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Fixed-Film, Fluidized-Bed Bioreactors for Biooxidation of Coal Conversion Wastewaters: Progress Report for the Period October 1, 1983–September 30, 1984

G. W. Strandberg
R. M. Worden
J. D. Hewitt
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Chemical Technology Division

FIXED-FILM, FLUIDIZED-BED BIOREACTORS FOR BIOOXIDATION OF COAL CONVERSION WASTEWATERS: PROGRESS REPORT FOR THE PERIOD OCTOBER 1, 1983—SEPTEMBER 30, 1984

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CONTENTS

ABSTRACT 1

1. INTRODUCTION 1

2. EXPERIMENTAL PROCEDURES 2

2.1 BIOREACTOR DESIGN AND OPERATION 2

2.2 ANALYTICAL TECHNIQUES 3

2.3 NITROGEN STRIPPER 5

3. RESULTS 5

3.1 BIODEGRADABILITY STUDIES 5

3.2 BIOREACTOR PERFORMANCE 7

3.3 SLUDGE PRODUCTION 11

3.4 BATCH KINETIC TESTS 15

3.5 OXYGEN AVAILABILITY STUDIES 16

3.6 BIOMASS ASSAYS 17

4. BIOREACTOR MODELING 20

5. ECONOMIC EVALUATION 26

6. ACKNOWLEDGMENTS 31

7. REFERENCES 32

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ABSTRACT

Actual coal gasification wastewaters have been treated successfully using a fixed-film, fluidized-bed bioreactor. Phenol removal exceeded 99% and COD removal was typically 75-85% for 50% strength wastewater. Batch kinetic tests showed potential for further improvement in bioreactor kinetics. A bioreactor model has been developed to guide further process development. A preliminary economic evaluation of a commercial scale process indicated that there is potential for as much as a 50% reduction in both capital and operating costs by use of fluidized-bed bioreactor technology rather than conventional activated-sludge technology.

1. INTRODUCTION

Conventional biooxidation processes (e.g., activated sludge) are currently proposed to reduce the concentration of dissolved organic components of coal gasification wastewaters. These systems require relatively long wastewater retention times of days and entail large capital investment and substantial land area.

An alternative technology for the biooxidation of dissolved organics is under development at Oak Ridge National Laboratory (ORNL).[1,2] This technology is the fixed-film, fluidized-bed bioreactor, which offers several advantages relative to conventional biooxidation technologies. Higher organic removal rates at low hydraulic retention times permit

smaller reactors, and hence lower capital costs. The fixed-film systems are also more resistant to stress factors than suspended growth systems.

Process development work is being carried out at ORNL to demonstrate the technical feasibility of the fixed-film, fluidized-bed bioreactor for treating coal gasification wastewaters. Synthetic and actual coal gasification wastewaters have been treated in two laboratory-scale bioreactors for ~2 years. These studies demonstrated that the bioreactors exhibit long-term stable operation with synthetic and dilute actual wastewaters. Bioreactor performance is affected by oxygen availability, liquid flow rate, biomass loading and wastewater strength. Batch kinetic experiments suggest a dependence on phenol and oxygen concentrations below 10 mg/L and 2 mg/L, respectively.[1]

For ~1 year an actual coal gasification wastewater obtained from the Morgantown Energy Technology Center, (METC) Morgantown, WV, has been treated. This report details the results of experiments to determine the effects of wastewater strength, wastewater components, and other operational parameters on bioreactor performance. Also, the initial framework for a bioreactor model and a preliminary economic evaluation of a commercial scale process are presented.

2. EXPERIMENTAL PROCEDURES

2.1 BIOREACTOR DESIGN AND OPERATION

Details of the design and operation of the fixed-film, fluidized-bed bioreactor have been described previously.[1,2] Briefly, the bioreactor consists of a glass column (5 cm ID and 1.5 m tall) containing a population of microorganisms naturally attached to 590 to 250 μm (30-60 mesh)

anthracite coal particles (Fig. 1). Wastewater and oxygen are introduced at the bottom of the bioreactor and fluidize the biomass/coal bed.

2.2 ANALYTICAL TECHNIQUES

Samples of influent and effluent wastewater were routinely analyzed for phenols using the 4-aminoantipyrene (4-AAP) colorimetric assay method.[3] Under certain conditions, this method approximates the total concentration of the major wastewater phenolics (phenol, o-cresol, and m,p-cresol have been identified by high pressure liquid chromatography).[4] However, during operation with high strength feed and high recycle, substantial 4-AAP-reacting components accumulated which did not appear to be phenols. Therefore, the major phenolics were also quantitated by gas chromatography. A 2-mm-ID, 1.8-m-long glass column packed with 250 to 175 μm (60-80 mesh) Tenax GC (Alltech Assoc., Deerfield, IL), operated isothermally at 190°C was used to separate the phenols.

Ammonia and sulfides were estimated using CHEMets water analysis test kits (CHEMetrics, Inc., Warrenton, VA). Chemical oxygen demand (COD) was determined using the Hach procedure.[5] Total suspended solids (TSS) and volatile suspended solids (VSS) were measured according to Standard Methods for the Examination of Water and Wastewater.[6]

The reaction of microbial cells with iodonitrotetrazolium violet was studied using a modification of the procedure of Arcuri[7] in an attempt to develop a viable cell assay.

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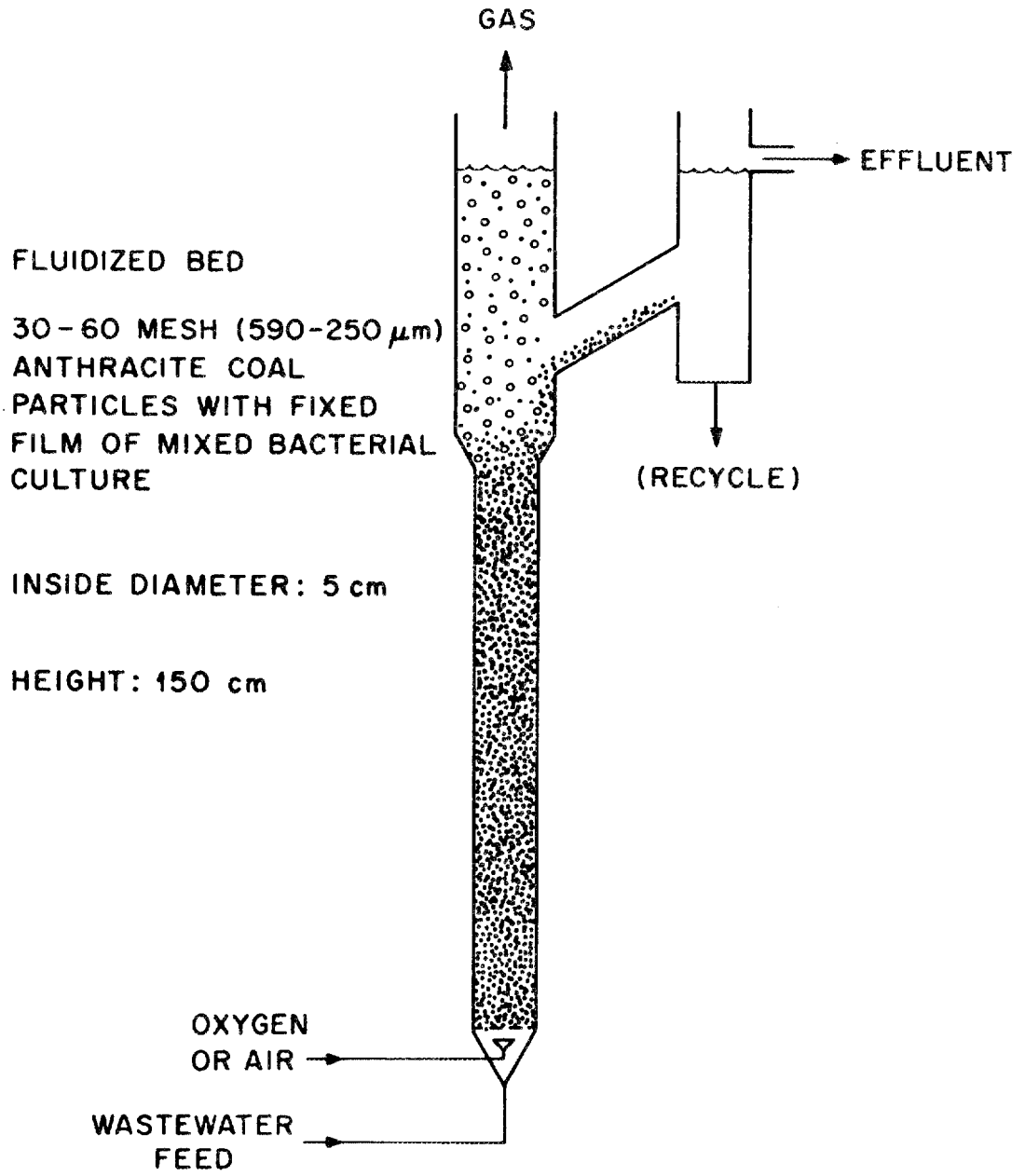

