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Preliminary Study on Treatment of Contaminated Groundwater From the Taylorville Gasifier Site

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HWRIC RR 017

Preliminary Study on Treatment of Contaminated Groundwater from the Taylorville Gasifier Site

by

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Printed in January 1988

Illinois Department of Energy and Natural Resources

HWRIC RR 017

PRELIMINARY STUDY ON TREATMENT OF CONTAMINATED GROUNDWATER FROM THE TAYLORVILLE GASIFIER SITE

Prepared For

State of Illinois Department of Energy and Natural Resources
Hazardous Waste Research and Information Center
Savoy, Illinois

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ABSTRACT

Groundwater and soil at the site of an abandoned coal gasification plant in Taylorville, Illinois have been contaminated with compounds associated with coal conversion process waters. A preliminary study to assess the feasibility of using ethanol as a means of increasing the solubility of compounds adsorbed within the soil matrix followed by treatment of the ethanol/groundwater extract in an expanded-bed anaerobic granular activated carbon (GAC) reactor was conducted. Results of the study indicate that compounds in the groundwater are highly adsorbable on GAC, and do not interfere with the anaerobic degradation of ethanol in the reactor. Soil extractions with varying ethanol/water ratios were able to remove many additional low water solubility compounds from the soil.

EXECUTIVE SUMMARY

Groundwater and contaminated soil were obtained from the site of an abandoned coal gasification plant in Taylorville, Illinois for a short-term preliminary treatability study. The proposed treatment scheme involves injection of ethanol at the site to increase the solubility of compounds adsorbed on the soil matrix, followed by treatment of the groundwater/ethanol extract in an expanded-bed anaerobic granular activated carbon (GAC) reactor. Hydrophobic contaminants removed by the ethanol would be expected to be easily adsorbed on the GAC in the reactor, while the ethanol itself would be readily degradable by the anaerobic culture in the reactor.

To assess the feasibility of the proposed treatment system, the ability of the GAC to adsorb contaminants already present in the liquid phase at the site must be determined. The ability of the anaerobic culture present as a fixed film on the GAC to provide biodegradation of the ethanol in the presence of these same compounds must be demonstrated, and the potential for removal of additional compounds from the soil with ethanol must be also be demonstrated.

Due to the short duration of the study, an adequate analytical technique for quantitatively identifying the compounds associated with the contamination was not developed. Analysis for this study was performed by qualitative gas chromatography (GC). Water obtained from the site was subjected to fixed-column and batch (isotherm) adsorption experiments. These studies indicated that 10-12 of approximately 50 major peaks present in the liquid phase at the site were not strongly adsorbed on GAC, and that the adsorbable compounds did not begin to persist until loadings in excess of 10 liters of groundwater per gram of GAC were reached. An oily phase present with the water eventually clogged the packed-bed column, but would not likely interfere with operation of an expanded-bed reactor.

Two laboratory-scale expanded-bed anaerobic GAC reactors with active methanogenic cultures were operated for a 2 month period. One reactor received groundwater as extracted from the site, while the other received groundwater supplemented with 5.63 ml of ethanol per liter of feed. Both reactors were supplemented with a nutrient

solution containing salts and vitamins essential to the growth of anaerobic bacteria. The ethanol-fed reactor produced methane equivalent to 93% of the influent COD during the operating period, indicating almost complete conversion of influent ethanol without inhibition due to contaminants. The other reactor showed evidence of methane production, but it is not known whether this methane was produced by biodegradation of contaminants in the water, or by endogenous respiration of the biomass previously present in the reactor. The effluents from both reactors consistently showed traces of only 3-5 compounds present in the groundwater.

Extractions of soil were performed using various blends of ethanol and water. An XAD resin was used to remove compounds from these extracts for analysis. There were signs that this technique was not able to recover all compounds from the extracts. GC analysis clearly showed the presence in these extracts of compounds which were not present in the groundwater at the site. GC analysis of these extracts showed approximately 3 times as many peaks as the groundwater.

The results of this study suggest that the treatment scheme proposed for the Taylorville site is feasible. Before such a process can be implemented, however, additional research is needed to: 1) develop a reliable, minimal cost analytical technique for identifying the compounds associated with the groundwater and soil extracts, 2) determine the completeness of soil decontamination that is possible through the use of ethanol extraction, and 3) operate an expanded-bed anaerobic GAC reactor on ethanol/water extracts to assess the effects of the additional compounds recovered on performance of the system.

1. INTRODUCTION

Numerous sites in the State of Illinois have groundwater which has been contaminated by substantial concentrations of hazardous organic compounds, including many on the U.S. Environmental Protection Agency (USEPA) list of priority pollutants. A number of these sites are located under abandoned or unused coal gasification plants. One such site is located in Taylorville, Illinois (Illinois Environmental Protection Agency Site # 0218160007), where operation of a gasifier some 40-50 years ago and subsequent abandonment of the site have led to highly contaminated soil and groundwater within the plant site.

Aqueous-phase effluents from coal conversion processes contain a variety of organic contaminants. Singer *et al.*[4] classified these into the following six major groups:

1. Monohydric Phenols
2. Dihydric Phenols
3. Polycyclic Hydroxy Compounds
4. Monocyclic N-Aromatics
5. Polycyclic N-Aromatics
6. Aliphatic Acids

Compounds within these groups are characterized by varying degrees of solubility in water, and by varying degrees of biodegradability. Contaminants previously identified in groundwater extracted from the Taylorville site are mainly from groups 3 and 4 in the above classification, and are almost exclusively characterized by low solubility in water, and by resistance to biodegradation. It is possible that highly soluble contaminants have already migrated from the site, and that those compounds which are biodegradable have already been metabolized by bacteria in the soil.

In addition, it is probable that there are numerous compounds of very low solubility that are remaining within the soil matrix itself and not leaching into the groundwater. Compounds with higher solubility will also remain partially adsorbed within the soil matrix when present in excess of solubility. Thus, treatment of the water alone at such a site deals

with only part of the contamination problem. Ideally, decontamination of the site should include extraction of those compounds which are adsorbed within the soil matrix.

2. OBJECTIVES OF STUDY

This study was undertaken as a short-term preliminary investigation of the feasibility of applying the expanded-bed granular activated carbon (GAC) anaerobic reactor to treatment of groundwater and soil extractions from a gasifier site such as Taylorville. The expanded-bed anaerobic GAC reactor is a fixed-film biological treatment system in which GAC is used as the attachment medium. As has been shown with real and synthetic coal conversion wastewaters, such a system allows simultaneous adsorption of refractory compounds which may be toxic or inhibitory to the biological activity, while allowing anaerobic degradation of biodegradable compounds in the water.[1-3]

Because of the low concentrations and limited biodegradability of contaminants at the site, it is unlikely that biological treatment would be economical or effective in treating contaminated groundwater. Conventional activated carbon treatment is more applicable, but withdrawal and treatment of the water alone will not be a practical way to decontaminate the site because of the slow release of low-solubility contaminants from soil to water.

Injection of a water-miscible solvent to increase the solubility of contaminants is one way to deal with this problem. The solvent should be non-toxic, and easily removed from the water during treatment. An injection/withdrawal system would have to be properly designed to ensure that any contaminants mobilized by the solvent would not migrate from the site. If a biodegradable solvent which is not adsorbable on GAC is selected, the expanded-bed anaerobic GAC reactor could be used to degrade the solvent while adsorbing compounds liberated from the soil without wasting carbon capacity.

A solvent which meets the above criteria is ethanol. Ethanol is water-miscible, non-toxic, readily available, relatively inexpensive, and completely biodegradable anaerobically. Based on these criteria, ethanol was selected for investigation as a possible means of removing contaminants from the soil at the Taylorville site for treatment in an expanded-bed anaerobic GAC reactor.

