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A WASTEWATER TREATMENT TRAIN FOR FIXED BED COAL
GASIFICATION

Semi-annual Progress Report for Period May 1—October 31, 1980

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December 1, 1980

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U. S. DEPARTMENT OF ENERGY

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A WASTEWATER TREATMENT TRAIN
for
FIXED BED COAL GASIFICATION
Semi-annual Progress Report
for the period 5/1/80 to 10/31/80

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ABSTRACT

The objective of this research is to develop a series of procedures that enable wastewater from a stirred fixed bed gasification process to be treated in an environmentally acceptable manner.

Experiments are conducted on a laboratory scale using samples of gasifier wastewater. The linkage of processes used include sulfide stripping, pH adjustment followed by free and fixed ammonia removal, pH adjustment for chemical precipitation of organics, and biological treatment in an activated sludge type configuration.

The pre-treatment technique employed provides almost 50% organic removal from the wastewater prior to biological processing; with the organics being accumulated into the sludge phase. The interaction of generated sludges with RCRA regulations is the subject of additional research.

A series of continuous biological reactors is operational with hydraulic detention times of 1.0 days, and sludge ages in excess of 20 days. A removal in excess of 80% of COD is accomplished by the biological reactors when the wastewater is pre-treated by the manner developed.

Keywords:

Coal gasification
wastewater
activated sludge

phenolics
environmental control technology

SEMI-ANNUAL RESEARCH PROGRESS REPORT

Contract # DE-AC21-80MC14372

A Wastewater Treatment Train for Fixed Bed Coal Gasification

report for the period 5/1/80 to 10/31/80

by

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The overall objective of this research is to develop a series of techniques that enable wastewater from the METC stirred-fixed bed gasification plant to be treated to the extent required for ultimate discharge and/or reuse. Biological processing of gasification wastewaters is selected as the core technique to be utilized for a broadbrush approach to carbonaceous removals. Biological techniques have the ability to degrade a wide variety of organic constituents, have shown commercial applicability to refinery and coke plant wastewaters, and have shown applicability to fluidized bed coal gasification wastewaters(1).

As a "living" unit operation on the list of available techniques for environmental control, biological processes have defined requirements regarding the nature and condition of wastewaters that may be thus handled. Consequently, suitable pre-treatment techniques must be developed along with the development of the biological operation to assure acceptable overall treatment. The available biological "treatability data" for the refinery industry, coke plant industry, and bench scaled coal conversion wastewaters reflects wide variations in process efficiencies and stabilities.

If we accept the premise that biological systems must follow the same laws of nature, observed temporal deviations in process efficiency and process stability must stem from deviations in the nature of the feed and ambient conditions of the biological reactor. Accordingly, a substantial effort was conducted as part of this research to develop a rational gasifier wastewater pre-treatment train to prepare wastewater for subsequent feed to an aerobic biological reactor of the "activated sludge" design. As part of overall research goals, definitions of the capabilities of biological processes and biokinetic rate equations are developed.

To date, the University of Pittsburgh has received three different shipments of METC gasifier wastewater. In all cases, the raw wastewater contains significant levels of sulfide and ammonia. Initial perceptions of the wastewater are that it is an amber colored material with considerable phenolic-cresol like odors. High levels of ammonia are evident by smell; high levels of oily materials are visually evident. Table #1 presents a preliminary characterization of the first two wastewaters received; the third shipment is now undergoing chemical characterization analysis and will be reported in subsequent project reports.

The two samples differ considerably in overall level of organic content, and in the qualitative makeup of the organic fraction. The first sample has a phenol/TOC ratio of 0.069, while the second has a more realistic value of 0.44. Data compiled by Neufeld et al (1) indicates that a representative range for phenol/TOC ratio is as shown on table #2. Further conversations with DOE-METC indicated that the first wastewater is considered to

TABLE #1

CHARACTERIZATION OF WASTEWATER

<u>Shipment #1</u>		<u>Shipment #2</u>
Item	Concentration	Concentration
Phenol	970 mg/L	2375 mg/L
COD	53,024 mg/L	13,350 mg/L
TOC	14,102 mg/L	5374 mg/L
TIC	30 mg/L	242 mg/L
Total Residue	72,334 mg/L	1349 mg/L
Fixed Residue	1,334 mg/L	143.2 mg/L
Volatile Residue	71,000 mg/L	1205.8 mg/L
Freon Sol. Oil & Grease	356 mg/L	1495.0 mg/L
Acetone Sol. Oil & Grease	1633 mg/L	106.3 mg/L
pH	7.5	8.0
Alkalinity (pH4.5)	2100 mg/L	23,750 mg/L
SCN	----	372 mg/L
NH ₃	11,000 mg/L	3200 mg/L
Phenol/TOC ratio	.069	.44