Fig. 1. Fixed-film, fluidized-bed bioreactor.

2.3 NITROGEN STRIPPER

The ammonia and sulfides concentrations in the wastewater were reduced using a nitrogen-sparged stripper at an elevated temperature. The stripping unit consisted of a ~200 L stainless steel drum modified as shown in Fig. 2. Approximately 100 L of wastewater was transferred to the stripper and heated to ~90°C; nitrogen gas was then introduced at the bottom at a flow rate of 15 L/min. After stripping for 8 to 9 h, the ammonia concentration was reduced to ~1500 and 2000 mg/L from an initial 15,000 and 16,000 mg/L, respectively, for two different wastewater samples. The sulfides concentration for both samples was reduced from 200 to 400 mg/L to <1 mg/L. After stripping, the wastewater was allowed to cool to ambient temperature and transferred to the bioreactor feed reservoir. Supplementary mineral salts and micronutrients were added prior to introducing the wastewater to the bioreactor.

3. RESULTS

3.1 BIODEGRADABILITY STUDIES

Recirculating decanter wastewater from a fixed-bed gasification test was received from the Morgantown Energy Technology Center (METC). This wastewater was substantially different in composition from the wastewater which was treated earlier (from the Holston Army Ammunition Plant, Kingsport, TN).[1] The METC wastewater was characterized (Table 1) and shown to have a substantial fraction (~2%) of dispersed oil (which was removed by filtration), high concentrations of ammonia (~15,000 mg/L) and sulfides (200 to 400 mg/L) and was basic (pH 8.5). It contained ~13,000 mg/L of carbon, of which ~50% was organic and ~50% inorganic (primarily carbonate). High

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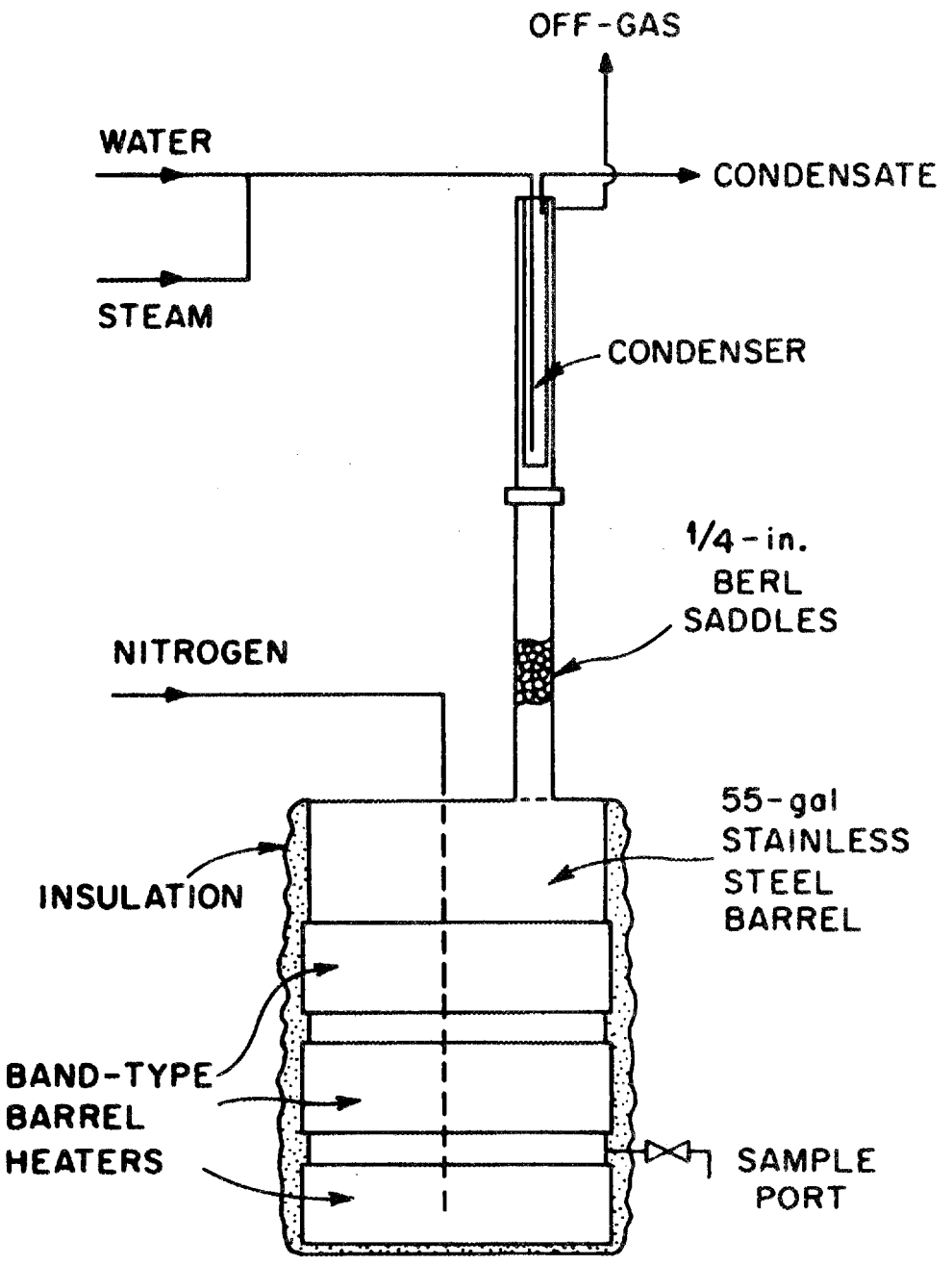

Fig. 2. Batch nitrogen stripper for removal of ammonia and sulfides from raw wastewater.

Table 1. Composition of METC recirculating decanter wastewater

Parameter	Concentration (mg/L)
COD	50,000
TOC	6500
Ammonia	15,000
Sulfides	200-400
Phenolics	6000 (4-AAP) 8000 (HPLC)

pressure liquid chromatographic analysis[4] of solvent extracts revealed that the major organics were monohydric phenol (3800 mg/L), o-cresol (1150 mg/L) and m,p-cresol (3970 mg/L). In order to determine the treatability of this wastewater, shake flask tests (see ref. 1 for methodology) were conducted. Table 2 shows that coal/biomass taken from an operating bioreactor was able to readily reduce the concentration of 4-AAP phenols and COD in the wastewater. Degradation rates of monohydric phenol alone and phenol added to METC wastewater were similar. The slight decrease in activity with METC wastewater alone may be due to the fact the microbial population was not previously adapted to this wastewater.

3.2 BIOREACTOR PERFORMANCE

Dilute, filtered (to remove oil), mineral-supplemented (but unstripped) METC wastewater was introduced to the bioreactor without recycle to initiate treatment. Over a period of a few weeks, the strength of the wastewater was gradually increased to a maximum of ~3%. The degradation rate was ~6 mg/(L coal•min).