To apply expanded-bed anaerobic GAC technology to a wastewater, the adsorptive properties of compounds in the water must be determined. This is necessary in order to determine if there are any non-adsorbable compounds in the water, and to estimate the rate

at which carbon will become saturated with adsorbable compounds. The second point is especially important in a biologically active system, as competitive adsorbtion may lead to desertion of less strongly adsorbed species by more strongly adsorbed species at higher loadings, resulting in possible inhibition of the biofilm in the reactor.

In this project, two fluidized-bed anaerobic GAC reactors were operated to treat groundwater extracted from the Taylorville gasifier site. One was fed only groundwater, and the other was fed groundwater supplemented with 5.63 ml of ethanol per liter of groundwater. Both reactors were supplemented with nutrients essential to the maintenance of an anaerobic culture. To assess the adsorptive properties of the groundwater, a fixed-bed GAC adsorption column was operated, and an adsorption isotherm was conducted. To assess the potential for ethanol/water mixtures to enhance solubility of contaminants found on soil from the site, contaminated soil was extracted with varying proportions of ethanol and water.

3. Materials and Methods

3.1 Groundwater and Soil. The groundwater used in this study was obtained from the Taylorville gasifier site, which is illustrated in Figure 1. Four 55-gallon barrels were filled from well number GW 4. Due to the low yield of this well and the lack of time available for the study, a fifth barrel was filled from the pit where the old gas holding tank was located in the excavated area on site. This water was from below the water table, and had accumulated at the surface of the excavation. The barrels were transported to the University of Illinois campus, where they were proportionally blended to provide a uniform water for the investigations performed in the study. The collection, handling, and storage of the water may have resulted in some loss of highly volatile compounds in the water prior to treatment.

After blending, the water was found to have a pH of 6.35, and a total (unfiltered) chemical oxygen demand (COD) of 120 mg/l. Dissolved organic carbon (DOC) proved to be a poor means of analysis, as volatile compounds in the water were stripped along with CO_2 during sample purging. Nitrogen-purged water was found to have a residual DOC of 16-20 mg/l.

Contaminated soil was obtained from the soil/water interface within the excavated area at the site, adjacent to where the old gas holding tank was located. Two 5-gallon plastic buckets were filled with saturated soil, and were subsequently stored at 4°C prior to use.

3.2 Gas Chromatography. Analysis for organic contaminants in the groundwater, soil extracts, and effluents form the treatment reactors was performed with a Hewlett-Packard 5840A gas chromatograph, fitted with the HP 18835B capillary inlet system, and a DB-1 30-meter fused silica capillary column (J and W Scientific, Inc., Folsam, CA). Each injection was temperature programmed at 10°C/minute, from 40°C to 170°C, using a split ratio of 50. Extractions were performed using methylene chloride in the manner outlined in Table 1. Gas chromatography-mass spectrometry was performed on selected samples using a Hewlett-Packard 5830 gas chromatograph interfaced with a Hewlett-Packard mass spectrometer, using the electron-impact positive ion mode. The gas

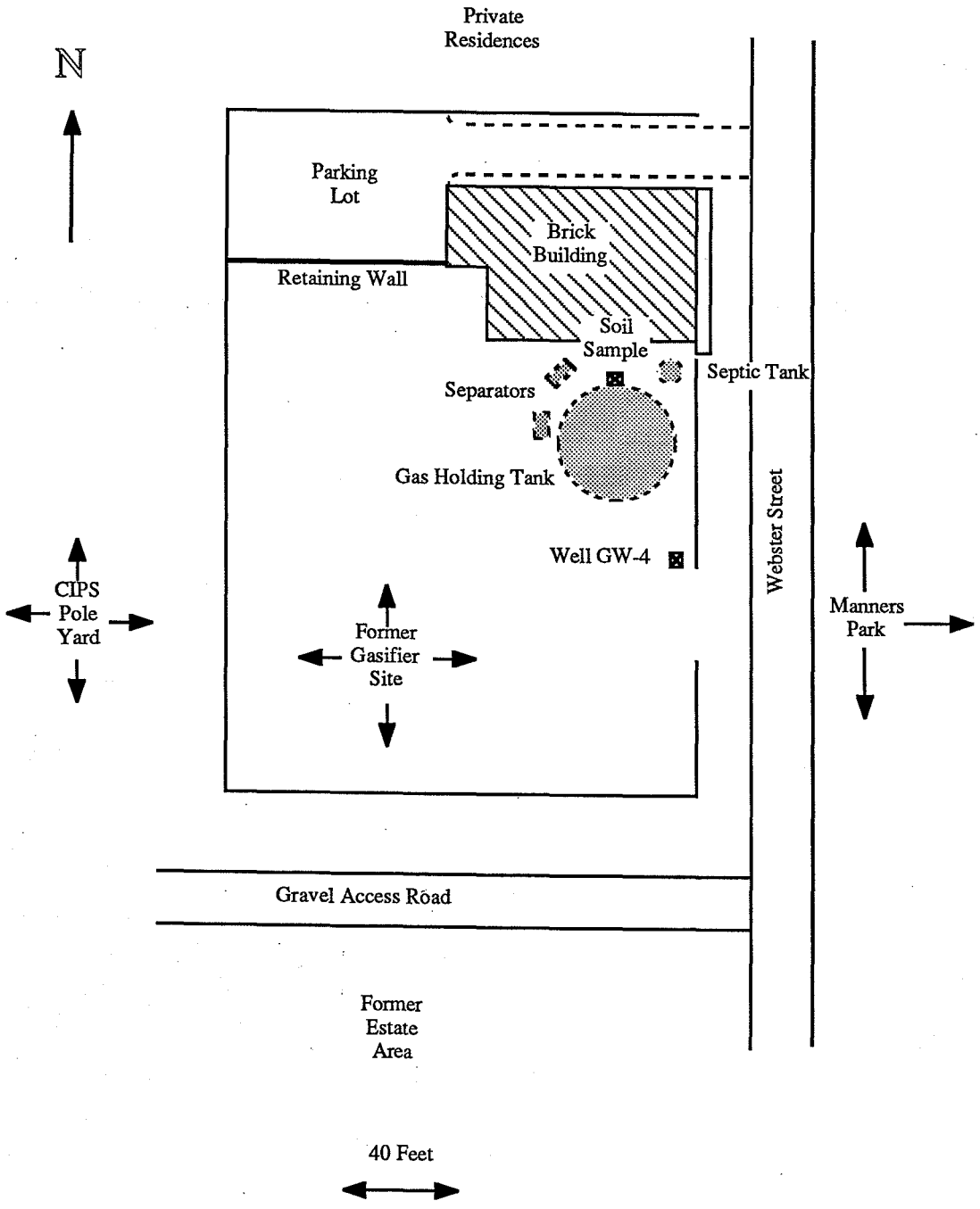

Figure 1: Schematic of Taylorville Gasifier Site Prior to Excavation
(Adapted from Reference 5)

Table 1: Procedure for Extracting Gas Chromatography Samples.

	Fixed-Bed GAC Adsorption Effluents	14-day Room Temp. Isotherm Supernatant	Expanded-Bed Anaerobic GAC Effluents
Sample Volume (ml)	200	150	400
pH Adjustment	Effluent to 7.0 after	Influent to 7.0 before	Reactors at 7.0 before
First Methylene Chloride Addition (ml)	3	3	6
Second and Third Methylene Chloride Additions (ml)	3	3	3
Volume of Methylene Chloride Injected (µl)	1	3	3

chromatograph was equipped with a DB-1 30-meter fused silica capillary column. The GC-MS unit was located at the University of Illinois Environmental Research Laboratory.

