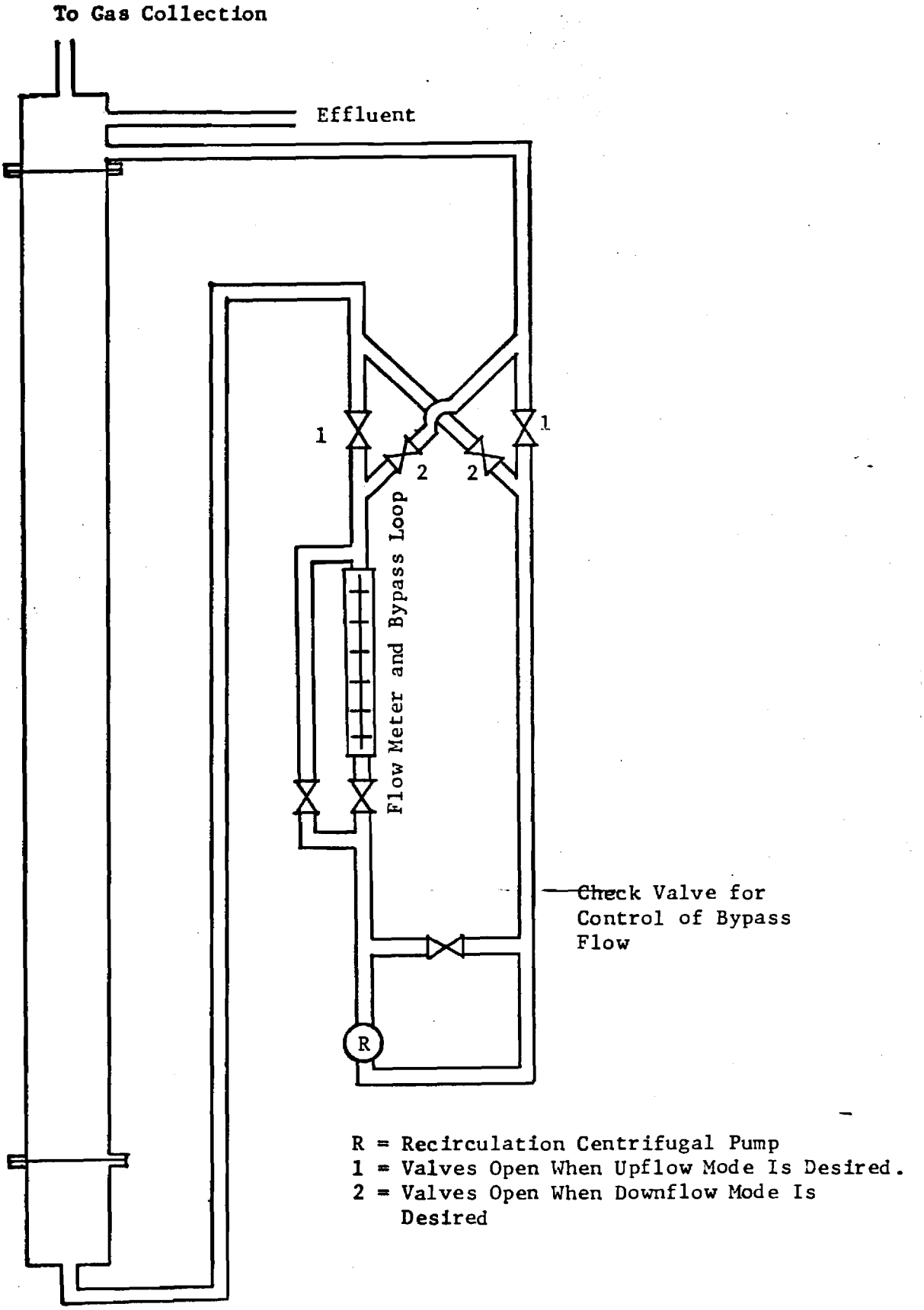

Figure 3. Schematic of Effluent Recirculation System

At the time of preparation of this report, the two-stage raschig ring and granular activated carbon packed anaerobic filter system is operating on a feed substrate containing the AFFF Ansul at a strength of 1000 mg/l of TOC in the feed. Two of the remaining 4 systems are presently in the first stage of acclimation to AFFF Ansul feed TOC strengths of 333 and 2000 mg/l, respectively while the remaining two systems are being acclimated to AFFF FC-780 feed TOC strengths of 333 and 2000 mg/l, respectively.

Synthetic Feed Substrate

The synthetic feed substrate to the currently operating two-stage anaerobic filter was prepared in two separate solutions. The AFFF Ansul was selected as the first AFFF concentrate to be studied. A solution of AFFF and distilled water was prepared in 20ℓ batches and fed to the anaerobic filter.

A dilution water solution was also fed to the columns from a separate 55ℓ reservoir. In addition to serving as a dilution water, this solution also contained biological nutrients, ammonium chloride and a phosphate buffer. The concentration of the constituents of the growth nutrients in the dilution reservoir was maintained at the levels indicated in Table I. In addition to these nutrients, additional ammonium chloride and a phosphate buffer were added and their strengths are presented with the operating data in Table II.

Analytical Methods

Samples collected from the two feed reservoirs (dilution buffer and concentrate reservoirs) and the respective two column effluents were analyzed according to the procedures in Standard Methods for the Examination of Water and Wastewater, 14th Edition, 1975, with the exception of the following analyses: (a) gas analyses were performed on a Fisher Model 25v Gas Partitioner using certified calibration standards (Matheson, East Rutherford, N.J.); and

(b) glycol analysis was performed on a Perkin Elmer Sigma I Gas Chromatograph. The column used was a 6 ft. long 2 mm I.D. glass column packed with 10% Carbowax 20 M on 80/100 Chromasorb W. Chromatographic conditions were: injection temperature 250°C, injection volume 1 microliter, detector temperature 300°C, oven temperature 160°C isothermal for five minutes followed by a temperature program which raised the temperature to 200°C at a rate of 10°C/min. Temperature was held at 200°C for 3 minutes resulting in a total run time of 12 minutes. A hydrogen flow rate of 30 ml/min, 240 ml/min of air and 30 ml/min of a helium carrier gas were employed.

Anaerobic Filter Acclimation

Phase 1 - After the two anaerobic filter columns were seeded, the AFFF concentrate was set at 10,000 mg/l TOC and it was pumped into the first anaerobic filter at a flow rate of 2.06 ml/min. The dilution buffer and nutrient solution was pumped at a flow rate of 18.55 ml/min, thus resulting in a feed TOC of 1000 mg/l. At the specified flow rates, an empty bed contact time of 12 hours was provided in each filter. Initially, significant gas production and COD and TOC reductions were observed. However, following this brief period of approximately 3 weeks, a marked decrease in gas production and COD and TOC reduction was evident. It should be noted here that almost all of the observed reduction COD and TOC during this period was due to adsorption onto the activated carbon surface.

Phase 2 - Because of the apparent slow acclimation of the process to the degradation of AFFF, it was decided to accelerate the acclimation process through the addition to the synthetic feed of 2000 mg/l of glucose. At the same time the TOC contribution of the AFFF was reduced to 333 mg/l. This resulted in a feed TOC of 1133 mg/l. It was felt that the addition of glucose will allow for the increase in the biomass strength within the filters and accelerate methane production. However, due to the readily

degradable nature of the glucose, the pH in the effluent from the first anaerobic filter dropped to a value of around 5 thus warranting an increase in the buffer content of the dilution water from a value of 0.01 moles/l which prevailed during phase one to a new strength of 0.1 moles/l which was maintained throughout the duration of this phase of the experiment. In addition, the ammonium chloride content of the buffer solution was increased to a value of 1.03 g/l in order to maintain a COD to nitrogen of 100:6. This ratio was maintained throughout the remainder of the study. The empty bed detention time in each of the two anaerobic filters was also increased to 24 hours for the remainder of the study in order to allow for more degradation to occur. Details of the operating conditions throughout this study are given in Table II.

A marked increase in growth was noticed following the increase in the NH_4Cl content of the feed. This is also obvious from Figures 4 and 5 where on day 31 of continuous operation gas production became evident at a daily rate of 1.03ℓ of methane from the first column and 0.47ℓ of methane from the second column. The total methane production rate from the treatment system which amounted to 1.5ℓ/day corresponds to an oxygen equivalent of 298 mg of COD per liter of feed solution. The feed COD during this phase of the experiment averaged at 2200 mg/l thus resulting in a production of methane gas equivalent to 13.6% of the feed substrate.

The reduction in COD across the treatment system was around 28% (see Figure 6) during this phase of the experiment which indicates that 14.4% of the COD fed into the system was either adsorbed onto the activated carbon to biomass. A 23% reduction in TOC was also recorded during this phase of the experiment (see Figure 7). The methane equivalent of the 2000 mg/l

TABLE II. Operating Conditions for Two-Stage Anaerobic Filter

Phase No.	Duration (days)	Empty Bed Contact Time (hours)	Flow Rate (ml/min)	Influent TOC Total (mg/l)	Influent TOC AFFF-TOC (mg/l)	Buffer Phosphate Content (m/l)	NH_4Cl Content (mg/l)
1	26	12/filter 24 total	20	1000	1000	-	153
2	24	24/filter 48 total	10	1133	333	0.1	306-1030
3	24	24/filter 48 total	10	733	333	0.06	611
4	12	24/filter 48 total	10	533	333	0.06	611-397
5	65 total 35 in operation	24/filter 48 total	10	867	667	0.06	680
6	13	24/filter 48 total	10	1200	1000	0.06	890
7	19	24/filter 48 total	10	1080	1000	0.03	840
8	Ongoing	24/filter 48 total	10	1000	1000	0.01	840

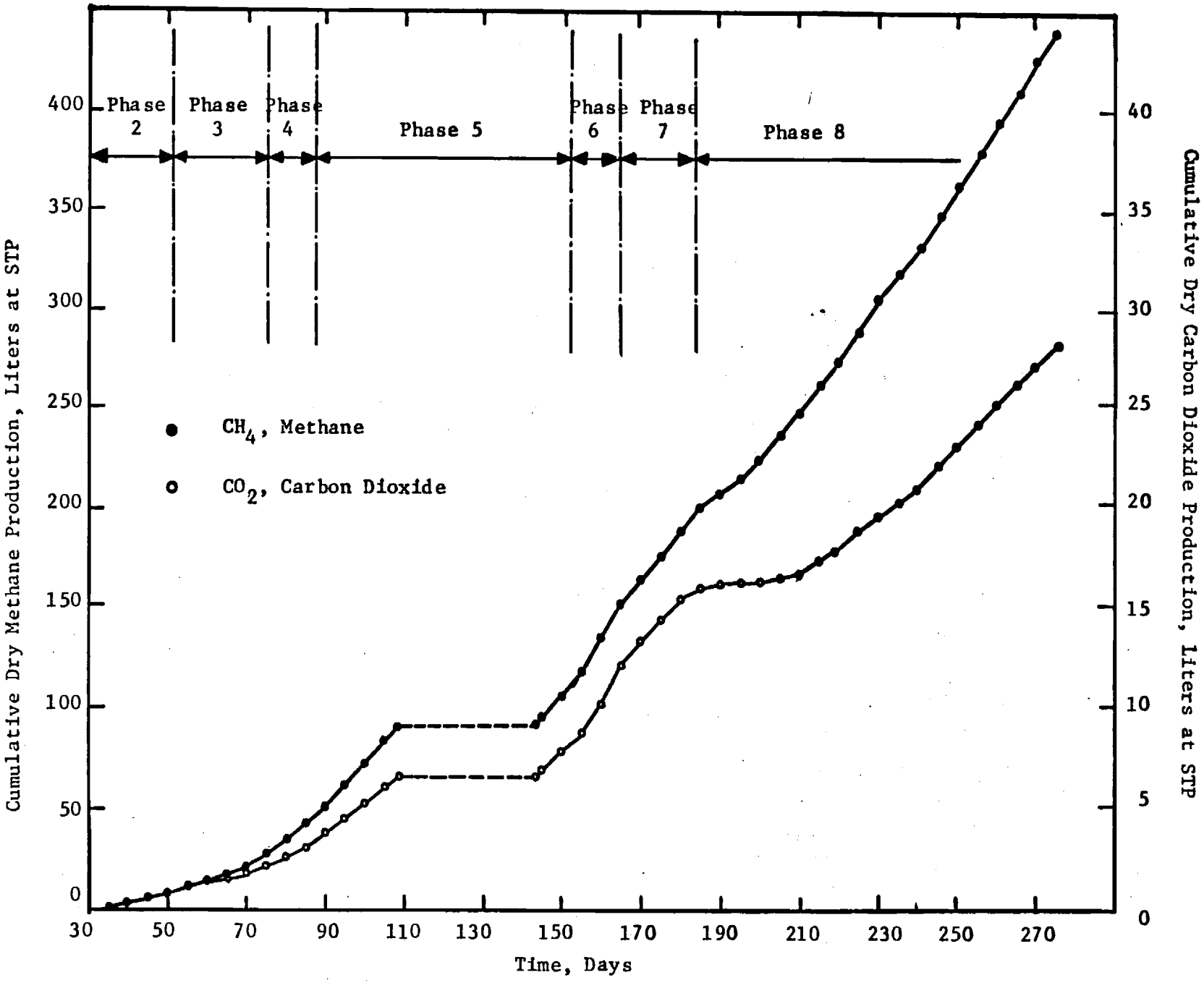

Figure 4. Methane and Carbon Dioxide Production from the Second-Stage Anaerobic Filter

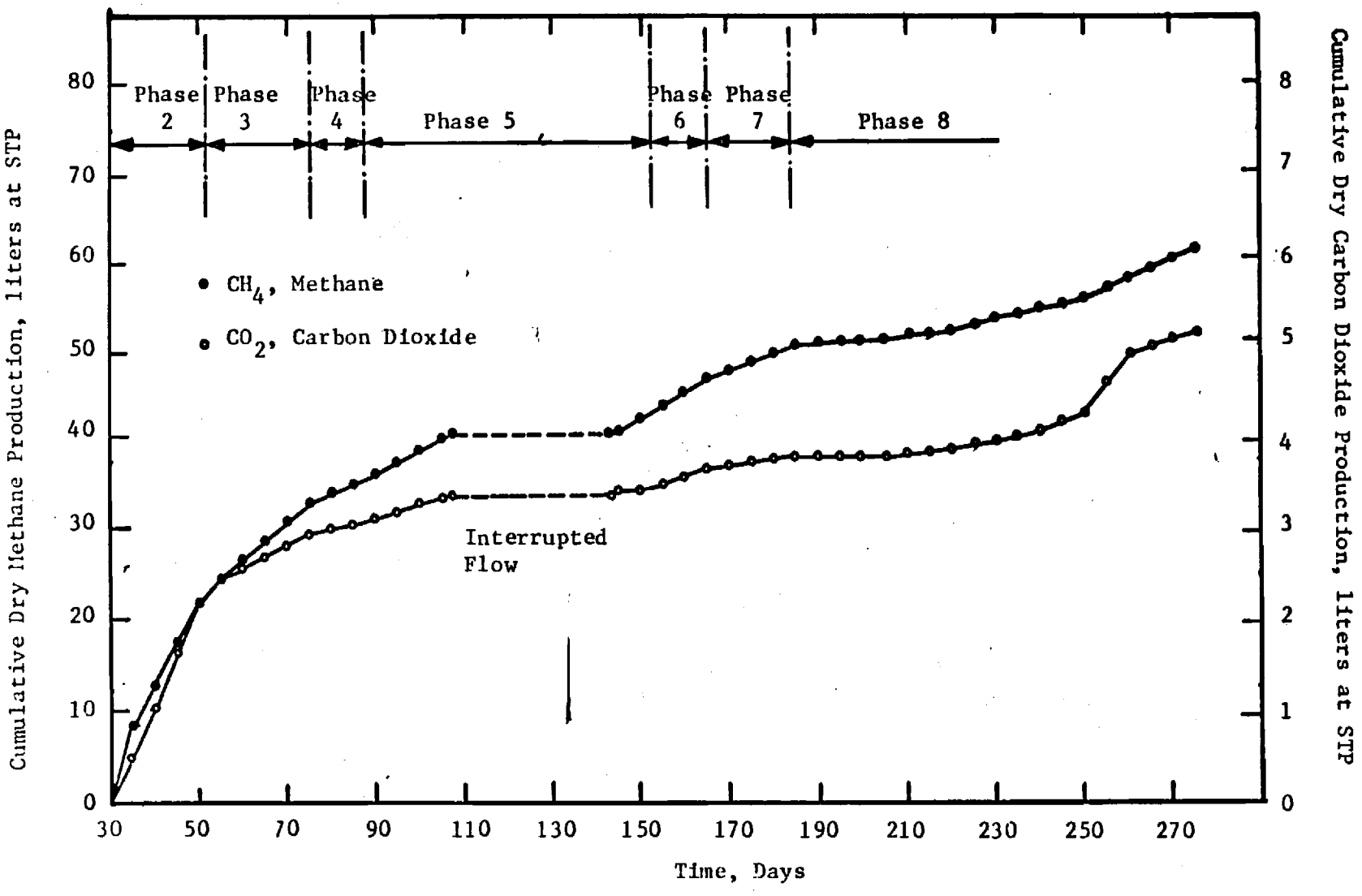

Figure 5. Methane and Carbon Dioxide Production from the First Stage Anaerobic Filter

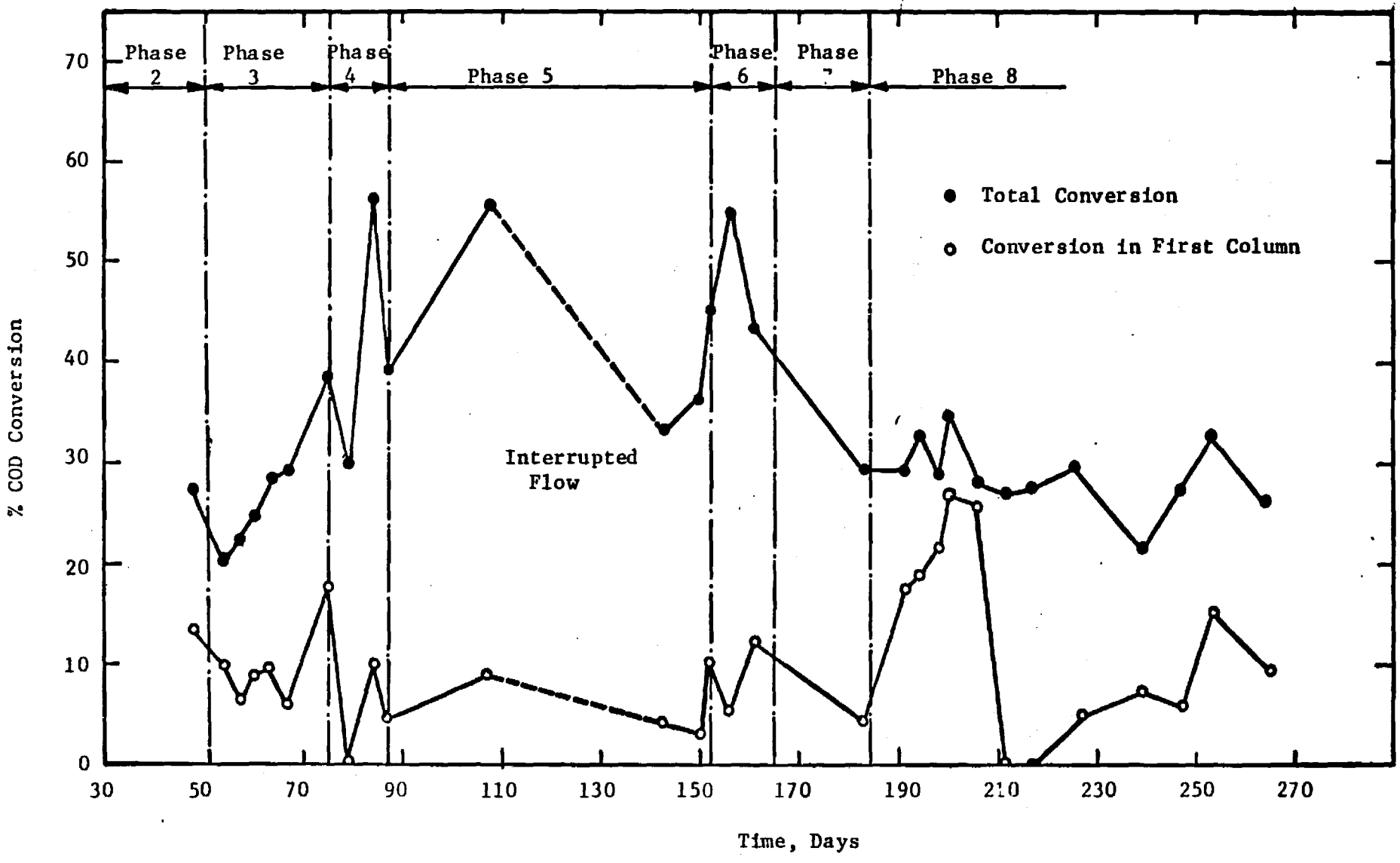

Figure 6. Chemical Oxygen Demand Conversion in Two-Stage Anaerobic Filter

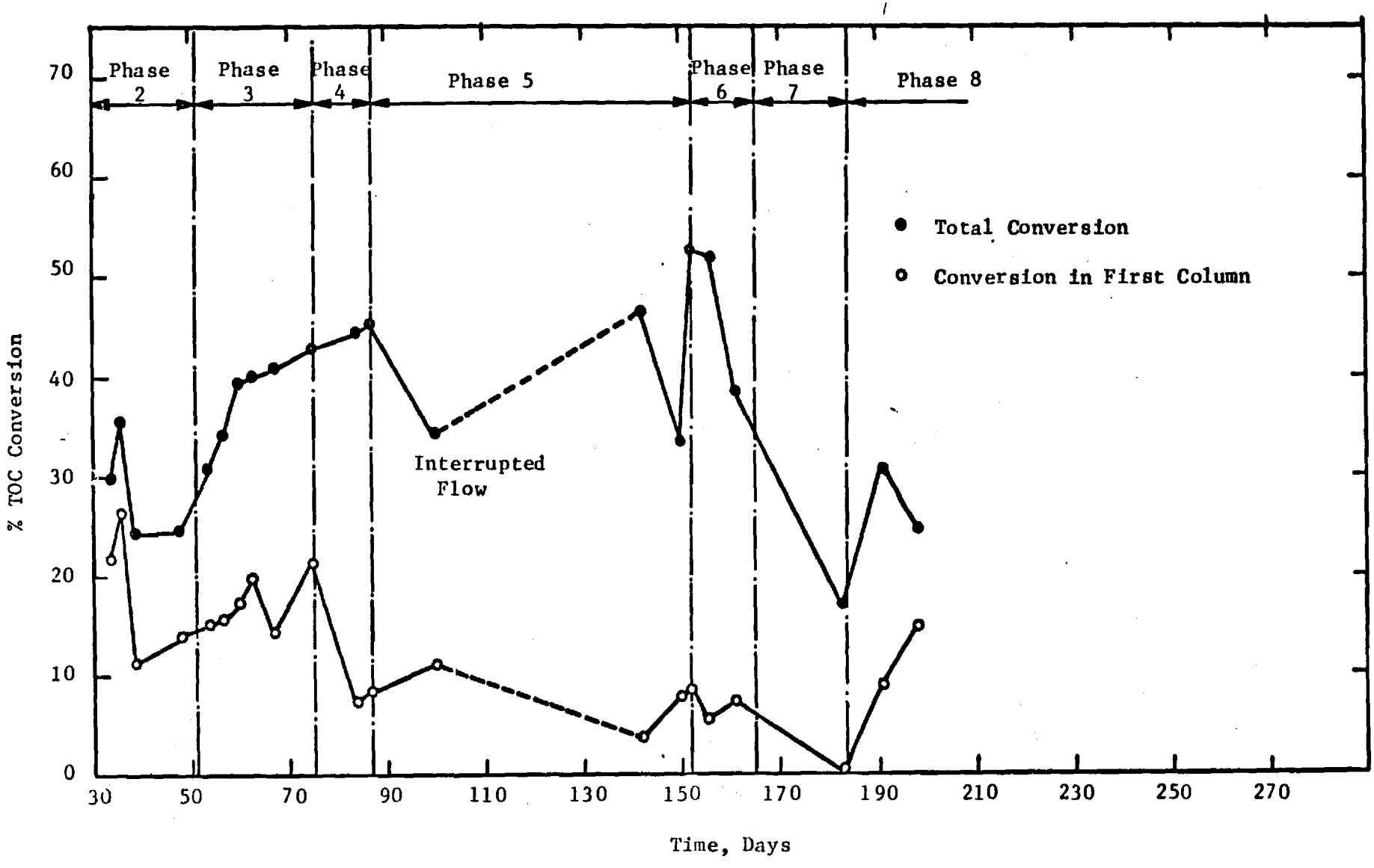

Figure 7. Total Organic Carbon Conversion in Two-Stage Anaerobic Filter

of glucose that was added translates to a maximum methane production rate of 10.8ℓ/day at STP. Consequently, only acclimation and not full glucose degradation was the objective of this phase of the experiment. Of interest, it is important to note that since methane production was observed from both columns, the reportedly sensitive methanogens were not inhibited by the constituents present in the AFFF concentrate.

Phases 3 and 4 - The acclimation protocol that was pursued from this point on was to gradually decrease the glucose in the feed from 2000 mg/l to 1000 mg/l and then to 500 mg/l while maintaining the AFFF TOC contribution in the feed at 333 mg/l. The objective of this reduction in the feed glucose concentration was to allow the microbial cultures in the anaerobic filters to be gradually exposed to AFFF as the predominant carbon source.

The decrease in the feed glucose concentration from 2000 down to 1000 mg/l resulted in an immediate reduction in the gas production from the first column (see Figure 4). Methane production from the first column during Phase 3 averaged at 0.40ℓ/day down from the previous production level of 1.03ℓ/day during phase 2. Methane gas production from the second column, however, increased slightly over the production rate observed during phase 2 to a new level of 0.74ℓ/day. Inspite of the limited data, it may be inferred from these results that the reduction in the glucose substrate resulted in more inhibition to gas production due to the presence of AFFF in the first column where activated carbon adsorption was not available.

During the third phase of the experiment the first column resulted in average reductions in COD and TOC of 7.5% and 17%, respectively, while the reduction in these parameters throughout the system averaged at 28% and 43%, respectively.

The response of the treatment system to a further reduction in the glucose content of the feed down to 500 mg/1 was exhibited by a further decrease in methane production from the first column and an increase in the production of methane from the second column. Methane production from the first column during the fourth phase averaged at 0.21ℓ/day while the rate of formation of methane from the second column averaged around 1.46ℓ/day for the same period. This results in a total methane production rate of 1.67ℓ/day which corresponds to glucose equivalent of 4.46 grams/day or 310 mg/1 of the feed substrate. The average COD and TOC conversions across the treatment system attained during phase 4 were 41.7% and 44.5%, respecitvely.

Gas chromatographic analysis for glycol in the AFFF Ansul according to the procedure outlined in the analytical emthods section resulted in one major peak at a retention time of 6.58 minutes. Two other peaks were also observed, however, they were considered negligible when compared to the major peak. The data in Figure 8 represent the concentration of glycol present in the feed and the effluents from the two columns. These data were reported as percent where a reference concentration of 100 percent glycol represents the glycol concentration present in a 1:100 dilution of the stock AFFF Ansul. During the third and fourth phases of the experiment, the relative strength of glycol present in the feed to the first column was set at 33.3 percent whereas the average concentration of glycol in the effluent from the first column was consistently around 10 percent. This indicates that a 70 percent reduction in glycol occurred in the first column during phases 3 and 4 thus raising the possibility that the glycol present in the feed was either partially reduced to volatile acids and subsequently methane and carbon dioxide or it was altered to another form that was not detected on the gas chromatogram. The concentration of glycol

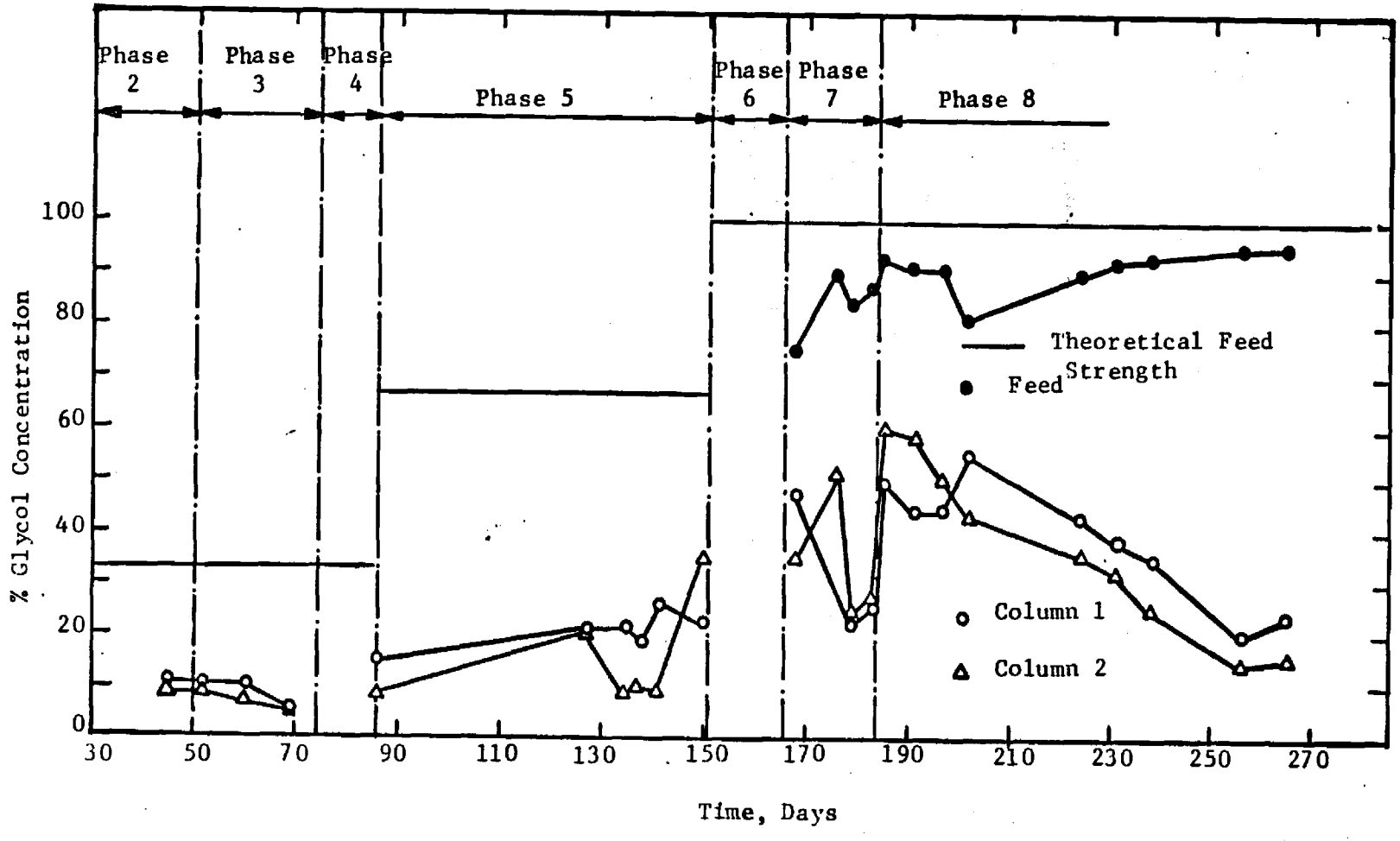

Figure 8. Glycol Concentration Across Treatment System

in the effluent from the second column varied from 9 percent on day 45 of continuous operation to 5 percent at the end of phase 4. This additional removal of glycol in the second column may be attributed to either additional biochemical conversion or to adsorption of the glycol onto the activated carbon surface.

Phases 5 and 6 - During these phases of the acclimation stage of this experiment the contribution of AFFF to the feed TOC was successively raised to 667 mg/l during phase 5 and later to 1000 mg/l during phase 6 while the concentration of glucose in the synthetic substrate was maintained at 500 mg/l. After 13 days of continuous operation into phase 5, the seal on the centrifugal recirculation pump of the anaerobic-activated carbon filter broke and the whole system was shut down for a period of 30 days. After this shutdown period pumping resumed and the response of the system, as depicted from the gas production data in Figures 4 and 5, was identical to that observed prior to breakdown. During the period of shutdown, the second column was exposed to a severe oxygen contamination and apparently this contamination did not retard gas production as measured after resumption of operations thus indicating the anaerobic-activated carbon filter to be a very resistant system to shock effects both in terms of absence of nutrients and exposure to oxygen for a period of 30 days.

The response of the first column to an increase in AFFF in the feed was a slight increase in gas production from a previous level of 0.21ℓ/day during phase 4 to a new level of 0.26ℓ/day of methane. Gas production from the second column, on the other hand, increased more markedly from a previous level of 1.46ℓ/day of methane. The net methane production from the system which averaged at 2.44ℓ/day at STP during phase 5 corresponds to 6.52 g of

glucose per day while the total glucose fed to the system was 7.2 g/day. Consequently, the increased methane production may be attributed partly to increased glucose degradation or a partial degradation of some of the organic constituents of AFFF.

During phase 6 of the experiment both anaerobic columns responded to a further increase in AFFF in the feed by immediate increases in the methane production rate. Methane production from the first column averaged at 0.31ℓ/day while the second column contributed a daily production of that gas of 3.4ℓ. Thus the net methane production rate from the system increased to 3.71ℓ/day which corresponds to 9.91 g of glucose per day. Since the methane production rate from the system exceeded the rate that may be anticipated if all the feed glucose was converted to methane, it may be concluded that the anaerobic filter was actually degrading some of the organic constituents of AFFF.

Phase 7 - During the seventh phase of this experiment which lasted for a period of 19 days, the glucose content in the feed substrate was decreased to 200 mg/1 while the TOC contribution of the AFFF constituents was maintained at 1000 mg/1. The immediate response of the system was a decrease in gas production from both anaerobic filters. Methane production from the first stage filter averaged at 0.2ℓ/day while the production rate of methane from the second column was 2.37ℓ/day. The net gas production of 2.57ℓ/day corresponds to 6.86 g of glucose per day which is appreciably greater than the 2.88 g of glucose fed to the system daily thus indicating an appreciable increase in the degradation of some of the organic constituents of AFFF.

Phase 8 - During the last and present phase of the experiment the glucose content of the feed substrate was eliminated thus reducing the organic carbon content of the feed to 1000 mg/1 of TOC totally attributable to AFFF.

Methane production was initially observed to decrease from both anaerobic filters as a result of the elimination of glucose from the feed. However, after 7 days of operation into this phase of the experiment methane production started increasing until it reached a level of 2.0ℓ/day on day 200 of continuous operation. Since that time methane production from the second column continued to increase and at present the second column is responsible for a methane production rate of 3.18ℓ/day at STP. It is of interest to note that during this phase of the experiment very little methane was produced from the first column until day 247 after which methane gas has been consistently produced from the first column at a rate of 0.244ℓ/day at STP.

An overall COD reduction of 30 percent has been obtained from the treatment system during this phase of the operation. Of interest, however, is the fact that the effectiveness of the first column in reducing the chemical oxygen demand of the wastewater has been increasing steadily while the overall conversion of COD in the treatment system remained uniform at 30 percent. No data on organic carbon conversion is available at present because of the breakdown of the TOC analyzer which is currently being repaired.

The data illustrating the system's efficiency in reducing glycol are presented in Figure 8. The first column has been responsible for a consistently increasing efficiency in the conversion of glycol, which at present is averaging at 24 percent in the first column effluent while the feed waste gas a theoretical strength of 100 percent. Very little additional glycol conversion appears to be occurring in the second column, which is at present contributing to a 5 to 10 increase in glycol removal.

Analyses for the volatile fatty acids in the effluents from the first and second anaerobic filters were conducted during this phase of the experiment.

Acetic and n-butyric acids were consistently found in the first column effluent. The concentration of acetic acid ranged from 300 to 700 mg/l while the concentration of butyric acid ranged from 350 to 1200 mg/l. No volatile acids were detected in the effluent from the activated carbon packed column indicating complete utilization of the acids within that column where they were degraded to methane and carbon dioxide.

Future Work

The remaining four systems are currently in the acclimation stage. Two of the reactor systems are being acclimated to treat AFFF Ansul at feed TOC strengths of 333 and 2000 mg/l, respectively. The other two systems are being acclimated to treat AFFF FC-780 at feed TOC concentrations of 333 and 2000 mg/l, respectively.

Preparation is currently underway to build a 2-stage aerated lagoon to further treat the effluent from the first two-stage anaerobic filter. Preliminary results indicate that while the feed waste will produce a very stable foam upon aeration, the effluent from the second column may be aerated with no foaming problems. This may be due to the complete or partial breakdown of the surface active agents in AFFF and as a result the effluent from the anaerobic filter system becomes more amenable to aeration and further aerobic treatment.

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ANAEROBIC ACTIVATED CARBON FILTER FOR THE TREATMENT OF AQUEOUS FILM FORMING FOAM (AFFF) WASTEWATER

QUARTERLY PROGRESS REPORT
July, 1980

by

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New Units

Filter Modifications:

The four new units were seeded with one liter of effluent from an anaerobic sludge digester at the Atlanta Clayton Sewage Treatment Plant. They were then operated in an upflow mode using as substrates: a) AFFF Ansul feed TOC strength of 333 and 2000 mg/l respectively for two units and b) AFFF FC-780 feed TOC strengths of 333 and 2000 mg/l, respectively for the other two units.

After 15 days of operation, problems were encountered with carbon fines and suspended solids being carried out of the carbon packed anaerobic filters and into the recirculation pumps. This caused rapid wear of the pump seals which resulted in premature seal failure and consequent leaks in the pumps. In addition, the suspended solids caused plugging of some recirculation lines resulting in a decrease in the recirculation flow and consequently a loss of bed fluidization. Also, with the loss of suspended solids from the filters, the expected acclimation and establishment of a viable microbial population appeared to be proceeding extremely slowly.

Because of the foregoing operational problems, the set of four anaerobic activated carbon filters were modified as follows (Figure 1):

1) Drain valves were inserted into the inlet port at the base of each column.
2) The activated carbon was removed from the first column of each set and replaced with Raschig Rings.
3) An outlet with a removable cap was placed in the recirculation line at the top of the column in order to allow the column to be backwashed and the backwash water discarded.
4) An additional sampling port was attached to the top of the first column.

