EFFECT OF SLUDGE AGE ON THE BIOLOGICAL TREATABILITY

OF A SYNTHETIC COAL CONVERSION WASTEWATER

by

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Abstract

Aerobic biological processes appear to be the focal point of any overall scheme for treating coal conversion wastewaters since a significant number of the major constituents of these wastes are biodegradable. Accordingly, suitable design and operating criteria for biological treatment facilities need to be developed. The studies to be described in this paper have been conducted using a synthetic wastewater which was formulated to be representative, in its organic composition, of actual wastewaters from coal gasification and coal liquefaction processes. The wastewater contains twenty-eight organic compounds, inorganic nutrients, and pH-buffers.

The synthetic coal conversion wastewater was fed to several bench-scale activated sludge reactors, operated at different solids retention times (sludge ages). Effluents from the reactors were analyzed by gas chromatography and high performance liquid chromatography to assess the degree of removal of the various constituents in the raw feed, and to identify reaction products following biological treatment. Additionally, acute toxicity studies using fathead minnows were conducted to evaluate the biological impact of the treated wastewaters on aquatic life. Acute mammalian cytotoxicity and Ames mutagenicity analyses were also performed on the reactor effluents to assess their potential impact on human health. This paper presents selected results of some of these analyses.

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INTRODUCTION

In order to evaluate the biological treatability of wastewaters
generated during the course of coal gasification and coal liquefaction, a
synthetic coal conversion wastewater was formulated and fed to several
bench-scale activated sludge reactors. The composition of the synthetic
wastewater is shown in Table 1; the basis for formulating the wastewater in
this manner has been presented previously.[1,2] The synthetic wastewater
contains twenty-eight organic compounds representing the major classes of
organics identified in actual coal conversion wastewaters, and essentially
all of the specific organic compounds which have been reported to be
present at high concentrations are included. The theoretical total organic
carbon (TOC) concentration of all the components is 4,636 mg/l. The high
concentrations of pH-buffering agents were provided in order to avoid the
operational problems reported earlier due to inadequate control of pH.[1]
It is unlikely that pH control will be a problem in treating real coal
conversion wastewaters in view of the abundant amounts of carbonate
alkalinity in the real wastewaters.[3]

PROCEDURES

The synthetic wastewater was made up in 200-liter batches and stored in
a stainless steel tank. Carbon-filtered Chapel Hill tap water was used as
dilution water to which the twenty-eight constituents, shown in Table 1,
were added. This was accomplished by adding appropriate quantities from
concentrated stock solutions, prepared periodically from reagent-grade
chemicals and stored under refrigeration until use. It was found that in
order to prepare some of the concentrated solutions, an organic solvent was
required to maintain solubility of the component organics. Accordingly,
methanol was employed for this purpose. The TOC attributable to the
methanol was approximately 140 to 200 mg/l. This represents a change in
procedure from that reported in an earlier paper.[1]

A series of 25-liter biological reactors were fed the synthetic
wastewater. The wastewater was introduced into each reactor by a
variable-speed peristaltic pump. Some of the reactors were operated as
chemostats, i.e. continuous-flow, completely-mixed activated sludge systems
with no recycle of solids (biomass). For these systems, the solids
residence time (SRT) or sludge age was equal to the hydraulic retention
time (HRT). Detention times of 3, 5, 7.5, 10, 20, and 40 days were
investigated during this phase of the study. The pumps feeding the 3- and
5-day reactors were operated continuously, while the pumps feeding the
other reactors were activated by a clock which operated them for a
pre-determined period once every half-hour. The other reactors were
operated with sludge recycle, on a modified fill-and-draw basis. In these
systems, the reactors were fed continuously or intermittently as described
above, but the effluent line from the reactor was kept closed, allowing the
volume of the mixed liquor to increase. At various times, the air supply
to the reactors was turned off for a short time (usually 30 min.), allowing

Table 1.   COMPOSITION OF SYNTHETIC COAL CONVERSION WASTEWATER

COMPOUND	CONCENTRATION, mg/1
1. Phenol	2000
2. Resorcinol	1000
3. Catechol	1000
4. Acetic Acid	400
5. o-Cresol	400
6. p-Cresol	250
7. 3,4-Xylenol	250
8. 2,3-Xylenol	250
9. Pyridine	120
10. Benzoic Acid	100
11. 4-Ethylpyridine	100
12. 4-Methylcatechol	100
13. Acetophenone	50
14. 2-Indanol	50
15. Indene	50
16. Indole	50
17. 5-Methylresorcinol	50
18. 2-Naphthol	50
19. 2,3,5-Trimethylphenol	50
20. 2-Methylquinoline	40
21. 3,5-Xylenol	40
22. 3-Ethylphenol	30
23. Aniline	20
24. Hexanoic Acid	20
25. 1-Naphthol	20
26. Quinoline	10
27. Naphthalene	5
28. Anthracene	0.2

$$\text{THEORETICAL} \quad \Sigma TOC \quad == \quad 4636 \text{ mg/1}$$

NH_4Cl (1000 mg/1 as N)	3820
$MgSO_4 \cdot 7H_2O$	22.5
$CaCl_2$	27.5
$NaHCO_3$	300
FeNaEDTA	0.34
PHOSPHATE BUFFER: KH_2PO_4	852
K_2HPO_4	2176
$Na_2HPO_4 \cdot 7H_2O$	3340

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the solids (biomass) in the reactor to settle. A portion of the supernatant liquor was then withdrawn from the reactor, and the volume and solids content of the remaining mixed liquor was adjusted to provide the desired hydraulic detention times and solids residence times. Other details describing the design and operation of the reactors have been reported previously.[1,2]

It should be noted that there was a significant color change in the synthetic feed solution, from clear to amber to brown, over the several days during which it was used to feed the reactors. Attempts were made to evaluate possible changes in wastewater composition during this time through periodic measurements of TOC and chromatographic scans using high performance liquid chromatography (HPLC). No changes in TOC were detected and the chromatographic analyses established that, while some changes do occur, these changes appear to be minimal.

Routine sampling of each reactor was performed three times a week. Parameters measured included temperature, pH, dissolved oxygen, mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), and total organic carbon (TOC). Other samples were collected as desired for the measurement of biochemical oxygen demand (BOD) and chemical oxygen demand (COD), and for more detailed analysis including analyses for specific organic compounds using HPLC and GC/MS, aquatic toxicity, and assessment of potential human health effects.

RESULTS OF REACTOR PERFORMANCE

Figure 1 illustrates the failure of the biological systems to treat the full-strength synthetic wastewater. Both the chemostat and recycle systems, with solids retention times of 20 and 40 days, respectively, failed almost immediately despite attempts to gradually acclimatize the microorganisms to the wastewater. A second attempt was made by reducing the ammonia content of the synthetic feed to 250 mg/l as N in order to avoid potential ammonia toxicity, but again the reactors failed.

In order to overcome the possibility of toxicity due to other constituents of the synthetic wastewater, the synthetic feed was diluted to 25% of that shown in Table 1. Other investigators[4,5] have had to resort to similar dilution procedures in order to treat coal conversion wastewaters biologically. The resulting diluted version has a theoretical TOC of 1,159 mg/l, making it comparable to wastewaters used in biotreatability experiments being conducted by others.

Figures 2 through 6 demonstrate the performance of the 5-, 7.5-, 10-, 20-, and 40-day chemostats treating the quarter-strength synthetic wastewater. It is obvious that the gross toxicity effects observed for the full-strength wastewater have been overcome. The effluent TOC, in general, decreases with increasing retention time, reflecting improved treatment efficiency. (The influent TOC during this period of operation was measured to be 1,040 ±120 mg/l.) It should be noted that the scales for each of the figures are not the same, so that care must be exercised in comparing the results. No difficulties were encountered in controlling pH due to the high buffer intensity of the raw feed; the pH held steady at 6.9 to 7.4 compared to difficulties experienced in earlier studies.[1]
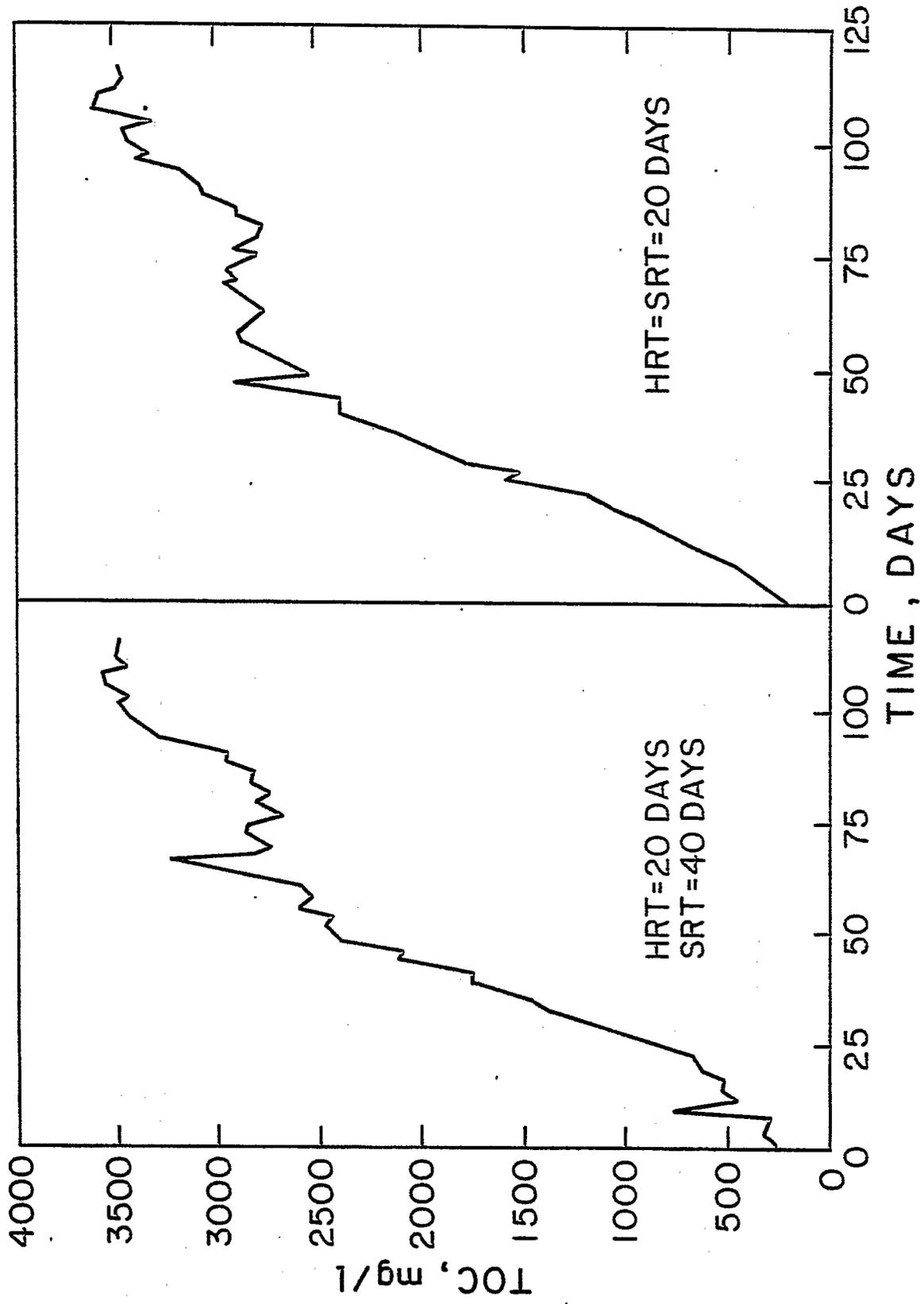
Figure 1. Failure of biological reactors to treat full-strength synthetic wastewater.
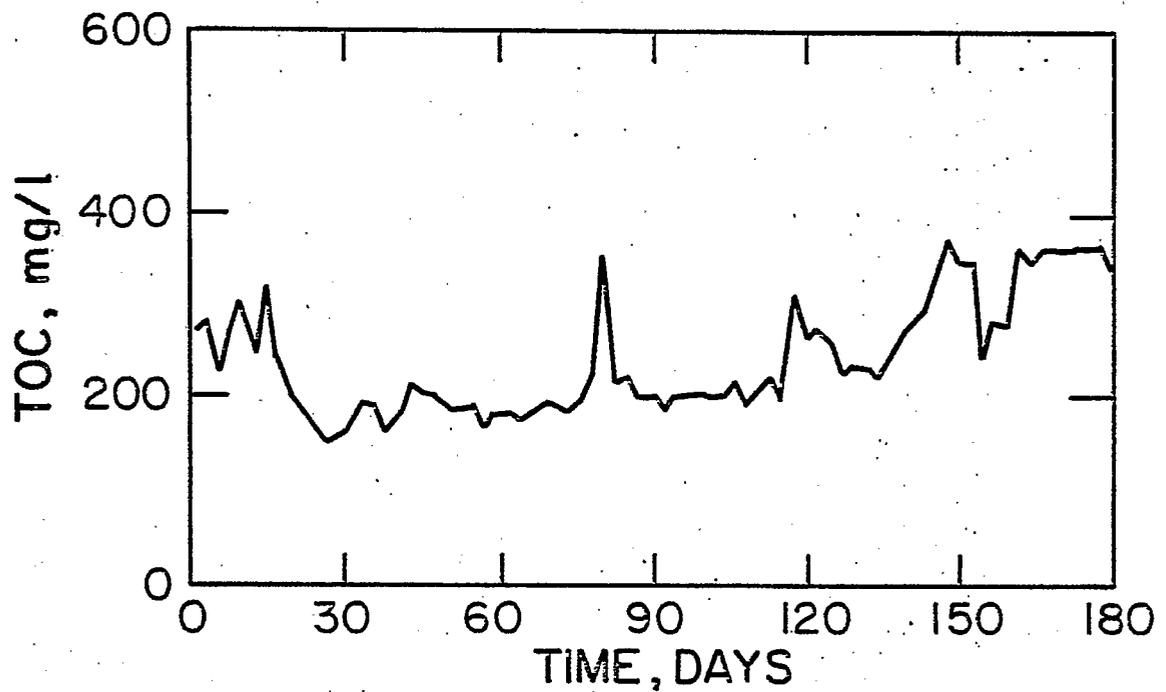
Figure 2. Effluent TOC from 5-day reactor.
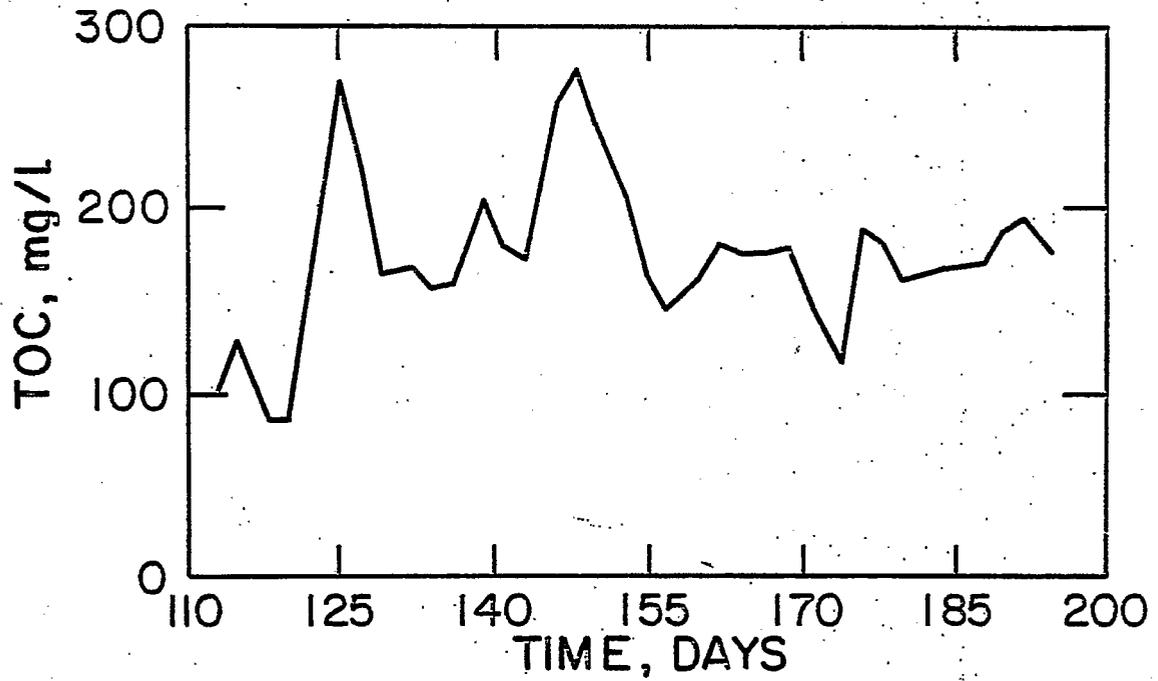
Figure 3. Effluent TOC from 7.5-day reactor.
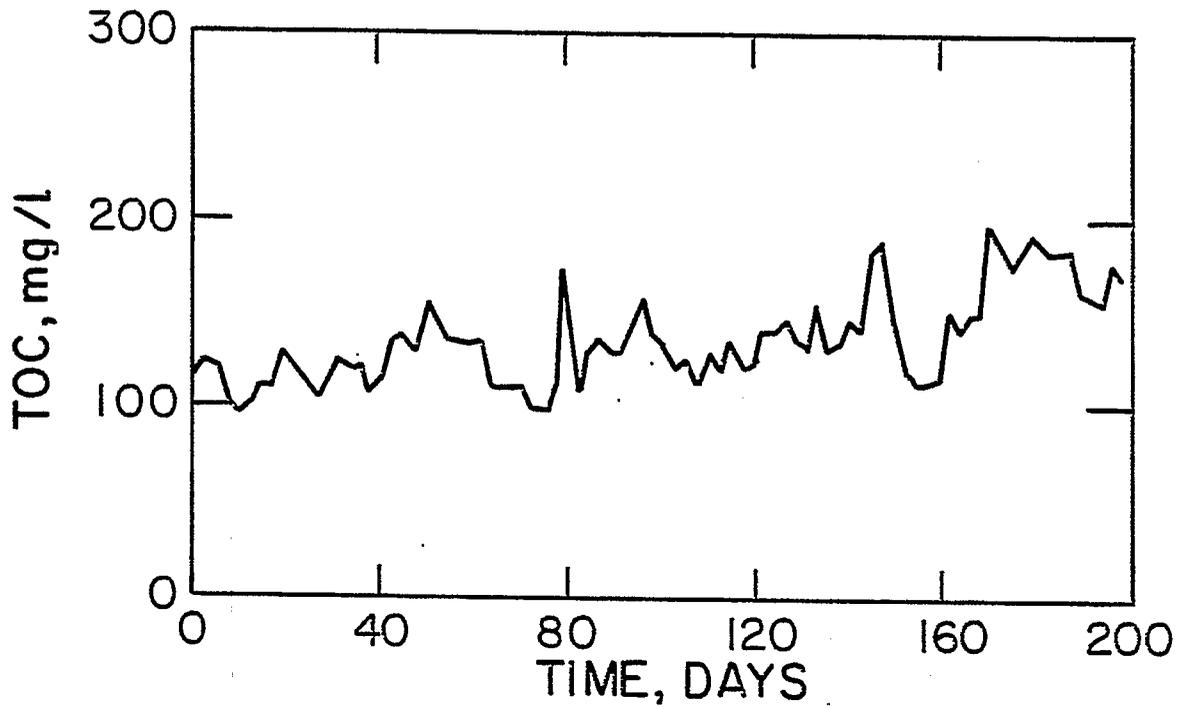
Figure 4. Effluent TOC from 10-day reactor.
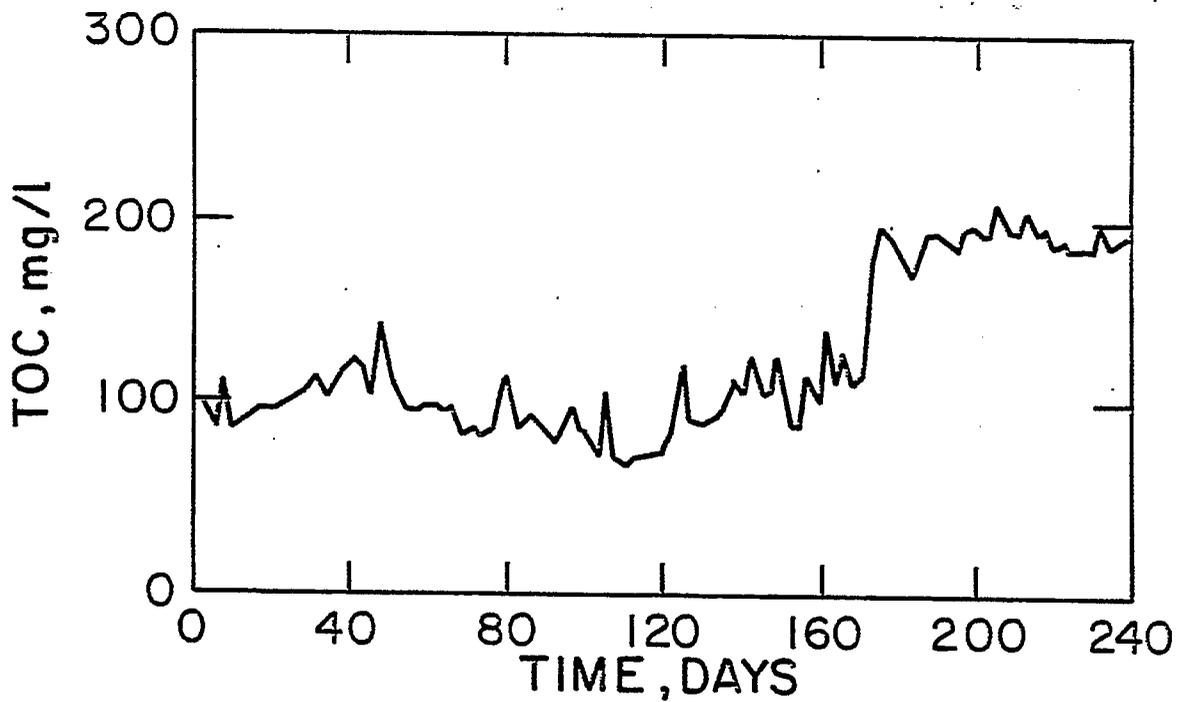
Figure 5. Effluent TOC from 20-day reactor.
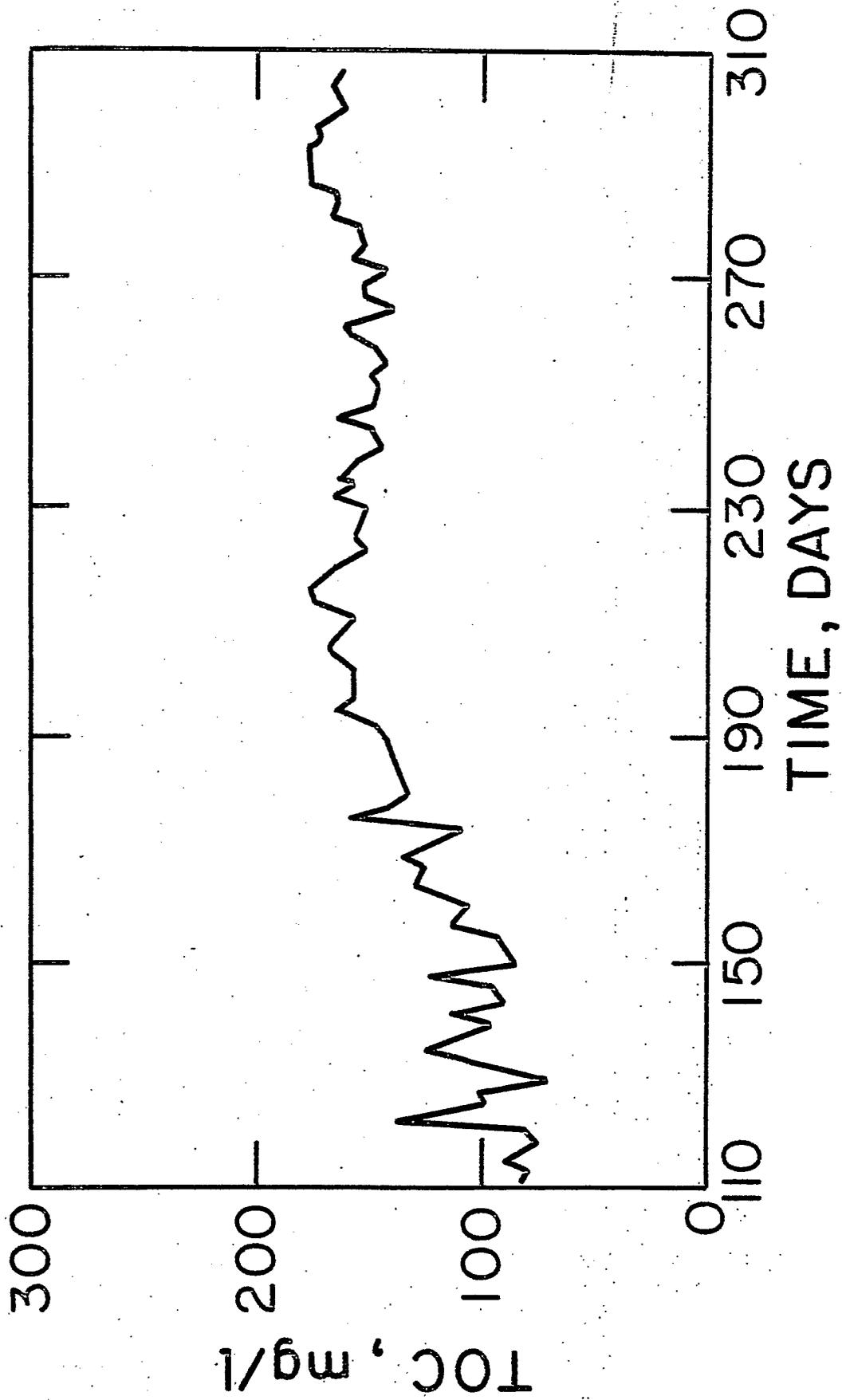
Figure 6.   Effluent TOC from 40-day reactor.