Table 2. Biodegradability of METC wastewater

Substrate	Time (min)	4-AAP phenols (mg/L)	Estimated degradation rate [mg/(L coal•min)]
Monohydric phenol	0	108.6	
	10	94.6	
	20	77.2	26
	30	54.2	
	40	30.4	
	70	0	
Monohydric phenol (35 mg/L) + METC wastewater (~0.5% v/v)	0	82.8	
	10	66.9	
	20	49.9	25
	30	29.8	
	40	7.6	
	70	1.6	
METC wastewater (~1% v/v)	0	55.4	
	10	42.5	
	20	26.6	21
	30	11.8	
	40	3.8	
	70	2.3	

The operation of the bioreactor was then converted to a recycle mode to allow an increase in the effective residence time within the bioreactor to treat higher strength wastewater. A summary of the performance of the bioreactor during recycle at various influent phenols concentrations and recycle ratios is presented in Table 3. The recycle ratio is the fraction of the liquid effluent recycled to the inlet, divided by the fraction discharged from the bioreactor system. Stable operation was observed as long as the influent phenols concentration was maintained below ~150 mg/L. It was subsequently determined using a synthetic feed that the bioreactor could handle phenol concentrations of at least 400 mg/L at 75 to 85% recycle. Thus, the instability observed at high phenols concentrations with the METC wastewater was likely due to other wastewater components.

Table 3. Performance of bioreactor on METC wastewater during recycle (bed volume 1.3-1.7 L; temperature, 30°C)

Phenols concentration (mg/L)		Effluent recycle ratio	Degradation rate [mg/(L bed•min)]
influent	effluent		
25	3	3.0	9
40	8	0.7	12
38	12	1.6	16
39	19	1.3	9
52	25	0.5	11
66	35	0.7	10
65	41	3.7	10
147	129	3.7	8
202	180	3.7	11

Ammonia and sulfides were suspected as the inhibitory components in the METC wastewater. Therefore, the wastewater was stripped to reduce the concentration of ammonia and sulfides to ~1500 mg/L and <1 mg/L, respectively. Results in Table 4 show that 50% strength wastewater was readily treated and a wastewater strength of up to 83% was effectively treated for a few days. For a short duration (due to a pump malfunction), 100% wastewater was tolerated without a problem. Also the ability of the bioreactor to substantially reduce the COD of the wastewater is shown.

The phenols concentrations were generally maintained at less than 100 mg/L in the bioreactor at the feed flow rates and recycle ratios used. On occasion, bioreactor concentrations of ~200 mg/L were maintained

Table 4. Bioreactor performance with concentrated METC wastewater[a]

Date	Feed concentration stripped wastewater (%)	Phenolics degradation rate[b] [mg/(L bed•min)]	COD degradation rate [mg/(L bed•min)]	COD removal (%)
6/28/84	34	5	24	80
6/29/84	36	6	25	80
7/2/84	100	5	32	87
7/3/84			39	80
7/4/84	55	8	33	87
7/5/84	52	11	32	85
7/6/84	83	8	32	87
7/9/84	83	4	30	81
7/10/84	52	6	28	77
7/11/84	52	9	27	75
7/12/84	52	7	27	75
7/13/84	50	9	32	87
7/17/84	50	4		
7/19/84	28	6		

[a]Bed volume, 1.3-2.0 L; liquid recycle, 0.6 L/min; oxygen flow rate, 85-130 mL/min; temperature, ~30°C.

[b]Phenol concentrations in the bioreactor were generally 20-60 mg/L.

without problem. Future studies will determine maximum phenols concentrations that can be tolerated.

Gas chromatographic (GC) analysis showed that the actual concentrations of the identifiable phenolics (phenol, o-cresol, m,p-cresol) are in the range of <1 to 5 mg/L in the effluent. This is substantially lower

than the 20 to 40 mg/L indicated by the 4-AAP assay, so 4-AAP apparently reacts with other wastewater components or degradation products. The degradation rates based on changes in 4-AAP-reactive material and GC-analyzed phenols are essentially the same. Greater than 99% of the GC-measured phenols were degraded.

Effluent COD values were generally in the range of 1150 to 2500 mg/L and appeared to increase with feed strength; there was an approximate 75 to 85% reduction in COD. The theoretical COD for phenol is ~2 g O_2/g phenol. Thus, a comparison of the phenol and COD degradation rates in Table 4 indicates that about two-thirds of the COD reduction is attributable to phenol degradation, while one-third is attributable to biodegradation of other species.

3.3 SLUDGE PRODUCTION

The amount of solid waste material or sludge generated from the treatment of coal conversion wastewater is an important consideration in the development of a treatment process. The solid waste produced by the fixed-film, fluidized-bed bioreactor is a combination of coal fines and biomass cells. An attempt was made during this study to determine the amount of sludge produced in normal bioreactor operation by taking into consideration the output of solids in the reactor effluent and the accumulation of biomass within the reactor.

The total suspended solids (TSS) assay was used to determine the amount of dry solids in the reactor effluent. Figure 3 shows the results of TSS measurements made on a daily basis; Fig. 4 represents the measurement of an entire day's effluent collected in 100 to 200 mL increments.