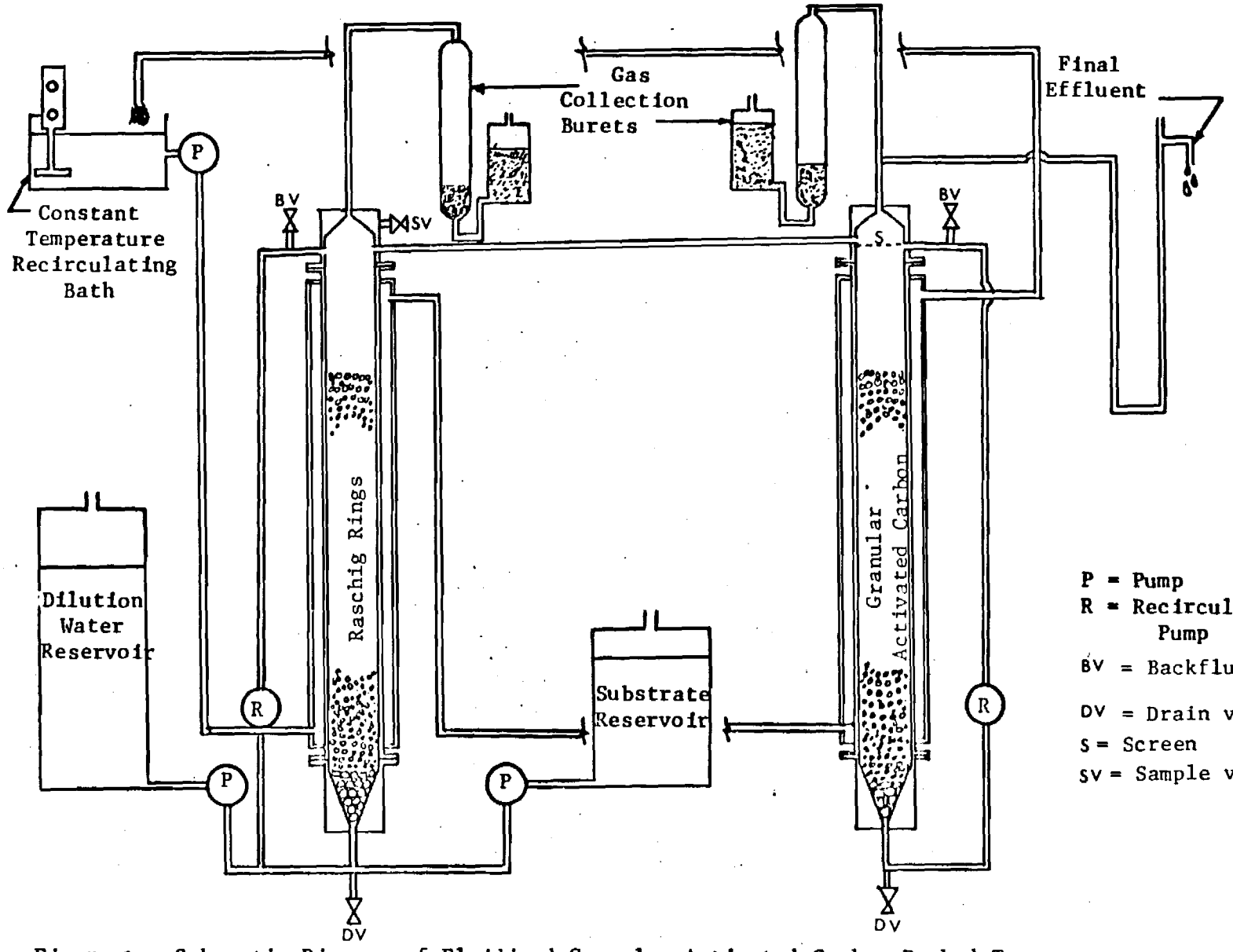


Figure 1 Schematic Diagram of Fluidized Granular Activated Carbon Packed Two Stage Anaerobic Bioreactor

5) A stainless steel screen was inserted in the top of the second column to retain all activated carbon within the column.

Following the above modifications, the first column in each set, which now contained Raschig Rings, was seeded with one liter of effluent per day from the original anaerobic activated carbon filter for a period of seven days. However, it was apparent that this was not a viable means of seeding all four systems due to the relatively small amount of effluent available. Therefore, each Rashig Ring column was seeded with seven liters of primary anaerobic digester sludge obtained from the Atlanta Clayton Sewage Treatment Plant.

Feed substrate was then pumped to the columns at a flow rate of one milliliter per minute, while the dilution water-buffer mixture was fed at a flow rate of nine milliliters per minute.

The organic feed substrate for reacclimating the columns is as follows:

Column Sets one and two: 3.33% AFFF Ansul plus 5000 mg/l glucose.

Column Sets three and four: 3.33% AFFF, FC-206 plus 5000 mg/l glucose.

Initial data (Figures 2-5) show almost immediate production of methane and carbon dioxide from all columns. As the columns acclimate, the concentration of glucose in the substrate will be decreased, with a concurrent increase in AFFF feed concentration, until the systems are being fed AFFF wastewater as their only carbon sources, as was done with the previous system.

Previously Operating Anaerobic Activated Carbon Filter

Continuous operation of the original anaerobic-activated carbon filter has resulted in apparent steady-state conditions being achieved in terms of COD conversion, glycol conversion and methane production.

Cumulative Gas Production From The Anaerobic Filter Number One

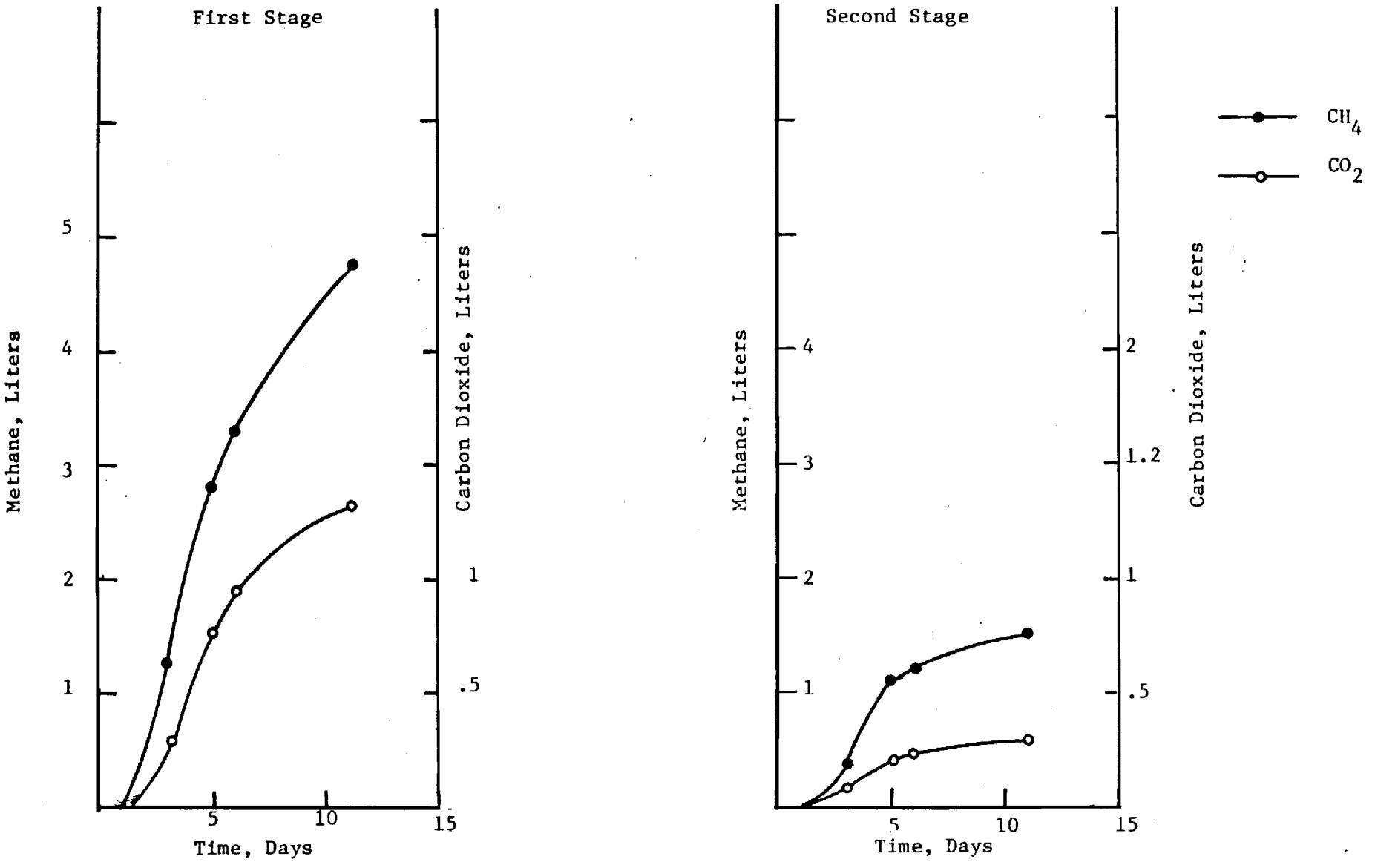


Figure 2

Cumulative Gas Production From The Anaerobic Filter Number Two

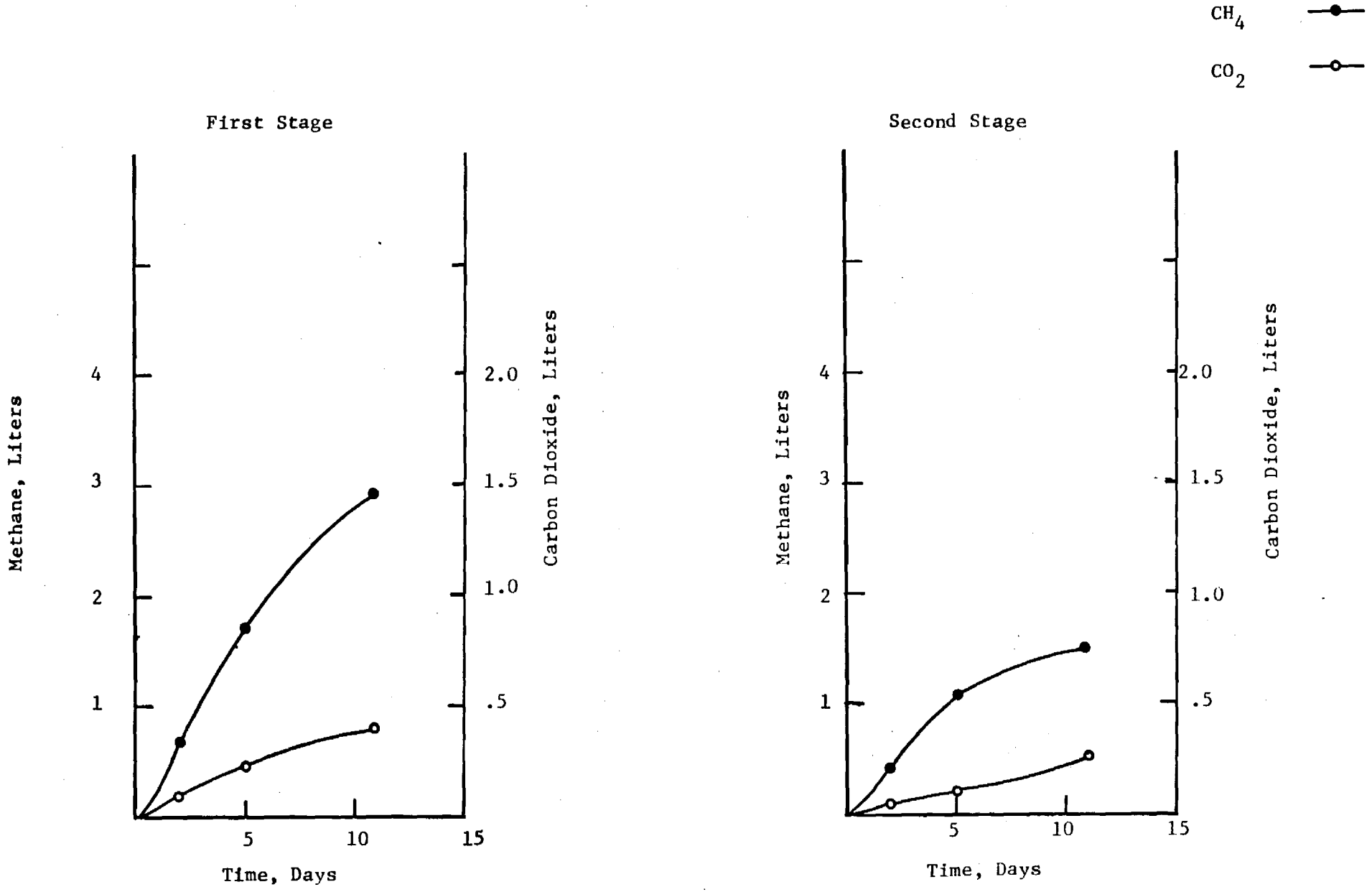


Figure 3

Cumulative Gas Production From The Anaerobic Filter Number Three

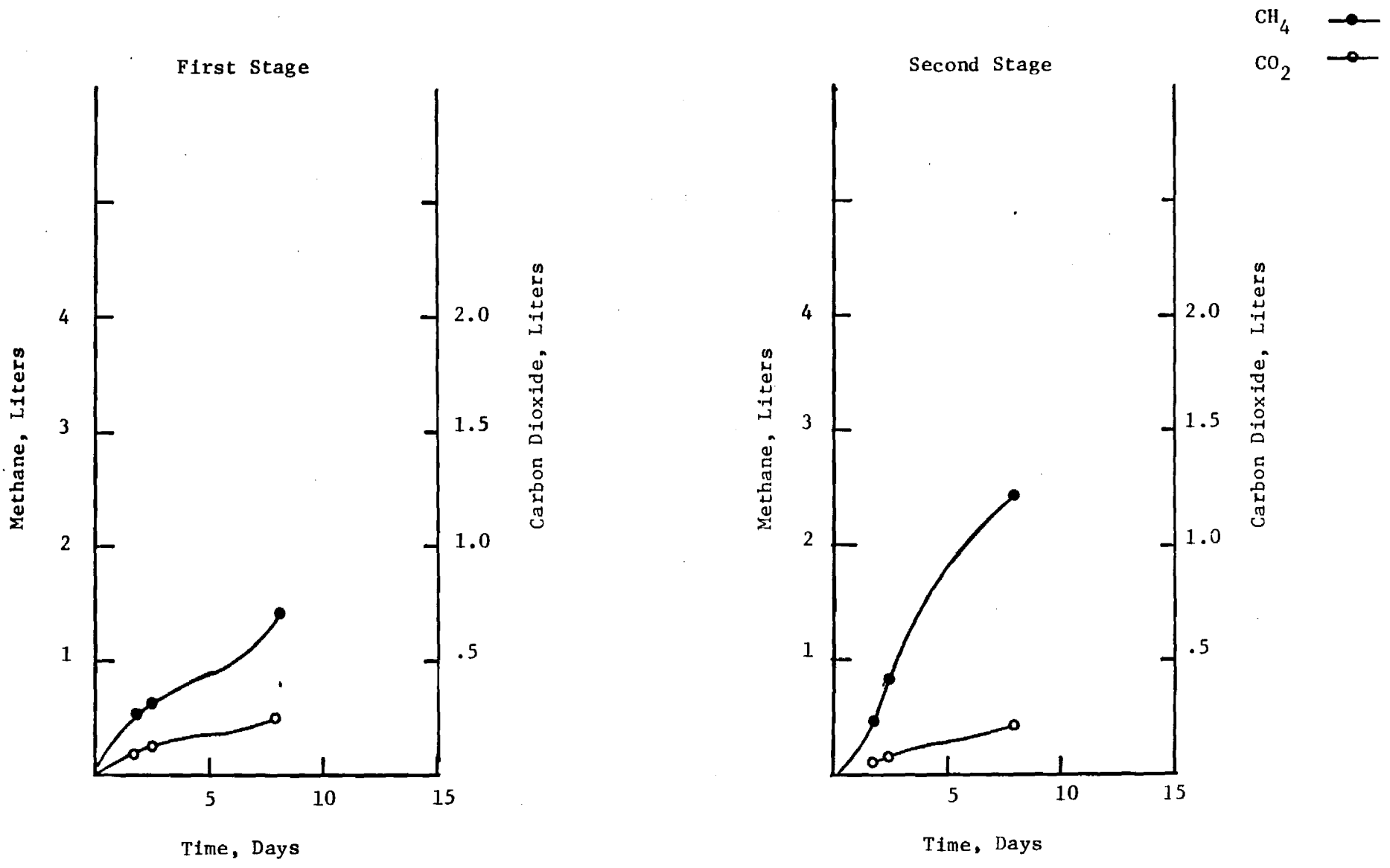


Figure 4

Cumulative Gas Production From The Anaerobic Filter Number Four

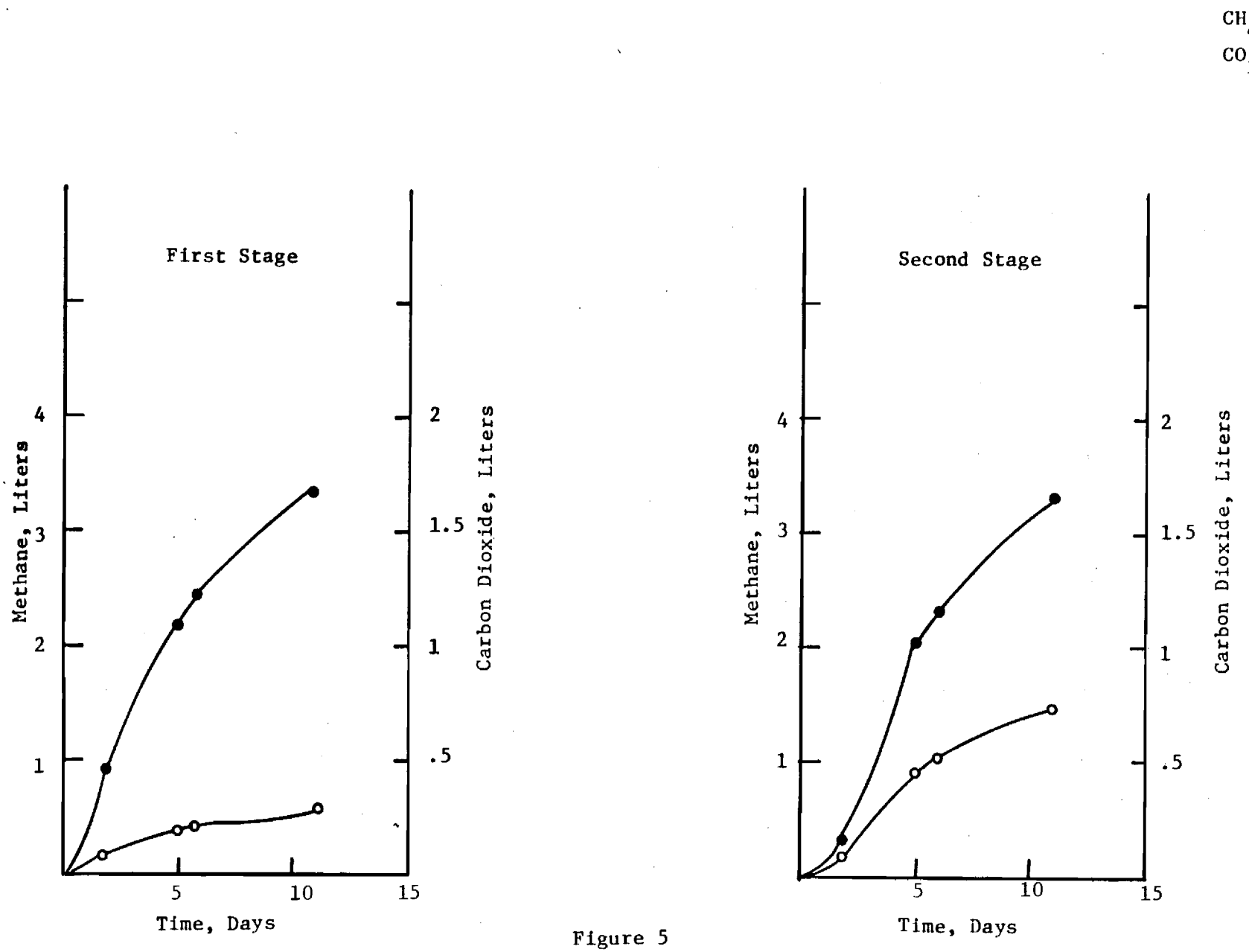


Figure 5

COD Conversion

The first column (Figure 6) results in an average conversion of 14% based on COD while the second column removes an additional quantity of COD to yield a total conversion of 30%. These are increases of 8% and 5% respectively since the last quarterly report.

Glycol Conversion

Glycol conversion efficiency (Figure 7) has contined to increase in the first column until it is now removing 88% of the influent glycol while the second column is only contributing another 2-3% glycol removal for an overall removal efficiency of 90-92%.

Methane Production

Methane production has continued to slowly increase from column one (Figure 8) and still has not reached a steady gas volume production for any extended period of time. For the period of day 270 to 280, it produced methane at a rate of 0.15 1/day. This rate has increased to 0.45 1/day for the period from day 345 to day 355 of continuous operation. However, the second column (Figure 9) in the treatment system has shown a relatively constant rate of methane production of 3.3 liter/day for the period from day 270 to day 355 of continuous operation.

Aerated Lagoon System

The effluent from the second column of the anaerobic activated carbon filter is now being fed to a two stage aerated lagoon. Currently no quantitative data is available on the operation of this system. However, qualitatively there have been no problems with foaming in either aerated reactor and there appears to be less foam in the second aerated reactor.

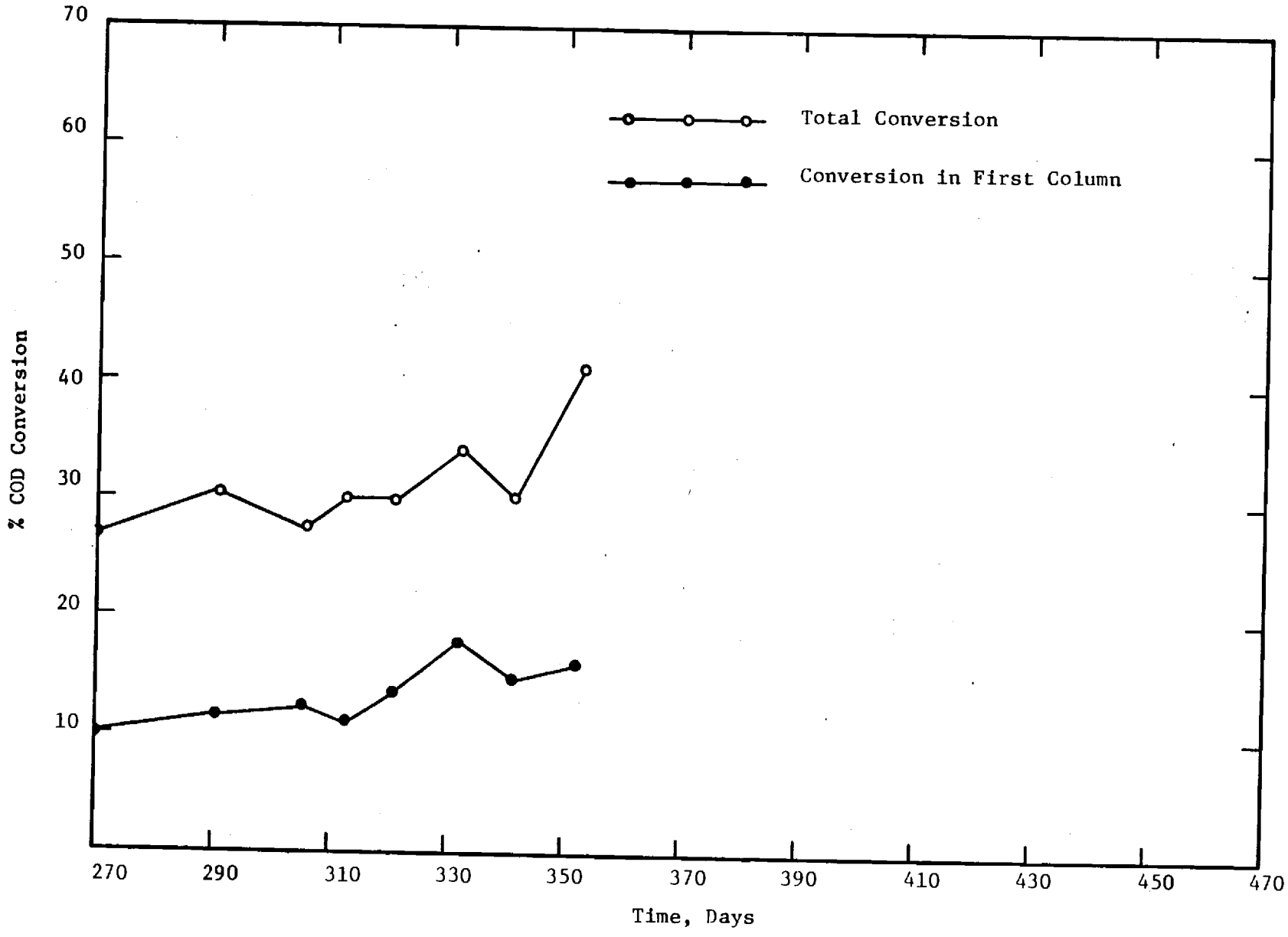
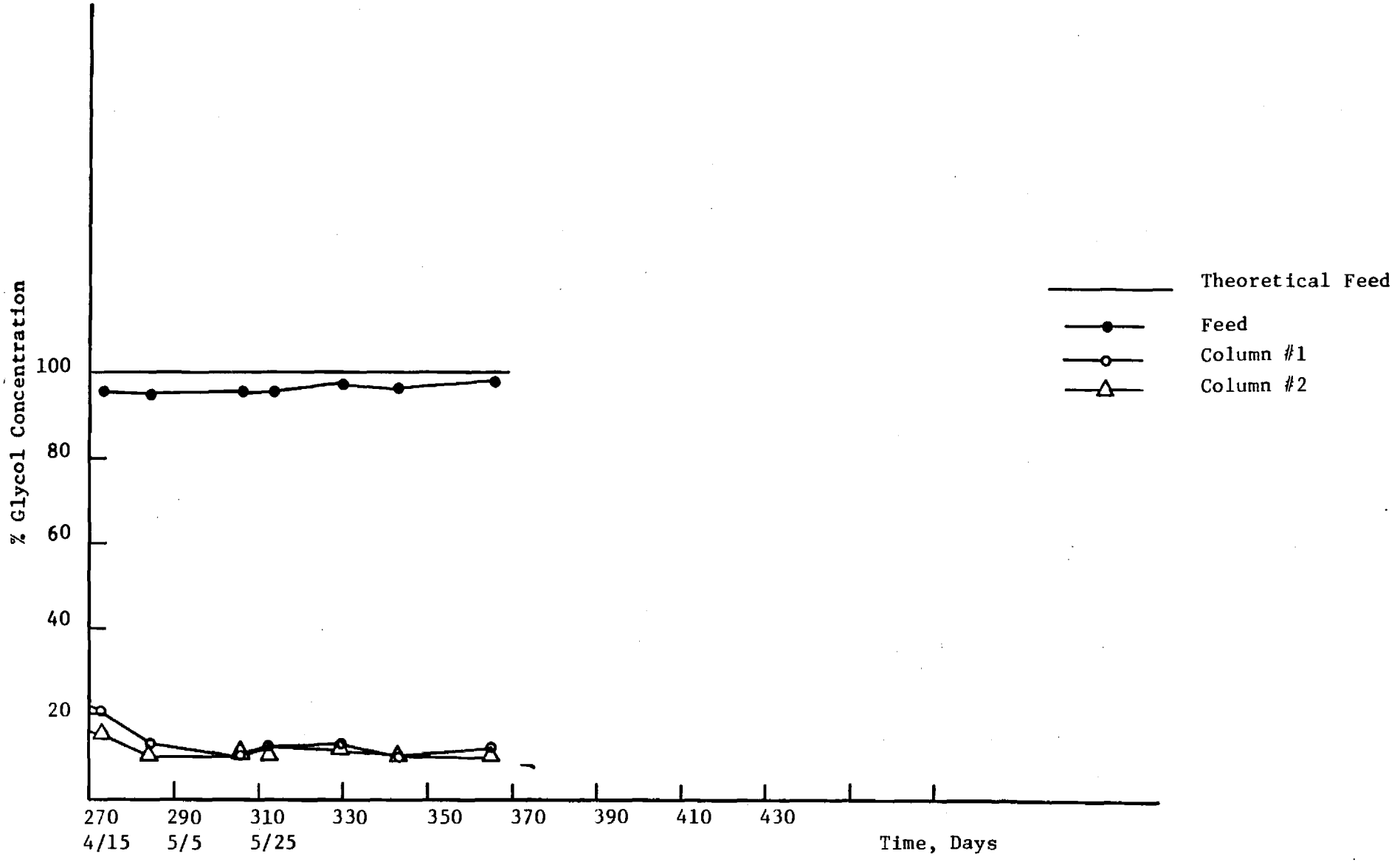

70
60
50
40
30
20
10
% COD Conversion
Total Conversion
Conversion in First Column
270
290
310
330
350
370
390
410
430
450
470
Time, Days

Figure 6



Glycol Concentration Across Treatment System

Figure 7

Methane and Carbon Dioxide Production from the First Stage Anaerobic Filter

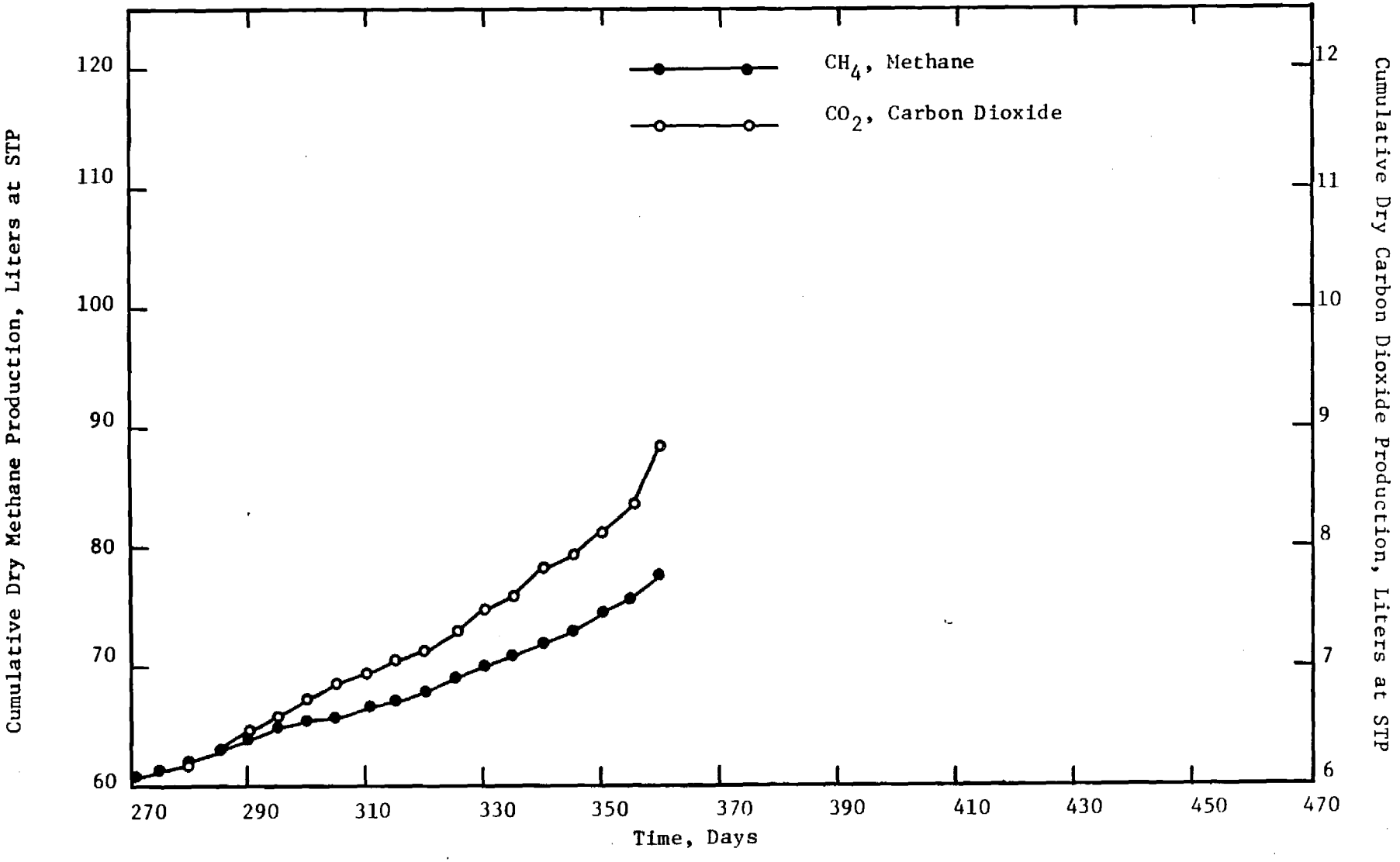
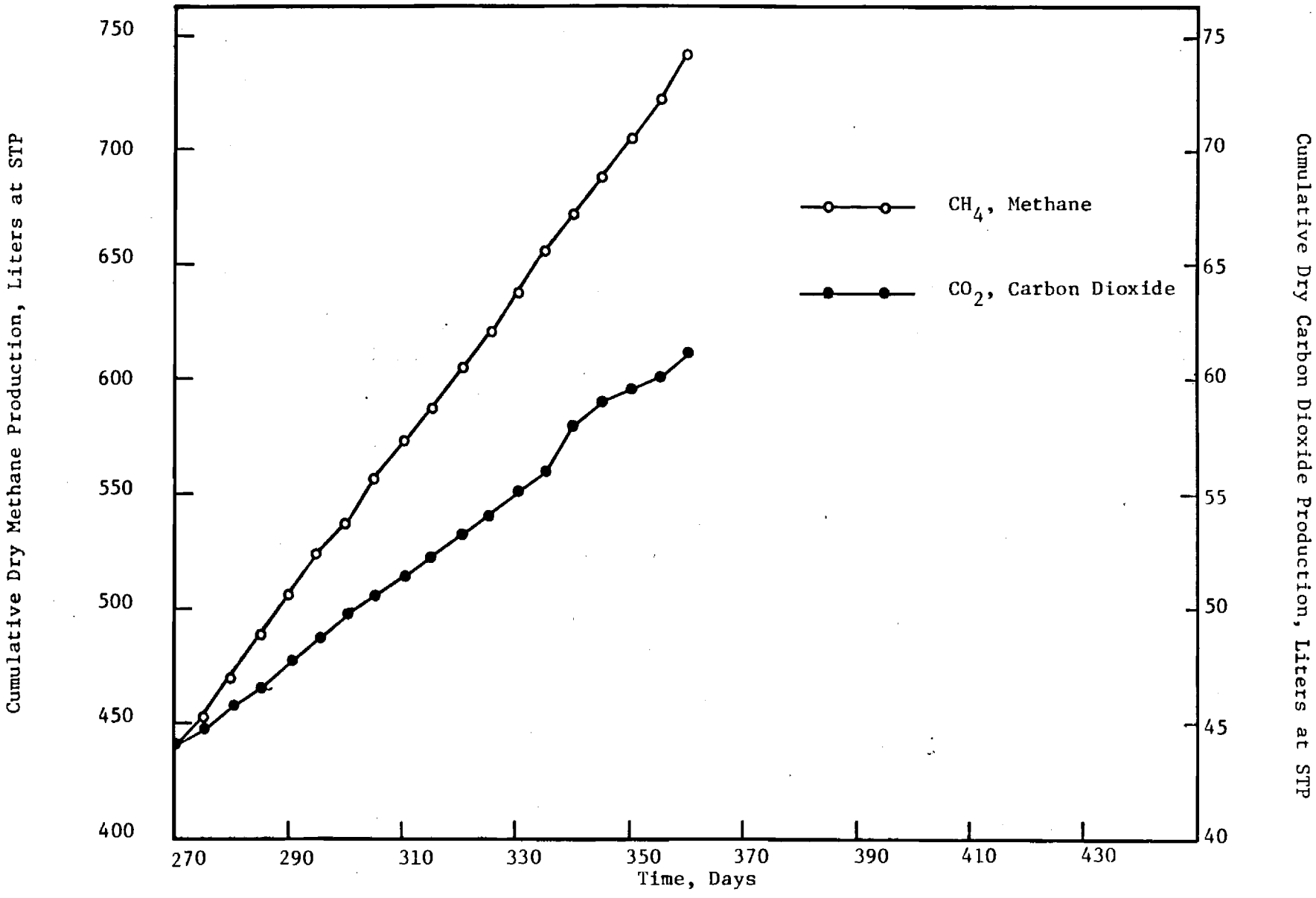


Figure 8

Future Work

As soon as the new reactor systems have been acclimated to treat AFFF Ansul and FC-206 at loadings of 333 and 2000 mg/l TOC feed strength, steady-state operational data will be collected. In addition, results from the treatment of the effluent from the anaerobic activated carbon filter by aerated lagoons will be evaluated.



Methane and Carbon Dioxide Production from the Second-Stage Anaerobic Filter

Figure 9

ANAEROBIC-ACTIVATED CARBON FILTER FOR THE TREATMENT OF AQUEOUS FILM FORMING FOAM (AFFF) WASTEWATER

QUARTERLY PROGRESS REPORT
August 1980

by

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Introduction

The present research effort is directed towards an examination of the effectiveness of a two stage anaerobic filter in the treatment of wastewaters emanating from fire fighting training exercises at military installations. In addition to fuel oil and gasoline, combustion products, and suspended solids, these wastewaters contain the constituents present in the fire fighting agent used. Such agents, commonly referred to as Aqueous Film Forming Foam (AFFF) contain various glycols and surfactants in addition to various fluorocarbon compounds.

For the purposes of the present research, five two-stage anaerobic filter treatment systems were constructed. The first column of all units was packed with Raschig rings while all other columns were packed with granular activated carbon. The granular activated carbon packed columns are fluidized by effluent recycle and the use of activated carbon is believed to result in concentration polarization and toxicity reduction in addition to providing a microbial attachment surface.

Experimental Apparatus

Two types of experimental systems were employed in this study. One anaerobic system was constructed with Raschig rings serving as a contact medium in the first column while the second column which was equipped with effluent recycle was packed with granular activated carbon (GAC), Figure 1. Four additional units were constructed in a similar manner, however, in this instance both columns of each reactor system were equipped with effluent recycle and both were packed with GAC. Problems were encountered with

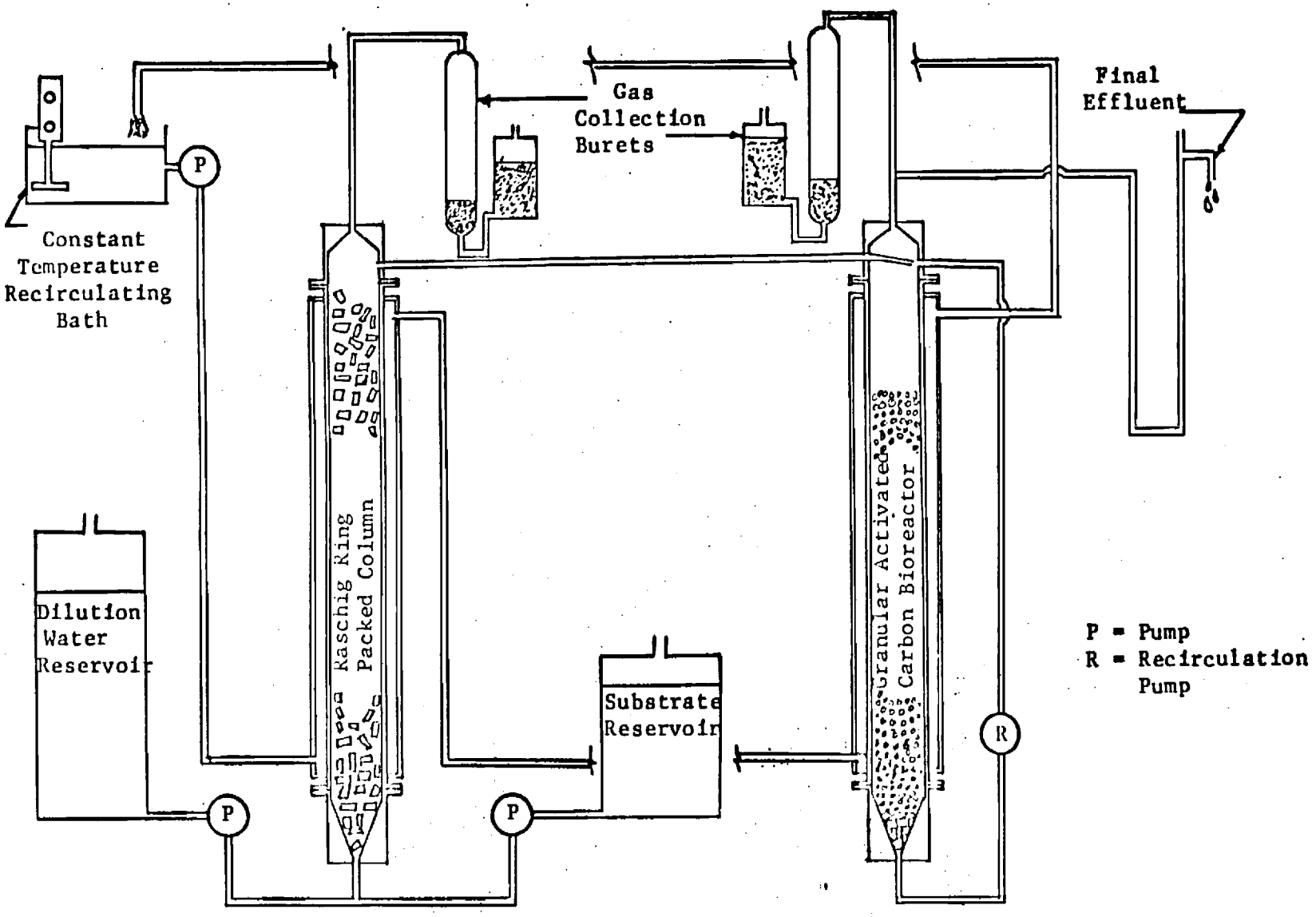


Figure 1. Schemetic Diagram of Raschig Ring - Granular Activated Carbon Packed Two-Stage Anaerobic Bioreactor

carbon fines and suspended solids being carried out of the first stage GAC packed anaerobic filter and into the recirculation pumps. In addition, the suspended solids caused plugging of some recirculation lines resulting in a decrease in the recirculation flow and consequently a loss of bed fluidization. Also, with the loss of suspended solids from the filter, the expected acclimation and establishment of viable microbial population appeared to be proceeding extremely slowly. No reliable data on the analysis effluent streams could be produced during that period.

