Item ID Number:	00105
Author	Cobb, H.D.
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Report/Article Title	Biodegradation of Phenolic Paint-Stripping Waste: Laboratory Evaluation of a Fixed Film Batch Reactor
Journal/Book Title	
Year	1979
Month/Day	May
Color	
Number of Images	119
Description Notes	F09635-77-C-0156; JON 21037W77; Program Element 63723F

Cobb, H.D., et al
1979

Biodegradation of Phenolic paint-stripping waste: Laboratory evaluation of a fixed film batch reactor

Microbiology

ESL-TR-79-11

BIODEGRADATION OF PHENOLIC PAINT-STRIPPING WASTE: LABORATORY EVALUATION OF A FIXED FILM BATCH REACTOR

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MAY 1979

FINAL REPORT
OCTOBER 1977-JANUARY 1979

ENGINEERING AND SERVICES LABORATORY
AIR FORCE ENGINEERING AND SERVICES CENTER
TYNDALL AIR FORCE BASE, FLORIDA 32403

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: ESL-TR-79-11
2. GOVT ACCESSION NO.:
3. RECIPIENT'S CATALOG NUMBER:

4. TITLE (and Subtitle): BIODEGRADATION OF PHENOLIC PAINT-STRIPPING WASTE; Laboratory Evaluation of a Fixed Film Batch Reactor
5. TYPE OF REPORT & PERIOD COVERED: Final Report Oct 1977 - Jan 1979
6. PERFORMING ORG. REPORT NUMBER:

7. AUTHOR(s): Howell D. Cobb, Jr; John W. Egan; William E. Olive, Jr; Daniel J. Hansen
8. CONTRACT OR GRANT NUMBER(s): F08635-77-C-0156

9. PERFORMING ORGANIZATION NAME AND ADDRESS: Laboratory of Cellular Physiology, Trinity University, San Antonio TX 78242
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: JON 21037W77; Program Element 63723F

11. CONTROLLING OFFICE NAME AND ADDRESS: HQ AFESC/RDVW, Tyndall AFB FL 32403
12. REPORT DATE: May 1979
13. NUMBER OF PAGES: 110

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):
15. SECURITY CLASS. (of this report): UNCLASSIFIED
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Available in DDC

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Trickling filter	Reactor genetics
Phenol	Chromium
Paint stripper	Toxic waste
Biodegradation	Fixed-film

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

USAF aircraft and ground support equipment require the protection of durable epoxy-polyurethane surface coatings. Maintenance of such painted surfaces using phenol - and chromium-containing strippers has created a waste disposal problem that is aggravated by the centralization of large aircraft depainting operations. The present investigation studied performance of a selectively-seeded, dedicated-function, trickling filter-type biodegradation unit. The specific waste target was the concentrated phenolic waste water produced at the Kelly
(continued)

Block 20 continued.

AFB-ALC depaint facility. Three filter units utilizing a top-down fluid-air flow batch operation were built at Trinity University, San Antonio, TX. Experiments were run examining solid support media choice, bed length and volume, ventilation requirements, hydraulic surface loading, phenol concentration and loading, rate kinetics, chromium tolerance, starvation response, and temperature effects. Results indicate that a small plastic bio-ring medium in this type filter operation, coupled with a genetically selected ecoysytem of column microorganisms, is an effective means of dealing with this waste stream. Requiring only coarse (#18 mesh) pretreatment filtration, the three 3 ft^3 columns showed essentially zero-order kinetics, handling concentrations of 1000 ppm at a hydraulic loading of 6.1 gpm/ft^2 with an average removal rate of 3 GM/Hr per ft^3 of reactor at 20°C (68°F) and 5.7 $GM/Hr/ft^3$ at 30°C (86°F). Effluent phenol concentrations of less that 1 ppm were achieved. Compressed air at 0.16 cfm/ft^2 supplied adequate filter ventilation. Phenol:nitrogen:phosphorus ratios of 1:10:48 were adequate for maximal rates; TRIS buffer at 1 g/L maintained optimum pH at 7-8. (A sensor-controlled pH-stat system might replace the buffer with inexpensive alkali pH adjustment.) Concentrations up to 3500 ppm phenol, and starvation for periods up to six weeks, were tolerated with recovery to normal within 72 hours; overnight and weekend shutdowns were routinely handled with no effect on rate. Routine process effluent contained only low amounts of fine suspended solids. Bed depths up to 11.5 ft yielded similar rates-per-unit-volume.

It was theorized that the batch process with its alternating starvation/loading cycles selects for a microbial community better able to cope with occasional wider swings in this cycle. A thin-film reactor conserves the genes of its adapted community more efficiently than other reactor types. The combination of a batch operated thin-film reactor could, on theoretical grounds, be expected to show stability under conditions which would normally upset the function of a continuous-flow system. This study showed that such a system could also offer competitive phenol removal rates.

The data summarized in this report suggests that a batch fixed film process may have advantages over other biological unit processes for some phenolic wastestreams. Further, the literature surveyed indicates that various recovery schemes and physical/chemical treatment processes such as incineration, adsorption, and chemical oxidation may be more appropriate technologies for the treatment of certain phenolic wastes. The selection of a process for a particular wastestream should, then, involve an evaluation of all existing technologies, including the batch process described here, from a treatment efficiency, capital cost, and operation and maintenance standpoint.

PREFACE

This report was prepared by the Laboratory of Cellular Physiology, Trinity University, San Antonio, Texas under Contract No. F08635-77-C-0156 with the Civil and Environmental Engineering Development Office (CEEDO). Detachment 1, Armament Development and Test Center (ADTC)/ECW, Tyndall AFB FL (26 Oct 77 - 30 Sep 78). Effective 1 March 1979 CEEDO was inactivated and became the Engineering and Services Laboratory (ESL), a directorate of the Air Force Engineering and Services Center located on Tyndall AFB Florida 32403.

Capt Jay A. Farmwald was program manager for this work.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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I. INTRODUCTION

A. BACKGROUND

The Air Force maintains five Air Logistics Centers (ALC's) which support large-scale paint stripping operations. These centers are responsible for the maintenance, depainting, and repainting of operational aircraft and ground support equipment. Current Air Force paint systems employ polyurethane topcoats with epoxy primers. Depainting these materials requires the use of paint removers which contain significant concentrations of phenol and chromium (see Table 1) (1). The resultant waste water represents the single major source of phenolic waste within the Air Force.

Although 1983 EPA guidelines do not include prescribed technology for phenolic paint stripping wastes per se, the ability of industrial and municipal processing installations to meet the extremely low phenol concentration discharge requirements (0.02 ppm for Best Available Control Technology Economically Achievable--BACTEA) (2) will be affected by loadings from paint stripping facilities. The problem is aggravated by the centralization of large aircraft depainting operations.

Process alternatives for the treatment of phenolic waste waters have been heavily investigated by both the Government and private industry. Systems examined have included various recovery schemes, incineration, adsorption, chemical oxidation, and biological degradation. For point-source streams

totaling less than 50 gpm at 2000 ppm, recovery of phenols does not appear economically feasible (3). Incineration is energy-intensive and practical only where generated heat can be used for additional purposes. Activated charcoal adsorption may be practical, depending strongly on waste component impact on carbon renewal capacity, on costs associated with stringent pretreatment filtration, and on long-term operating costs. Chemical oxidation schemes can be dependable and effective on high-strength point-source waste; but if more than one target toxicant is present, the number of treatment steps may increase. Its normal use is as an adjunct--either a pretreatment or polishing step--to some other treatment process. Commercial analysts have found installation costs for bioprocessing systems to be slightly higher than activated carbon, but operating costs to be significantly lower (4). For an excellent summary and further references the reader is referred to an article by K. H. Lanouette (5).

The Air Force is continuing to evaluate alternative processes in their efforts to meet current interim and future final discharge standards in a cost-effective manner. Control technologies have been demonstrated for permanganate and ozone oxidation (6) and carbon adsorption (1). The use of existing military biological treatment facilities has also been evaluated (7). However, since the date of that Air Force investigation point-source treatment technology has advanced.

B. BIOPROCESSING ALTERNATIVES

Biological treatment of phenolic wastes has proven economical and reliable for certain industrial wastes at large and intermediate scales (2,4,8,9). Generally, biological process design, system cost, and full-scale reaction rates vary, depending on the exact nature of the waste water to be treated. Due to the complex kinetics that can occur when other toxic compounds or alternate carbon sources are present, the common engineering practice is to evaluate the efficiency of bioprocessing on the specific waste stream (5,10). Most applications of biological phenol degradation have been in the petrochemical and plastics industries (4,11,12,13), where activated sludge systems operating in the continuous-flow mode were early introduced (14,15). This treatment scheme evolved from the standard municipal facility experience, not entirely from recognized advantages of the method. Augmentation of municipal and industrial facilities sludge populations with adapted or mutated organisms has helped to improve process reliability (16,17); longer cell retention times can conserve these adapted organisms and lead to improved efficiency (5,18,19). Trickling filter operations have been investigated and proven feasible, especially for low-flow waste streams (20). High recycle rate filters are the rule. In larger systems, trickling filters have been used for "roughing" high-strength phenolic industrial waste in conjunction with oxidation lagoons (21,22,23,24). Commercial toxic waste water treatment engineering companies offer a variety of bioprocessing

approaches: The normal procedure includes development of strains suited to the particular waste stream, in a manner similar to that involved in this study, followed by seeding of an appropriate type reactor.

A unique aspect of ALC depainting waste streams is the high chromium content of the strippers currently in use. Several commercial concerns market mixtures of "adapted, mutated" sludge organisms designed for seeding municipal and industrial waste facilities. These products are based primarily on soil pseudomonad organisms such as Pseudomonas putida, and Pseudomonas aeruginosa (17), and have proven useful in other systems (25). However their kinetics in this system are not documented, and of the mutant strains on the market, none are recommended by their makers to operate at the chromium concentration of the KAFB facility raw waste stream (17.5-59.5 ppm) (1, 7). (See Table 1 and Section III. D. 5.) Dilution to the required 2 ppm tolerance level would entail an increase in waste stream volume of X20, on the average.

Novel experimental systems such as fluidized bed bioreactors (25) have reported high degradation rates, but influent streams are required to be very dilute, and such reactors have hypercritical flow regimes; that combination of conditions makes them unsuitable for applications where constant attention is not desirable.

In the current study, the application of a genetically-adapted ecosystem to a narrowly defined waste stream

TABLE 1

ANALYSIS OF PAINT STRIPPER AND PAINT STRIPPING WASTEWATER

NOTE: All values in mg/l

COMPONENT	PAINT STRIPPER	PAINT STRIPPING* WASTEWATER
PHENOL	200,000	1040 - 4060
METHYLENE CHLORIDE	600,000	75 - 2000
SURFACTANTS	100,000	120 - 4000
PARAFFIN WAX	50,000	- - - - -
METHYL CELLULOSE	40,000	- - - - -
WATER	10,000	- - - - -
CHROMIUM TOTAL	2,400	17.5 - 59.5
CHROMIUM +6	2,400	- - - - -
TOTAL PHOSPHATE (AS P)	- - -	10 - 28
SUSPENDED SOLIDS	- - -	107 - 303
VOLATILE SOLIDS	- - -	458 - 2700
TOTAL SOLIDS	- - -	800 - 3830
COD	- - -	9200 - 36400
COD FILTERED (0.45u)	- - -	7250 - 35100
TOC	- - -	2710 - 14400
TOC FILTERED (0.45u)	- - -	2520 - 13600
OIL AND GREASE	- - -	8.4 - 66.3

* As reported by Perrotti (3) for the San Antonio ALC (KAFB) wastestream.

(a dedicated function system) is observed at the pilot scale. Research and reaction data are obtained using a batch trickling filter process on point-source paint stripping waste water generated at the San Antonio ALC depaint facility. The results demonstrate that the specific high phenol/chromium waste stream can be economically and efficiently detoxified to low levels on site using a biological system. The utilization of a batch process protocol to maintain selective pressures on the ecosystem is partly responsible for the unusual system kinetics, and suggests that full benefit of genetic engineering is not being obtained using standard treatment techniques.

II. PHASE ONE: DEVELOPMENT OF SEED CULTURES AND MEDIA

A. ISOLATION AND MAINTENANCE OF BACTERIAL STRAINS

Initial sampling for phenol degraders for use in these experiments was done in the paint stripping room (Bldg 375 KAFB), at locations expected to harbor microorganisms already exposed to concentrations of stripping waste. Bushnell and Haas (26) reported that hydrocarbon degraders would most likely be found in areas where such selective forces might already have acted.

Samples on sterile cotton swabs were used to inoculate phenol agar slants (for composition, see Table 2) at the stripping site; the slants were then transported to our laboratory where they were incubated for four days at 37°C., then used to inoculate flasks containing 50 ml of phenol broth (see Table 2). After incubating for two days at 37°C., broth cultures were streaked for isolation onto phenol agar plates. The isolated colonies appearing on these plates were separated, yielding 24 possible strains, based on colony morphology.

Tests for the ability to efficiently metabolize phenol in a broth medium were run on each isolate. Strains J10, J13, J20 and J24 (see Section II.C.) were selected for further study. These stocks were maintained on phenol agar slants and plates, transferred semi-monthly, and were never exposed to other carbon sources.

TABLE 2.
MEDIA COMPOSITIONS

NOTE: All amounts given in grams/liter unless otherwise specified.

BMS (Basal Mineral Salts)	
MgSO4	0.1
CaCl2	0.01
NH4NO3	1.0
FeCl3	0.0005
NaCl	0.1
K2HPO4	2.0
KH2PO4	1.0
H20 to make	1 L
pH	8.0

Phenol Broth	
Phenol	0.5
BMS to make	1 L
pH	8.0

SMW (Synthetic Waste Water)		
		Flask Column
Phenol	0.50 - 1.0	
Sigma 7-9 TRIS	6.00 - 1.0	
NH4NO3	0.24 - 0.5	
KH2PO4	0.09 - 0.2	
Tap Water to make	1 L - 1 L	
pH	8.0 - 8.0	

Phenol Plates & Slants	
Phenol	0.5
Agar	20.0
BMS to make	1 L
pH	8.0

AMW (Actual Waste Water, Fortified)		
Initial Feeding Formula (each experiment)		Intra-Experiment Feedings
KAFB waste water(*)		KAFB WW 125 mL/L
Paint Stripper (*)		Paint Stripper (*)
Sigma 7-9 TRIS	1.0	Sigma 7-9 TRIS 1.0
NH4NO3	0.5	NH4NO3 0.5
KH2PO4	0.2	KH2PO4 0.2
Tap Water (*)		Recycled Spent Waste to make 1 L
pH	8.0	pH 8.0

* The amounts of tap water (for dilution), and of paint stripper required to fortify AMW to desired run concentration varied with actual KAFB waste phenol concentration.

TABLE 3.

TAP WATER ANALYSIS, SAN ANTONIO, TEXAS

SPECIES	PPM	SPECIES	PPM
Ca^{++}	74.3	CO_3^{--}	259.3
Mg^{++}	14.8	SO_4^{--}	25.4
Na^{++}	8.5	Cl^-	15.1
Fe^{++}	0.02	NO_3^{--}	1.65
Mn^{++}	0.002		

B. MEDIA FORMULATIONS

For any microorganism to operate efficiently, certain mineral requirements must be met. Table 2 lists the various media that were developed for the study's two phases. Discussed fully here are those which apply to the growth parameter "flask" experiments; the others are more thoroughly handled in their appropriate Sections.

The Basal Mineral Salts (BMS) medium met all the basic mineral requirements for these organisms and was well-buffered within the physiological pH range (pH 7 - 8). Its formulation was derived on the basis of prior experience with phenolic degraders (27). This became the standard medium against which performance by others was measured in the flask growth studies. However, supplementation of this magnitude in an operational degradative facility was recognized as undesirable, and very likely unnecessary.

An analysis of San Antonio tap water (Table 3) revealed that, with the exception of nitrogen and phosphorus, most of the required minerals were present in concentrations sufficient to sustain cell densities of 1 mg/ml (28). Based on the assumption that bacterial cells contain approximately 8% nitrogen and 1 - 2% phosphorus, it was estimated that supplementation of tap water base by 0.242 g/L NH_4NO_3 and 0.091 g/L KH_2PO_4 would be required to maintain this density, or a Ø:P ratio of 1:48.2, and a Ø:N ratio of 1:10.

A concentration of 6 g/L TRIS* was used to buffer at the desired pH for flask runs, but this proved unnecessarily high; a much lower amount was used in the Pilot Plant Synthetic Waste Water (SWW) medium. The SWW formulation thus represented an economical basic recipe, which was varied experimentally to determine the stringency of mineral and carbon source requirements. It was recognized that, under field conditions, tap water mineral contributions would be significantly augmented by additions from aircraft parts, metal pallets, drain trough gratings, the paint and stripper themselves, the concrete floor, etc.; and that other carbon sources would be present. These parameters were left until the final phase for study (see Section III. D.).

* TRIS (hydroxymethyl) aminomethane 99.0-99.5% Buffer Grade Sigma Chemical Co., St. Louis, Missouri.

C. SEED CULTURE GROWTH STUDIES

Flask phenol broth culture growth studies were conducted on selected bacterial strains. The primary criteria established to select these strains from the 24 isolates were rapidity of growth in phenol broth, colony morphology and vigor on phenol agar plates. Strains J10 and J13, both pseudomonads, and strains J20 and J24, almost identical subspecies in the Coryneform group, were chosen for the growth studies.

Organisms from stock subcultures were used to inoculate spinner flasks containing one liter of phenol broth. After cultures achieved useful turbidimetric density in log phase, the cells were harvested by centrifugation (5000 G) and resuspended in a small volume of BMS medium. Nephelometer flasks containing either BMS-based phenol broth, or SWW test media were inoculated with sufficient cell suspension to yield an initial cell concentration of 0.1 mg/ml (dry weight-to-volume), and placed on an Eberbach reciprocating shaker for incubation at room temperature (25° C).

Throughout all phases of this study, cell concentrations were determined turbidimetrically with a Klett-Sommerson colorimeter. One ml samples were drawn at predetermined intervals and quickly frozen, pending phenol and pH determinations. Phenol concentration was measured with a Barber Coleman Series 5000 gas chromatograph, equipped with a flame ionization detector (FID), under the following conditions: column packing

10% SP-2100 on 80/100 Supelcoport; column temp. 180° C., injector temp. 190° C., detector temp. 225° C., nitrogen flow 63 ml/min., air at 40 psig., hydrogen at 20 psig; and sample size 3 ul.

The preliminary growth and phenol metabolism experiments indicated that growth rates of J20 and J24 were about three times those of J10 and J13, and that phenol metabolism rates of J20 and J24 were about one-half those of J10 and J13. Typical performances are presented in Figure 1.

The disparities between growth versus phenol metabolism exhibited by the pseudomonads were disconcerting. It was clear that these organisms were degrading the phenol incompletely. Pigment buildup in the broth was substantial, a phenomenon reported by other investigators (29, 30). Since rapid column seeding was regarded as a prime quality in the prospective inoculants, Coryneform strains J20 and J24 were selected for use. An added incentive was their heavy mucoid colony appearance, promising the quick development of a substantial slime layer on the Pilot Plant's support media, which would in turn contribute a foothold for other incidentally introduced organisms as the column ecosystem evolved. (See Section III.D.10.)

Figure 2 illustrates growth curves and phenol utilization rates typical of J20 and J24. The figure shows response to a variety of mineral salts compositions.

When raised on SWW, J20 achieved phenol utilization

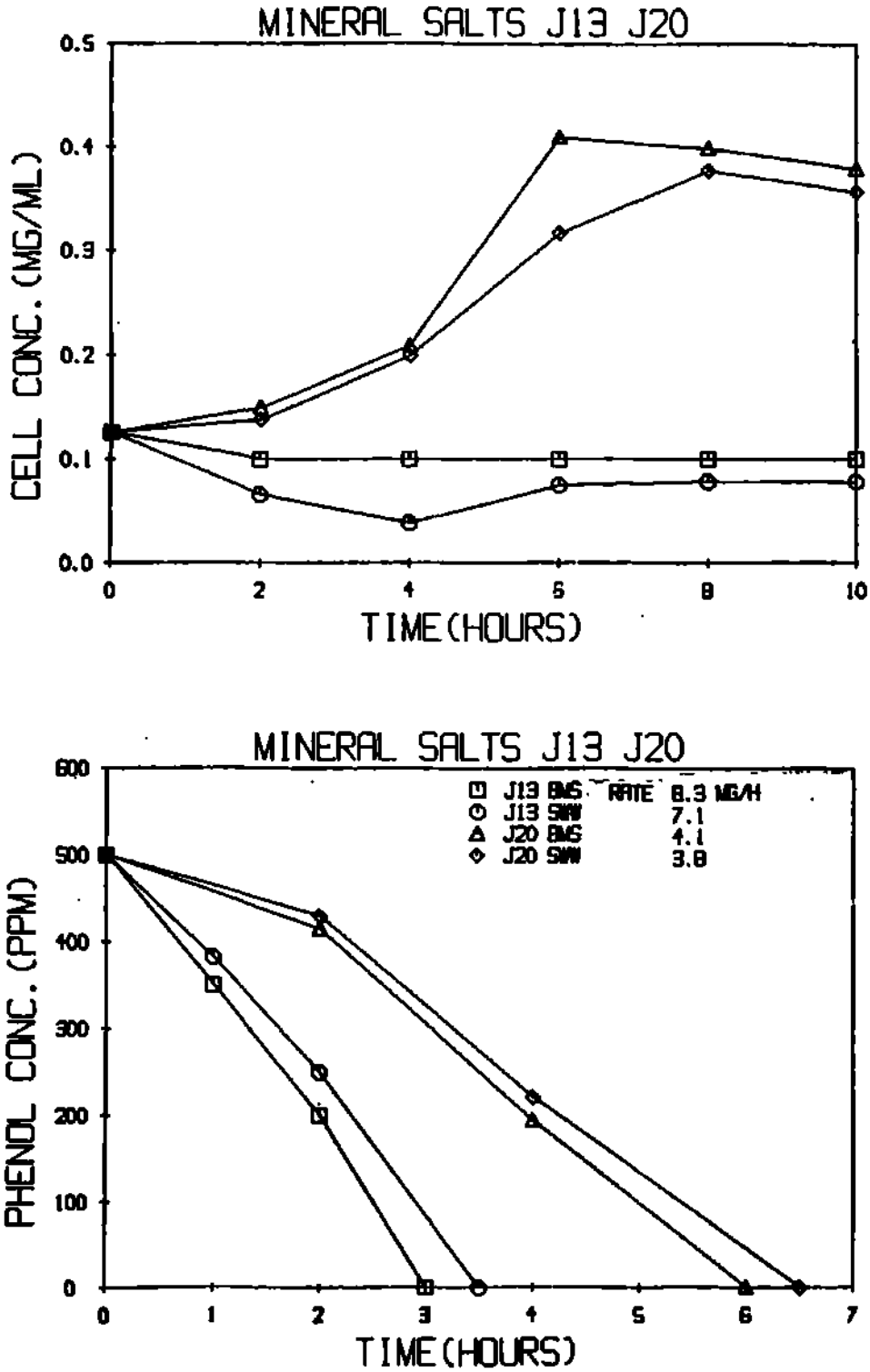


FIGURE 1. Growth and phenol utilization by strains J13 and J20 in two selected formulations of mineral salts.