Table #2

Phenol/TOC Ratios for Various
Coal Conversion Processes (after ref #1)

<u>Coal Type</u>	<u>Process</u>	<u>Phenol/TOC (lb/lb)</u>
Lignite	SYNTHANE-PDU	0.265
Lignite	GFETC-400psi	0.819
Lignite	HYGAS	0.292
Sub-bituminous	SYNTHANE	0.395
Dituminous	SYNTHANE	0.432
	METC	0.44

for comparison purposes, the
phenol/TOC ratio for $C_6H_5OH = 1.3$

be non-representative and was collected from a side stream, while the second sample was more representative of larger scaled operations. While chemical characterization of the third sample is not yet complete, preliminary data indicates that it is more like the second sample in chemical constituents.

Pre-treatment

Upon receiving the first shipment of gasifier wastewater, it became apparent that increased attention to development of a pre-treatment train was in order.

The pre-treatment technique developed to treat this first shipment is a linkage of steps as follows:

Step 1: Air Stripping This is accomplished in the laboratory via an air stone inserted into the wastewater. Such aeration liberates noticeable quantities of H_2S and other volatile organic fractions.

Step 2: Lime Addition Lime (as $CaOH$) is added to the aerated wastewater in sufficient quantities to bring the pH to the range of $10\frac{1}{2}$ to 11. A mixing time of at least 30 minutes is utilized to assure completion of any reactions.

Step 3: Filtration to remove lime sludge A large Buchner funnel with coarse grade Whatman filter paper is utilized to remove excess lime added in step #1. The resultant sludge is brown in color indicating the presence of organic materials. The ratio of VSS/SS of this sludge is measured to be about 13%.

Step 4: Ammonia Stripping Ammonia is stripped batch wise in a modified fifteen gallon electric glass lined hot water heater. Air is introduced at the bottom of the laboratory ammonia stripper and the temperature of water inside the stripper is maintained at 140°F. The wastewater is kept in the ammonia stripper until the total ammonia in solution is at a concentration of about 500 mg/L. The wastewater is then removed from the ammonia stripper and placed into a large glass jar where it is subsequently cooled. The pH of the wastewater coming out of the ammonia stripper is within approximately 1 pH unit of the pH going into the ammonia stripper.

Step 5: The wastewater after ammonia stripping is then filtered through large Buchner funnels in a manner similar to that of step 3. A sludge is formed which is blackish in nature and contains on the average of 72½% volatile solids, thus most of the sludge removed at this step is organic in nature.

Step 6: The wastewater is further acidified to a pH of about 3 using sulfuric acid. Mixing is maintained for a period of about five minutes to achieve completion of reactions.

Step 7: The wastewater, which is now at pH 3, is allowed to settle or is filtered. This sludge developed in step 6 settles very very rapidly with the resulting sludge consisting of approximately 49% volatile material.

Step 8: NaOH is then added to the wastewater so that the final pH is approximately 7. This water is now considered sufficiently pre-treated to be feed to the biological reactors.

Step 9: Biological Reaction Phase: In this phase, the pre-treated bio-feed is diluted to 10% wastewater, 20% wastewater, 30% wastewater, and 40%wastewater, and is fed on a continuous basis to completely mixed activated sludge type reactors. The reactors are held at sludge ages of about 20 days (or more), with hydraulic retention times of only 1.0 day. Hydraulic retention times of less than 1 day may be achieved using this configuration; however, we are limited by the availability of feed to the overall experimental scheme to attempt shorter times at this point in time. It is envisioned that more concentrated wastewater feed may be readily treated by this pre-treatment and bioreactor configuration.

Pre-treatment Results

The purpose of judicious adjustment of pH followed by filtration was to remove organic carbonaceous materials which would otherwise have to be removed in the biological reaction step. The philosophy taken is that removal of organic materials by any means prior to the biological step is desirable, since the energy required for aeration and oxygenation in the biological step is thus minimized. The price to be paid by conducting this pretreatment is that of addition of acid and base at various points to accomplish judicious pH adjustment. It is not clear at this point in research whether any of the pH adjustment steps

may be eliminated or perhaps combined. Such elimination or combination would result in the subsequent reduction of chemical requirements, and the reduction in numbers of different types of sludges and pieces of equipment to contend with on a commercial scale.

Figure 1 is a schematic of the overall pretreatment train used to prepare the METC wastewater for biological digestion as now used at the University of Pittsburgh.