Filter Modifications

Because of the foregoing operational problems, these four sets of anaerobic activated carbon filter systems were modified as follows (Figure 2):

1. Drain values (DV) were inserted into the inlet port at the base of each column.
2. The GAC in the first column was replaced by Raschig rings.
3. An outlet with a removable cap (BV) was placed at the top of the recirculation line in order to allow the column to be backwashed and the backwash water to be discarded.
4. An additional sampling value (SV) was attached to the top of the first column.
5. A stainless steel screen (S) was placed inside the upper portion of the second column in order to retain all activated carbon within the column. During the period of low liquid recirculation, gas binding of carbon particles tended to lift the particles upward and plug the recirculation line.

Following the above modifications, these systems have been in normal operating conditions since June 1980.

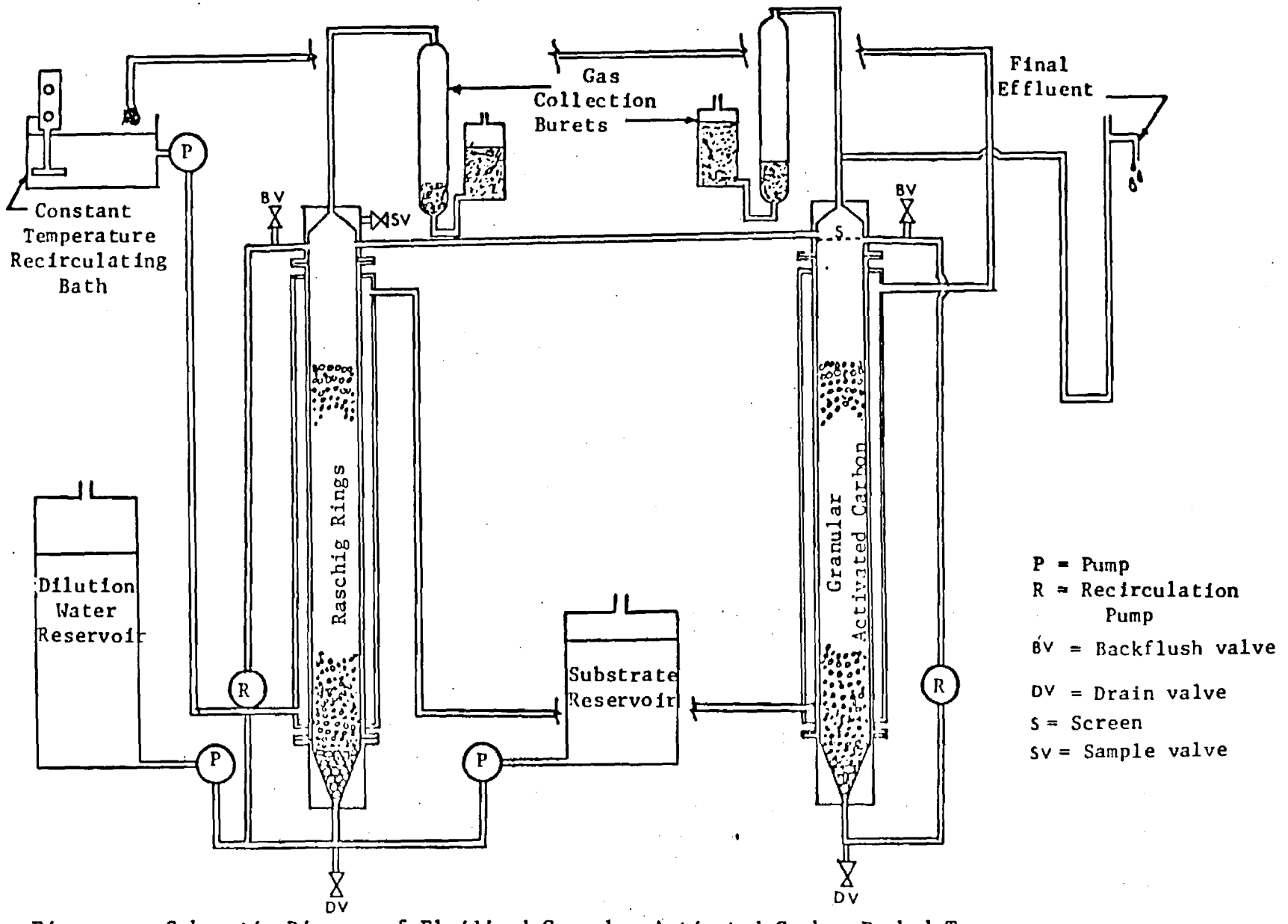


Figure 2 Schematic Diagram of Fluidized Granular Activated Carbon Packed Two Stage Anaerobic Bioreactor

Details of Filter Design

Feed Pumps. The AFFF is diluted with distilled water to any desired concentrations in a 20-ℓ concentrate reservoir (Figures 1 & 2). This diluted substrate is fed into the reactor feed using a positive displacement FMI pump, Model RP G-20 (Fluid Metering Incorporated, Oyster Bay, NY) having a maximum flow rate of 5.4 ml/min and a maximum operating pressure of 50 psi. No other nutrients are added to this reservoir in order to prevent any biodegradation within the reservoir and the feed lines.

Dilution water containing the phosphate buffer and ammonium nutrients necessary for active biodegradation are pumped from another 55-ℓ reservoir using a positive displacement pump Model RP G150 (Fluid Metering Incorporated, Oyster Bay, NY). This pump has a maximum flow rate setting of 96 ml/min and a maximum operating pressure of 20 psi. The flow from the two reservoirs is mixed in a tee connection prior to entry into the first-stage anaerobic filter.

Raschig Ring Packed Anaerobic Filter. This filter consists of a water jacketed plexiglas column having the following features:

i. inner column (10.1 cm in internal diameter by 182-cm long) which will serve as the actual roughing anaerobic filter chamber.

ii. a water jacket (15.25 cm in internal diameter by 170-cm long) to allow the unit to be operated at a constant and controllable temperature through the circulation of water from a constant temperature bath (Model T31, HAAKE, Inc., Werk Karlsruhe, West Germany) through the jacket.

iii. influent header is constructed using a plexiglas column section and plates and its inner structure, which is 20-cm long, is tapered into an inverted conical shape in order to allow for better distribution of the influent flow. This unit is equipped with a perforated plate to allow for the introduction of the mixed feed solution.

iv. effluent structure: a conical shape structure is used to minimize the trapped gas volume and is equipped with fittings for connection to the gas collection system, connection to the effluent structure from this unit and a sampling port.

v. gas collection system consisting of two 4.5-ℓ gas burets, two leveling bottles and sampling ports to allow for monitoring of both the quantity and composition of the gaseous products produced and for the release of the excess gas produced.

Granular Activated Carbon Packed Filters. This unit is identical in structure to the roughing unit except that it is equipped with a 1/3 HP centrifugal pump in the operating unit and a 1/2 HP centrifugal pump in the four new units (Teel Pump, Dayton Electric Manufacturing Company, Chicaog, Ill.). The purpose of this pump is to recriculate the aqueous contents of the carbon filled filter and maintain this carbon fluidized in order to minimize gas trapping onto the carbon. Details of the recirculation system are presented in Figure 3.

Filter Packings and Start Up of the Currently Operating (Old) System as Well as the New Setups

The roughing anaerobic filters of the previously operating systems (referred to as an old system later) as well as the four new setups were packed with 1.27-cm (0.5 inch) Raschig rings to a depth of 193 cm (6.33 ft). The packed columns have a porosity of 58.33% and specific surface area of 337.18 m^2/m^3 (102.65 ft^2/ft^3). Because of its relatively high porosity and surface area, this packing is ideal for the roughing filter where a high growth rate and sludge accumulation are anticipated.

The old anaerobic activated carbon filter system was packed in a similar manner with an initial depth of 128 cm (4.20 ft) and backwashed down to a depth of 100 cms (3.28 ft) in order to eliminate carbon fines.

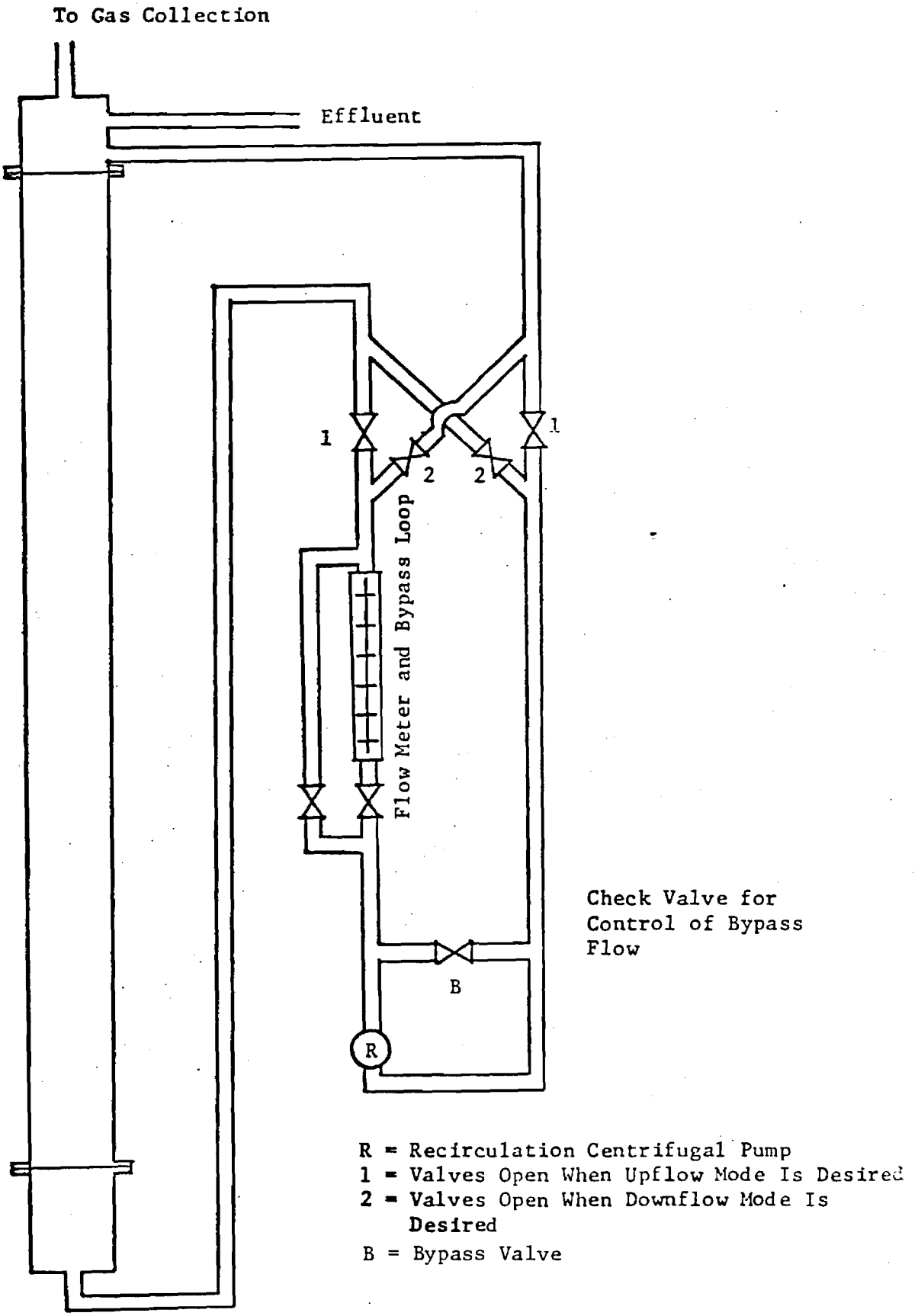


Figure 3. Schematic of Effluent Recirculation System

The activated carbon used in this study is Calgon FMC 6 x 16 U.S. mesh size with an average particle size of 2.27 mm. However, after backwashing, a larger average particle size was retained in the filter. The second filter columns of the new setups were packed with 2.5 Kg of Calgon FMC 6 x 16 U.S. Mesh size granular activated carbon and backwashed to a depth of 115 cm .

The columns of an old system were seeded with an anaerobic sludge from the underflow of an anaerobic digester at the Atlanta Clayton Sewage Treatment Plant; and the columns of the new system, following the modifications listed before, were seeded with primary anaerobic digester sludge from the same source.

The dilution water reservoir is filled to capacity with dechlorinated and deaerated tap water to which nutrients and a phosphate buffer are added. In addition to serving as a nutrient, the phosphate mixture is designed to provide a buffer to the waste at the desired operating pH. The levels of addition of the phosphate, ammonium and other nutrients is higher than what is estimated to be needed for the successful operation of the system. The concentration of the various nutrients in the dilution water reservoir are given in Table 1. The flow rate of the dilution water was set at 9.0 ml/min while the concentrate flow rate was set at 1.0 ml/min such that the feed concentration to the first column will be only 10 percent of the stock concentrate.

The flow rate of 10 ml/min is selected in order to provide an empty bed contact time of 24 hours in each of the reactors.

The recirculation flow rate on the anaerobic granular activated carbon packed filters is adjustable through the control of the bypass valve (B) as shown in Figure 3. This rate can be varied in order to determine the

TABLE I. Concentration of Nutrients in Buffer Solution

Compound	Concentration (mg/l)
$FeCl_3 \cdot H_2O$	4.83
$MnCl_2 \cdot 4H_2O$	0.71
$Zn\ Cl_2$	0.49
$CoCl_2 \cdot 6H_2O$	0.43
$Na_2B_4O_7 \cdot 10H_2O$	0.17
$Na_3C_6H_5O_7$ (sodium citrate)	26.33
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.31
KH_2PO_4	60.98
$NaH_2PO_4 \cdot H_2O$	37.09
$(NH_4)_2SO_4$	23.66
NH_4Cl	112.00
$CaCl_2 \cdot 2H_2O$	26.55
$MgCl_2 \cdot 6H_2O$	36.42
Vitamin Extract*	0.16 ml

*The Vitamin Extract was prepared by adding 10 grams of a multivitamin to 333 ml of 95% ethanol and 667 ml of distilled water. The solution was allowed to stir for 10-12 hours at 60°C, settled for 24 hours and decanted. The decanted solution was the vitamin extract.

minimum recirculation flow rate that would allow for economic and efficient operation of the system.

At the time of preparation of this report, the old system was operated on a feed substrate containing the AFFF Ansul at a strength of 1000 mg/l of TOC in the feed. Two of the remaining 4 systems were in the third phase of acclimation to AFFF Ansul feed TOC strengths of 333 and 1000 mg/l, respectively, while the remaining two systems were acclimated to AFFF FC-206 feed TOC strengths of 333 and 1000 mg/l, respectively. The current stage of phase 3 operation will be described later.

Synthetic Feed Substrate

The synthetic feed substrate to the old anaerobic filter system was prepared in two separate solutions. The AFFF Ansul was selected as the first AFFF concentrate to be studied. A solution of AFFF and distilled water was prepared in 20ℓ batches and fed to the anaerobic filter.

A dilution water solution was also fed to the columns from a separate 55ℓ reservoir. In addition to serving as a dilution water, this solution also contained biological nutrients, ammonium chloride and a phosphate buffer. The concentration of the constituents of the growth nutrients in the dilution reservoir was maintained at the levels indicated in Table I. In addition to these nutrients, additional ammonium chloride and a phosphate buffer were added and their strengths are presented with the operating data in Table II.

Analytical Methods

Samples collected from the two feed reservoirs (dilution buffer and concentrate reservoirs) and the respective two column effluents were analyzed according to the procedures in Standard Methods for the Examination of Water and Wastewater, 14th Edition, 1975, with the exception of the following analyses: (a) gas analyses were performed on a Fisher Model 25v Gas

TABLE II. Operating Conditions for Two-Stage Anaerobic Filter

Phase No.	Duration (days)	Empty Bed Contact Time (hours)	Flow Rate (ml/min)	Influent TOC Total (mg/l)	Influent TOC AFFF-TOC (mg/l)	Buffer Phosphate Content (m/l)	NH_4Cl Content (mg/l)
1	26	12/filter 24 total	20	1000	1000	-	153
2	24	24/filter 48 total	10	1133	333	0.1	306-1030
3	24	24/filter 48 total	10	733	333	0.06	611
4	12	24/filter 48 total	10	533	333	0.06	611-397
5	65 total 35 in operation	24/filter 48 total	10	867	667	0.06	680
6	13	24/filter 48 total	10	1200	1000	0.06	890
7	19	24/filter 48 total	10	1080	1000	0.03	840
8	Ongoing	24/filter 48 total	10	1000	1000	0.01	840

Partitioner using certified calibration standards (Matheson, East Rutherford, N.J.); (b) glycol analysis was performed on a Perkin Elmer Sigma I Gas Chromatograph. The column used was a 6-ft. long 2-mm I.D. glass column packed with 10% Carbowax 20 M on 80/100 Chromasorb W. Chromatographic conditions were: injection temperature 250°C, injection volume 1 microliter, detector temperature 300°C, oven temperature 160°C isothermal for five minutes followed by a temperature program which raised the temperature to 200°C at a rate of 10°C/min. Temperature was held at 200°C for 3 minutes resulting in a total run time of 12 minutes. A hydrogen flow rate of 30 ml/min, 240 ml/min of air and 30 ml/min of a helium carrier gas were employed; and (c) Shake Test —The foaming property of the samples was used to approximate the surfactant concentration. The foaming property was determined by the method commonly referred to as the shake test. This determination consisted of placing a 100 ml sample in a 250 ml graduated cylinder with a secured fitting glass stopper. The sample was then shaken vigorously for 30 seconds and allowed to settle for 5 min, after each time the foam volume in ml was recorded. The result of this method can be represented by the volume of foam. The shake test has been used successfully in the membrane treatment process to replace the less reliable fluorocarbon determination. However, the validity of using the shake test to monitor the surfactants in the anaerobic filter process is yet to be determined.

Results and Discussion

The Old System

Continuous operation in phase 8 (1000 mg/l of TOC totally attributed to AFFF) of the old carbon filter has resulted in apparent steady-state conditions achieved in terms of COD and glycol conversions, as well as methane

production. About 44% overall COD conversion is achieved at the time of this report preparation as shown in Figure 4. About 80% glycol conversion is observed across the system, consistently (Figure 5). However, methane production shows a slower but continuous rate of increase (Figure 6 and 7). The first stage (Figure 6) shows a gas production rate of 0.15 lit/day during the period between 270 to 280 day; this rate increased to 0.45 lit/day from day 345 to 355 of continuous operation. The second stage of the treatment system (Figure 7) shows a relatively constant rate of methane production at 3.3 lit/day during the period from day 270 to day 355 of continuous operation. A total consumption of volatile acids was observed in the second stage. However, a volatile acids concentration of less than 100 mg/l was observed in the first stage. The results of the shake test showed approximately 43% reduction of foam by the first stage and approximately 79% reduction of foam by the entire system.

Two-Stage Aerated Lagoon

The effluent from the second stage of the old anaerobic carbon filter is now being fed to a two-stage aerated lagoon. A 50% COD reduction across the two-stage aerated lagoons was realized at the time of this report writing. Thus resulting in a total overall reduction of COD to approximately 75% across the entire anaerobic/aerobic system consisting of two anaerobic filters and two aerated lagoons in series. A substantial reduction in foam was observed in the second stage of the aerated lagoon. Quantitative data on the two-stage aerated lagoon system will be presented in the future.

Phase 1 of the New Systems

All of the four new setups were fed with a feed of 330 mg/l TOC of Ansul/FC-206 plus 500 mg/l of glucose during this phase I acclimation period. Setup #1 and #2 were fed with Ansul whereas setup #3 and #4 FC-206. No conclusive results were obtained during this phase of operation owing to

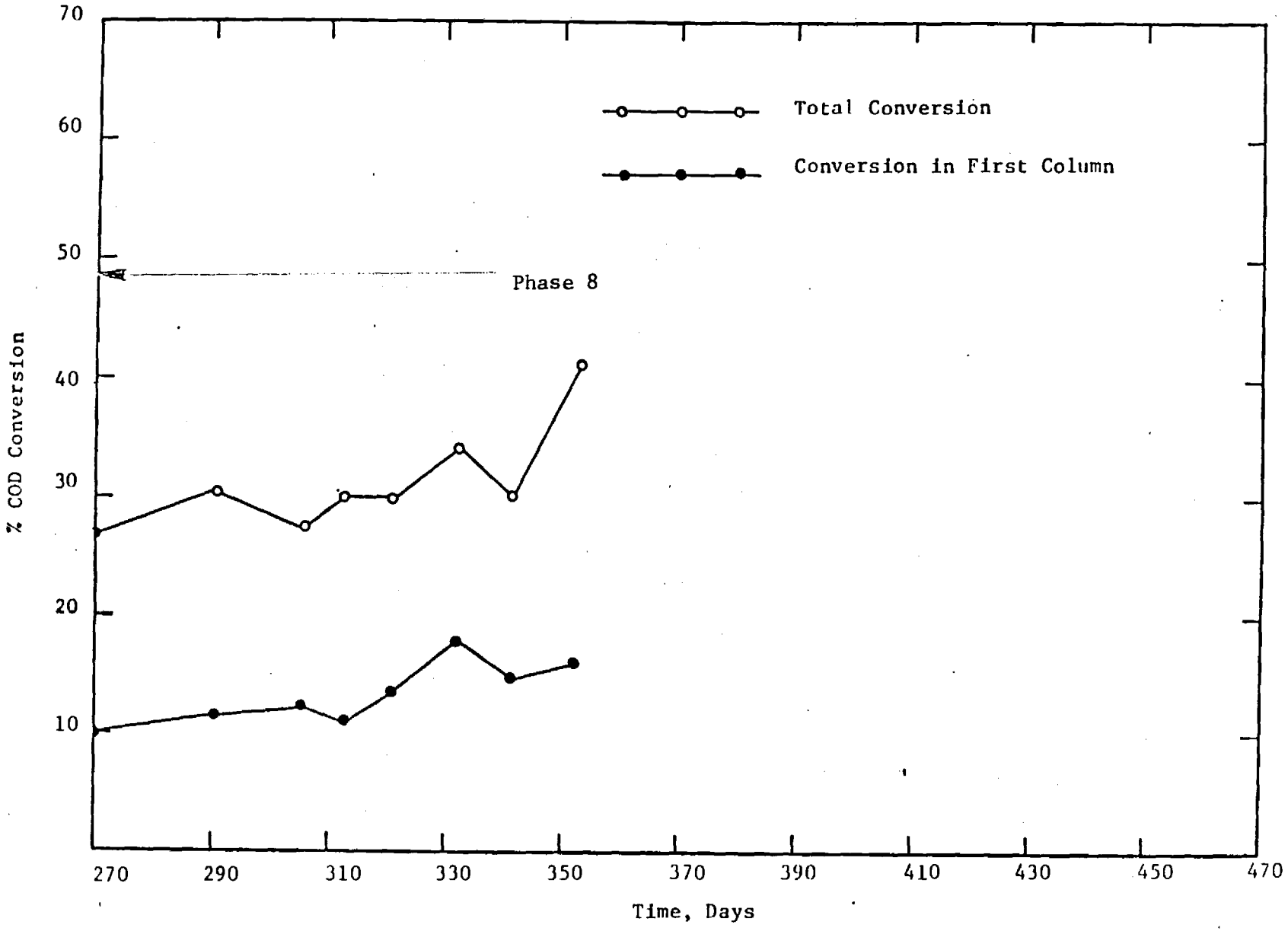
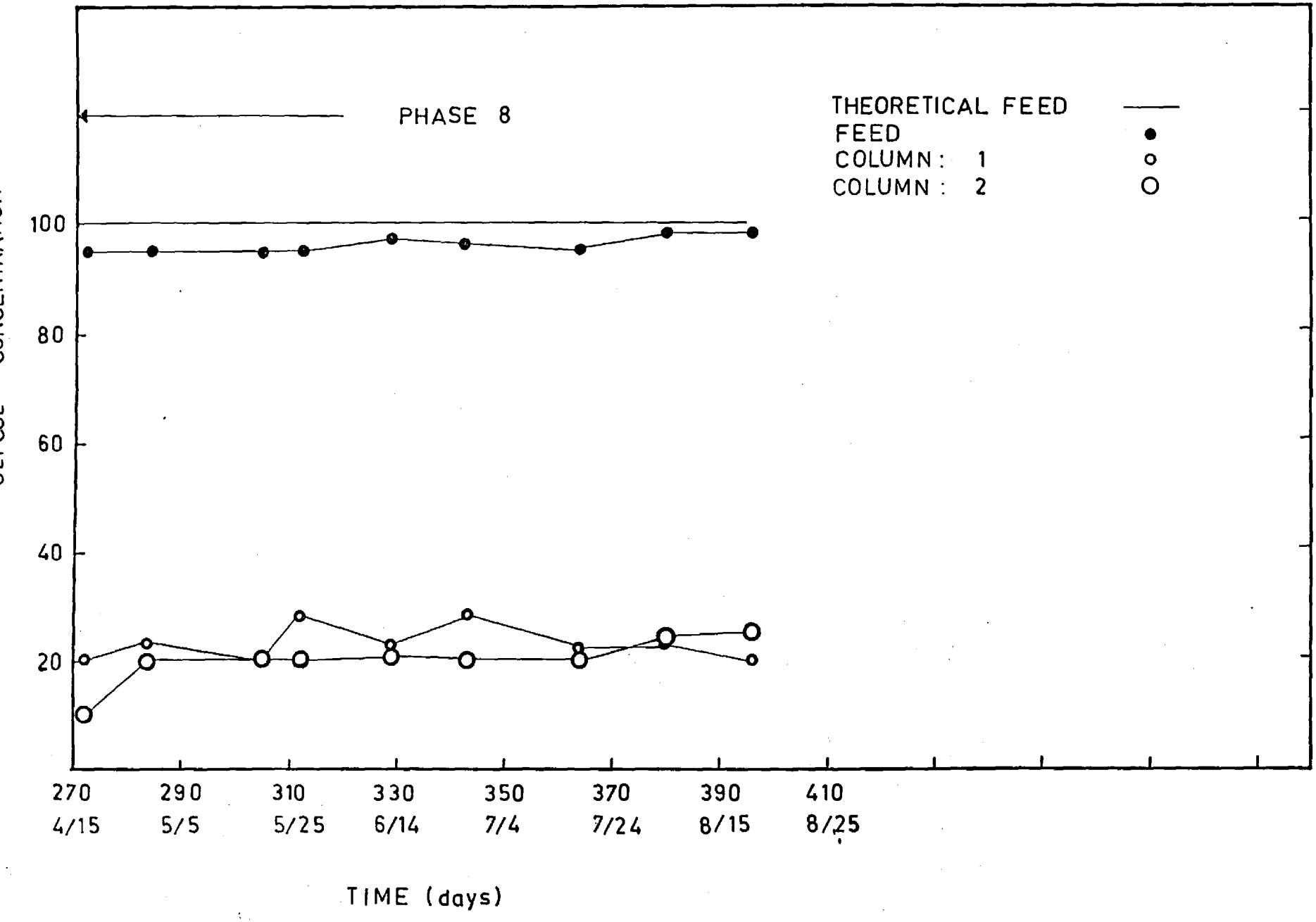

70
60
50
40
30
20
10
% COD Conversion
Total Conversion
Conversion in First Column
Phase 8
270
290
310
330
350
370
390
410
430
450
470
Time, Days

Figure 4



GLYCOL CONCENTRATION ACROSS THE OLD SYSTEM

FIGURE - 5

Methane and Carbon Dioxide Production from the First Stage of the Old Anaerobic Filter

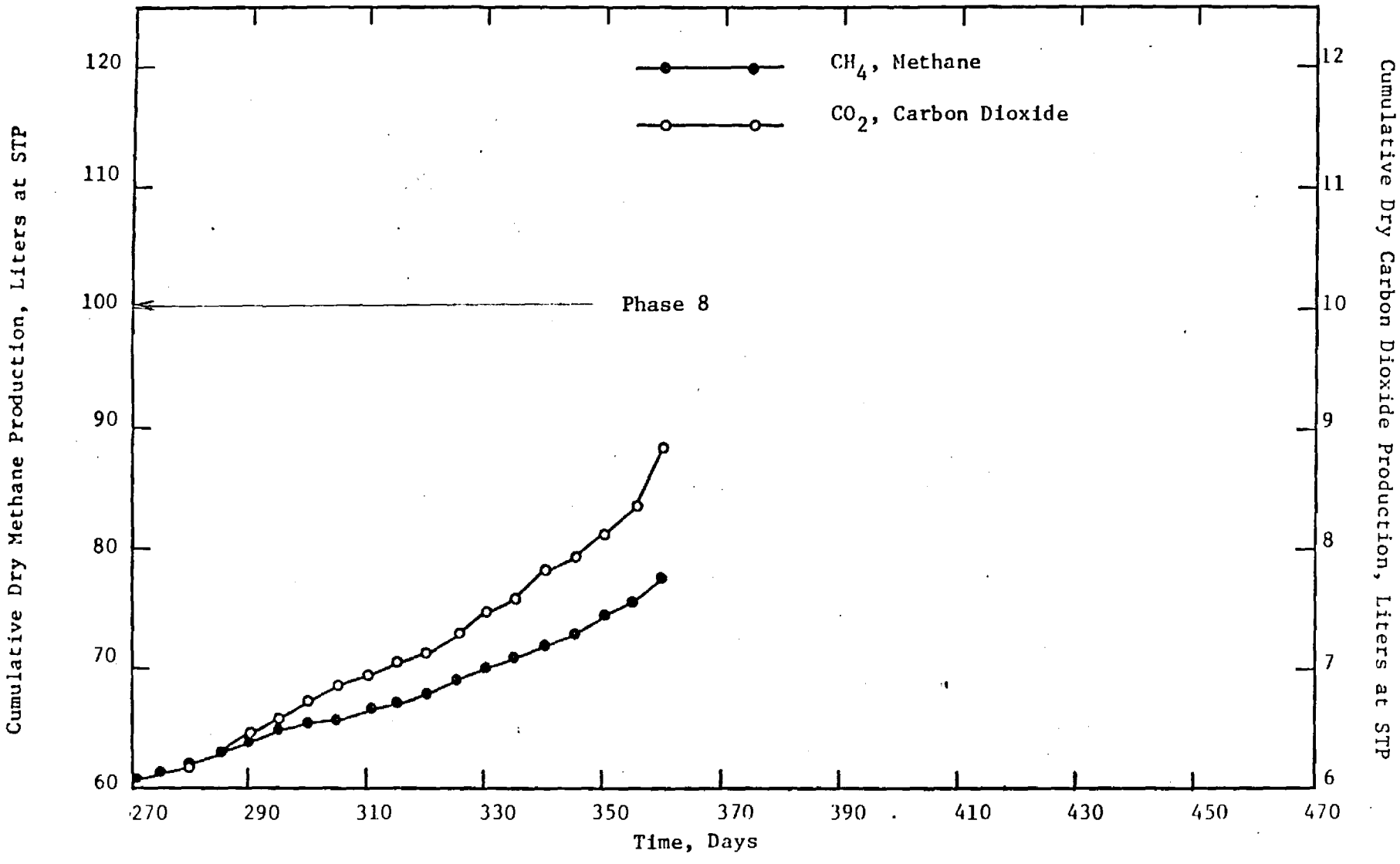
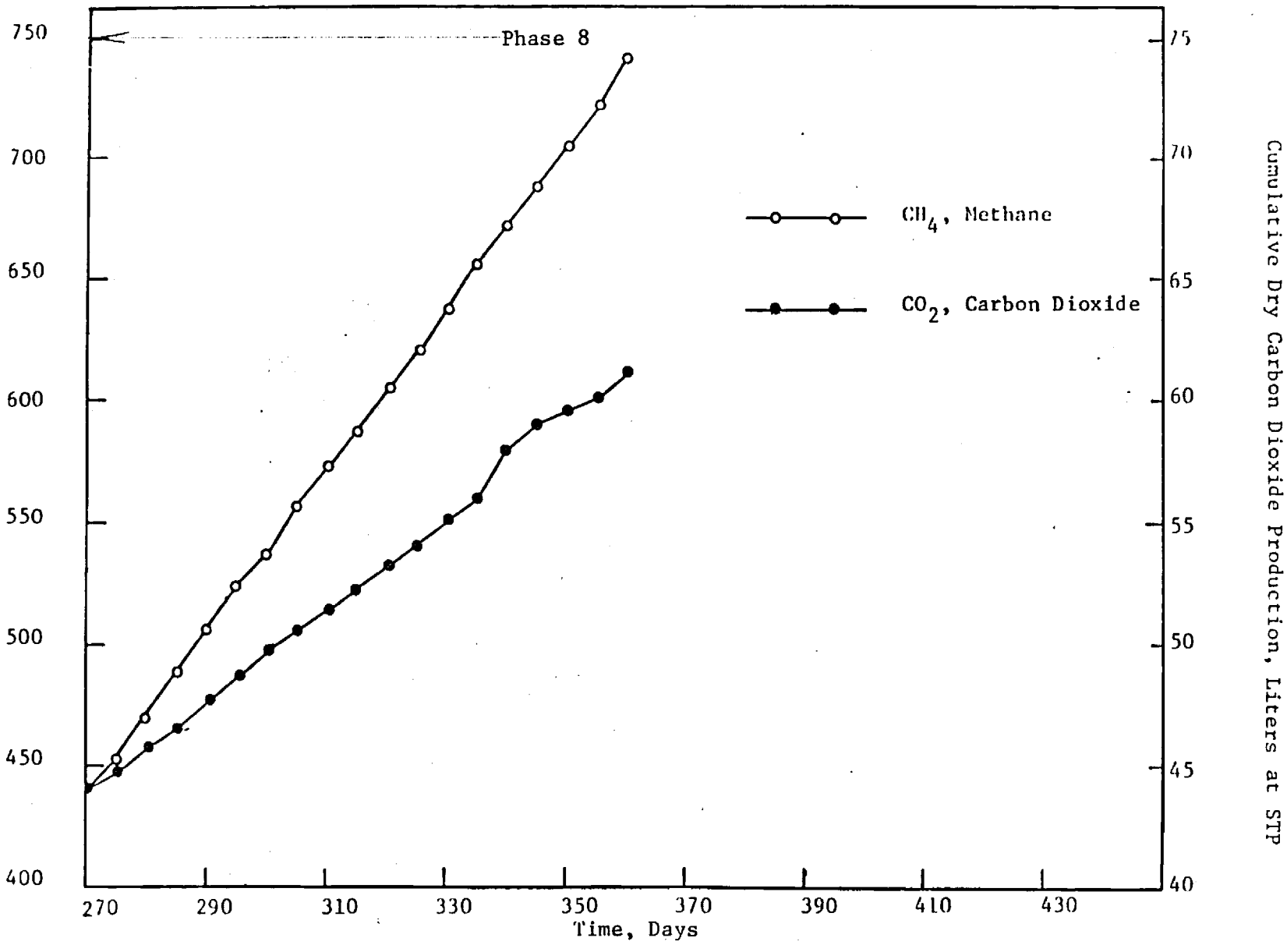


Figure 6



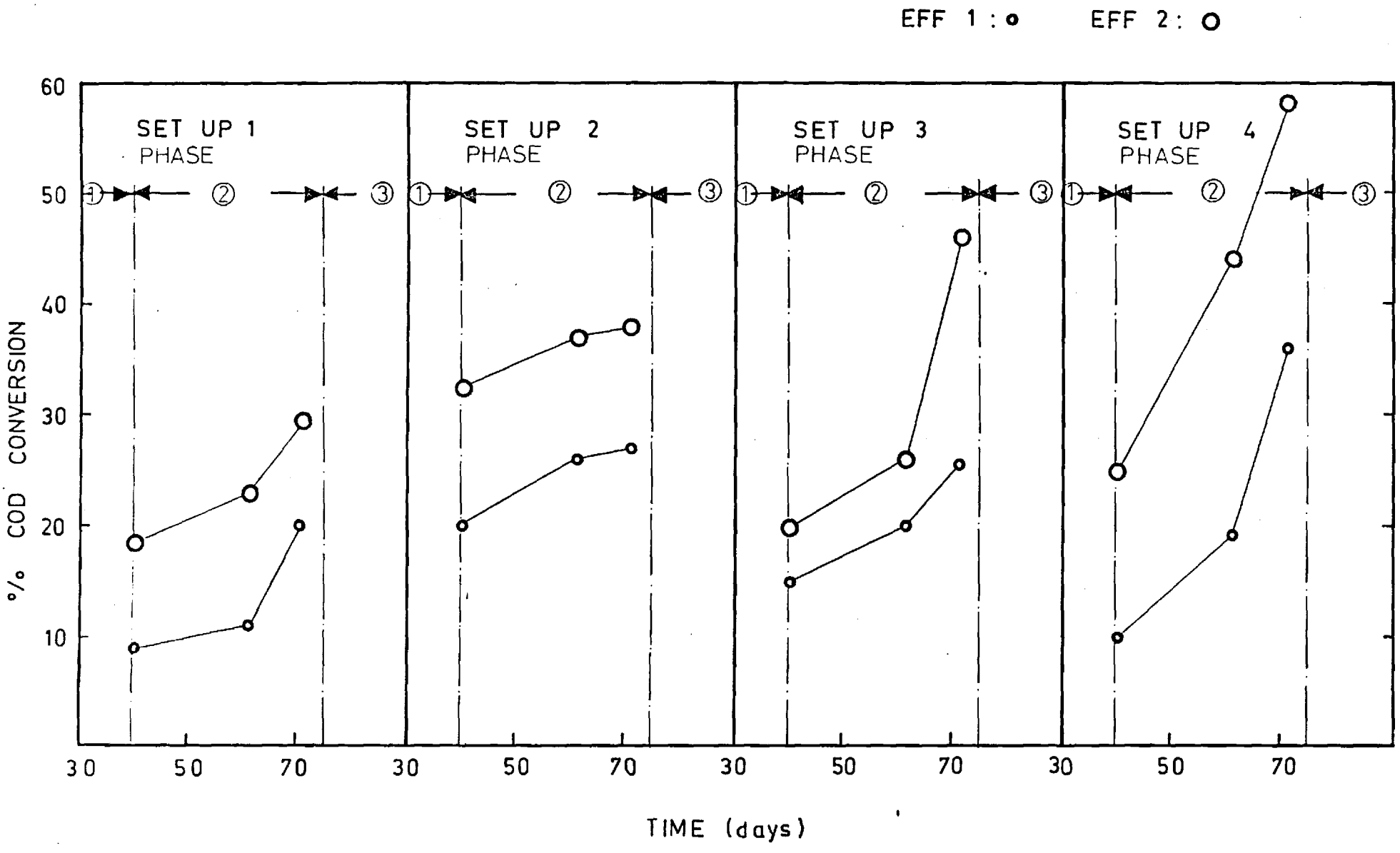
Methane and Carbon Dioxide Production from the Second-Stage of the Old Anaerobic Filter

Figure 7

the operational problems encountered on the loss of sludge and plugging of pipes. During this period only the influent as well as the effluent was continuously monitored. Feed pH of approximately 7.3 and the effluent pH of approximately 6.7-6.9 was found in all four systems indicating a proper operation in the desirable pH ranges.