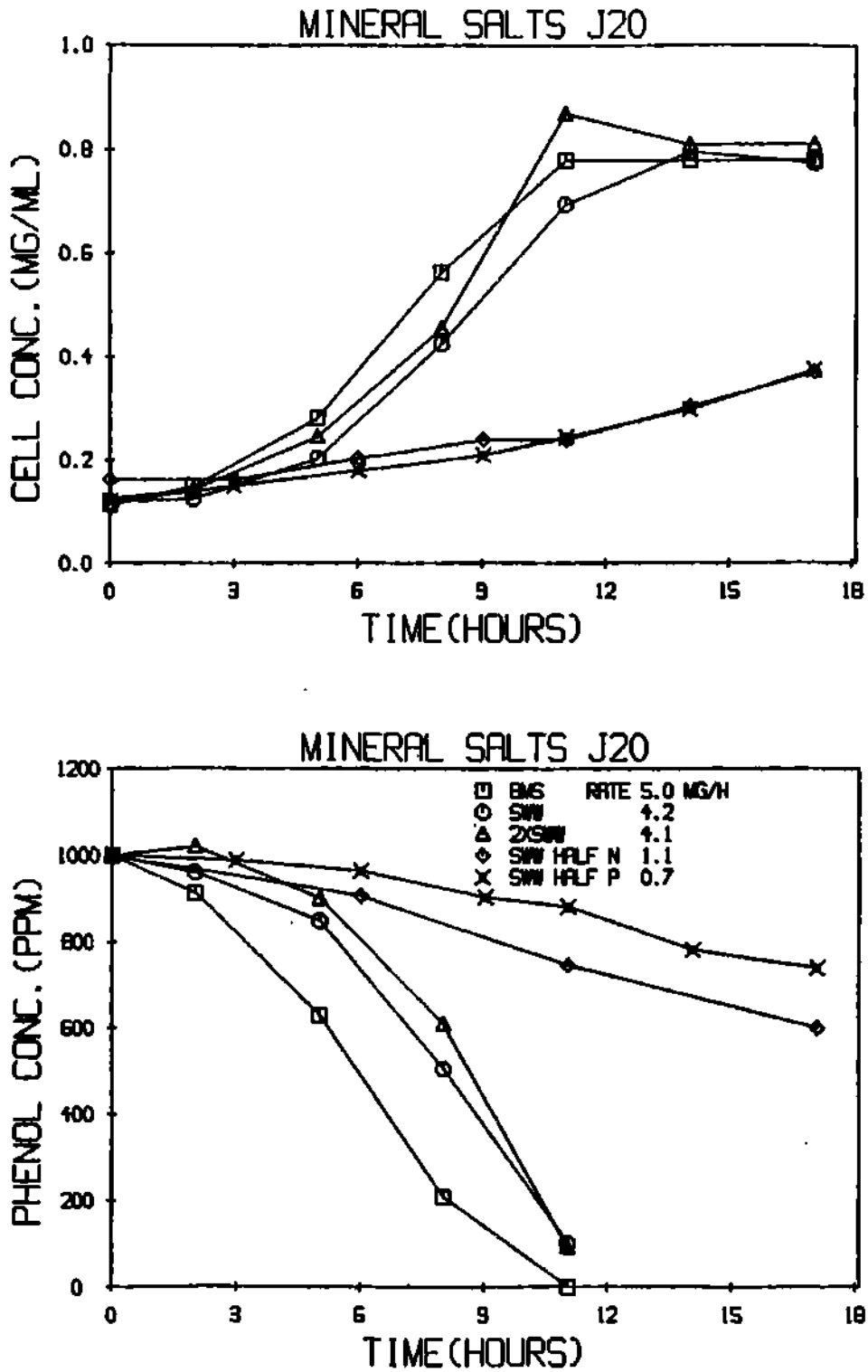


FIGURE 2. Growth and phenol utilization by strain J20 in five selected formulations of mineral salts media. 2XSWW= double SWW mineral salts; SWW ½N and ½P= half the NH_4NO_3 and KH_2PO_4 concentrations of SWW. Rates are in milligrams per hour (mg/hr).

rates of 4.2 mg/hr, comparing favorably to its performance on BMS (5.0 mg/hr). A doubling of the nitrogen and phosphorus component concentrations in the SWW failed to increase phenol degradation rates, although the additional minerals did produce slightly higher cell densities. However, reduction by one-half of either nitrogen or phosphorus produced drastic reductions in the rates of phenol utilization and growth.

From these studies it was concluded that San Antonio tap water is capable of providing a significant proportion of total mineral needs for the inoculant strains selected; that additional mineral input from paint, paint stripper, and other sources would, under field conditions, provide a still larger share. This confirms that it will only be necessary to provide a cheap nitrogen and phosphorus source to a pilot plant, together with a means to maintain a near-optimum pH, in order to assure satisfactorily high rates of microbial phenol metabolism on the Kelly waste.

III. PHASE II: PILOT PLANT STUDIES

A. PLANT DESIGN

1. Rationale for Batch Approach

Rose (31), Grady (32) and others have argued that it is possible to extend batch findings to continuous flow applications in trickling filter operations. From the testing standpoint, where inhibition may be involved, it is easier to obtain kinetic data from batch runs than to attempt such data extraction from transient loadings of continuous-flow systems (33). But more than just experimental convenience recommends a batch approach to the Kelly AFB paint stripping waste. As is discussed in Section IV, trickling filter batch processes may conserve engineered bacterial gene constellations better than the more common means of waste bioprocessing. Space and configuration requirements for trickling filters are more appropriate to retrofitting an operation than activated sludge systems. Trickling filter operating costs are primarily controlled by energy used in recycle pumping and forced aeration. These costs compare favorably to activated sludge facilities which, due to higher biomass densities in the mixed liquor, require a more expensive form of forced aeration and heavier-duty sludge pumps. Trickling filter batch operations are more suited to intermittent waste production and variable phenol concentration. Furthermore, their output tends to require less secondary treatment, carrying less suspended solids. And effluent quality may be controlled simply by altering batch time. Much

work on sequencing batch reactors has been done by Irvine's group (34 , 35 , 36 , 37); periodic operations in other fields demonstrate advantages that apply equally to unsteady-state bioprocessing techniques (38 , 39).

When applied to the Kelly problem, the combination of advantages and untried possibilities made study of the batch mode seem a worthwhile alternative to more conventional continuous-flow treatment.

2. Pilot Plant Design

While the Phase I experiments were in progress, the design of the Pilot Plant system was finalized and its construction implemented. Three identical units were built, capable of independent operation for simultaneous studies, and also able to operate in a closed-loop, or "tandem" mode for the study of factors related to filter volume and depth.

Figure 3 is a detailed schematic of an individual trickling filter unit. The two major structural parts are the column (one foot in diameter, four feet six inches high), and the 160-liter (42.3-gallon) base reservoir. Each column can be loaded with an appropriate support medium; in this case, either ceramic or plastic bio-saddles, or plastic bio-rings (see Section III.B below). A Flotec R2P1 variable-flow pump allows cycling of phenolic waste (synthetic or actual) over the column support media, with surface loadings from 3.3 to 6.7 gpm/ft^2. Compressed air is provided to each unit via a metered inlet at the top of the column, and through a 1"-diameter sparging stone low in the reservoir. Liquid flow rates are monitored with a Cole-Parmer magnetic flow meter; air flow is monitored and controlled with a ball-type metering valve at each entry site. Isolated column operation, or closed-loop, tandem mode operation is effected by the settings of valves in the liquid circuits.

Liquid line access is provided below the flow meter site; access to the reservoir and column effluent

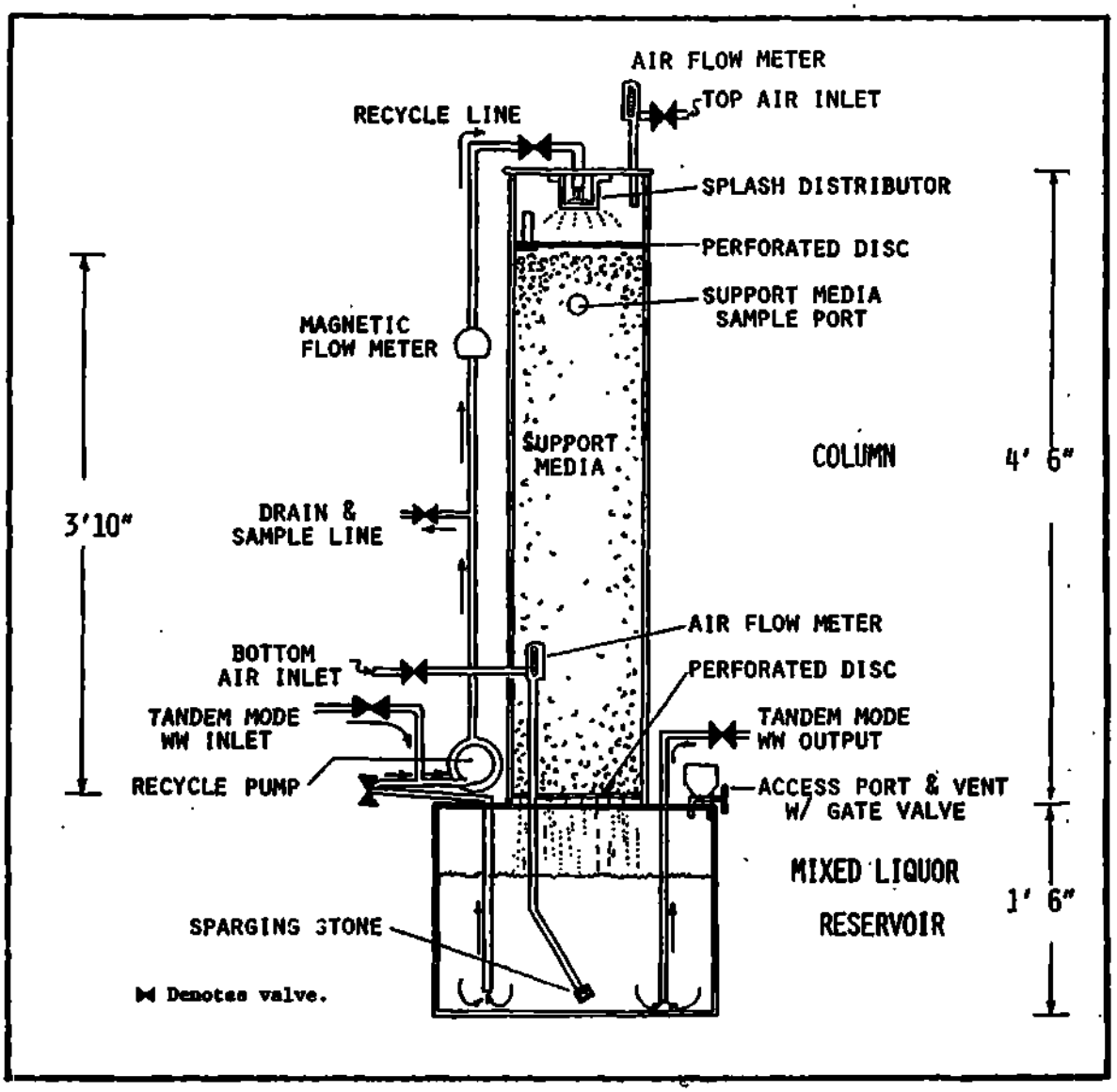


FIGURE 3. Trickling filter pilot plant schematic.

stream is through a large-orifice gate valve in an upper corner; access to the column support media is through a frontside plugged port at the three-foot line of the column.

Throughout the study, the battery of filter units was housed inside a controlled environment chamber allowing maintenance of ambient temperature within ±0.5° C. of desired value (Figure 4). Except where noted, all studies were conducted at 20° C. (68° F.)(See Table 4).

TABLE 4.
STANDARD RUN CONDITIONS

PARAMETER	SYMBOL	METRIC	ENGLISH
REACTOR VOLUME	V_R	85 L	3 ft^3
REACTOR CROSS-SECTIONAL AREA	A_R	7.3 dcm^2	0.785 ft^2
FILTER BED DEPTH (ONE COLUMN)	D_b	11.6 dcm	3.82 ft
FILTER HYDRAULIC FLOW RATE	q_R	18 L/min	4.8 gpm
HYDRAULIC SURFACE LOADING	L_s	2.5 L/min·dcm^2	6.1 gpm/ft^2
FILTER VENTILATION LOADING	f_v/A_R	2.1 L/min·dcm^2	0.68 ft^3/min·ft^2
MIXED LIQUOR TANK VOLUME	V_T	160 L	42.3 GAL
MIXED LIQUOR BATCH VOLUME	V_{ML}	10-120 L	2.6-31.7 GAL
SYSTEM HYDRAULIC LOADING	L_H	see § IV. C.	see § IV. C.
MIXED LIQUOR AERATION RATE	f_{ML}	15 L/min	0.53 ft^3/min
TEMPERATURE	T	20±1° C	68±2° F
INITIAL pH	pH	8.0	8.0
ORGANIC LOADING (INITIAL)	L_o	2.82 g/L·day	177 lb/1000 ft^3·day
INITIAL PHENOL CONCENTRATION	$[\emptyset]_o$	500-600 ppm	500-600 ppm

dcm^2 = 100 cm^2

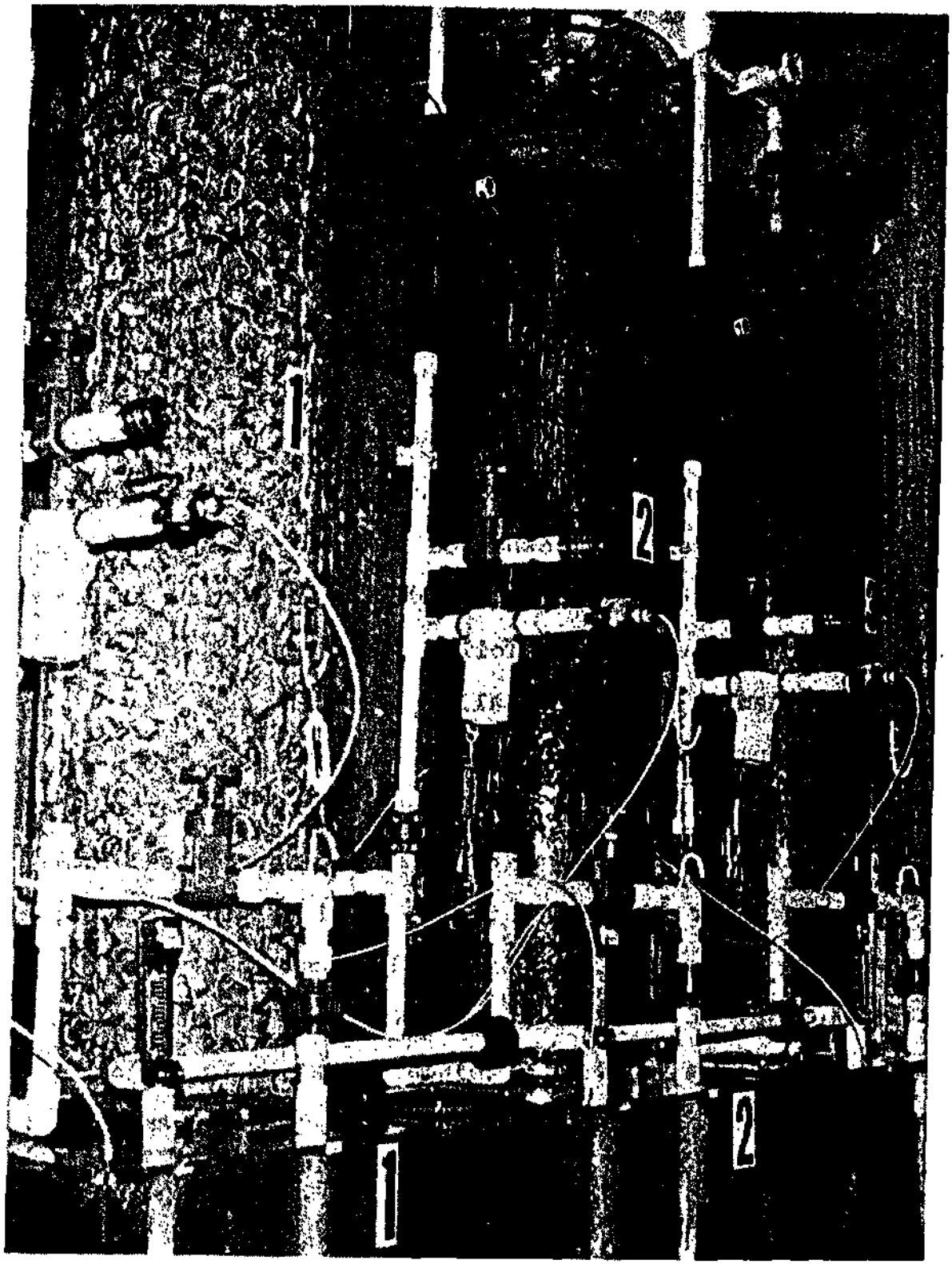


FIGURE 4. Triple columns of the phenolic waste biodegration pilot plant located in an environmental chamber at Trinity University. Note the three experimental packing materials.

B. COLUMN SEEDING

To obtain a large inoculum for commencing column operations, a Virtis Model 43-100 Fermenter containing 16 liters of phenol broth was inoculated with strains J20 and J24. Phenol concentrations and pH were monitored and maintained at nominal levels until the cell density had increased to approximately 1.2 mg/ml. During microscopic examination it was determined that approximately 10% of the population consisted of a pseudomonad invader closely resembling strain J13. Inasmuch as sterile technique was not to be imposed on column handling, it was decided to allow the mixture to become the primary inoculum, and to follow subsequent expected population changes microscopically.

Column seeding was accomplished using 4.5L of the primary seeding mix diluted to 40L with Synthetic Waste Water (SWW). This liquid phase was then recycled over the columns in tandem mode for 30 min. to insure equal seeding inocula; then valving was switched to isolated column mode. At a surface loading of 6.7 gpm/ft^2 with 15 L/min forced aeration through the bottom inlet, the columns were run for 20 days. During this attachment phase, phenol concentration and pH were monitored. When phenol concentration would near depletion, five liters of spent liquor (1/8th of V_{ML}) would be removed and replaced with fresh SWW media containing Tris buffer, NH4NO3, KH2PO4, and supplemented with enough reagent phenol to bring the waste liquor up to 500 ppm.

C. SUPPORT MEDIA SELECTION

1. Support Media Design Requirements

One objective of this study was to select a support medium material for a phenolic waste degradation trickling filter unit which would yield a satisfactory compromise between engineering considerations and chemical/biological demands.

It is known that the degradation potential of trickling filters is heavily dependent upon filter biomass. Biomass growth, in turn, can be maximized with support media having large specific area (surface area-to-volume ratios), and by low liquid flow rates. Unfortunately these are precisely the conditions which lead to flow blockage by particulates and sloughing biomass. Processes using once-through bottom-up fluid-air flow design have encountered this problem, which increases maintenance costs and down time, offsetting the high efficiencies of such units. As in the classic municipal trickling filter, such processes have found filamentous growths particularly annoying. Their solutions have included extremely fine (25-micron) pretreatment filtration and periodic support media replacement, both highly undesirable procedures for industrial operations which routinely produce large amounts of particulates in their waste. It was felt that, with a small sacrifice in potential rate, a system design incorporating much higher hydraulic surface loadings, coupled with coarser support media, might avoid these difficulties.

2. Methods and Materials

It was hypothesized that there would exist an optimum specific area, a (surface area/unit volume), for the packing medium which would support an active, stable biomass, tolerant of particulate loading. To test this parameter, two medias were chosen exhibiting a wide range of a: a plastic saddle with a=20.67 dcm^2/L (63 ft^2/ft^3); and a plastic bio-ring with a=34.12 dcm^2/L (104 ft^2/ft^3).*

Further, the surface characteristics of the support media in a high rate filter might prove critical for biomass anchorage, channeling patterns, composition of the final organism population, and thus for phenol degradation performance. The most important changes would be those in the nature of the biomass population. Large shear forces would demand a far more tenacious slime layer. To test for surface effects, a ceramic saddle* comparable in specific area to the plastic saddle was selected, with a=25.59 dcm^2/L (78 ft^2/ft^3). These solid media are illustrated in Figure 5.

From the engineering point of view, plastic substrates present a much greater ease in handling than the ceramic saddles. There is a seven-fold savings in weight per unit volume using plastic saddles. (This advantage is only negligibly reduced for the bio-rings which, with a higher packing density, weigh slightly more per unit volume than the plastic saddles.) Both of the substrate materials are satisfactorily inert and durable. In fact, the principal

* Plastic saddle: Actifil 01-0100; plastic bioring: Actifil 10-0160; ceramic saddle: Actifil 20-0160; Norton Co., Akron, Ohio.

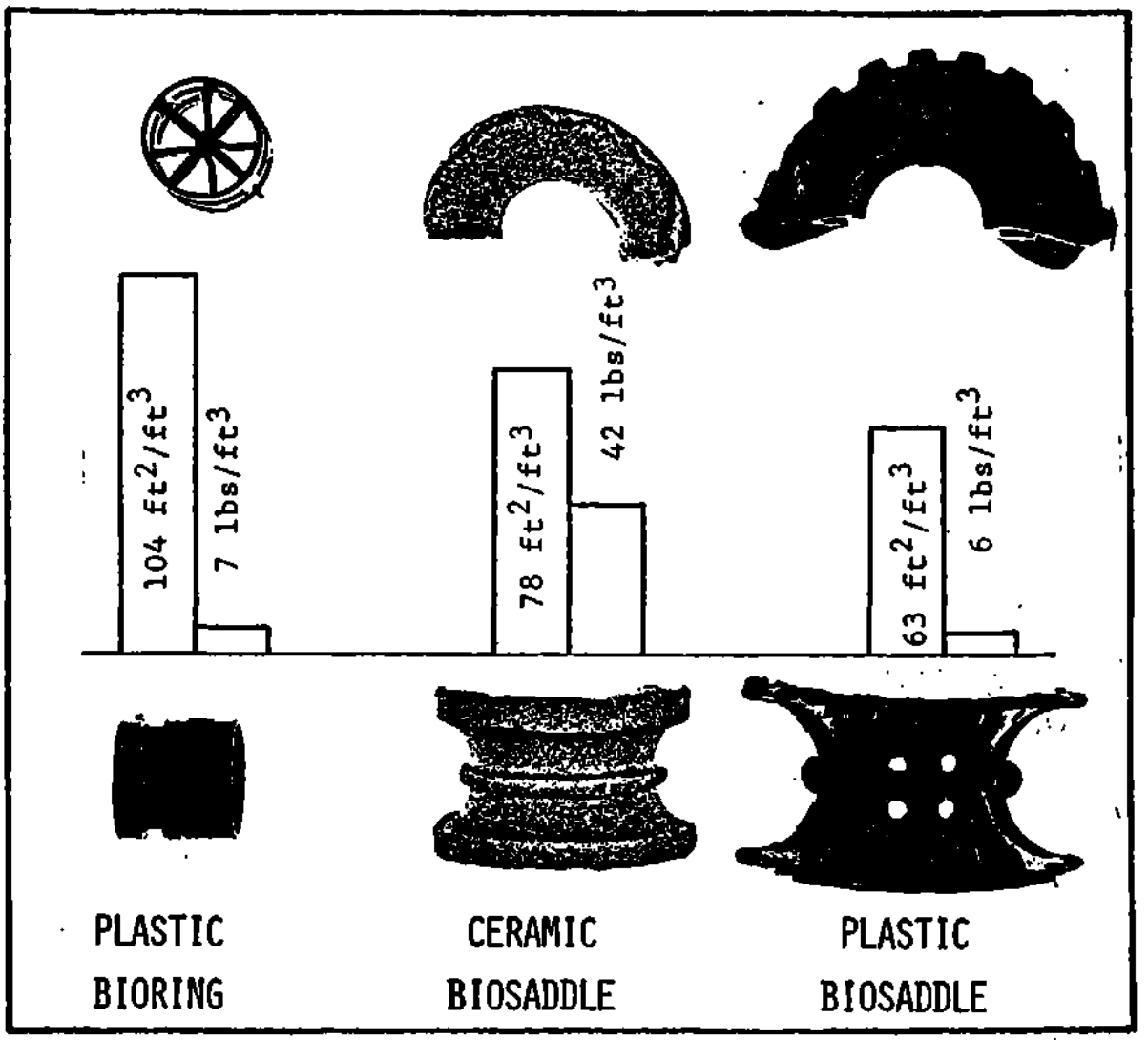


FIGURE 5. Three types of support media studied, shown from two perspectives at actual size, with a graphic depiction of their relative weight and surface area/unit volume.

points remaining in doubt were related to packing density effects on hydraulic flow, and the suitability of the smooth plastic surface as an anchor site for our developing ecosystem of phenol degrading organisms.