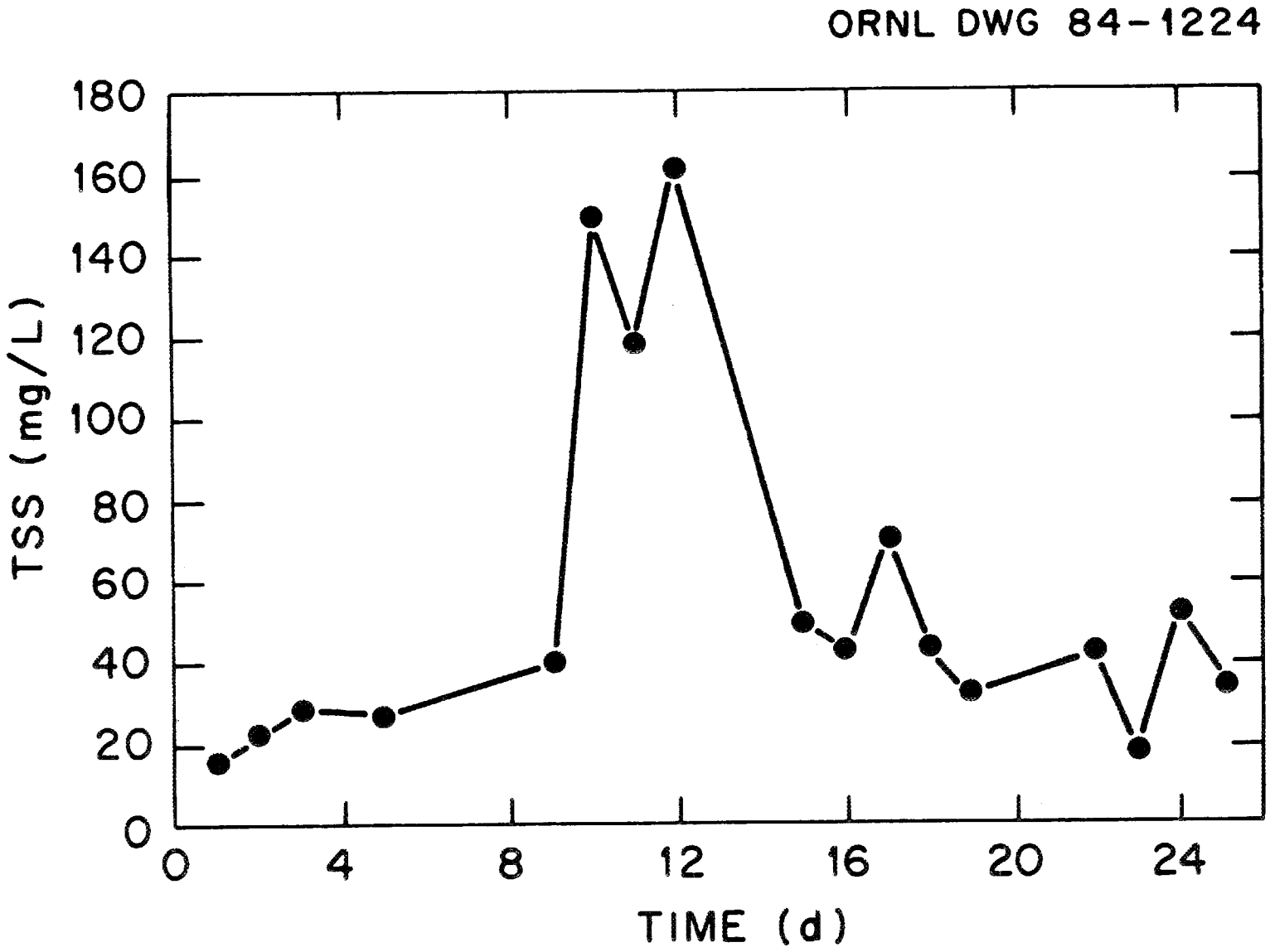

Fig. 3. Total suspended solids in bioreactor effluent as determined from daily grab samples.

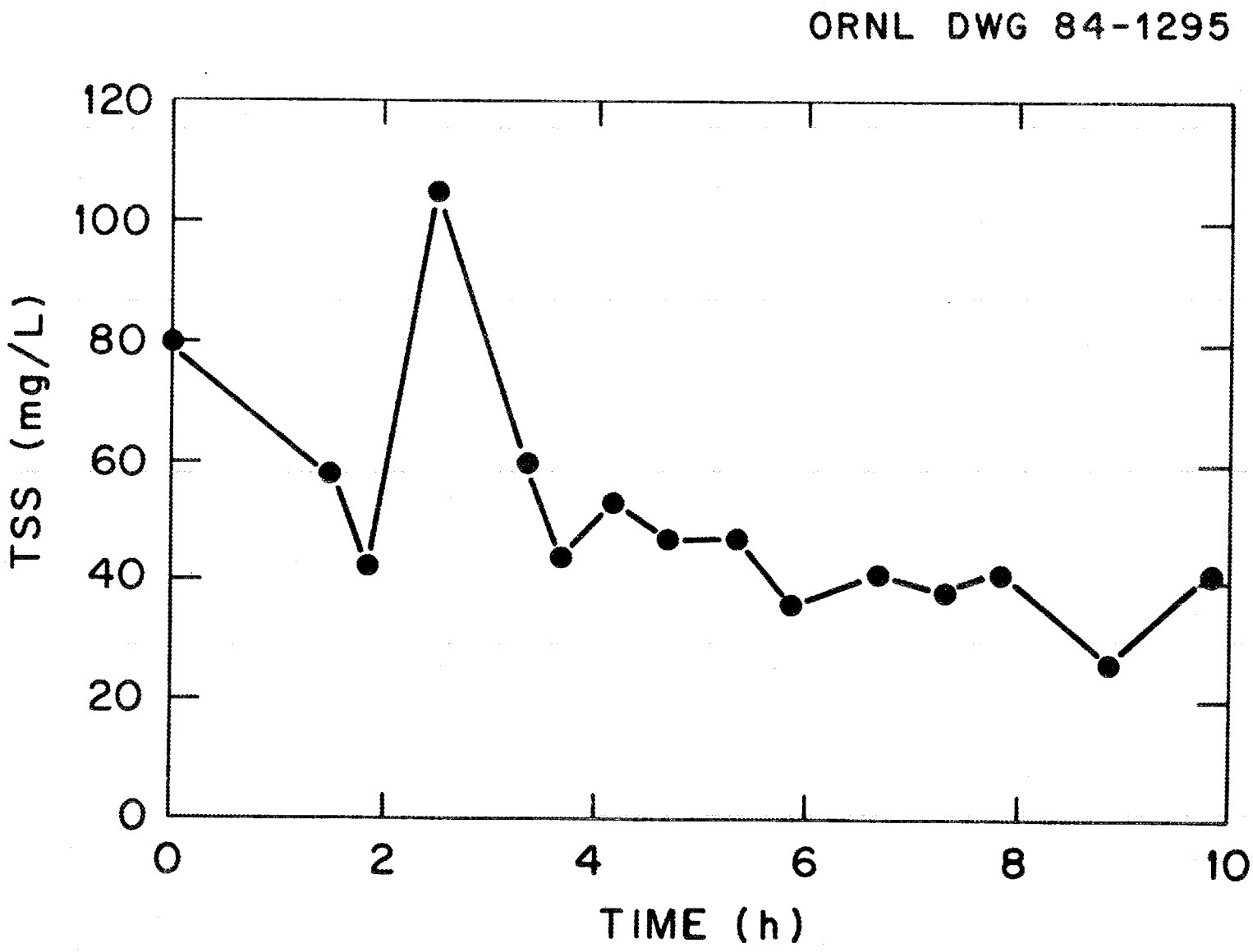

Fig. 4. Total suspended solids in total bioreactor effluent over a 10-h period, measured in 100 to 200 mL fractions of effluent.

The normal concentration of dry solids appeared to be around 30 to 40 mg/L, but higher TSS values were common. Normal shedding of biomass, washout of materials with increased flow rates, and a variety of other factors can be reasons for temporarily high solids outputs. The large discharge of solids over days 10 to 15 in Fig. 3 are believed to be related to a pulse of full-strength wastewater on approximately day 10. Integration of the data in Fig. 3 indicates an average dry solids concentration of 55 mg/L in the bioreactor effluent. Similarly, the data in Fig. 4 indicate an average value of 51 mg/L. The VSS content was consistently ~90% of the TSS value, which indicated very little coal in the effluent.

An accumulation of ~100 mL (74 g dry weight) of coal/biomass was removed from the settling arm of the bioreactor each week during normal operation. The fraction of the dry weight representing biomass was judged to be less than 1%, based on earlier experience with such systems. If the settled coal is assumed to have contained 1% biomass, then the accumulation of dry cells in the settling arm was 0.11 g/d. With an average effluent TSS value of 55 mg/L and an average effluent flow rate of 4.5 mL/min, the dry biomass discharged with the effluent was 0.36 g/d. Thus, the total estimated production of dry biomass was 0.47 g/d.

During the sludge production study, the average phenol degradation rate was 7.3 mg/(L bed•min), the settled bed volume was fairly steady at 1.3 L, and thus 13.7 g/d of phenol was degraded. Overall biomass production during the study was therefore 0.034 g dry biomass/g phenol degraded. Biomass is ~90% water by weight, so this value represents ~0.34 g wet sludge/g phenol degraded. Cell growth on the coal particles and reactor walls would have to be taken into account if the reactor were only operated

for a short time; but by the time the measurements mentioned above were performed (beginning day 18 of operation), cell growth on these surfaces was well established, and generation and removal of biomass had reached an essentially steady state. Bed expansion due to film growth was negligible during the study.

3.4 BATCH KINETIC TESTS

The reaction rates presented in Table 4 show no apparent effect of wastewater strength and are similar to those obtained with dilute wastewater and synthetic feeds. Batch kinetic tests were performed to determine maximum degradation rates under more ideal, controlled conditions. The initial degradation rates of monohydric phenol and wastewater phenols were determined by adding phenol or concentrated wastewater to shake flasks containing coal/biomass from the bioreactor in either distilled water or clarified (centrifuged) effluent (50% strength feed) from the bioreactor. High initial degradation rates of 35 to 40 mg/(L bed•min) in all the cases indicated that the culture is equally active on synthetic substrates and actual wastewaters. However, the batch reaction rates were substantially greater than the rates in the continuous bioreactor. This same phenomenon had been noted earlier with synthetic feeds.[1] Earlier experience had also shown that higher reaction rates were obtained at higher liquid and oxygen flow rates. Two short-term experiments were done with the higher strength wastewater at a 50% increase in liquid flow rate and a 100% increase in oxygen flow rate; no enhancement of reaction rate was seen in either test. In any case, it would seem likely that reaction rates can be improved in the fluidized-bed bioreactor once the rate-limiting phenomena are identified.