3.3 Expanded-Bed Anaerobic GAC Reactors. Two identical reactors were used to assess the treatability of the blended water obtained from the site. A schematic of one of these reactors is given in Figure 2. Each reactor consisted of a 4-inch inner diameter plexiglass tube, surrounded by a concentric tube which served as a temperature-control water jacket. Conical influent (bottom) and effluent (top) headers were fitted to the tube to complete the reactor. The liquid volume of each reactor was 10.4 liters. The influent header was filled with graded river gravel to provide flow distribution into the GAC bed. Each reactor was charged with 1.5 kg of 16 x 20 U.S. Standard mesh size Calgon F-400 GAC, washed with deionized water to remove fines and dried for 36 hours at 102°C prior to weighing. The unexpanded bed height in the reactor was 16 inches. The recycle system was powered by a centrifugal pump which withdrew water from the side of the effluent header, maintaining an expanded bed height of 24 inches, for a 50% bed expansion. Water from a constant-temperature bath maintained at 35°C was circulated through the water jacket of the reactor.

Blended groundwater was fed to the reactors from collapsible feed reservoirs through positive displacement pumps and Tygon tubing. The pumps fed into the suction side of the recirculation system. The feed flow rate to both reactors was 3 liters per day, resulting in an empty-bed hydraulic detention time of 15.56 hours (based on expanded-bed volume). The feed to one column, hereafter called "Column A," was supplemented with ethanol. The other column, referred to as "Column B" from here on, received water with no ethanol. Both feeds were supplemented with nutrients and alkalinity in the form of sodium bicarbonate to maintain reactor pH at 7.0 ± 0.2. The composition of the feed reservoirs is given in Table 2. The composition of the nutrient salt solution is given in Table 3.

The reactors were monitored daily for feed flow rate, gas production, and pH. An effluent volume of 300 ml was collected daily from each column, and the samples were composited every three days for analysis. Samples were stored at 4°C prior to analysis. Composited samples were analyzed for soluble and total chemical oxygen demand (COD),

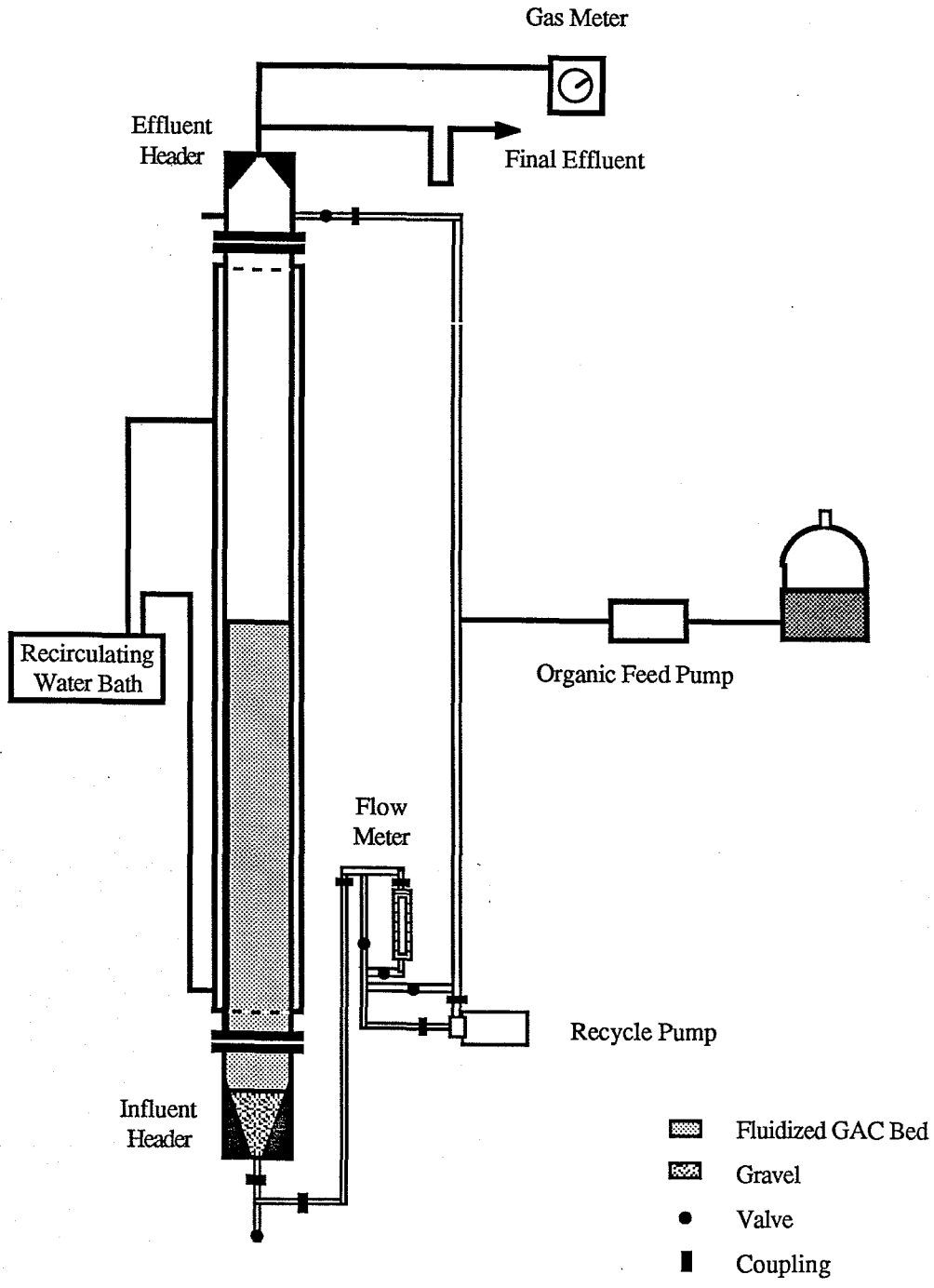

Figure 2: Schematic of Expanded-Bed Anaerobic GAC Reactor

Table 2: Composition of Feeds to Expanded-Bed Anaerobic GAC Reactors.

	Column A (ml per Liter)	Column B (ml per Liter)
Ethanol	5.625	---
Salt Solution	25.0	2.5
48 000 mg/l NH_4-N Solution	2.0	2.0
1N $NaHCO_3$ Solution	37.5	10.0
Influent COD (mg/l)	8400	120

Table 3: Composition of Nutrient Salt Solution.

Compound	Concentration, mg/l
KH_2PO_4	13610.0
$NaH_2PO_4 \cdot H_2O$	8280.0
$MgCl_2.6H_2O$	8130.0
$CaCl_2 \cdot 2H_2O$	5880.0
$Na_3C_6H_5O_7$	5877.5
$FeCl_3$	647.4
$MnCl_2 \cdot 4H_2O$	158.2
$ZnCl_2$	108.9
$CoCl_2 \cdot 6H_2O$	95.2
$(NH_4)_6Mo_7O_{27} \cdot 4H_2O$	69.3
$CuCl_2 \cdot 2H_2O$	68.3
$NaB_4O_7 \cdot 10H_2O$	38.3

and for organic compounds via gas chromatography. Samples for soluble COD were filtered through 0.45μm membrane filter paper.

3.4 Fixed-Bed Carbon Adsorption Column. As a preliminary means of assessing competitive adsorption properties of the groundwater, the apparatus illustrated in Figure 3 was used to perform a fixed-bed column adsorption test. 1 g of 30 x 40 mesh F-400 GAC was placed in a 1.75-cm ID glass tube. The GAC was packed between 16 x 20 mesh silica sand, to promote a uniform flow distribution and minimize end effects. The sand was held in place at both ends by a plug of glass wool, and the column was capped at both ends by rubber stoppers with glass tubes inserted to allow flow.