Figure 2 is a bar-graph plot of TOC removal at key sampling steps within the pre-treatment train. Figure 2 shows that the initial TOC (total organic carbon) of the raw wastewater is approximately 12,800 mg/L. After air stripping and lime pH adjustment, the TOC appears to be somewhat unchanged. Indeed, even after ammonia stripping, there is only a small reduction in overall TOC of the wastewater. The liquid phase corresponding to step number 5 (the first sludge produced after ammonia stripping) has a TOC of about 10,500 mg/L, while the supernate has a TOC of about 7,000 mg/L after further pH adjustment. The overall TOC removal by such judicious pH adjustment and precipitation is about 47%. This organic removal represents a reduced loading to the aerobic biological reactor step, and in a commercial scaled operation would similarly result in a decrease of oxygen and energy required for processing. The sludge that is generated by the pre-treatment step, however, must be disposed of in a manner consistent with recent RCRA hazardous waste regulations. Further

FIGURE #1
Process Flow Diagram

FIGURE #2

TOC LEVELS AT VARIOUS POINTS IN

PRETREATMENT TRAIN

research is envisioned in this area.

Figure 3 is a similar plot of phenol levels at the same sampling steps in the pre-treatment train. This figure indicates that phenol is not removed to any great extent during the course of treatment. Thus, the organics that are removed in the pre-treatment train are non-phenolic in nature and most likely only partially degradable.

The data presented on figures 2 and 3 are for the first shipment of gasifier wastewater. The second shipment of gasifier wastewater was received in a series of several drums. It was noted during the course of experimentation that the contents of each drum was different from each other, and noticeably different than the first shipment. The quantities of sludge produced from materials in each of the barrels varied considerably from barrel to barrel with more sludges being produced from barrels which were clearly more contaminated and less sludges being produced from barrels being less contaminated. By carrying out the pre-treatment step as indicated on figure 1 for the large variations in raw wastewater feed, a reasonably consistent quality of pre-treated wastewater was able to be provided to the biological reactor step.

Results of Biological Testing to Date

As indicated above, four continuous culture activated sludge type bio-reactors were maintained at dilutions of the pre-treated bio-feed of 10% gasifier water, 20% gasifier water, 30% gasifier water and 40% gasifier wastewater. Each

Figure #3

PHENOL LEVELS AT VARIOUS POINTS IN
PRETREATMENT TRAIN

of the reactors had a sludge age of at least 20 days, and carefully controlled hydraulic retention times of 1.0 days. The pH of the reactor was controlled with a Horizon brand pH controller equipped with acid and base feed pumps. The pH was controlled to approximately 7.0 plus or minus 0.1. When the pH exceeded any of these limits, the appropriate acid or base feed pump would be automatically turned on for pH readjustment.

During the startup phases of biological reactors, and periodically during the course of the experimentation, considerable foam was noted on the surface of the aeration tanks. Nalco brand anti-foam agent was applied dropwise for foam reduction. The use of anti-foam was applied sparingly since steel industry experience with anti-foam indicates that continuous applications often result in sludge deflocculation and loss of bio-sludge over the weir of secondary clarifiers.

Figure 4 is a plot of reactor number 1 effluent and reactor level VSS versus time into the run for, what was determined to be, a steady state period. Also on figure 1, are plots of feed and effluent soluble TOC versus time during the course of the run. As may be seen from this figure, the average influent TOC to the bio-reactors was 180 mg/L with an effluent averaging 52 mg/L. The dotted lines on each of the figures represent one standard deviation above and below the mean values. The values of the mean plus one standard deviation and the mean minus one standard deviation are also listed on the figures with the data points as indicated. Similar data for the 20% gasifier feed is shown on figure number 5, while similar data for reactor number 3 at 30% gasifier wastewater is shown on figures 6, and 6A. Similar steady state data for reactor

REACTOR NO.1 - 10% GASIFIER WATER

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FIGURE #4

Reactor and Effluent VSS vs Time

Feed and Effluent TOC vs Time

REACTOR NO. 2 - 20% GASIFIER WATER

Reactor and Effluent VSS vs Time

Feed and Effluent TOC vs Time

REACTOR NO. 3 - 30% GASIFIER WATER

Figure #6

Reactor and Effluent VSS vs Time

REACTOR NO. 3 - 30% GASIFIER WATER

Feed and Effluent TOC vs Time

FIGURE 6-A

number 4 at 40% gasifier wastewater is shown on figure number 7 and figure number 7A. As shown on figure number 7A, the influent TOC to reactor number 4 was 656.8 mg/L with an effluent TOC of 187 mg/L indicating an overall removal efficiency during the steady state period of about 72% on a soluble total organic carbon basis.

Figure 8 is a summary plot of percent TOC removal versus fraction of gasifier wastewater in the feed. It can be seen that for the four cases considered, approximately 72% TOC removal was maintained.