To insure similar startup conditions in media evaluation runs, fresh SWW was added according to the previously discussed protocol and circulated through all three columns in series for 30 min. to insure an equal distribution of microbes in the liquid phase. Experiments were conducted at batch volumes of 20, 40, 80, and 120 liters at hydraulic surface loadings of 2.47L/min·dcm^2 (6 gpm/ft^2) for approximately 50 hrs. each. When phenol concentrations approached low levels, one-quarter of the waste water volume was replaced with an equal volume of fresh standard SWW, plus additional reagent phenol sufficient to bring the entire liquid phase volume to the desired concentration. (This procedure was more economical of water and chemicals than discarding and replenishing the entire liquid phase.) During the run, 5 ml samples were taken from the mixed liquor reservoir at appropriate intervals and frozen until GC analysis could be performed. Turbidimetric and pH measurements were obtained at the time of sampling. At the end of each volume run the entire liquid phase was discarded.

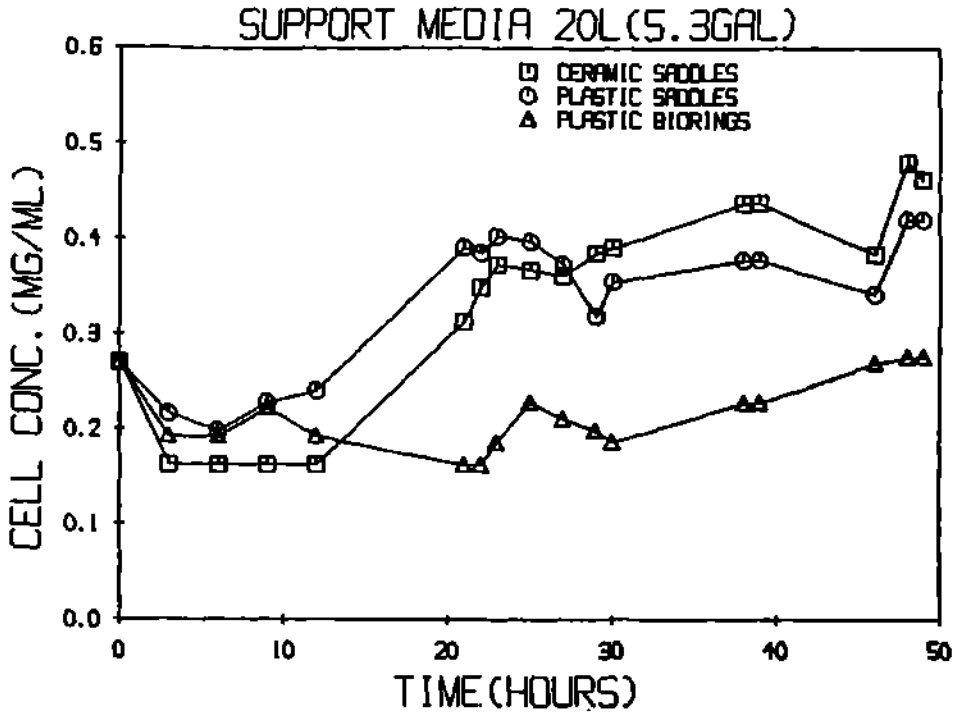
3. Media Performance

The phenol degradation rate curves in Figure 6 show that the bio-rings have a slight but persistent advantage over the other two support media. The relatively low overall rates are indicative of the immaturity of all three columns. (These are overall rates, expressed in Table 5 as grams/hr·ft^3 for each condition.).

Observations of surface attachment and wall growth confirmed that all three support materials presented no hazard to colonization. However, Column 3, packed with bio-rings, exhibited more rapid biomass development and much less wall growth than the coarser materials. The close packing of the bio-rings against the column walls and each other prevented the gross channeling of waste flow that tended to develop with saddles. This effectively reduced superficial flow velocities, favoring attachment.

Later experience with the bio-ring material unequivocally demonstrated that growth densities attained in these early support media experiments were far from the maximum possible, and that these initial rates of phenol degradation were low compared to those attained months later as the column ecosystems matured.

The cell growth patterns seen in the upper graphs of Figure 6 are variations on the classic curve. The two saddle materials yield similar trends; the bio-ring data is more erratic. Since all columns were begun initially with



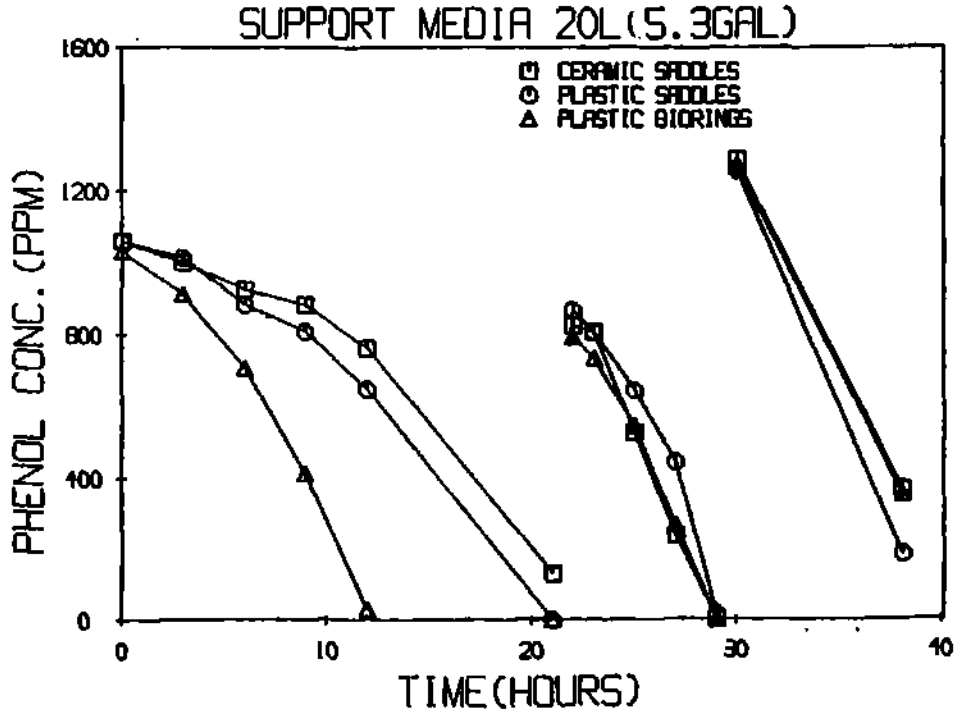


FIGURE 6a.

FIGURE 6 a-d. Cell growth and phenol utilization rates for the three types of support media at batch volumes of a) 20L; b) 40L; c) 80L; and d) 120L. Interruptions in rate curves occur at intra-run feedings. See Table 5 for rate data.

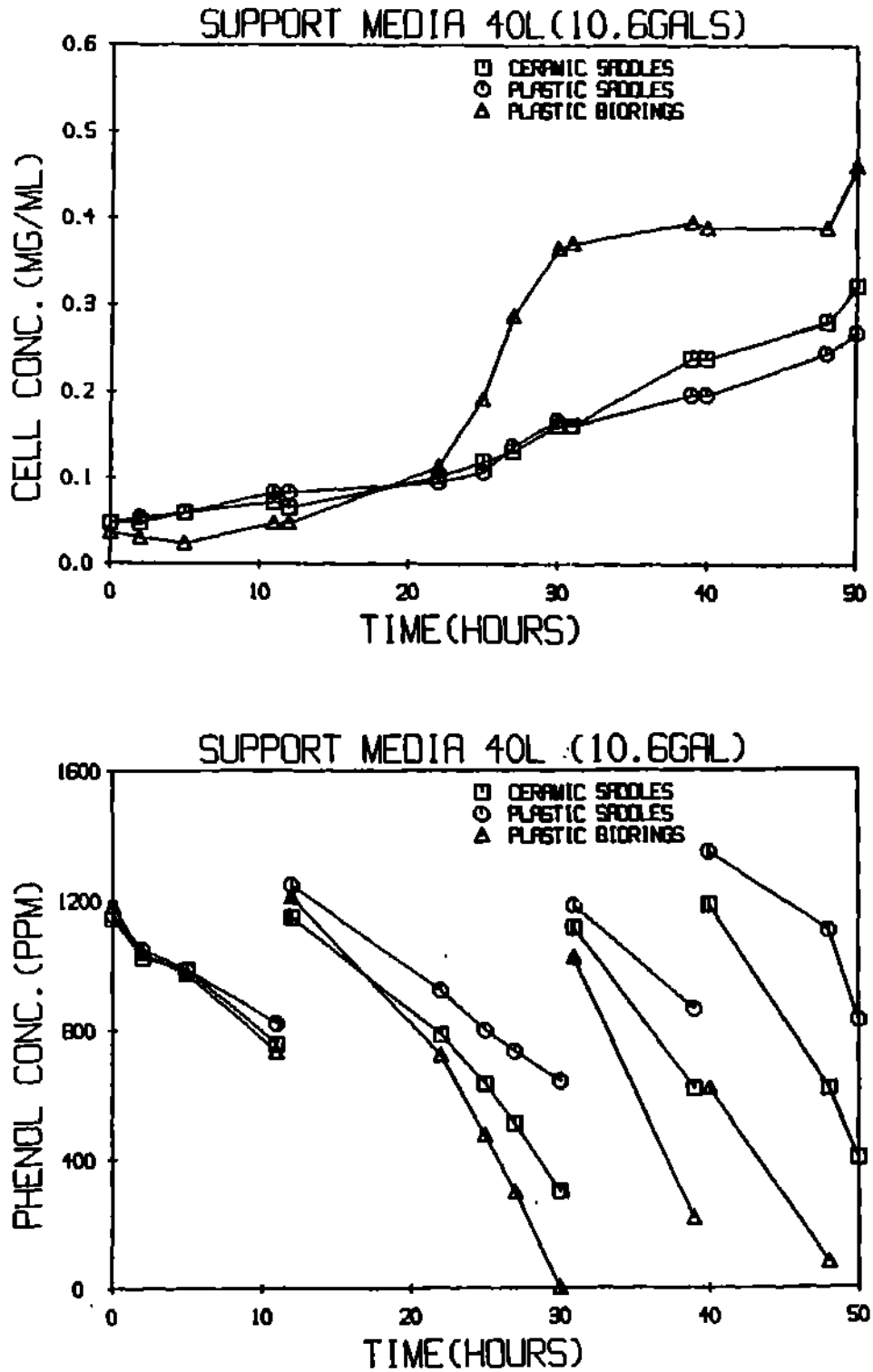
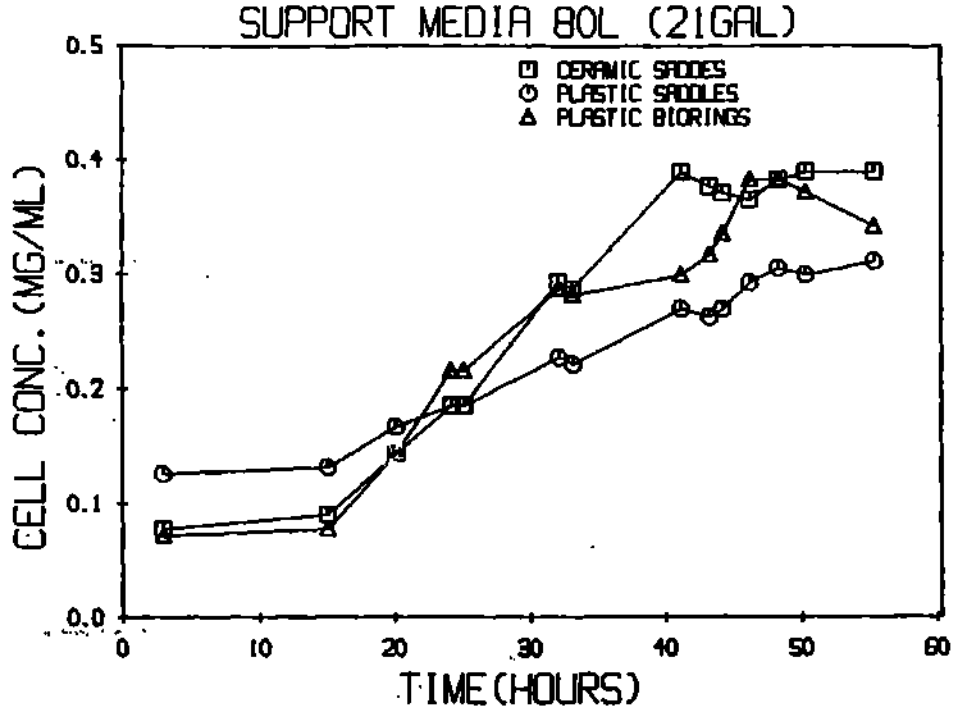

SUPPORT MEDIA 40L(10.6GALS)
CERAMIC SADDLES
PLASTIC SADDLES
PLASTIC BIORINGS
CELL CONC.(MG/ML)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0
10
20
30
40
50
TIME(HOURS)
SUPPORT MEDIA 40L (10.6GAL)
CERAMIC SADDLES
PLASTIC SADDLES
PLASTIC BIORINGS
PHENOL CONC.(PPM)
0
400
800
1200
1600
0
10
20
30
40
50
TIME(HOURS)

FIGURE 6b.


SUPPORT MEDIA BOL (21GAL)
CERAMIC SADDES
PLASTIC SADDLES
PLASTIC BIORINGS
CELL CONC. (MG/ML)
0.5
0.4
0.3
0.2
0.1
0.0
0
10
20
30
40
50
60
TIME(HOURS)

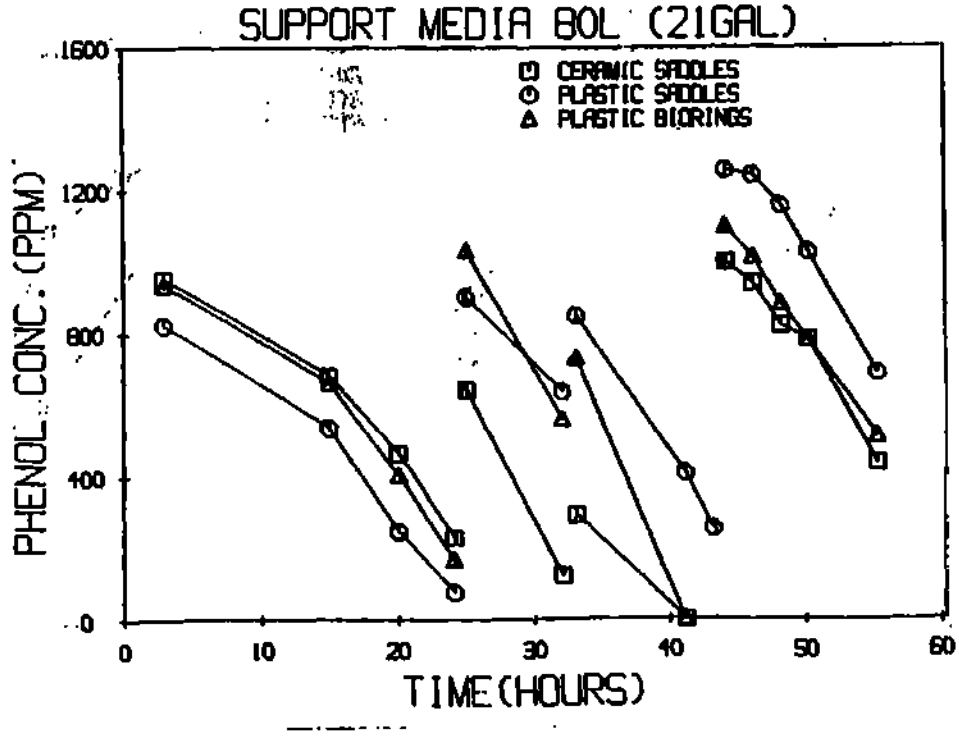
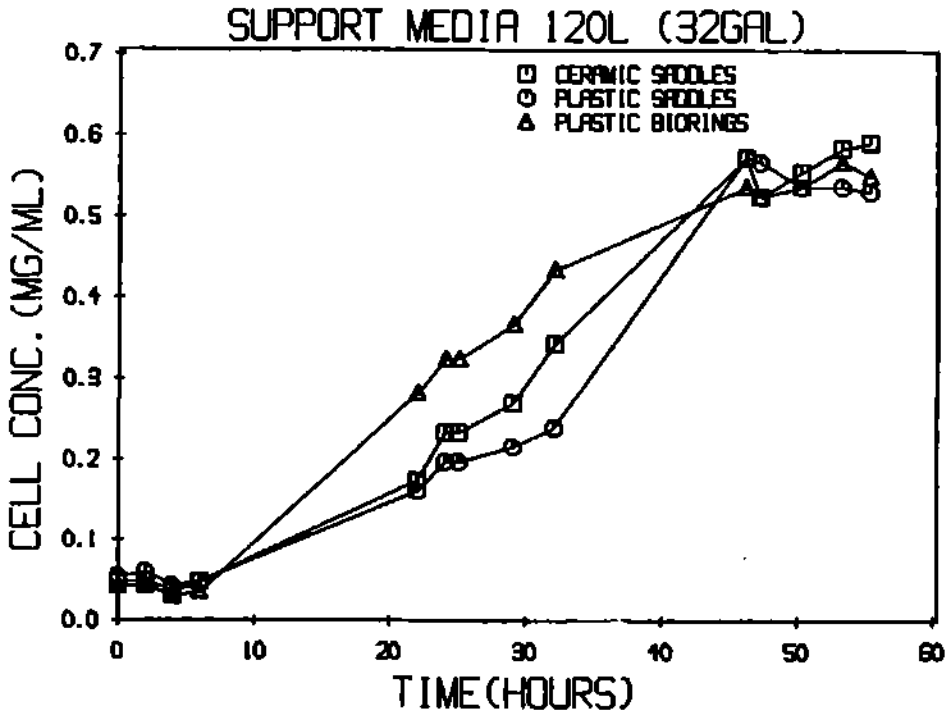

SUPPORT MEDIA BOL (21GAL)
CERAMIC SADDLES
PLASTIC SADDLES
PLASTIC BIORINGS
PHENOL CONC. (PPM)
1600
1200
800
400
0
0
10
20
30
40
50
60
TIME(HOURS)

FIGURE 6c.


SUPPORT MEDIA 120L (32GAL)
CERAMIC SADDLES
PLASTIC SADDLES
PLASTIC BIORINGS
CELL CONC. (MG/ML)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
10
20
30
40
50
60
TIME(HOURS)

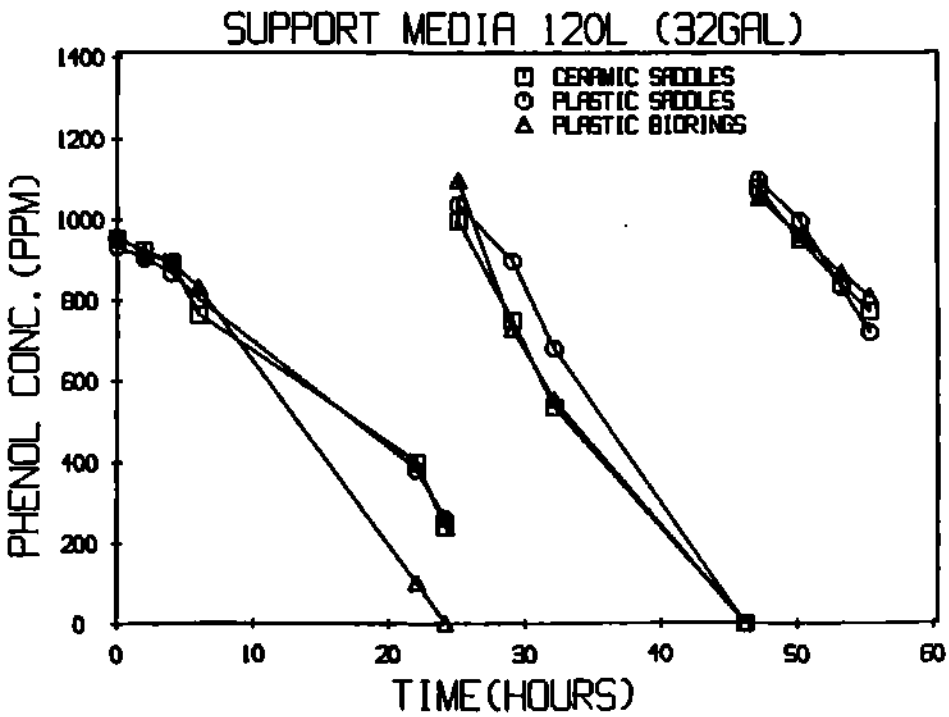

SUPPORT MEDIA 120L (32GAL)
CERAMIC SADDLES
PLASTIC SADDLES
PLASTIC BIORINGS
PHENOL CONC. (PPM)
0
200
400
600
800
1000
1200
1400
0
10
20
30
40
50
60
TIME(HOURS)

FIGURE 6d.

the same liquid phase populations and identical chemical environments at each T_o, the variation seen at 20L and 40L for the bio-rings is difficult to explain. However in both these cases the rate data in Table 5 puts bio-ring performance first. Evidentally microbes attached to the support medium were already appreciably enhancing Column 3's efficiency. In later experiments utilizing the bio-rings, this trend toward very low liquid phase cell densities coupled with high phenol removal efficiency became quite pronounced. There are clear effluent processing advantages to low particulate concentrations in the filter effluent.

In calculating rates for this initial set of experiments, a quantity we term the "bound liquid volume", V_b (fully discussed in the following section), was not taken into account. We were unaware of the effect at the time. However subsequent reevaluation of data for these early experiments has unequivocally shown that V_b is very small for immature columns, as would be expected from the analogy of a "sponge effect": very few absorption sites are available on the stationary phase of a filter at low biomass densities--there is not much of a column "phenol sponge".

Additionally, at this early stage the filter units were not being ventilated, but were sparged in the liquid phase, a condition affecting absolute but not relative performance.

In electing the bio-rings as medium of choice

for all subsequent experiments, we were persuaded by its advantages in both major areas of concern: First, the extreme light weight of the basic material promised to greatly ease structural requirements for large facilities. Second, biomass attachment on the vast surface area offered much greater potential for rapid attainment of high zoogleal film densities in a compact reactor. The higher surface porosity of the ceramic material, said to promote rapid microbial attachment, did not enable that massive medium to approach the performance of the bio-rings.

TABLE 5.

RATE DATA FOR COLUMN SUPPORT MEDIA (PACKING) EXPERIMENTS

NOTE: All rates in grams/hour·ft^3 of support medium

SUPPORT MEDIA	VOLUME				AVERAGES
	20L	40L	80L	120L	
PLASTIC BIORINGS	1.4	1.5	1.9	2.2	1.7
PLASTIC SADDLES	1.1	0.7	1.3	1.7	1.2
CERAMIC SADDLES	1.1	1.0	1.5	1.8	1.3

D. ACTUAL WASTE WATER EXPERIMENTS

1. Methods and Materials

Stringent testing of the pilot plant and its ecosystem was performed using waste water obtained from the Kelly Air Force Base paint stripping facility at Bldg. 375. (This same waste water has been characterized previously by Perrotti (1) for bench and pilot scale carbon adsorption studies. A summary of his findings appears in Table 1.) The waste was pumped directly from the facility discharge sump through a #18 USA Standard Testing Sieve* into 15 gal. drums. Care was taken to obtain waste only during or shortly after active paint stripping operations, allowing observation of maximum concentration conditions. (Since the sump is regularly drained by pumping into sanitary sewer lines, the phenol concentration of waste water fluctuates widely as alternating strip and wash operations are performed.) The drums were then transported back to the laboratory at Trinity University, where they were tested and stored at 20°C. until used. The phenol concentration of raw actual waste water (AWW) was found to vary between 750 and 3500 ppm during the five month collection period, which correlates well with Perrotti's findings.

At the close of the column packing selection phase, Columns 1 and 2 were emptied, washed, and repacked with the

* Provided by personnel of Det 1, HQ ADTC/ECW, USAF Systems Command, Tyndall AFB, Florida.

Actifil 10-0160 bio-ring material. Synthetic waste feeds were then provided and the assembly was run in the tandem (closed-loop) mode for two weeks. At that time, individual column runs indicated comparable rates for all three columns; units 1 and 2 were then considered seeded and ready for experimental use.