Attempts to treat the quarter-strength wastewater with a 3-day residence time failed. Immediately after feeding of the 3-day reactor commenced, the effluent TOC began to rise and within a few days approached the influent TOC. This pattern was observed a second time, implying that the wastewater cannot be treated with such a low solids residence time.

A closer look at the TOC data in Figures 2 through 6 shows that, in general, reasonably steady performance was maintained for about 130 to 170 days, after which the effluent TOC increased somewhat. In fact, there appears to be a slight upward trend in the TOC data over the entire period of observation. Accordingly, it may be inappropriate to speak of steady-state behavior, despite the rather consistent performance of the reactors over this long observation period. Some of the observed fluctuations in TOC may be attributed to mechanical difficulties which were encountered at various times during this period of reactor operation. These included failures of the air compressor, feed pumps, and timing devices leading to occasional losses in the air supply and to under- and overfeeding of the reactors, respectively. Additionally, a significant increase in the ambient temperature began at about the 160th day of operation and this may have severely impacted the performance of the reactors.

Some of these TOC fluctuations ultimately became rather extreme, as shown in Figure 7, resulting in failure of the 5-, 7.5-, and 10-day reactors despite up to six months of relatively stable performance. The variability in reactor behavior is clearly illustrated in Figure 8 which depicts the performance of the 20-day chemostat for more than one year of operation. There appears to be a six-month metastable period during which the effluent TOC averaged about 100 mg/1, followed by another three-month metastable period during which the effluent TOC averaged about 175 mg/1. The last three-month period of operation is marked by wide fluctuations in performance. These results suggest that, while dilution of the wastewater to 25% of full-strength overcomes the gross toxicity problem associated with the raw wastewater, treatment of the diluted wastewater by a chemostat system, such as an aerated lagoon, even at very long detention times, provides variable performance and is inherently an unstable system.

Accordingly, additional studies were carried out in reactors involving sludge recycle. Figure 9 shows the results of three reactors operated at a solids residence time of 20 days, with hydraulic retention times of 2, 5, and 10 days. Figure 10 shows performance data covering a twelve-month period for a second reactor with a 10-day hydraulic retention time and a 20-day sludge age. The extent of treatment, as measured by the effluent TOC for each reactor, appears to be approximately the same, with effluent TOCs averaging 200-225 mg/1 (slightly higher and more variable for the 2-day HRT reactor). Comparing these effluent values to the influent TOC of the quarter-strength synthetic feed, the reactors provided an 80-83% reduction in TOC. The major "bumps" observed in the 10-day reactors, at 35 days (Figure 9) and 225 days (Figure 10) were caused by mechanical problems; the reactors were apparently able to overcome these operational malfunctions and return to a steady level of performance.

The conclusions reached from the data in Figures 9 and 10 are that a sludge age (SRT) of 20 days results in the same level of treatment,
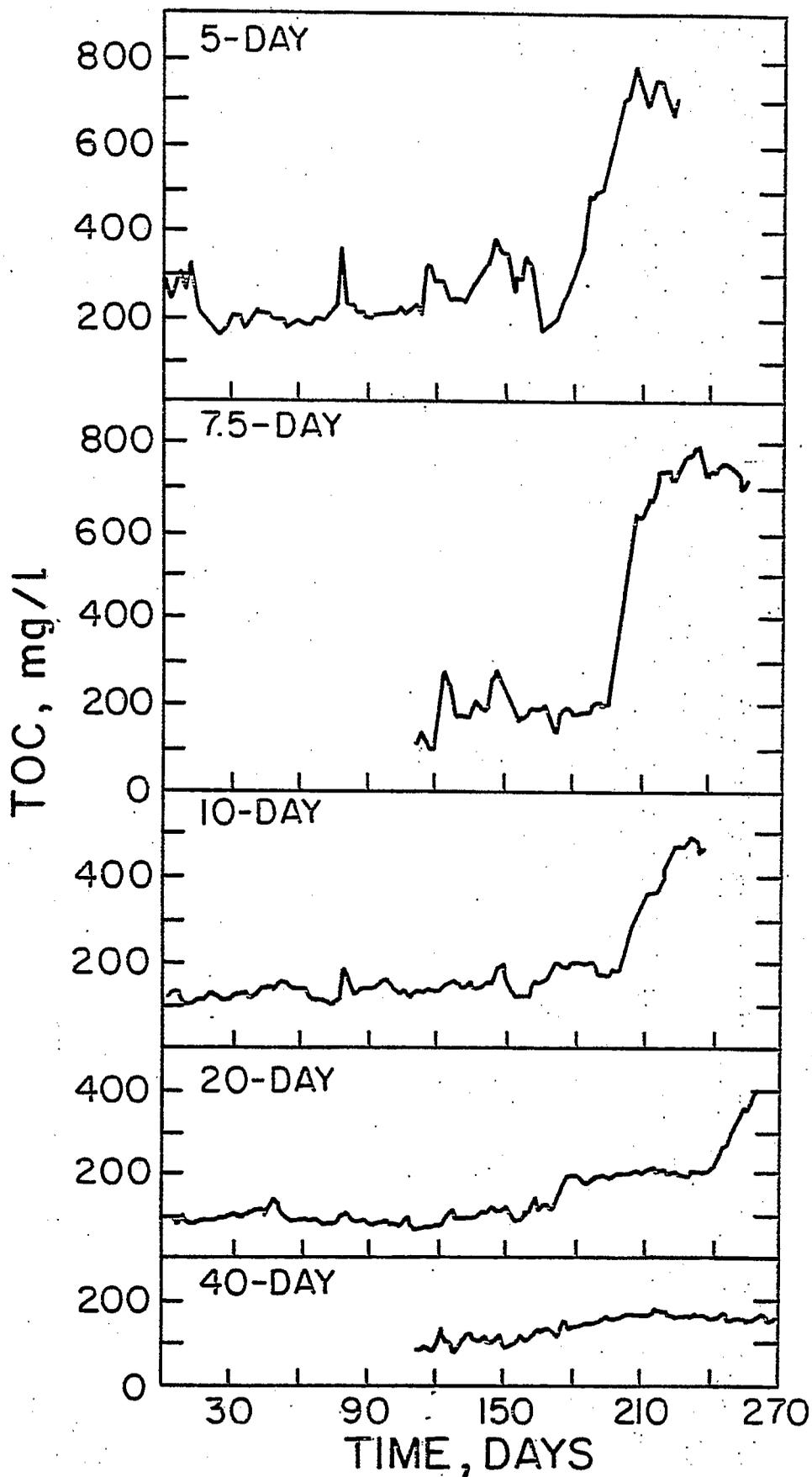
Figure 7. Summary of performance of chemostats treating 25% synthetic wastewater at different detention times.
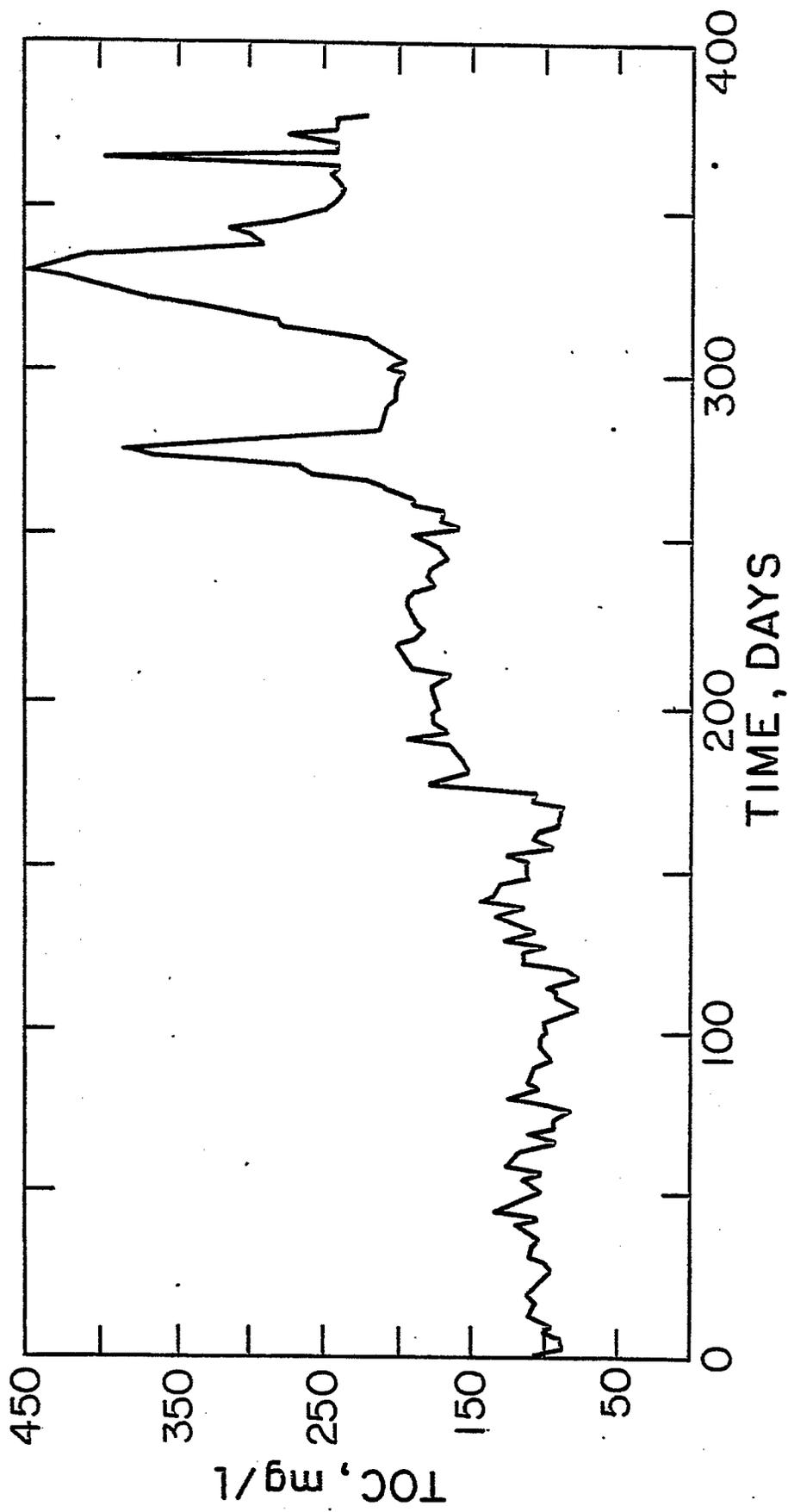
Figure 8. Long-term performance of 20-day chemostat treating 25% synthetic wastewater.
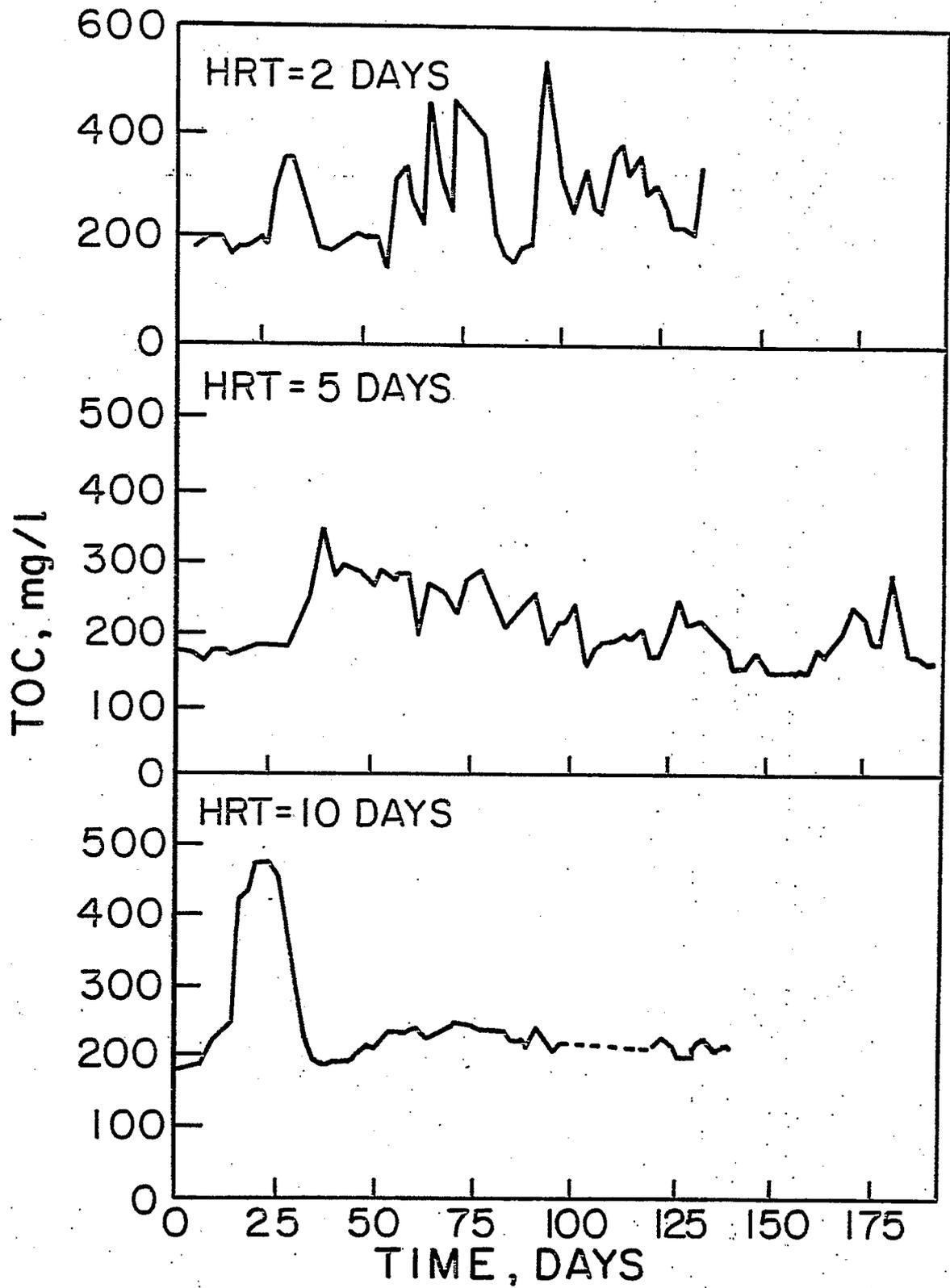
Figure 9. Summary of performance of recycle reactors treating 25% synthetic wastewater with 20-day sludge age and different hydraulic retention times.
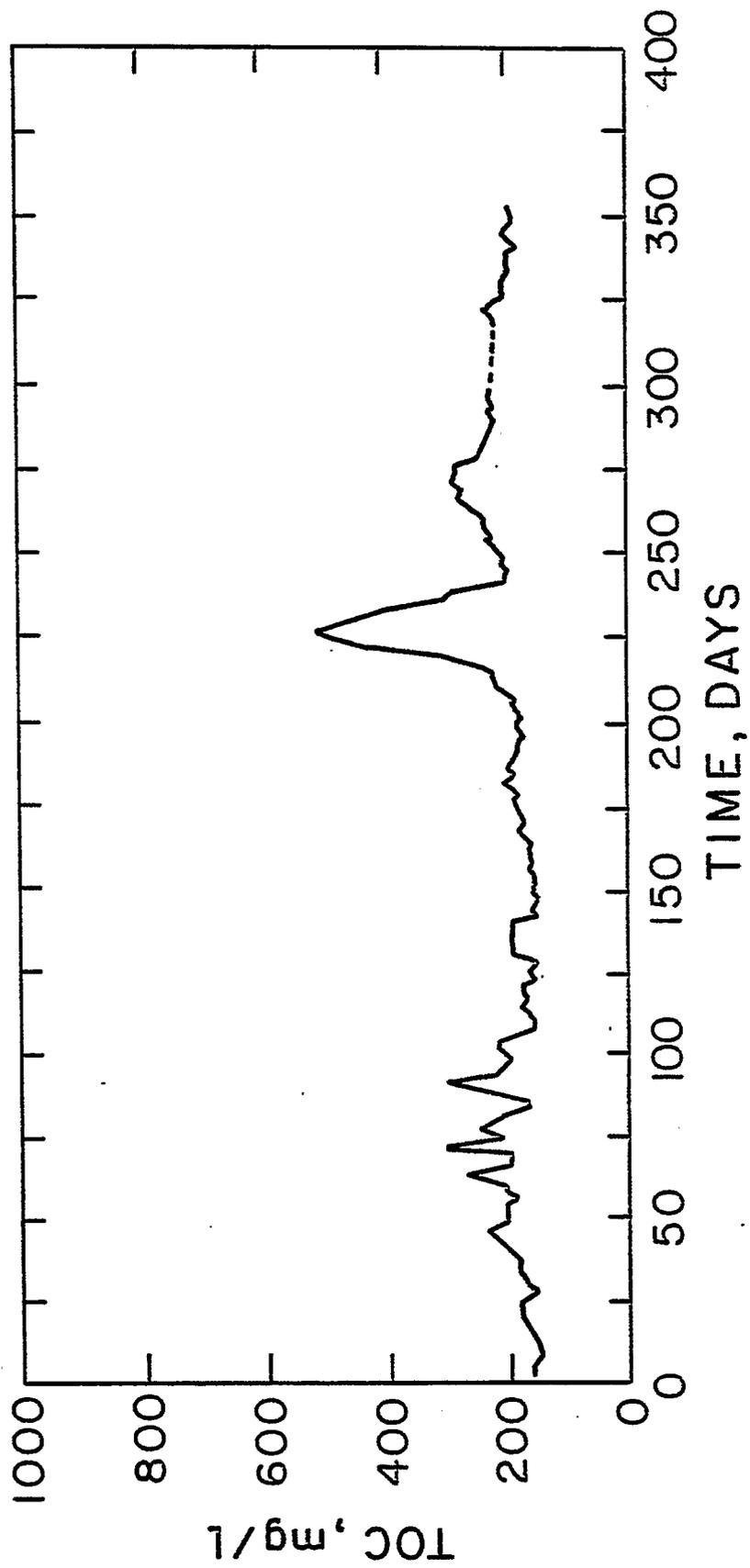
Figure 10. Long-term performance of recycle reactor with 20-day sludge age and 10-day hydraulic retention time.