Figure 9 is a plot of TOC removal rate, measured as pounds TOC removed per pound VSS per day, as a function of TOC in the effluent. This is a first attempt at measuring biokinetics. As may be seen by this figure, a visual relationship appears to be a horizontal line and not a line with intercept at the origin. This may be expected since the sludge ages for all reactors were in excess of 20 days, a value which from prior research indicates virtual complete degradation of the biologically degradable fraction of TOC. By dividing the effluent TOC by the fraction of wastewater to the biological reactor, an average value of non-degradable TOC of about 473 mg/L becomes apparent. The data as shown on figure 9 implies that even if one could treat raw gasifier wastewater without any dilution, a residual soluble total organic carbon of approximately 473 mg/L would still result. It is unclear whether BAT standards for coal conversion facilities would dictate removal of this non-degradable fraction. The phenolic level, however, of this non-degradable fraction may be considered as being 0.

REACTOR NO.4 - 40% GASIFIER WATER

Reactor and Effluent VSS vs Time

Figure #7

REACTOR NO. 4 - 40% GASIFIER WATER

FIGURE # 7-A

Feed and Effluent TOC vs Time

FIGURE #8

BIOLOGICAL TREATMENT
OF
METC GASIFIER WASTEWATER

FIGURE #9

TOC Removal Rate vs TOC

Figure 10 represents preliminary results in calculations of sludge production parameters for the biological reactors using pre-treated gasification wastewater. As shown on this figure, a value of yield coefficient, "a" is 0.83 lbs VSS/lb TOC removed, while the decay coefficient, "b" equals 0.05 per day. These values may be incorporated to estimate an overall quantity of bio-sludge on a dry weight basis which must be disposed of from a commercial sized coal conversion wastewater treatment facility. These values agree quite closely with other values developed by Neufeld using Synthane wastewaters(1).

Figure 11 is a plot of percent COD removal versus fraction of gasifier wastewater in feed. This figure, conceptually similar to figure 8 for soluble organic carbon, indicates an overall COD removal of approximately 84% for the 10, 20, and 30% fraction of gasifier wastewater in bio-reactor feed with a somewhat lower percent COD removal at the 40% gasifier wastewater feed. The significance in having a higher fraction of COD removal by biological degradation as compared to TOC removal is that many of the organics removed appear to be those which exert COD's and hence are readily oxidizable during the COD tests. Accordingly, those materials which are not removed in the biological degradation step must be either of an aromatic nature (since aromatics usually do not oxidize well under the conditions of the COD test) or of a high molecular weight polycyclic nature which also are not oxidized readily under the conditions of the COD test. Such information however is only qualitative and speculative in assessing the characterization of the non-degradable fraction of TOC from the overall pre-treatment and biological treatment steps.

FIGURE #10

Evaluation of Sludge Production Parameter

FIGURE #11

Summary of Results and Conclusions

1. A linkage of simple processes has been developed to pre-treat gasifier wastewater from the stirred bed METC facility which prepares such wastewater for biological wastewater treatment. The pre-treatment train consists of steps of aeration, ammonia stripping, and pH adjustment which results in approximately 50% removal of soluble organic carbon materials prior to reaching the biological treatment step. The pre-treatment train concentrates these organic materials into readily dewaterable sludges which must be further disposed of.
2. Steady state conditions have been achieved in the biological reaction step at sludge ages in excess of 20 days, with hydraulic detention times of 1 day. Consistent results have been achieved for TOC removals; with TOC removals averaging approximately 72% overall and COD removals averaging 84% overall.
3. A 40% solution of gasifier wastewater has been found to be treatable in our biological systems. Prior research by other investigators has shown that 40% gasifier wastewater may be treatable in biological reactors however, such treatment has resulted in unstable operation. No such unstable operation has been found to exist for this system.
4. Lime addition results in the formation of sludges before and after the ammonia stripping operation. The sludges produced during the course of the pre-treatment train have been found to range from 13% volatile matter for the lime sludge prior to ammonia stripping, to 72½% volatile matter for sludges produced just after ammonia stripping. It is envisioned that polymerization is taking place in the

in the hot alkaline environment of the ammonia stripper which results in organic removal into the sludge phase.

Continuation of Research

Research is continuing in the area of increasing the fraction of gasifier wastewater treated to the biological reaction step. In addition, preliminary evaluations are being made of heavy metals in the aqueous phase at each of the points around the pre-treatment step. Evaluations are being made to attempt to close the material balance for inorganic materials added and subsequently removed in sludge phases around the pre-treatment step. Characterizations are also being made at each sampling point in the pre-treatment step as to organic removal, phenolic removal, cyanide removals, and other key pollutional species.

Acknowledgement

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References

- 1) Neufeld, R.D., Drummond, C.J., Johnson, G.E.
"Biokinetics of Activated Sludge Treatment of SYNTHANE Fluidized Bed Gasification Wastewaters"
Preprints of papers presented at the Fuels Division, American Chemical Society Meeting at Anaheim, CA, March 12-17, 1978, volume 23 #2, pp175-186 (available from the American Chemical Society, Washington, D.C.)