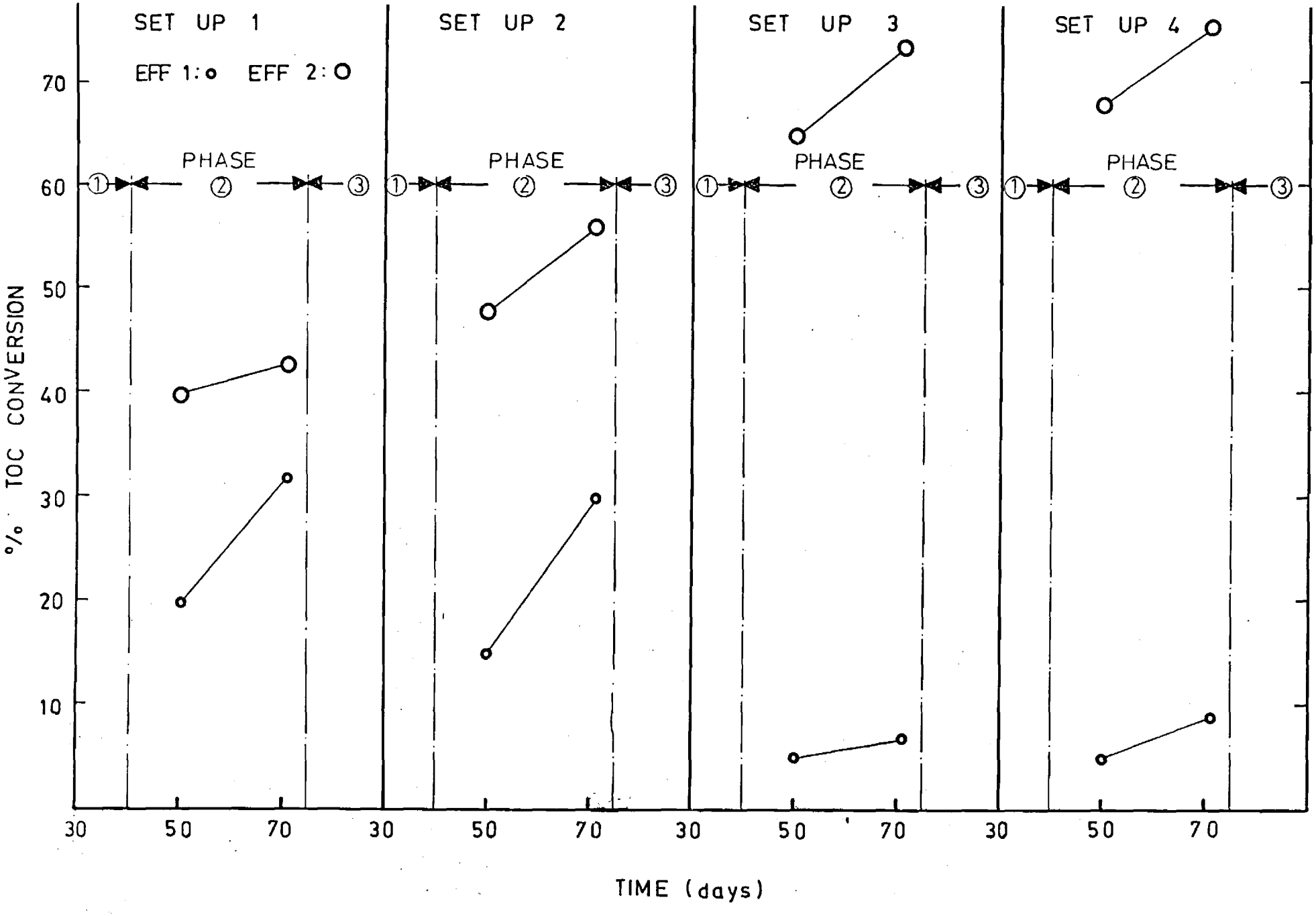
Phase 2

After a measurable amount of gas production was observed the concentration of glucose in the feed was reduced to 200 mg/l. Gross parameters like COD (Figure 8), TOC (Figure 9) and methane production (Figures 10a-d) across each system were measured. An overall reduction in COD of approximately 30% in setup #1 and 37% in setup #2(3330 mg/l Ansul + 2000 mg/l glucose as the 10 x concentrated substrate) is observed (Figure 8). The second stage of both these setups shows an additional 10% reduction in COD over the first stage that is packed with Raschig rings. However, an overall COD reduction of approximately 46% from setup #3 and approximately 58% (3330 mg/l FC-206 + 2000 mg/l glucose as the 10 x concentrate) from setup #4 is observed in Figure 8, whereas the first stages of these setups show a COD reduction of approximately 25% and 36%, respectively. This increased removal of COD is in good agreement with the TOC reduction (Figure 9) and gas production rates (Figures 10 c and d) for setups #3 and #4 in which a drastic reduction of approximately 74% in TOC (Figure 9) and an increased methane production of approximately 8 1/day in the second stage of setup #3 (Figure 10c) and 5 1/day in the second stage of the setup #4 (Figure 10D) are observed. The gas productions in setup #1 and 2 (Figure 10a and b) are comparatively lower. An overall glycol conversion (Figure 11) greater than 95% is observed in the setup #2, 3 and 4 whereas setup #1 shows a 70% overall conversion of glycol. However, the first stages (Raschig ring reactors) of setups #1 and 2 (Figure 11) show a higher glycol conversion (approximately



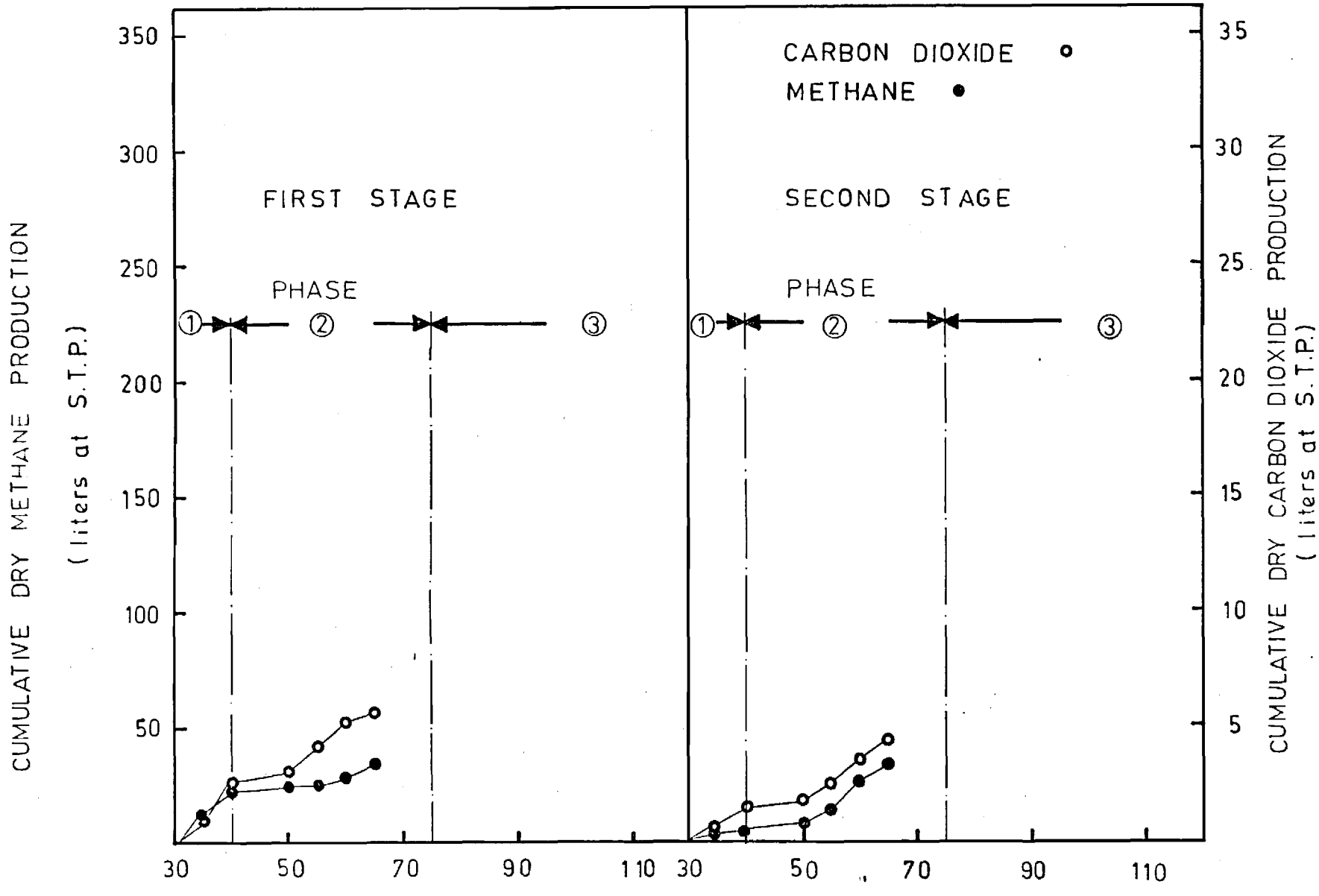
CHEMICAL OXYGEN DEMAND CONVERSION IN TWO STAGE ANAEROBIC FILTE

FIGURE - 8

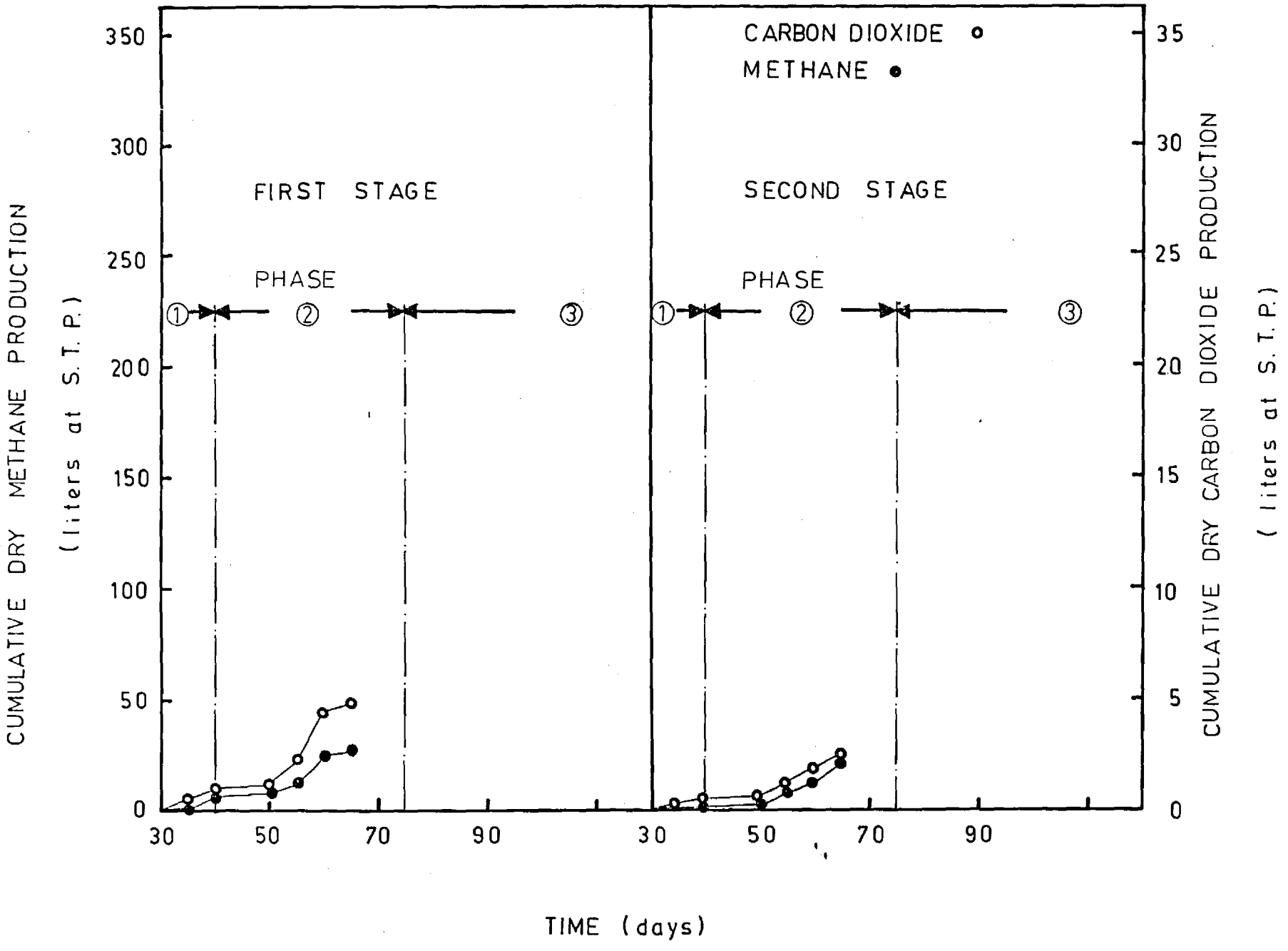


TOTAL ORGANIC CARBON CONVERSION IN TWO STAGE ANAEROBIC FILTER

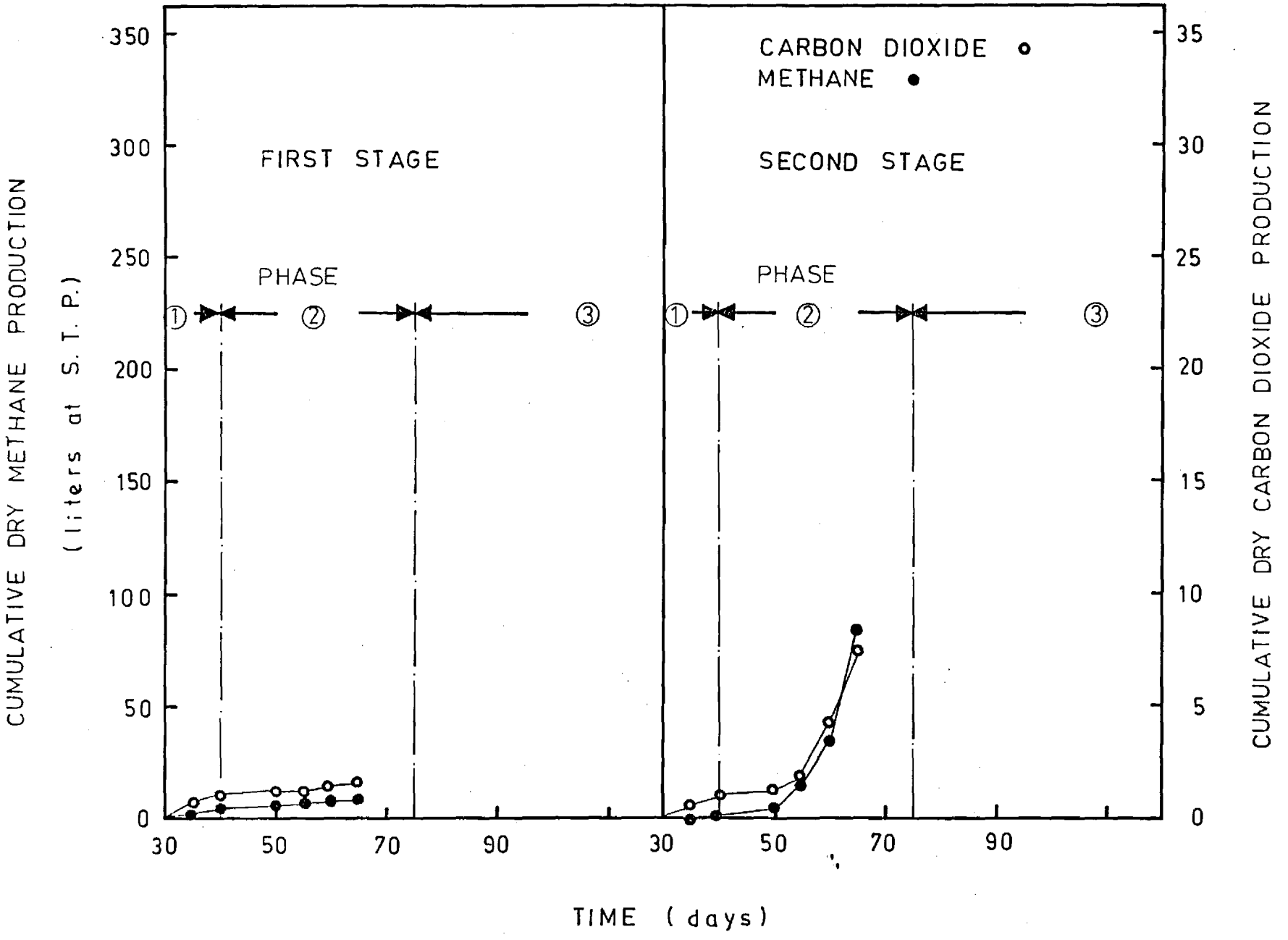
FIGURE - 9



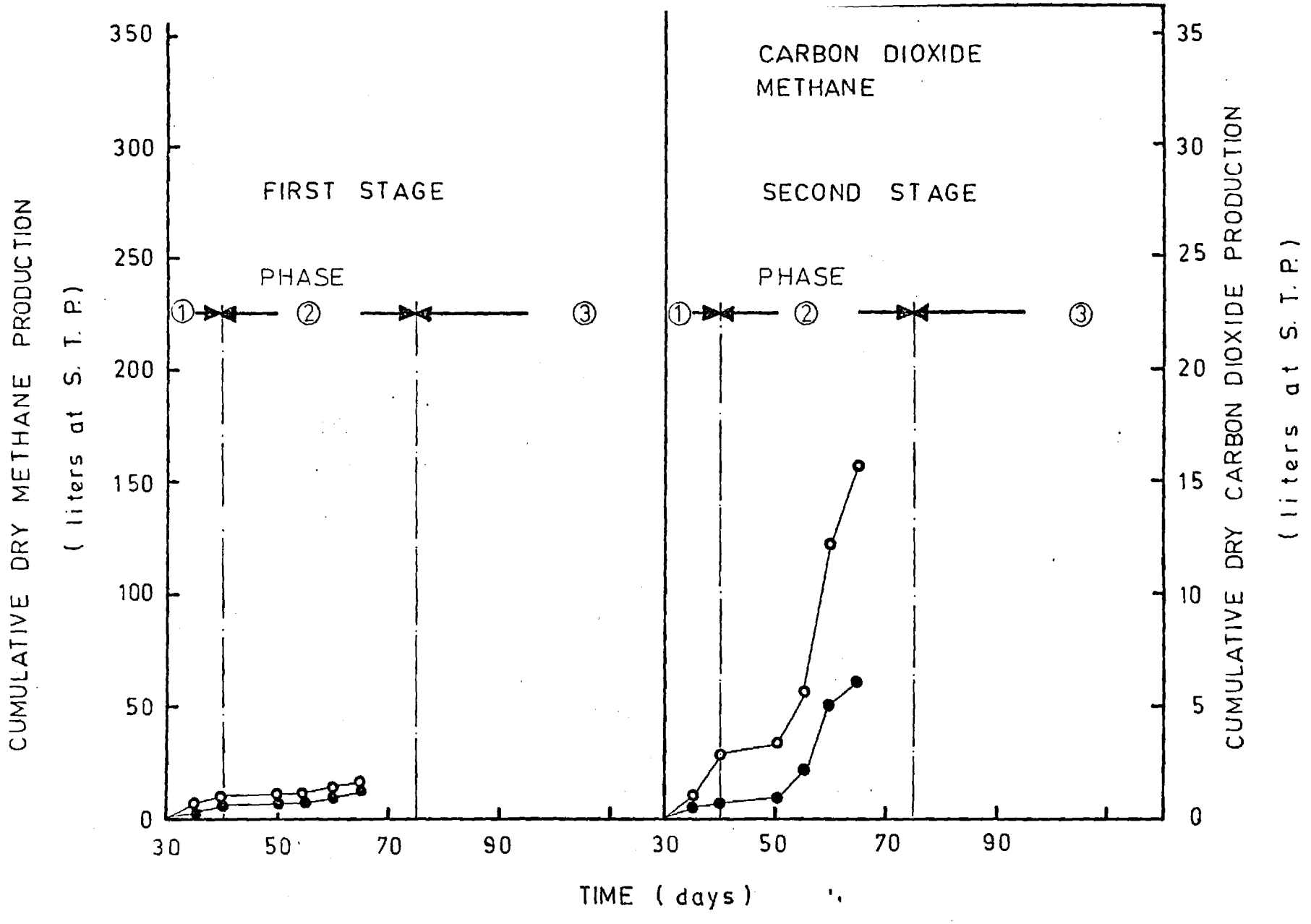
SET UP 1 FIGURE 10 a



SET UP 2 FIGURE 10 b



SET UP 3 FIGURE 10 c



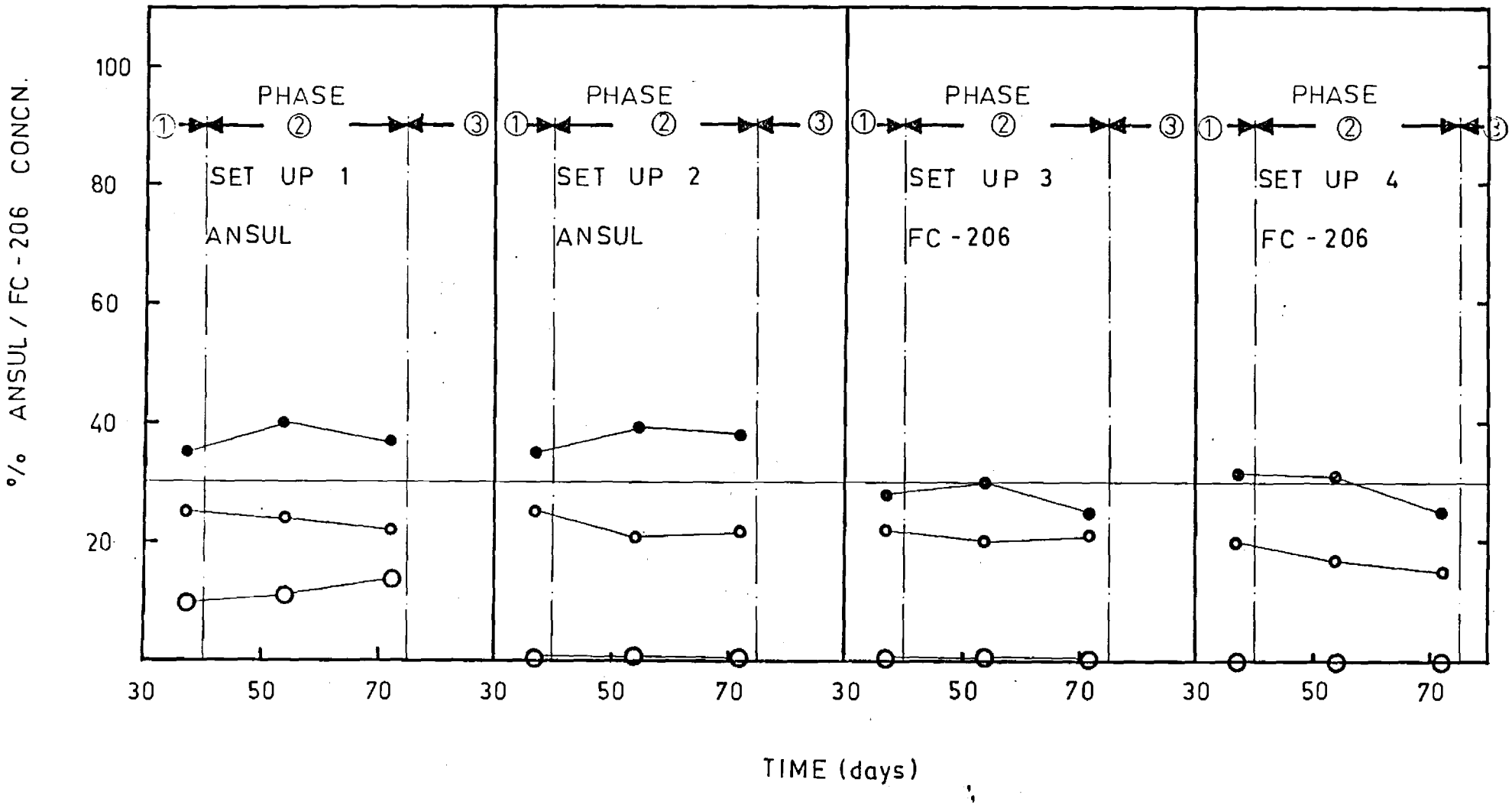
SET UP 4 FIGURE 10 d

50%) than the setups #3 and #4 (19% and 40%, respectively). Results of shake-test for foaming property of the effluents showed approximately 41% foam reduction by the first stage and approximately 97% foam reduction from the second stage of the setups #1 and 2. The effluents from the second stage of setups #3 and 4 showed approximately 96% foam reduction which is comparable to that from setups #1 and 2. However, the second stages of setups #3 and #4 showed a very little foam reduction. Most of the foam reduction was done by the first stages of these setups.

Volatile fatty acid concentration and pH of the effluents from these systems were used to monitor the operation of all four setups. The first stage of all columns showed total volatile fatty acids (TVFA) concentrations ranging from 100 to 200 mg/l. Effluents from the second stage, however, showed trace amounts or absence of TVFA. Acetic acid, propionic acid and butyric acid were the major constituents of TVFA measured. pH of the effluents were in the acceptable range of 6.7 to 6.9.

From the present data, it appears that FC206 shows a better biodegradability as well as carbon adsorptivity. Setups #3 and 4 which are fed with FC-206 show a higher gas production rate (Figure 10c,d), a higher COD reduction (Figure 8) and almost total conversion of glycol (Figure 11) across these systems. The reduction of COD, TOC, glycol and foaming characteristics of the AFFF feed can probably be attributed to the action of both biodegradation and carbon adsorption. The bacteria from the first stage provide the seed for the second stage filled with the fluidized activated carbon. Microorganisms in the second-stage carbon column see a potentially reduced strength of wastes due to:

1. Partial breakdown by the bacteria in the first stage that is packed with Raschig rings; and



GLYCOL CONCENTRATION ACROSS THE NEW SYSTEMS

FIGURE - 11

2. Adsorption of the less readily available substances onto the activated carbon

Phase 3

In view of the promising results obtained in phase 2 of this study, the AFFF concentration of the feed fed to setups #2 and #4 was increased from 333 mg/l TOC to 1000 mg/l of TOC in terms of AFFF concentrations, whereas the glucose concentration is remained unchanged at 200 mg/l. The other two systems were run on the feed containing 333 mg/l TOC of AFFF with no glucose addition. Phase 3 was started on day 45 and is currently in progress at the time of preparing this report.

ANAEROBIC-ACTIVATED CARBON FILTER FOR THE TREATMENT OF AQUEOUS FILM FORMING FOAM (AFFF) WASTEWATER

by

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October 1980

SCHOOL OF CIVIL ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

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FINAL REPORT
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ABSTRACT

The present research effort was directed towards an examination of the effectiveness of a two-stage anaerobic filter in the treatment of wastewaters emanating from firefighting training exercises at military installations. In addition to fuel oil and gasoline, combustion products, and suspended solids, these wastewaters contain the constituents present in the firefighting agent used. Such agents, commonly referred to as Aqueous Film Forming Foam (AFFF) contain various glycols and surfactants in addition to various fluorocarbon compounds.

For the purposes of the present research, five two-stage anaerobic filter treatment systems were constructed. The first column of all units was packed with Raschig rings while all other columns were packed with granular activated carbon.. The granular activated carbon packed columns were fluidized by effluent recycle and the use of activated carbon was believed to result in concentration polarization and toxicity reduction in addition to providing a microbial attachment surface.

Diluted solutions of Ansul and FC-206 AFFF concentrates were fed to these systems. Inorganic nutrients and buffer were added to the feed in order to assure proper operation of the biological system. Feed concentrations varying from 333 mg/l to 1000 mg/l of TOC of these AFFF agents were studied. It was found that a 50% reduction in COD, along with 90% reduction of some of the major constituents, such as the foaming agents and glycols, were accomplished with the two-stage anaerobic system consisting of a fluidized carbon column. A further reduction of 40% COD with no foaming problems was obtained with an aerobic lagoon system receiving effluent from the anaerobic system fed with 1000 mg/l of TOC of a AFFF concentrate.

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SUMMARY

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I. INTRODUCTION

Firefighting training exercises at military installations consume large quantities of water and firefighting chemical agents, and result in intermittent waste streams containing high pollution strength and toxic potential. The firefighting agents as a group are known as Aqueous Film Forming Foam (AFFF). There are currently three major brands of AFFF used by the military: Anusl, 3M FC-206, and 3M FC-780. All three of these are similar in composition. Generally AFFF consists of fluorochemicals and hydrocarbon surfactants, solvents (such as ethylene glycol and its derivatives) and water. During firefighting exercises and equipment function tests, a 3.5% to 6% solution of AFFF concentrate is used alone, or in combination with purple K powder (potassium bicarbonate).

Wastewater generated from firefighting exercises contains the AFFF stock constituents, residual fuel oil and gasoline, combustion products, and suspended solids. All of these constituents are considered to have some adverse impact on the receiving environment. Toxicity studies have indicated that AFFF alone has a 48-hour TLm of 150 ppm (v/v) to oyster larvae (1). Research efforts, therefore, have been directed toward developing an effective method for treating this wastewater.

AFFF concentrate is a costly material, and the treatment of AFFF wastewater has proven to be complex. In a recent study with membrane processes to treat AFFF, Chian et al. (2) demonstrated that all the active ingredients of AFFF concentrate were rejected well by a DuPont B-10 hollow fiber, aromatic polyamide fiber reverse osmosis (RO) membrane, whereas 25% of the foam forming property of AFFF was lost in the brine of the ultrafiltration (UF) membrane using Abcor's HFK and HFJ tubular modules. The firefighting properties of the AFFF constituents recovered by the UF/RO

processes were quite encouraging. An economic analysis of the recovery system indicates that the return on investment could be as short as two months with a 6% AFFF wastewater. However, in order for the membrane process to be economically attractive, a concentration of at least 1.5% of AFFF active constituents in wastewater should be present. For a less concentrated wastewater, e.g., containing less than 1% AFFF active ingredients, other less capital intensive treatment processes should be investigated. The present research effort was directed towards an examination of the effectiveness of an innovative two-stage anaerobic filter system in the treatment of wastewaters emanating from firefighting training exercises at military installations. In addition to the AFFF constituents, fuel oil and gasoline, combustion products, and suspended solids are known to be present in the firefighting wastewater. The latter are however, not included in this study.

For the purposes of the present research, five two-stage anaerobic filter treatment systems were constructed. The first column of all units was packed with Raschig rings, while all other columns were packed with granular activated carbon. The granular activated carbon packed columns were fluidized by effluent recycle. The use of activated carbon is believed to result in concentration polarization and toxicity reduction in addition to providing a microbial attachment surface. These systems were fed with dilute AFFF solutions of varying concentrations fortified with a necessary amount of inorganic nutrients as well as buffers.

II. RESEARCH OBJECTIVES

Chian et al. have demonstrated the feasibility of treating the high-strength AFFF wastewater by membrane processes (2). For a low-strength AFFF wastewater other treatment alternatives should be investigated. This wastewater, however, cannot be treated by direct aerobic biological treatment due to the stable nature of the foam formed during aeration. The objective of this study was to examine the treatability of low-strength AFFF wastewaters with a two-stage anaerobic filter system. The first-stage filter, filled with Raschig ring as a contact media, served as a roughing filter and a fatty acid generating unit, whereas the second-stage unit containing fluidized granular activated carbon (GAC) was used for further treatment of the waste. The adsorptive properties of the GAC would tend to enhance methane fermentation.

The performance of these systems were evaluated as related to its reduction in the conventional parameters (COD, TOC and methane generation) as well as its reduction in the glycol and foaming ability. A final-stage aerobic lagoon system was used to polish the effluent from the anaerobic filter.

III. MATERIALS AND METHODS

Two types of experimental systems were employed in this study. One anaerobic system was constructed with Raschig rings serving as a contact medium in the first column while the second column equipped with effluent recycle was packed with granular activated carbon (GAC), Figure 1. Four additional units were constructed in a similar manner, however, in this instance both columns of each reactor system were equipped with effluent recycle and both were packed with GAC.

Feed Pumps. The AFFF was diluted with distilled water to any desired concentration in a 20-ℓ concentrate reservoir (Figure 1). This diluted substrate was fed into the reactor using a positive displacement FMI pump, Model RP G-20 (Fluid Metering Incorporated, Oyster Bay, NY) having a maximum flow rate of 5.4 ml/min and a maximum operating pressure of 50 psi. No other nutrients are added to this reservoir in order to prevent any biodegradation within the reservoir and the feed lines.

Dilution water containing the phosphate buffer and ammonium nutrients necessary for active biodegradation are pumped from another 55-ℓ reservoir using a positive displacement pump Model RP G-150 (Fluid Metering Incorporated, Oyster Bay, NY). This pump has a maximum flow rate setting of 96 ml/min and a maximum operating pressure of 20 psi. The flow from the two reservoirs is mixed in a tee connection prior to entry into the first-stage anaerobic filter.

Raschig Ring Packed Anaerobic Filter. This filter consists of a water jacketed plexiglas column having the following features:

i. inner column (10.1 cm in internal diameter by 182-cm long) which served as the actual roughing anaerobic filter chamber.

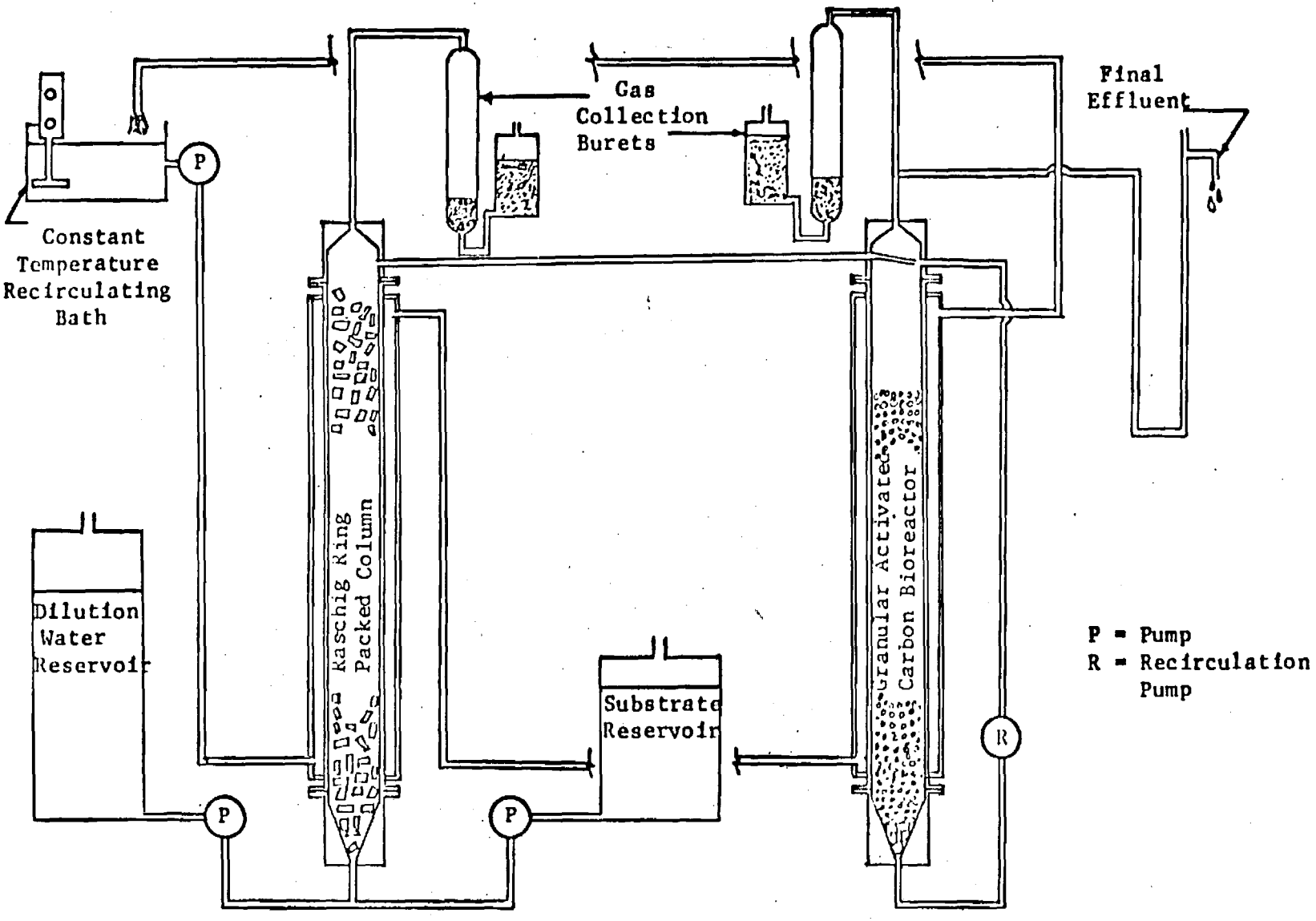


Figure 1. Schemetic Diagram of Raschig Ring - Granular Activated Carbon Packed Two-Stage Anaerobic Bioreactor

ii. a water jacket (15.25 cm in internal diameter by 170-cm long) which allowed the unit to be operated at a constant and controllable temperature through the circulation of water from a constant temperature bath (Model T31, HAAKE, Inc., Werk Karlsruhe, West Germany) around the jacket.

iii. influent header was constructed using a plexiglas column section and plates and its inner structure, which is 20-cm long, was tapered into an inverted conical shape in order to allow for better distribution of the influent flow. This unit was equipped with a perforated plate to allow for the introduction of the mixed feed solution.

iv. effluent structure: a conical shape structure was used to minimize the trapped gas volume and is equipped with fittings for connection to the gas collection system, connection to the effluent structure from this unit and a sampling port.

v. gas collection system consisting of two 4.5-ℓ gas burets, two leveling bottles and sampling ports to allow for monitoring both the quantity and composition of the gaseous products produced and releasing the excess gas produced.