3.5 OXYGEN AVAILABILITY STUDIES

The biodegradation of phenols in these systems is highly oxygen dependent. General experience with the bioreactors and the significantly higher reaction rates achieved in shake-flask tests suggest that a major limiting factor in the bioreactors is oxygen availability. The effect of O_2 in the gas phase on phenol degradation was examined during an interim period when the bioreactor was operating on a synthetic feed (monohydric phenol); the results are shown in Table 5. The liquid flow rate was ~0.5 L/min and the influent phenol concentration varied from ~50 to ~70 mg/L during this period. The gas flow rates were increased for the air + O_2, and air only, tests in order to increase the gas-liquid mass transfer coefficient. However, the decreased oxygen concentration in the gas decreases the driving force for mass transfer, which more than offsets the increased mass transfer coefficient. Note that for the 50:50 air:O_2 mixture, the gas flow rate was increased by ~40% relative to the pure O_2 case, while the O_2 concentration is decreased by ~40%. Thus, the total oxygen throughput is the same in both cases. The net result of decreasing the oxygen concentration in the influent gas is a decrease in phenol degradation rate (i.e., the bioreactor is oxygen-limited).

Table 5. The effect of gas composition on the phenol degradation rate

Gas composition (by volume)	Average degradation rate [mg/(L bed•min)]	Gas flow rate (mL/min)	O_2 in gas (%)
Pure O_2	10.4	55	100
50:50 air:O_2	7.6	75	~60.5
Air	3.7	145	~21

A second bioreactor similar to that shown in Fig. 1 has been maintained on a synthetic feed (monohydric phenol) and was used to examine the effects of off-gas recycle. Two potential benefits could be realized by using that procedure. (1) At a given rate of oxygen supply, the gas flow in the bed can be increased, which increases the transfer rate of oxygen from the gas phase to the liquid phase. (2) Also, since only a relatively small fraction of the oxygen is transferred to the liquid as the bubbles rise through the bed, off-gas recycle provides for further absorption and hence improved oxygen utilization.

Preliminary tests of off-gas recycle resulted in only slight increase in the degradation rate under the conditions used. We feel that additional studies are needed.

3.6 BIOMASS ASSAYS

An understanding of the various phenomena that occur in fixed-film, fluidized-bed bioreactors is important to ultimate realization of their process potential. One significant aspect to this understanding is a knowledge of the biomass loading within the bioreactor, and in particular, the ratio of active biomass to total biomass. The microbial films that develop on the inert support particles vary in thickness depending on factors that are presently unidentified. The films likely consist of both metabolically active and inactive cells. Since the overall bioreactor reaction rates are dependent upon the transfer of metabolites into and out of the films, too thick a film may retard metabolite transfer. Also, if the film is largely composed of inactive cells, it may occupy too much of the reactor volume.

We have been attempting to develop appropriate assay procedures for total and active biomass. The difficulty in developing a total biomass assay is compounded with a support medium such as coal because the coal is composed of similar elements (e.g., carbon and nitrogen) and in similar ratios as the microorganisms themselves. Nevertheless, we have had some success in establishing rudimentary assays.

The total biomass assay entails the mechanical/chemical removal of biomass from the coal. After oven drying (105°C, 45 min), a known weight of the coal/biomass sample is gently agitated in the presence of ~4 N NaOH for a few min, and the dislodged biomass is then removed by suction. The treated coal is washed, dried, and weighed. The biomass concentration is estimated by the decrease from the starting weight.

We have also attempted to estimate total biomass concentration by a differential ashing procedure used to determine the amount of activated charcoal in the powdered activated carbon treatment (PACT) process.[8] The method depends on the greater volatility of biomass at high temperature (400 to 500°C) compared to charcoal. Our experience with the method indicated that there was significant, unexplainable, scatter in the data and that the method was not sufficiently accurate.

The method of Arcuri[7] was used to estimate active biomass in the fixed-films. This assay is based on the ability of viable cells to reduce iodonitrotetrazolium violet (INT). The reduced dye (red color) is extracted from the cells with acetone and quantified spectrophotometrically. The method shows promise, but further development is needed. For example, Fig. 5 shows that there is a linear relationship between the amount of acetone-extractable, reduced INT produced and the amount

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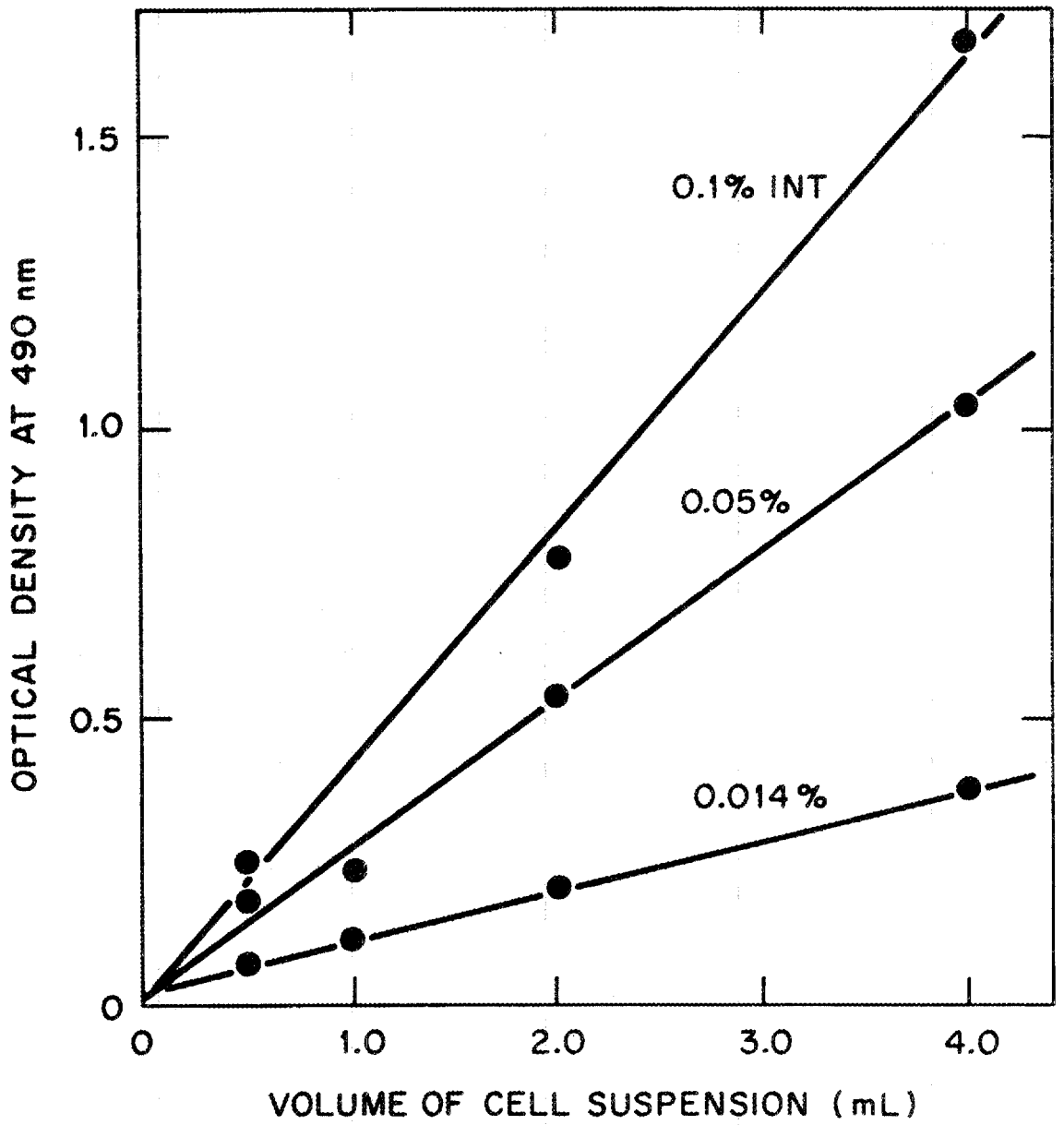

Fig. 5. Dependence of acetone-extractable INT color on quantity of cells.

of cells present. This experiment was done with cells from an actively growing culture of Pseudomonas alcaligenes (isolated from one of our bioreactors). The method appears to work with biofilms from bioreactors being fed synthetic wastewaters. However, with biofilms from reactors being fed actual wastewater, acetone-extractable materials are encountered which interfere with the spectrophotometric assay.