The Actual Waste Water experiments followed an SOP similar to that used during the media performance studies with the following exception: after running the initial batch of mineral salts-fortified AWW, subsequent batches within the experiment were brought to standard initial phenol concentration by draining one-eighth of the spent liquid volume, and replacing that volume with fortified AWW, per the formulation detailed in Table 2.

Although turbidimetric measurements were regularly taken on samples from the mixed liquor during runs, their utility was compromised by an unexpected phenomenon. Where in earlier runs cell densities had followed a standard growth curve with substrate disappearance (Figure 6), virtually all experiments in the AWW phase demonstrated a reverse trend. Immediately on run startup the mixed liquor would give relatively high Klett readings--due to the innate turbidity of the AWW, washdown from the filter, and sediment mobilized by the fill procedure. These readings would rapidly decline to a constant level around 35 Klett units--equivalent to approximately .2 mg/ml suspended

solids (Figure 7)--and stay there throughout even a long run. Consequently the usual estimates of biomass production based on mixed liquor cell densities have not been made. It is possible to say, however, that mixed liquor cell densities were never high during the AWW studies, and were significantly lower than those 'normal' growth curves recorded for the early experiments, done when the filter biomass was immature.

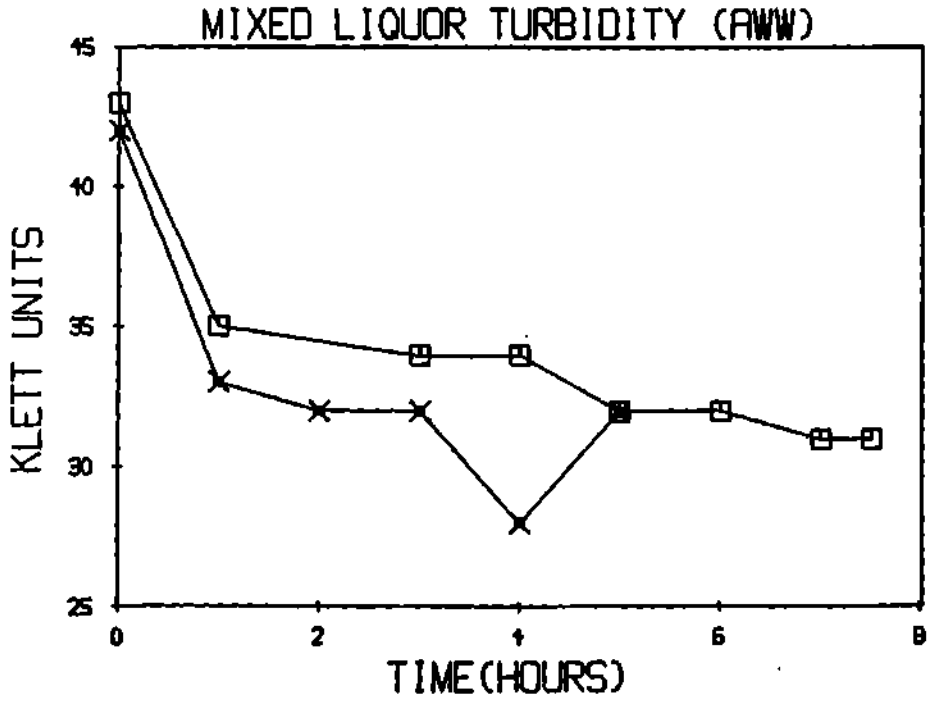


FIGURE 7. Mixed liquor turbidity from mature column runs at a batch volume of 80L.

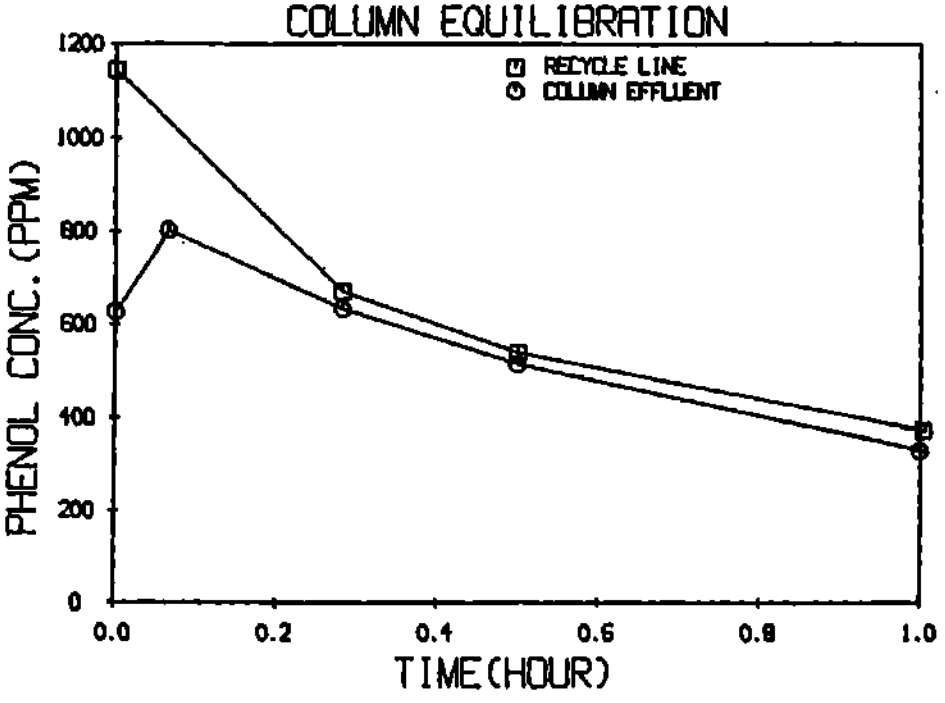


FIGURE 8. "Column sponge" effect during equilibration period. Samples were taken simultaneously from the recycle line and column effluent.

2. Bound Volume Absorption Effect

Biomass established on the column was observed to have a strong absorptive affinity for phenol at the onset of a run. At startup, samples of column effluent typically showed a phenol concentration 50% lower than influent samples of the same plug, with a rapid decline in difference leading to a state of equilibrium over a 30 to 60 minute period (see Figure 8). This "column sponge" effect presented early difficulties in interpreting system dynamics.

There are two possible mechanisms which may account for this effect. On the one hand, there is evidence of phenol-specific adsorption in the biomass, which could be due to microbially-produced compounds with a binding affinity for phenol, such as certain extracellular enzymes. A second mechanism would be absorption, either specific or nonspecific. Specific absorption would describe phenol diffusion into slimes with high phenol diffusion constants. Nonspecific absorption would apply to slimes showing no distinct diffusion "preference" for phenol over other soluble organics. To facilitate mathematical handling of the effect, we elected to adopt a diffusion model for the purposes of this study.

A counterpart to the "column sponge" exists in activated sludge systems (19, 40) and has been put to work in the contact stabilization process. But for other activated sludge systems, initial apparent high rates of substrate uptake must be accounted for only during unsteady-state situations,

such as with hydraulic or organic loading transients (41, 42, 43, 44, 45). Inasmuch as transient states are normally abated by system design, the effect has drawn little attention.

Batch systems, on the other hand, typically exhibit extremes of substrate concentration oscillation. The "sponge" effect can become paramount in determining absolute rates (mass/time) in cases where reactor volume (and the sponge volume) and mixed liquor batch volume do not differ greatly--as in pilot scale projects.

Conceptually, the sponge effect is due to diffusion-equilibration of phenol in the newly recharged mixed liquor with absorptive sites in the filter biomass (see Figure 11), consisting of water, polymeric secretions, bacterial and fungal cells and cellular debris. Theoretical diffusion properties of such bacterial films have been discussed (46, 47), but model equations have limited pragmatic value. There are indications that these materials can show surprising adsorptive specificities, unique to both the particular biomass and substrate of interest.

A high rate trickling filter exposed to limited numbers of carbon sources appears to evolve a characteristic substrate absorptive capacity range. For operational purposes, we have termed this capacity the "bound volume", V_b, defined as that additional water volume which, when added to the initial mixed liquor volume V_{ML}, will result in dilution of the initial absolute mass of substrate added, ϕ_{t_o}, to an effective initial

equilibrium concentration of $[\emptyset e]_{t_o}$, or

$$[\emptyset e]_{t_o} = \frac{\emptyset_{t_o}}{V_b + V_{ML}} \qquad (1)$$

Rearranging,

$$V_b = \frac{\emptyset_{t_o}}{[\emptyset e]_{t_o}} - V_{ML} \qquad (2)$$

Except for inflections following equilibration, and at the low end of $[\emptyset]$, the kinetics of substrate removal for this system are essentially linear. If a zero order rate is assumed during the equilibration period, then $[\emptyset e]_{t_o}$ may be determined as indicated in Figure 9, or:

$$[\emptyset]_t = \left[\frac{[\emptyset]_{t_i} - [\emptyset]_{t_{i-1}}}{t_i - t_{i-1}} (t_i - t_o)\right] + [\emptyset_c]_{t_o} \qquad (3)$$

Rearranging:

$$[\emptyset e]_{t_o} = [\emptyset]_t - \left[\frac{[\emptyset]_{t_i} - [\emptyset]_{t_{i-1}}}{t_i - t_{i-1}} (t_i - t_o)\right] \qquad (4)$$

No attempt was made in this study to thoroughly examine V_b, nor to model its variation. It was treated as an operational parameter, empirically derived. V_b appeared to increase to a steady-state plateau of 35L as the filter biomass

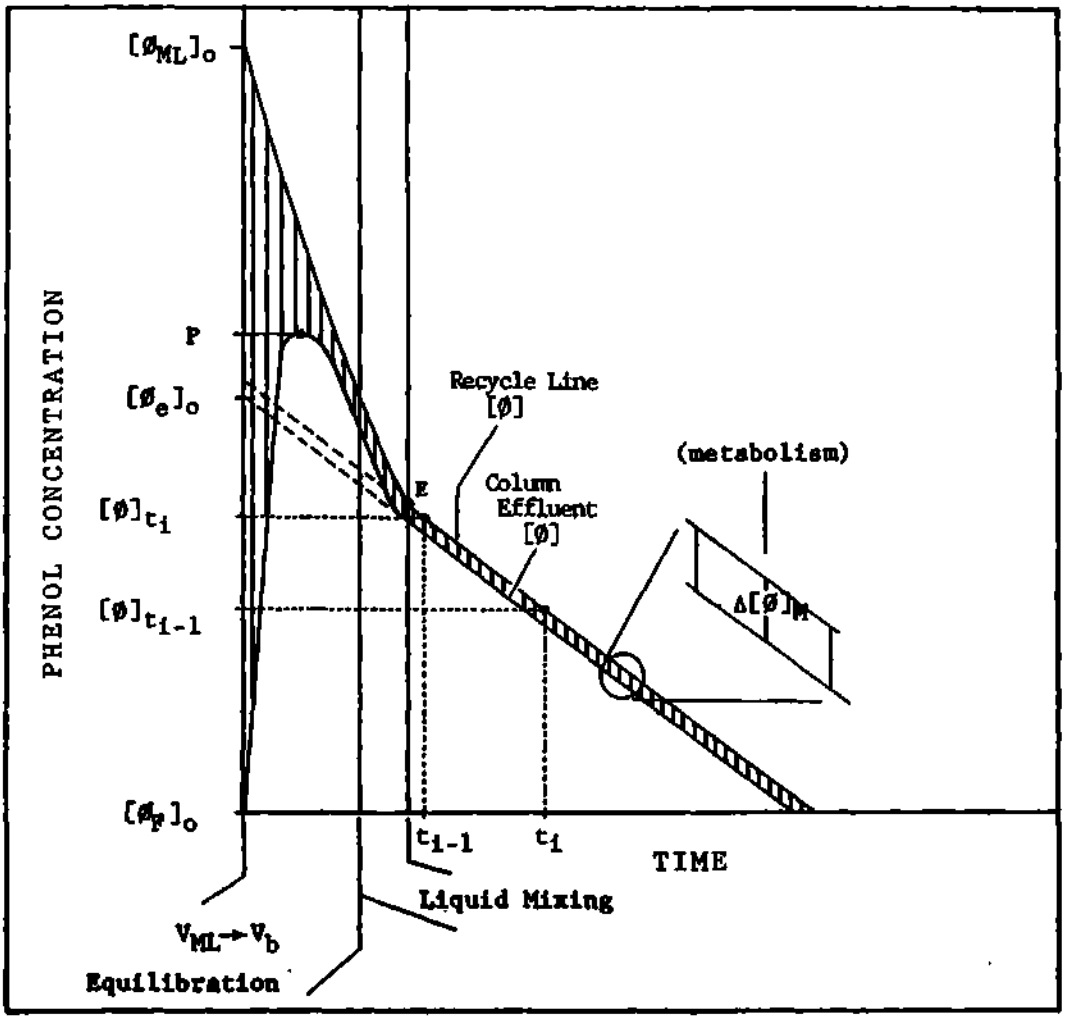


FIGURE 9. Representation of the equilibration process and its relationship to rate calculation using $[\phi_e]_{t_o}$. $[\phi_{ML}]_o$ is the mixed liquor phenol concentration just prior to commencement of batch recycle. $[\phi_F]_o$ is the filter effluent phenol concentration of the first slug through after startup. Sampling of recycle line and column effluent shows a rapid convergence to a steady-state difference. P represents the point at which mass transfer of mixed liquor-borne phenol into the column slime (and V_b) no longer dominates metabolic removal. Continued steep slope of recycle line curve to E is due to lag in liquid mixing of low-phenol column effluent with V_{ML} in batch reservoir. Exact determinants of P have not been defined; in our system, turnover occurred within five minutes of startup, and showed variation with batch size. After equilibration $\Delta[\phi]_M$ was found to represent the instantaneous metabolic rate of the filter bed. If metabolic rate is assumed linear during equilibration, as after, then extension of recycle and column effluent lines to Y-intercept yields a useful imaginary quantity, $[\phi_e]_o$, conceptualized as the phenol concentration of the combined volumes, $V_{ML}+V_b$. In view of the massive amount of phenol originally entering V_b, one can visualize V_b as constantly at equilibrium with the recycling waste stream, minus an amount due to metabolism. Therefore the calculation of rate from recycle line (i.e., mixed liquor) phenol concentration data alone must consider the waste volume acted upon by the biomass to include $V_{ML}+V_b$ (48).

matured, from which value it deviated only when the columns were stressed by starvation or phenol overload. The fact that V_b was essentially independent of $\emptyset_{t_o}$, giving similar values over the wide range of $[\emptyset e]_{t_o}$ derived, was supporting evidence that the actual microbial metabolism of phenol during the equilibration period was indeed linear. As a point of interest, a "bound" volume of 35L, if evenly distributed over the specific surface area of the column packing media, would form a layer 0.12 cm thick, a not unlikely value for the observed film depth.

The impact of the bound volume effect was greater on this study than would be the case in field type units, where the recycling mixed liquor volume would normally far exceed the range of bound volume on the filter bed. Pilot scale data herein reports [Ø] as measured in the mixed liquor in ppm. However, rates in ppm/hr can be compared only within a run. Between runs, the absolute rate in grams/hour-ft^3 must be used. The absolute rate between any two points can be determined using $(V_{ML} + V_b)$ as the volume term. In all cases where absolute rates are reported, it has been calculated using the formula:

$$R = \frac{\left([\emptyset]_{t_i} - [\emptyset]_{t_{i-1}}\right)(V_{ML} + V_b)}{V_R\,(t_i - t_{i-1})} \qquad (5)$$

to yield the rate in g/hour-ft^3 of reactor volume, where both $[\emptyset]_{t_i}$ and $[\emptyset]_{t_{i-1}}$ are mixed liquor phenol concentrations measured <u>after</u> equilibration, at times t_i and t_{i-1}.

3. Aeration Effects

For this study, it was realized that ventilation served a dual purpose, the first being provision of oxygen to a dense biomass requiring a theoretical O_2-to-phenol mass ratio of 2.4:1 (5). The second purpose stemmed from the presence of highly volatile methylene chloride ($CH_2CH\ Cl$), a major paint stripper component, with the potential for interfering with microbial metabolism in the filter. As shown in Figure 10, in order to rule out oxygen limitation, forced rather than diffusion ventilation was elected; this method also served to prevent buildup of toxic volatiles. In the liquid phase, where we expected some microbial growth and phenol metabolism to take place, sparging was introduced to supply any additional oxygen demand. Vortex currents generated by the rising bubbles also aided in mixing the returned column effluent.

When aerating the mixed liquor phase, compressed air was admitted through a 1"-diameter sparging stone located near the bottom of the liquid reservoir, then vented out the reservoir access port. When ventilating the filter, compressed air was admitted through the inlet located at the top of the column, passed down through the support medium and expelled through the outlet (access) port. This separation allowed a semi-quantitative analysis of the roles played by ventilation versus mixed liquor aeration.

Mueller (49) has pointed out that oxygen may become the rate limiting nutrient in high organically loaded

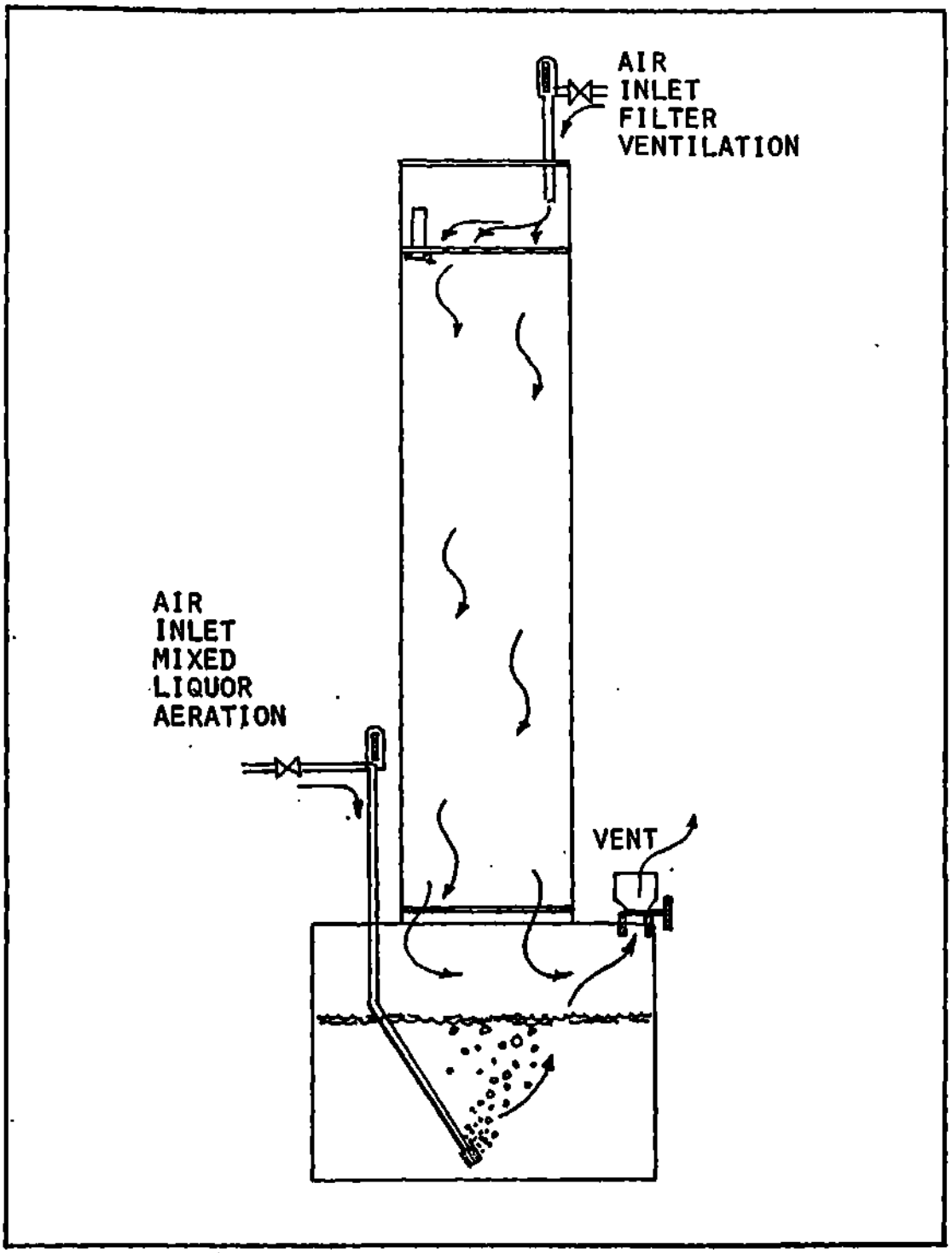


FIGURE 10. Air flow patterns for filter ventilation and mixed liquor aeration.

filters. Metcalf and Eddy, Inc. ([19]) discuss this, and recommend that air be supplied in the range of 0.03-0.30 L/min·dcm^2 (0.1 - 1.0 cfm/ft^2), either by natural convection or forced ventilation, in an effort to keep that layer of bulk liquid closest to the ambient air at saturation.

Figure 11 illustrates 'model' and 'actual' conditions existing in the Pilot Plant filter bed. The model provides for a layer of stagnant fluid on the biomass, called the "bound volume", V_b, which represents the effect of all non-metabolic absorption sites for phenol within the biomass (2. above). Flowing down over this is the mobile waste liquor layer. Conventionally all these "layers" are treated as differentiated and of defined thickness. In reality, as indicated in the inset drawing, the exceedingly complex surface of the slimes--its actual surface area far greater than that provided by the media specific surface area, a--is well-exposed to ventilating gas flow, with the depth of the overlying fluid layers, both flowing and stagnant, varying locally over a wide range.

Oxygen from the waste stream as well as from ventilating air is available for biological oxidation by diffusion into the biomass. By-products and CO_2 diffuse out of the slime into the flowing liquid phase, eventually coming to equilibrium with the ventilating gas stream. Most models depict this as occurring through the differentiated liquid layers. But scanning electron microscopic observation of the

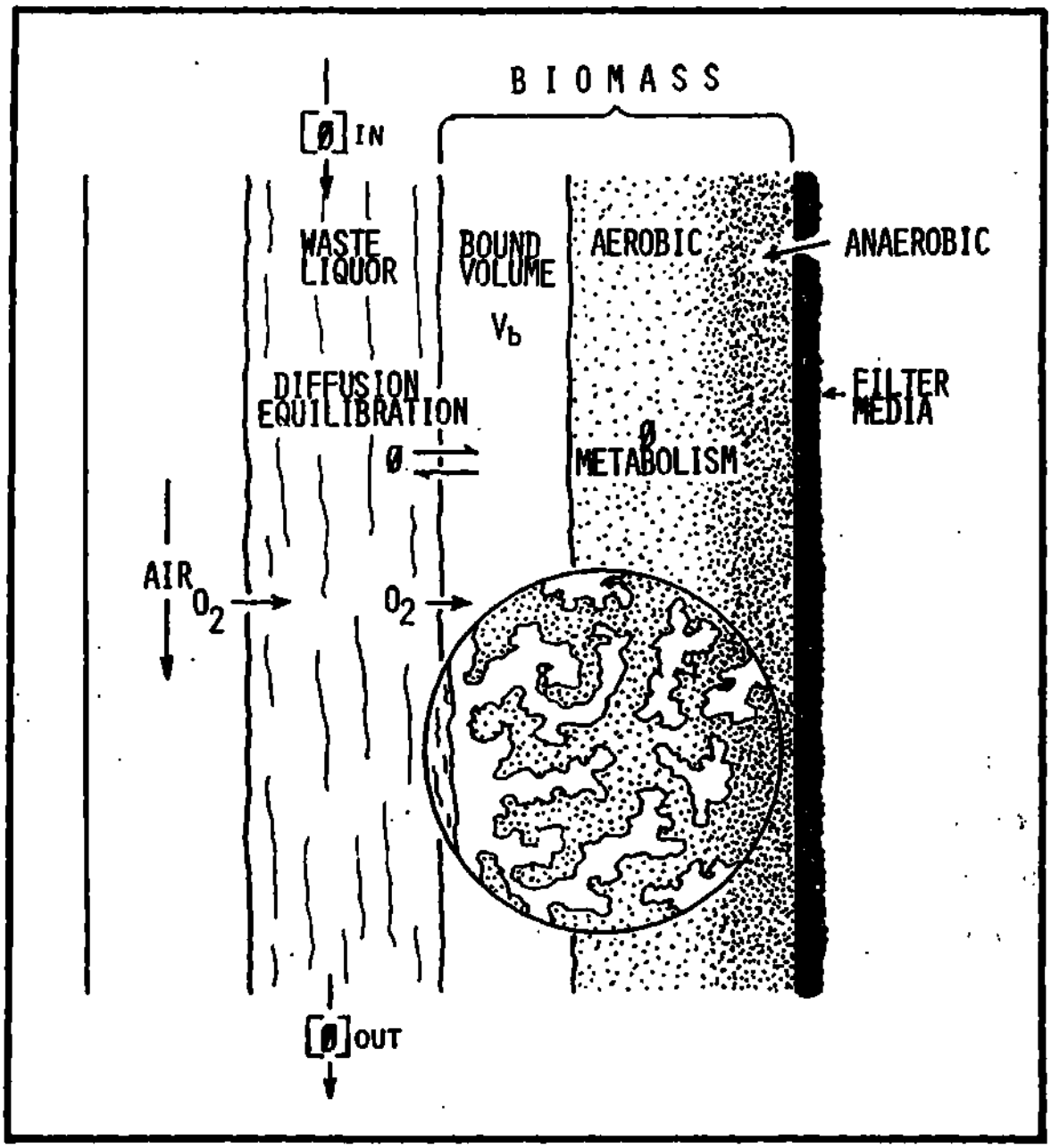


FIGURE 11. A conceptual model illustrating bound volume, V_b, and its relationship to conditions existing in a thin-film reactor.

slimes makes this simple picture seem incomplete; the biomass surface is highly textured on both a gross and fine scale.