The column was operated in an upflow mode. Groundwater was delivered to the column from an aspirated glass reservoir via Tygon tubing, by a positive displacement pump calibrated at 15 ml/minute. Effluent passing from the top of the column was collected in 200 ml sample bottles, and the pH was immediately adjusted to 7.0 ± 0.2 with strong NaOH and/or HCl solutions. The column was operated continuously for 35 hours. Effluent samples were analyzed for COD and by gas chromatography.

3.5 Adsorption Isotherm. A second means of determining adsorptive properties of the groundwater on GAC was provided by an adsorption isotherm run at room temperature, using a 14 day equilibration time to ensure equilibrium. For this isotherm, blended groundwater was adjusted to pH 7.0 prior to the test. Samples were prepared in 160 ml bottles in the following manner: 1) The desired mass of pulverized F-400 GAC was weighed and placed into the bottle 2) Approximately 100 ml of groundwater was placed in the bottle 3) The bottle was temporarily capped and shaken gently for approximately 30 seconds to wet the carbon 3) The bottle was filled to the top with additional groundwater (final liquid volume: 160 ml) to exclude head space 4) The bottle was capped with a rubber seal and crimped. The bottles were placed in a rotating cylindrical shaker at ambient room temperature (23-25°C), and allowed to equilibrate for 14 days. Following this period, samples were filtered through 0.45μm membrane filter paper and analyzed for soluble COD and by gas chromatography.

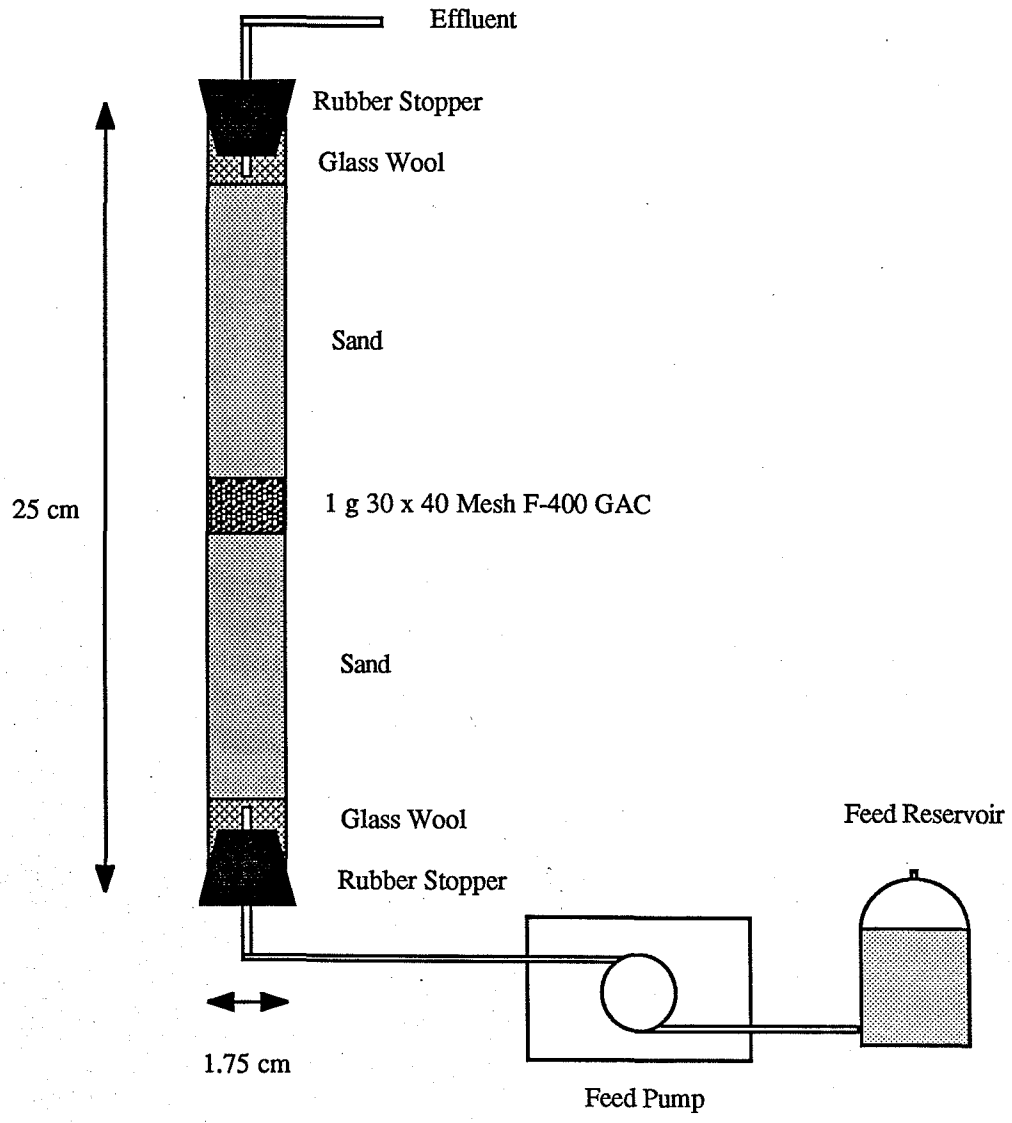

Figure 3: Schematic of Fixed-Bed Carbon Adsorption Column Apparatus.

3.6 Ethanol/Water Soil Extractions. The ability of various blends of ethanol and water to extract contaminants from soil removed from the Taylorville site was investigated by allowing soil samples to equilibrate with an extracting liquid phase in sealed bottles devoid of head space. 200 g samples of saturated soil were placed in amber 1 liter bottles, which were filled with solutions containing 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100% ethanol. An additional bottle was filled with 200 g saturated soil and methylene chloride. The liquid volume required to fill the bottles to the top was approximately 940 ml. The bottles were inverted and shaken twice a day for a period of 3 weeks to mix the soil sample and promote mass transfer of contaminants from the soil to the liquid.

Samples were prepared for gas chromatographic analysis by using an XAD resin (Amberlite XAD-2). The resin had been cleaned in the following manner: 1) Rinsed with a 2% solution of ammonium carbonate for 20 minutes 2) Rinsed with distilled water 3) Sequential extractions in a Soxhlet apparatus with distilled water, methanol, and diethyl ether 4) Final rinse with methanol and distilled water. 100-200 ml of supernatant from the each extraction bottle was passed through a 1.0μm glass fiber filter, adjusted to pH 2-2.5 with sulfuric acid, and passed through a 1-cm diameter, 10-cm long glass column containing 5g of clean XAD resin, secured between two plugs of glass wool. Sorbed organic compounds on the resin were removed by backwashing with 45 ml of methylene chloride. The methylene chloride was concentrated to 2-5 ml by evaporation in a Kuderna-Danish apparatus prior to injection of a 3μl sample in the GC. This sample preparation technique allowed partial escape of some volatile compounds, but capture of polar, non-volatile compounds. Fresh resin was used for each sample, and a blank of 100 ml methanol was run to assure that the resin was not contaminated. The soil extraction performed in methylene chloride was injected directly into the GC, with no sample preparation.

4. Results and Discussion

4.1 Groundwater Analysis. A typical chromatograph of influent groundwater from the composited drums used in these studies is given in Figure 4. Samples of groundwater used in the treatability studies were also analyzed by gas chromatography-mass spectrometry in an effort to characterize the contaminants to as great an extent as possible. The GC-MS unit was operated using a capillary column identical to the GC unit in the lab, and a similar temperature program. Several compounds were tentatively identified, but the complexity of the water and the nature of the organics present makes positive identification difficult. A list of compounds identified is given in Table 4, along with a list of compounds identified in previous site investigations.[6] According to the GC-MS analysis, the major peaks on the influent chromatograph are associated with benzene (retention time = 0.90 in Figure 4), toluene (2.17), indene (3.93), and napthalene (5.78).