4. BIOREACTOR MODELING

A dynamic model for biooxidation of phenolics in the fixed-film, fluidized-bed bioreactor is being developed. The integrated model consists of a bioparticle model and a reactor model. The bioparticle model postulates that a spherical, inert pellet is coated with a uniform homogeneous biological film. Substrates (phenol and oxygen) diffuse into the film from the bulk liquid and react at a rate, R, which is described by the following double-Monod relationship:

$$R_{phenol} = K_{max}\left(\frac{C_{O_2}}{K_{O_2} + C_{O_2}}\right)\left(\frac{C_p}{K_p + C_p}\right), \tag{1}$$

$$R_{O_2} = \gamma R_{phenol}\ , \tag{2}$$

where C_{O_2} and C_p are the concentrations of oxygen and phenol, respectively; K_{O_2} and K_p are the half-saturation Monod constants; K_{max} is a kinetic coefficient; and γ is a stoichiometric coefficient. Diffusion and reaction of phenol and oxygen within the film are governed at steady state by

$$D_p\left\{\frac{d^2C_p}{dr^2} + \frac{2}{r}\frac{dC_p}{dr}\right\} = R_{phenol}\ , \tag{3}$$

$$D_{O_2}\left\{\frac{d^2C_{O_2}}{dr^2}+\frac{2}{r}\frac{dC_{O_2}}{dr}\right\}=R_{O_2}\ , \tag{4}$$

with boundary conditions

$$r = \text{outer radius of film; } C_p,\ C_{O_2} = \text{bulk phase concentrations}\ , \tag{5}$$

$$r = \text{inner radius of film; } \frac{dC_p}{dr}=\frac{dC_{O_2}}{dr}=0\ . \tag{6}$$

The parameters D_p and D_{O_2} are the diffusivities of phenol and oxygen in the film. These equations are used to calculate phenol and oxygen concentration profiles in the film, and provide the reaction kinetics term for the reactor model based on the flux of substrate at the particle surface.

One set of results from this bioparticle simulation is shown in Table 6 and Fig. 6. The "active film thickness" is defined by the point at which the limiting substrate concentration has decreased to ~1% of its value at the external surface of the film. The phenol concentration at

Table 6. Dependence of "active film thickness" on substrate concentrations

Oxygen (mg/L)	Phenol (mg/L)	Active film thickness (μm)	Limiting substrate
0.1	50	40	oxygen
1.0	50	100	oxygen
10.0	50	220	phenol

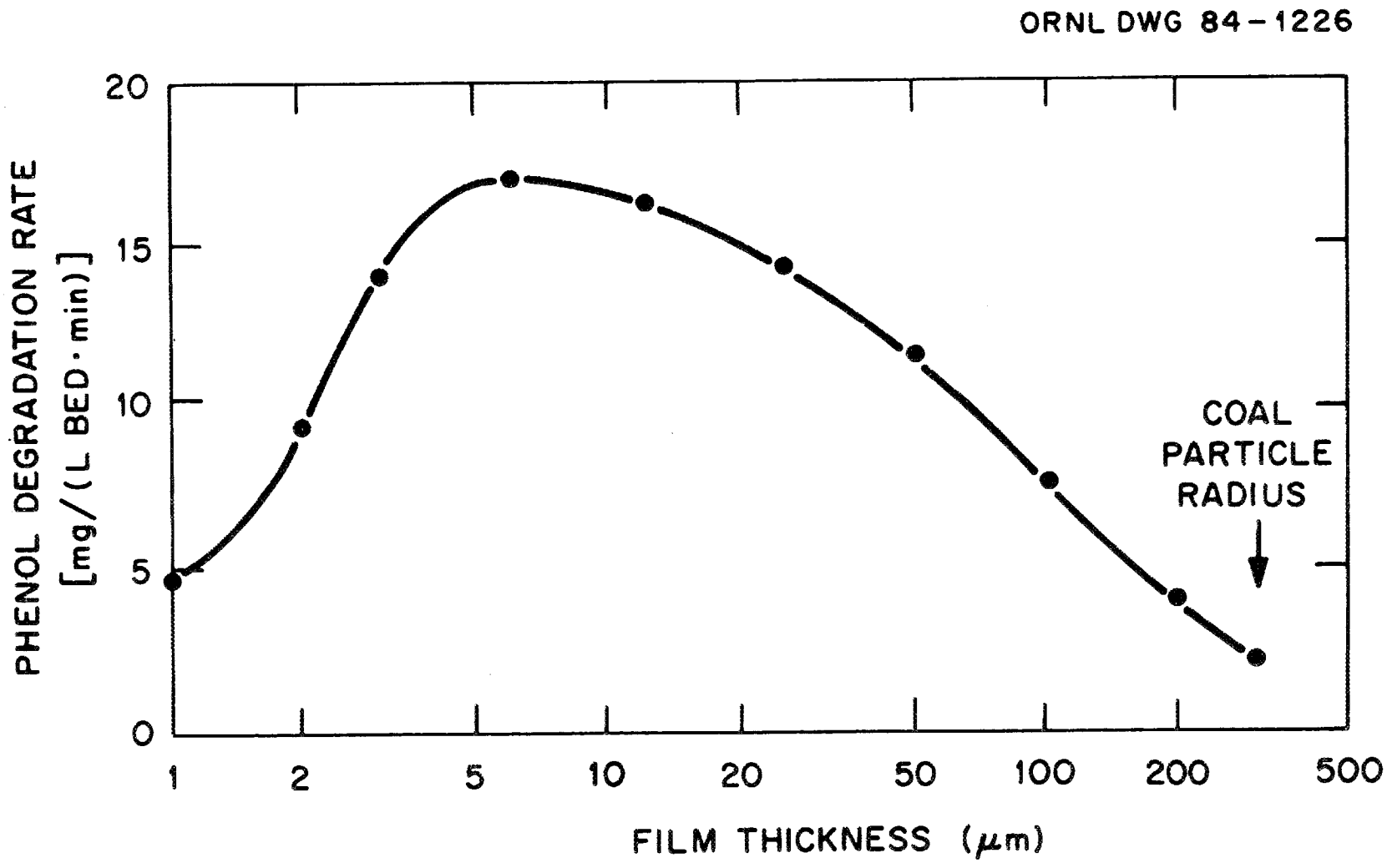

Fig. 6. Degradation rate in bioreactor as a function of film thickness (model simulation).

the surface was set at 50 mg/L, while various oxygen concentrations were used. Other parameter values are shown in Table 7. The films may be either oxygen limited or phenol limited, depending on the bulk liquid concentrations.

Figure 6 shows that the phenol degradation rate goes through a maximum as the film thickness is increased; the "optimum" film thickness appears to be ~5 to 10 μm. At low film thickness, the specific reaction rate increases as the film thickness increases due to addition of more "catalyst." However, at larger film thickness the specific rate decreases due to expansion of the bed volume (i.e., larger particles) and due to films which exceed the active film thickness.