regardless of the hydraulic residence time, but that control of the system is more difficult at lower HRTs, resulting in more variable performance. The long-term results shown in Figure 10 for the recycle system compared to the long-term results shown in Figure 8 for the 20-day chemostat demonstrates clearly the greater stability of the recycle system. Hence, more data on reactor performance under different conditions of operation (SRT and HRT) need to be developed using recycle systems in order to establish suitable design criteria for treating coal conversion wastewaters.

However, before this objective can be considered further, the question of toxicity of the wastewater constituents, associated with the failure of the reactors treating full-strength synthetic wastewater (see Figures 1 and 2), needs to be addressed. It should be noted that the full-strength reactors were started up using mixed liquor from the quarter-strength reactors, and gradually increasing the feed concentration from 25% to 100% strength. Accordingly, the microorganisms comprising the mixed liquor in these reactors should have been acclimatized to the wastewater constituents, at least at the lower dilution rate. Nevertheless, shortly after the wastewater feed reached full-strength, failure resulted, reflecting the accumulation of constituents in the reactor which were toxic to the microorganisms. As indicated previously, parallel results for the full-strength synthetic wastewater with the ammonia concentration reduced to 25% strength indicated that ammonia alone was not the causative agent in bringing about failure of the full-strength reactors.

In order to begin addressing the toxicity question in a systematic manner, a full-strength phenolics feed was formulated, the composition of which is shown in Table 2. This phenolics feed contains only the major phenolic constituents of the 28-component synthetic wastewater (compare Tables 1 and 2). The theoretical TOC of the phenolics feed is 3739 mg/l; hence, the seven constituents of the phenolics feed comprise 80.7% of the TOC in the 28-component synthetic wastewater (TOC = 4636 mg/l). It should be noted that the full-strength phenolics feed contains ammonia at a concentration 25% of that in the synthetic wastewater.

The full-strength phenolics wastewater was fed to a chemostat with a solids residence time of 20 days and to a recycle reactor with a solids residence time of 40 days and a hydraulic retention time of 20 days. The results are shown in Figure 11. Major fluctuations in the performance of each of the reactors are apparent. Most of these fluctuations appear to be related to documented mechanical problems associated with the operation of the feed system and the air supply. Again, the recycle system behaves in a more stable manner than the chemostat. Although some of the fluctuations were rather extreme, the reactors have recovered and have been treating the phenolic wastewater for more than four months, providing effluent TOC concentrations as low as 200-250 mg/l. Comparing this output to the TOC of the raw feed, this amounts to a 94-95% reduction in TOC. The concentration of total phenols in the treated water, as measured by wet chemical analysis on four occasions during this period, averaged 0.22 mg/l.

These results indicate that the full-strength phenolics wastewater, with a phenol concentration of 2000 mg/l, is biologically treatable. Hence, the toxicity problems associated with the 28-component full-strength

Table 2.   CHARACTERISTICS OF PHENOLICS FEED

CHEMICAL		CONCENTRATION, mg/l
1.	Phenol	2000
2.	Resorcinol	1000
3.	Catechol	1000
4.	o-Cresol	400
5.	p-Cresol	250
6.	3,4-Xylenol	250
7.	2,3-Xylenol	250
	Theoretical TOC ===	3739 mg/l as C
	NH_4Cl (250 mg/l as N)	955
	$MgSO_4 \cdot 7H_2O$	22.5
	$CaCl_2$	27.5
	$NaHCO_3$	300
	FeNaEDTA	0.34
	PHOSPHATE BUFFER:	
	KH_2PO_4	852
	K_2HPO_4	2176
	$Na_2HPO_4 \cdot 7H_2O$	3340

Figure 11. Biological treatability of full-strength phenolic wastewater.

synthetic wastewater must be due to one of the other minor constituents in the synthetic feed. Based upon parallel biodegradability studies of model compounds reported elsewhere,[6] leading candidates responsible for the toxicity problems include the pyridine and quinoline species, indole, acetophenone, and aniline. This toxicity question is being explored further by adding various of these additional constituents to the full-strength phenolics mixture, and feeding this "spiked" phenolic wastewaters to different biological reactors containing acclimatized mixed liquor from the reactors represented by Figure 11.

RESULTS OF DETAILED CHEMICAL ANALYSES AND BIOASSAYS OF REACTOR EFFLUENTS

Treated effluent from the chemostats treating the quarter-strength synthetic wastewater were collected at various times during the course of their operations and analyzed for residual BOD, COD, and phenols using standard methods of analysis.[7,8] Additionally, samples were subjected to specific organic analysis by high performance liquid chromatography (HPLC) and gas chromatography/mass spectrometry (GC/MS). Aquatic bioassays involving algae, fish, and Daphnia, and mammalian cytotoxicity and Ames mutagenicity analyses were also conducted as a means of assessing the aquatic and health impacts, respectively, of the biologically-treated wastewater. Selected results from these detailed analyses are presented here. The results need to be interpreted with some care in view of the variability in reactor performance discussed above.

Wet Chemical Analyses

Table 3 shows the BOD, COD, and concentration of phenols in the effluent from the biological reactors for the days indicated. These values, compared to the measured influent concentrations, reflect the excellent degrees of treatment which were achieved, especially during the times when the reactors were performing in a reasonably stable manner. It should be noted that the concentration of phenols was measured using the 4-aminoantipyrine procedure[7,8] which responds only to certain of the phenolic constituents. It is apparent from Table 3 that BOD and phenols are virtually completely removed by the reactors having a solids retention time of at least 20 days, while COD and TOC removal does not improve to any great extent if the SRT is increased beyond 7.5 days. There appears to be approximately 100-160 mg/l of TOC with a COD of about 350-450 mg/l which is non-biodegradable in nature.

HPLC Analysis

Table 4 presents the results of HPLC analyses of the reactor effluents on the days indicated. Fresh samples of the reactor effluent were collected, filtered through 0.7 um glass fiber filters, and injected directly into the HPLC. Separation of the wastewater components in the samples was achieved using a 60-minute water/acetonitrile solvent gradient on a Waters uBondapak C_{18} analytical column. The eluted compounds were detected by both UV absorbance at 280 nm and fluorescence at 275 nm excitation and 310 nm emission wavelengths. Quantitation of the individual phenolic compounds shown in Table 4 was accomplished from the fluorescence measurements using effluent samples spiked with various quantities of the constituents in question. In some cases, the concentrations in the table

Table 3.   SUMMARY OF WET CHEMICAL DATA ILLUSTRATING
REACTOR PERFORMANCE. (All values in mg/l.)

	DAY	BOD	COD	PHENOLS
Raw Feed		1,780	2,830	575
5-day Reactor	126	112	670	—
	131	—	—	54
	133	126	670	—
	140	235	850	—
	147	485	1,160	—
	154	430	1,080	94
	161	360	825	—
	168	150	1,025	—
	169	—	—	33
	175	186	940	—
7.5-day Reactor	164	—	—	0.70
	168	10	570	—
	175	3	435	—
	185	6	445	—
	192	10	465	—
	194	—	—	1.16
10-day Reactor	126	5	480	—
	133	5	430	—
	140	5	460	—
	154	8	460	—
	161	9	470	0.62
	168	6	410	—
	175	6	460	—
	185	8	380	—
	192	6	465	—
	198	11	400	3.3
20-day Reactor	126	3	310	—
	133	2	370	0.43
	136	— —	—	0.35
	140	4	355	—
	147	— 2	320	—
	150	— 2	—	0.35
	154	2	360	—
	157	—	∆	0.29
	161	3	350	—
	168	2	400	—
	175	3	420	—
	185	2	415	—
	192	1	385	—

Table 3.   (continued)

	196	–	–	0.19
	198	3	420	–
	203	–	–	–
	204	–	–	0.18
	210	3	450	–
	217	–	–	–
	218	–	–	0.22
	224	–	460	–
	226	3	–	–
	231	4	465	–
	233	–	–	0.25
40-day Reactor	193	–	340	–
	198	1	345	–
	205		–	0.11
	210	2	420	–
	212	–	–	0.18
	219	–	–	0.12
	224	–	430	–
	226	1	–	0.15
	231	–	–	–
	240	–	–	0.10
	252	1	375	–
	254	–	–	0.11
	259	1	–	–
	273	3	–	–
	282	–	–	0.09

Table 4.   CONCENTRATIONS OF MAJOR PHENOLIC COMPOUNDS IN REACTOR EFFLUENTS (mg/l).

COMPONENT	RAW FEED	5-DAY REACTOR DAY 163	5-DAY REACTOR DAY 175	7.5-DAY REACTOR DAY 188	10-DAY REACTOR DAY 176	20-DAY REACTOR DAY 176	20-DAY REACTOR DAY 185	40-DAY REACTOR DAY 303
PHENOL	500	0.9	0.6	<0.2	<0.4	<0.2	<0.1	<0.13
O-CRESOL	100							
P-CRESOL	62.5							
	162.5	22.2	30.2	0.2	0.8	<0.005	<0.02	0.036
3,4-XYLENOL	62.5							
2,3-XYLENOL	62.5							
3,5-XYLENOL	10							
	135	33.6	31.4	1.0	2.5	1.4	<0.01	0.007
2,3,5-TRIMETHYLPHENOL	12.5	9.0	7.0	0.6	1.3	<0.08	<0.02	<0.004
CATECHOL	250	<0.5	<0.5	<0.2	<0.5	<0.2	<0.1	<0.02
RESORCINOL	250	<0.5	<0.5	<0.2	<0.5	<0.2	<0.1	<0.02
TOC	1159	362	362	182	182	105	155	165

are shown as being less than a certain value; this value represents the detection limit of the fluorescence detector for that compound at the sensitivity used for that sample.

The HPLC results show that the removal of the phenolics increases with increased detention time and that phenol, resorcinol, and catechol are almost completely removed by the 5-day reactor. The cresols are completely removed (to concentrations less than 1 mg/l) within 7.5 to 10 days while a retention time of 20 days is required to reduce the concentrations of the xylenols and trimethylphenol below 1 mg/l. (It should be noted that the HPLC fluorescence procedure utilized is not capable of distinguishing among the various isomers of a given compound.) The HPLC results are in accordance with the phenol results reported in Table 3 in which the wet chemical aminoantipyrine procedure was employed.

The results in Table 4 are significant from the standpoint of reactor performance in that they show that the major phenolic constituents of the synthetic wastewater are removed by the biological reactors, and that the residual TOC in the effluent from the reactors is non-phenolic in nature. Parallel HPLC analysis using the UV detector indicates that a major portion of the residual TOC is comprised of highly polar compounds, e.g. aliphatic acids, presumably cellular metabolites arising from the biological degradation of the phenolics.

Acute Fish Toxicity

Samples of reactor effluent were collected continuously, over a 24-hour period, from the reactor overflow ports, and centrifuged and filtered to remove suspended solids. The samples were then frozen at -20°C. The low flow rates for some of the reactors, particularly those with long detention times, necessitated daily collection of the effluent over a relatively long time period until enough of the effluent could be collected to perform the bioassay. After a sufficient quantity of sample was available, the frozen samples were thawed and aliquots of the effluent were diluted with dechlorinated tap water to the desired concentration. Fathead minnows (Pimephales promelas) were used for the fish bioassay. Ten liters of each dilution were placed in a series of 5-gallon pickle jars, and 15 fish were added to each jar. Each test concentration was done in duplicate, so that a total of 30 fish were exposed to each concentration.

Figure 12 is a plot showing the percent mortality of the fish exposed for 96 hours to various dilutions of the raw feed and the various reactor effluents. The estimated 96-hour LC50 values, i.e. the lethal concentrations of the various wastewater samples causing death of 50% of the fish after 96 hours of exposure, are 1.1%, 6.6%, 33%, and 51%, respectively, for the quarter-strength synthetic feed and the 5-, 10-, and 20-day reactor effluent samples. As expected, toxicity decreases as the extent of the biological treatment increases.

Table 5 is a summary showing the characteristics of the wastewaters tested along with the LC50 values calculated from the results in Figure 12. The fact that the TOC concentration of the sample from the 10-day reactor is lower than that of the 20-day reactor is attributed to the composite nature of the samples. The samples were collected over a
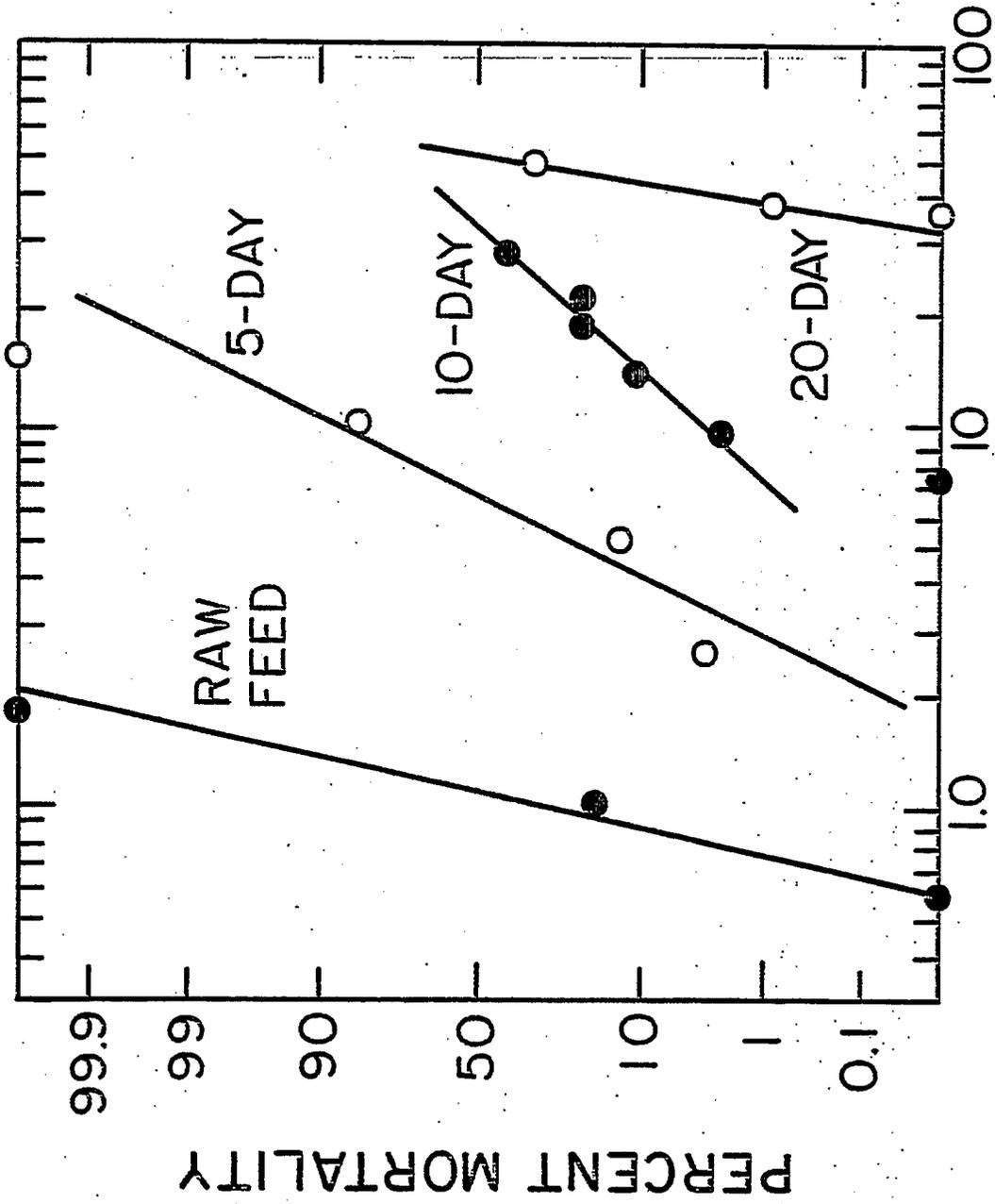
Figure 12. Acute toxicity of raw and treated synthetic wastewater to fathead minnows.