Granular Activated Carbon Packed Filters. This unit was identical in structure to the roughing unit except that it was equipped with a 1/3 HP centrifugal pump in the previously operating unit and a 1/2 HP centrifugal pump in the four new units (Teel Pump, Dayton Electric Manufacturing Company, Chicago, Ill.). The purpose of this pump was to recirculate the aqueous contents of the carbon filled filter, and to maintain this carbon fluidized in order to minimize gas trapping onto the carbon. Details of the recirculation system are presented in Figure 2. The recirculation flow rate of the anaerobic granular activated carbon packed filter can be adjusted through

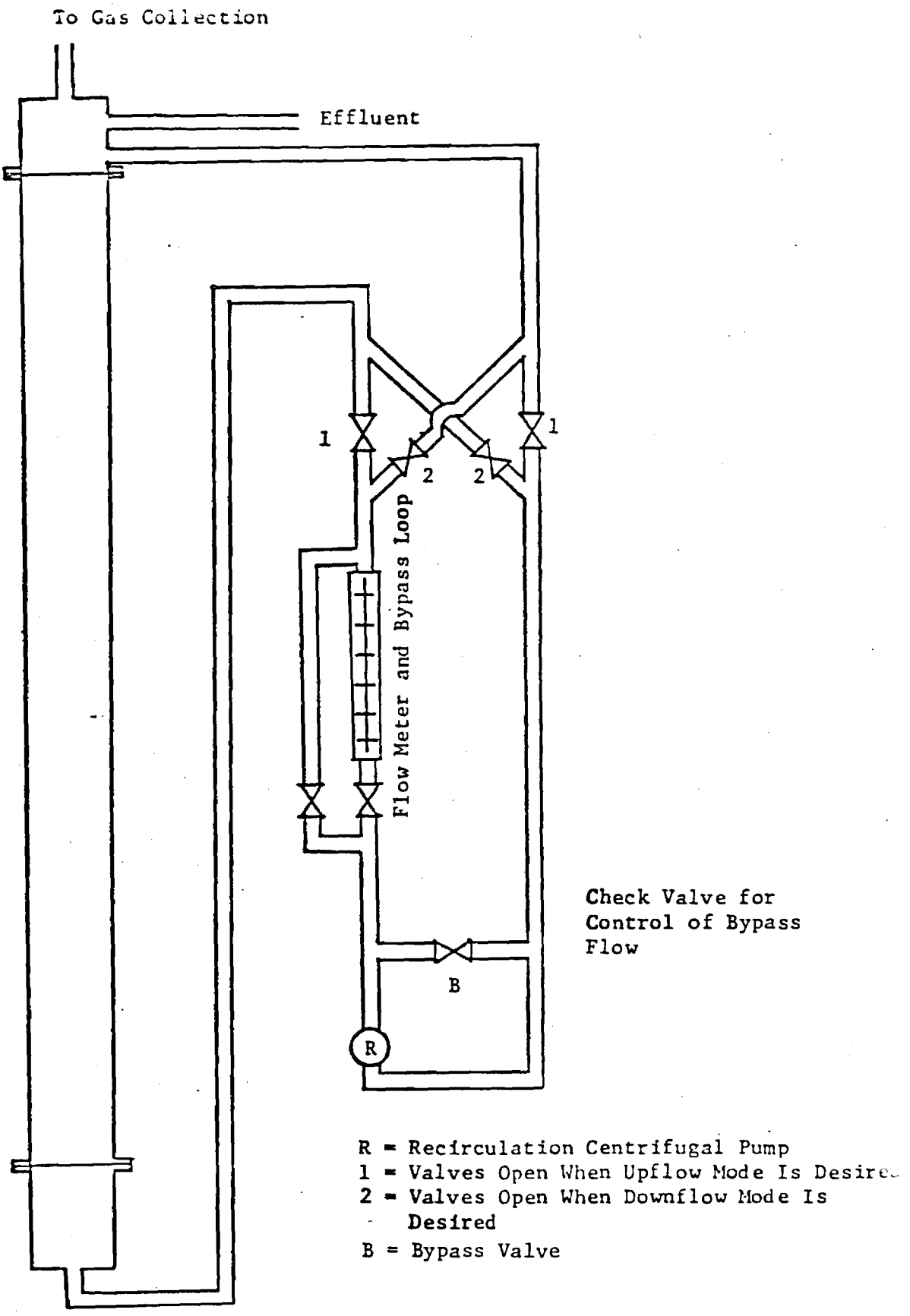


Figure 2. Schematic of Effluent Recirculation System

the control of the by-pass valve (B) as shown in Figure 2. This was necessary in order to determine the minimum recirculation flow rate which would allow for economic and efficient operation of the system.

FILTER MODIFICATIONS

To avoid the problems encountered in carbon plugging of the recirculation system, the following modifications were made. Figure 3 shows the schematic diagram of the modified system.

1. Drain valves (DV) were inserted into the inlet port at the base of each column.
2. The GAC in the first column was replaced by Raschig rings.
3. An outlet with a removable cap (BV) was placed at the top of the recirculation line in order to allow the column to be backwashed and the backwash water to be discarded.
4. An additional sampling valve (SV) was attached to the top of the first column.
5. A stainless steel screen (S) was placed inside the upper portion of the second column in order to retain all activated carbon within the column, since during the period of low liquid recirculation, gas binding of carbon particles tended to lift the particles upward and plug the recirculation line.

FILTER CONTACT MEDIA

The roughing anaerobic filters of all the five systems were packed with 1.27-cm (0.5 inch) Raschig rings to a depth of 193 cm (6.33 ft). The packed columns have approximately a porosity of 58% and a specific surface area of 337 m^2/m^3 (103 ft^2/ft^3). Because of its relatively high porosity and surface area, this packing is ideal for the roughing filter where a high growth rate and sludge accumulation are anticipated.

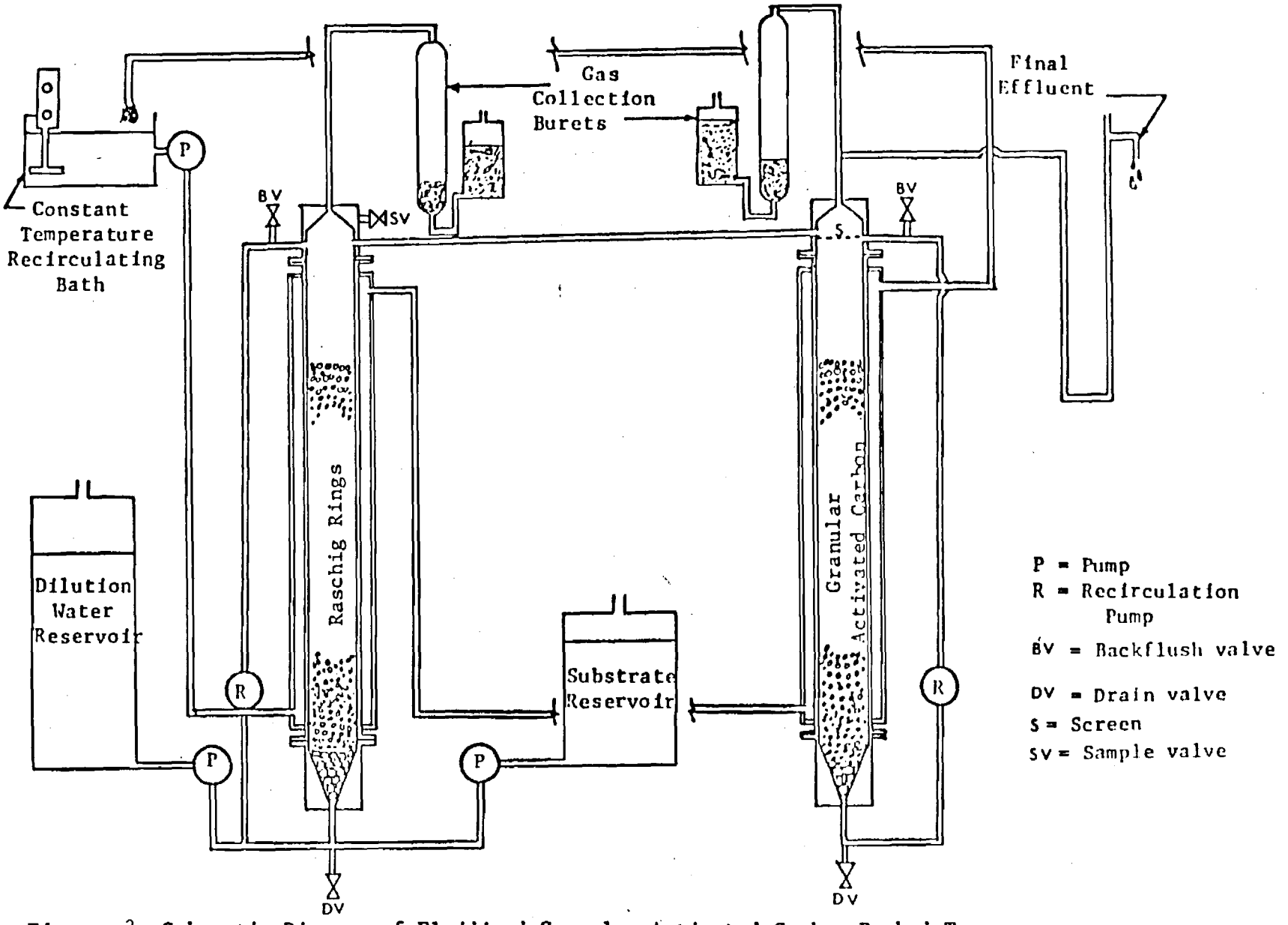


Figure 3. Schematic Diagram of Fluidized Granular Activated Carbon Packed Two Stage Anaerobic Bioreactor

The second-stage activated carbon filter of all the five systems were packed with an initial GAC depth of 128 cm (4.20 ft) and backwashed down to a depth of 100 cms (3.28 ft) in order to eliminate carbon fines. The activated carbon used in this study was Calgon FMC 6 x 16 U.S. mesh size with an average particle size of 2.27 mm. However, after backwashing, a larger average particle size was retained in the filter. The second filter columns of the four new setups were packed with 2.5 Kg of Calgon FMC 6 x 16 U.S. mesh size granular activated carbon and backwashed to a depth of 115 cm.

The columns of an old system were seeded with an anaerobic sludge from the underflow of an anaerobic digester at the Atlanta Clayton Sewage Treatment Plant; and the columns of the new system, following the modifications listed before, were seeded with primary anaerobic digester sludge from the same source.

The dilution water reservoir was filled to capacity with dechlorinated and deaerated tap water to which nutrients and a phosphate buffer were added. In addition to serving as a nutrient, the phosphate mixture was designed to provide a buffer to the waste at the desired operating pH. The levels of phosphate, ammonium and additions of other nutrients were higher than what was estimated to be needed for the successful operation of the system. The concentration of the various nutrients in the dilution water reservoir are give in Table 1. The flow rate of the dilution water was set at 9.0 ml/min while the concentrate flow rate was set at 1.0 ml/min such that the feed concentration to the first column will be only 10 percent of the stock concentrate.

The flow rate of 10 ml/min was selected in order to provide an empty bed contact time of 24 hours in each of the reactors.

SYNTHETIC FEED SUBSTRATE

The synthetic feed substrate to the old anaerobic filter system was prepared in two separate solutions. The AFFF Ansul was selected as the first AFFF concentrate to be studied. A solution of AFFF and distilled water was prepared in 20ℓ batches and fed to the anaerobic filter.

A dilution water solution was also fed to the columns from a separate 55ℓ reservoir. In addition to serving as a dilution water, this solution also contained biological nutrients, ammonium chloride and a phosphate buffer. The concentration of the constituents of the growth nutrients in the dilution reservoir was maintained at the levels indicated in Table I. In addition to these nutrients, additional ammonium chloride and a phosphate buffer were added and their strengths are presented along with the operating data in Table II.

With the addition of four more systems, AFFF FC-206 concentrate was also studied along with the AFFF Ansul. Varying TOC loading conditions of these two AFFF concentrates were simultaneously studied in the four new systems designated later in the report as, Setup 1, 2, 3 and 4.

A TOC loading of 330 mg/l Ansul was applied to Setup 1, whereas a higher TOC loading of 1000 mg/l of Ansul along with 2000 mg/l of glucose was applied to Setup 2. Setup 3 and 4 were loaded similarly but with AFFF FC-206 concentrate. These were the conditions for the phase I acclimation period. After the acclimation period, glucose was eliminated from feeds to Setups #1 and 3 and reduced to 200 mg/l to Setups 2 and 4.

TABLE I. Concentration of Nutrients in Buffer Solution

Compound	Concentration (mg/l)
$FeCl_3 \cdot H_2O$	4.83
$MnCl_2 \cdot 4H_2O$	0.71
$Zn\ Cl_2$	0.49
$CoCl_2 \cdot 6H_2O$	0.43
$Na_2B_4O_7 \cdot 10H_2O$	0.17
$Na_3C_6H_5O_7$ (sodium citrate)	26.33
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.31
KH_2PO_4	60.98
$NaH_2PO_4 \cdot H_2O$	37.09
$(NH_4)_2SO_4$	23.66
NH_4Cl	112.00
$CaCl_2 \cdot 2H_2O$	26.55
$MgCl_2 \cdot 6H_2O$	36.42
Vitamin Extract*	0.16 ml

*The Vitamin Extract was prepared by adding 10 grams of a multivitamin to 333 ml of 95% ethanol and 667 ml of distilled water. The solution was allowed to stir for 10-12 hours at 60°C, settled for 24 hours and decanted. The decanted solution was the vitamin extract.

TABLE II. Operating Conditions for Two-Stage Anaerobic Filter

Phase No.	Duration (days)	Empty Bed Contact Time (hours)	Flow Rate (ml/min)	Influent TOC Total (mg/l)	Influent TOC AFFF-TOC (mg/l)	Buffer Phosphate Content (m/l)	NH_4Cl Content (mg/l)
1	26	12/filter 24 total	20	1000	1000	-	153
2	24	24/filter 48 total	10	1133	333	0.1	306-1030
3	24	24/filter 48 total	10	733	333	0.06	611
4	12	24/filter 48 total	10	533	333	0.06	611-397
5	65 total 35 in operation	24/filter 48 total	10	867	667	0.06	680
6	13	24/filter 48 total	10	1200	1000	0.06	890
7	19	24/filter 48 total	10	1080	1000	0.03	840
8	Ongoing	24/filter 48 total	10	1000	1000	0.01	840

ANALYTICAL METHODS

pH

The pH of the influent and effluent was measured immediately after sample withdrawal using a Fisher Accumet pH meter, Model 144 (Pittsburgh, Pa.).

TIC and TOC

The total inorganic carbon (TIC) and the total carbon (TC) of the influent substrate and effluents from all of the columns were measured using a Beckman 915 Total Organic Carbon Analyzer (Fullerton, CA). All samples were filtered through a 1-μm Gelman membrane filter (Ann Arbor, Mich.) prior to the analysis. The TOC content of the samples was subsequently determined as the difference between TC and TIC.

COD

The chemical oxygen demand (COD) of the organic matter present in the feed and effluents from all columns was determined by the COD test as described in Section 508 of Standard Methods for Examination of Water and Wastewater, 14th Edition (1975). All samples were filtered through a 1-μm Gelman membrane filter prior to analysis.

Gas Analysis

Gas analyses were performed on a Fisher Model 25V Gas Partitioner, using certified calibration standards (Matheson, East Rutherford, NJ) in conjunction with a Fisher Thermal Stabilizer Model 27 and a Coleman Recorder, Hitachi 165 (Pittsburgh, Pa.). Helium was used as the carrier gas. The helium carrier column was a 76.2-cm (30 in) long aluminum column with a 0.64-cm (0.25 in) outer diameter. This column was packed with 30% diethylhexylsebacate on 60 x 80 mesh columnpak followed by a 183-cm (6 ft) long by 0.48-cm (0,188 in) O.D. aluminum column packed with 5A molecular sieve 60 x 80 mesh. The helium gas flow rate was set at 80 ml/min.

Glycol Analysis

Glycol analysis was performed on a Perkin Elmer Sigma I Gas Chromatograph. The column used was a 183-cm (6 ft) long by 2-mm I.D. glass column packed with 10% Carbowax 20 M on 80/100 Chromasorb W. Chromatographic conditions were: injection temperature 250°C, injection volume 1 microliter, detector temperature 300°C, oven temperature 160°C isothermal for five minutes followed by a temperature program which raised the temperature to 200°C at a rate of 10°C/min. Temperature was held at 200°C for 3 minutes resulting in a total run time of 12 minutes. A hydrogen flow rate of 30 ml/min, 240 ml/min of air and 30 ml/min of a helium carrier gas were employed; standard curves for the two AFFF concentrates are included in Figures 4, 5a and 5b.

Shake Test

The foaming property of the samples was used to approximate the surfactant concentration. The foaming property was determined by the method commonly referred to as the shake test. This determination consisted of placing a 100-ml sample in a 250-ml graduated cylinder with a secured fitting glass stopper. The sample was then shaken vigorously for 30 seconds and allowed to settle for 5 min, after each time the foam volume in ml was recorded. The result of this method can be represented by the volume of foam. The shake test has been used successfully in the membrane treatment process to replace the less reliable fluorocarbon determination. However, the validity of using the shake test to monitor the surfactants in the anaerobic filter process is yet to be determined.

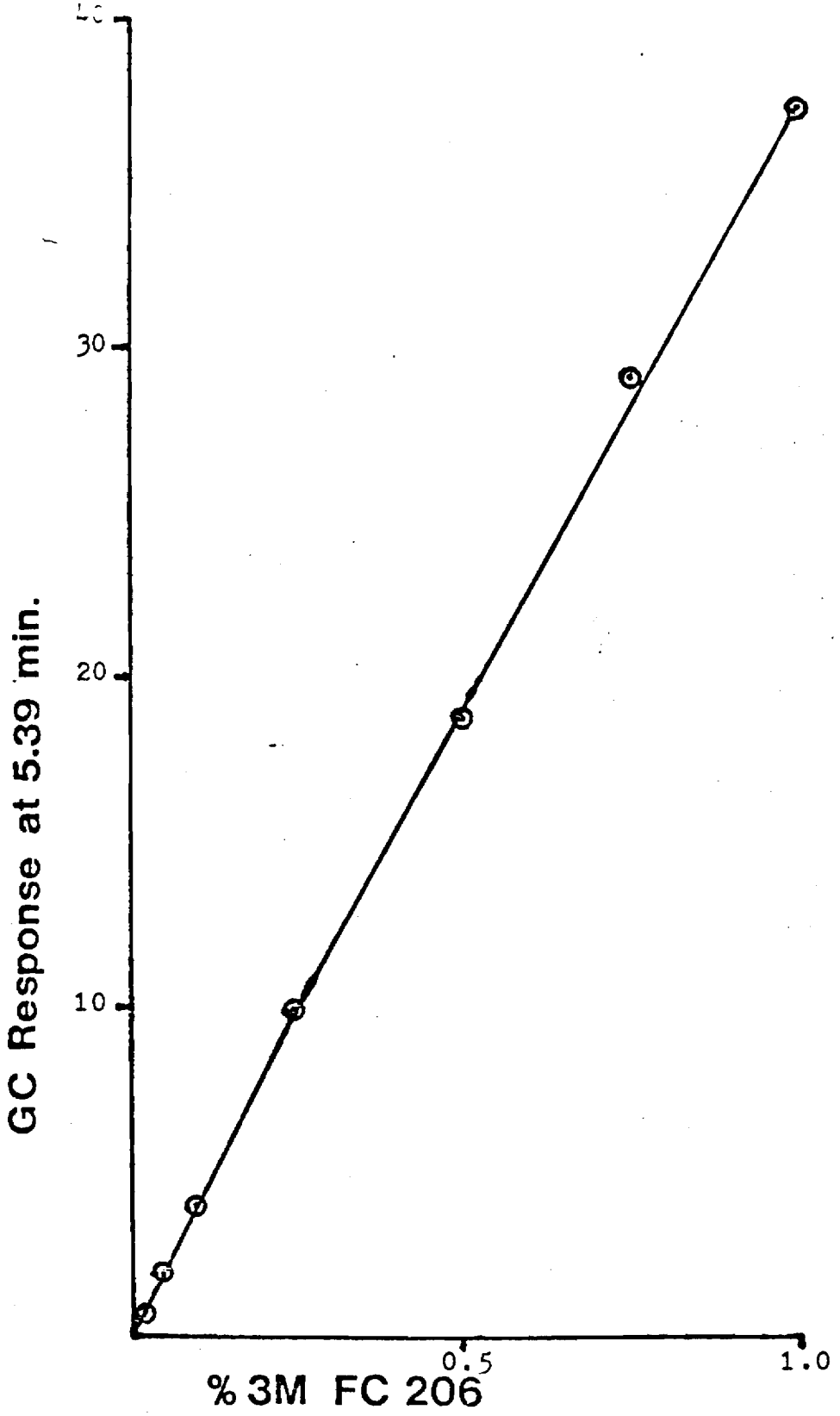


FIGURE 4 - Glycol Determination 3M FC 206 Standard Curve

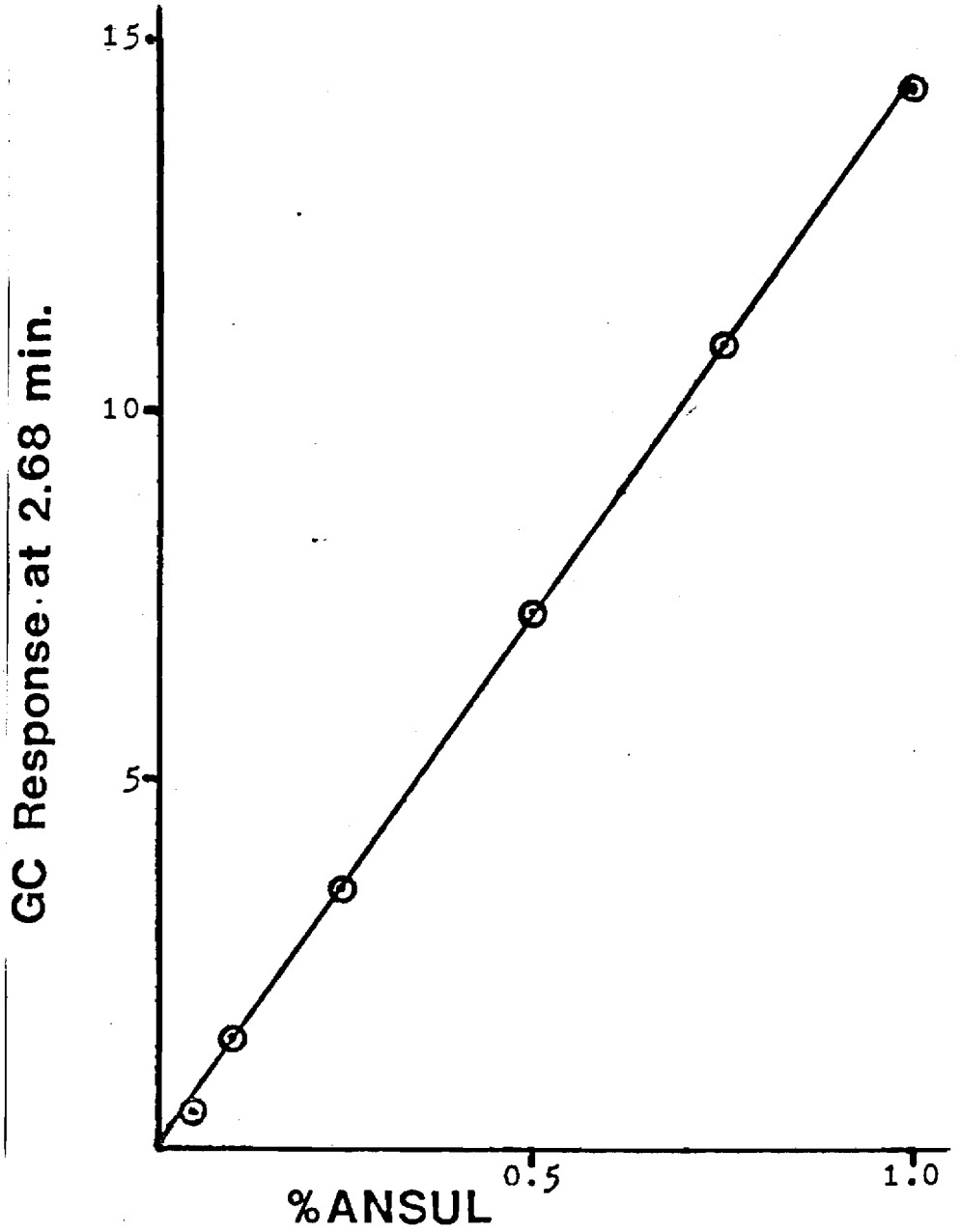


FIGURE 5a- Glycol Determination ANSUL Standard Curve

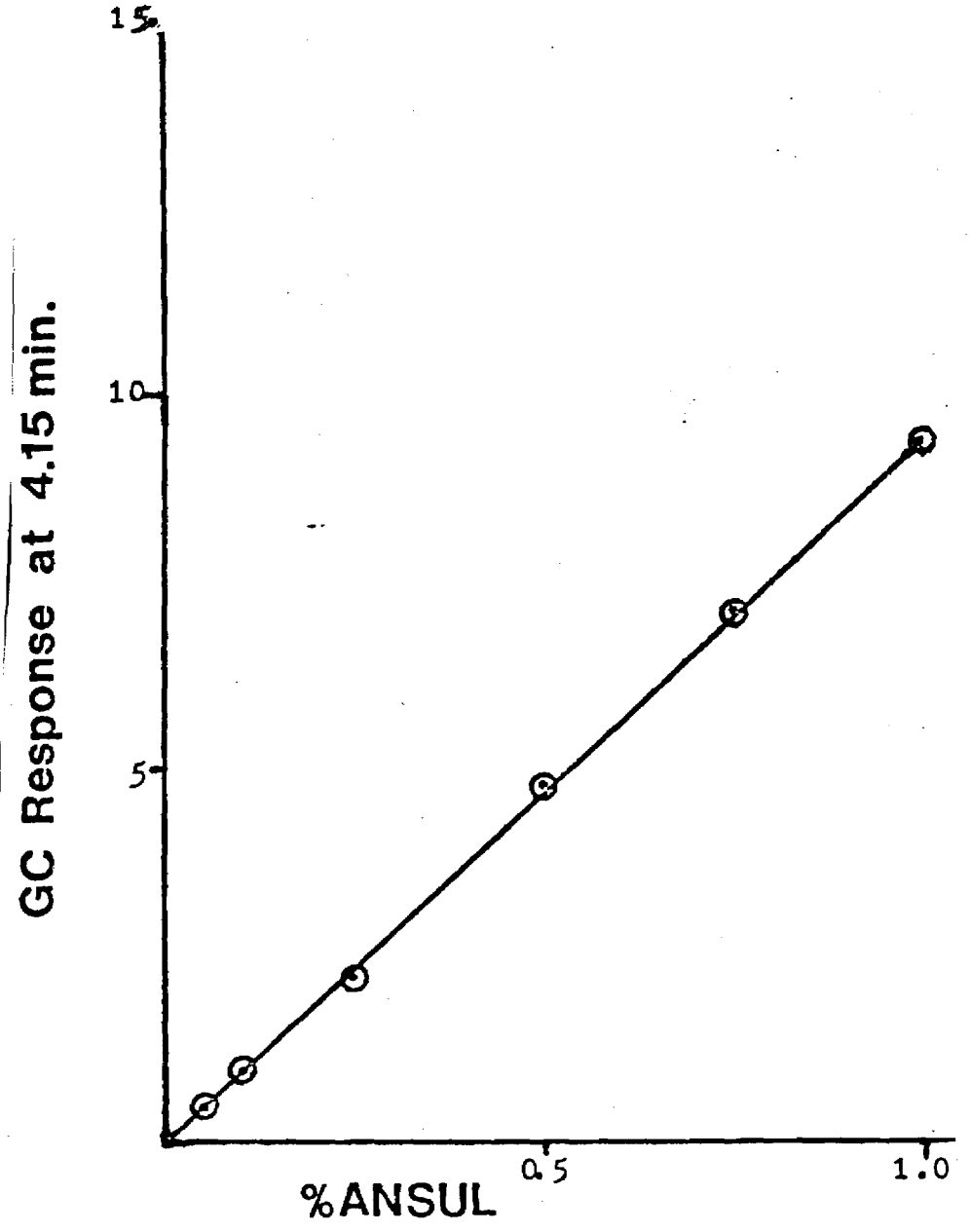


FIGURE 5b- Glycol Determination ANSUL Standard Curve

IV. RESULTS AND DISCUSSION

Old System

After 254 days of continuous operation of the old system in phase-8 (1000 mg/l TOC totally attributed to AFFF Ansul, Table II), an apparent steady-state condition was achieved in terms of COD and glycol conversion, as well as methane production. Approximately 40-44% total COD conversion has been consistently observed from the day 354 onwards (Figure 6). An overall glycol conversion of 80% has been observed consistently in the effluent from the second-stage reactor as shown in Figure 7. Methane production rate of 0.15 ℓ/day was observed from the first-stage reactor during the initial period of Phase 8, upto day 280. This rate increased to 0.35 ℓ/day between day 345-355 of continuous operation and again dropped back to 0.22 ℓ/day. After that it is observed as approximately remaining constant up to day 451 of continuous operation (Figure 8). The second stage of the treatment system show a relatively constant and high rate of methane production (Figure 9) at 3.1 ℓ/day during the period from day 270 to day 355, and at 2.8 ℓ/day during the period from day 355 to day 451 of continuous operation. A total consumption of volatile acids was observed in the second stage, however, a volatile acids concentration of less than 150 mg/l was observed in the first stage. The results of the shake test showed approximately 38-40% reduction of foam by the first stage and approximately 80-82% reduction of foam by the entire system. A reduction of 40-45% TOC was observed from the second-stage reactor effluent. Since the Phase-8, starting from day 183, was in continuous operation for 254 days in the absence of glucose addition, the glycol and foam contents are solely attributable to the anaerobic degradation mediated by the carbon adsorption.

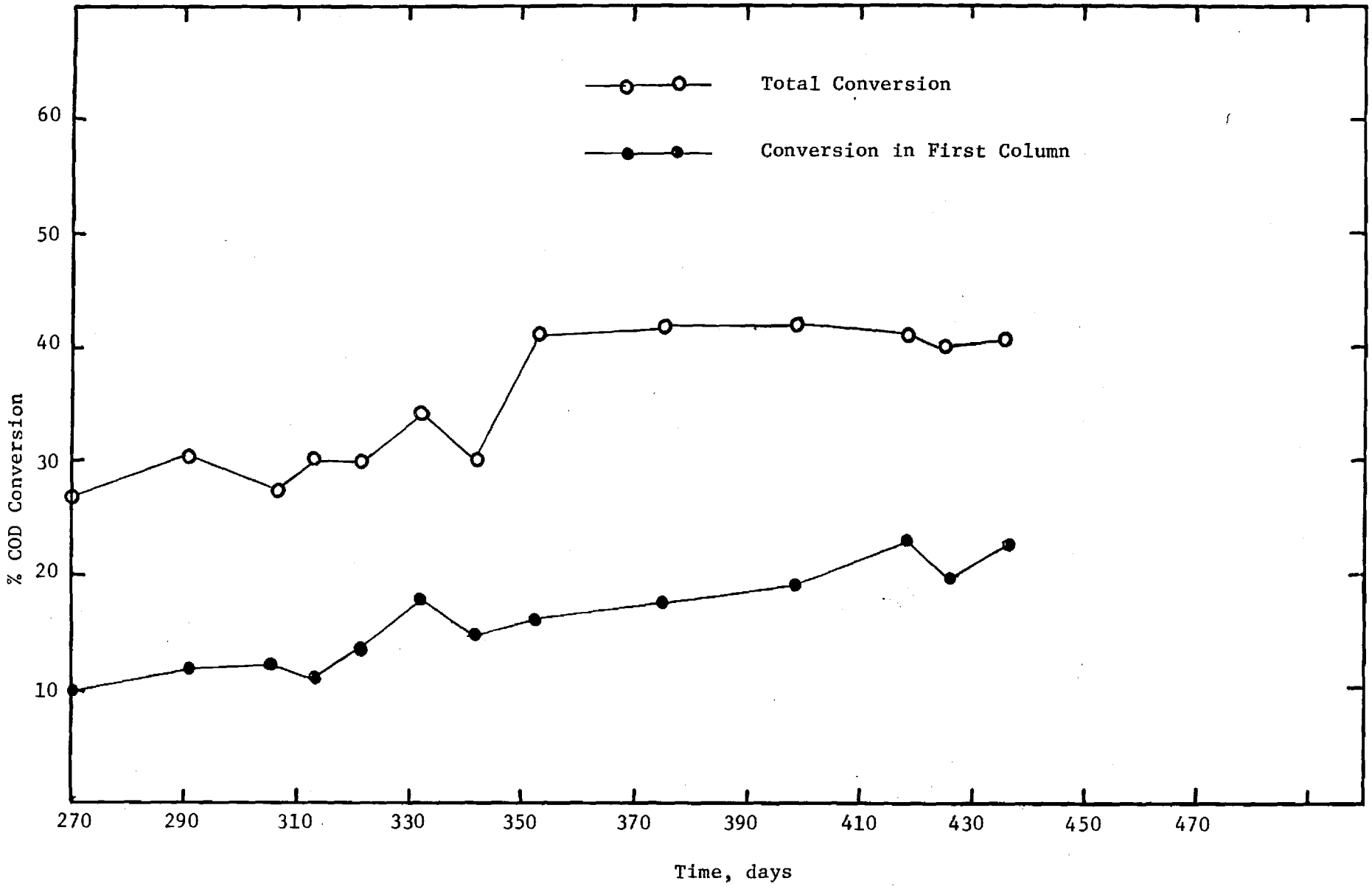
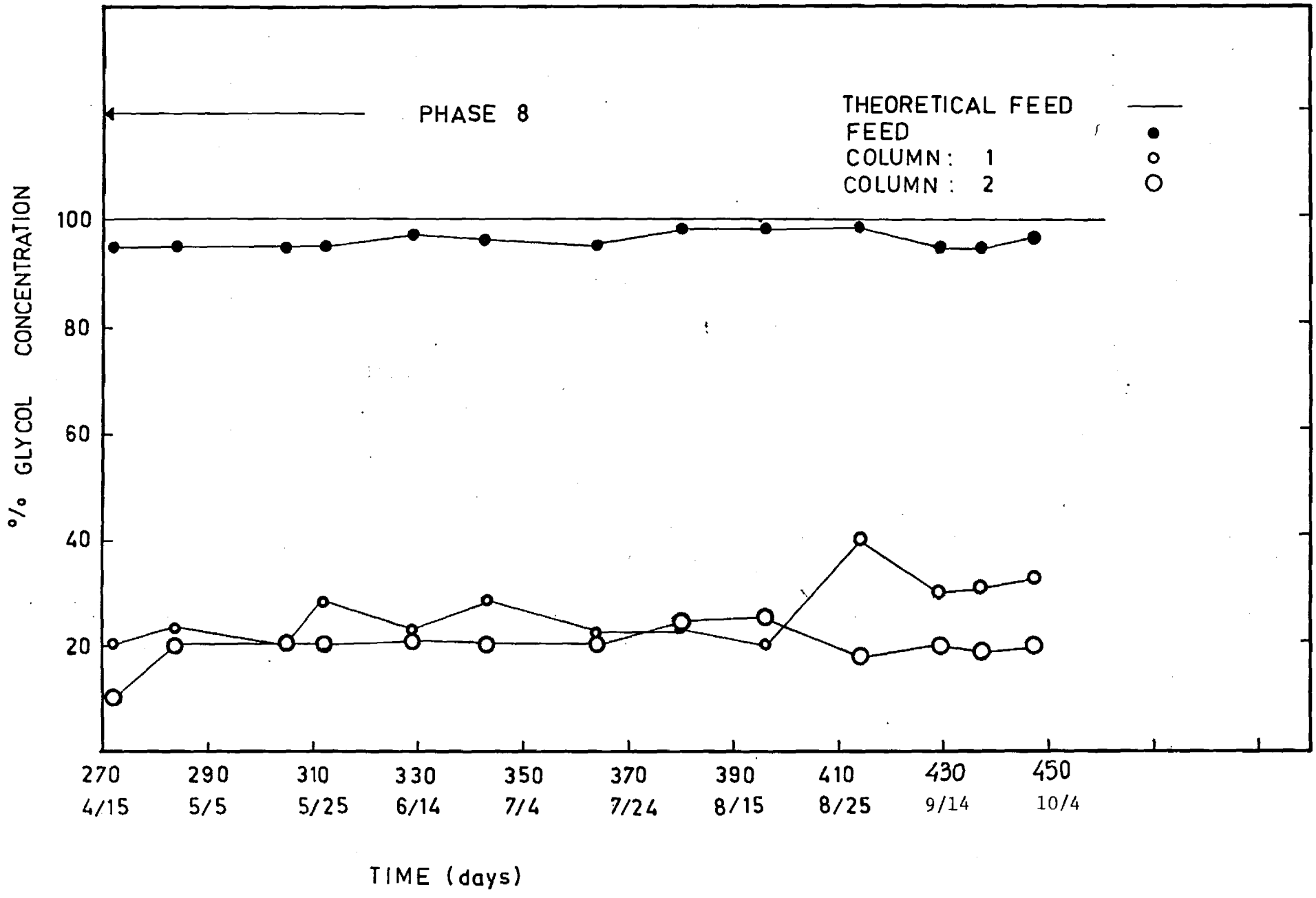


Figure 6. COD Conversion Across the System



GLYCOL CONCENTRATION ACROSS THE OLD SYSTEM

FIGURE 7

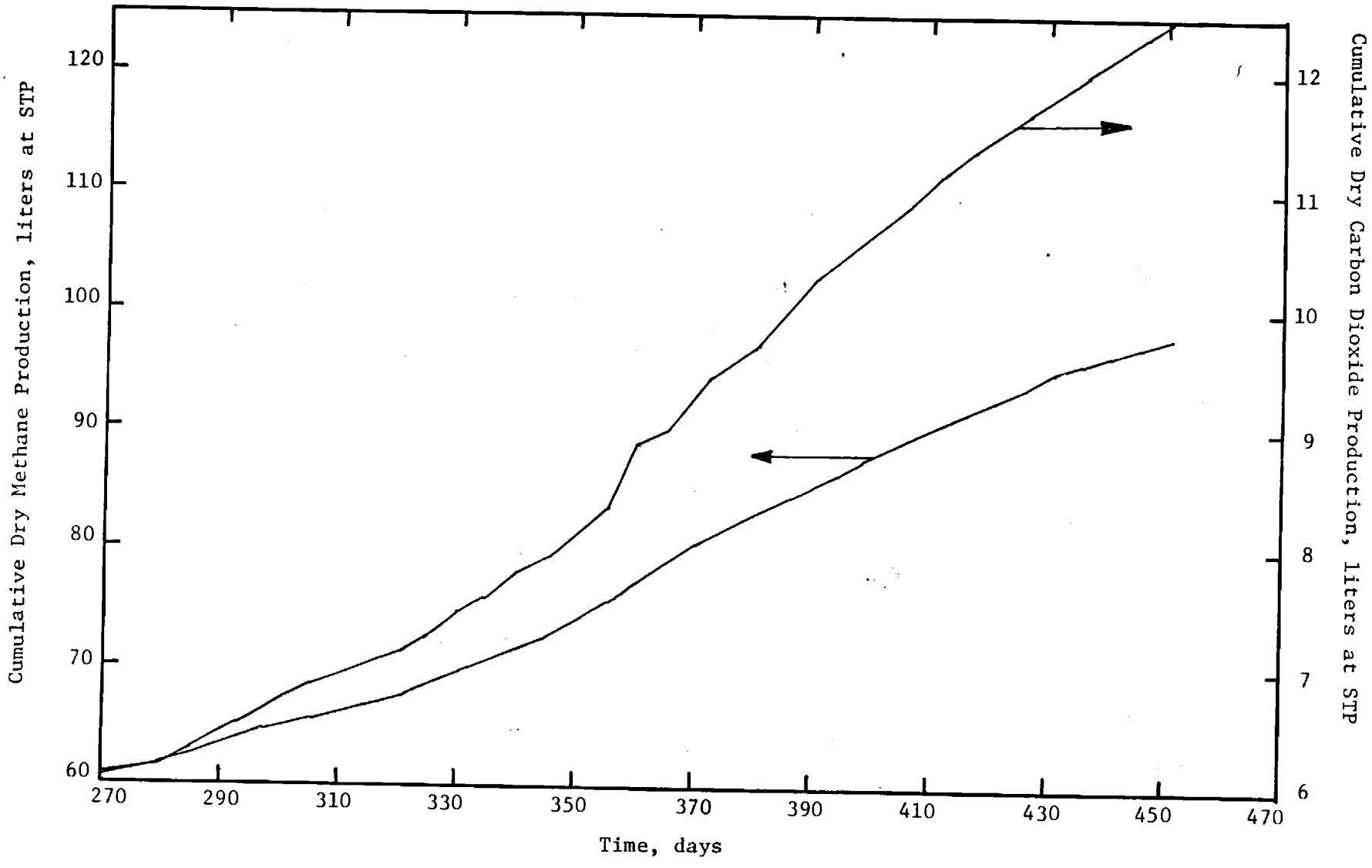


Figure 8. Methane and Carbon Dioxide Production from the First-Stage Anaerobic Filter