Virtually direct access to ventilating gases is a requirement for optimal oxygen transfer, expecially where a thick zoogleal film is involved. On the other hand, mass transfer of phenol would seem to require greater exposure of the film to the waste liquor stream. Calculations based on the known volume of mobile fluid on the column (V_t), and the probable volume of biomass, indicate that the transiting waste liquor volume would theoretically be distributed in a layer of extreme thinness over the biomass surface. Under actual operating conditions such uniformity is never the case. It is therefore likely that oxygen and phenol availablity exist simultaneously as limiting factors at different sites at the microecological level. An optimal supply of both materials would occur under somewhat turbulent filter flow conditions. A combination of random feed distribution (locally irregular hydrodynamic flow) and ventilating gas flow would therefore contribute to removal efficiencies in the filter.

Figures 12 and 13 illustrate column influent and effluent oxygen concentrations under ventilation and non-ventilation conditions. It is clear from the effect on metabolism that ventilation is a far more significant source of oxygen than the dissolved gases in the influent stream. (The decreasing rates in Figure 13 reflect oxygen limitation setting in as trapped ventilating gas was depleted after ventilation

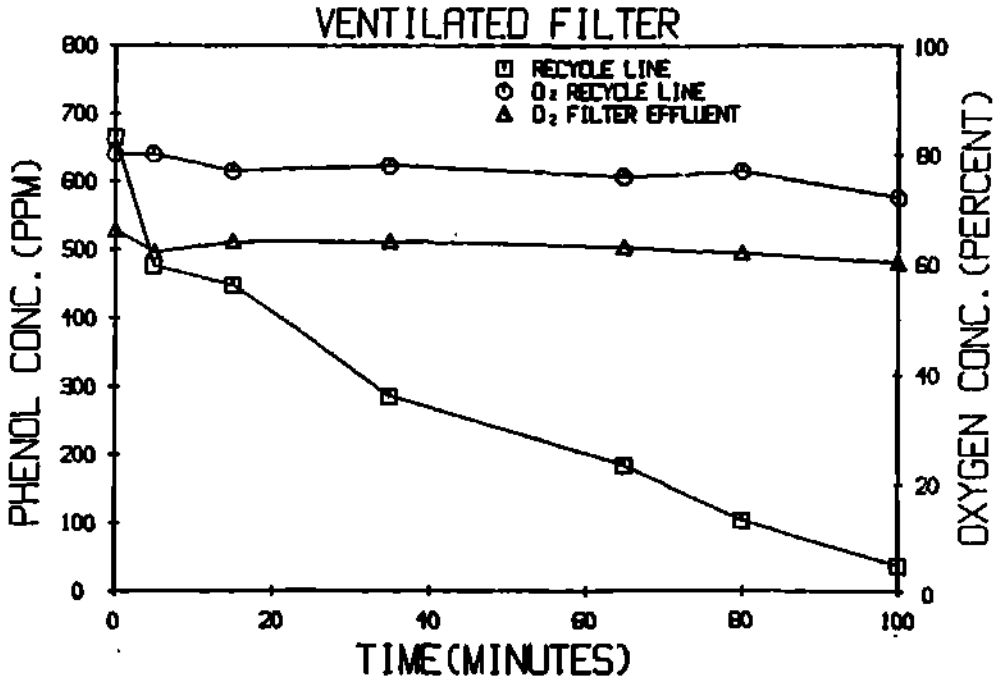


FIGURE 12. Recycle line and column effluent % oxygen saturation levels during a normal run with both mixed liquor sparging and filter ventilation. The initial equilibration period is included in the graph to show that assumption of linear removal during this period is supported by O_2 data.

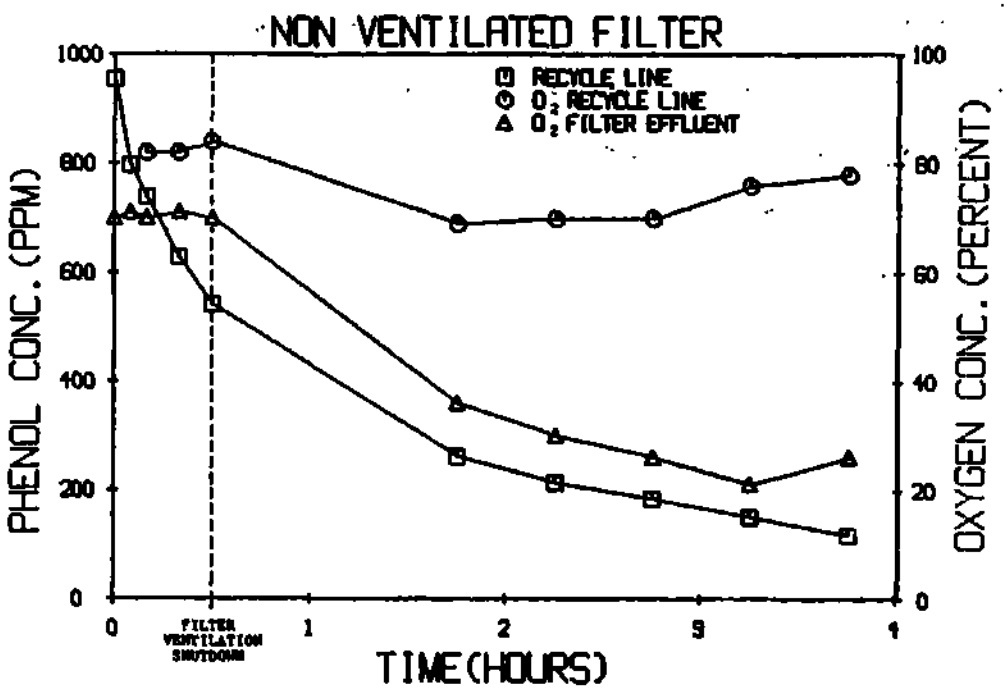


FIGURE 13. The importance of gas-phase O_2 in the filter bed can be inferred from the rapid depletion of column effluent dissolved O_2 following ventilation shutdown at T+30m, even though mixed liquor sparging continued. Again equilibration period data is included.

shutdown at equilibrium, T+30 min.)

Table 6 gives rates obtained for several protocols of aeration. A series of unreported experiments determined that batch size did not significantly alter rates; however, runs were made at 40 and 120 L (10.6 and 31.7 gals.) as spot checks of variation. No reasons were found to change the assessment.

The tabulated results reconfirm filter shutdown when not ventilated, leaving a mixed liquor phase which is inactive. The low degradation rates are due to oxygen-limited metabolism on the column since, under the reverse condition, with the column ventilated and no liquid sparging, rates are normal. There is essentially no anaerobic phenol metabolism in this system. Aeration of both phases together at 15 L/min did not produce any significant change in performance, indicating no oxygen transfer advantage to sparging the mixed liquor in either a scaled-up batch or continuous-flow facility.

For standard conditions throughout this study, air was supplied at 2.05 L/min·dcm^2 (.67 cfpm/ft^2). Oxygen was not limiting for ventilation rates within the range of values tested. There was a modest trend toward slightly higher performance at the highest rates; however, it is likely that the extra energy required to supply roughly twice the air volume to the column in order to obtain a mere 7 percent increase in removal rate would not be cost effective.

A third aeration approach attempted briefly in this study was counter-current ventilation. In this mode,

sparged air from the mixed liquor was forced to flow up through the filter and allowed to exit at the top. Waste liquor holdup on the column was appreciable, and under the control of the filter hydraulic loading. Possibilities for use of this mode, and certain other ramifications, are further discussed in 4.C., below.

TABLE 6.
AERATION EFFECTS

Filter Ventilation	Mixed Liquor Aeration	Phenol Utilization Rate	
		40 L	120 L
L/min·dcm^2	L/min	grams/hr·ft^3	
4.11	15	---	3.5
2.05	15	3.1	3.2
2.05	0	3.1	---
1.37	10	2.9	---
0.69	5	2.7	---
0.00	15	0.9	0.5

4. Loading Effects

a. Parameters

Primary design parameters for fixed film systems include organic loading L_o (mass of substrate/reactor volume time); hydraulic surface loading, L_s (reactor influent flow volume/reactor cross-sectional area time).

Process efficiencies in fixed film systems are a function of organic loading because of the upper limit on total biomass related to maximum film thickness, support media specific surface area, $\underline{a}$, and reactor volume, V_R. One aspect of organic loading--the substrate concentration--becomes load-limiting in systems where substrate removal follows anything other than zero-order kinetics (50), and especially where a significant carbon source exhibits concentration-dependent toxic or inhibitory effects. Such a target substrate affects its own degradation rate, as well as that of other waste components, placing design constraints on substrate concentration limits and control provisions. This situation applies to phenol-loaded systems, and is of major importance when phenol constitutes the primary carbon source in the waste stream, as it does for the Kelly AFB paint stripping facility. Findings related in d., below, explore factors bearing on substrate loading and concentration effects.

Hydraulic surface loading, q_R/A_R--where A_R is the reactor cross-sectional area--is an operational variable with complex effects. Fluid motion through a trickling filter, as a source of shear forces acting on the biomass, exerts powerful selective effects on filter organisms and establishes upper limits on film thickness. Its interplay with hydrodynamic characteristics of reactor, media, and biomass establishes the mean hydraulic retention time, θ_H, and transit volume, V_t, of the filter. Combined with the characteristic porosity of the column media, it also controls filter sensitivity to influent particulates. In this study, the base drain arrangement was nonrestrictive of fluid flow; media effects were characteristic for the packing material and constant; biomass effects stablized after maturity (V_b plateau); and the value of q_R, the reactor influent flow rate, was not varied widely enough to alter θ_H significantly. For a thorough discussion of the effects of liquid residence time in low and high rate filters, see the article by Klemetson (51).

In cases where concentration and hydraulic loading considerations establish organic loading limits, in both continuous-flow and batch systems, the desired organic loading (capacity) is achievable through manipulation of reactor volume. (Effects of changes in V_R are handled in D.7. below) Within a given reactor volume, one may alter structural retention characteristics to increase V_t in order to obtain phenol removal from a larger number of particles per pass

through the filter, thereby increasing the effective column rate. Although an indirect aspect of hydraulic effects, this was not included in the variables examined in this study. Reference is made to incidental findings related to V_t in c., below.

b. Reactor Flow Regime

Dye tracer slugs were used to verify flow characteristics through the reactor and to measure the mean hydraulic retention time, θ_H (19). Ten ml of erythrosin red dye in aqueous solution were injected into the waste stream entering the filter dispersion head. Samples were collected from the column effluent at 5 second intervals, and optical absorbance determined at 525 nm on an Hitachi-Perkin Elmer Model 139 UV-VIS spectrophotometer. The plot of absorbance versus time in Figure 14 represents a 5th order computer approximation combining multiple trials under identical conditions. Technically, the small degree of longitudinal dispersion exhibited qualifies this filter configuration as an "arbitrary flow" reactor whose flow may be approximated by ideal plug flow relationships (52, 53).

c. Hydraulic Surface Loading Effects

One of the design goals for this dedicated function trickling filter was high immunity to blockage, coupled with relaxed requirements for waste stream pretreatment

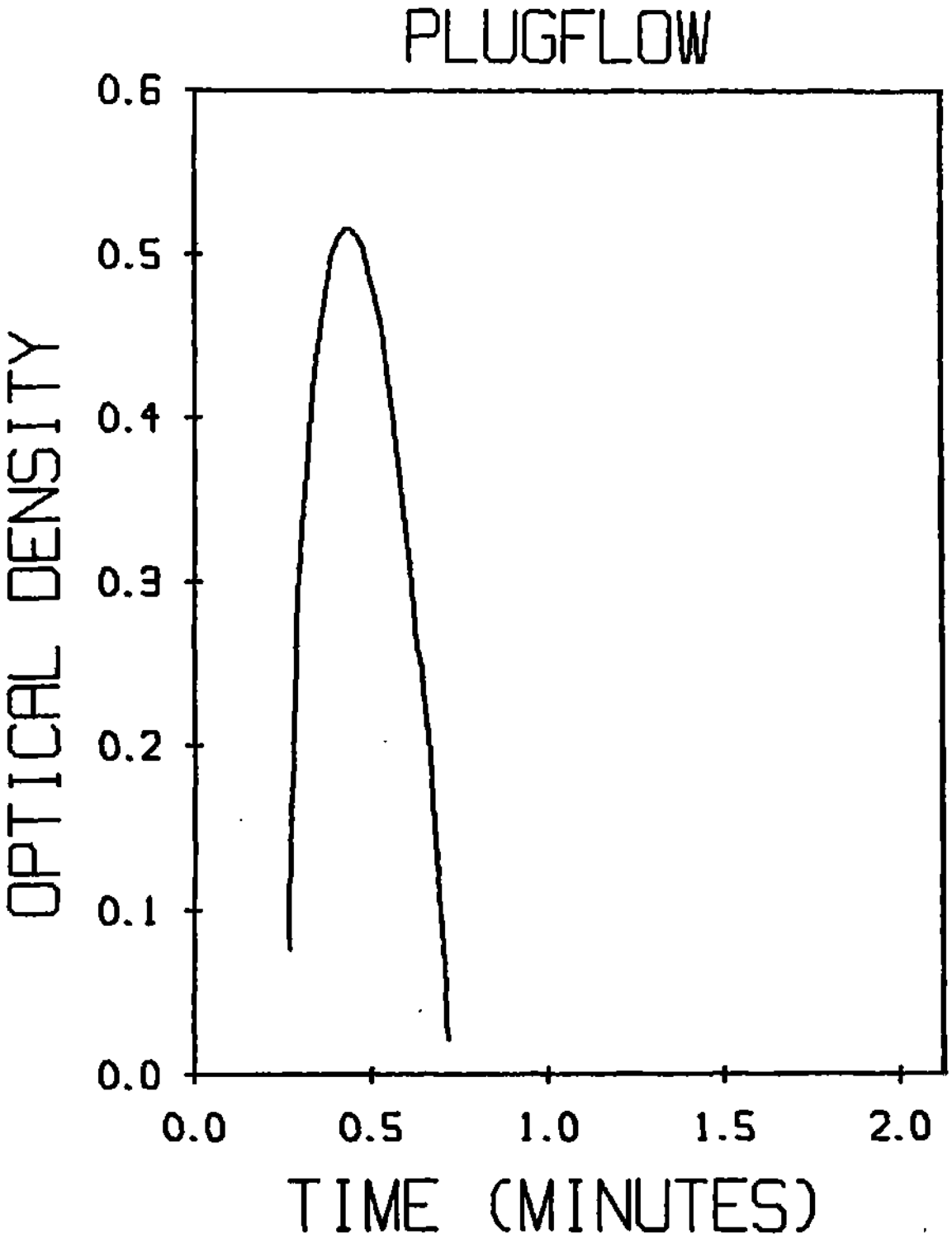
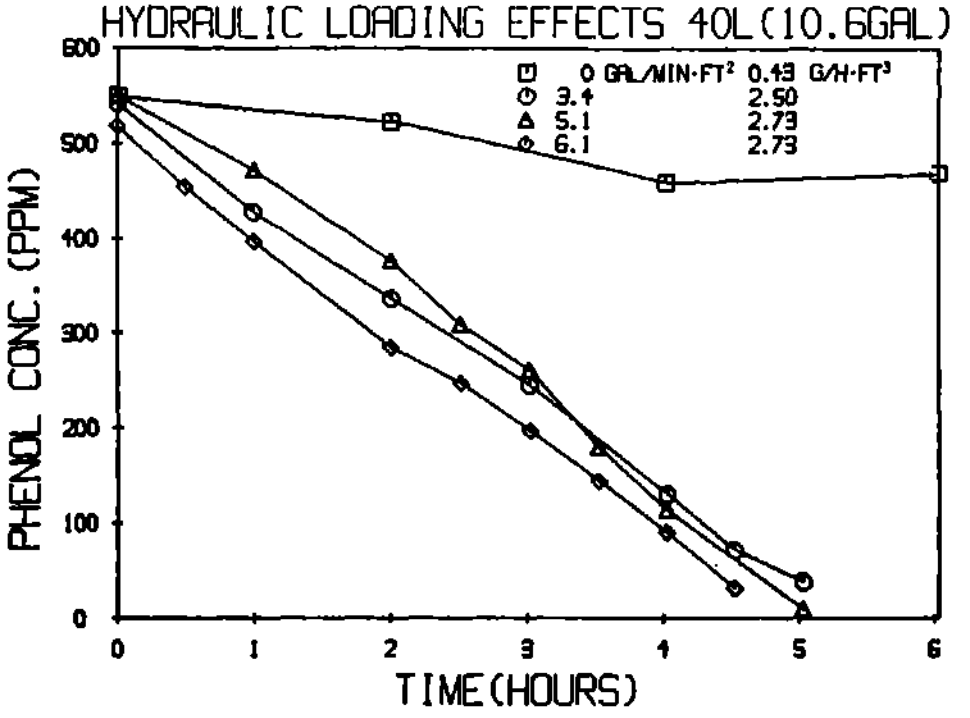


FIGURE 14. Dye tracer pulse revealing approximate plug-flow regime for normal filter conditions.

clarification. A second goal was highest rate compatible with compact reactor structure. The latter dictated that high specific area packing media be used, in order to obtain a large active biomass (Section III. C., above). The smaller diameter packing and denser biomass, in turn, meant higher waste flow rates through the filter would be needed.

The effect of surface loading, L_s, on phenol removal rate is illustrated in Figure 15. These experiments were conducted in batch mode at initial phenol concentrations between 500 and 600 ppm in order to minimize any concentration effects on rate. (Growth studies had earlier indicated linear rates for initial concentrations in this range).

The span in L_s, from 1.37L/min·dcm^2 to 2.74L/min·dcm^2 (3.3gpm/ft^2 to 6.7 gpm/ft^2), plus the zero loading condition, represented the delivery range available from the Flotec R2P1 pumps yielding satisfactory dispersion of waste at the column head. Modest effects on rates were noted, increasing with flow, indicating that an optimum was reached between 5-6.7 gpm/ft^2. The rate that was selected for standard operating conditions throughout the rest of the study was 6 gpm/ft^2, thus the standard operating procedure (SOP) encompassed an optimum value insofar as metabolic rates were concerned. The zero-flow condition represented, of course, only mixed liquor metabolism since there was no waste water contact with the column. The low value of 0.2 g/hr reemphasized



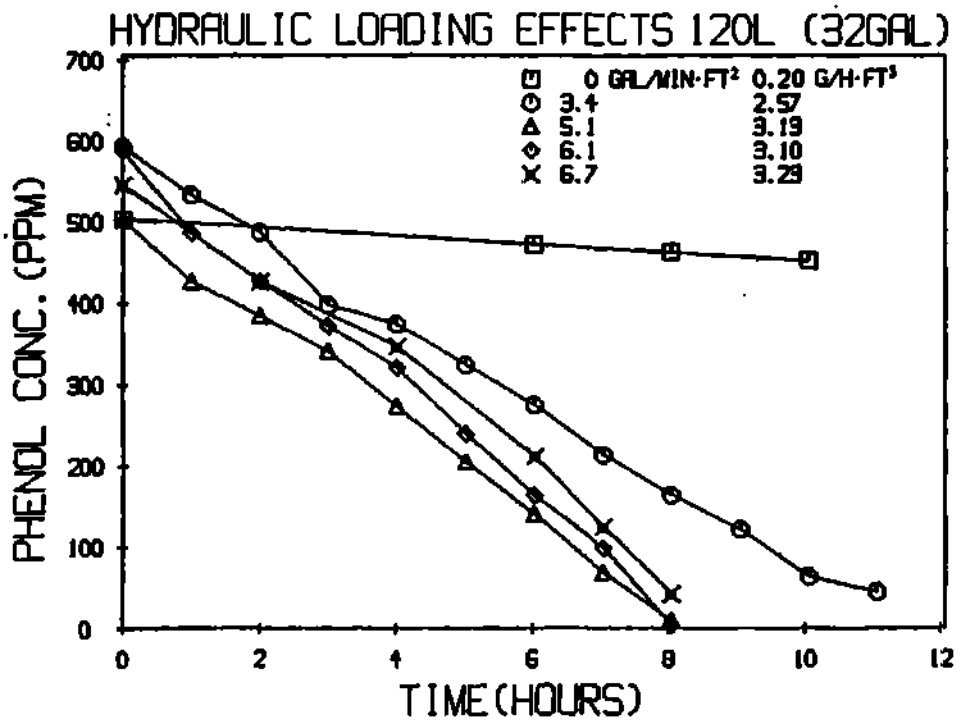


FIGURE 15. Phenol degradation rates observed at selected hydraulic loadings at 40L and 120L batch volumes.

the small contribution of mixed liquor metabolism to overall performance in this sytem.

Column transit volume, V_t, was observed to increase from 4L at the low flow to 7L at the high flow rate, measured as the immediate decrease in V_{ML} when new batch recycling was begun, minus the plumbing volume. Effluent oxygen concentration data demonstrated only relatively slight reductions from the near saturated state existing at the filter head with standard condition air flow (see D.3. above). Therefore it was considered unlikely that the modest rate increases observed were due to better aeration at the dispersion head. An increase in dispersion efficiency and in V_t was probably responsible, with more of the biomass in contact with phenol-bearing waste liquor at any given time. The implication is that a reactor design yielding a larger V_t might improve system efficiency.

A brief series of experiments early in the study sought to evaluate a countercurrent mode of ventilation, as was briefly mentioned in D.3. above. Air was bubbled through the mixed liquor, then forced to flow upward through the filter against the descending waste liquor flow, exiting at the top. A large fluid buildup was observed on the column, and foaming at the top required entrapment. Observed rates were significantly higher than the most recent base rates.

Degradation rates under several countercurrent air and hydraulic flow values are presented in Table 7. Even at an air up-flow of 0.69 L/min·dcm^2 (0.18 cfpm/ft^2)--equal to the lowest top-down flow ever applied in the study--phenol degradation occurred at a rate virtually equal to top-down nominal. Phenol removal moderately increased at the highest ventilation. However, hydraulic loading changes resulted in the strongest effects on unit removal efficiency. The high rate in Table 7 of 5.7 g/hr·ft^3 is equivalent to a phenol loading of 4.83g/L·day (302.7 lb/1000ft^3·day) while operating in a batch mode.

TABLE 7.