4.2 Expanded-Bed Anaerobic GAC Reactors. The two reactors described earlier were seeded with biomass from an anaerobic reactor treating a non-hazardous substrate. To promote growth of a viable methanogenic culture on the GAC in the reactors, nutrients and a 1000 mg/l solution of acetate were fed at a flow rate of 1 liter/day for a period of one month. Groundwater and nutrients as described in Table 3 were then fed for a period of 2 months, at a flow rate of 3 liters/day.

Performance of an expanded-bed anaerobic GAC reactor can be described in terms of a mass balance on COD across the reactor. This method was used to assess the fate of the ethanol in the feed to Column A. COD fed to the system can have one of four fates: biological conversion to methane, escape to liquid effluent, adsorption on GAC, or incorporation into biomass. A slight amount of the methane produced will dissolve and escape with the liquid effluent, depending on the partial pressure of methane in the product gas and the temperature of the reactor. Periodic partial replacement of GAC in the system was not practiced in this study, simplifying the mass balance to:

$$\text{Influent} = \text{Methane} + \text{Liquid Effluent} + \text{Change in Accumulation}$$

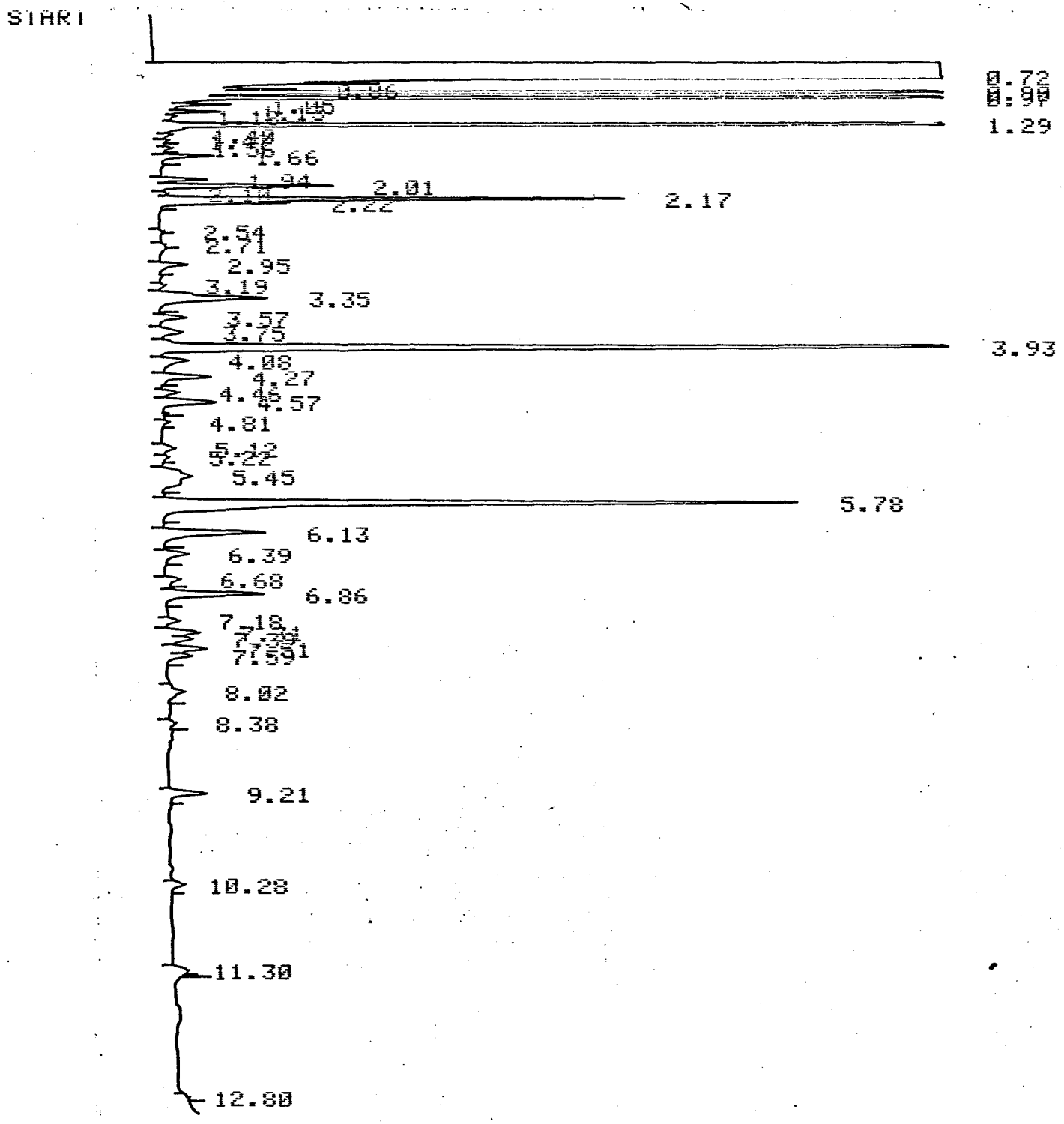

Figure 4: Typical Chromatograph of Influent Groundwater

Table 4: Tentative Identification of Compounds in Taylorville Gasifier Groundwater.

Compound	Retention Time, minutes
By GC-MS, This Study	
Toluene	2.8
$(CH_3)_2$ Benzene	5.6
Styrene	6.1
$(CH_3)_2$ Benzene	6.2
Indene	9.4
CH_3 Phenol	10.1
$(CH_3)_2$ Phenol	11.3
Methyl Indene	11.4
$(CH_3)_2$ Phenol	11.6
Napthalene	11.7
$(CH_3)_4$ Benzene	11.8
Vinyl Benzaldehyde	12.1
Indanone	13.0
CH_3 Napthalene	13.5
CH_3 Napthalene	13.7
Acenapthalene	15.5
Unknown	17.6
Unknown	20.8
Unidentified Alkanoic Acids	23.8
	25.6
Unidentified Alkyl Compounds	25.8
	26.7
	27.5
	28.3
	29.1

By Previous Site Investigation:[6]

Benzene	Toluene
Styrene	Xylene
Napthalene	2-Methylnapthalene
Acenapthalene	Dibenzofuran
Phenanthrene	Anthracene
Fluoranthene	Pyrene
Benzo Anthracene	bis(2-Ethylhexyl)Phthalate
Chrysene	Benzofluoranthene
Thiophene	Benzopyrene

where all terms are expressed in equivalent units (grams of COD or liters of methane). Conversion from methane to COD is based on the fact that 1 gram of COD yields 0.35 liters of methane at standard temperature and pressure (STP). Accumulation in this case refers to both carbon adsorption and biosynthesis of cell mass attached to the GAC.

A mass balance performed on Column A indicates almost complete conversion of ethanol to methane. Figure 5 shows influent and effluent COD expressed as equivalent methane, along with gas COD. These values are plotted cumulatively in Figure 6. As this figure shows, over the duration of the experiment, 93% of influent COD was converted to methane, with only 2% escaping as liquid effluent. The remaining 5% of the influent load was adsorbed on the GAC in the system or converted to biomass. When feed was stopped at the end of the study, gas production dropped off almost immediately, suggesting that little if any of the adsorbed material was biodegradable. Any methane produced through degradation of contaminants in the water would be insignificant compared to that attributable to degradation of ethanol in the feed.