Table 5.   RESULTS OF ACUTE TOXICITY TESTS

USING FATHEAD MINNOWS

SAMPLE	TIME OF COLLECTION	TOC, mg/l	PHENOLS, mg/l	96-HOUR LC50, %	TOC AT LC50, mg/l	PHENOLS AT LC50, mg/l
RAW FEED	-----	1150	516	1.1	12.7	5.7
5-DAY REACTOR	Day 149-165	328	94	6.6	21.7	6.2
10-DAY REACTOR	Day 149-171	150	0.62	33	49.5	0.2
20-DAY REACTOR	Day 149-219	189	0.22	51	96.4	0.11

relatively long period of time, as noted, during which some degree of
reactor instability was observed (see above discussion). The concentration
of phenols, however, as measured by the wet chemical method, is in
accordance with expectations, i.e. lower concentrations with increasing
reactor detention times. The aquatic toxicity of the reactor effluent
seems to be more closely related to the concentration of residual phenols
and to the detention time of the reactors than to the residual TOC
concentration; the LC50 for the sample from the 20-day reactor is 51%
compared to 33% for the 10-day reactor sample despite the fact that the TOC
of the latter is lower. Hence, the concentration of residual TOC, by
itself, is not a satisfactory indicator of the aquatic toxicity of the
treated wastewater. More information as to the composition of the various
treated samples needs to be known.

Table 5 also shows the concentration of TOC and phenols at the percent
dilution corresponding to the LC50s for each of the samples. It is
apparent that the constituents comprising the residual TOC become
correspondingly less toxic as the degree of treatment, as indicated by the
detention time of the reactor, increases. Furthermore, a comparison of the
last column in Table 5 with acute fish toxicity results for phenol alone
(see Figure 13 where the 96-hour LC50 for phenol is shown to be 28 mg/l)
indicates that the resulting toxicity of each of the composite samples,
including the raw feed, cannot be attributed solely to phenol. The
residual concentration of phenols at the LC50 dilution is, in each case,
significantly less than the 28 mg/l LC50 for phenol. Hence, the aquatic
toxicity of the treated samples must be due to constituents other than
phenol, or to synergistic effects involving phenol and other constituents.

Mammalian Cytotoxicity

In order to evaluate the effectiveness of biological treatment in
alleviating potential human health effects associated with coal conversion
wastewaters, a clonal toxicity assay employing Chinese Hamster Ovary (CHO)
cells[9] was used to compare the relative acute toxicities of the effluents
from the biological reactors and the quarter-strength raw synthetic
wastewaters. Effluent samples from the reactors were collected,
centrifuged, aliquoted in small bottles, and stored at -80°C. Individual
aliquots of the frozen samples were thawed immediately prior to use,
filtered through a 0.2 um Nuclepore polycarbonate filter, and diluted with
various amounts of deionized water and growth medium to obtain the desired
concentrations.

Two hundred CHO cells were plated per tissue culture dish and allowed
to incubate and attach for 3 hours in a normal cell growth medium. The
medium was then removed and the appropriate dilution of the wastewater was
added. After an exposure period of 20 hours, the test solution was
removed. The cells were washed and reincubated in normal growth medium for
7 days. At the end of this incubation period, the colonies were fixed,
stained, and counted.

Figure 14 is a plot of percent survival of the CHO cells for various
dilutions of the different reactor effluents tested and the
quarter-strength synthetic raw feed. The source of the different samples
and the day of collection are shown in Table 6. Again, it should be noted
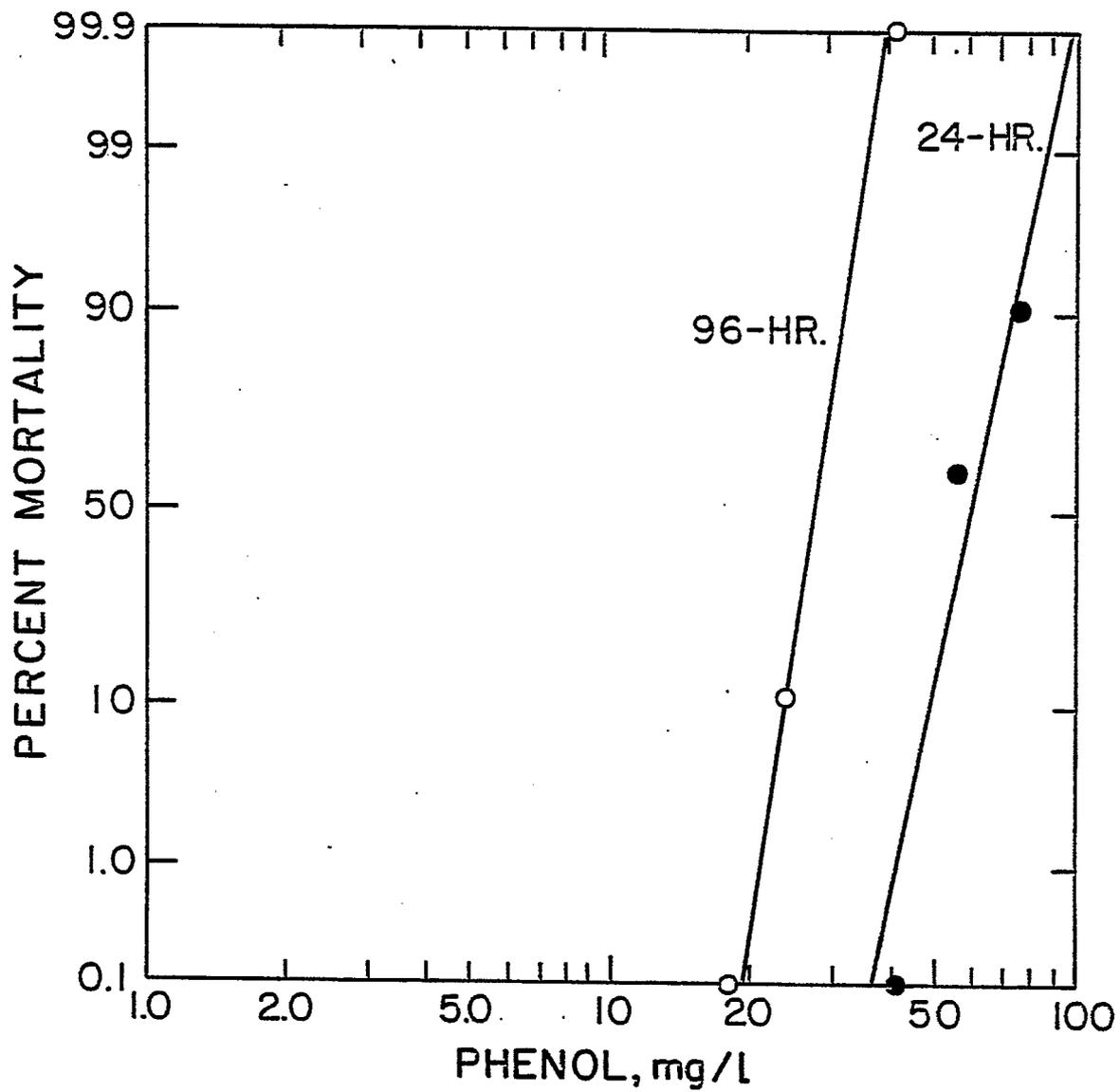
Figure 13. Acute toxicity of phenol to fathead minnows.
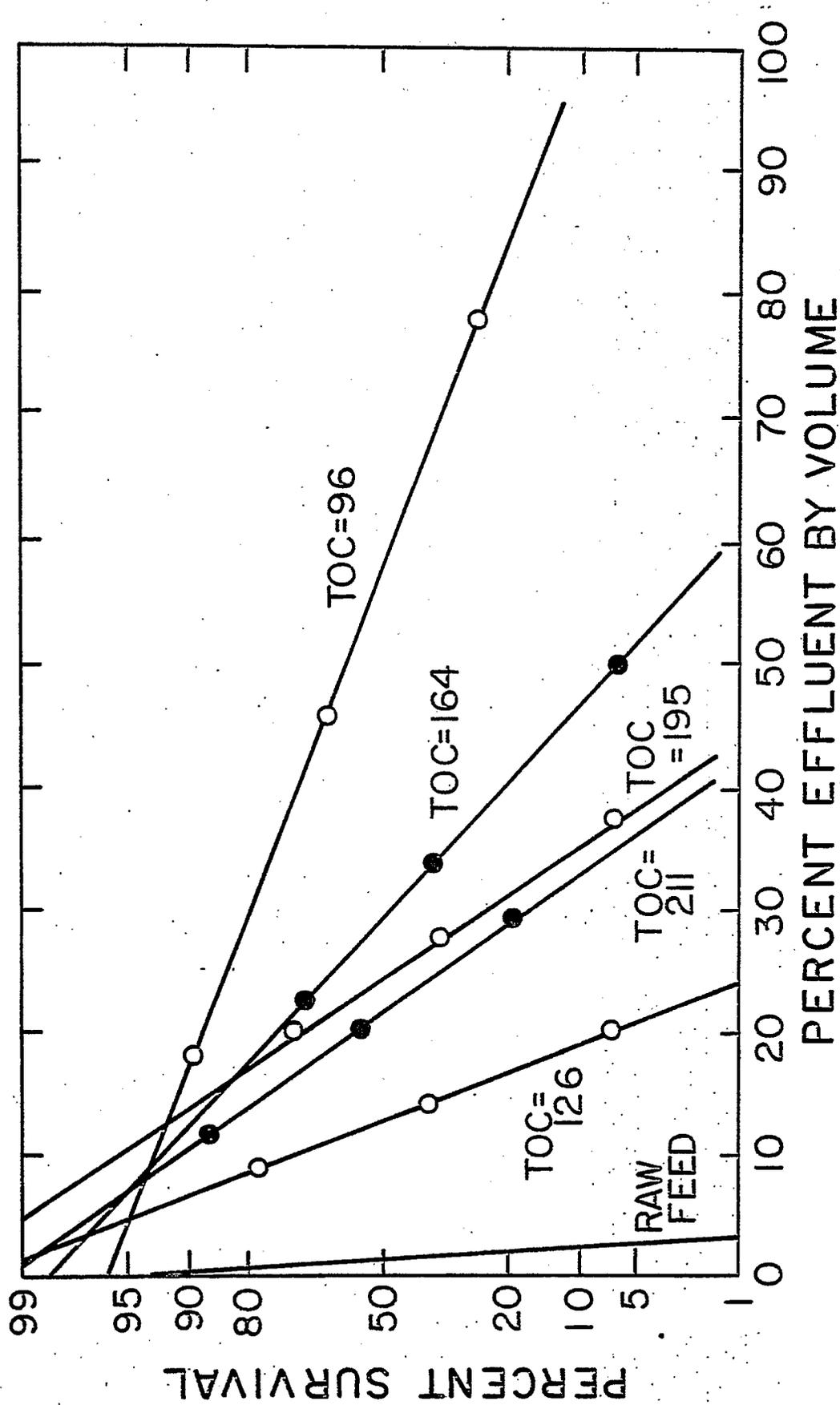
Figure 14. Cytotoxicity of raw and treated synthetic wastewater to Chinese hamster ovary cells.

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Table 6.   RESULTS OF CHO ACUTE MAMMALIAN CYTOTOXICITY TESTS

SAMPLE	DAY OF COLLECTION	TOC, mg/l	LC50, %..
Raw Feed	----	850	1.2
5-day Reactor	114	211	21.6
10-day Reactor	114	126	12.6
20-day Reactor	114	96	58.1
20-day Reactor	219	195	24.5
40-day Reactor	314	164	29.1

that the variability in reactor performance results in TOC values which are not entirely consistent with each other. For example, on two different dates, the effluent TOC concentrations from the 20-day reactor were 96 and 195 mg/l, resulting in very different cytotoxic responses. Figure 14 shows that, with the exception of the 10-day reactor and its corresponding TOC concentration of 126 mg/l, CHO toxicity decreases as effluent TOC decreases. The concentrations of each sample resulting in 50% lethality of the CHO cells, i.e. the LC50 values, are shown in Table 6. In contrast to the fish bioassay results, TOC appears to be a reasonably good indicator (with the exception of the 10-day reactor sample) of mammalian cytotoxicity. The anomalous behavior of the 10-day reactor cannot be explained.

Ames Mutagenicity

The _Salmonella typhimurium_ mammalian-microsomal system was used to analyze the potential mutagenic activity of the raw and treated synthetic wastewater. All five Ames tester strains recommended for screening purposes were employed in this investigation. Two of the strains (TA100 and 1535) are capable of detecting mutagens which cause base-pair substitutions, while the other strains (TA98, 1537, and 1538) have the ability to detect frameshift mutagens. Standard experimental procedures for the plate incorporation assay, as outlined by Ames[10], were followed with one exception: due to the low concentrations of many of the chemicals present in the wastewater, 0.5-2.0 ml sample volumes were assayed instead of the standard 0.1 ml of sample per plate. The volume of the top agar overlay containing the various sample volumes was kept constant at 5.0 ml.

One-liter samples of reactor effluent were collected, centrifuged, aliquoted into smaller volumes, and stored at $-80^{\circ}C$. Immediately prior to use, the wastewater was thawed and filtered through a 0.2 um Nuclepore polycarbonate filter. Each of the effluent samples as well as the raw feed was first examined to determine an acceptable range of sample volumes which would not be toxic to the bacterial strains and therefore would not preclude the mutagenicity testing.

The experimental scheme for determining the mutagenicity of the samples involved the assay of all the samples using one strain at a time, both with and without metabolic activation using an S-9 preparation of Arochlor 1254-induced rat liver microsomes. Positive control mutagens dissolved in dimethyl sulfoxide (DMSO), DMSO (solvent control), and an aqueous control were always assayed along with the wastewater samples. Mutagenicity studies were initiated with strain TA98 which has previously been reported to exhibit significantly increased mutation rates in the presence of the products of coal conversion processes.[11]

Table 7 demonstrates some of the results of the mutagenicity testing with strain TA98. A low level of direct-acting mutagenicity was found in the raw synthetic wastewater when assayed using 1.0 ml sample volumes per plate. Such activity was not observed in any of the reactor effluent samples, even when tested at 2.0 ml sample volumes. (The 5-, 10-, and 20-day reactor effluent samples were collected on Day 114 while the 40-day reactor effluent sample was taken on Day 314.)

Table 7.   DIRECT-ACTING MUTAGENICITY OF RAW AND TREATED

WASTEWATER SAMPLES WITH STRAIN TA98

	REVERTANTS/PLATE			MEAN	REVERSION RATIO*
Aqueous Control	31	26	32	30	(1)
1 ml Raw Feed	66	62	57	62	2.1
2 ml Reactor Effluents					
5-day	33	29	36	33	1.1
10-day	31	34	36	34	1.1
20-day	29	26	28	28	1 (0.93)
40-day	27	30	30	29	1 (0.98)
1 µg Daunomycin**	500	560	726	595	21.0
DMSO***	25	35	25	28	(1)

*Mean revertants on sample plate/mean revertants on control plate

**Used as positive control

***Solvent control for Daunomycin

Direct mutagenic activity was found in the raw wastewater with strains TA98 and TA1537, both of which detect frameshift mutagens. The mean reversion ratio with TA98 for five trials using the raw feed was 2.0 (see Table 8). Such a two-fold increase in the number of revertants over the control is the generally-accepted criterion for positive mutagenicity results. The mean reversion ratio with TA1537 for three trials (not shown) was 4.6. Results with TA1538 indicate that this strain was less sensitive to the frameshift mutagens in the raw wastewater than strains TA98 or 1537. There were no two-fold increases in reversion ratios found for any of the effluent samples, as demonstrated in Table 8 for the TA98 strain.

The synthetic wastewater also contains weak indirect mutagenic activity (not shown). Such activity requires the presence of a metabolic activation system (such as S-9 discussed above) for detection. When TA1535, a base-pair substitution detector, was used in the presence of S-9, the mean reversion ratio was 2.1 for three trials using the synthetic wastewater. No such increase was apparent for the effluent samples. Results were negative with the other commonly-used base-pair substitution strain, TA100, for the treated as well as the raw wastewater samples.

At this point, it can be concluded that biological treatment, even with a solids residence time of only 5 days, is capable of reducing the mutagenic activity associated with the raw synthetic wastewater to undetectable levels at the concentrations examined. These mutagenicity studies are continuing.

CONCLUSIONS

Based upon model studies using a synthetic coal conversion wastewater at 25% of full-strength and aerobic biological processes with and without solids recycle, coal conversion wastewaters appear to be biologically treatable. TOC, COD, and BOD removal increase with increasing solids residence time. Phenol is virtually completely removed with a sludge age of 5 days, while the cresols and xylenols require 7.5 to 10 days and 20 days, respectively, for removal to levels below 1 mg/l. Some difficulties were encountered in attaining stable reactor operation and steady-state performance was difficult to achieve. The reactors with sludge recycle demonstrated greater stability compared to the chemostats.

The full-strength synthetic coal conversion wastewater was found to be non-treatable biologically, presumably due to the presence of constituents at toxic levels in the full-strength sample. The toxicants do not appear to be any of the major phenolic components (i.e. phenol, resorcinol, catechol, cresols, xylenols). Studies are continuing to identify the constituent(s) responsible for the toxic behavior of the full-strength wastewater.

Bioassays of the raw and treated quarter-strength synthetic wastewater show that the acute toxicity of the raw wastewater to fish and to mammalian cells is markedly reduced as a result of biological treatment and that the reduction in toxicity increases with increasing sludge age. Additionally, at the concentrations tested, biological treatment reduces the mutagenic activity associated with the raw synthetic wastewater to undetectable levels..

Table 8.   SUMMARY OF TA98 REVERSION RATIOS*

WITH RAW AND TREATED WASTEWATER SAMPLES

Without Metabolic Activation (S-9)

TRIAL	RAW FEED (1.0 ml)	REACTOR EFFLUENTS (2.0 ml)			
		5-DAY	10-DAY	20-DAY	40-DAY
1	1.8	1.4	1.0	1.1	1.0
2	2.1	1.1	1.1	1.0	1.0
3	1.9	---	---	---	---
4	2.5	---	---	---	---
5	2.0	---	---	---	---
MEAN	2.0	1.3	1.1	1.0	1

*All ratios based on triplicate plates/sample.

ACKNOWLEDGEMENTS

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TREATMENT AND REUSE OF

COAL CONVERSION WASTEWATERS

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This paper presents a synopsis of recent experimental activities to evaluate processing characteristics of coal conversion wastewaters. Treatment studies have been performed with high-BTU coal gasification process quench waters to assess enhanced removal of organic compounds via powdered activated carbon-activated sludge treatment, and to evaluate a coal gasification wastewater treatment train comprised of sequential processing by ammonia removal, biological oxidation, lime-soda softening, granular activated carbon adsorption, and reverse osmosis. In addition, treatment studies are in progress to evaluate solvent extraction of gasification process wastewater to recover phenolics and to reduce wastewater loading of priority organic pollutants. Biological oxidation of coal gasification wastewater has shown excellent removal efficiencies of major and trace organic contaminants at moderate loadings, addition of powdered activated carbon provides lower effluent COD and color. Gasification process wastewater treated through biological oxidation, lime-soda softening and activated carbon adsorption appears suitable for reuse as cooling tower make-up water. Solvent extraction is an effective means to reduce organic loadings to downstream processing units. In addition, preliminary results have shown that solvent extraction removes chromatographable organic contaminants to low levels.

TREATMENT AND REUSE OF

COAL CONVERSION WASTEWATERS

INTRODUCTION

Experiments have been performed at Carnegie-Mellon University to characterize coal gasification process wastewaters, to evaluate basic wastewater treatment properties, and to assess wastewater management strategies. The purpose of this paper is to review recent experimental activities in these areas, and to indicate directions for future research.

COAL GASIFICATION WASTEWATER MANAGEMENT

Figure 1 presents a general schematic representation of water streams important in coal gasification process water balances. Major streams include those associated with the boiler and cooling tower systems, process condensates, treatment blowdowns, and slurry/sludge waters. Process influent water streams generally include: water for coal slurry feed, water for direct contact gas cooling or quenching, and water for removal and/or quenching of char, ash, or slag. Process steam requirements include steam to gasifier and make-up steam to CO shift reactor. Process effluents are categorized as slag or ash quench water, raw product gas quench condensate, CO shift condensate, acid gas removal condensate and methanation condensate. The nature and quantities of these process water and effluent streams are highly process specific. The disposition of these streams for particular high BTU coal gasification processes is discussed in Luthy, et al., 1980[1], for the CO_2-Acceptor, Bi-Gas, Hygas, Synthane, and Lurgi processes.