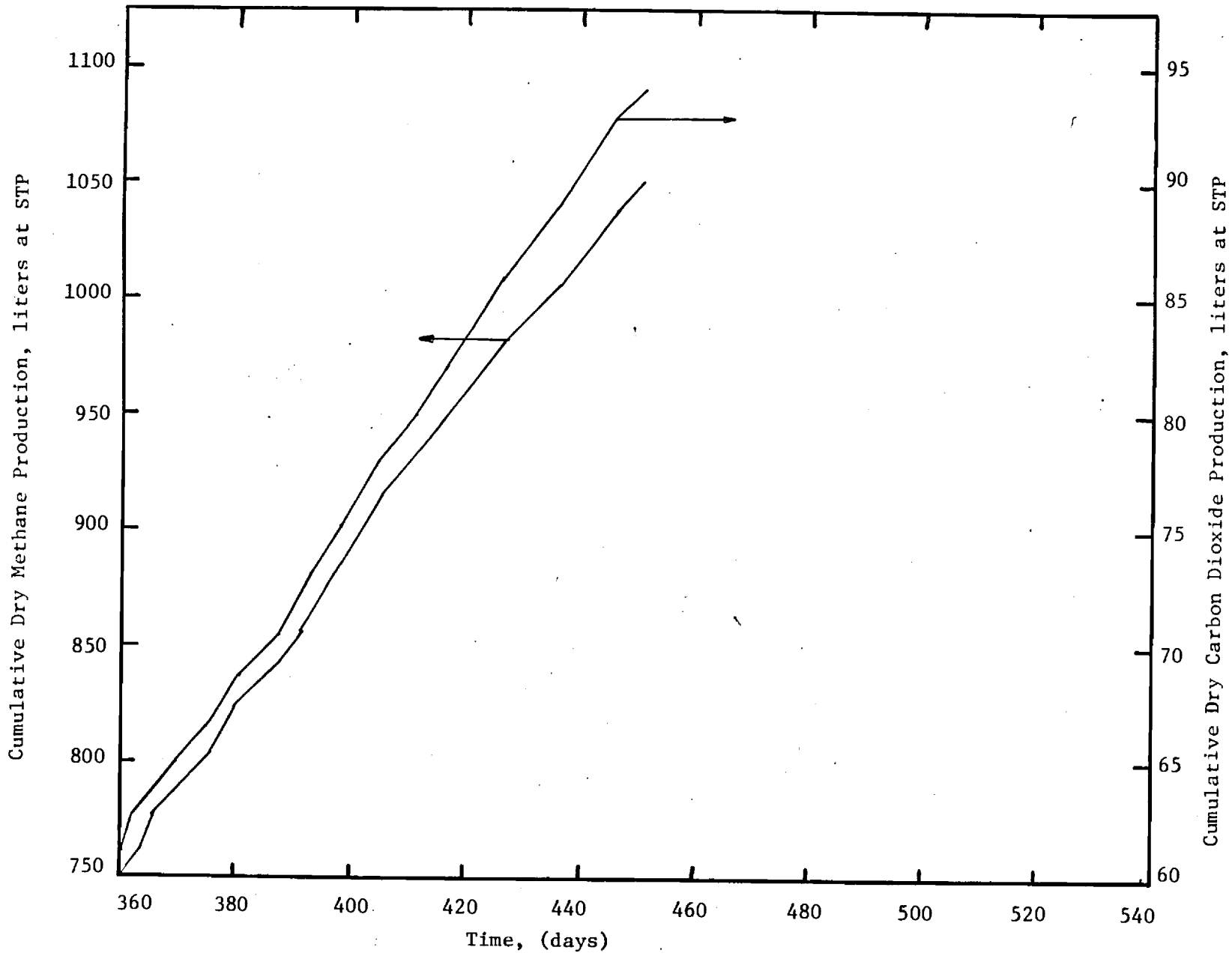


Figure 9. Methane and Carbon Dioxide Production from the Second Stage Anaerobic Filter

Two-Stage Aerated Lagoon

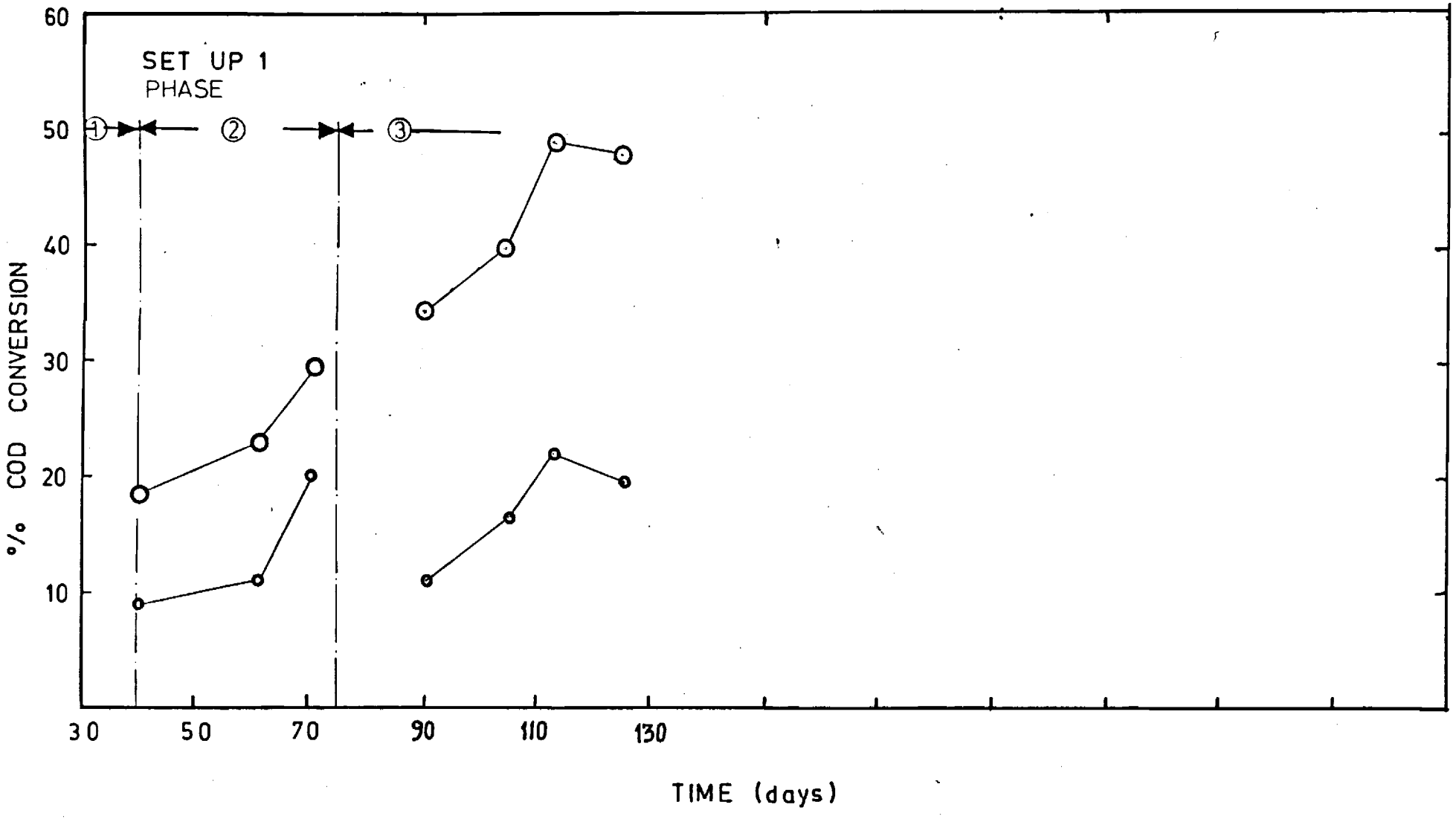
The effluent from the second stage of the old anaerobic carbon filter was fed to a two-stage aerated lagoon. A 50% COD reduction across the two-stage aerated lagoons was realized. Thus resulting in a total overall reduction of COD to approximately 75-80% across the entire anaerobic/aerobic system consisting of two anaerobic filters and two aerated lagoons in series. A substantial reduction in foam was observed in the second stage of the aerated lagoon. Quantitative data on the two-stage aerated lagoon system will be presented in the future.

Phase 1 of the New System

All of the four new setups were initially fed with a feed containing 330 mg/1 TOC of Ansul and FC-206 plus 5000 mg/1 of glucose during this Phase I acclimation period. Setup #1 and #2 were fed with Ansul whereas Setup #3 and #4 FC-206. No conclusive results were obtained during this phase of operation owing to the operational problems encountered on the loss of sludge and plugging of pipes by carbon. During this period only the influent as well as the effluent pH was continuously monitored. Feed pH of approximately 7.3 and the effluent pH of approximately 6.7-6.9 was found in all four systems indicating a proper operation in the desirable pH ranges.

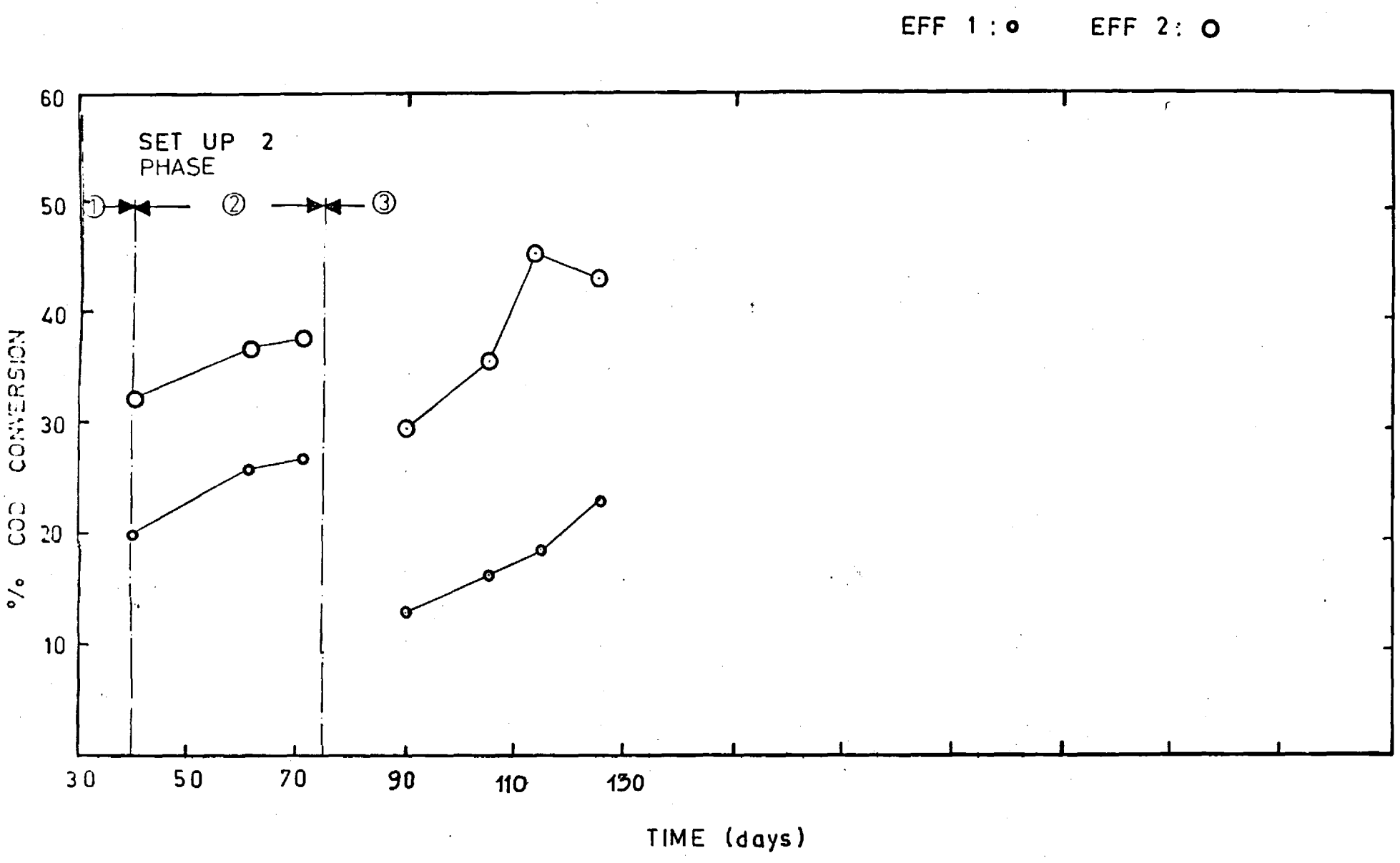
Phase 2

After a measurable amount of gas production was observed the concentration of glucose in the feed was reduced to 200 mg/1. Gross parameters like COD (Figure 10-13), TOC (Figure 14-17) and methane production (Figure 18-21) across each system were measured. An overall reduction in COD of approximately 30% in Setup #1 and 37% in Setup #2 (3330 mg/1 Ansul + 2000 mg/1 glucose as the 10 x concentrated substrate) is observed at the end of Phase 2 operation (Figure 10 and 11). The second stage of both these setups shows