Column B showed no measurable gas production during operation with groundwater feed, but did show signs of biological activity. Full degradation of the 120 mg/l influent COD would result in methane production equivalent to 126 ml/day. Gas in the head space above the column was determined to have a methane content of 20-30% throughout the operating period. Liquid effluent in equilibrium with this gas at 35°C, by Henry's law, would have a methane content of approximately 4.3 mg/l. At a feed rate of 3 liters/day, this translates to 18.2 ml of methane escaping as dissolved gas in the liquid effluent per day, or 14.4% of the influent potential. This methane was produced by biological activity, either through degradation of organic compounds in the feed, or by endogenous respiration of biomass accumulated in the reactor during the start-up phase.

The presence of viable biomass was verified near the end of the study by spiking one feed batch with the same concentration of ethanol as in the feed to Column A. Gas production immediately increased to levels comparable to that of Column A, and tailed off immediately after the ethanol was discontinued in the feed. The sudden pickup in methane production during this period suggests that biomass in the reactor was being sustained by degradation of organic compounds in the groundwater itself, but that concentrations of

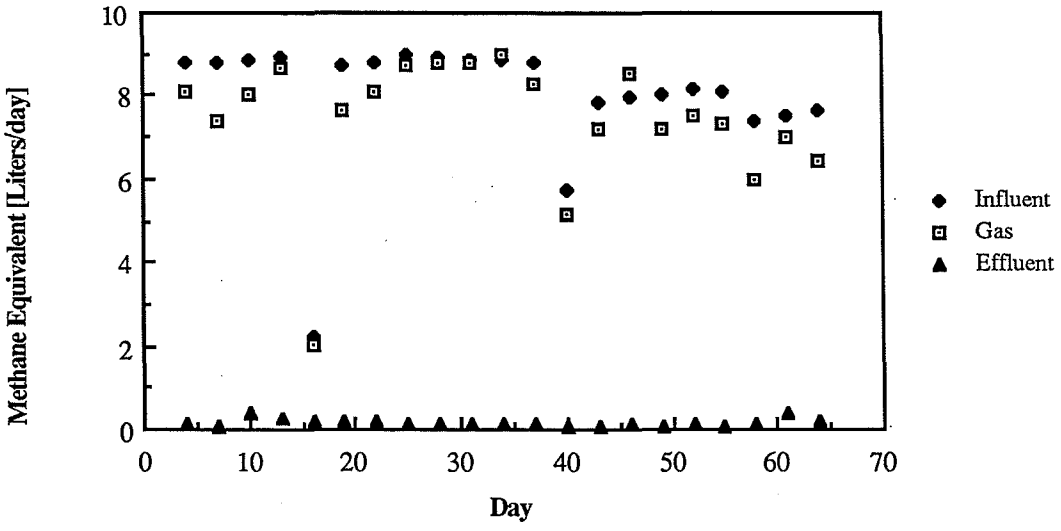

Figure 5: Influent and Effluent Methane Equivalent and Gas Production for Column A.

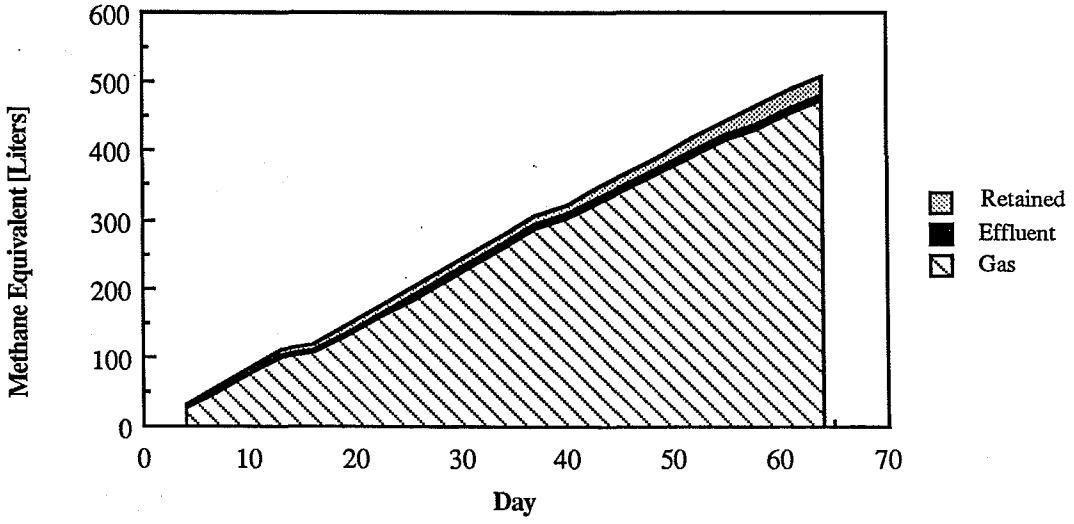

Figure 6: Cumulative Fate of Influent COD to Column A.

these compounds were not sufficient to cause measurable gas production until the introduction of ethanol to the reactor.

Analysis of effluent samples from Columns A and B indicated traces of several organic contaminants in both columns. Typical chromatographs of effluents from Columns A and B are given in Figures 7 and 8, respectively. Effluent COD from both columns fluctuated throughout the study, as tabulated in Table 5. Column A effluent averaged 37.2 mg/l soluble and 153.5 mg/l total COD, while Column B effluent averaged 25.2 mg/l total COD. Soluble effluent COD for Column B was essentially equal to the total value, as there was no suspended matter in the samples.

4.3 Fixed-Bed Carbon Adsorption Column. Results from operation of this column proved inconclusive due to the presence of oily compounds associated with the groundwater. These compounds slowly covered the support sand in the column with an orange-yellow coating which may have sorbed compounds before they reached the GAC. As a result, significant breakthrough of compounds was not observed by gas chromatographic analysis of effluent samples. By the end of the experiment, over 32 liters of water had been passed through the column. Likewise, COD analysis of effluent samples showed no clear breakthrough of organic compounds.

Eventually, the buildup of oily residue plugged the column, causing failure of the bottom tubing connection. Some of the sand near the bottom of the column was removed and replaced with fresh sand, and additional water was passed through the column. Two effluent samples taken following sand replacement showed reduced COD and organic contamination, suggesting absorption of organic compounds by the film forming on the fresh sand. A sample of sand removed from the column was extracted with 5 ml of methylene chloride in a separatory funnel, and GC analysis of the extract indicated the presence of many compounds present in the water.

4.4 Adsorption Isotherm. A room-temperature isotherm was undertaken in an effort to separate the effect of carbon adsorption from that of oil-film absorption in determining characteristics of the groundwater. GC analysis of residual compounds from the isotherm samples is summarized in Table 6, which includes only those compounds that