COUNTERCURRENT FILTER VENTILATION EFFECTS

NOTE: All phenol utilization rates in g/hr·ft^3

Filter Ventilation Loading (Countercurrent mode) L_g= 5.05 gpm·ft^2 $f_{HL}=f_v$			Hydraulic Surface Loading (Countercurrent mode) f_{HL}= 0.53 cfm f_v/A_g= 0.68 cfm·ft^2		
0.23 cfm·ft^2	0.45 cfm·ft^2	0.67 cfm·ft^2	3.03 gpm·ft^2	5.05 gpm·ft^2	7.07 gpm·ft^2
2.99	3.13	3.42	2.17	3.76	5.70
Top-Down Nominal Base Rate		2.73	Top-Down Nominal Base Rate		2.73

Observation confirmed that the major impact of waste liquor surface loading was on the transit fluid volume, V_t. Countercurrent airflow served to obstruct the base drain configuration, and to increase turbulence in the filter bed flow. The net effects were: Longer hydraulic retention times, greater biomass contact with transiting liquid, longer ventilating air contact time, and improved reactor efficiency.

Unfortunately, the mixed liquor tank was unable to contain the resulting pressure, dampening our spirits considerably. Aeration procedures were returned to low pressure, top-down normal. The episode underscored the potential of transit volume as a design variable affecting trickling filter efficiency, and countercurrent ventilation as a means of controlling it. Section IV.C.3. offers a discussion of applications.

d. Organic Loading and Substrate Concentration Effects

To determine the kinetics and loading tolerance of the system, batches were run at a volume of 20L under initial phenol concentrations varying from 700 to 3300 ppm. Figure 16a illustrates raw data obtained. The trend toward linearity is noteworthy. In Figure 16b. the rate-vs-concentration relationships are more apparent, including a clearcut, mounting depression of overall rate with increased initial loading. (The curves in Figure 16b. were obtained by treating raw data points with a least-squares-fit, 2nd order approximation, then calculating rates between generated data points. This procedure would smooth out between-point variability and might be criticized as disguising Monod trends; however, as the raw data shows, this does not appear to be the case, down to very low phenol concentrations. Additionally this procedure is useful in clarifying the role of $[\emptyset]_o$ in determining overall rate.)

The known toxicity of phenol was expected to alter the conventional Monod rate-vs-substrate concentration relationship, depicted by the dashed curve in Figure 17 (54). But the uniqueness of the filter's biomass made it impossible to predict what form this alteration might take. In earlier work we had reported on inhibitory effects of high cresol concentrations (>1400 ppm) on pure culture growth systems demonstrating apparent non-Monodian kinetics (27). Yang

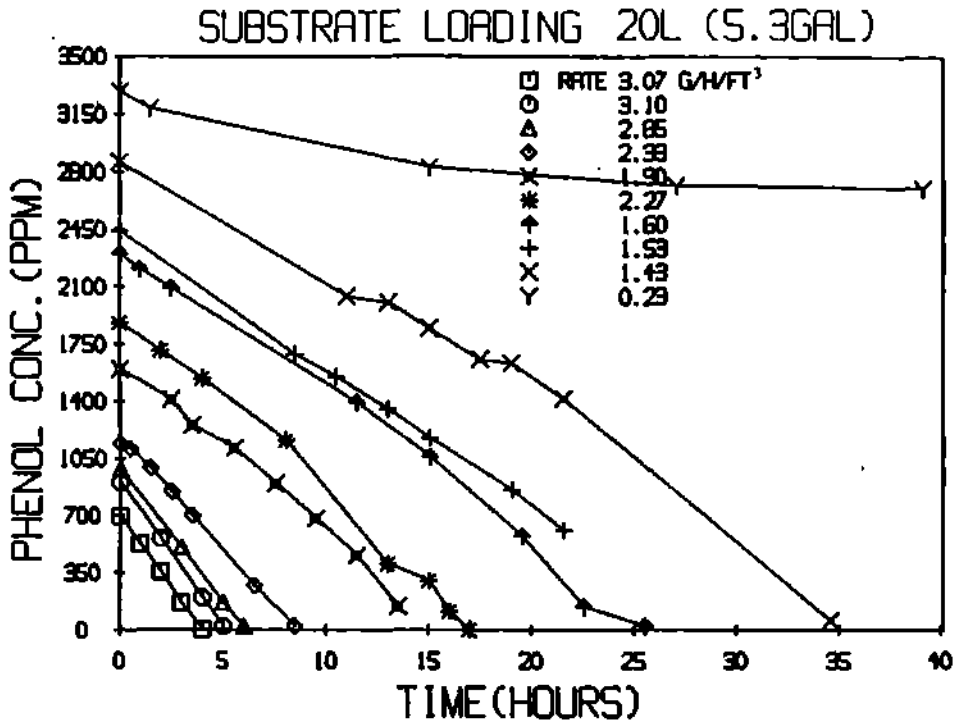


FIGURE 16a. Raw data for substrate loading runs.

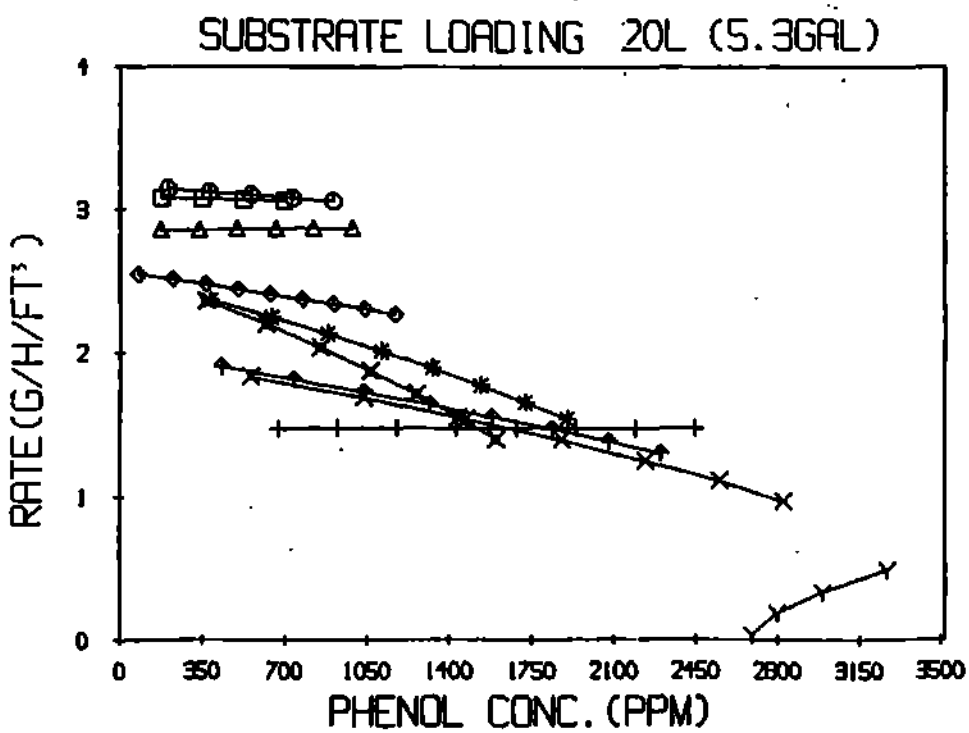


FIGURE 16b. Rate vs. concentration plot, using 2nd order approximations of raw data, showing the overall inhibition of batch rates at the test volume with increasing $[\emptyset]_o$ (hence higher organic loading).

and Humphrey (55) found classical Monod kinetics in their work with Trichosporon cutaneum (a yeast) and Pseudomonas putida pure and mixed batch cultures, for phenol concentrations up to 100 ppm, and severe inhibition of phenol uptake rate beyond that. Activated sludge studies of transient loading surges for continuous-flow nonphenolic waste treatment systems have reported an inhibitory phenomenon (40), but inhibition due to nontoxic organics probably involves different mechanisms.

Rate data for the Pilot Plant system plotted in Figure 16b portray an unexpected dimension of inhibition. Within a given run, degradation can be approximated by near-zero-order kinetics to a low substrate concentration. But the envelope rate curve (ABCDE) resembles a modified noncompetitive enzyme inhibition equation of the form

$$R = \frac{R_{max}}{1 + (K_s / [\emptyset]_o) + ([\emptyset]_o / K_i)^2} , \qquad (6)$$

where R = batch reaction rate corresponding to some $[\emptyset]_o$ (R assumed constant for a given $[\emptyset]_o$, i.e. zero-order kinetics);

R_{max} = highest initial rate measured over the non-inhibiting range of $[\emptyset]$;

K_s = Monod's half-velocity constant for R_{max};

$[\emptyset]_o$ = initial batch phenol concentration;

K_i = the inhibition constant for phenol, which for this unusual type of inhibition interaction can be

written as

$$K_i = \frac{[I]}{\left[\frac{R_{max}}{R} - \left(1+\frac{K_s}{[\emptyset]_o}\right)\right]^{\frac{1}{2}}} \qquad (7)$$

where phenol may be doing double duty as substrate and inhibitor, I; i.e., $[I] = [\emptyset]_o$. In these experiments, $K_i \approx 2000$ ppm, $R_{max} \approx 3.3$ g/hr-ft^2, $K_s \approx 1$ ppm.

The curve envelope ABCDE suggests a homotropic inhibitory action on a K3-type regulatory enzyme (56), but the family of curves representing actual runs at specific $[\emptyset]_o$'s does not support such a simple explanation (see Figure 16b). Some possibilities include: a) one or more of the primary enzymes in the degradation scheme--perhaps the membrane-associated hydroxylase (Figure 18)--are exhibiting a complex, time-dependent regulatory effect; b) the long term rate inhibition is due to a mechanism involving more than mere inhibition of ring-fissioning enzymes, possibly extending to suppression of RNA synthesis and/or translation throughout the biomass; c) the control may be exerted by some other component(s), either of the waste water or of phenol degradation; or d) the effect may be some combination of these or other unrecognized mechanisms.

Applied to the test ecosystem, the utility of equation (6) lies in its ability to predict the system initial rate R, once R_{max} has been established at the non-

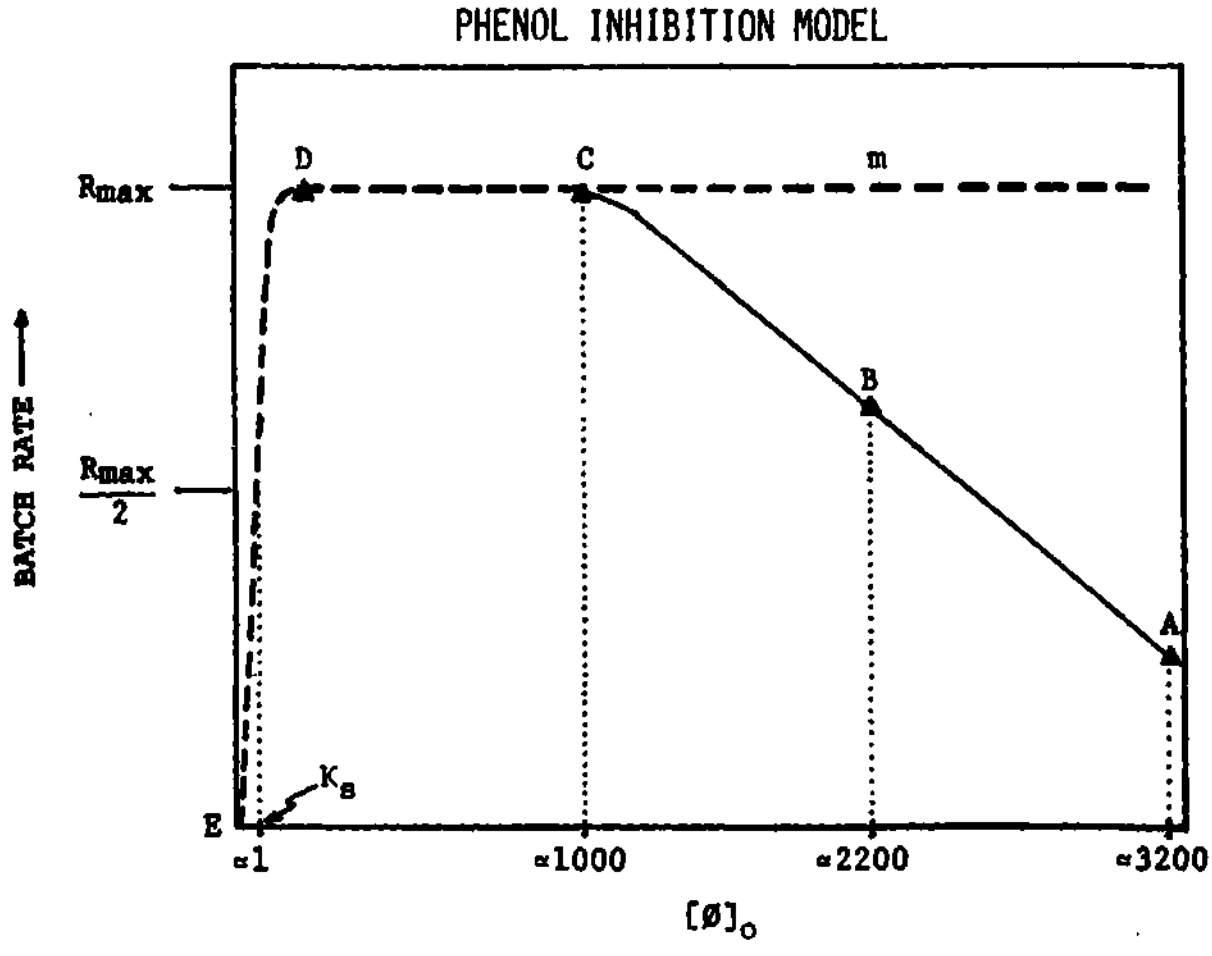


FIGURE 17. A graphic representation of standard Monod model m (heavy dashed curve), together with inhibition model for phenol in this system. Batches with initial concentrations $[\emptyset]_o$ falling along the line from A to D show near zero-order rates to very low ppm. For $0 \leq [\emptyset]_o \leq 1000$ ppm (C to E), Monod-type kinetics apply, and all batch rates follow the dashed curve to C. K_s for this system is low, perhaps below 1 ppm. R_{max} is approximately 3.3 g/hr-ft^3 at 20°C.

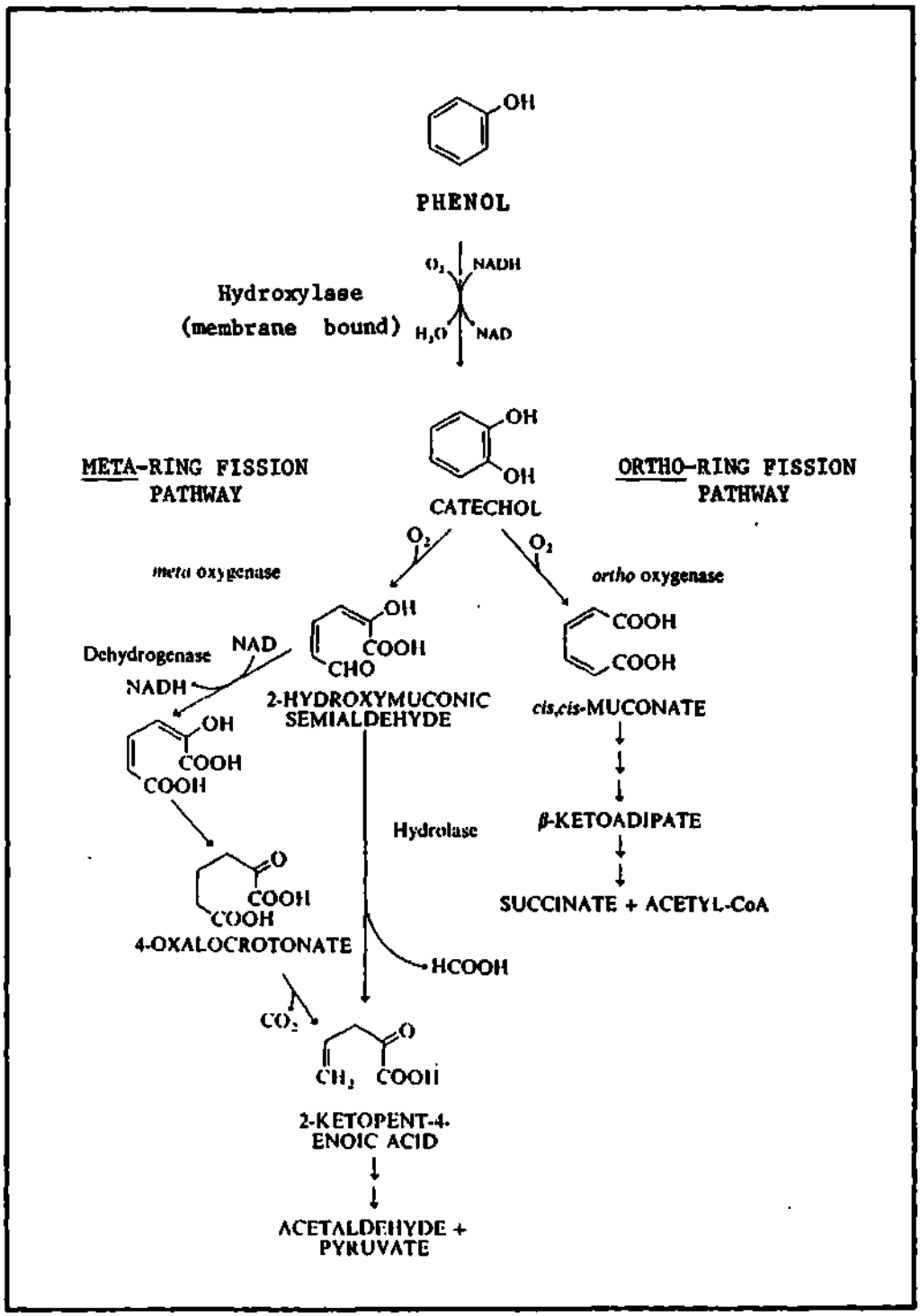


FIGURE 18. Ortho- and meta-ring fission pathways known to exist in the Trinity ecosystem. The hydroxylase enzyme is believed to be membrane-bound, and may be the initial target of inhibiting effects of phenol.

inhibitory phenol concentrations. Further, since near zero order (linear) rates can be expected to very low [Ø], R has been assumed representative of the overall rate for the batch begun at that concentration, with the following proviso:

For these loading runs, the next batch run at "normal" loadings ($[Ø]_o$ ~ 800 ppm) gave standard baseline rates, indicating that the phenomenon was transitory rather than lethal. Between-batch processing time was on the order of two hours. It may be that the overall rate inhibition would lift <u>within</u> a run, provided that the batch time were long enough. Batch time lengthens for larger V_{ML} to V_R ratios. In such cases, R would not necessarily represent a close approximation of the run maximum, nor would it be zero-order.

Without further experimentation it is difficult to assess the importance of the inhibition effect reported here. Studies reporting overall Monod kinetics have not described this phenomenon (37 , 46 , 57). Those demonstrating zero-order kinetics have generally not tested the upper limits of their ecosystems to the same extent, nor have their routine treatments of their test units been as consistently demanding as those utilized in this study (10 , 19).

In any case, taking the volume of the Pilot Plant reactor to be 85L (3 ft^3), removal rates of 2.7 g/l day (169 lb/1000 $ft^3 \cdot$day) have been routinely handled by this system under stated standard conditions at 20° C., with mixed liquor phenol concentrations of 1000 ppm for hydraulic loadings between 3.3 and 6.7 gpm/ft^2. Within a range of

~1$\leq$[Ø]$\leq$1000 ppm the system kinetics are approximately zero-order. (Under counter-current aeration conditions, preliminary rates of 4.83 g/L·day--303 lb/1000 ft^3·day--were achieved.) These results are comparable to those of pilot-scale activated sludge systems, which found that 120 to 250 lb/1000 ft^3·day loadings were the highest practical without excessive foaming (5,14,15).

5. Chromium Tolerance

Perhaps the most serious aspect of the Kelly waste water is the high concentration of chromium in the toxic hexavalent state encountered even after washdown dilution. In a technical report (7), the Air Force Environmental Health Laboratory found that a maximum concentration of 0.14 mg/L (0.14 ppm) chromium in the waste influent to a biological treatment facility could be tolerated with a reduction efficiency of about 50%. Higher concentrations led to rapid poisoning of the sludge mass. Currently, one of the better commercial pre-adapted bacterial preparations on the market (PHENOBAC), may be used only on waste water where hexavalent chromium is present at less than 2 ppm (17). KAFB stripping facility chromium concentration is routinely 20 times that (see Table 1).

Heavy metals toxicity tests on the J-series of organisms had earlier shown sensitivity only to silver ion (Ag^{++}) (58). Inasmuch as the presence of chromium in the waste water never appeared to influence phenol utilization, and the Contract Statement of Work did not mention a concern for this parameter, chromium tests were done only periodically during this study. The performance of the Coryneforms and the remainder of the column ecosystem is dramatically in evidence in Table 8. These represent the only four runs on which chromium data was taken. Reductions of hexavalent chromium as high as 99.4% were achieved in 3.5 hours, with initial concentrations of 16.5 ppm. Performance varied, with a low of 36.4% reduction from 16.5 ppm;

TABLE 8.

CHROMIUM REDUCTION

NOTE: All values in mg/l.*

Batch Number	1		2		3		4	
Chromium	TOTAL	+6	TOTAL	+6	TOTAL	+6	TOTAL	+6
Batch Start	16.5	16.5	12.3	9.0	27.7	16.5	11.8	11.8
Batch Finish	7.2	0.1	4.3	0.1	22.0	10.5	1.8	1.8
Batch Time (Hr)	3.5	3.5	3.5	3.5	3.5	3.5	2.5	2.5
Percent Reduction	56.4	99.4	65.0	98.9	20.6	36.4	84.7	84.7

*Chromium assays performed by Chemical Processes Lab (MANCB) KAFB. Total chromium reported as tri + hexavalent.

the higher total chromium in Batch 3 may have influenced +6 reduction.

A curious aspect of the test results is the apparent removal of chromium from the waste water. The columns developed a yellow coloration during the AWW runs; it is possible some chromium becomes locked up in the biomass. One would expect removal of chromium to decline with time to some equilibrium, balanced by sloughing of chromium-rich biomass into the effluent. Yet Batch 4, accomplished some 4 months after the first three batches, demonstrates the highest total chromium removal. The metal sequestering mechanism of the Trinity filter ecosystem is an intriguing puzzle which remains to be adequately investigated.

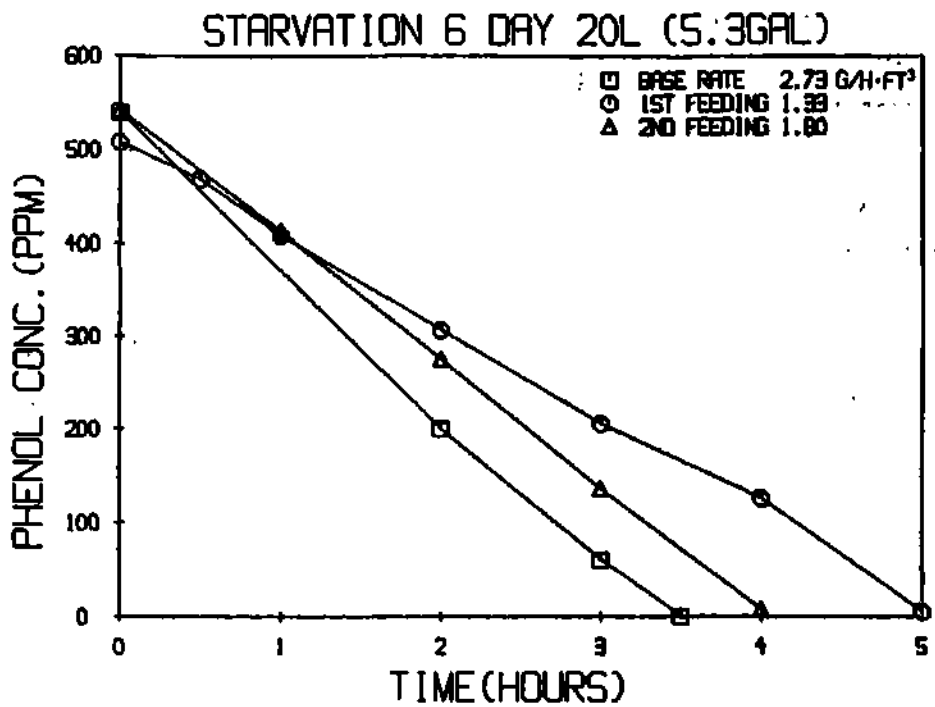


FIGURE 19. Six day starvation test.