Specific process water treatment and distributional configurations are also strongly dependent on the particular gasification process being considered. Thus various water management schemes exist for different gasification processes. Some aspects of these schemes are well understood and have become generally accepted as necessary in achieving a process water balance. For example, raw makeup water is typically softened and serves as process water, as cooling water, and as supply to the boiler feed water treatment system. In contrast some aspects of high BTU coal gasification process water balance are unique to this industry. This is especially true with respect to treatment and reuse of heavily contaminated phenolic wastewaters. In this case little previous experience is available to detail issues associated with treatment and reuse of these wastewaters; consequently, current research interest is focused on evaluation of specific treatment characteristics for purposes of engineering design and environmental assessment. There is also much interest in evaluating wastewater treatment characteristics in order to achieve a product water of suitable quality for reuse in the gasification process.

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Figure 1. Major water streams in a coal gasification process water balance.

Considerations Regarding Water Reuse

Medium and high-BTU coal gasification processes are net consumers of water. The ability to achieve complete water reuse may have a significant impact on the feasibility of a commercial-scale facility, especially for semi-arid western regions and for eastern sites not contiguous or adjacent to large rivers. A general design assumption should hold that all major wastewater streams be considered for reuse, including high organically contaminated streams and saline brines. Dirty water should be cleaned only for reuse and not for discharge to a receiving water; any water suitable for discharge is acceptable for reuse. Returning water to a source is not economic when water must be cleaned to satisfy stringent environmental regulations. Furthermore, treatment for reuse is likely to require less severe processing than treatment for discharge.

Various water management schemes exist for a given gasification process. These depend on the exact nature of the particular waters and on the quality constraints for which waters will be reused. Though specific processes may differ in water management configurations, it is apparent that the cooling tower is the most likely target for wastewater reuse. Treatment for reduction of high ammonia and organic loadings is necessary, while some extent of demineralization and removal of residual organic contaminants will be necessary to achieve a water within quality constraints governing cooling tower makeup. Minimum quality constraints governing acceptable levels of organic contamination in cooling tower make-up are not clearly understood and must be evaluated. Also the fate of toxic hazardous wastewater contaminants during wastewater treatment and during cooling tower operation must be assessed. These factors will ultimately determine the most appropriate treatment scheme to achieve water reuse in a cooling tower.

WASTEWATER CHARACTERISTICS AND SCALABILITY

High-BTU coal gasification processes may be divided into two general classifications with respect to levels of organic contamination in process condensates: 1) those processes which produce little or no phenolics, oils, and tars, and 2) those processes which produce substantial quantities of these materials. Among those processes which produce organic contaminants a further division may be made between those which are significant producers of tars and heavy oils. General data for comparison of coal refinery condensates are presented in Luthy, 1979.[2]

The production of organic contaminants during coal gasification is related to gasifier physical configuration and operating conditions. Processes tending to show little or no organic contamination may be either entrained flow or fluidized bed gasifiers that operate at temperatures greater than approximately 1050°C (1900°F) and produce ash as slag or agglomerates. Examples of such processes are Bi-Gas, Combustion Engineering, Koppers-Totzek, U-Gas, and Westinghouse. Gasifiers having high coal devolatilization temperatures, such as the CO_2-Acceptor process at 830°C (1500°F), also produce a cleaner product gas which in turn yields condensates free of organic contamination (Fillo, 1979[3]). Other

important gasifier operating variables which relate to production of organics are gas residence time, coal particle size and heat-up rate, and the extent of gas-solids mixing (Nakles, et al., 1975[4]). Examples of gasification processes which produce effluents with organic contamination are Hygas, Synthane, slagging fixed-bed, Lurgi, and Wellman-Galusha.

It should be recognized that published information on coal gasification process wastewater characterization necessisarily reflects a difference in process scales and use of various coals. Since much of the available data are for analysis of condensates from process development units or pilot plants, it should be expected that any changes anticipated between pilot plant and commercial scale gasifier operating conditions may have significant effects on gasifier effluent production, especially with respect to organic contamination. Thus, scalability of pilot plant data is a major issue in evaluating coal conversion pilot plant effluent composition and distributional trends. Factors to consider may include coal type and pretreatment, coal-to-steam ratio, gasifier geometry and operating parameters, and raw product gas quench system design and operation.

Wastewater treatment experiments performed at Carnegie-Mellon University have utilized process quench waters from the Hygas and slagging fixed-bed coal gasification pilot plants. While these process condensates may not be representative in a quantititative sense of wastewaters which would be expected in a demonstration or commercial scale process, it is anticipated that the majority of organic and inorganic species observed in these effluents may be expected to exist in a commercial facility, though relationships between mass emissions and concentrations may be somewhat different. In as much as the scope of the investigations were to obtain basic information on biological and physico-chemical treatability characteristics of gasification effluents, the pilot plant wastewater samples were envisioned as providing a reasonable matrix of representative contaminants which may be expected in presently conceived commercial facilities.

TREATMENT STUDIES WITH COAL GASIFICATION CONDENSATES

There exists only a limited number of published studies on treatment of organically contaminated coal gasification process wastewaters, especially for the new generation of gasification processes under development. Most of those studies have focused on physicochemical treatment for reduction of tars, oils, and ammonia prior to biological oxidation, and on basic biological oxidation characteristics of these wastewaters. These data are largely based on experience gained from laboratory bench-scale experimentation.

Experimental biological oxidation studies have been reported for Lurgi coal gasification process effluent (Cooke and Graham, 1965[5]), Synthane (Johnson, et al., 1977[6]; Neufeld, et al., 1978[7]; and Drummond, et al., 1979[8]) and Morgantown Energy Technology Center (METC) pilot coal

gasification wastewaters (Sack, 1979[9]), and H-Coal pilot coal liquefaction effluent (Reap, et al., 1977[10]). In addition, biological oxidation studies have been performed with pilot coal gasification process effluents obtained from the Hygas pilot plant operated by the Institute of Gas Technology in Chicago, Illinois (Luthy and Tallon, 1980[11]) and the slagging fixed-bed pilot plant operated by the Grand Forks Energy Technology Center (GFETC) in Grand Forks, North Dakota (Luthy, et al., 1980[12]).

A discussion of performance data and biological oxidation kinetic values for treatment of coal conversion wastewaters is presented in Luthy (1979[2]). A general conclusion from these investigations is that wastewaters processed for removal of ammonia by steam stripping followed by activated sludge treatment for removal of degradable organic matter will show high removal efficiencies for BOD, COD, phenolics and thiocyanate. Nitrification has been demonstrated in several investigations. However, because of the nature of coal gasification process condensates, activated sludge treated wastewater will contain relatively high concentrations of residual organic material. This material is associated with effluent COD and color and is characteristic of oxidation of complex phenolic wastes.

REMOVAL OF TRACE ORGANIC CONTAMINANTS

Less information is available on the trace organic composition of coal gasification wastewaters and removal efficiencies for these compounds during treatment. Singer, et al. (1978) summarizes organic characterization data for coal conversion effluents. Information on removal efficiencies for specific organic compounds from synthetic coal conversion wastewater mixtures is presented in Singer, et al. (1978[13], 1979[14]).

Stamoudis and Luthy (1980[15]) provide results of screening gas chromatography/mass spectrometry analysis of Hygas and GFETC pilot plant wastewater to determine removal efficiencies during biological oxidation. In these investigations wastewater was pretreated by lime addition and air stripping to reduce excess alkalinity and ammonia prior to biological oxidation. The biological reactors were complete-mix, single-stage air activated sludge reactors, with GFETC wastewater being treated at 33% strength and Hygas condensate at 100% strength. General operating parameters and performance characteristics for the biological reactors employed for evaluation of removal efficiencies of organic constituents are summarized in Stamoudis and Luthy (1980[15]). Samples of reactor influent and effluent were prepared for GC/MS analysis by extraction with methylene chloride using generally accepted techniques into acid, base and neutral fractions.

It was found that approximately 99% of influent extractable and chromatographable organic material, on a mass basis, was derivatives of phenol and represented in the acid fraction of the influent samples. Activated sludge processing removed most of the organic constituents,

with compounds of the acidic fractions being removed almost completely. High removal efficiencies were also observed for compounds in the basic fraction, with the exception of certain alkylated pyridines. The extent of removal of compounds in the neutral fractions was dependent on chemical structure. Aromatic hydrocarbons containing aliphatic substitutions and certain polynuclear aromatic compounds were only partially removed. A general broad conclusion from this study was biological oxidation provides good to excellent removal for most compounds present in the coal gasification process wastewater.

Followup studies were conducted with GFETC slagging fixed-bed pilot plant wastewater pretreated in the same fashion as above in order to compare removal of organic contaminants by activated sludge and powdered activated carbon (PAC)-activated sludge treatment. Details of the experimental procedures and results are presented in Luthy, et al. (1980[1]).

A high suface area PAC (Amoco PX-21) was selected for use in this study on the basis of results from wastewater batch adsorption isotherm testing. PAC-activated sludge treatment was evaluated at sludge ages of twenty and forty days with PAC mixed liquor equilibrium concentrations of 0, 500, 1500, and 5000 mg/l. The reactors were operated for an appropriate balance period to achieve steady state operation.

Activated sludge treatment with no addition of PAC showed excellent removal of phenolics and BOD. Phenolics were reduced to less than 1 mg/l from influent values of 1300-1500 mg/l; BOD was reduced to about 30 mg/l from influent concentration of 3600-3800 mg/l. COD removal efficiencies were 85% and 88% at removal rates of 0.37 and 0.24 mg COD removes/mg MLVSS-day at sludge ages of twenty and forty days, respectively.

PAC-activated sludge treatment gave significantly lower effluent COD and color with increasing equilibrium carbon concentrations. In addition, somewhat lower effluent concentrations of BOD, phenolics, ammonia, organic-nitrogen, and thiocyanate were achieved by PAC-activated sludge treatment compared to activated sludge treatment. PAC-activated sludge treatment reduced foaming problems and gave a sludge with good settling properties. Effluent characteristics were not significantly different for PAC-activated sludge treatment at a sludge age of twenty and forty days. In general, PAC-activated sludge treatment in this study gave as good or better effluent characteristics than previously reported results with other industrial wastes. A highly nitrified effluent was produced by PAC-activated sludge treatment at a sludge age of forty days. This effluent appears suitable for reuse as cooling tower make-up water with respect to macro-organic contaminants.

Samples of biological reactor effluent with sludge age of forty days and mixed liquor PAC concentrations of 0, 500, 1500, and 5000 mg/l were screened for base and neutral fraction organic compounds. Base and neutral fraction capillary column chromatograms of all four reactors

were very similar. Characterization of sixteen compounds, representing some of those which were found not to be completely removed in the previous GC/MS study with slagging fixed-bed wastewater, gave similar GC flame ionization detector responses in effluent samples for all four reactors with concentration levels of these compounds in the range of several mg/l. These results confirmed that biological oxidation of coal gasification wastewaters removes organic contaminants to low levels, however PAC-activated sludge treatment does not necessarily provide significantly lower effluent concentrations of certain trace organic compounds under conditions in which the biological oxidation process has been optimized. The PAC results can be explained in part on competition adsorption between very low concentration of base and neutral fraction compounds and very high concentration of oxidized and/or polymeric substances resulting from biological treatment of phenolic wastes. These later substances are similar to humic materials and are associated with residual effluent COD and color. These substances are removed significantly by PAC-activated sludge treatment, and they likely compete with trace organic contaminants for adsorption on the powdered activated carbon.

EVALUATION OF A COAL GASIFICATION WASTEWATER TREATMENT TRAIN

A sample of Hygas pilot plant Run 79 coal gasification quench condensate has been processed through sequential wastewater treatment unit operations to evaluate treatment technology to achieve wastewater reuse. The unit operations investigated in this study are shown in Figure 2 and include: ammonia removal, biological oxidation, lime-soda softening, activated carbon adsorption, and reverse osmosis.

The raw wastewater contained approximately 0.86 meqv/l of alkalinity and 0.94 meqv/l of ammonia at pH of 7.7. These results plus batch steam stripping tests showed that approximately 97% of the ammonia can be liberated in one unit operation without chemical addition. Removal of the remaining fraction of ammonia will require addition of lime or caustic. If lime is used, this will result in a significant increase in wastewater hardness (>1000 mg/l as $CaCO_3$). In this study, steam stripping was simulated by liming to precipitate alkalinity and air stripping to remove ammonia. The residual hardness in stripped wastewater was in the same range regardless if free- and fixed-leg steam stripping or liming and air stripping were used for ammonia removal.

Biological oxidation at a COD removal rate of 0.16 mg COD removed/mg MLVSS-day gave 90% reduction in COD from an influent value of 6900 mg/l, and 99% reduction in BOD from an influent value of 3500 mg/l. There was also 96% removal of thiocyanate and reduction of phenolics to 0.7 mg/l. Biologically treated wastewater contained about 30 mg/l BOD, 700 mg/l COD, and 1200 mg/l hardness (as $CaCO_3$). It was judged that if biologically treated wastewater were to be used as make-up to a cooling tower, that the COD was sufficiently high to promote potentially significant biological activity, and that calcium and sulfate levels could lead to scaling and fouling problems. Therefore, removal of calcium hardness was evaluated by lime-soda softening,
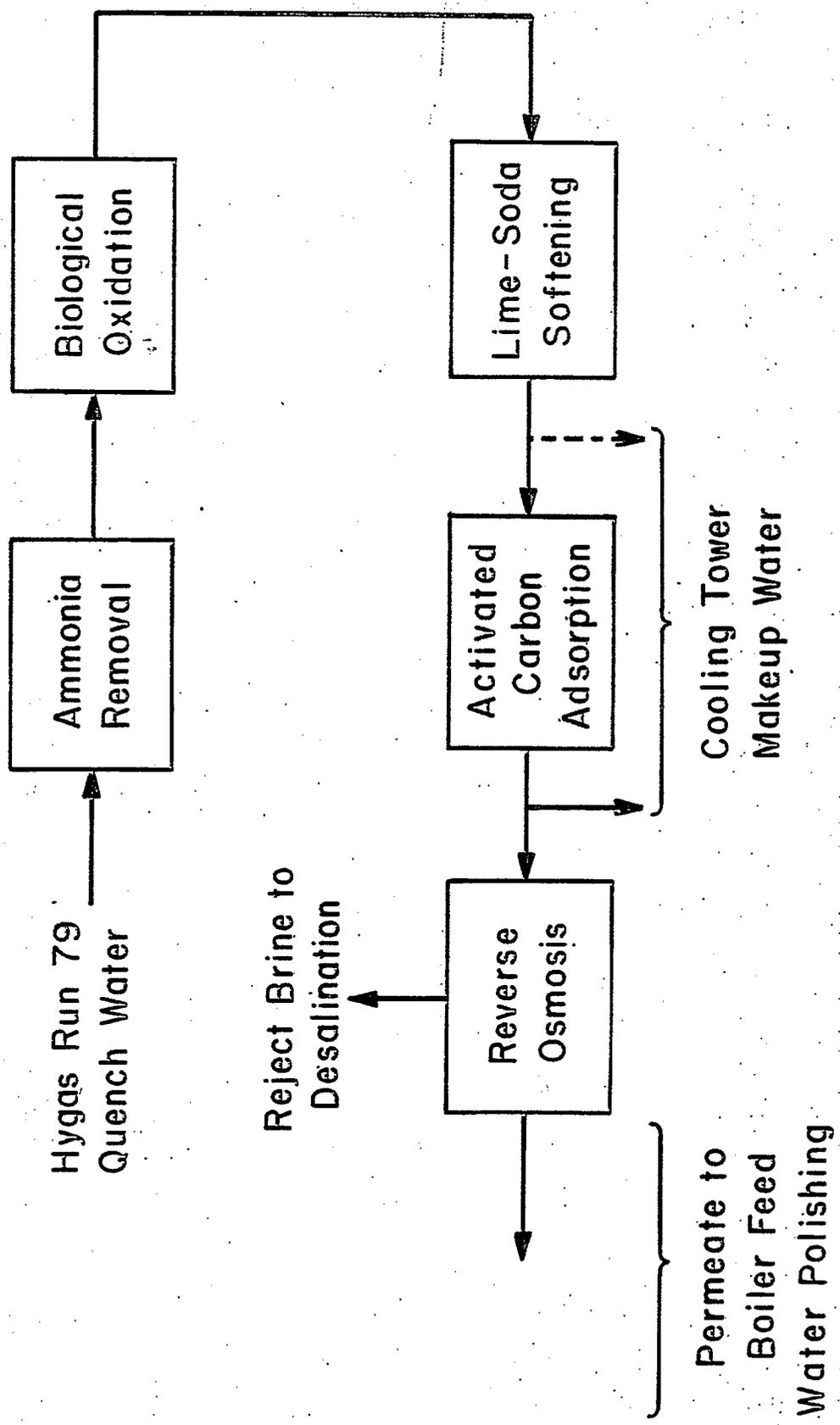
Figure 2. Bench Scale Treatment Train to Evaluate Processing Characteristics of Hygas Process Quench Condensate.

and removal of COD was assessed by granular activated carbon treatment of softened wastewater.

Most of the calcium hardness in biological reactor effluent existed as non-carbonate hardness owing to the consumption of alkalinity during biological oxidation. Thus, lime-soda softening required proportionally more soda than lime. This resulted in the replacement of residual wastewater equivalents of hardness by equivalents of sodium. Lime-soda softening reduced wastewater hardness to practical limits (30-40 mg/l as $CaCO_3$). These tests also indicated that flocculation and/or filtration would be necessary to clarify sludge formed by the softening operation. Granular activated carbon adsorption column testing of softened biological effluent was conducted at pH of 7, a contact time of seventeen minutes, and a loading of about 1.2 gpm/ft^2. These tests showed that approximately 80% of COD and 95% of residual color could be removed by carbon adsorption.

Hygas wastewater processed by ammonia removal, biological oxidation, lime-soda softening, and activated carbon adsorption was judged to be of sufficient quality for reuse as cooling tower make-up water. At this time it is not possible to predict the degree of cooling tower biological activity which may be induced by residual COD of about 100 mg/l in carbon treated effluent, although it is suspected that a biocidal program could control this problem.

Reverse osmosis experiments were conducted with granular activated carbon treated wastewater. Reverse osmosis treatment with a hollow fiber polyamide membrane produced a clear colorless product, with a TDS level comparable to tap water. Low levels of organic contaminants (COD = 20 mg/l) did permeate the membrane. It is believe that these compounds were low molecular weight, and that they permeated the membrane owing to preferential sorption at the membrane-solution interface. Product water from reverse osmosis treatment is suitable for reuse as make-up to a boiler feed water polishing facility.

Reverse osmosis membrane fouling was not observed in this study under operation at 75 percent conversion. Addition of a polyphosphate inhibitor is thought to have been at least partially responsible for this. A decline in membrane flux did occur, but this was primarily a result of membrane compaction. Comparison of polyamide and cellulose triacetate hollow fiber membranes showed that the polyamide membrane provided a higher quality product water while the cellulose triacetate membrane provided higher flux rates.

This investigation showed that a possible treatment scheme for reuse of phenolic coal gasification effluents may include provisions for ammonia stripping, biological oxidation, softening, and activated carbon adsorption. These unit processes will provide a water with sufficient quality for reuse as cooling tower make-up water. Further study is required to assess the possibility of excessive biological activity and/or emissions of trace compounds to the environment as a

result of wastewater reuse in cooling towers. Resolution of this problem may depend on large pilot cooling tower studies and on operational experience gathered at demonstration plants.

Reverse osmosis appears to be an attractive technique to remove wastewater dissolved solids. If reverse osmosis is employed in treatment system design, the resulting product water will be of sufficient quality to be used as a boiler feedwater source. However, further study needs to be undertaken to determine the extent of membrane fouling that could possibly occur under long term steady state operation. It is probably best to evaluate reverse osmosis treatment units at the pilot scale once demonstration plants have been built.