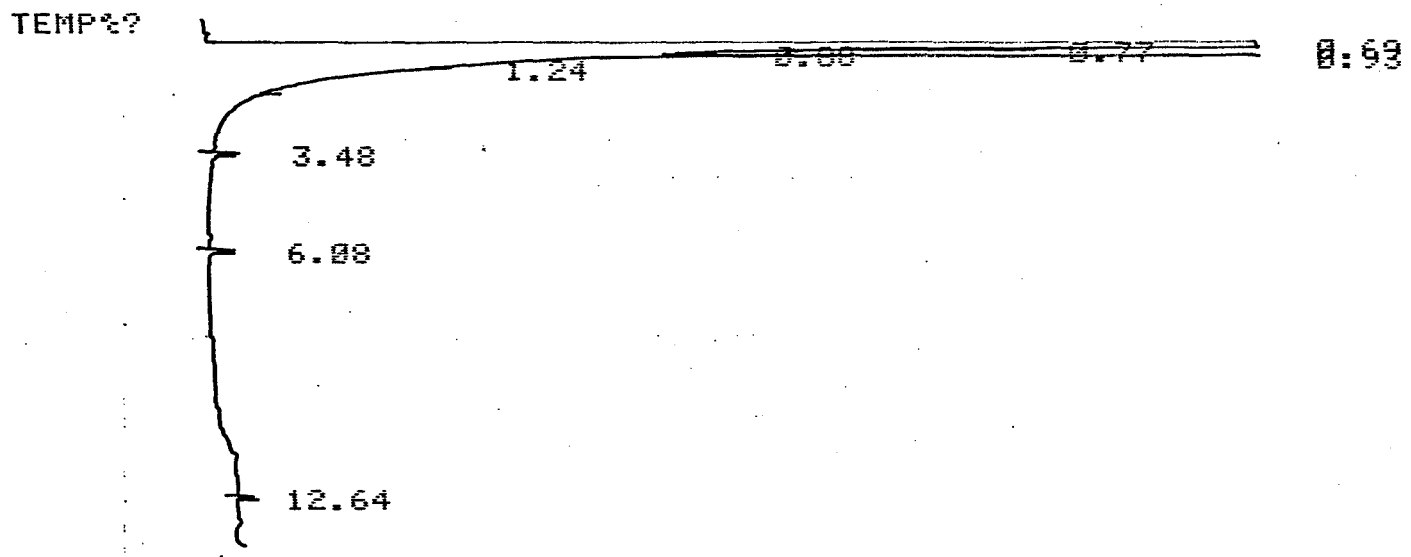

Figure 7: Typical Chromatograph from Column A Effluent

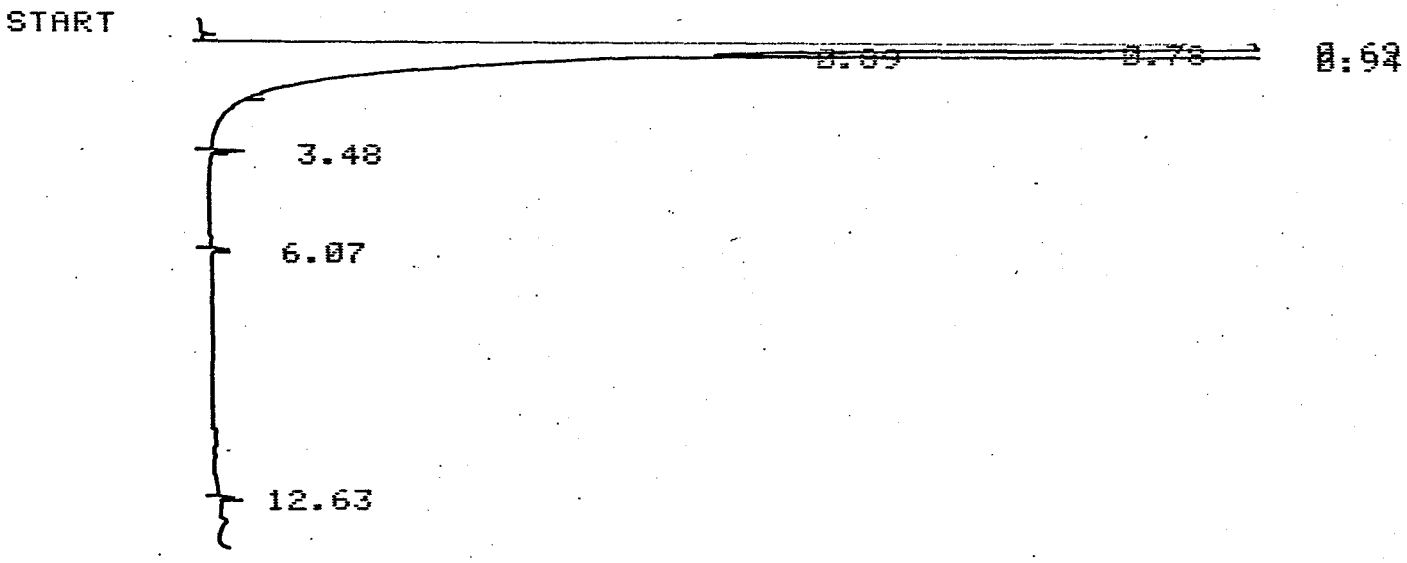

Figure 8: Typical Chromatograph from Column B Effluent

Table 5. Influent and Effluent COD for Columns A and B.

Day	All Values in mg/l				
	Column A			Column B	
	Influent (Nominal)	Effluent		Influent (Nominal)	Effluent
		Total	Soluble		Total
0	8400			120	
4	8400	142	40.5	120	9.4
7	8400	60	1.7	120	11.8
10	8400	365	89.4	120	16.9
13	8400	242	BDL	120	BDL
16	8400	215	1.7	120	18.6
19	8400	155	52.6	120	13.5
22	8400	169	76.9	120	33.7
25	8400	103	52.6	120	37.1
28	8400	110	32.1	120	18.6
31	8400	135	35.4	120	32.1
34	8400	112	77.6	120	42.2
37	8400	132	5.1	120	25.3
40	8400	87	38.8	120	23.6
43	8400	69	23.6	120	28.7
46	8400	104	17.5	120	16.7
49	8400	94	70.9	120	94.5
52	8400	103	38.8	120	37.3
55	8400	71	22.6	120	19.3
58	8400	116	35.4	120	23.6
61	8400	416	42.2	120	26.7
64	8400	225	26.0	120	18.7

BDL = Below Detectable Limits

Table 6: Results of Isotherm Analysis.

Loading (ml Water per g GAC)	Soluble COD (mg/l)	Chromatogram Peak Areas Retention Time (minutes)															
		0.87	0.90	0.97	1.05	1.13	1.29	2.95	3.36	3.58	4.27	4.46	4.57	6.12	6.85	10.27	11.30
107	2.5	627	749	9644	170	101	1881			164				4		208	
128	3.4		209	10940			58			138				104		193	
160	8.4	500	872	8936	409	301	1821			134						142	69
178	10.1	597	1024	9858	528	428	2082			158						191	119
200	3.4	200	629	11160	139	165	2052			202						153	65
229	16.9		1027	12990	445	314	1343			233						178	98
267	11.8	384	657	10700	244	184	854			198						159	93
320	3.4	375	671	10590	153	51	912			168						176	12
400	10.1	373	709	12120	178	111	884			176						176	56
457	16.9	781		12800	252	194	629			197						233	22
533		405	797	11050	286	179	862			152						168	44
640	16.9	351	771	10220	240	192	838			170	23		83			243	17
800	15.2	481	712	10460	285	191	1184			179						340	224
1067		433	745	11000	334	240	1279			178						297	60
1600	3.4																
1778	10.1		374	10070		37	303			176						231	
2000	20.2	388	606	9138	251	191	849			163						177	51
2286	28.7		456	10590	165	95	377			203						274	171
2667		332	485	7022	204	149	595			119						190	21
3200	20.2	373	665	10440	269	176	854			195						241	25
4000	23.6		332	8772	69	24	122			153						198	96
5333	33.7		399	9228	60	23	117			142						149	69
8000	28.7		696	9552	207	159	671		54	151				21		456	25
16000			791	9262	210	172	647	33	123	162	150	52	141	476	137	117	177
32000	45.5		1069	10300	137	81	563	118	331	201	324	113	281	1375	641	152	102
Blank 1	124.5	404	22980	9384	70	29	9690	163	913	169	371	112	449	931	690	184	27
Blank 2	119.6	540	19610	9826	201	140	9818	186	1108	175	415	112	519	929	759	69	58

were observed to persist in the aqueous phase. Chromatographs for loadings of 320 and 16000 ml groundwater/gram GAC are given in Figures 9 and 10, respectively.

These results indicate the presence of both strongly adsorbable and poorly adsorbable compounds in the groundwater. The results suggest that for many compounds (those shown in Figure 3 that do not appear in Table 6), saturation of GAC does not occur, even at loadings in excess of 32 liters of groundwater per gram of GAC. To identify the nature of the compounds that persisted at lower loadings, the sample corresponding to a loading of 1778 ml/g was sent for GC-MS analysis. The results were compared to an influent sample to determine the percent removal at this loading. This information is summarized in Table 7.