The reactor model for conceptual testing is a stirred-tanks-in-series model. At steady state the phenol and oxygen mass balances for each tank are

$$Q(C_{P_{in}} - C_{P_{out}}) = R_{phenol}V \ , \tag{7}$$

$$Q(C_{O_{2_{in}}} - C_{O_{2_{out}}}) + K_La(C^*_{O_2} - C_{O_2}) = R_{O_2}V \ , \tag{8}$$

where Q is the liquid flow rate, V is the bed volume, and $K_La(C^*_{O_2} - C_{O_2})$ is the rate of transfer of oxygen from the gas to the liquid.

Table 7. Parameter values used in simulation reported in Tables 6 and 8

Coal particle radius	300 μm
Bed volume (clean coal)	0.42 L
Number of tanks in series	1
Liquid residence time in bed	6 min
Influent phenol concentration	50 mg/L
Influent oxygen concentration	1.0 mg/L
$C^*_{O_2}$ (pure oxygen)	40 mg/L
D_p	5.0×10^{-7} cm^2/s
D_{O_2}	7.7×10^{-6} cm^2/s
K_p	1.0 mg/L
K_{O_2}	0.01 mg/L
K_{max}	10 μg phenol/(cm^3 biomass•s)
K_La	1×10^{-3} s^{-1}
γ	1.0 g oxygen/g phenol

Results of several simulations using this simple model are shown in Table 8. The parameter values listed in Table 7 are believed to be reasonable estimates, but they are by no means "best" values. For the case of one tank, the degradation rate is maximized at a film thickness of ~10 μm. Oxygen was the limiting substrate; the steady-state oxygen concentration was as low as 0.015 mg/L in the case of the thickest film. This highlights the importance of gas-liquid oxygen transfer whose increase would enhance the bulk phase oxygen concentration and hence increase the biooxidation rate.

Table 8. Effect of film thickness on bioreactor performance (model simulation)[a]

Film thickness (μm)	Effluent phenol (mg/L)	Effluent oxygen (mg/L)	Settled bed volume (L)	Phenol degradation rate [mg/(L bed•min)]
300	34.6	0.015	3.36	2.29
200	34.6	0.025	1.95	3.96
100	34.6	0.0474	1.00	7.73
50	34.7	0.0721	0.667	11.54
25	34.7	0.0920	0.534	14.4
12	34.7	0.105	0.472	16.3
6	34.8	0.113	0.446	17.0
3	37.9	2.42	0.434	13.9
2	41.9	5.38	0.428	9.45
1	46.0	8.35	0.424	4.71

[a] Parameter values are given in Table 7.

It is interesting to note that the volumetric degradation rates in Table 8 and Fig. 6 are similar to those observed experimentally. No doubt this agreement is largely fortuitious, but nevertheless it is encouraging.

Preliminary simulations also were done to investigate the effects of liquid mixing in the bioreactor and the oxygen transfer rate. The simulation for one stirred tank was compared with a simulation for five equal-size tanks in series with the same total volume as the single tank. When substrate concentrations are very high (producing zero-order kinetics) or very low (allowing little reaction to occur), the 1-tank and 5-tank models predict essentially identical performance. However, with intermediate conditions the 5-tank model gives a higher quality effluent than does the 1-tank model, as shown in Table 9. The results in Table 9 differ from those in Table 8 principally in the value of K_La. The 10-fold larger

K_La in Table 9 allows for sufficient oxygen transfer to remove the severe oxygen limitation and permits more variation in the reaction rates.

Table 9. Effect of axial mixing and oxygen transfer on bioreactor performance (simulation). Parameter values are given in Table 7 <u>except</u> that $K_La = 1 \times 10^{-2}\ s^{-1}$ and particles are homogeneous biofilm, 500 μm radius, no coal

	1 tank		5 tanks	
	phenol (mg/L)	oxygen (mg/L)	phenol (mg/L)	oxygen (mg/L)
Influent to tank 1	100	1.0	100	1.0
Effluent from tank 1	6.1	11.1	71.4	0.676
Effluent from tank 2			43.0	0.671
Effluent from tank 3			14.8	0.733
Effluent from tank 4			3.01	10.3
Effluent from tank 5			0.44	21.2

In the future the details of the model will be expanded, better parameter values will be developed, and unsteady-state capabilities will be added to perform dynamic simulations.

5. ECONOMIC EVALUATION

An economic comparison was made between a conventional activated sludge process[9] and a conceptual fluidized bed process. The wastewater stream to be treated was 0.64 million gallons per day (mgd) containing 1450 mg/L of phenols, which represents a 50% raw wastewater stream. Process specifications for the activated sludge plant were taken from Ref. 9. Effluent from the process is to contain <2 mg/L.

The conceptual activated sludge and fluidized bed processes for treatment of coal gasification wastewater were presumed to be oxygen-blown. The size of the aeration tank for the air-blown system[9] was reduced by 50% to approximate the improvement in performance expected for an oxygen-blown system. However, better mixing is required in oxygen-blown systems to support the higher concentration of microorganisms, so the capital costs are relatively similar. No costs were charged in this analysis for oxygen because it was assumed that these costs would be comparable for the activated sludge and the fluidized bed systems.

The conceptual fluidized bed design was based on a phenols degradation rate of 20 mg phenols/(L settled bed•min). This rate is believed to be a reasonable goal based on batch kinetic studies. This reaction rate leads to a total settled bed volume of 32,200 gal, which is then increased by 50% to allow for bed expansion. The resulting net bioreactor volume is thus 48,300 gal, which may be compared with 320,000 gal for the activated sludge plant.

The high reaction rate will not be maintained at very low concentrations of phenol (e.g., down to 2 mg/L). Therefore, a "polishing" fluidized bed bioreactor of 5,000 gal was added to reduce the phenols from ~10 mg/L down to the final effluent value.

The geometry of the fluidized bed bioreactor is dependent on the effluent recycle (if any) and the maximum desirable phenols concentration in the bioreactor. An additional key requirement is a sufficient linear flow velocity to fluidize the bed, which is ~36 cm/min. The relationships among tank dimensions, recycle ratio, and phenols concentration are shown in Fig. 7. Minimal recycle is desirable to minimize pumping costs. A