EVALUATION OF A PROPOSED TREATMENT TRAIN FOR A DEMONSTRATION PLANT

Figure 3 shows a simplified schematic of a proposed wastewater treatment system for a slagging Lurgi process to gasify Illinois No. 6 bituminous coal (Continental Oil Company, 1979[16]). Wastewater treatment at this proposed facility handles streams discharging to an oily water sewer, Rectisol process blowdown, solvent extracted wastewater from ammonia recovery, and sanitary wastewater. As shown in Figure 3, the treatment train for wastewater from ammonia recovery passes to an equalization basin and then to a dissolved air flotation unit. Wastewater is then treated biologically in an extended aeration basin of three days hydraulic detention time. Effluent from the biological reactors is clarified, processed through polishing filters, and then pumped through granular activated carbon columns for removal of residual organics. Wastewater from the activated carbon unit is pumped to the utilities cooling tower.

The utilities cooling tower supplies cooling water to equipment having ordinary or carbon steel metallurgy. Makeup to the utilities cooling tower is obtained from various sources of which blowdown from the process cooling tower comprises the largest portion of the total. Makeup from wastewater treatment comprises about 17% of the total demand. The plant is designed for zero discharge of wastewater. The key units for this are multi-stage and Carver-Greenfield evaporators. The multi-stage evaporator concentrates an approximate one percent feed to an approximate 30 weight percent salt solution. The condensate is recovered in the utility cooling tower and the salt solution is concentrated to an approximate 60 weight percent aqueous slurry. The concentrated salt mixture is chemically fixed and trucked to a landfill. Continental Oil Company recommended that semi-commercial evaporators be constructed and evaluated prior to constructing large units because no commercial experience exists with wastewater from a gasification facility, and there may be problems with scaling and foaming.

Figure 4 shows a schematic representation of experiments in progress to evaluate essential features of a wastewater treatment train of the

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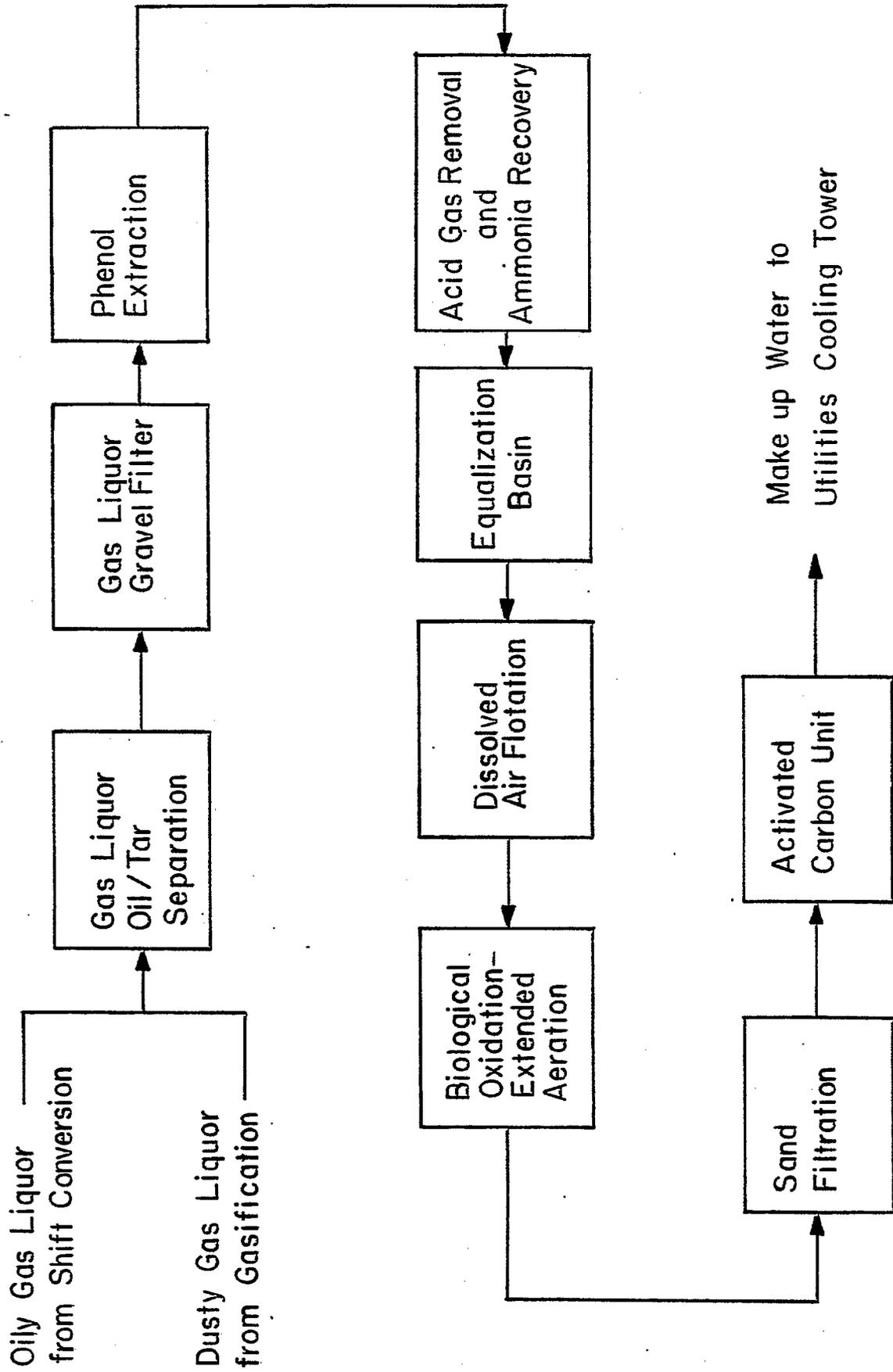
Figure 3. Proposed wastewater management scheme for a Lurgi plant gasifying Illinois No. 6 bituminous coal (Continental Oil Company, 1979).

Slagging Fixed-Bed Wastewater

↓

Trace Organics Characterization
by GC/MS and HPLC

↓

Solvent Extraction
with MIBK

↓

Ammonia Stripping

↓

Organics Characterization
(GC/MS and HPLC)

Activated Sludge	PAC/Activated Sludge
↓	↓
Organics Characterization (GC/MS and HPLC)	Organics Characterization (GC/MS and HPLC)
↓	↓
Granular Activated Carbon Adsorption (HPLC Analysis)	Lime-Soda Softening (HPLC Analysis)
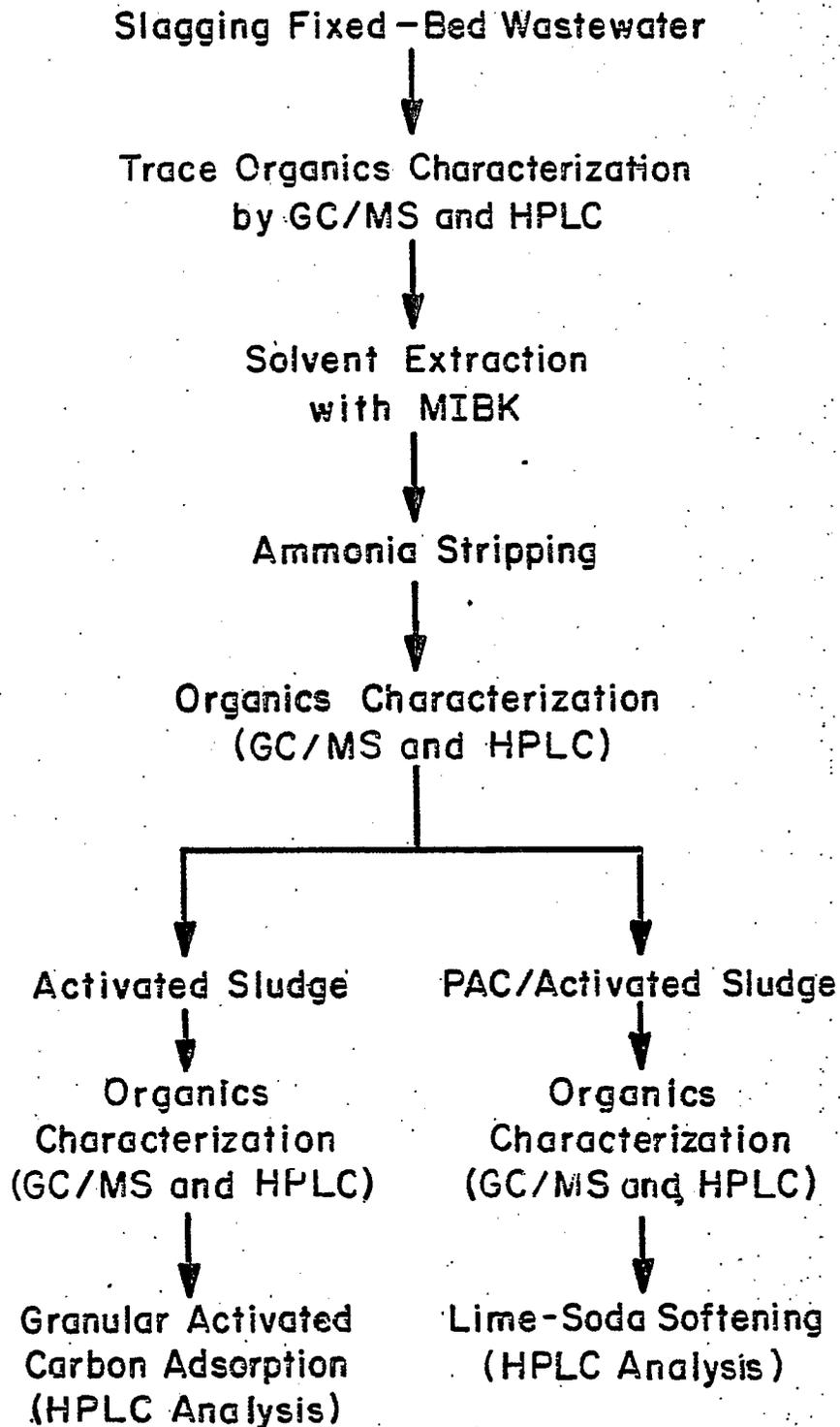
Figure 4. Experiments in progress to evaluate essential features of a coal
gasification wastewater treatment train.

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type discussed above. This study utilizes GFETC slagging fixed-bed lignite wastewater without dilution. Wastewater is processed through solvent extraction, steam stripping, and biological oxidation with and without PAC addition. Effluent from biological oxidation with no PAC is treated by granular activated carbon adsorption, while effluent from the PAC-activated sludge reactor is evaluated for lime-soda softening characteristics. High pressure liquid chromatographic analyses are being performed after each treatment step to assess removal of polycyclic aromatic hydrocarbons. Screening GC/MS analyses are being conducted on raw, solvent extracted-ammonia stripped, and activated sludge and PAC-activated sludge effluent to characterize removal efficiencies for trace organic contaminants. At this writing, experiments have been completed through biological oxidation. Gas chromatography and GC/MS scans have been made for raw, solvent extracted-ammonia stripped, and PAC-actived sludge effluent. A report on the results of this investigation should be available for distribution later this year.

Several representative solvents were screened for use in the solvent extraction step. As a result of this analysis methylisobutyl ketone was selected for use owing to its measured high distribution coefficient for phenolics. Wastewater was processed through five sequential extraction steps at a solvent-to-liquid ratio of 1:15. This reduced phenolics from 5500 mg/l to about 5 mg/l. Concomitant with phenolics removal there was 88% reduction of COD (32,000 to 3900 mg/l) and 89% removal of BOD (26,000 to 2900 mg/l). Preliminary evaluation of GC/MS data suggests that there is on the order of 99%+ removal for most organic compounds through solvent extraction and ammonia stripping.

It has been demonstrated that solvent extracted wastewater can be processed by either activated sludge and PAC-activated sludge treatment without the need for dilution. Additionally, solvent extracted wastewater does not show tendency to foam excessively as observed in previous investigations. Effluent BOD values were in the range of 30 mg/l for both activated sludge and PAC-activated sludge treatment. PAC treatment showed generally better removal efficiency for TOC, COD, ammonia-nitrogen, organic-nitrogen, SCN$^-$, and color. Initial assessment of GC/MS scans of extracts from activated sludge and PAC-activated sludge treated wastewater indicates that organics are reduced to extremely low levels, generally less than several micrograms per liter.

This work has shown that solvent extraction offers several distinct wastewater processing advantages. Aside from recovering phenolics for use as a fuel or chemical commodity, there is achieved a marked reduction of trace organic compounds. If the extract is to be used for fuel, then there is the possibility of combusting toxic/hazardous organic compounds to thermal extinction. Solvent extraction reduces organic loading to a biological oxidation facility, and it may also serve as a physico-chemical treatment step to moderate shock loadings of organics. Solvent extracted coal gasification process wastewater is easier to treat biologically than wastewater which would otherwise contain much higher levels of organics.

FUTURE WORK

It is planned to continue these investigations in order to understand removal efficiencies and fates of trace organic compounds during treatment of wastewaters derived from production of synthetic fuels. Preparations are being made to perform experiments with slagging fixed-bed wastewater generated from conversion bituminous coal. Data gained from this study will be used to develop a model for predicting the fates of various trace organic contaminants during treatment with special emphasis on modeling removal of trace organics during solvent extraction. It is also proposed to conduct analogous investigations with oil shale and tar sand condensates where the objective of these studies would be to characterize and evaluate removal of organic compounds via proposed treatment trains for demonstration facilities.

ACKNOWLEDGMENTS

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PILOT PLANT EVALUATION OF H2S, COS, AND CO2 REMOVAL

FROM CRUDE COAL GAS BY REFRIGERATED METHANOL

by

R. M. Kelly, R. W. Rousseau, and J. K. Ferrell

Acid gas removal systems are a necessary part of coal gasification processes. Carbon dioxide must be removed from gasifier product gas to improve the energy content of the gas and several sulfur compounds must be taken out to protect downstream process catalysts as well as reduce potential sulfur emissions.

At North Carolina State University, an integrated coal gasification- gas cleaning test facility is being used to study the environmental and process implications of several different acid gas removal solvents. Details of the plant facilities and operating procedures may be found in a recent EPA technical report (Ferrell et al., EPA-600/7-80-046a, March 1980) (1). This paper presents some of the initial results from acid gas removal pilot plant operation, discusses several aspects of methanol use for acid gas removal and outlines future experimental work on this part of the process.

INTRODUCTION

The choice of a solvent for acid gas removal in a coal gasification process depends upon several factors. Consideration must be given to the type of gasification scheme used, the sulfur content of the coal, the end use of the product gas and, most importantly, the process chosen for off-gas sulfur recovery. For both economic and environmental reasons, most large-scale coal gasification processes currently planned in the United States include some type of sulfur recovery unit. In general, the higher the sulfur content of the stream being sent to the recovery unit, the more favorable the economics. The type of solvent chosen, therefore, should exhibit some selectivity between the product gases, the sulfur compounds, and carbon dioxide.

Both chemical and physical solvents have been considered for use in acid gas removal systems for coal gasification. The choice of one type of solvent over the other depends to a large extent on the partial pressure of the acid gases in the gas stream to be treated. Chemical solvents are preferred for low to moderate acid gas partial pressures, while physical solvents would be preferred at high acid gas partial pressures (see Figure 1). This basis of comparison reflects only the capacity of a particular type of solvent for acid gases and accounts neither for the selectivity between carbon dioxide and sulfur gases nor for the effectiveness of the solvent in treating specific sulfur compounds.

Very little information is available concerning the fate of certain sulfur compounds in either physical or chemical solvents. In a study undertaken to evaluate sulfur emission controls for the Western Gasification Company's coal gasification project in New Mexico, it was estimated that 1% of the total sulfur fed to a Lurgi gasifier would report as carbonyl sulfide. This takes on additional significance when considering that this represents almost 2.2 tons/day of sulfur(2). Because hydrogen sulfide and carbonyl sulfide are not absorbed/stripped with the same efficiency in most solvents, failure to account for each compound could result in unexpectedly high sulfur emissions.

As part of our research program, we plan to evaluate the effectiveness of both physical and chemical solvents in removing acid gases from both gasifier product gas and synthetic gas mixtures. Also, the build-up in the solvent of sulfur, nitrogen, and hydrocarbon species will be monitored. The results reported here are from experiments using a gas produced during fluidized bed gasification of Western Kentucky No. 11 coal char with emphasis on the fate of H2S and COS in the acid gas removal system.

FIGURE 1

EQUILIBRIUM DIAGRAM

FIGURE 1 — EQUILIBRIUM DIAGRAM. Plot of GAS MOLE FRACTION (vertical axis) versus LIQUID MOLE FRACTION (horizontal axis), showing curves for CHEMICAL SOLVENT and PHYSICAL SOLVENT, with horizontal reference lines at Y_1 and Y_2, and vertical reference lines at X_{p_1}, X_{c_1}, X_{c_2}, and X_{p_2}.
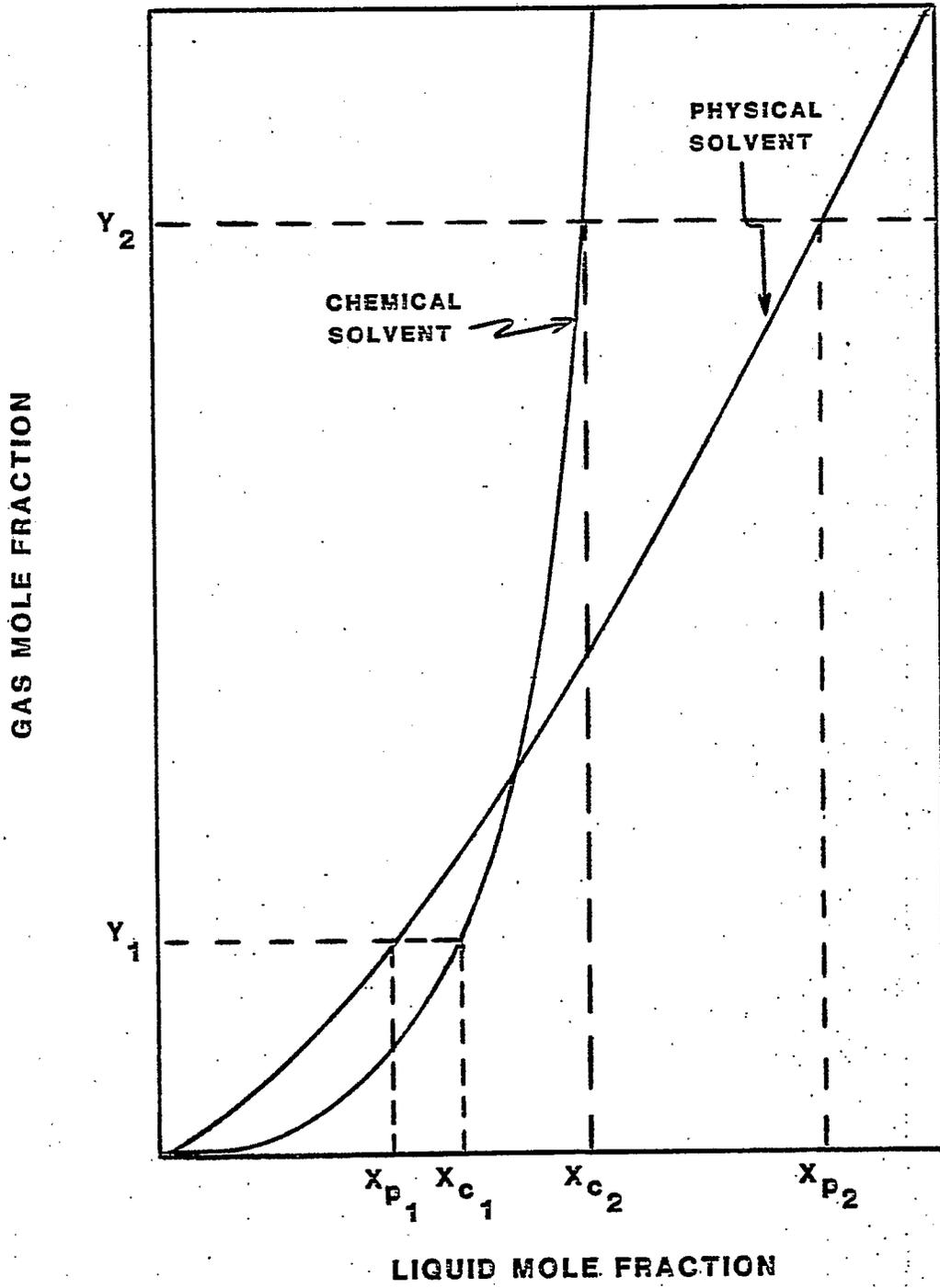
PROCESS DESCRIPTION

Figure 2 shows a process flow sheet for the acid gas removal system (AGRS) used in this study. It was designed to operate with four different solvents:

1. refrigerated methanol

2. hot potassium carbonate

3. monoethanolamine

4. dimethyl ether of polyethylene glycol(DMPEG)

With minor modifications, other solvents could also be used. Feed gas from either the gasifier or from a mixing manifold can be used in making process measurements.