6. Starvation Recovery

Paint stripping at any facility is an intermittent process, and circumstances are conceivable during which phenol availability to the columns might be restricted for extended periods of time. Waste processing facilities exposed to intermittent phenolics input have historically presented severe loss-of-acclimation problems to industry (5, 15).

In keeping with the "ecosystem training" treatment philosophy, our standard procedure included routine overnight and weekend starvation periods. Except when runs happened to occupy these time periods, the filters were allowed to run out of phenol; recycle of spent waste was continued. Prior to experiments, test batches were run to check for base rate changes. During nine months of such experiments, no significant variations were found in base rate for even the first after-weekend runs. But to study the capacity of our ecosystem to withstand longer periodic substrate shortage, a Six Day Starvation Test was performed. The protocol for this set called for running a batch (20L) of AWW under standard operating procedures, to establish a column base rate (see Figure 19). After GC analysis confirmed less than 1 ppm residual phenol, this same spent waste water was recycled for an additional six days with no further replenishments of any kind. At the end of this time, two successive runs were made in which nominal substrate loadings were applied in a mixed liquor volume of 20L. The column exhibited no lag time in phenol uptake, and was operating at approximately 50% of base

rate on the first run. Within 48 hours column performance had returned to base rates, and computed V_b had reached 33L from a low of approximately 18L, indicating that the biomass had reached its normal plateau.

A much more severe test was inadvertently imposed on Column 1. For more than six weeks, mechanical difficulties forced the complete shutdown of this unit. During this long period the system merely sat, liquid phase drained out, and slowly dehydrated. When started up once again, without re-seeding, utilizing AWW and standard initial run conditions, a great deal of suspended solids was observed flushed into the liquid phase tank. However the phenol degradation rate was 40% of nominal (1.33 g/hr.ft^3 overall), and three subsequent runs showed rapidly increasing overall rates with a return to baseline within 72 hours. Clearly the ecosystem established on the columns possesses a useful resilience, even in the face of unusually traumatic conditions.

The linear kinetics of these runs were again at odds with data from standard waste treatment theory. To exist during the starvation period, column organisms would be forced to switch over to metabolism of other carbon sources. Two major pools of stored carbon were recognized: a) intracellular storage granules, such as the plentiful metaphosphate inclusions microscopically observed in the Coryneforms; and b) the extracellular polymeric secretions and dead cell lysates of the slime itself.

Tests of pure culture Coryneforms recovered from the columns had shown a complete loss of phenol pathway enzymes after even short 2-generation exposures to rich carbon sources such as tryptic soy and/or glucose media (Egan, Olive and Burkholz, unpublished observations). However, the presence of high phenol-metabolizing enzyme levels was repeatedly verified in column slime material subjected to up to 8 weeks of continuous starvation.

Figure 20 is a graphic interpretation of preliminary data from an allied investigation into the genetics of J-series organisms ([59]). Using a YSI Model 53 Biological Oxygen Monitor, suspensions of freshly obtained slime material, and of pure culture Coryneform bacteria recently isolated from the filters, were compared for their ability to use phenol as a metabolic substrate. Each of the first two steps in the breakdown of phenol involves consumption of a molecule of oxygen (Figure 18); an increasing rate of disappearance of dissolved O_2 in the test cell upon addition of phenol indicates the presence of the ring-fission enzymes.

The figure shows the dramatic difference between phenol-induced and non-induced (tryptic-soy-raised) column J20s. Phenol-induced column J20s allowed to enter cryptic growth in a phenol-depleted SWW medium were non-induced for phenol. But column slime suspensions, even when starved for phenol for more than eight weeks, showed strong and immediate uptake of O_2. These results support the interpretation that one or more slime

organisms possess "constitutive induction" ring-fission enzyme control. A discussion of the genetic as well as practical importance of these findings appears in Section IV.A.

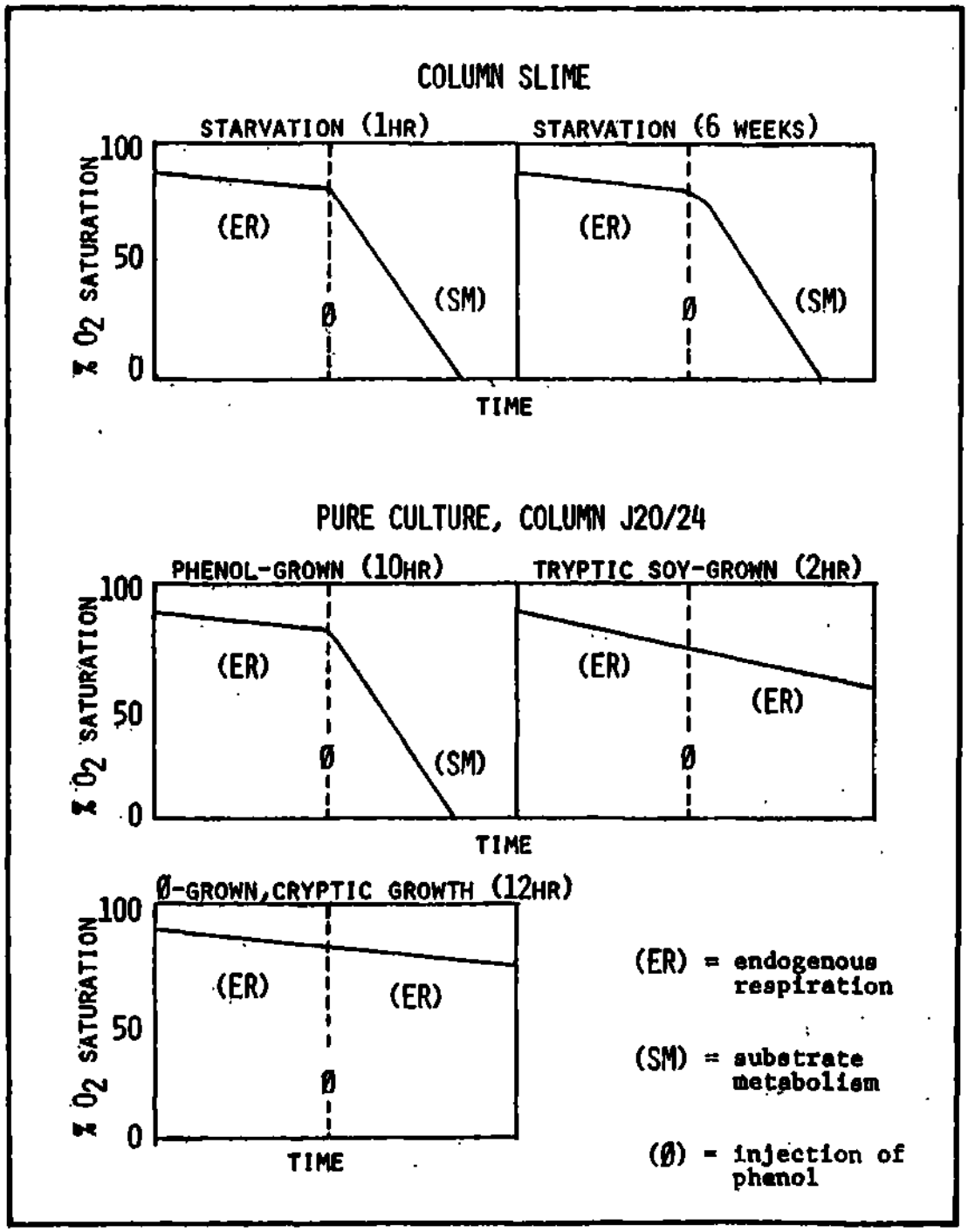


FIGURE 20. Oxygen consumption due to phenol metabolism for filter slime and pure culture organisms grown on either phenol or tryptic soy. Curves illustrate that phenol-starved filter slime maintains high phenol enzyme levels over long periods of time.

7. Bed Volume and Depth Effects (Tandem Mode)

Effects of changes in reactor volume, V_R, and flow path length were studied by utilizing the "tandem run" mode of the triple tower Pilot Plant. In the tandem mode, a single mixed liquor volume was cycled in a closed loop through all three towers (Figure 21).

Comparison of the rate-per-unit-volume obtained at 3 ft^3 of the packed bed volume (one-column rate) to that obtained at 9 ft^3 (three-column rate), shows a modest increase traced to slight differences in V_b between columns (see Figure 22). Here, the fluid streams were redistributed at each 3.83-ft interval by the splash heads; in an actual scale-up, the increased bed depth may interact with hydraulic factors in a way not completely predictable from the pilot scale. The pooling represented by the mixed liquor tank volumes probably had little effect on the observed rates, as we had demonstrated in prior runs.

Our protocol of batch treatment, which conserved significant portions of the spent waste water as part of the diluent for new concentrated waste input, may have been expected to lead to slight toxic by-product buildup in the mixed liquor. This might have accounted for the clear dichotomy in importance of the mixed liquor versus filter removal activities, except that, immediately following the periodic total replacement of V_{ML}, no significant differences

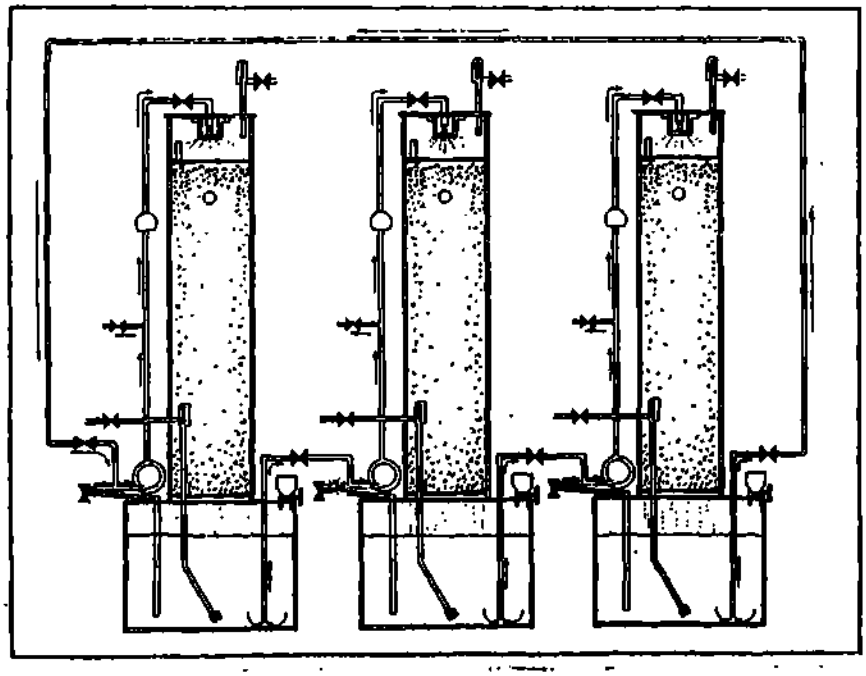


FIGURE 21. Tandem mode operation. Arrows indicate flow direction of waste water. 120 L was the total batch volume for both the tandem and isolated column run.

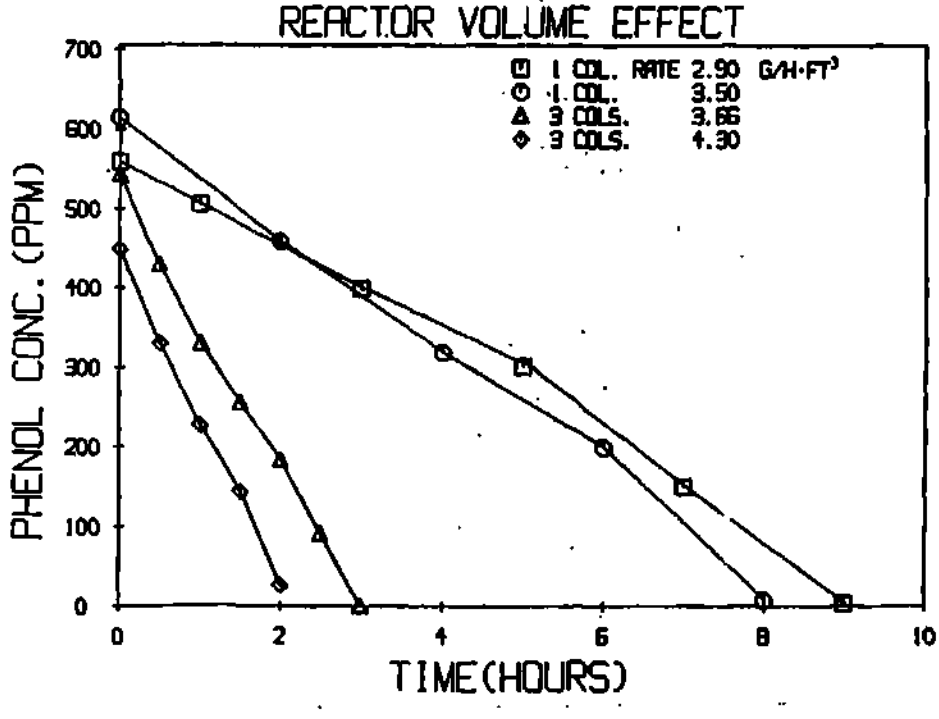


FIGURE 22. Phenol degradation rates for 120 L runs in an isolated column, versus rates in tandem mode. $V_b \approx 35$ L for each column in circuit.

in either rate or liquid phase growth were detected. During very long batch times, in cases where the mixed liquor volume V_{ML} is rather large compared to V_R, this circumstance might alter. One would expect more growth in V_{ML} if it is left to progress long enough. But, if batch times are short, efforts to improve liquid phase phenol removal contributions by aeration may prove uneconomical and unnecessary.

Implications for scaled-up batch and continuous-flow systems are discussed in Section IV. C.

TABLE 9.

RATE DATA FOR TEMPERATURE EXPERIMENTS

NOTE: All rates in grams/hour·ft^3

COLUMN TEMP C	VOLUME				AVERAGE RATES
	20 L	40 L	60 L	80 L	
20	3.9	3.8	---	3.9	3.9
30	6.0	6.2	5.6	---	5.9

8. Temperature Studies

Temperature conditions for the majority of experiments in this study were established by the technical tasks assigned under the Contract Statement of Work. The temperature of interest was 20° ±1° C. Previous studies by this laboratory ([28]) had established that test organisms originally isolated from the Kelly AFB facility were capable of growth and utilization of phenols at temperatures of 15° C., 25° C., and 35° C. The primary test temperature (20° C), reflects the mean annual temperature in the San Antonio area, and was chosen to evaluate pilot plant operation for that reason.

To check expectations of performance under other ambient temperature conditions, this lab ran an additional series of studies with the current pilot plant at a temperature of 30° C. Comparison of results with those obtained at the nominal annual mean are given in Table 9. Performance at 30° C. was approximately 1.8 times the average rate for 20° C., a result expected due to the well-known tendency for enzyme reaction velocities to double for each 10° C. rise ([19]).

Implications of this data are clear. At higher than mean temperatures, a trickling filter unit of this type would have an effectively increased efficiency of approximately

$$R_T = R_{T_{20}} \times (1.8) \exp\left(\frac{T-20}{10}\right) \qquad (8)$$

where T is the new temperature in °C.,

R_T is the rate at the new temperature,

$R_{T_{20}}$ is the average rate experienced at 20° C.,

and $\exp\left(\frac{T-20}{10}\right)$ is an exponential term indicating the fraction of a ten-degree-Centigrade interval represented by the temperature increase or decrease.

At operating temperatures that are ten degrees below annual mean, the degradation rate for biological systems might therefore be expected to be about 44.5% of its value at the mean. There is much to be gained from maintaining warmer temperatures, and reactor design should incorporate suitable features.

Temperature stabilization may be obtained by several means: insulation; locating compact columns within environmentally controlled areas; controlling liquid phase storage temperature; providing a cold-weather heating system for the units (e.g., a passive solar-type heat exchange system); or any combination thereof.

9. Biomass Evolution

Ordinary multiple-target waste processing reactors exhibit several stages of biomass development from startup through maturity (60). Beginning with representatives of relatively few microorganism species, colonization by fortuitous arrivals will commonly bring in bacteria, algae, fungi (including yeasts), protozoans, and finally many higher life forms including worms, arthropod larvae, snails, etc. It might be expected that toxic waste dedicated-function reactors would show a much more restricted clientele.

Initially, the filter biomass consisted entirely of bacteria. Upon dilution onto nutrient agar plates, only the original J20/24 mixture of Corynebacterium sp. and invading Pseudomonas sp. were identified. Over sixty days, during the synthetic waste water experiments, a distinct segregation took place. The pseudomonads came to dominate the mixed liquor phase, with the Coryneforms found principally on the column and in the light foam atop the mixed liquor.

Shortly after the introduction of KAFB actual waste water, a colonizing species of Penicillium was identified. Additionally, the pseudomonad population in the liquid phase dropped dramatically. The cause of this decrease has not been discovered; it does not appear to be due to waste toxicity, since these pseudomonads (as well as other strains from laboratory stock) grow well on AWW agar plates in pure culture. It is possible that an antibiotic substance, perhaps produced

by the fungus population on the columns, is limiting microbial growth in the liquid phase.

After ninety days of operation on AWW, colonization by nematodes and mites was observed. The microscopic, transparent mites resembled Platyseius tenuipes, commonly found in activated sludge sewage processing plants. These mites survived in mixed slime cultures grown on 1000 ppm phenol agar plates. They appeared to thrive on bacterial polysaccharide secretions adhering to the whiskerlike conidiophore processes of fungal growths. The nematodes, too, appeared immune to the phenolic environment, both in the filter beds and on agar plates.

Microorganisms isolated from the very mature columns demonstrated curious interdependencies. The Coryneforms retained their overall genetic integrity, based on morphology, growth substrate preferences, and pigmentation. However, the only identifiable pseudomonad species recovered showed surprising fastidiousness, growing on phenol agar only in the presence of the Coryneform. By contrast, at least two varieties of Penicillium were isolated, one able to grow on all phenolic substrates tested (phenol and the cresols), the other specific for para-cresol. Fruiting bodies were in evidence on the fungi after 5 days' growth on phenol agar. These organisms have been maintained for further study.

The original appearance of the biomass as it began to build in small catchments was a clumped olive drab floc on the young filter bed packing. When changeover to AWW

was accomplished, it had already assumed a more filamentous texture. Within a month of exposure to the Kelly waste, its color had altered to a red-orange mottled yellow. Conceivably this change was due to the accumulation of chromium compounds in the slimes.

Examination of bio-rings withdrawn from the columns has shown that the biomass is irregularly clumped on available surfaces, of a crumbly flocced texture, and is by no means "slimy". Electron microscopic observation reveals a surprisingly uniform ground forming a highly invaginated, almost honeycombed structure; a picture of a virtual column "sponge".

Though the filters attained a predictably low species diversity, those organisms successfully colonizing the filters presented a strange assortment. In nontoxic multiple-target installations, the biomass ecology can be very critical to proper filter functioning (60). The exact contribution to stability by these dedicated function filter inhabitants, however, remains to be evaluated.

IV. DISCUSSION

A. GENETIC ASPECTS OF DEDICATED FUNCTION REACTORS

Originally, biological waste processing systems handled low-toxicity, multiple-target wastes. The fortuitous populations of such systems evolved genetic control mechanisms appropriate to a rich environment where metabolic versatility was encouraged. Recently, when toxic wastes were introduced as additional targets for such systems, it was found that the nutritional hyper-versatility of bacteria such as the soil pseudomonads made them especially useful as "buffer organisms" in a complex biomass, able to switch to consuming the toxic substrate when its concentration rose, limiting its toxic effects on the whole population. Deliberately adapted and mutated, they became the first biotechnological tools of the waste water engineer, augmenting the fortuitous populations in common use. Still--as with non-augmented reactor populations--problems of shock load shutdown and variable efficiency have persisted, apparently due to dilution or loss of critical genes in the biomass. Regular reseeding, coupled with designed increases in cell retention time--up to 50 days--have been necessary to counteract these problems (5).

Point-source toxic wastes, however, present an unusual opportunity for bioprocessing not encountered in multiple-target facilities---not even in the relatively specialized industrial park waste processing plants now in existence. These limited-target streams are unique to the

process generating them; the combination of toxic components, concentration ranges, and production schedule presents a specific, narrowly-defined genetic challenge to a biological system. Genetic response to that challenge is equally specific: Even uncontrolled toxic waste reactor populations show limited variety, reflecting the selection pressure of a hostile but constant environment.

To seed a limited-target facility with artificially, genetically streamlined organisms is one obvious way to govern biomass development; but this does not carry the idea of controlled reactor populations to its most practical, logical conclusion. As indicated in Figure 23 , common toxic waste process protocols can actually select against those expensive lab-reared genes, simply by removing some of the selection pressures that spawned them. To make the most of the metabolic power than can be constructed in microorganisms today, the waste processing protocols must maintain those gene constellations by applying appropriate selective pressures. The more narrowly defined the waste, the more advantage may be taken of genetic streamlining. This is the utility of point-source treatment using a dedicated function reactor.

Reactor conditions in continuous-flow systems can be described as environmentally stable. If microorganisms can take best advantage of a fixed environment, as suggested above, then unsteady-state batch treatment systems would seem to be at odds with an effort to streamline and specialize the biomass

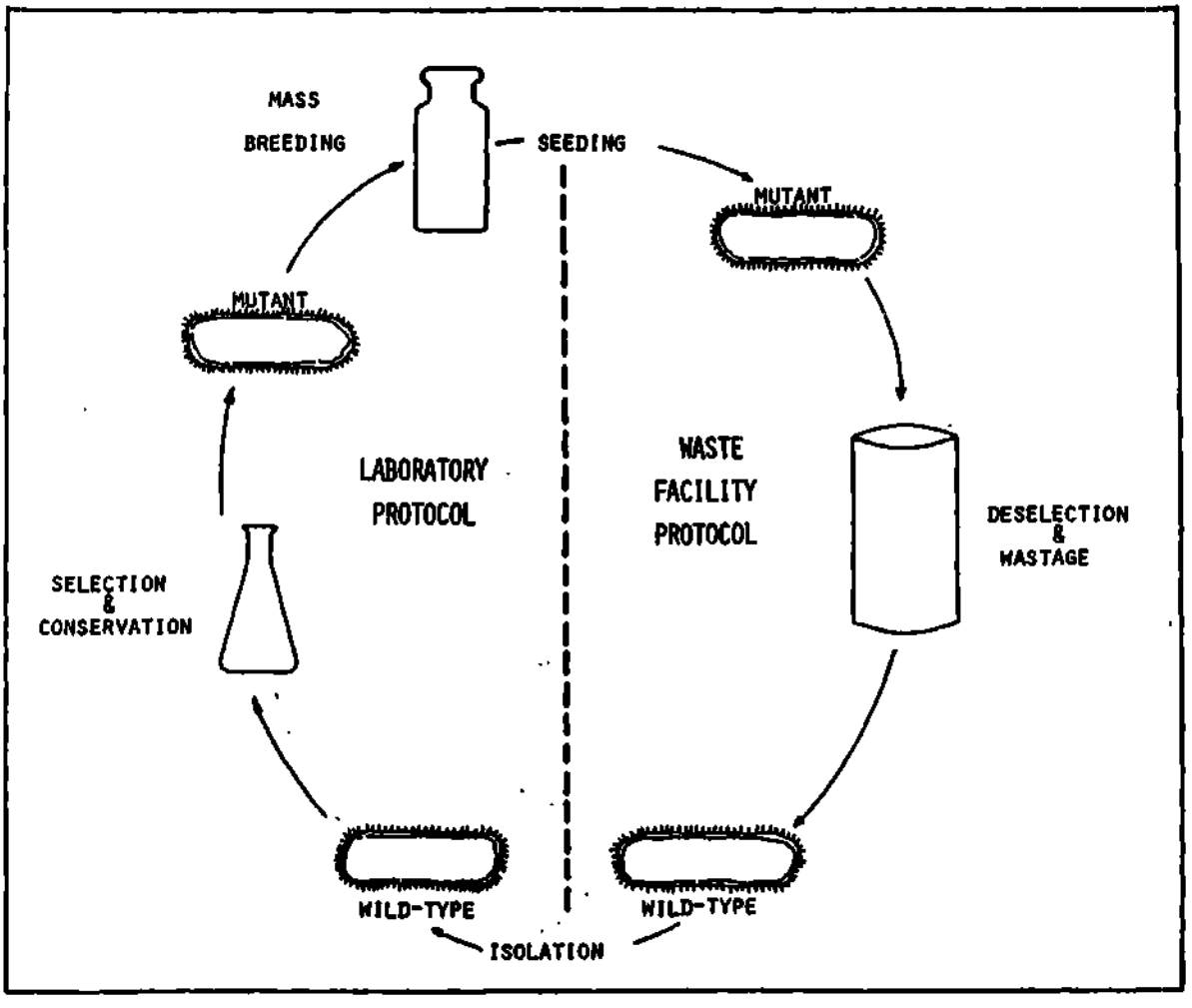


FIGURE 23. Inefficient coupling of laboratory selective protocol with non-selective treatment facility application in standard systems.

population. This might be true if "fixed environment" meant "steady-state". But there are good arguments that this is not the case.