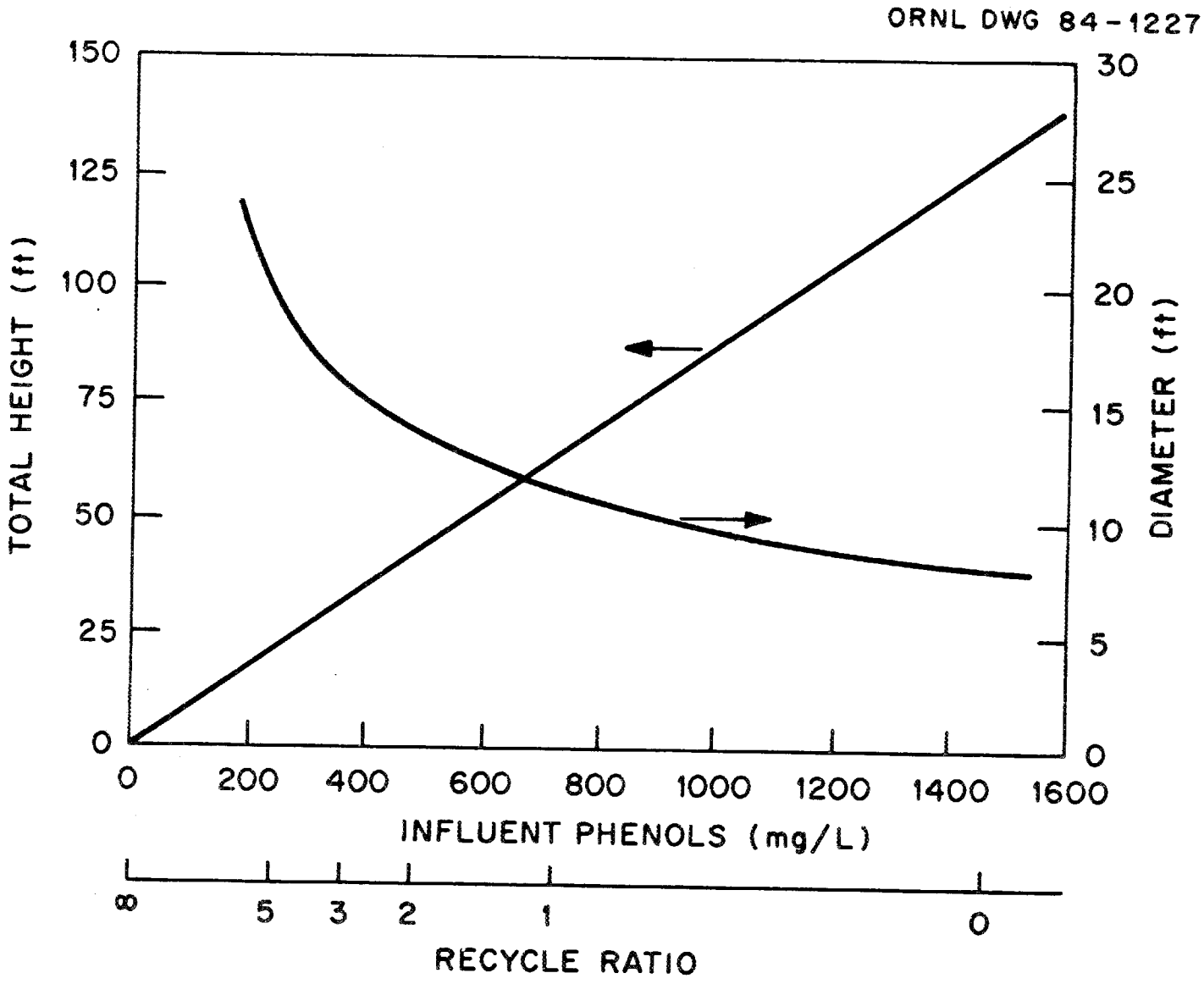

Fig. 7. Geometry of 48,300 gal fluidized-bed bioreactor to treat 0.64 mgd of wastewater containing 1450 mg/L of phenols. The phenols degradation rate is specified to be 20 mg/(L settled bed•min).

recycle ratio of unity will maintain the maximum phenols concentration below 750 mg/L; this operating condition was chosen as a reasonable design. Experimental work is underway to demonstrate bioreactor operation at this phenols concentration using 50% wastewater. A bioreactor diameter of 11 ft and a total height of 65 ft are indicated in Fig. 7. This height in one unit would require special construction for structural stability, so two main reactors in series, each ~33 ft high, were specified. The conceptual process flowsheet is shown in Fig. 8.

Sludge production in the fluidized bed process is ~0.3 to 0.4 g wet sludge/(g phenol degraded) when treating 50% wastewater (see Sect. 3.3). This is comparable to (although slightly greater than) sludge wastage in activated sludge processes. Sludge from the fluidized bed appears as TSS in the effluent, and there is negligible bed expansion due to growth of biomass and consequent carryover of coal. Coal make-up was ignored for this analysis.

The economic comparison of the two treatment processes is shown in Table 10. The fluidized bed process has only ~40% of the capital cost of activated sludge and also ~40% of the operation and maintenance costs. However, both processes are described and costed at the conceptual level, and there are considerable uncertainties in process performance and cost. These results do suggest that the fluidized bed process may have potential economic advantage if the technical performance of the process can be developed to achieve the (reasonable) design performance used in this analysis.

ORNL DWG 84-1228

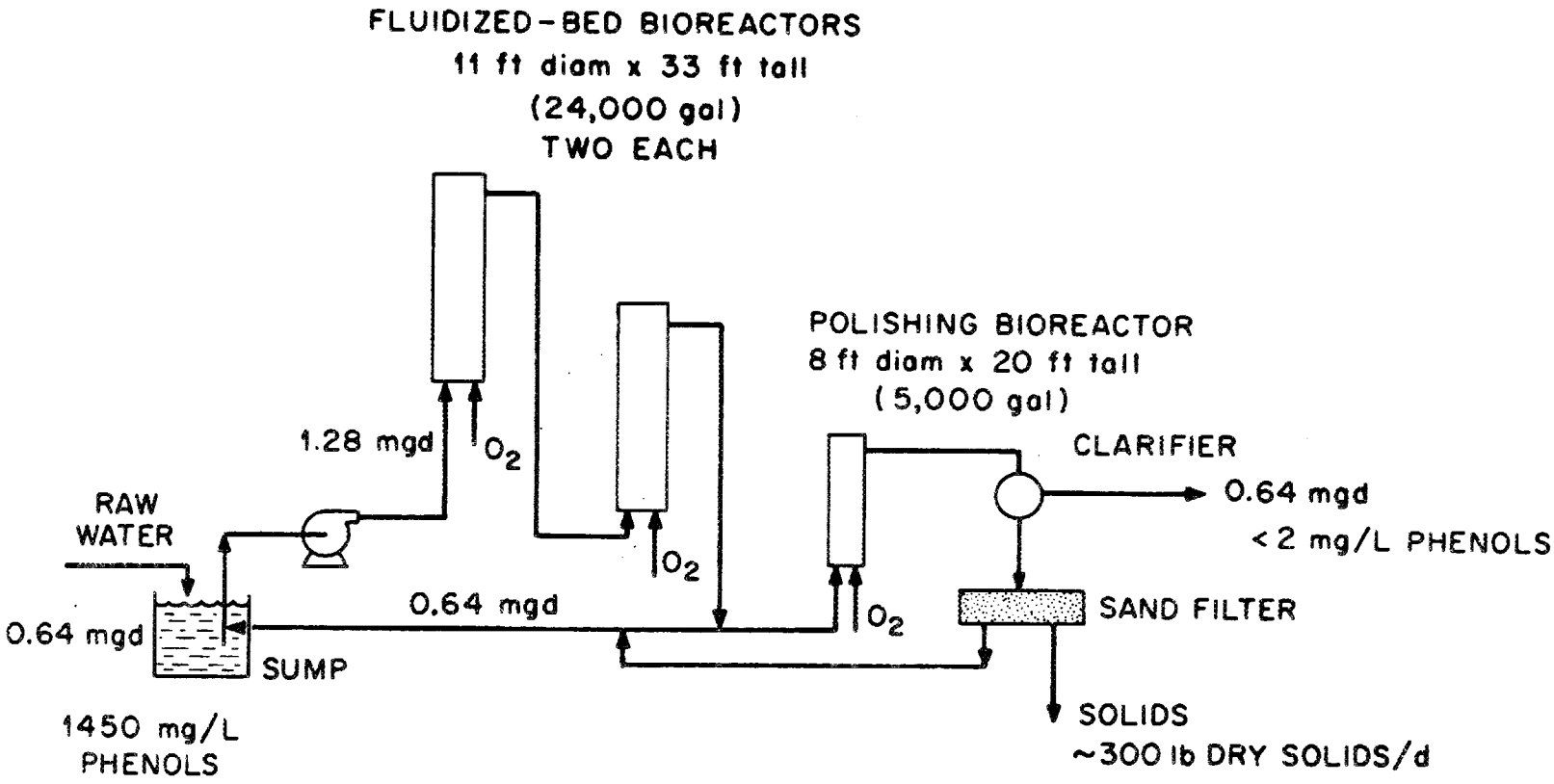

Fig. 8. Conceptual flowsheet for fluidized-bed bioreactor process.

Table 10. Comparison of fluidized bed and activated sludge (10^3 \$)

Item	Activated sludge	Fluidized bed
Capital costs (includes construction)		
Tanks	250	58
Pumps, mixing	200	100
Blowers	250	50
Clarifier	50	50
Piping	75	25
Sand bed	25	35
Engineering and contingencies (30%)	250	95
Total	1,100	414
Operation and maintenance costs [\$20/(man•h); \$0.05/kWh]		
Blowers	92	38
Pumps	43	15
Clarifier	4	4
Sand bed	2	3
Total	141	60

6. ACKNOWLEDGMENTS

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