The AGRS consists of an absorber-flash tank-stripper combination with the necessary auxilliary equipment. The flash tank can be operated at pressures ranging from atmospheric to 28 atmospheres absolute. For good system performance, it is normally operated around 8 atmospheres absolute. The absorber and stripper are both packed columns, each containing three sections of packing, any or all of which can be used in mass transfer studies. Both are insulated and approach adiabatic operation. Operating ranges and column characteristics are given in Table 1.

A refrigeration system provides sufficient cooling to feed methanol to the absorber at temperatures as low as 236 K (-35 F). Inert gas (nitrogen) is used to strip the methanol of acid gases but a reboiler is available for thermally stripping (regenerating) the chemical solvent systems.

Plant operation is monitored and regulated from a control room using graphical displays on a video terminal and a Honeywell TDC 2000 process control computer. Signals from 96 process sensors (temperatures, pressures, flow rates, and differential pressures) are sent to a PDP-11/34 plant data acquisition system.

All chemical analyses are done on the premises with occasional GC/ mass spectrometry done by EPA contractors. In the future, when the char used as gasifier feed is replaced by coal, the recirculating AGRS solvent will be checked for hydrocarbon build-up as well as for any trace materials of environmental or process signficance.

FIGURE 2

ACID GAS REMOVAL SYSTEM (AGRS)
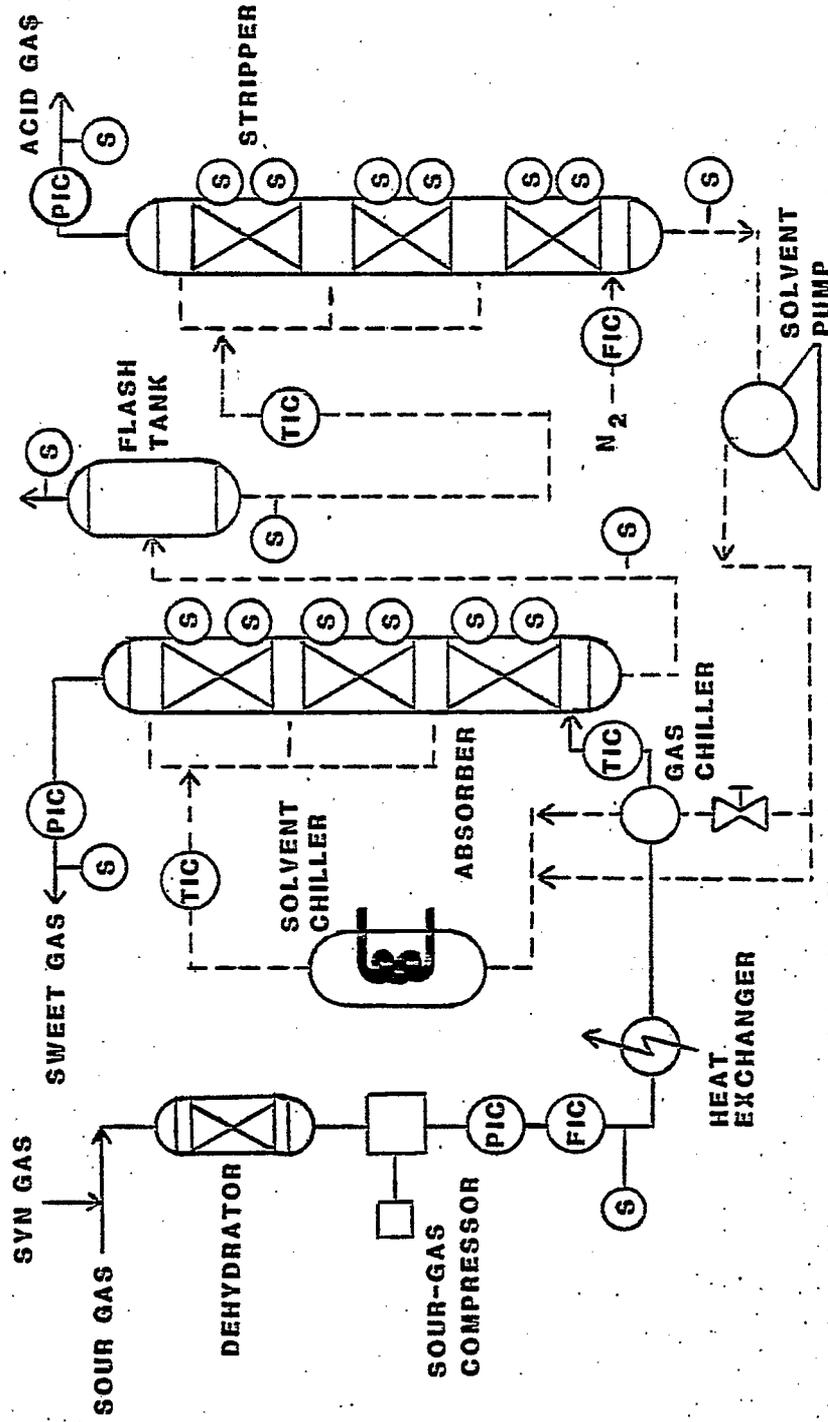
FIC = Flow Indicator and Controller
PIC = Pressure Indicator and Controller
TIC = Temperature Indicator and Controller
S = Sample Port

TABLE 1

COLUMN SPECIFICATIONS AND OPERATING RANGES FOR REFRIGERATED METHANOL

	Absorber	Stripper
Total Packed Height	21.3 ft	21.3 ft
column Diameter	5 inches	6 inches
No. of Packed Sections	3	3
Packing Type	Ceramic Intalox Saddles	Ceramic Intalox Saddles
Packing Size	1/4 inch	1/4 inch
Operating Temperature	-35 F to -10 F	-10 F to 60 F
Operating Pressure	100-500 psig	10-25 psig
Liquid Flow Rate	0.5-1.5 gpm	0.5-1.5 gpm
Gas Flow Rate	10-20 $scfm_{32°F}$	2-10 $scfm_{32°F}$

MASS BALANCE RESULTS

One of the major objectives of all initial runs was to achieve a closed material balance around the pilot plant. This required the ability to operate the plant at a steady state 'for long periods of time. Also, accurate flow measurements and chemical analyses are necessary as are proper sampling techniques.

A considerable amount of time was spent in improving mass balance closure so that deviations of less than 10% resulted. Because all flow streams were measured by orifice flow meters and laminar flow elements, calibrations had to correct for the effect of chemical composition on flow stream properties. To account for differences between the gas used for calibration and the process gas, a density correction was provided for orifice meter calibrations and a viscosity correction was provided for laminar flow element calibrations. These corrections were made to the flow rate measurements recorded by the data acquisition system and reported in a run summary.

While there is still room for improvement, the mass balance closure was adequate to reach some conclusions concerning the distribution of various compounds in the system. Improvement in the current mass balance closure will come from improved sampling techniques, especially for sulfur species, as well as better process control to enhance the quality of the steady state.

USE OF METHANOL AS AN ACID GAS REMOVAL SOLVENT

The choice of an acid gas removal system in coal gasification processes requires consideration of both process and economic factors. The residual levels of sulfur compounds and carbon dioxide, and their disposition in the AGRS, usually serve as the bases for decision. The options available include hot gas clean-up, direct conversion, physical and chemical solvents and no acid gas removal at all. Any process requiring the removal of both carbon dioxide and sulfur compounds at high acid gas partial pressures will probably use a physical solvent.

Although there are a score of proposed physical solvent processes for acid gas removal, only a few have been proven commercially. SELEXOL (DMPEG), developed by the Allied Chemical Corporation, and Rectisol (refrigerated methanol), developed by the Lurgi Corporation, are most frequently mentioned in coal gasification applications. Both are capable of achieving high degrees of carbon dioxide and sulfur gas removal and show sufficient selectivity for specific acid gases. The initial part of our study focused on the use of refrigerated methanol.

Figure 3 shows the solubilities of various gases in methanol as a function of temperature (3). This plot shows only the solubility of

FIGURE 3

SOLUBILITY OF GASES IN METHANOL (2)
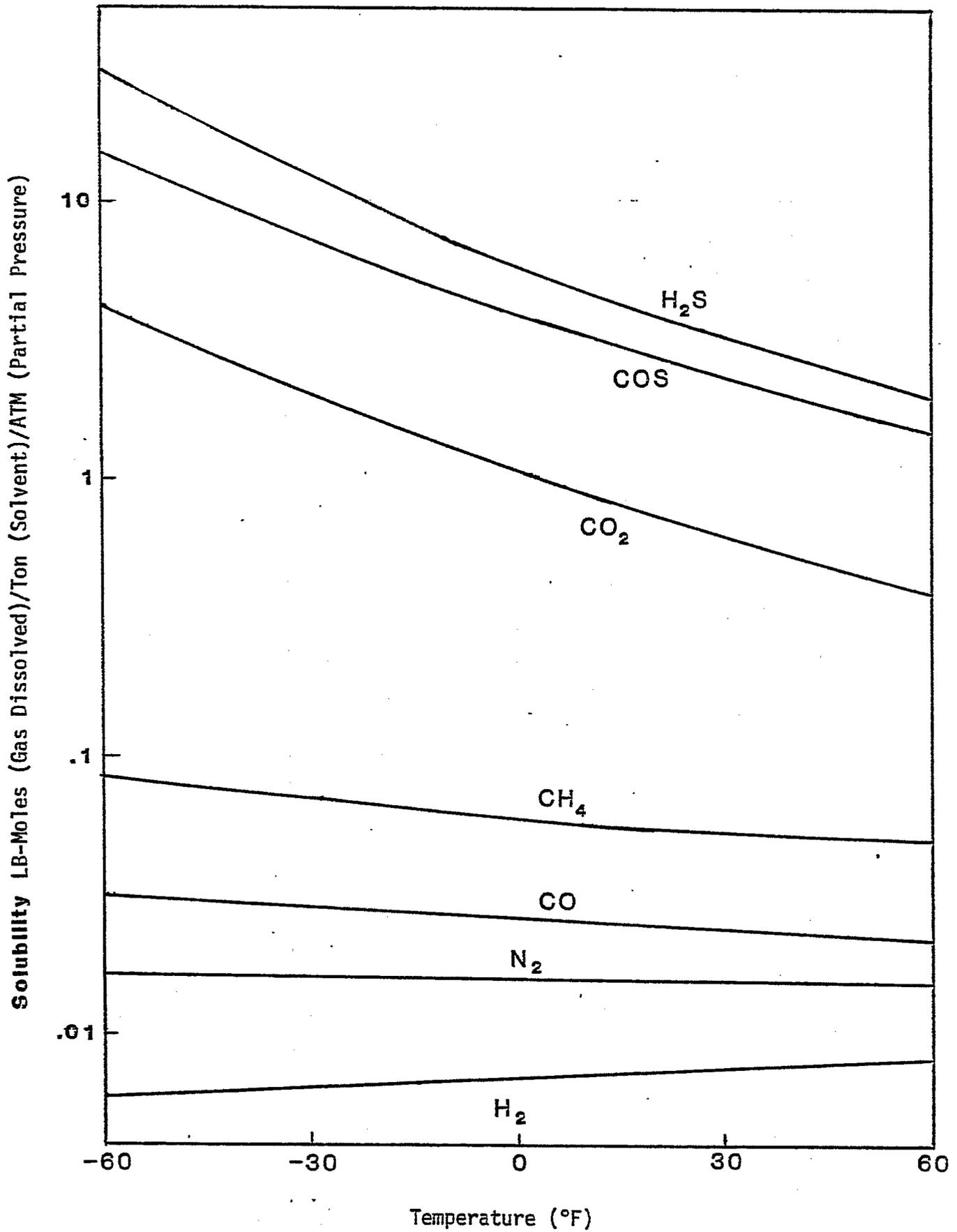
each gas at a partial pressure of one atmosphere and does not reflect the thermodynamic non-idealities associated with the multicomponent system at higher pressures. Nevertheless, there are several points that can be made regarding the general behavior of these constituents in methanol.

In general, all gases shown here have an increased solubility with decreasing temperature and increasing partial pressure. Hydrogen and nitrogen are notable exceptions. Hydrogen solubility increases with temperature while nitrogen solubility is insensitive to temperature. The three acid gases (H2S,COS,CO2) are considerably more soluble than the other permanent gases and differ somewhat among themselves in solubility. At individual partial pressures of one atmosphere, the ratios of solubilities of various gases at a temperature of -40 F are shown in Table 2. Thus, one might conclude that the acid gases can be separated from the permanent gases and from each other given an appropriate separation scheme. In practice, however, thermodynamic factors and mass transfer restrictions make complete separation difficult.

Clearly, the evaluation of an acid gas removal system must consider both the ability of the solvent to remove acid gases to sufficiently low levels as well as its ability to separate carbon dioxide from the sulfur compounds. The absorber-flash tank-stripper combination used in this study cannot be operated to remove selectively the specific acid gases but removal efficiencies of each acid gas can be determined over a range of operating conditions. This information will then be used in developing a mathematical model to describe pilot plant operation and extended to predict both removal efficiencies and selectivity for other configurations. The necessary vapor-liquid equilibrium information is being developed in a parallel study and some results are already being used (4,5). Also, several pilot plant runs using synthetic gas mixtures are being used to determine process parameters. The final product of this study will be a computer simulation package useful in evaluating several process configurations for acid gas removal with methanol.

INITIAL RESULTS - REFRIGERATED METHANOL

Tables 3, 4, and 5 summarize some initial results of the current research program. It should be pointed out that the objective of these runs was not to remove as much of the acid gases as possible but rather to evaluate the effect of changing certain process variables on removal efficiencies. These runs represent a portion of a larger experimental program which is still in progress and will be the subject of a future report.

TABLE 2

RELATIVE SOLUBILITIES IN METHANOL AT -40°F (233K)

Gas	$\dfrac{\text{Solubility of Gas}}{\text{Solubility of } H_2}$	$\dfrac{\text{Solubility of Gas}}{\text{Solubility of } CO_2}$
H_2S	2540	5.9
COS	1555	3.6
CO_2	430	1.0
CH_4	12	
CO	5	
N_2	2.5	
H_2	1	

TABLE 3

OPERATING CONDITIONS

	30	35	36	37
Absorber				
Pressure (atm.abs.)	28.2	28.2	21.4	31.6
Height of Packing (ft)	7.1	7.1	7.1	21.3
Inlet Liquid Flow Rate ($\frac{16\ moles}{hrft^2}$)	60.7	72.1	72.6	71.1
Inlet Liquid Temp. (°F)	-34.1	-36.3	-32.4	-36.3
Inlet Gas Flow Rate ($\frac{lb\ moles}{hrft^2}$)	16.2	15.9	16.4	16.6
Inlet Gas Temp. (°F)	54.0	53.9	57.5	59.9
Flash Tank				
Pressure (atm. abs.)	7.8	7.8	7.8	7.8
Stripper				
Pressure (atm. abs.)	1.7	1.7	1.7	1.7
Height of Packing (ft)	21.3	21.3	21.3	21.3
Stripping N_2 flow ($\frac{lb\ moles}{hrft^2}$)	0.9	0.9	0.9	0.9
Stripping N_2 Temp. (°F)	75.0	75.0	75.0	75.0

TABLE 4

RATIOS OF ACID GAS CONCENTRATIONS IN PROCESS STREAMS				
Run #		Sour Gas	Sweet Gas	Flash Gas	Acid Gas
30	CO_2/H_2S	27.0	30.4	68.1	28.1
	H_2S/COS	21.7	16.0	14.7	21.7
	CO_2/COS	585.7	486.7	1004.7	611.1
35	CO_2/H_2S	34.7	25.7	80.7	36.4
	H_2S/COS	17.9	12.3	13.8	15.5
	CO_2/COS	622.4	316.7	1117.1	566.0
36	CO_2/H_2S	23.4	6.2	59.3	31.4
	H_2S/COS	18.6	17.0	15.0	16.7
	CO_2/COS	435.4	105.0	887.6	524.0
37	CO_2/H_2S	29.0	15.6	76.1	31.4
	H_2S/COS	18.4	13.7	14.6	17.4
	CO_2/COS	533.0	213.3	1112.1	546.5

TABLE 5

ABSORBER OPERATION

	30	35	36	37
Pressure (atm absolute)	28.2	28.2	21.4	31.6
Ht. of packing (ft)	7.1	7.1	7.1	21.3
L in (# moles/hr-ft^2)	60.7	72.1	72.6	71.1
G in (# moles/hr-ft^2)	16.2	15.9	16.4	16.6
G out (# moles/hr-ft^2)	11.5	11.4	12.8	12.1
T_L in (°F)	-34.1	-36.3	-32.4	-36.3
T_L out (°F)	3.5	-0.6	-1.7	7.2
T_G in (°F)	54.0	53.9	57.5	59.9
Liquid Temperature rise (°F)	37.6	35.7	30.7	43.5
H_2S in (ppm)	9096	8072	8918	8631
H_2S out (ppm)	476	371	682	405
% removed	96.3	96.7	94.0	96.7
COS in (ppm)	423	449	476	475
COS out (ppm)	32	34	37	27
% removed	94.3	94.5	94.2	95.8
CO_2 in (%)	24.6	28.0	20.9	25.1
CO_2 out (%)	1.5	1.0	0.4	0.6
% removed	95.8	97.6	98.4	98.1

Mass balance reports for the runs listed in Tables 3, 4, 5 are included in the Appendix.

In general, AGRS balances meet the established criteria of less than a 10% deviation from complete closure. In cases where more than a 10% deviation was measured, flow meter and chemical analysis problems have been cited and will be corrected in future runs. Because solvent losses are an important consideration in using methanol, this analysis has recently been incorporated into the research program and results are reported in runs 35 and 37. This will be done routinely in the future. Failure to account for methanol losses in the gas exiting the flash tank and in the acid gas stream is probably a factor in mass balance overestimation.

Calculated liquid compositions exiting each vessel are reported as determined by difference. In the past, liquid samples between columns and at the stripper exit were taken as were samples from the column packing. Sampling and analytical problems led to the temporary abandonment of this practice but it will be reinstated in the future. The liquid exiting the stripper, however, is usually sampled and analyzed for residual acid gases. A check was also made of the hydrocarbon content of the solvent after approximately 60 hours of operation. No detectable hydrocarbons were found which is not a suprising result considering the fact that char and not coal was used as a feedstock to the gasifier (6). Future experiments call for the gasification of coal-char mixtures where the build-up of hydrocarbons in the methanol will be monitored and compared to the results obtained for char gasification.

The results presented here are from the clean-up of gases generated by the gasification of Western Kentucky No. 11 bituminous coal char. This char contains very little volatile matter (less than 2.0%) so that the sulfur gases produced will generally be the product of the gas phase hydrolysis of H2S, the predominant sulfur gas form. This means that most of the sulfur gases fed to the AGRS will be in the form of H2S, COS, with small amounts of CS2. Traces of methyl mercaptan, ethyl mercaptan, methyl sulfide and thiophene were also found in some gas streams but their irregular appearance prevent any quantitative conclusions concerning their distribution in the AGRS. These sulfur species are probably related to the volatile matter present in the feed char. Present efforts include a more detailed look at the fate of the less concentrated sulfur species.

DISCUSSION OF RESULTS

1. System Performance

The results presented in Tables 3, 4, 5 and in the Appendix represent system performance for a series of runs made at fairly low liquid to gas (L/G) ratios. These results verify the expected order of solubility for the three acid gases in methanol and show how these

gases distribute in the acid gas removal system. Although the system is considerably simpler than a commercial process, it does contain the three basic unit operations (absorption, flash vaporization, and stripping) found in the Rectisol process.

Overall system performance can be discussed using run AM-30 as an example. This run was made using 7.1 feet of packing in the absorption column and 21.3 feet of packing in the stripper. Because current emphasis is on absorber operation, each of the four runs shown here utilized the total packed height of the stripper so that esentially clean methanol could be fed to the absorber. This was verified through the analysis of the methanol leaving the stripper.