The object of dedicated function treatment is to metabolize specific toxic wastes and attain a desired discharge concentration. This means that, at some point in the process, the biomass will be consuming this waste at very low concentrations. In a typical continuous-flow system, process design maintains a low substrate concentration throughout the biomass continuously. Influent lines may carry high substrate loads at high concentrations, but the actual levels delivered to the biomass are deliberately diluted down, using recycled effluent and/or some other diluent. In many waste facilities this protocol is an absolute necessity, because only a small portion of the biomass is made up of organisms actually able to consume the substrate; and many of these are not "switched on" to it both because it is dilute, and because it is only one of many other target carbon sources. This means that, if the enzyme systems responsible for oxidizing phenol follow Monod kinetics, then reactor efficiency at low concentrations may be significantly less than that possible at higher concentrations. In an activated sludge continuous-flow facility, the reactor may be operating near the half-velocity concentration most of the time; its removal efficiency per unit volume could be much less than maximal.

By contrast, a batch treatment system--particularly

where an active biomass is always available, as in a trickling filter bed--spends only a fraction of its operating time at the low concentration condition. Throughout most of the batch cycle, the biomass is exposed to high enough substrate levels to sustain maximal reaction rates. If Monod kinetics apply, rates will drop to levels similar to that encountered in continuous-flow only after most of the substrate load has been degraded. This implies that a smaller batch reactor and system volume could yield the same organic loading capacity as that provided by a larger activated sludge continuous-flow system.

The above argument would not hold if rates were totally zero-order and of the same magnitude for both a batch and continuous-flow trickling filter system. Our study did in fact demonstrate near-zero order rates to very low phenol concentrations for the batch-operated Trinity trickling filters. This does not at all imply that the same kinetics would exist if the same system were operated in a continuous-flow mode (see Figure 24): Since the effluent is maintained at some steady-state concentration, and the influent feed line is presumably equalized upstream of the filter, the filter is always presented with a constant, diluted input concentration while running. No depth of the bed would be operating under zero substrate concentration (in a high rate filter, the concentration stratification is not so marked as in a low rate filter), so about the same removal efficiency could be expected from all bed depths. However, the very constancy of the environment may

lead to undesirable genetic alterations in the biomass.

As mentioned earlier, the laboratory selection process usually involves both selection against organisms unable to tolerate high toxicant loadings, and selection for those which grow best on or use the most target substrate. In addition to selecting our column organisms in this manner, our protocol for the pilot plant also included regular starvation periods of 12 to 48 hours (overnight and weekends), coupled with the regular phenol shock loading that a 1000 ppm batch feeding entails. The resistance of the biomass to long periods of dehydration and complete starvation was directly influenced by this treatment. Possibly even the linear kinetics observed were also a result of such protocol-generated selective pressures.

As was demonstrated in Section III.D.3., the phenol oxidizing enzyme activity of the filter slime did not decline even after many weeks of phenol starvation. This would be characteristic of mutant, "constitutive enzyme" genes--enzyme production genes whose induction, or "switching on," was no longer tied to the presence of phenol or a phenol metabolite. In other constitutive mutations it has been shown that enzyme production control has been shifted to some common cellular metabolic intermediate such as succinate, or an amino acid (61). In a dedicated function unit, this would mean that one could not shock the biomass with sudden nominal loadings, as may occur after even brief periods of target absence in typical activated sludge systems. Also, as substrate (phenol)

concentration dropped during processing, this decline would not lead to the usual "switching off" of crucial enzyme production genes; and this would tend to erase the familiar "Monod drop" in rate at low substrate concentration.

It is difficult to estimate the degree of change that might occur if our normal treatment protocol were to be permanently discontinued, but certainly the tendency would be for both shock load and starvation resistance to decline as critical population genetic configurations were allowed to mutate away from those originally selected under the laboratory protocol. This would be the situation in any facility where organisms were originated under one set of conditions, then left to operate under another.

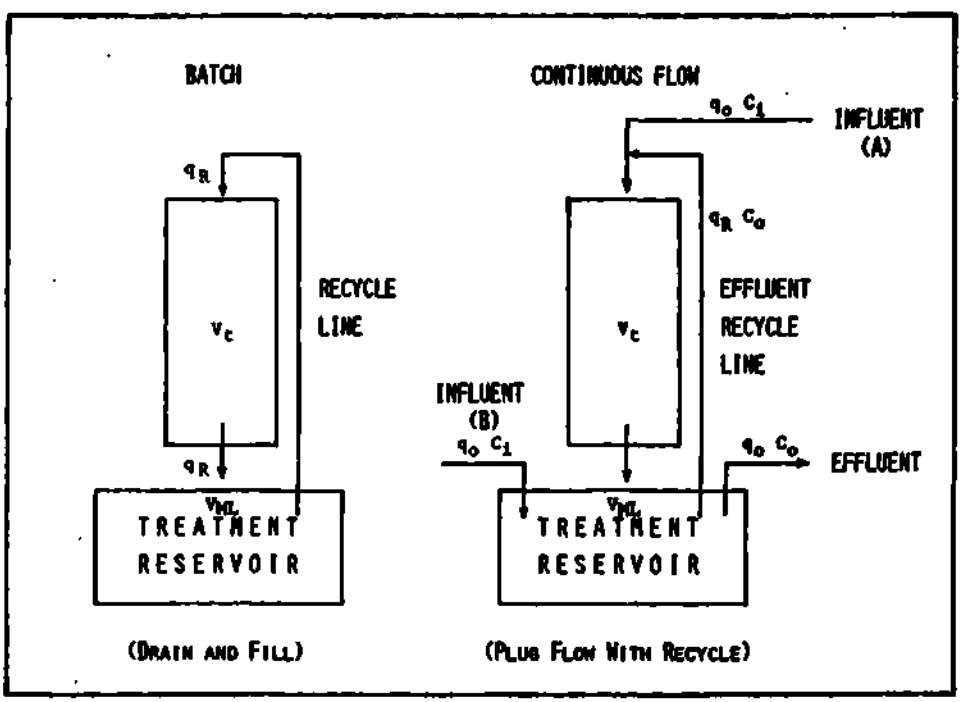


FIGURE 24. Batch and continuous flow schematics for trickling filters. Continuous flow applications may use either influent injection site A or B.

B. PROCESS PROTOCOLS

1. General

The overall objective of this study was to evaluate a bioprocessing approach to handling the phenolic paint stripping waste generated at the Kelly AFB facility. To obtain this information, a batch approach was utilized for a number of reasons. We felt that:

a. The application of genetic engineering to waste processing demanded efficient control of reactor environment in order to conserve desirable mutant traits. Resistance to starvation could best be maintained by continuing selection pressures for this trait in the operating filter biomass; shock load resistance would follow from regular exposure to sudden high loadings, in a manner similar to the isolation/selection protocols.

b. Batch pilot scale rate equations would be reasonably predictive of performance for large-scale reactors, provided good distribution was planned and the relationship between hydraulic loading and bed depth (mass velocity) on reaction rate was evaluated. As Rose (31) maintained, because of the complex fluid dynamics, direct scale-up should be attempted only if such a relationship could be estimated, or if the pilot plant was of the same bed depth as the proposed large unit. This study evaluated rates at bed depths of 3.83 ft (11.67 dcm), 7.66 ft (23.34 dcm), and 11.49 ft (35.02 dcm) for constant hydraulic loadings, and found rates to remain constant

on a per-unit-of-volume basis (Section III.D.7.).

c. As has since been stated by Irvine and Richter ([37]), the application possibilities of batch processing have been overlong neglected.

2. Batch

At a time when discharge standards are tightening, a batch operated reactor has the advantage of controlled discharge quality. Provided production rate and reactor capacity are matched, effluent phenol concentrations are governed by batch processing time.

When waste flows are irregular, as is often the case when control technologies are applied at the point-source, batch operations are to be preferred. With a properly selected, conditioned biomass, as this study has shown, intermittent short-term shutdown can be accomplished with little effect on reactor efficiency, and with only mild transient effects even for long-term shutdowns. This indicates a much greater degree of resilience is possible than has generally been attributed to batch operations in the past. We believe this is a function of "teaching" the biomass how to cope with such challenges, by designing them into the protocol.

The higher labor and handling costs associated with batch facilities can be lessened if modern process control technology is considered. A batch system built around reliable fluid switching, under electronic control, properly fail-safed and provided with back-up critical parts, will demand little

more technical expertise to operate--and less human attention--than well-designed continuous-flow facilities.

3. Continuous-flow

The kinetic data summarized in this report were derived using a batch reactor which operated in a low dispersion plug-flow regime. Grady (62), Smith (63), and others have stated that continuous-flow trickling filter installations could be designed based on batch data using plug-flow relationships. Smith warns, however, that parameters affecting rate must be given appropriate values in the scale-up, and that it is frequently difficult to insure that conditions such as temperature and flow turbulence remain equivalent.

For constant flow waste streams, or regularly periodic streams of predictable phenolic content, a continuous-flow system has certain advantages. Traditionally this mode requires a low level of skilled supervision, and fluid switching is kept to a minimum. Parameters are chosen so that the average output of the reactor falls within guidelines. This means, of course, that ungoverned changes in input concentration or other factors can cause effluent to exceed regulation limits. If this is to be prevented, it is necessary to provide toxicant concentration test capabilities, and a means to adjust appropriate parameter values to bring effluent back within guidelines.

A disadvantage of the continuous-flow process is, again, that the filter biomass is not prepared to deal with transients, and may not be able to handle forced shutdown periods

as handily as the oscillation-acclimated batch system.

4. Design Equations

a. Kinetics

As discussed in Section III.D.4.c., the overall inhibiting effect of phenol on microbial metabolism in this system results in a zero-order batch rate that is based on the initial phenol concentration. Or, from equation (6):

$$R = \frac{R_{max}}{1 + (K_s/[\emptyset]_o) + ([\emptyset]_o/K_i)^2}$$

where $R_{max} \simeq 3.3$ g/hr-ft^3

$K_s \simeq 1$ ppm

$K_i \simeq 2000$ ppm.

Temperature effects are related to rate by equation (8):

$$R_T = R_{T_{20}} \times (1.8) \exp\left(\frac{T-20}{10}\right).$$

A generalized rate expression for phenol, based on Kornegay's derivation (64) for Monod kinetics has been proposed below. Due to our inability to directly measure biomass produced in our system, we have been unable to verify the applicability of this model. However, its basic precepts do not violate what is known of system performance:

$$R\, V_R = -r_A\, D_b dz, \qquad (9)$$

$$r_A = \left[\frac{k[\emptyset]}{K_s + L + [\emptyset]} \Big/ Y \right] \quad a \cdot x \cdot d \qquad (10)$$

R V_R = rate of decay of Ø within the reactor;

D_b = depth of reactor bed;

$[\emptyset]$ = phenol concentration ($0 \leq [\emptyset] \leq 1000$ ppm);

K, K_s = Monod coefficients;

L = diffusion coefficient of phenol;

Y = growth-yield coefficient;

x = mass of organisms per unit volume of active film;

a = specific surface area of bed media;

d = depth of the active zoogleal film.

For a given medium, organism population, temperature and pH, waste water makeup, hydraulic loading rate and aeration sufficiency, all the terms become constant except for $[\emptyset]$. We are currently working on a theoretical treatment relating the measurable parameter, V_b, to biomass on the filter, hoping to find a useful replacement for the conceptual terms a·x·d, and possibly L, in Kornagey's expression.

Design equations for batch, plug-flow, and plug-flow with recycle may be derived through a mass balance on phenol through the system:

b. Batch

For a batch system, one obtains

$$t_b = \frac{V_{ML}}{V_R} \int_{C_1}^{C_o} \frac{1}{R} \, dC \qquad (11)$$

where t_b - batch time;

V_{ML} = mixed liquor volume;

V_R = reactor volume;

R = rate of phenol degradation per unit volume of reactor;

C_i = initial concentration;

C_o = final concentration.

For zero-order kinetics, this reduces to

$$t_b = \frac{V_{ML}}{RV_R} \Delta[\emptyset] \qquad (12)$$

where $\Delta[\emptyset]$ = desired change in effluent $[\emptyset]$.

In a system such as that depicted in Figure 24, when operated in a batch mode, the batch volume stored in the treatment reservoir, V_B, may be defined as

$$V_B = Q_P\ (t_b+t_f+t_d+t_s), \qquad (13)$$

where $V_B = V_{ML}$;

Q_P = raw waste production rate;

t_b = batch process time;

t_f = batch fill time;

t_d = batch drain time;

t_s = a safety allowance;

R, V_R, and $[\emptyset]_o$ have their usual connotations.

The value of V_b, the bound volume , may also have to be taken into consideration in a suitable algorithm if a microprocessor unit is monitoring both raw waste and batch liquor $[\emptyset]$, in order to account for the initial rapid equilibration

effect described in Section III.D.2. If V_b is linearly related to biomass volume, it may be expected to be approximately equal to 40% of the reactor volume, V_R. Depending upon batch volume (V_{ML}), V_b may remain a significant parameter even in a scaled-up batch reactor.

c. Plug-flow

Although untried for this system, a mass balance equation for a simple plug-flow reactor operating in continuous-flow mode is

$$V_R = q_o \int_{C_i}^{C_o} \frac{1}{R} \, dC \qquad (15)$$

and for plug-flow with recycle,

$$V_R = (q_R + q_o) \int_{\frac{(q_o C_i + q_R C_o)}{(q_R + q_o)}}^{C_o} \frac{1}{R} \, dC \qquad (16)$$

q_o = raw waste influent flow rate;

q_R = recycle rate of effluent through filter;

and all other variables have their usual meanings.

This equation is sometimes expressed in terms of the "recycle ratio", $\frac{q_R}{q_o}$. Part of the importance

of this term derives from the loading limits of the reactor. For instance, in our system, 1000 ppm (C_{max}) is the highest combined raw waste-plus-recycled effluent phenol concentration compatible with maximal filter rate. This sets a minimal recycle ratio, depending upon the maximal expected raw waste phenol concentration. In the case of the Kelly AFB facility, this would be about 4500 ppm (C_i); and generally

$$\frac{q_R}{q_o} \geq \frac{(C_i - C_{max})}{(C_{max} - C_o)}, \quad C_i \geq C_{max} . \qquad (17)$$

But, in addition, the recycle ratio is also controlled by the required hydraulic loading. Inasmuch as the primary effect of hydraulic loading in the Trinity filters was to modulate the transit volume, V_t, on the column--thus affecting mixed liquor retention time, and through that, the rate--it is clear that some trade-offs are possible between designed retention volume and the hydraulic regime. These manipulations were beyond the scope of the study. It would be safe to say that a much lower hydraulic loading than was actually used could be permitted, providing V_t was increased by structural design or counter-current ventilation scheme, and provision was made for the increased sensitivity to blockage that a lower flow implies.

The preceding discussion applies to a continuous-flow system. For batch mode, equation (15) holds if C_i = initial batch phenol concentration, and C_o = final batch phenol concentration. In an on-site pilot plant, provision for operation in both a batch and continuous-flow mode might be made for further evaluation of these parameters.

V. CONCLUSIONS

A. The Kelly AFB-ALC paint stripping facility waste stream can be efficiently handled by a biodegradative process at the point-source.

B. Batch operations conducted over long periods of time appear to condition trickling filter biomass to both starvation and shock loading, eliminating the need for continuous reseeding by lab-reared stock.

C. A batch-operated top-down air-fluid flow trickling filter, seeded with the Trinity University genetically tailored ecosystem of microorganisms, can routinely process initial phenol concentrations of up to 1000 ppm with an average removal rate of 3.3 g/hr-ft^3 of reactor at 20°C., in the presence of total chromium concentrations ranging from 11.8 to 59.9 ppm. Effluent phenol concentrations of less than 1 ppm are achievable.

D. Plastic bio-ring type support medium with a specific surface area $\underline{a}$ = 104 ft^2/ft^3 (diameter = 0.43 in.) provides anchorage for a dense biomass, imposing only coarse pretreatment filtration (#18 mesh).

E. Filter bed depth scale-up to 11.5 ft should be possible if adequate waste stream dispersion and ventilation (0.22 cfm/ft^2) are maintained. Hydraulic surface loadings, L_s, between 3.4 - 6.7 gpm/ft^2 yielded comparable rates of phenol degradation; one rate-controlling factor influenced by L_s was the transit volume, V_t, on the column. Indications are that V_t-increasing configuration or flow-scheme changes, such as counter-current

air-fluid flow, could do much to increase the already high performance of this type unit, even at lower L_s.

F. Combined starvation and dehydration interludes supplying no inputs of any kind for more than six weeks were survived with rapid (72-hr) recovery to normal performance levels with neither special treatment nor reseeding. Routine 12-hr and 72-hr overnight and weekend 'down' periods were tolerated with no alterations in base rates.

G. Operation at 20°C. (68°F.) gave average rates of 3.3 $g/h \cdot ft^3$ with 99.9% phenol removal; operation at 30°C. (86°F) increased rates to 5.7 $g/h \cdot ft^3$ with 99.9% removal.

H. All trace minerals and some bulk requirements are satisfied by the combination of tap water and waste water components. A Ø:P ratio of 1:48 and Ø:N ration of 1:10 were adopted as sufficient supplementation for this pilot operation. KH2PO4 and NH4NO3 were used in this study; other possible phosphorus or nitrogen sources include urea or diammonium phosphate $(NH4)_2PO4$. Analyses indicate that the Kelly waste water itself may provide some of the phosphorus requirement.

I. In-system conditions should be maintained at pH 6-9, with an optimum range between 7-8. In an on-site system, buffer may be used, or pH governed by sensor-controlled addition of inexpensive NaOH or NH_4OH.

J. Batch operation of this system results in low, fine suspended solids concentrations in the effluent (0.2 mg/ml = 200 ppm), indicating that a field system could dispense with

even a simple sand clarifier if discharge was to another waste facility.

K. Reaction kinetics are approximately zero-order over the range $1 \leq [\phi] \leq 1000$ ppm; phenol inhibition results in a complex but near-zero-order, initial concentration-dependent rate for batch startup concentrations between 1000 and 3500 ppm.

L. Standard steady-state continuous-flow operation of this process, if kinetics remained approximately zero-order, would require a reactor of similar volume to the batch reactor. However the kinetics of this study may be peculiar to a filter biomass utilized in a batch mode. Detailed design equations have been developed and are presented in Section IV.B.4.

M. Both automated batch and continuous-flow systems are currently in use. Application of automated process control to the Kelly problem would mean a more efficient system with little change in personnel or skill levels required of the maintaining organization.

VI. RECOMMENDATIONS

A. It is recommended that the Air Force consider implementation of a pilot scale on-site trickling filter bioprocessing system at the KAFB depaint facility.

B. Economics of architecture and scale suggests structuring control design and pilot plant capacity to allow continued usefulness of pilot-scale facilities in a scale-up.

C. Two moderate-size trickling filter units would permit flexibility of experimental design for evaluating batch, sequenced batch, and continuous-flow operation, as well as the testing of other parameters. Continuity of treatment during maintenance would also be possible.

D. Figure 25 is a sketch of a possible on-site pilot-scale facility. For maximum benefits from the process, the final clarifier should be dispensed with, and effluent ducted via the existing channel to the Kelly AFB industrial waste facility. The influx of adapted organisms would provide the facility with useful genetic augmentation.

E. Facility size and flow handling is a function of discharge requirements. Using a batch mode, effluent quality (phenol and chromium concentration) discharged to the industrial facility could be regulated at any convenient concentration, from less than 1 ppm upward.

F. In view of the rapidly developing capabilities of automated process control technology, it may be worthwhile from the standpoint of both economics and system efficiency to plan for its use even in such a low-flow application.

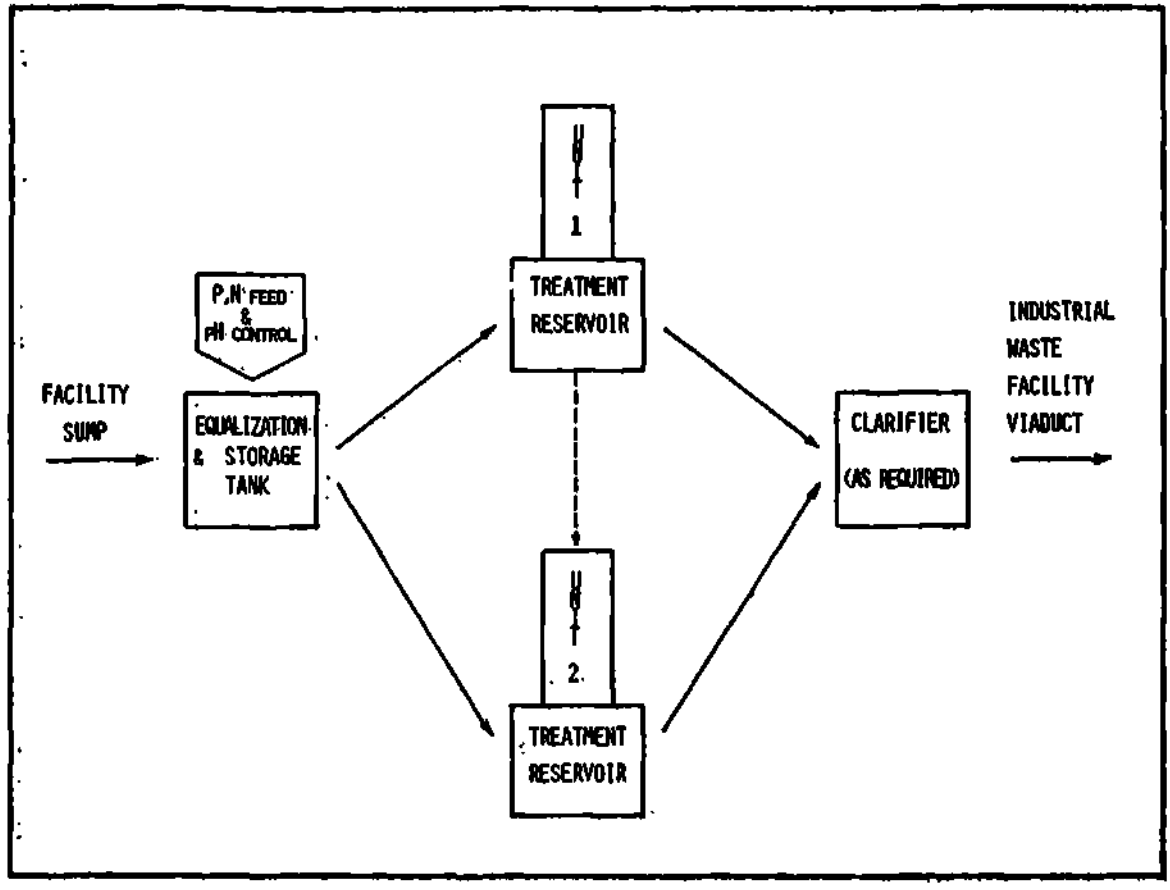


FIGURE 25. Simplified on-site pilot plant arrangement for KAFB-ALC depaint facility. Liquid circuits would allow parallel or series operation in batch, sequencing batch, or continuous-flow mode.

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