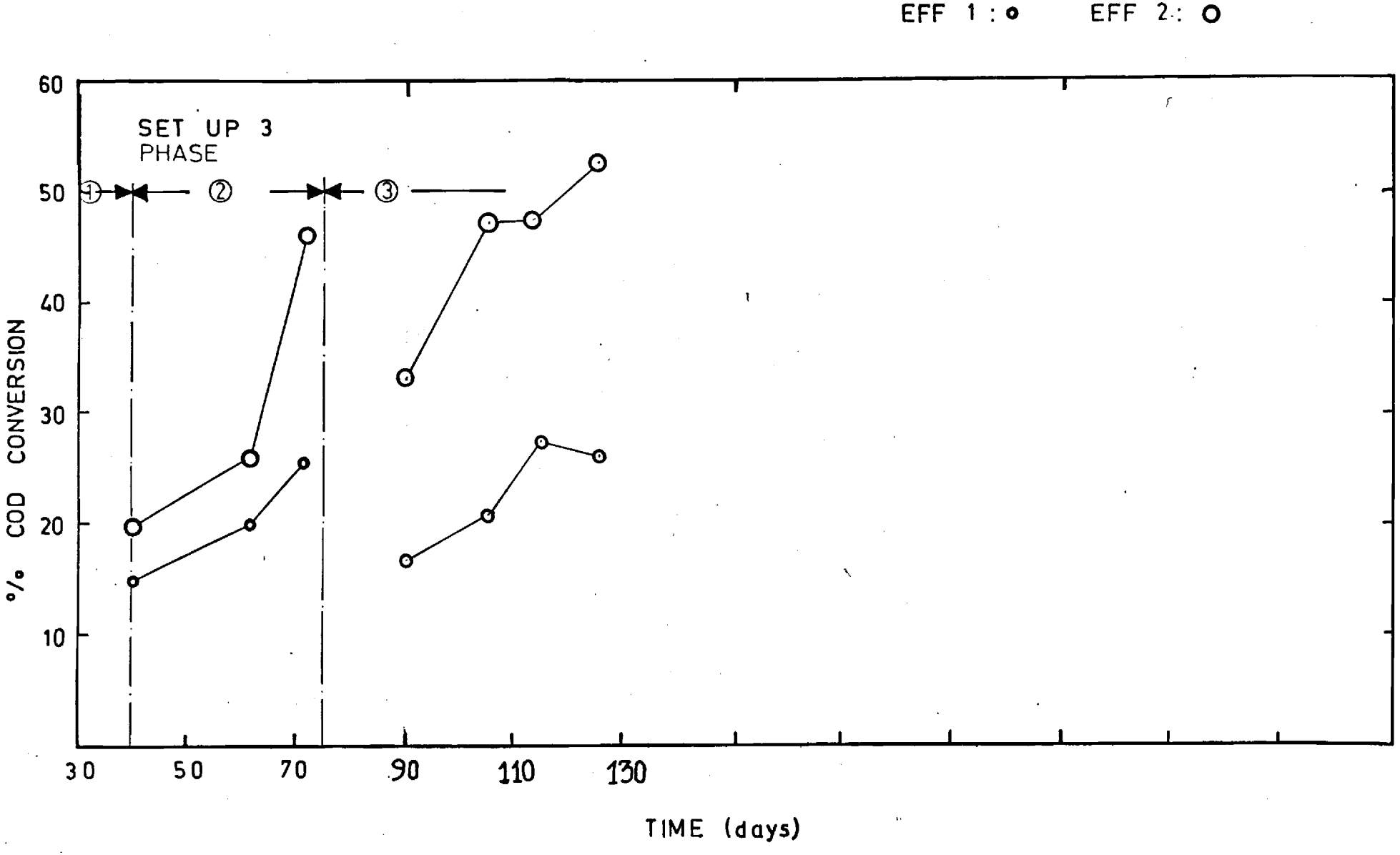
CHEMICAL OXYGEN DEMAND CONVERSION IN TWO STAGE ANAEROBIC FILTE

FIGURE - 10



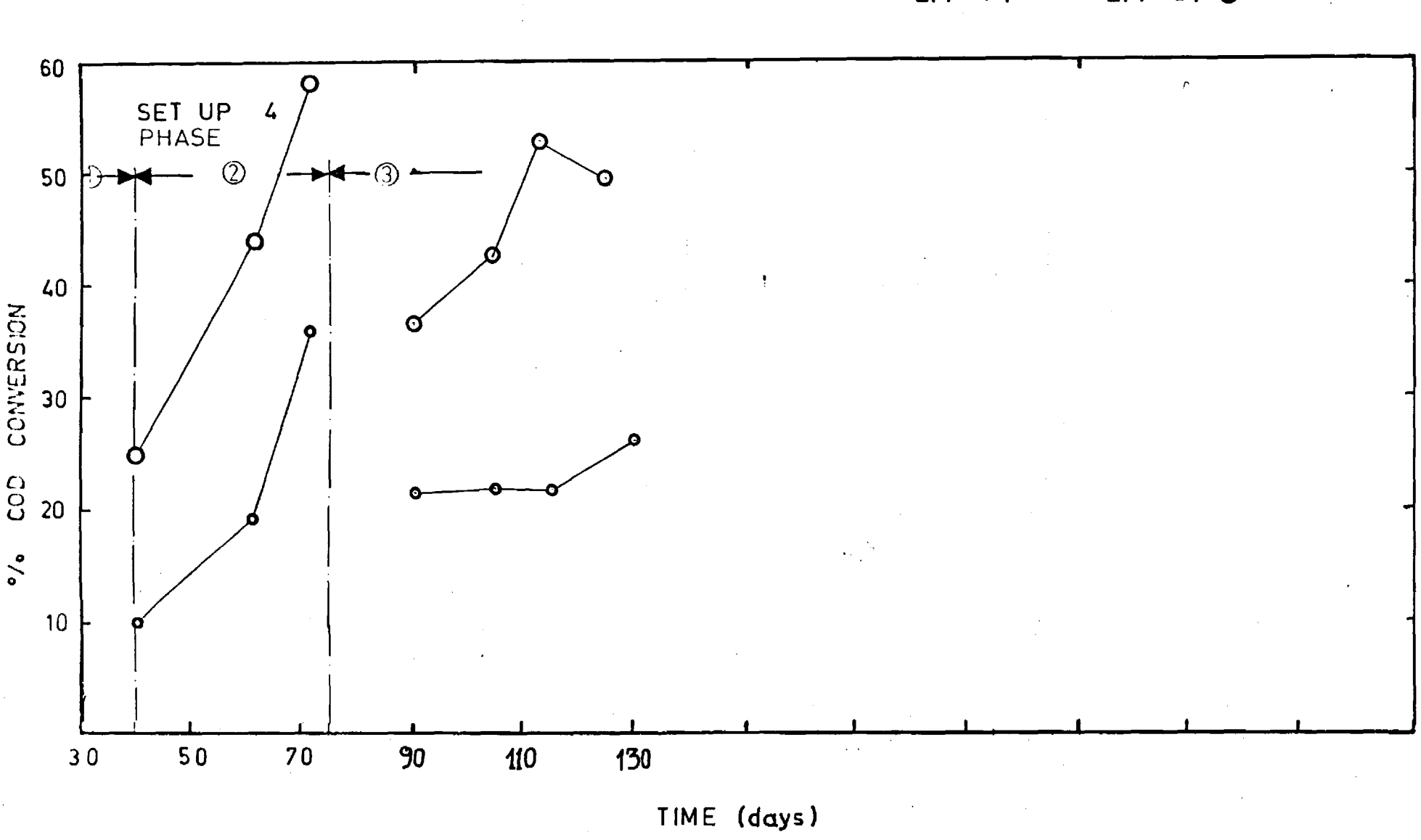
CHEMICAL OXYGEN DEMAND CONVERSION IN TWO STAGE ANAEROBIC FILTEI

FIGURE - 11



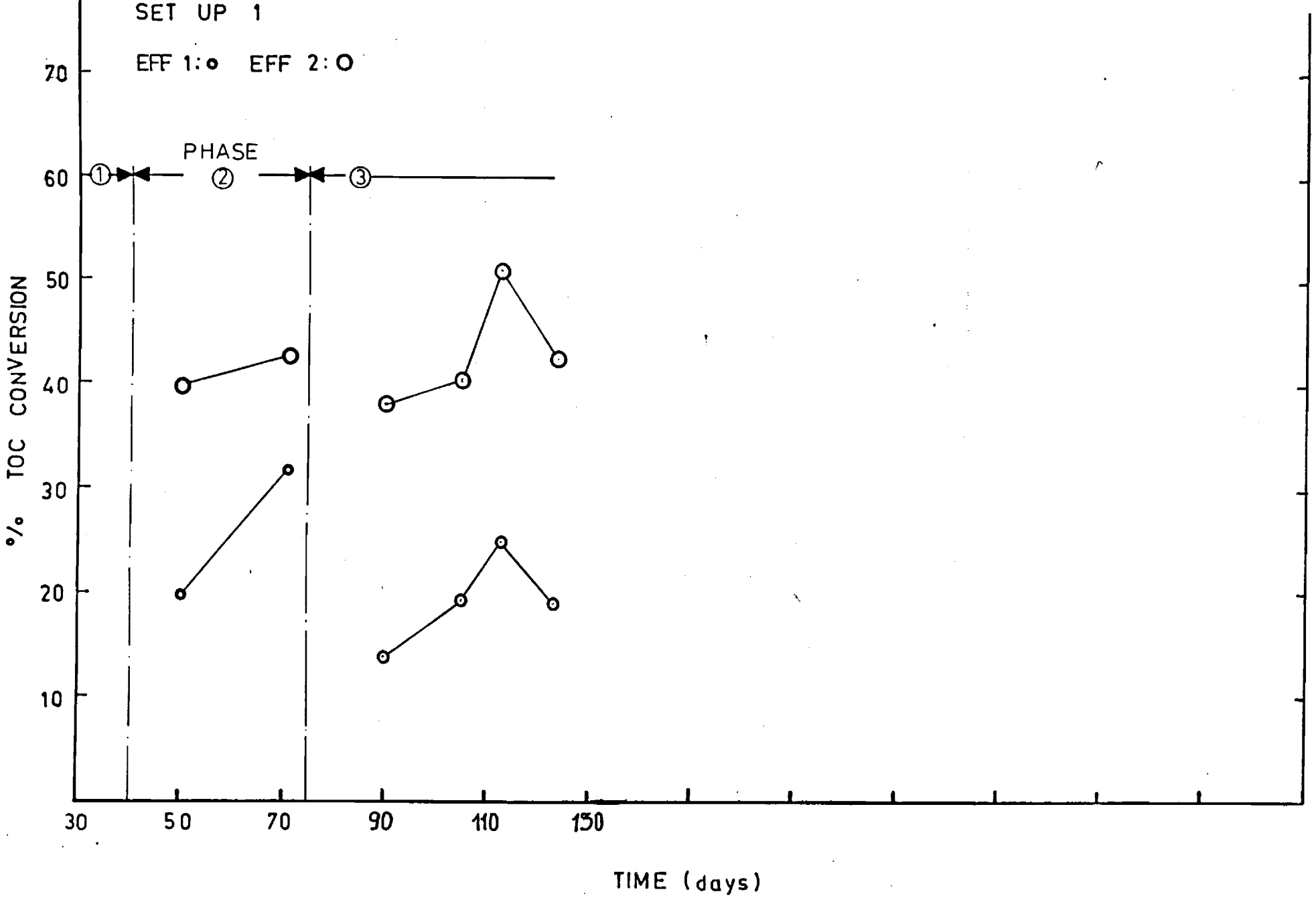
CHEMICAL OXYGEN DEMAND CONVERSION IN TWO STAGE ANAEROBIC FILTEI

FIGURE - 12



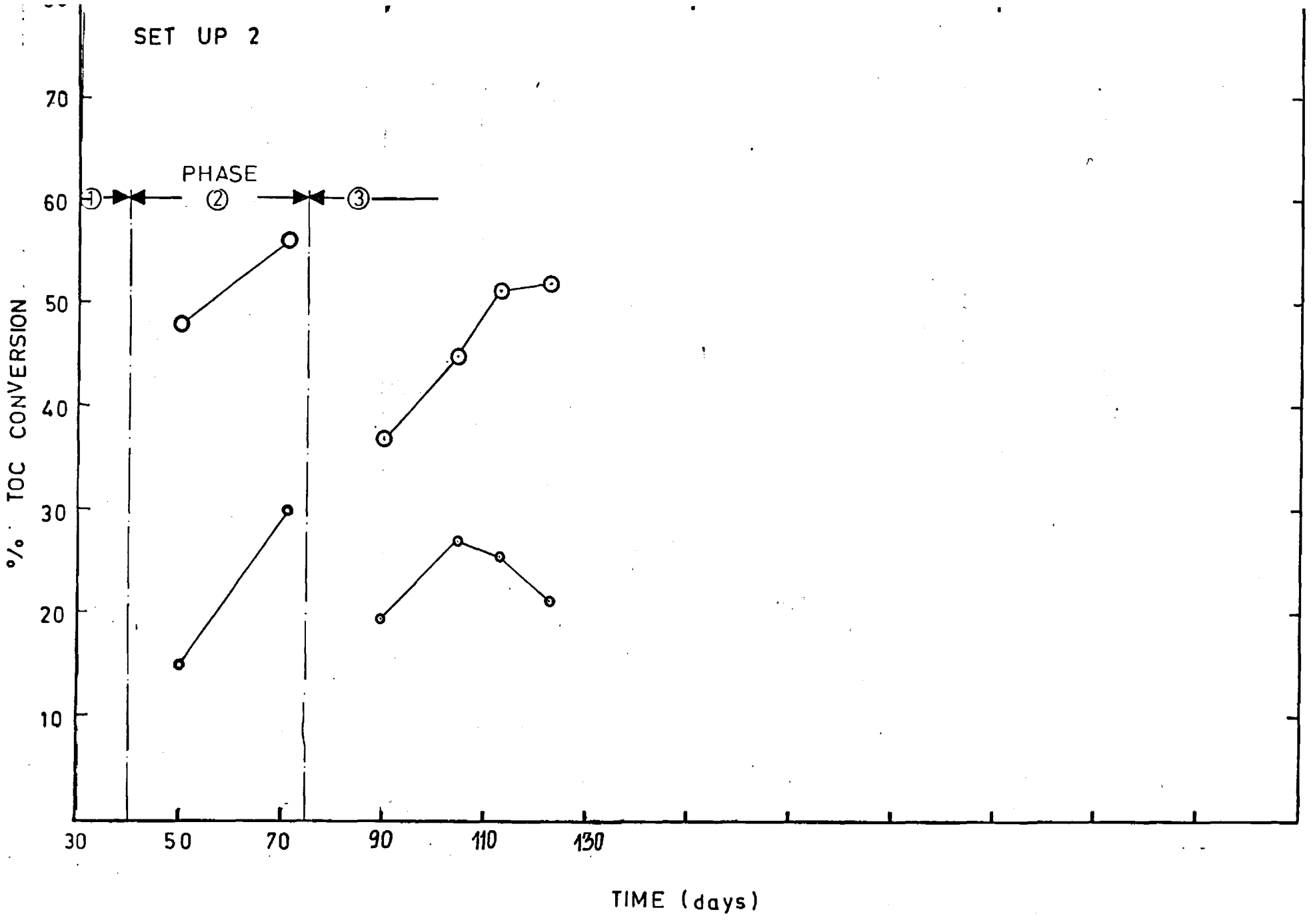
CHEMICAL OXYGEN DEMAND CONVERSION IN TWO STAGE ANAEROBIC FILTEI

FIGURE - 13



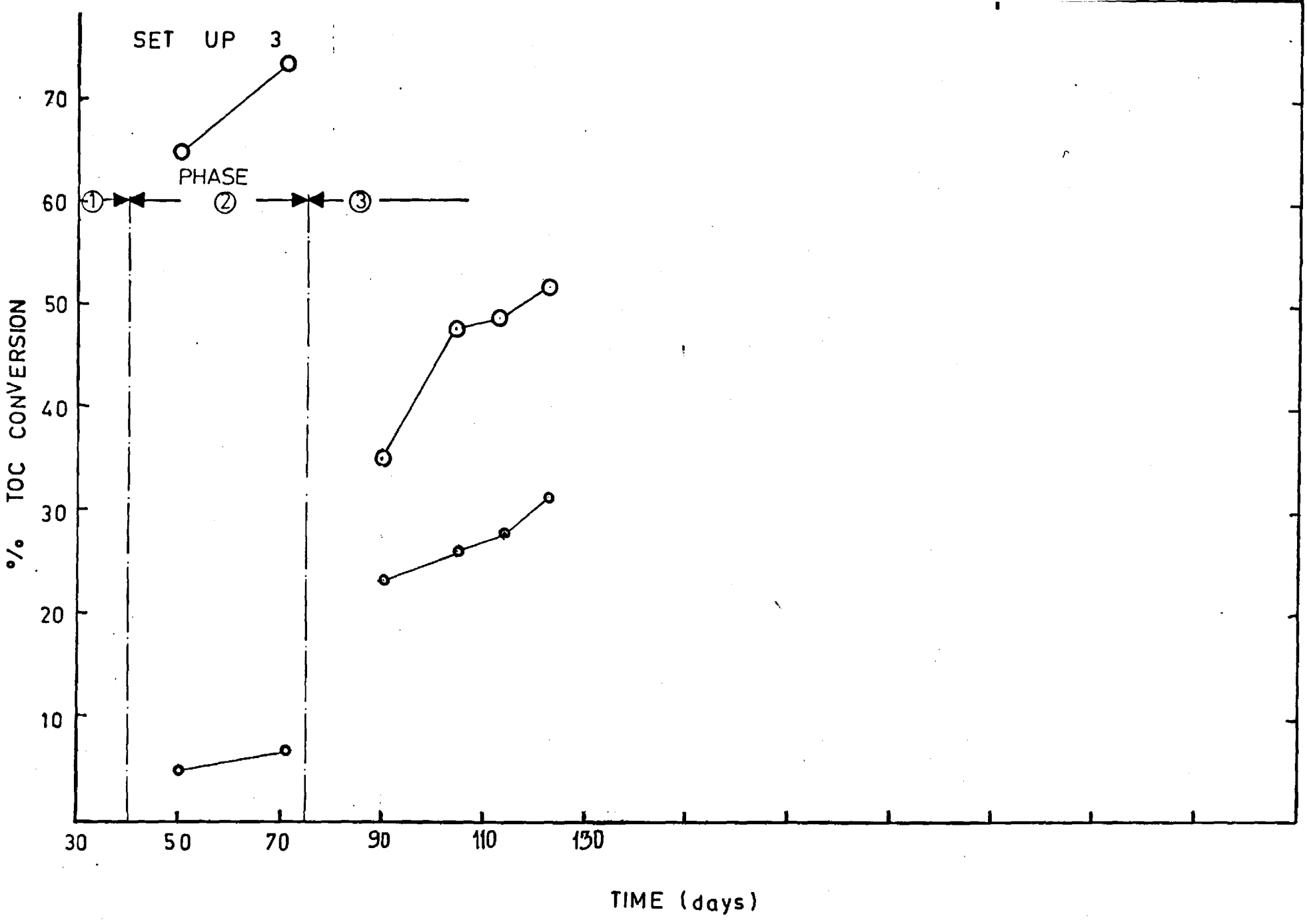
TOTAL ORGANIC CARBON CONVERSION IN TWO STAGE ANAEROBIC FILTER

FIGURE - 14



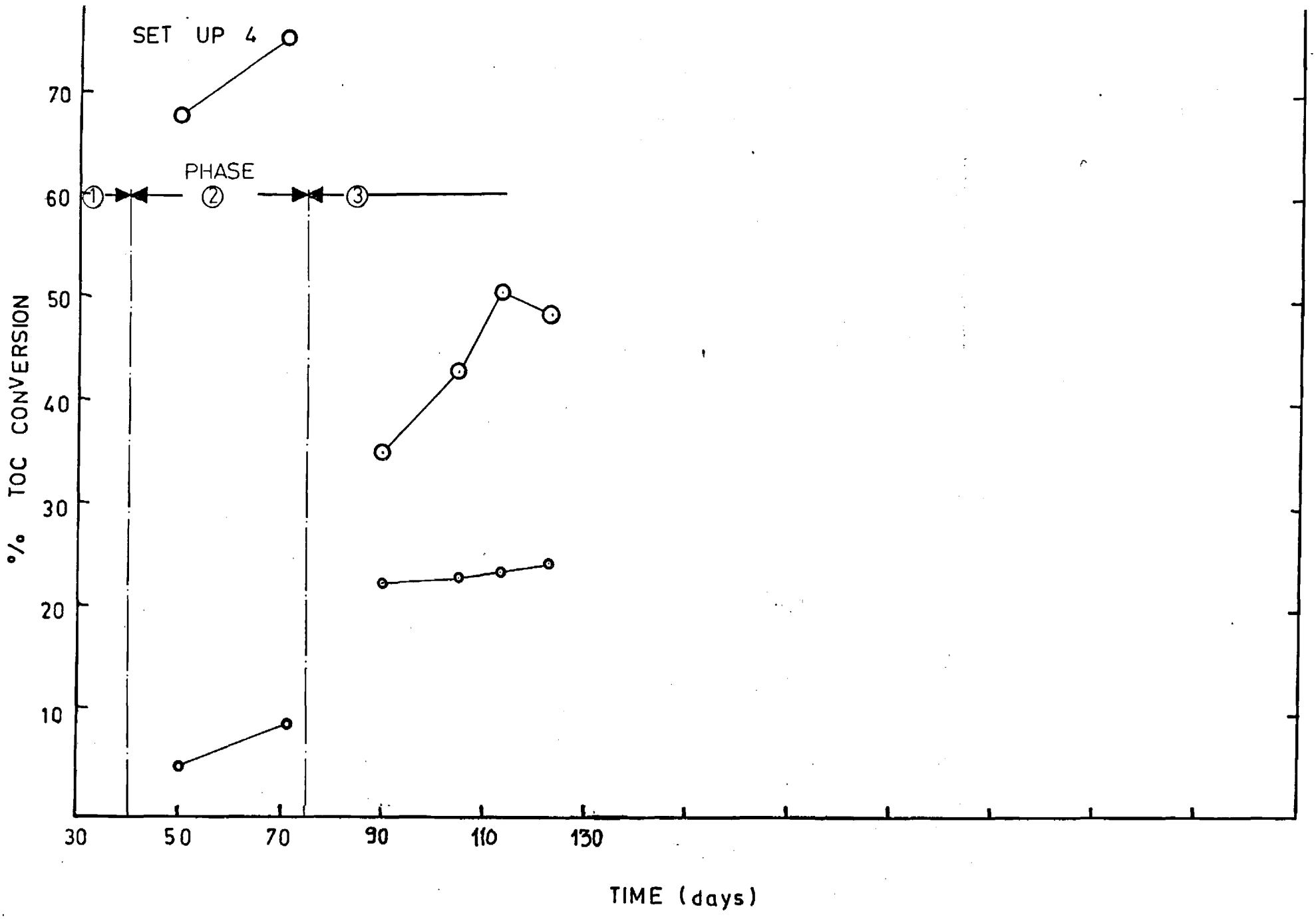
TOTAL ORGANIC CARBON CONVERSION IN TWO STAGE ANAEROBIC FILTER

FIGURE - 15



TOTAL ORGANIC CARBON CONVERSION IN TWO STAGE ANAEROBIC FILTER

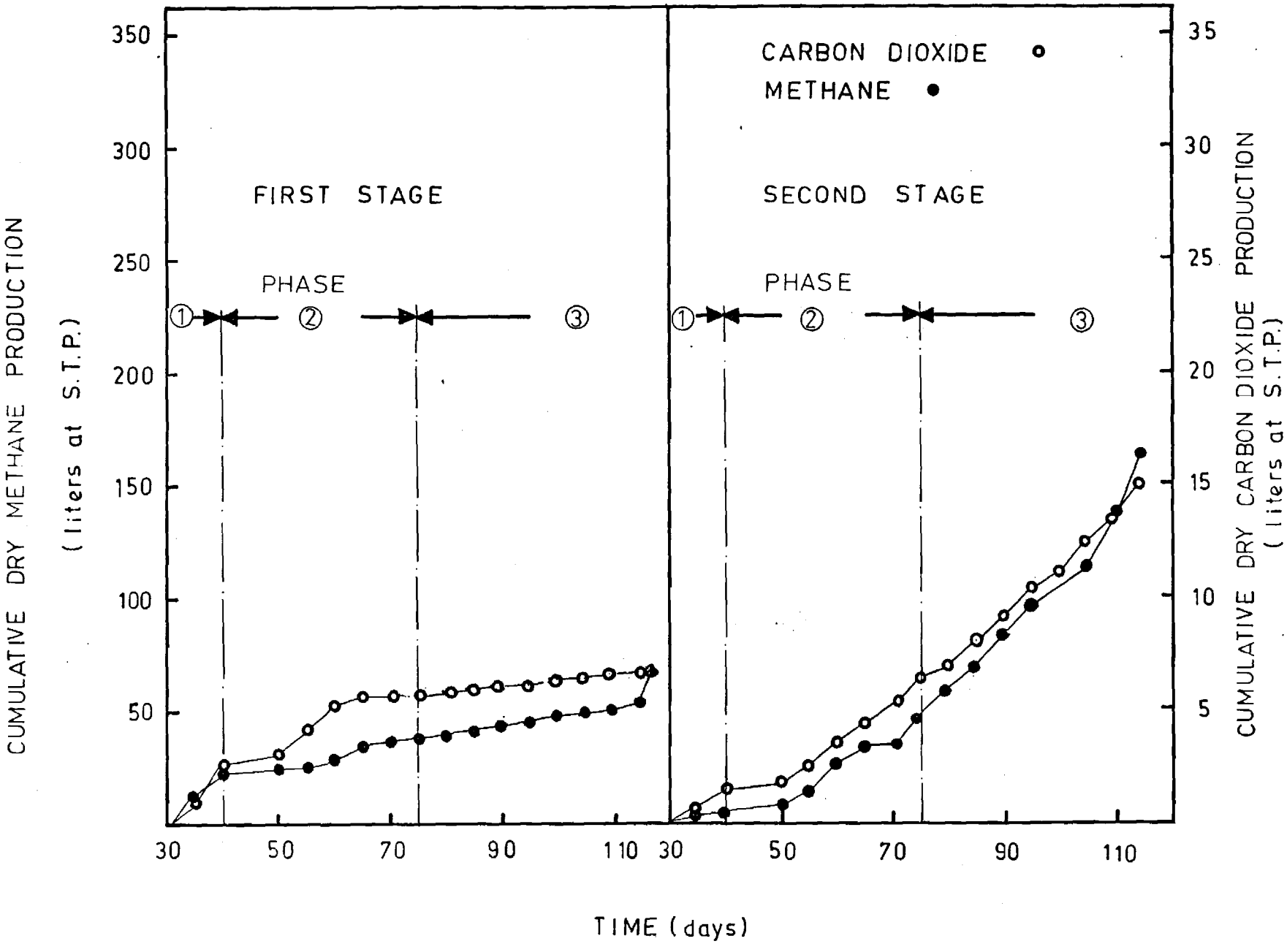
FIGURE - 16



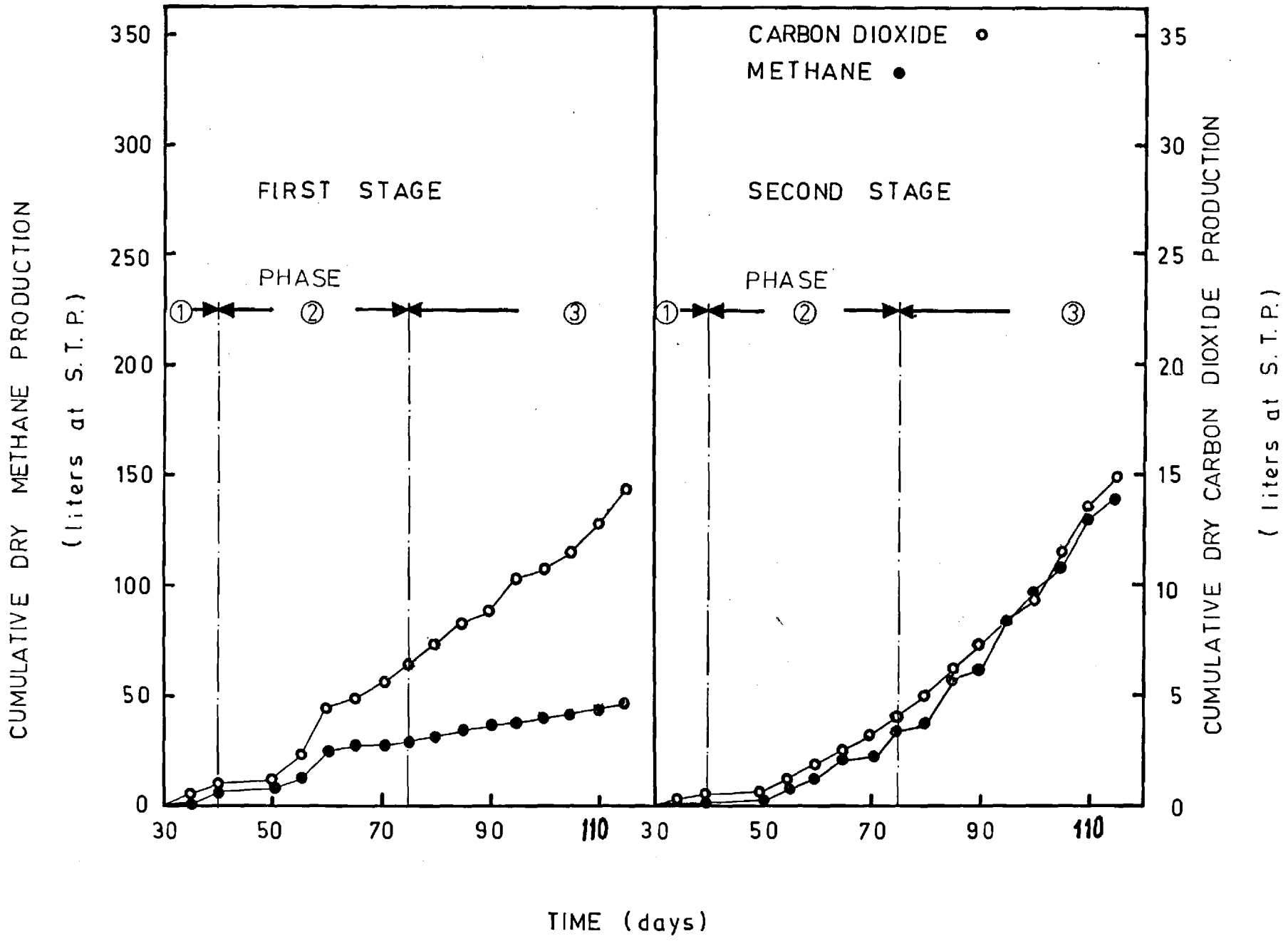
TOTAL ORGANIC CARBON CONVERSION IN TWO STAGE ANAEROBIC FILTER

FIGURE - 17

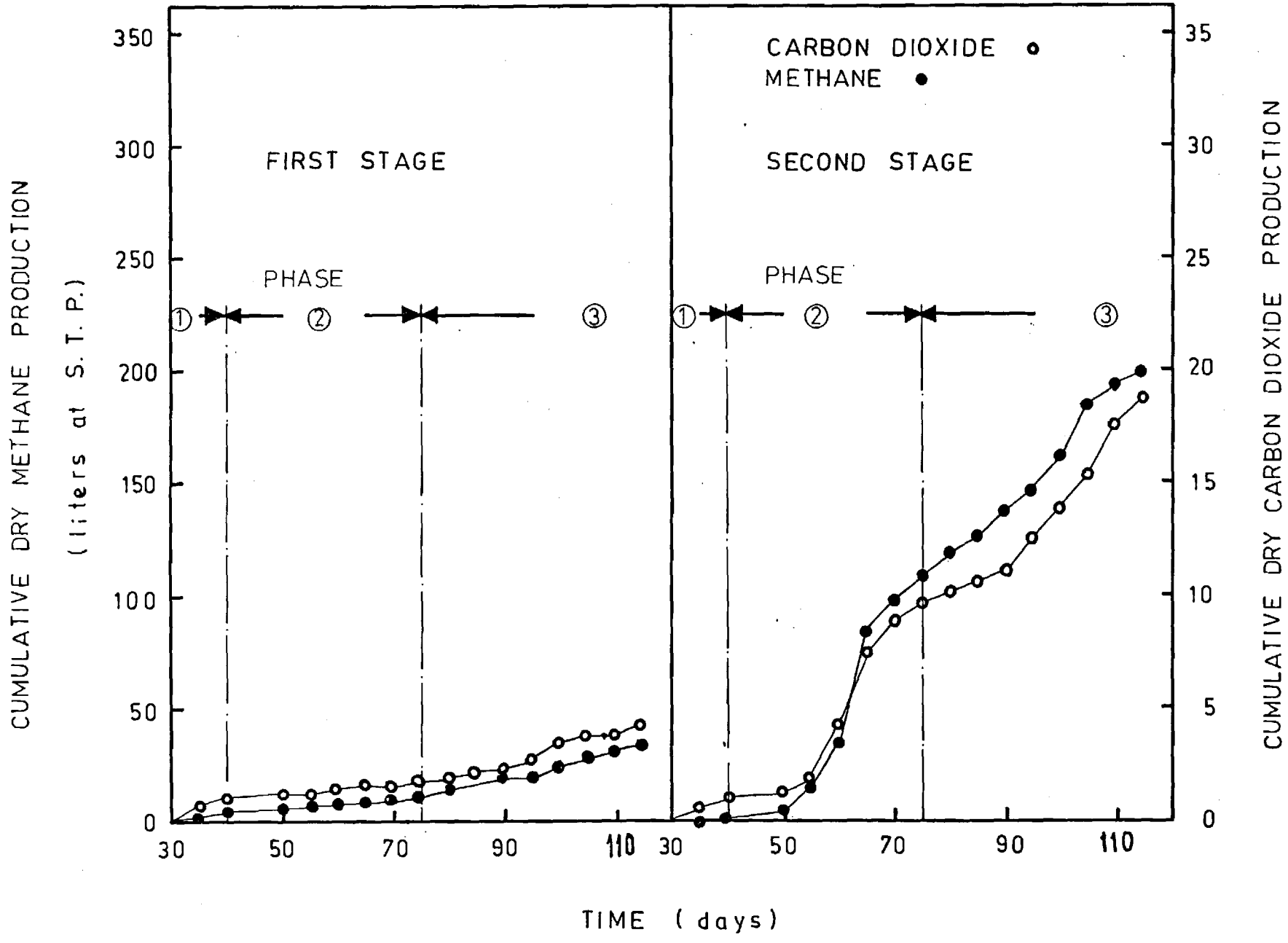
an additional 10% reduction in COD over the first stage that is packed with Raschig rings. However, an overall COD reduction of approximately 46% from Setup #3 and approximately 58% (3330 mg/1 FC-206 + 2000 mg/1 glucose as the 10 x concentrate) from Setup #4 is observed in Figures 12 and 13 during the same period, whereas the first stages of these setups show a COD reduction of approximately 25% and 36%, respectively. This increased removal of COD is in good agreement with the TOC reduction (Figures 16 and 17) and gas production rates (Figures 20 and 21) for Setups #3 and #4. A drastic reduction of approximately 74% in TOC (Figures 16 and 17) and an increased methane production of approximately 8 ℓ/day in the second stage of Setup #3 (Figure 20) and 5 ℓ/day in the second stage of the Setup #4 (Figure 21) are observed. The gas productions in Setup #1 and 2 (Figures 18 and 19) are comparatively lower. An overall glycol conversion (Figures 23, 24, 25) greater than 95% is observed in the Setup #2, 3 and 4 as shown in Figures 23, 24, and 25, whereas Setup #1 shows a 70% overall conversion of glycol (Figure 22). However, the first stages (Raschig ring reactors) of Setups #1 and 2 (Figures 22 and 23) show a higher glycol conversion (approximately 50%) than the Setups #3 and #4 (19% and 40%, respectively). Results of shake test for foaming properity of the effluents showed approximately 41% foam reduction by the first stage and approximately 97% foam reduction from the second stage of the Setups #1 and #2. The effluents from the second stage of Setups #3 and 4 showed approximately 96% foam reduction which is comparable to that from Setups #1 and 2. However, the first stages of Setups #3 and #4 showed a very little foam reduction. Most of the foam reduction was done by the second stages of these setups.



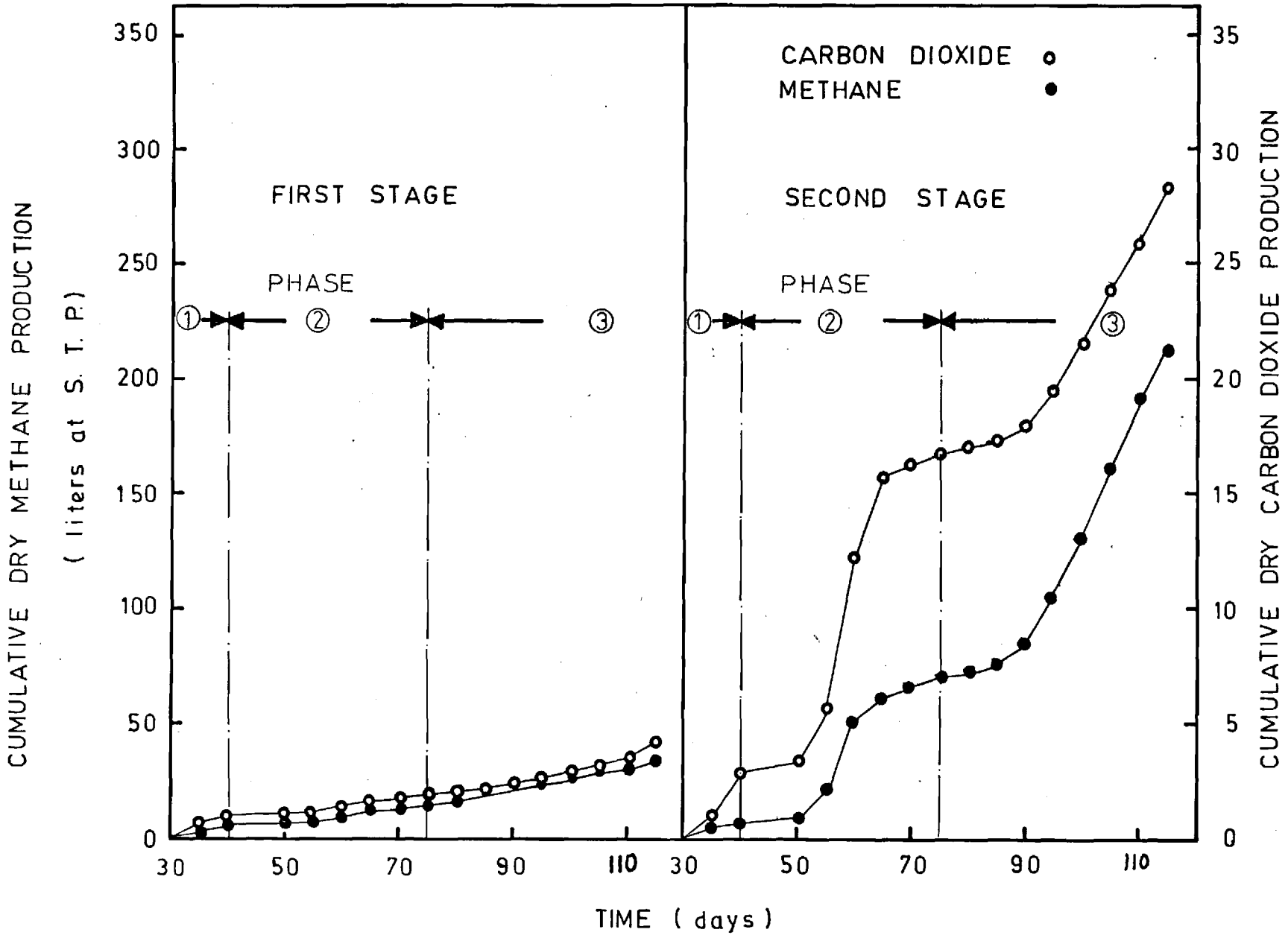
SET UP 1 FIGURE 18



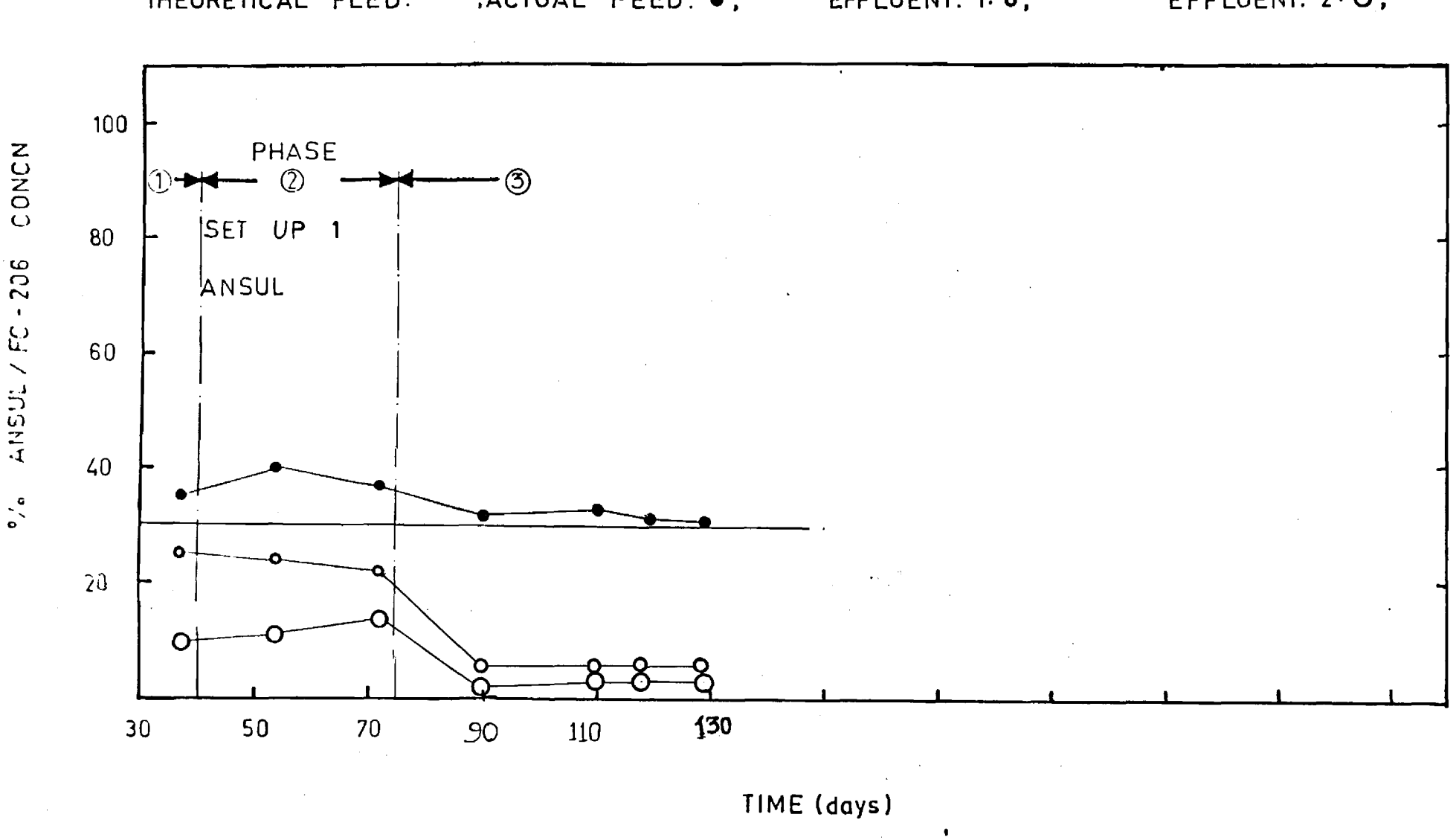
SET UP 2 FIGURE 19



SET UP 3 FIGURE 20

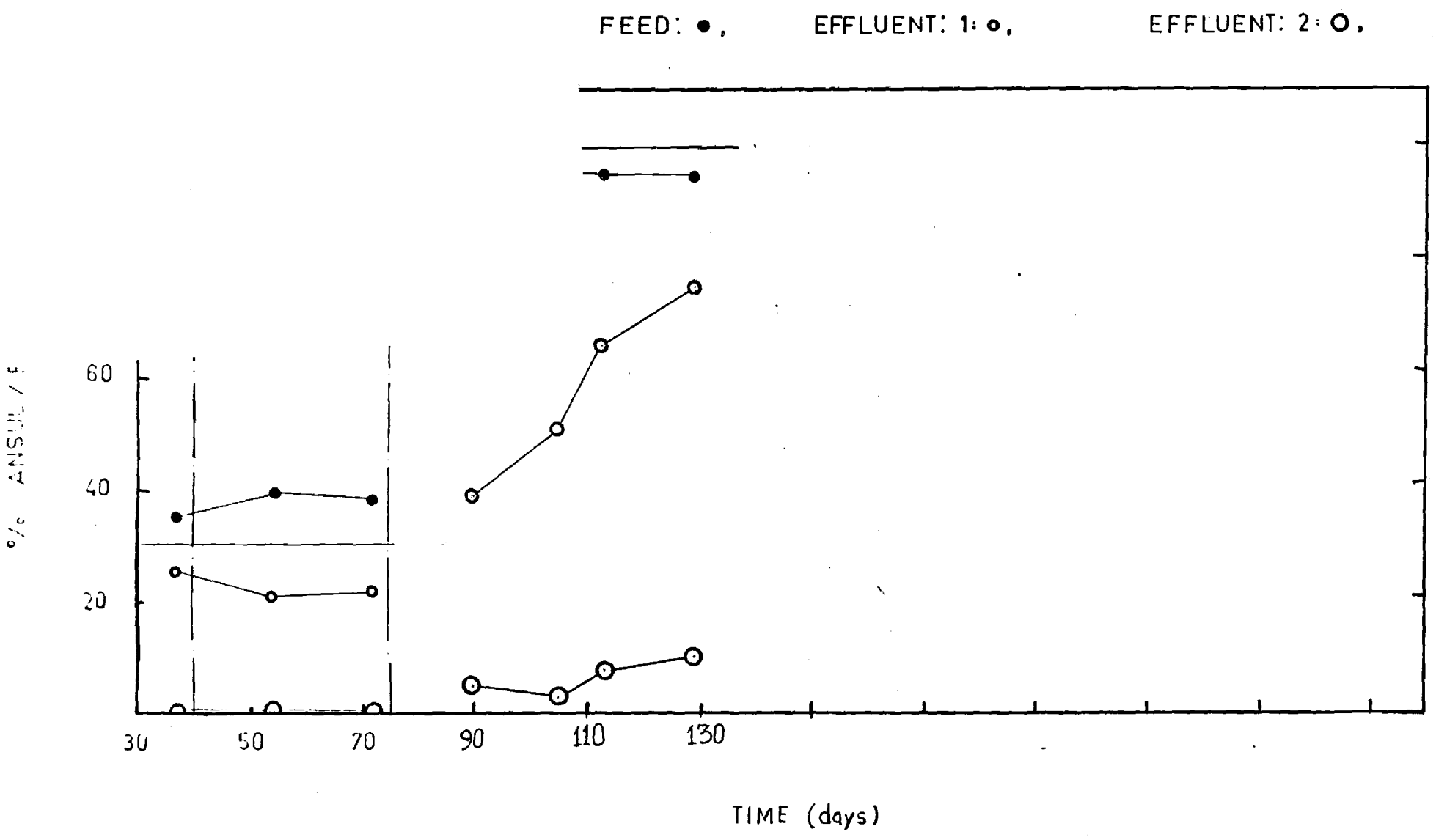


SET UP 4 FIGURE 21



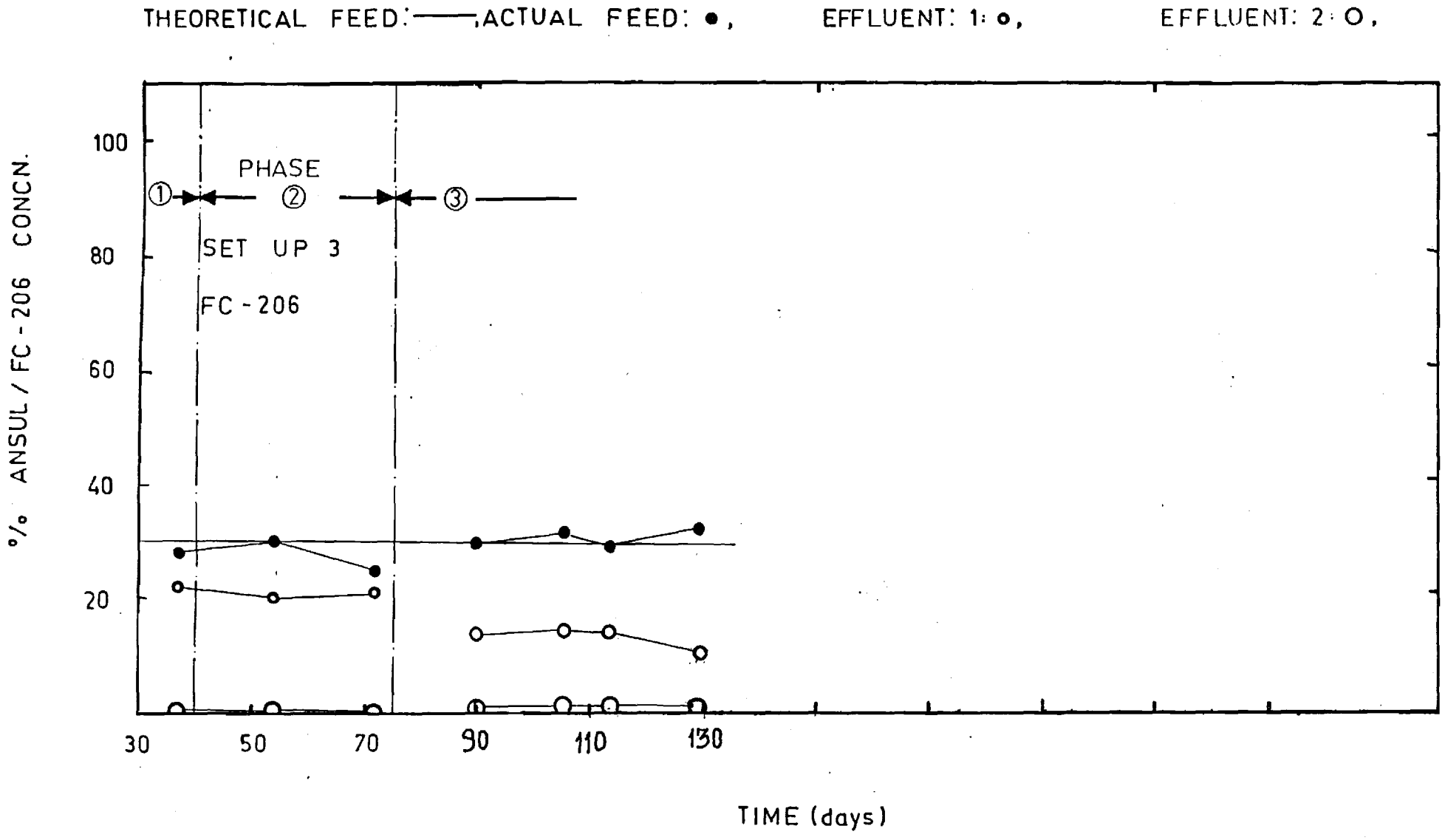
GLYCOL CONCENTRATION ACROSS THE NEW SYSTEMS

FIGURE - 22 .



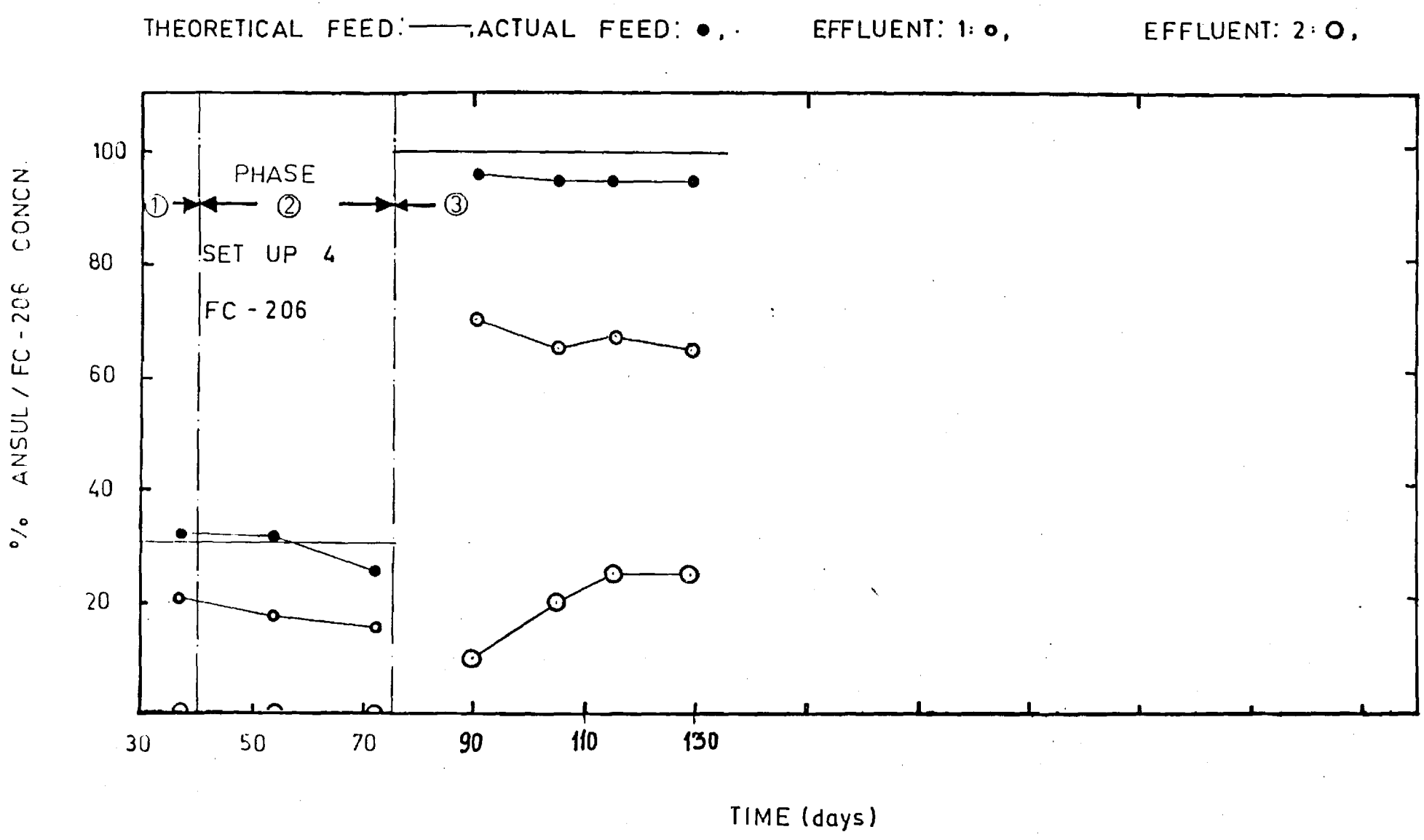
GLYCOL CONCENTRATION ACROSS THE NEW SYSTEMS

FIGURE 23



GLYCOL CONCENTRATION ACROSS THE NEW SYSTEMS

FIGURE - 24



GLYCOL CONCENTRATION ACROSS THE NEW SYSTEMS

FIGURE - 25

Volatile fatty acid concentration and pH of the effluents from these systems were used to monitor the operation of all four setups. The first stage of all columns showed total volatile fatty acids (TVFA) concentrations ranging from 100 to 200 mg/1. Effluents from the second stage, however, showed trace amounts or absence of TVFA. Acetic acid, propionic acid and butyric acid were the major constituents of TVFA measured. pH of the effluents were in the acceptable range of 6.7 to 6.9.

FC 206 showed a better biodegradability as well as carbon adsorptivity. Setups #3 and 4 which were fed with FC-206 show a higher gas production rates(Figures 20 and 21), a higher COD reduction (Figures 12 and 13) and almost total conversion of glycol (Figures 24 and 25) across these systems.

Phase 3

In view of the promising results obtained in Phase 2 of this study, the AFFF concentration of the feed ded to Setups #2 and #4 was increased from 333 mg/1 TOC to 1000 mg/1 of TOC in terms of AFFF concentrations, whereas the glucose concentration remained unchanged at 200 mg/1 starting from day 75 of continuous operation. Setups #1 and #3 were, however, run on the feed containing 333 mg/1 TOC of AFFF with no glucose addition starting from the same time.

A methane material balance can be performed across the system according to the following relationship:

$$\text{Methane Produced} = \frac{22.4\ell\ (COD_{in} - COD_{out})\ \text{mg/1} \times \text{flow rate ml/min} \times 24 \times 60}{64 \times 1000 \times 1000}$$

The methane production rate on day 65 is 8 ℓ/day at STP (Figure 20) across Setup #3. The equivalent methane COD as calculated from the above relationship was 8.8 ℓ/day at STP indicating a high activity of methane production. However, the total methane production from Setup #3 in Phase 3

(without glucose) on day 92 is 2.1 ℓ at STP (Figure 20) whereas the equivalent methane COD corresponds to 6 ℓ, thus indicating a higher adsorptive activity. A high methane production rate of about 5 ℓ/day at STP are seen in the second stage of Setup #3 and #4 is observed on day 110 (Figures 20 and 21) indicating an increasing bioactivity in the second stage reactor. The first stage of these setups also show an increased methane production rate from 0.2 ℓ/day to 0.4 ℓ/day, from day 92 to day 110 (Figures 20 and 21). It should be noted here that Setup #4 is fed at a higher concentration of FC-206 (1000 mg/1 TOC) with the addition of glucose (200 mg/1). Setup #2 (Ansul TOC, 1000 mg/1 and glucose, 200 mg/1) also shows a high total methane production of 4.4 ℓ/day at STP across the system (Figure 19).

Setup #1 (fed with 330 mg/1 of Ansul), however, shows a low methane production rate of 1.65 ℓ/day at STP across the system (Figure 18). Higher COD reductions of approximately 50% were observed across the system in Setups #1, #2, #3 and #4 on day 130 (Figures 10, 11, 12 and 13). High glycol conversion of approximately 90-95% was observed across the system in Setups #1, #2 and #3 and about 75% in Setup #4 during Phase 3 operation upto 130 days (Figures 22, 23, 24 and 25). The increased gas production in Setup #2 and #4 may be attributed partly to an increased degradation of some of the organic constituents of AFFF or partly to an increased glucose degradation. An increase in methane production rate in Setup #1 and #3 was observed even after cutting off the glucose feed and the same increase in methane production rate in Setups #2 and #4 was observed even after decreasing the glucose to (200 mg/1) the AFFF feed containing 1000 mg/1 of TOC. It may be concluded that some of the organic constituents of AFFF were indeed degraded in the anaerobic filters. The above conclusion is based on the glucose equivalent of methane. The rate of total methane

formation of 5.5 ℓ/day by the Setup #4, corresponds to glucose equivalent of 14.6 grams of feed substrate, which is appreciably higher than the 2.88 gq glucose fed to the system daily, thus indicating an appreciable increase in the degradation of some of the organic constituents of AFFF.

Degradation of glycols (Figures 22-25) and the loss of foam forming properties were indeed observed. However, the extent of degradation of these compounds are not known. Some intermediates may be formed which are reflected by its relatively low COD conversions of approximately 50% (Figures 10-13) on day 130 as compared to more than 90% reduction in both glycol (Figures 22-25) and the foam forming properties. These intermediates may not be degraded further in the anaerobic system for reason of unfavorable metabolic pathways. They may, however, be degraded effectively in an aerobic system. This is indeed the case as the aerobic system fed with the effluent from the old system receiving 1000 mg/l AFFF showed a 40% more reduction in COD.

V. CONCLUSIONS

The primary goal of this research was to demonstrate the treatability of AFFF ingredients by anaerobic biological treatment of firefighting wastewaters. The data presented in the previous section demonstrate that the AFFF wastewater is amenable to anaerobic biological treatment with the innovative two-stage anaerobic filters using a fluidized GAC column. The stable nature of the foam of the AFFF wastewaters which presents a major problem in treating these wastes aerobically, was successfully reduced (80% reduction) by the fluidized bed GAC anaerobic filter. With the addition of a two-stage aerated lagoon in conjunction with the GAC filter, a significant reduction in the COD and TOC of the anaerobic effluent was realized although more data are to be presented for the aerobic system. Higher reductions in pollutional strength of the wastes are expected with a system of such a combination of anaerobic filters followd by aerobic stabilization. The high methane production rate achieved by such a system can result in valuable energy conservation. The continuous operation of the carbon reactors for 450 days with an old system has proved that GAC present in this reactor is self regenerating and provides resistance against upsets and shock loads experienced during this period of operation. Based on the results of the four new setups (Figures 10-25), AFFF loading can be increased further with a shorter period of acclimation. Higher reductions in the pollutional strength can be anticipated with time, on the basis of data available from the successful working of the new setups. The reduction of COD, TOC, glycol and foaming characteristics of the AFFF feed by the two-stage anaerobic bioreactor can probably be attributed to the action of both biodegradation and carbon adsorption. The bacteria from the first stage

provide the seed for the second stage filled with the fluidized activated carbon. Microorganisms in the second-stage carbon column see a potentially reduced strength of wastes due to:

1. Partial breakdown by the bacteria in the first stage that is packed with Raschig rings; and
2. Adsorption of the less readily available substances on the activated carbon.

VI. RECOMMENDATIONS

In summary, the anaerobic system under study serves the purpose of pretreating the wastewater which would otherwise be unamenable to the aerobic system. The energy produced from the anaerobic system may well be sufficient enough to run the aerobic process which rendered the anaerobic/aerobic treatment process to be highly energy efficient. It is believed that any wastewater treatment system that meets this criterion of being energy efficient would be the process of the future. Further development of this anaerobic/aerobic system is therefore warranted.

VII. REFERENCES

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E-20-A02

PILOT PLANT STUDY ON THE RECOVERY OF AFFF FROM FIREFIGHTING WATERWAYS BY A UF-RO MEMBRANE SYSTEM

MEMORANDUM OF PROCEDURES (MOP)

March 31, 1981

by

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TABLE OF CONTENTS

I. OBJECTIVE

The purpose of this effort is to develop design criteria for fabrication of a UF-RO membrane system for AFFF recovery from firefighting wastewaters and to prepare test and evaluation procedure for the fabricated UF-RO system. The system test will demonstrate the technical feasibility and economics of using UF-RO to recover AFFF for reuse at the Navy and the Air Force firefighting training facilities.

In the current pilot-plant study, Georgia Tech will develop design crtieria and review with Ft. Detrick personnel for the fabrication of a UF-RO system for AFFF recovery test. Georgia Tech will also prepare a Memorandum of Procedure based on Georgia Tech lab experiment data for the test of the UF-RO system at a selected Navy site. Georgia Tech will then observe installation of the UF-RO test system, and assist in start up of the system at the Navy site.

II. BACKGROUND

Wastewater generated from firefighting training activities or firefighting equipment testings for fuel oil fire control, contains a foam agent called AFFF. The AFFF consists of fluorochemical and hydrocarbon surfactants, ethylene glycol and its derivatives have shown a significant adverse effect (toxicity) to the receiving environment. A cost-effective treatment and/or AFFF recovery processes must be developed for disposal of the AFFF-laden wastewater, so that the AFFF user facilities could best meet regulatory agency's requirements.

The Civil Engineering Laboratory (CEL) has been developing treatment alternatives for AFFF-laden wastewater since 1977. Georgia Institute of Technology (Georgia Tech) conducted experiments for CEL for the feasibility of using UF-RO membrane technology to treat AFFF-laden wastewater and to recover AFFF for reuse. The results of Georgia Tech study demonstrated that it was technically and economically feasible to use UF-RO system to separate and recover the AFFF for reuse. Recovered AFFF when tested at NRL, met fire extinquishing performance specs described in MIL-F-24385A. A pilot-scale study was recommended to fully establish the process feasibilities and economics of the AFFF recovery system. A complete design criteria for a field applicable full-scale system may be developed through the pilot-scale study.

USAMBRDL, Ft. Detrick has UF-RO membrane components that were used in MUST program. They may be made available for fabricating a pilot scale system with daily flow rate of about 4,000 gallons (based on 8 hours operation time).

Georgia Tech personnel were involved in the MUST system development. Later, they conducted a laboratory experiment for CEL to determine the feasibility of membrane technology for AFFF-laden wastewater treatment and AFFF recovery for reuse. It is beneficial to utilize Georgia Tech expertise and in-depth knowledge in the specific UF-RO system components for the fabrication and testing of the pilot-scale system. Design criteria and test procedure must be developed by Georgia Tech prior to the fabrication and test of the UF-RO pilot-scale system at a selected Navy fire-fighting site.

III. SYSTEM COMPONENTS DESCRIPTION

The UF-RO membrane system that was fabricated for the MUST program consists of two individual self-contained, skid-mounted units. They were designed to interface with each other by means of a transfer line connected directly. No provision was made to having a surge capacity between these two units. As such, it becomes difficult to operate the two units simultaneously. The major problem that may encounter by operating the two units simultaneously is the formation of cavitation in the RO pressure pump if the RO permeate is bled faster than the supply of UF permeate. This is especially true with the current system, i.e., the use of only a fraction of the existing UF modules. The remedies for it are to incorporate a surge tank between these two units, and to increase the membrane area of the UF modules with a concommittant decrease in the number of RO modules.