The mass balance report of AM-30 shows that each compound, with the exception of CO_2, was within 4.0% of complete closure. The CO_2 balance offset can be traced to flow meter calibration problems for the Acid Gas stream and also to failure to account for the methanol present in this stream. This problem also appeared in runs 36 and 37 and has been corrected for future runs. A mass balance of this quality gives added significance to the results obtained especially for the sulfur compounds. Methanol analyses of the three exiting gas streams were not done for this run, but other runs showed negligible amounts in the Sweet Gas with the concentration increasing for the Flash Gas and the Acid Gas. The increased presence of methanol in these streams was expected because they are at decreased pressure and increased temperature.

The choice of the operating pressure for the flash tank is based on several factors. The Rectisol process contains a series of flashing operations designed to remove the acid gases from the solvent and allow for some separation of the sulfur compounds from CO_2. In our system, operation at moderate pressures (4.4-11.2 atm. abs.) provides some insight into how these gases distribute. Also, flash tank operation indicates how closely our vapor- liquid equilibrium model predicts actual system performance. Moderately high pressures are a better test as to how well the VLE model handles departures from ideal behavior. Finally, trial and error has shown that this range of operating pressures is more compatible with overall system performance; the effect of process controller oscillation on sampling and steady state operation is reduced.

Stripper operating pressure was 1.7 atmospheres absolute for AM-30 and for the three other runs. In practice, stripper operating conditions are the result of a balance between temperature and pressure to minimize solvent losses and yet regenerate the solvent. The pressure used here represents the lowest that the stripper pressure controller could maintain and still avoid the adverse influence of process controller oscillation. Inlet temperature to the stripper was not controlled but will be used later to facilitate stripper simulation efforts.

Since the focus of these runs in on absorber performance, column pressure was varied along with liquid flow rate and inlet liquid tem-

perature. Variation in Sour Gas CO2 concentration introduced additional variation demonstrating the necessity for a mathematical model in process analysis. The model is described further in the next section.

The temperatures measured throughout the acid gas removal system are very important in terms of understanding the process. Since the sampling of liquid and gas from the column packing proved to be unsuccessful, column temperature profiles take on added significance in determining mass transfer rates. Current modeling efforts rely on comparisons of measured and predicted column temperature profiles. This profile is indicative of the rate of CO2 transfer because of the large heat effects associated with CO2 absorption in methanol.

The absorber temperature profiles are reported in the Appendix for all four runs and were measured with sensors located on the outside of the absorption column wall. For all runs, temperature sensor TT350, located at 4.8 feet above both the gas inlet and the bottom of the packing, did not stay fastened to the column wall and is probably inaccurate. In addition, the lowest temperature measured, TT353, at 0.3 feet, is probably located too close to the packing end and therefore not useful. These will be moved for future runs.

Both height of packing and height above the gas inlet are reported to point out that end effects have been minimized. In earlier runs, the gas inlet was located 7 inches below the bottom of the packing and significant end effects were observed in those runs. Because it is important in the modeling efforts to eliminate end effects, the bottom of the absorber was reconstructed to ensure that the mass transfer takes place in the column packing and not above or below it.

An interesting observation can be made concerning the temperature profile of the stripper. At the top of the column, the acid gases flash due to the pressure reduction of the solvent entering from the flash tank. This can be noted from the decreasing temperatures measured in the top part of the column. Further down the column, the temperature begins to increase as the influence of the warm stripping nitrogen is felt. A lower flash tank pressure would reduce this flashing effect as the pressure drop between the flash tank and the stripper would be less.

2. Acid Gas Distribution in the AGRS

Table 4 shows the ratios of acid gas concentrations for the various gas streams in the AGRS. The ratios of the acid gases exiting the stripper in the concentrated Acid Gas stream are the same as those in the entering Sour Gas stream. This is the expected result for non-selective physical solvent systems.

Because of problems with the analysis of low levels of CO2 in the Sweet Gas stream, not much can be said of the ratios involving CO2. However, it appears that H2S is removed at a slightly higher efficiency than COS when the ratios in the Sour Gas stream are compared to the

Sweet Gas stream. This is expected because H2S has a slightly higher solubility than COS over the temperature range used.

The Flash Gas ratios reflect the amount of CO2 initially fed to the system. Here, the ratios of CO2 to H2S and COS are about twice those found in the entering Sour Gas stream. Changing the flash tank operating presures would improve this selectivity. This indicates that there is the potential to concentrate the CO2 fed to the system through a flashing process. The ratio of the sulfur compounds (H2S:COS) is again less than that found in the Sour Gas. The fact that H2S is more soluble than COS means that proportionately less H2S will flash upon pressure reduction.

3. Absorber Column Performance

Table 5 contains the results associated with absorber column performance for four integrated runs treating a gas produced in the gasifier. An attempt was made to vary system conditions to show the effect on acid gas removal efficiencies. A comparison of the results from these runs underline the importance of mathematical modeling to analyze system performance.

All runs show an acid gas removal efficiency of at least 94.0% for the range of operating conditions used. Also, only small differences in component removal efficiencies can be seen despite the changes in packed height, liquid flow rate, and operating pressure. The reason for this can be explained by examining the inlet gas compositions for each run and by considering mass transfer limitations.

Gasifier operation will dictate both the composition and flow rate of the gas stream fed to the AGRS. For the four runs shown here, the inlet gas flow rate to the absorber varied only slightly but the CO2 content of the stream varied significantly. This affects the absorber column temperature profile as the magnitude of the absorption heat effect depends on the amount of CO2 absorbed. As the temperature increases, the amount of acid gases removed decreases.

This effect can be seen by comparing the results of runs 35 and 36 in Table 5. Although 35 was made at a higher absorber pressure and lower inlet liquid temperature, the acid gas removal efficiencies are approximately the same. A closer look shows that there is 7% more CO2 in the entering gas stream for run 35. The increased thermal effect tends to offset the expected increase in column removal efficiency.

Run 37, made with three times the packed height used in the other runs, resulted in only small improvements in acid gas removal efficiency. This indicates that for the range of operating conditions used, acid gas removal efficiency has reached an upper limit. improvements could be obtained with lower inlet temperatures, higher operating pressures and larger liquid flow rates.

The effect of changing liquid flow rates can be seen by comparing runs 30 and 35. The increase in the liquid flow rate from 60.7

lb-moles/hr/sq.ft. to 72.1 lb-moles/hr/sq.ft. improved CO2 removal efficiency by 1.8%. H2S and COS removal remained about the same probably because of mass transfer limitations. Future runs will be made at higher L/G ratios to examine more completely the effect of this variable on removal efficiency.

The results from these four runs clearly point to the need to develop a mathematical model to assist with the analysis of experimental results and provide a basis for analyzing more complicated process configurations. Although there exists the possibility of feeding synthetic gas streams to the AGRS, the most useful information comes from runs where gasifier product gas is used. Because of the variability associated with gasifier operation, a carefully structured experimental plan would be difficult to complete. The strategy used thus far has been to cover a wide range of operating conditions. Then, a mathematical model will be used to extend these results to process situations that cannot be studied with the pilot plant.

PROCESS MODELING

At present, mathematical modeling efforts have mainly dealt with describing the operation of the packed absorption column for the adiabatic case. A calculational technique first described by Feintuch and Treybal (7,8) for packed column design has been implemented on the computer and is currently used for analyzing runs where synthetic gas mixtures of carbon dioxide and nitrogen are fed to the absorption column. Thus far, only cases for the absorption of a single component have been modeled but a multicomponent case is currently being developed to describe the transfer of H2S, COS, CS2, CO2, H2, N2, CO, and CH4. Additional hydrocarbons will be added to this list as the experimental program moves into the gasification of coal-char mixtures.

The calculational technique described accounts for the mass and heat transfer resistances in both the liquid and gas phases. Solvent evaporation is also incorporated into the calculation. It is an essentially rigorous solution to a highly non-linear set of partial differential equations which treats a packed column as a true differential device without resorting to a stage -wise, tray tower analogy (8). The method involves dividing the tower height into differential sections and satisfying heat transfer, mass transfer, and equilibrium relationships for each section. Experimental verification of this technique for air-water-ammonia systems at ambient pressure and temperature has been shown by Raal and Khurana (9). Feintuch (8) suggests an extension of this technique to complex multicomponent systems but no literature data are available with which to compare the results. Initial indications from our work indicate that this calculational method applies to the multicomponent system studied here.

As a first step in model development, computer simulation for the adiabatic absorption of CO2 in methanol was tried. Results for a re-

cent synthetic gas run (AM-32) are presented in Figure 4. Here, the liquid temperature profile in the absorber is compared to the model prediction. Process conditions for AM-32 are shown in Table 6. Thus far, excellent agreement between model prediction and experimental data has been seen for column temperature profiles and removal efficiencies. The model also predicts both liquid and gas flow rate and composition profiles for both design and analysis approaches to packed column performance. The model has been used for simulation of systems containing H2S-N2- CH3OH and COS-N2-CH3OH. A multicomponent case is presently being developed for the components mentioned above. An upcoming EPA technical report will provide a more detailed description of mathematical modelng efforts.

FUTURE EXPERIMENTAL WORK

Figure 5 and Table 7 illustrate the present scope of our research program and plans for future work. Currently, we anticipate using a chemical solvent following the evaluation of refrigerated methanol and should begin this work sometime during 1981. A full evaluation of each solvent used includes experimental runs with both crude coal gas and synthetic gas mixtures. A computer simulation package for each system is planned. Also, vapor-liquid equilibrium model development will parallel all anticipated pilot plant studies. Capability to measure both binary and multicomponent VLE information exists and has already been utilized. This collection of information, along with an assessment of the fate of certain trace compounds, should provide the basis for evaluating the relative merits of the solvents proposed for acid gas removal in coal gasification processes.

FIGURE 4

PACKED ABSORPTION COLUMN
LIQUID TEMPERATURE PROFILE FOR
SYNGAS RUN AM-32

AM-32

——————— Computer Model Prediction.

⊙ Experimental Data

Height of Packing, Ft

T (°F)
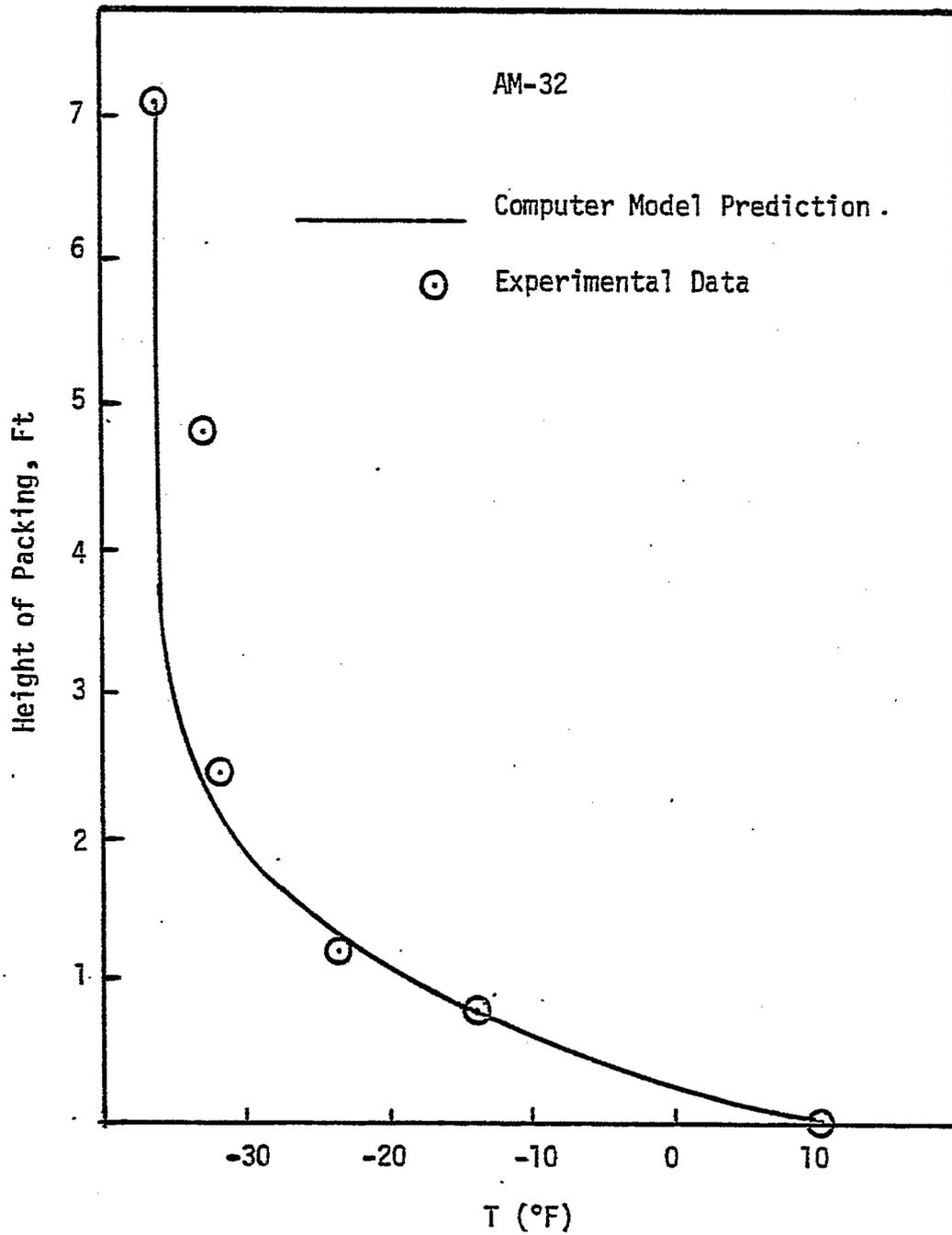
TABLE 6

PROCESS CONDITIONS FOR SYNTHETIC GAS RUN AM-32

Liquid Flow Rate	61.05 lb moles/hr/ft^2
T_L in	-36.1°F
Gas Flow Rate	17.31 lb moles/hr/ft^2
T_G in	57.4°F
Pressure	28.0 Atmospheres absolute
Inlet Gas Composition	33.73 mole percent CO_2 66.27 mole percent N_2
Outlet Gas Composition	0.92 mole percent CO_2 99.08 mole percent N_2
CO_2 Removal Efficiency	98.10%

FIGURE 5

AGRS RESEARCH PROGRAM

574
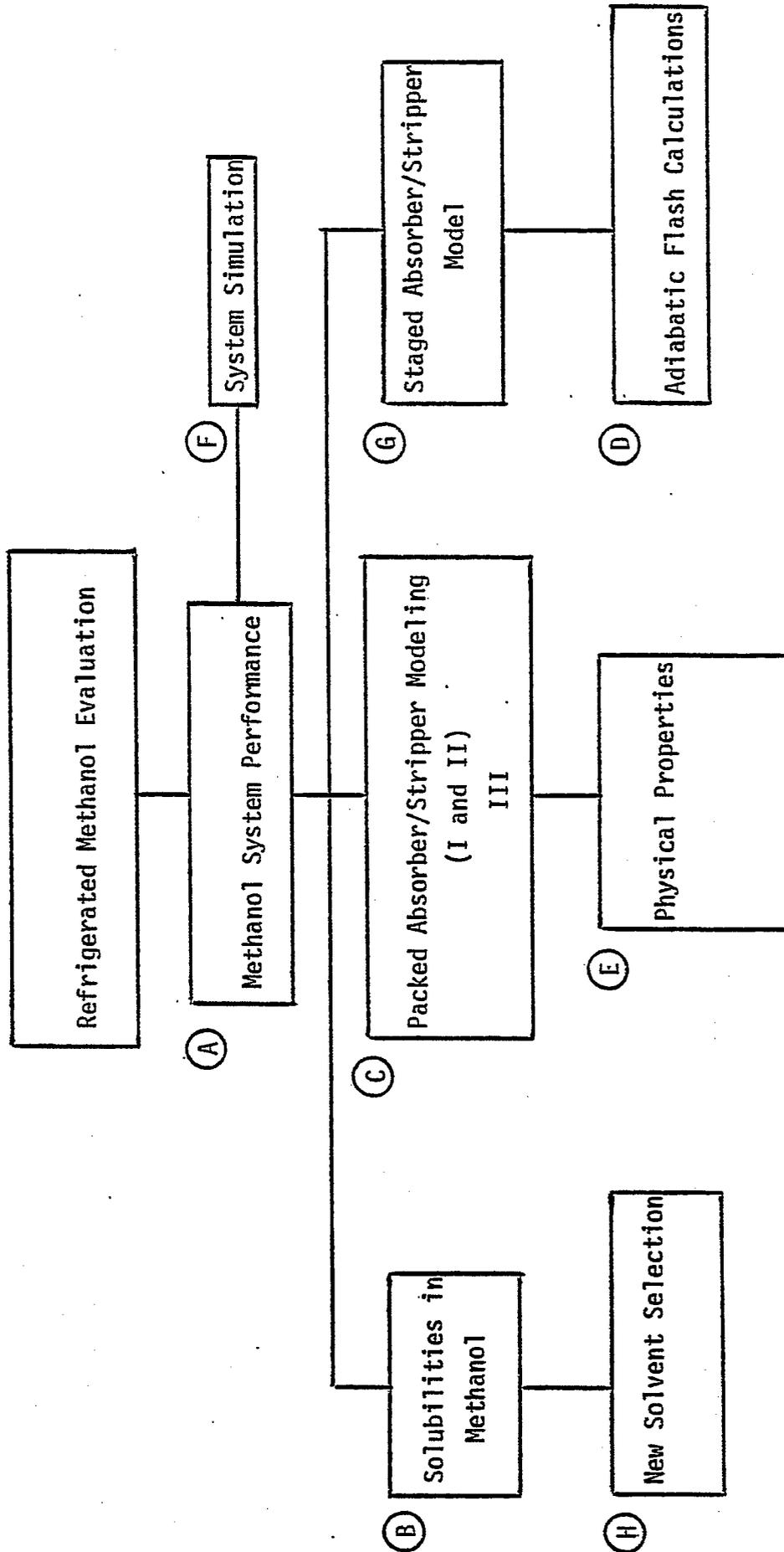
TABLE 7

A. Methanol System Performance

    1. CO2, H2S, COS and other sulfur gas removal

    2. Hydrocarbons, particularly aromatics, removal and accumulation in solvent

    3. Thermal behavior

    4. Relationship of gasifier operation to AGRS performance

    5. Comparison of SYNGAS and crude coal gas operations

    6. Methanol losses from absorber, flash tank and stripper

    7. Solvent stability

B. Solubilities in Methanol

    1. Use current VLE model (Ferrell, Rousseau and Matange, 1980) in absorber/stripper/flash tank calculations

    2. Use current VLE model to develop methods for calculating heats of solution

    3. Obtain VLE data on COS, CS2, and other important gases, and incorporate into VLE model

    4. Modify current model to use Wilson and/or UNIQUAC equations

C. Packed Absorber/Stripper Models I, II, and III

Model I (SIMPAK): considers a three-component system in which the carrier gas is insoluble

Model II (MCOMP): places no restrictions on number of components or solubility of carrier gas

Model III (von Stockar method): relies on an unsteady state description of the packed column, and is believed to have better convergence properties than approach of Model I and II

    1. Model development for packed columns

    2. Use of model in simulation of SYNGAS operation

3. Use of model in evaluation of crude coal gas operation

4. Use of model to guide selection of AGRS operating variables (e.g. N2 flow rate to stripper to maximize sulfur concentration of feed stream to sulfur recovery unit.)

D. Adiabatic Flash Calculation

1. Model flash tank in AGRS

2. Describe flashing.process as liquid enters stripper

E. Physical Properties and Equipment Parameters

1. Document, catalog and make available all physical properties, diffusivities and packing characteristics used in system

F. System Simulation

1. Bring all system elements together in a program to examine unit interactions and optimize operating conditions

G. Staged Absorber/Stripper Model

1. Extension of Packed column models to staged columns to provide necessary tools for system simulation

H. New Solvent Selection

1. Begin to consider next solvent system to study (e.g. hot potassium carbonate) and determine needed information to begin evaluation

2. Determine advantages/disadvantages of potential solvents

3. Provide basis for choosing desirable features of acid gas removal solvents from environmental, process, and energy considerations

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