Ultrafiltration System

The modified UF system has a total membrane area of 124 ft^2. Half of it will be lined with the Abcor's high flux HFM membrane. The system was designed to feed continuously along with a high capacity recirculation pump. The retentate (brine) is bled continuously from the recirculating system. Figure 1 shows the block diagram of the UF system. One advantage of this continuous feed and bleed mode of operation is to minimize the foaming problem. However, the main disadvantage of this mode of operation is that the system has to be operated at the concentration level of the retentate discharge stream which greatly reduce the permeate flux and intensify the concentration polarization effect on the membrane surface. This shortcoming, however, can be circumvented by incorporating a large

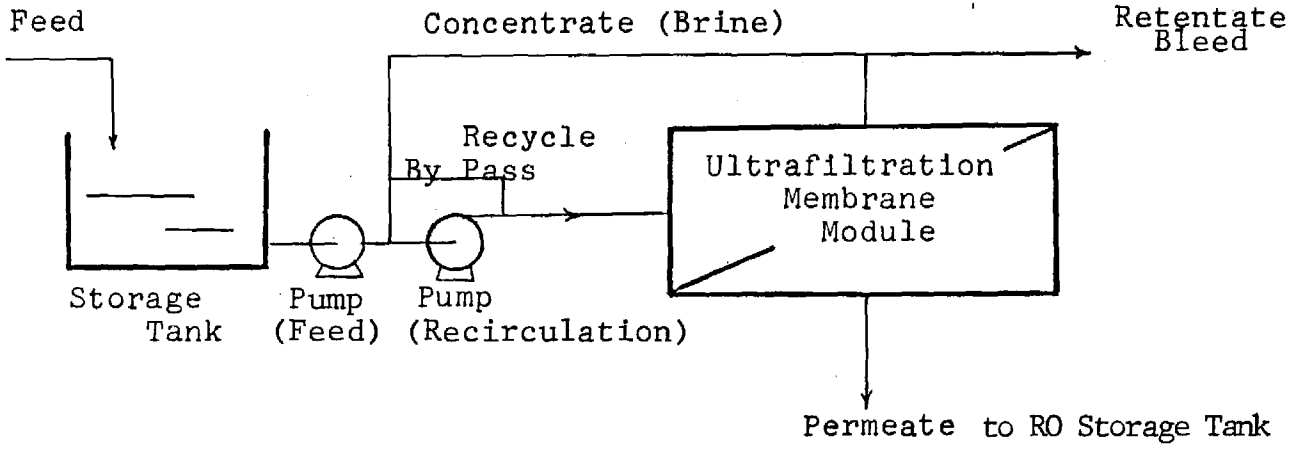

Figure 1 Continuous Feed and Bleed Operation of an Ultrafiltration System

UF feed tank into the system and operating in a batch mode. The retentate will then be bled to this feed tank instead of being discharged into the waste stream. By combining the batch operation with the continuous feed and bleed mode of operations, the problem of foaming and low flux can be resolved simultaneously. The only expense involved is the cost of a sizeable UF feed tank, together with all the necessary plumbing. The size of the UF tank should be the daily throughput capacity of the UF unit. According to the current design, the size of the UF feed tank can be estimated as follows:

$$124 \text{ ft}^2 \times 25 \text{ gal/ft}^2\text{-day} \times \frac{8 \text{ hr-day}}{24 \text{ hrs}} = 1033 \text{ gallons (operated at 25°c)}$$

If the system is to be operated at 50°c, the size of the feed tank should be 2000 gallons. Since the flux declines approximately 30% by operating at 50°c and 94% product water recovery rate (Figure 2), the size of the UF feed tank can be smaller depending upon what is available on the testing site. An UF feed tank is however, necessary to ensure a smooth operation of the system.

A schematic diagram of the modified UF pilot plant which incorporates the continuous feed and bleed mode of operation is shown in Figure 3. In this mode of operation, the majority of the feed is recirculated in a loop through the membrane modules by means of a high capacity recirculation pump. The UF permeate (ultrafiltrate) is collected in a storage feed tank for RO which also serves as the surge tank between the UF and the RO units. The make-up feed is introduced into the pumping loop by means of a feed pump which also develops the pressure (approximately 50

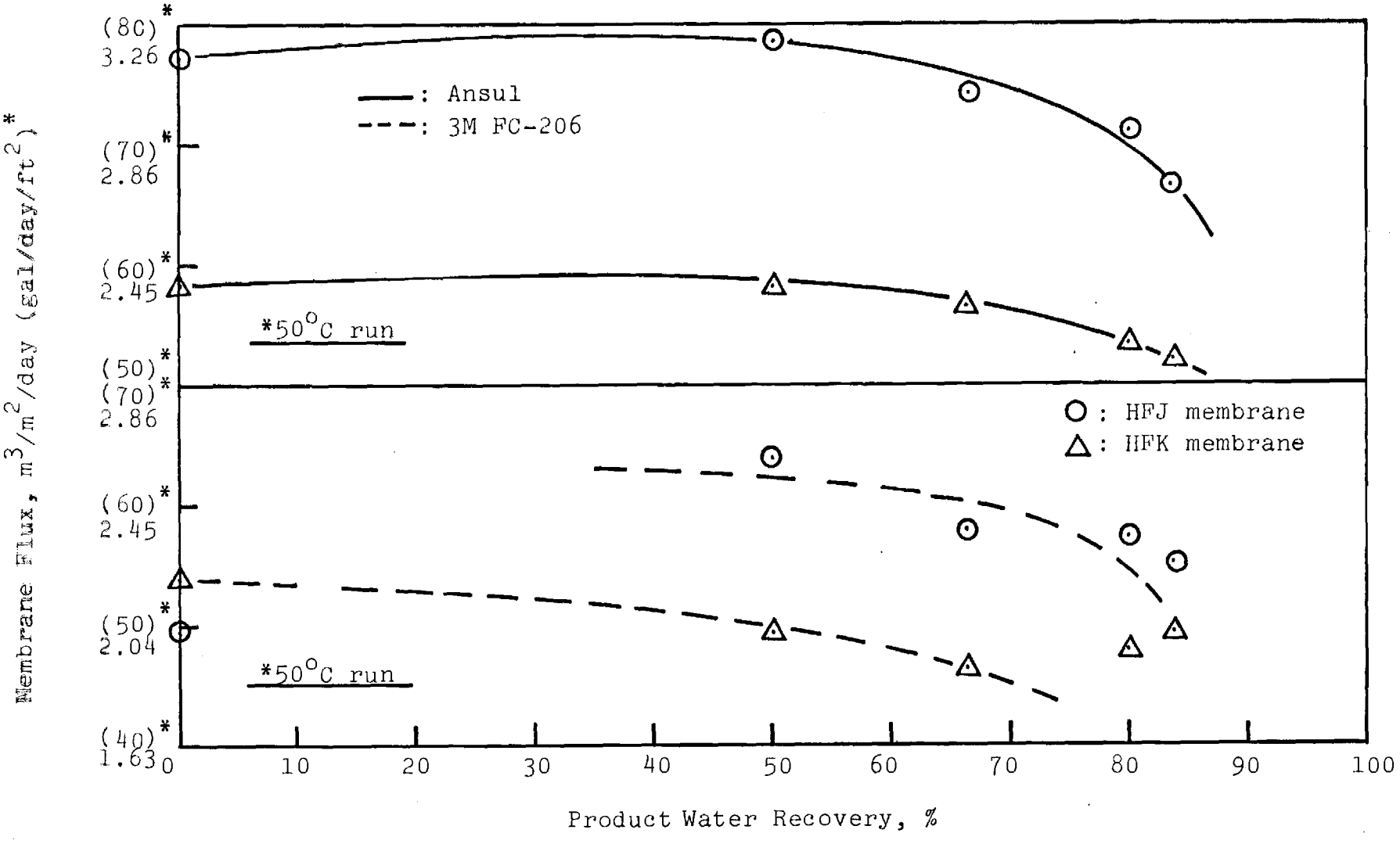

Figure 2. Ultrafiltration Membrane Flux as a Function of Product Water Recovery (6% AFFF Spiked Wastewater)

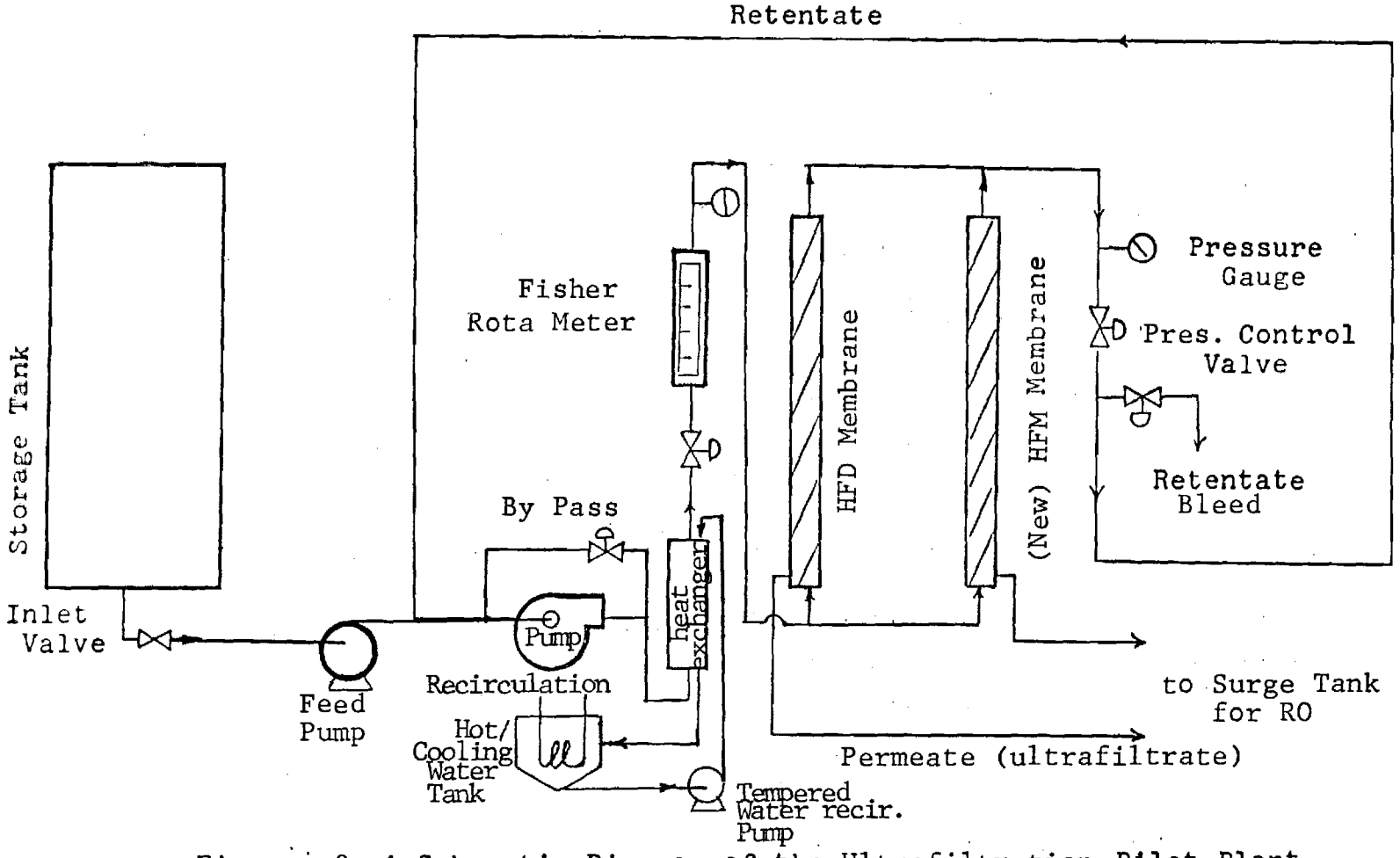

Figure 3 A Schematic Diagram of the Ultrafiltration Pilot-Plant

psig) required for the UF system. The retentate is constantly bled from the system through a bleed valve. The flow rate of the retentate should be between 1/16 to 1/20 of that of the permeate flow in order to accomplish a 94 to 95% product water recovery. The recirculation flow rate should be controlled between 35 to 50 gallons per minute as indicated by a Fisher rotameter. The temperature of the system can be controlled by means of a heat exchanger which is circulated with a tempered water. The tempered water is supplied by an auxiliary hot/cooling water tank and a small recirculation pump.

Reverse Osmosis System

Unlike UF, the desired product in RO is the retentate which contains the bulk of the AFFF constituents. The RO permeate can be used for makeup water for the firefighting exercises or discharged directly into the sewer or receiving stream. The MUST RO system consists of a positive displacement high pressure pump preceeded by a series of polishing filters and a chemical injection system. Four B-10 (DuPont) permeators are interconnected in a stage arrangement. The feed is introduced prior to the chemical injection system by means of a low pressure feed pump. Both permeate and retentate can be bled from the system as desired. Since the RO flux decreases rapidly as the product water recovery approaches to the 90% level (Figure 4), the combination of the batch and bleed mode of operation should be included in the design in lieu of the continuous feed and bleed mode of operation. This can be accomplished by directly introducing the RO retentate to the RO feed tank which interfaces between the UF and the RO units. A copper cooling coil should be installed in the feed to control the temperatures of the feed to the RO system

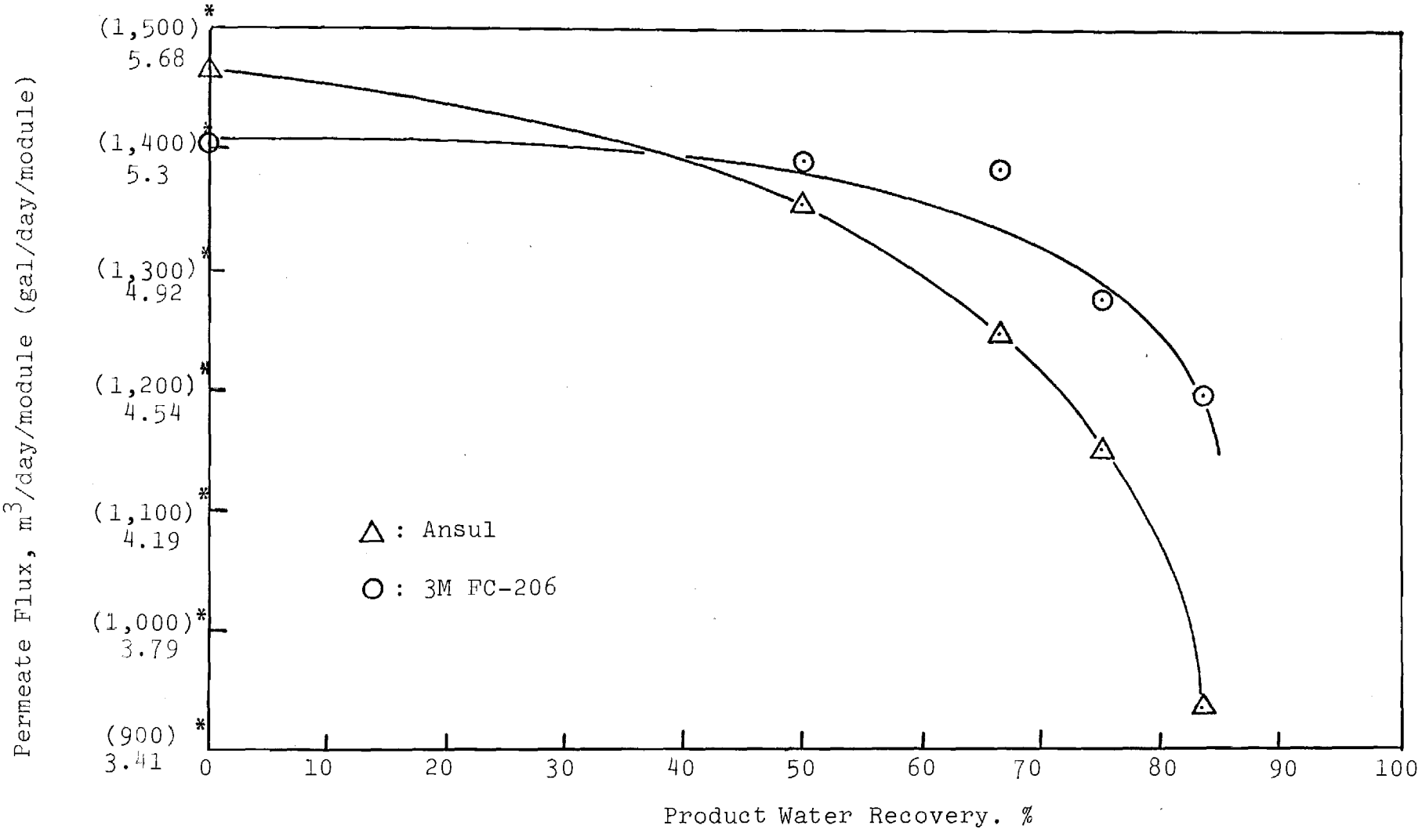

Figure 4. Reverse Osmosis Membrane Performance as a Function of Product Water Recovery (Feed Solution from 6% AFFF Spiked Wastewater)

in case when the UF system is operated at a high temperature. In order to maximize the flux of the RO modules, the size of the surge tank should be half of that of the UF feed tank, i.e., approximately 500 gallons.

A schematic diagram of the modified RO pilot plant which incorporates the combined mode of batch and bleed operations is shown in Figure 5. In this mode of operation, the majority of the feed is removed as RO permeate through the 4 B-10 modules interconnected in a staged 2-1-1 arrangement. The estimated permeation flow rate is 1600 gallons in an 8-hour period. The excess permeate can be recycled back to the intake of the low pressure feed pump which is incorporated in the original design of the MUST RO unit.

A memorandum was prepared by Chian regarding modifications of the MUST UF/RO system for the pilot-plant study (Appendix I).

IV. TEST MATERIALS

Firefighting agents used in military services are commonly referred to as Aqueous Film Forming Foam (AFFF) which contain fluorocarbons, hydrocarbon surfactants, solvents (such as various types of glycols) and water. Currently three major AFFF products are available on the market; namely, Ansul, 3M FC-206 and 3M FC-780. Since the composition of 3M FC-780 is similar to that of 3M FC-206 with the exception of its concentration, only the latter, together with Ansul, will be evaluated in this study.

Pilot-plant study on the capability of the UF-RO system in recovering the AFFF active ingredients will be conducted by using tap water and

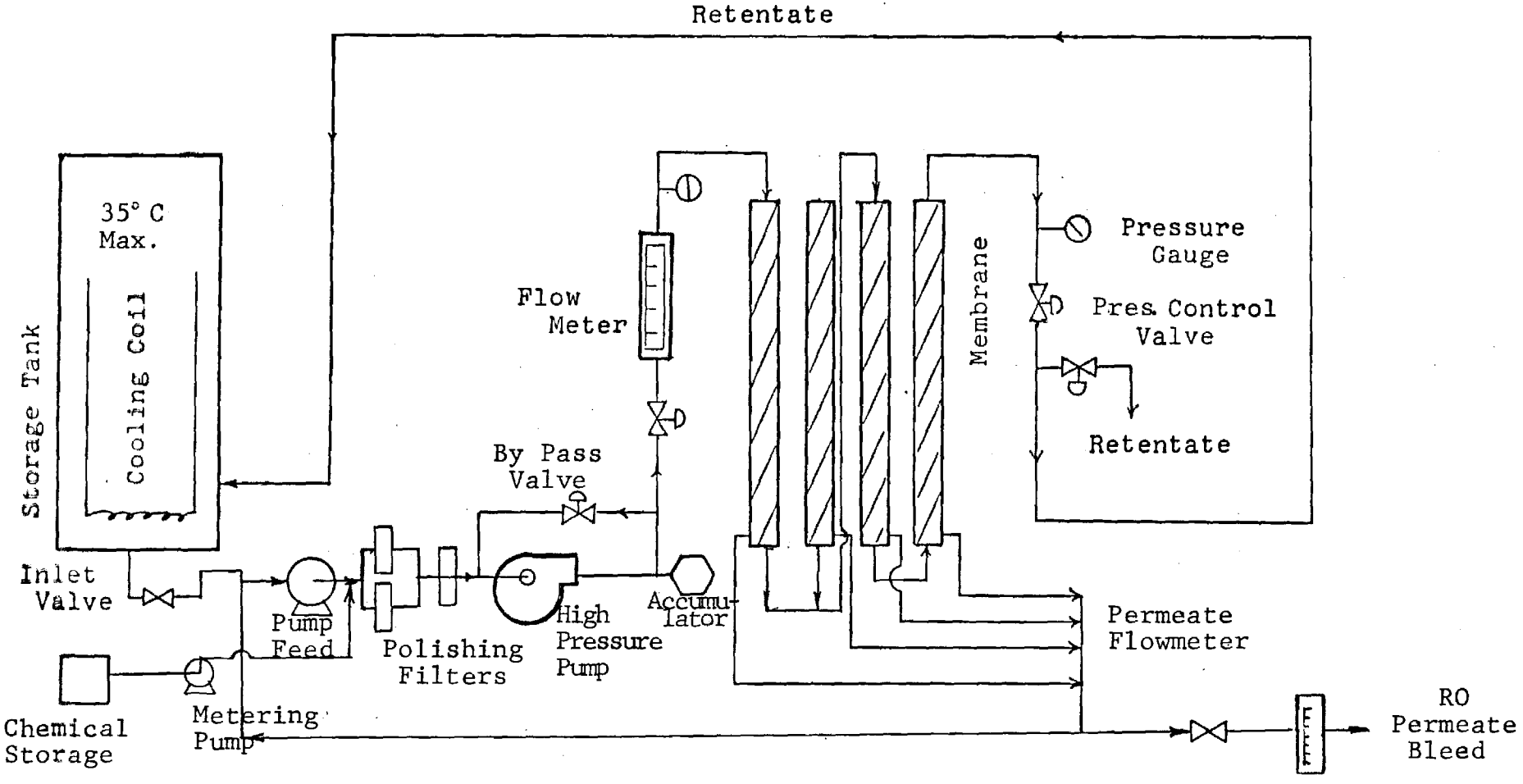

Figure 5 A Schematic Diagram of the Reverse Osmosis Pilot-Plant

various AFFF wastewaters spiked with 3-6% of Ansul and FC-206. The amount of these AFFF agents required for the entire duration of this pilot plant study could be as much as 500 to 1000 gallons for each of the 6% AFFF concentrates. While most of these AFFF concentrates can be recovered from the synthetic wastewater (i.e., tap water spiked with AFFF), up to one-third of the spiked AFFF in actual firefighting wastewaters is expected to be lost in the UF retentate. If every experiment requires the use of 1000 gallons of wastewater spiked with 6% AFFF concentrate (i.e., 60 gallons of AFFF per test), 20 gallons of it will have to be supplemented in the repeated experimentations. Therefore, it requires 700 gallons of AFFF concentrate to just run one test per week with the actual wastewater during the 8-month testing period.

In addition, chemicals are needed to adjust the pH of UF permeate and chelate the scale-forming calcium and magnesium salts for the subsequent RO experiments. The amount of sulfuric acid has to be determined based on the alkalinity of tap or waste waters used at the testing site. The amount of chelating agents, such as citric acid, sodium hexameta phosphate (SHPP), sodium tripoly phosphate, has also to be determined based on the results of water analysis of the City of San Diego City water. In general, the concentration of these additives used is approximately 100 ppm for a period of one-half hour at 200 psig during the regeneration step. Duponts PT-B citric acid mixtures which were developed specifically for regenerating B-10 "Permasep" permeator should be purchased for the pilot-plant study. Specific instruction are provided by Dupont for its application. There might be sufficient amount of Dupont's PT-B on stock in Fort Detrick which was procured originally for the MUST project. Although the testing solutions contain sufficient

amounts of surfactants, detergents such as Alconox or enzyme based Alconox, Biz, may be needed to clean both the UF and the RO unit. Generally 1/4 oz of detergent is used for each gallon of cleaning solution; a total of 1.5 lb detergent will be needed for each cleaning process utilizing 100 gallons of cleaning solution. On the basis of one cleaning per month, a total of 12 lbs of Alconox, or enzyme based detergent, will be needed.

V. TEST METHODOLOGY AND PROCEDURES

Analytical Methods

For the pilot-plant study, the most practical means of analysis of samples are to determine parameters that are simple and easy to measure on the testing sites and yet informative enough to assess the performance and to detect malfunction of the system. Analyses of those parameters which falls into this category include COD, pH turbidity, conductivity and shake tests. TOC analysis can be also used to check the results of COD test. This can be done later in the Civil Engineering Lab at Port Hueneme.

COD

The chemical oxygen demand (COD) of the organic matter present in the synthetic and actual wastewaters can be determined by the COD test as described in Section 508 of Standard Methods for Examination of Water and Wastewater, 14th Edition 1975. All samples shall be filtered through a 0.45 μm Gelman membrane filter or a fiberglass mat filter prior to analysis.

pH

The pH of the wastewater should be measured to determine suitability of the UF permeate for the RO process. pH can be determined using a direct or digit readout pH meter.

Turbidity

The turbidity of the RO feed and the UF membrane permeate should be measured to determine suitability of the feed for RO as well as intactness of the UF membrane. It can be determined using a potable Hach turbidity meter.

Shake Test

The foaming property of the samples can be used to approximate the surfactant concentration. The foaming property can be determined by the method commonly referred to as the shake test. This determination consists of placing 100 ml of a properly diluted sample in a 250-ml graduated cylinder with a securely fitted glass stopper. The sample should be shaken vigorously for 30 seconds and allowed to settle for five minutes. The volume of foam will then be measured after standing for five minutes. The results of this test can be represented by the volume of foam. The shake test has been used successfully by the AFFF Manufacturers and in the membrane and the anaerobic treatment processes to replace the less reliable and yet tedious surfactant and fluorocarbon determinations. However, the validity of using the shake test to monitor membrane rejection of this AFFF active ingredient, lies in the use of samples diluted with the same dilution water at the same concentration level. In other words, the volume of foam may not be proportional to the amount of surfactants in AFFF over a broad concentration range.

TOC

The total organic carbon (TOC) of the organic matter in the samples can be used to confirm the results of COD tests as well as to monitor possible changes of the AFFF compositions after the membrane treatment process. The COD/TOC ratio of AFFF concentrate varies between 3.4 to 3.6. A drastic difference in this ratio for the RO retentate may represent a significant change in the composition of the AFFF constituents after the UF process. TOC can be determined according to Standard Methods.

Conductivity

Conductivity measurement can be used to determine the amount of total dissolved solids (mainly ionic nature) in the samples. The results of this test can be used to assess the performance of the RO membrane. A high rejection of TDS* (e.g., 99% and better) accomplished by the B-10 module provides an assurance of high recovery of all AFFF active ingredients by the RO process. On the other hand, a poor rejection (e.g., 97% or less) indicates the deterioration of the B-10 module. Membrane rejection of TDS can be restored by treating the B-10 module with the Duponts' BT-B citric acid mixtures according to procedures supplied by Dupont. The conductivity or TDS can be determined using a Myron Cell (Myron Company, Los Angeles, CA, Model 0-5000 ppm, 3-range TDS meter-Telephone: 714-438-2021).

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*$\%\ \text{Rejection of TDS} = \dfrac{(\text{TDS})_{\text{feed}} - (\text{TDS})_{\text{permeate}}}{(\text{TDS})_{\text{feed}}} \times 100\%$

Evaluation of AFFF

In order to eliminate possible delays and confusion experienced with the test of recovered AFFF equipment required for the evaluation of AFFF according to the fire extinguishing test procedures of NRL, Washington, D.C., it should be made available, together with trained personnel, for the pilot-plant studies on the recovery of AFFF with the membrane processes.

Membrane Testing Procedures

The hydraulics and rejection of UF/RO system should be tested prior to any pilot-plant studies with either synthetic or actual wastewaters. Only when the system performs properly according to the following testing procedures, the membrane experiments should then be conducted.

Ultrafiltration

Membrane flux of tap water should be determined versus operating pressure at a constant temperature (e.g., 25°c). Figure 6 shows the flux-pressure data of Abcor's HFJ (currently designated as HFM) and HFK membrane determined at Georgia Tech. It can be used to compare if the membrane is severely fouled or cracked. The former is reflected by a flux which is appreciably lower than that shown in Figure 6 whereas the latter appreciably higher. Since it is desirable for the UF membrane to have a lowest possible rejection of all AFFF ingredients as well as a complete rejection of all suspended solids, membrane rejection of turbidity should be determined using a 500 ppm by weight of Bentonite suspension. UF rejection of turbidity can also be used to determine whether there is any leakage between the feed and the permeate sides of the system.

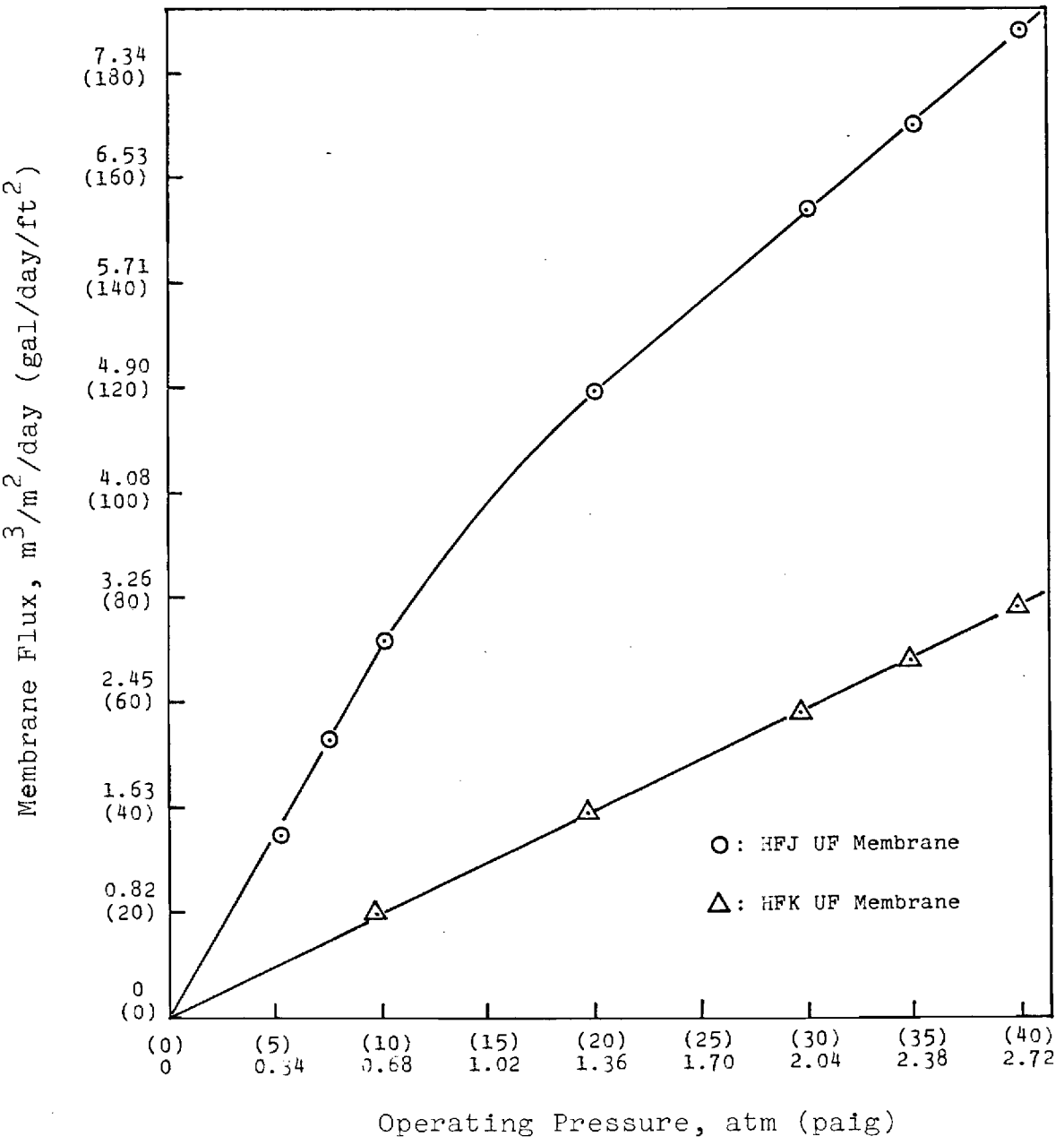

Figure 6. Abcor HFJ and HFK UF Membranes Pressure Effect Tap-Water Studies (Plotting Membrane Flux vs. Operating Pressure), at Constant Temperature, 25°C

Reverse Osmosis

The performance of the RO system can be determined by the membrane rejection of a 3500 ppm by weight of NaCl solution at a pressure of 600 psig and a feed flow rate of 6 gpm. A rejection of better than 99% of NaCl based on TDS measurement with a Myron Cell should be accomplished by the B-10 module prior to any experiments with wastewaters. Treatment of the B-10 module with the Duponts citric acid mixtures according to the procedures provided by Dupont is necessary should the rejection of NaCl solution be less than 97%. The B-10 should yield a permeate flow rate at 1.5 gallons per minute under the prevailing testing conditions.

Experimental Protocols

The experimental protocols to be conducted for the pilot-plant studies can be divided into three phases as outlined in Table 1.

After each phase of studies, the RO retentates which yields the highest level of foam forming property will be subject to firefighting tests with or without the supplemental of 1/3 of fresh AFFF (on TOC or COD basis) according to the testing procedures of NRL's. The fire extinguishing tests of AFFF should be conducted on the site, i.e., San Diego.

VI. DATA COLLECTION AND ANALYSIS

All data obtained from the membrane treatment should be recorded according to the format given in Table 2. Calculation of membrane rejection data and the results of fire extinguishing tests should be computed and recorded in Table. 3.

Table 1

Experimental Protocols for the Membrane Treatment of AFFF

Phase		Experiment	Parameters to be Evaluated
I	A.	UF of 6% AFFF synthetic wastewater	Membrane fluxes and rejections of COD, TOC and shake test data for 0, 50, 80, 90 and 95% product water recovery at 25°c and 50°c, respectively
	B.	RO % UF permeate collected with the synthetic wastewater	Membrane fluxes and rejections of TDS, COD, TOC and shake tests data for 0, 50, 80, 90, and 95% product water recovery at 25°c with and without chemical additions (such as STPP, SHPP or citric acid) and pH adjustment
II.	A.	UF of wastewater spiked with 6% of fresh AFFF concentrate	Same as I-A
	B.	RO of UF permeate collected from II-A	Same as I-B
III.	A.	UF/RO of wastewaters spiked with 6% of recovered AFFF concentrate	Same as II-A but run at an optimum temperature and as II-B with chemical addition pH adjustment
	B.	UF/RO of wastewaters spiked with 6% AFFF recovered under III-A	Same as III-A

Table 1 (continued)

Phase	Experiment	Parameters to be Evaluated
IV	A. Recovery of AFFF from unspiked wastewaters*	operated under optimum conditions conditions
	B. Recovery of AFFF from repeated use of AFFF recovered under IV-A	successive testing of recovered AFFF from actual wastewater
V	Disposal of retentate obtained form the UF process	Disposal alternatives such as drying bed, land filling, combustion, etc.

*i.e., wastewaters generated from experiments used for the evaluation of AFFF according to NRL procedures

Table 2

Data Collection for the Membrane Experiments

Code_____

Phase_____

AFFF_____

UF temp_____ °c

Chemicals_____

Date_____

Ultrafiltration

% Product Water Recovery	Flux, Avg GPD/ft^2	Feed						Permeate						Retentate			
		COD	TOC	Turb	Cond	ST*	pH	COD	TOC	Turb	Cond	ST*	pH	COD	TOC	Cond	ST*
0	✓	✓	✓	✓		✓		✓	✓	✓		✓	✓				
50	✓	✓		✓		✓		✓		✓		✓	✓				
80	✓	✓		✓		✓		✓		✓		✓	✓				
90	✓	✓		✓		✓		✓		✓		✓	✓				
95	✓	✓	✓	✓		✓		✓	✓	✓		✓	✓				

Reverse Osmosis

	Avg. GPD/ Module																
0	✓	✓	✓	✓	✓	✓		✓	✓		✓	✓					
50	✓	✓		✓	✓	✓					✓	✓					
80	✓	✓		✓	✓	✓					✓	✓					
90	✓	✓		✓	✓	✓					✓	✓		✓	✓	✓	✓
95	✓	✓	✓	✓	✓	✓		✓	✓		✓	✓		✓	✓	✓	✓

* Shake tests obtained with the same amount of dilution water

(✓) Check mark indicates data to be taken for the experiments

Table 3

Analysis of Experimental Data

Code_____

Ultrafiltration	% Rejection					
% Product Water Recovery	COD	TOC	Turb	Cond	ST*	Results of Fire Extinguishing Tests
0	✓		✓		✓	
50	✓		✓		✓	
80	✓		✓		✓	
90	✓		✓		✓	
95	✓	✓	✓		✓	✓
Reverse Osmosis						
0	✓	✓		✓	✓	
50				✓		
80				✓		
90				✓		
95	✓	✓		✓	✓	✓

* shake test

VII. TEST SCHEDULE

In reference to Table 1, the schedule for a 8-month period of field evaluation of the pilot-scale UF/RO system is given in Table 4.

Table 4

Schedule for the Field Tests

Phase	Experiments*	1981 8	9	10	11	12	1982 1	2	3
I	Performance test of UF/RO	—							
	A	—	—	—					
	B		—	—	—				
II	A				—				
	B					—			
III	A					—			
	B					—			
IV	A						—		
	B							—	
V									—

* Refer to Table 1 and Section V for UF/RO Membrane Testing Procedures

VIII. REFERENCES

1. D. B. Chan, "Development of Design Criteria and Test and Evaluation Procedures of a UF-RO Membrane System for AFFF Recovery from Firefighting Wastewaters - Statement of Work," March 1981.

2. E. S. K. Chian, T. P. Wu, and R. W. Roland, "Membrane Treatment of Aqueous Film Forming Foam (AFFF) Wastes for Recovery of AFFF Active Ingredients," Final Report, U. S. Navy, Civil Engineering Laboratory, October 1980.

3. R. P. Schmitt, "Recovery of AFFF Active Ingredients from Wastewater by the UF/RO Process," Final Report, V. J. Ciccone & Associates, Inc., Woodbridge, VA 22191, January 1981.

APPENDIX I

The following modifications for the design of the MUST UF/RO system were suggested as a result of inputs from both Dick Schmitt and Ed Chian during a visit with Dr. Dick Durrows on February 20, 1981.

UF System

-- One more bank of UF modules (28 10-foot tubes) relined with 62 ft^2 of Abcor HFM membrane shall be added. The total membrane areas for the entire UF unit will then be 124 ft^2. The estimated costs are $2,800 plus freight.

-- A feed tank for the UF unit is needed. The estimated cost is $3,000.

RO System

-- A vacumm or low-pressure shut-off switch is to be installed between the inlet to the high pressucre Cat pump and the outlet of the Cuno polishing filter.

-- An 1/2-gallon pressure accumulator (Greer Accumulution 3000 psi - Olaer Products, Los Angeles, CA) is to be installed vertically on top of the Cat pump.

-- Two pairs of stainless plugs are needed to cut off the feed flow to and the brine flow from two RO modules. (disregard this item).

-- A permeate flow meter is to be installed after the breed from the RO unit.

-- Water analysis data from a typical San Diego City water is needed.

-- pH and scale control is necessary. A supply of sodium hexaphosphate and citric acid is needed.

-- A surge tank that holds the fluid flow from the UF to the RO units along with the necessary fittings are to be provided.