4.5 Ethanol/Water Soil Extractions. The experimental findings of the soil extraction studies are the most important results of this research project, as it is the characteristics of these extracts that determine the ultimate applicability of the proposed treatment system to a gasifier site. The procedure used to extract compounds from the water/ethanol mixtures in this experiment was chosen due to a shortage of time. The results are useful for qualitative analysis of the number of additional compounds that can be removed, but are of limited usefulness as a means of comparing various ethanol/water mixtures.

This problem was caused by apparent overload of the XAD resin with the higher ethanol-content samples. The higher ethanol-content extracts had an intense yellow color. This color was visible, but less pronounced, for samples containing less ethanol. During adsorption of the less concentrated samples, the yellow coloring was removed upon passage through the XAD resin. For samples containing 50% or more ethanol, liquid passing through the resin retained a yellow hue, suggesting failure of the resin to fully capture the contaminants due to their presence at higher concentrations in the liquid phase and because of the increased solubility of polar compounds in the stronger ethanol solutions.

Although it is not possible to quantify accurately from this preliminary experiment, it is apparent that higher ethanol content leads to greater removal of contaminants from the

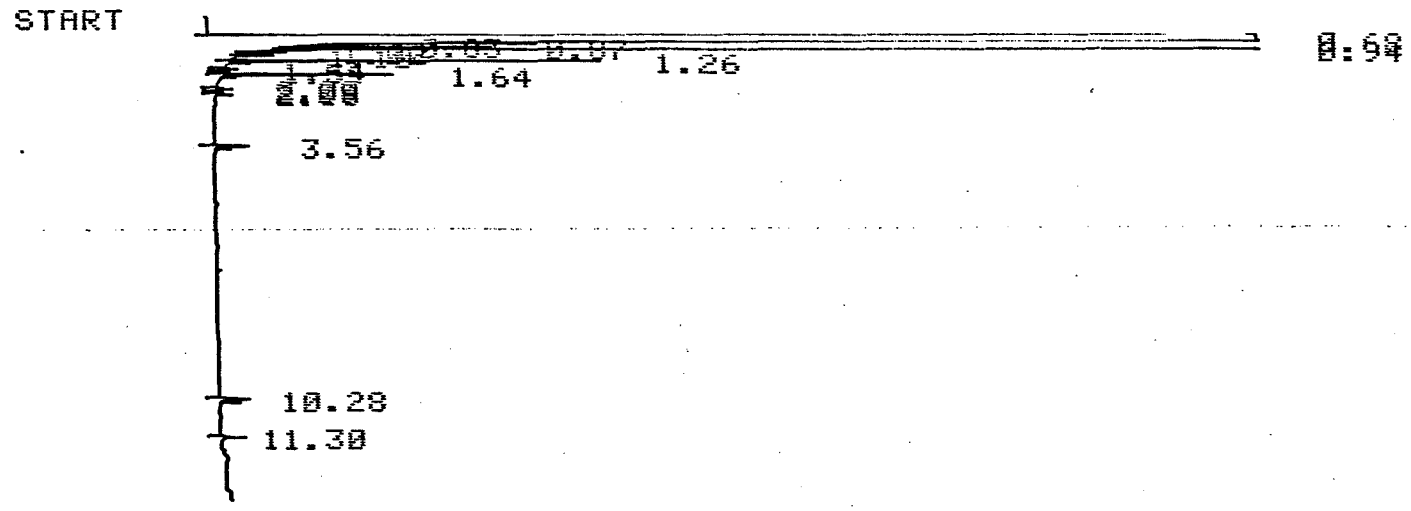

Figure 9: Chromatograph from Isotherm Sample Loaded at 320 ml Groundwater per gram of GAC

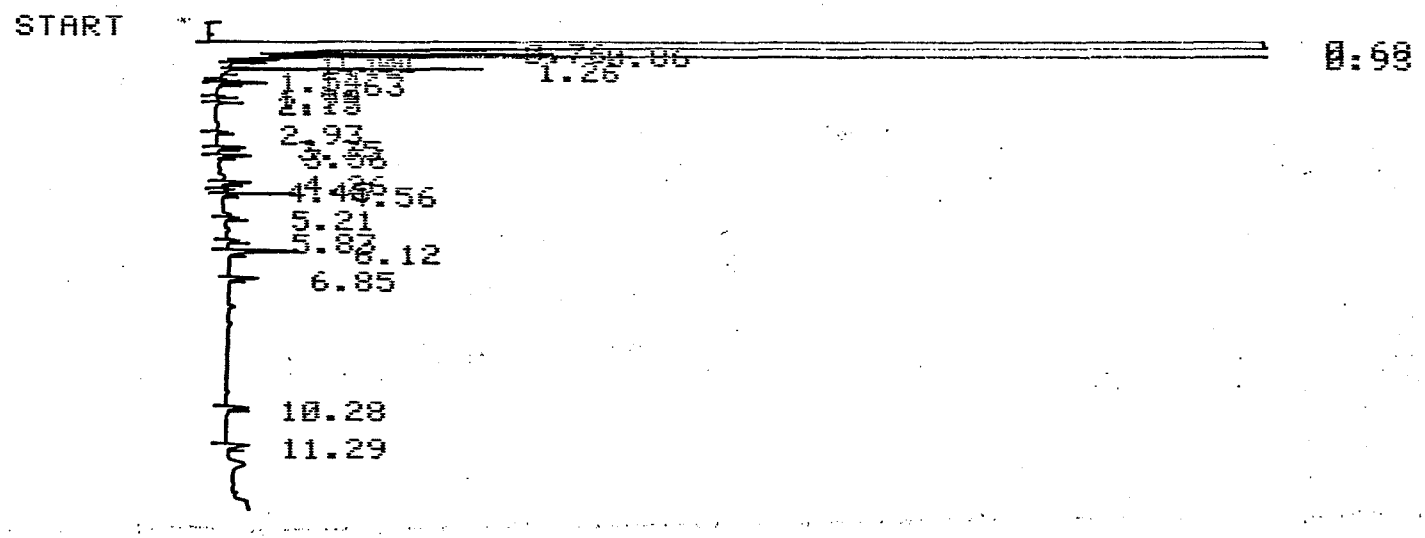

Figure 10: Chromatograph from Isotherm Sample Loaded at 16000 ml Groundwater per Gram of GAC

Table 7: Percent Removal of Compounds Appearing in Isotherm Supernatant at a Loading of 1778 ml Groundwater per Gram GAC.

Retention Time	Tentative Identification	Percent Removed
2.8	CH_3 Benzene	94%
12.1	Vinyl Benzaldehyde	26%
13.0	Indanone	77%
17.6 20.8	Unknown	0%
23.8 25.6	Unknown Alkanoic Acids	0%
25.8 26.7 27.5 28.3 29.1	Unknown Alkyl Compounds	0%

soil. Figure 11 shows the chromatograph from the extraction with 10% ethanol. Comparison with Figure 12, which shows the chromatograph from the 60% ethanol extraction, shows the increased concentration and number of compounds in the latter sample. Comparison of these chromatographs with the chromatograph from groundwater alone (Figure 4) shows that additional compounds being removed by the ethanol solutions have long retention times in the GC column. This suggests larger, more complex compounds, which apparently are not soluble in water alone. Extraction of soil into distilled water containing no ethanol produced a chromatograph similar to that of groundwater at the site.

Extraction of saturated soil directly into methylene chloride provided only limited removal of compounds, due to the immiscibility of methylene chloride in water. A chromatograph of such an extraction is given in Figure 13.

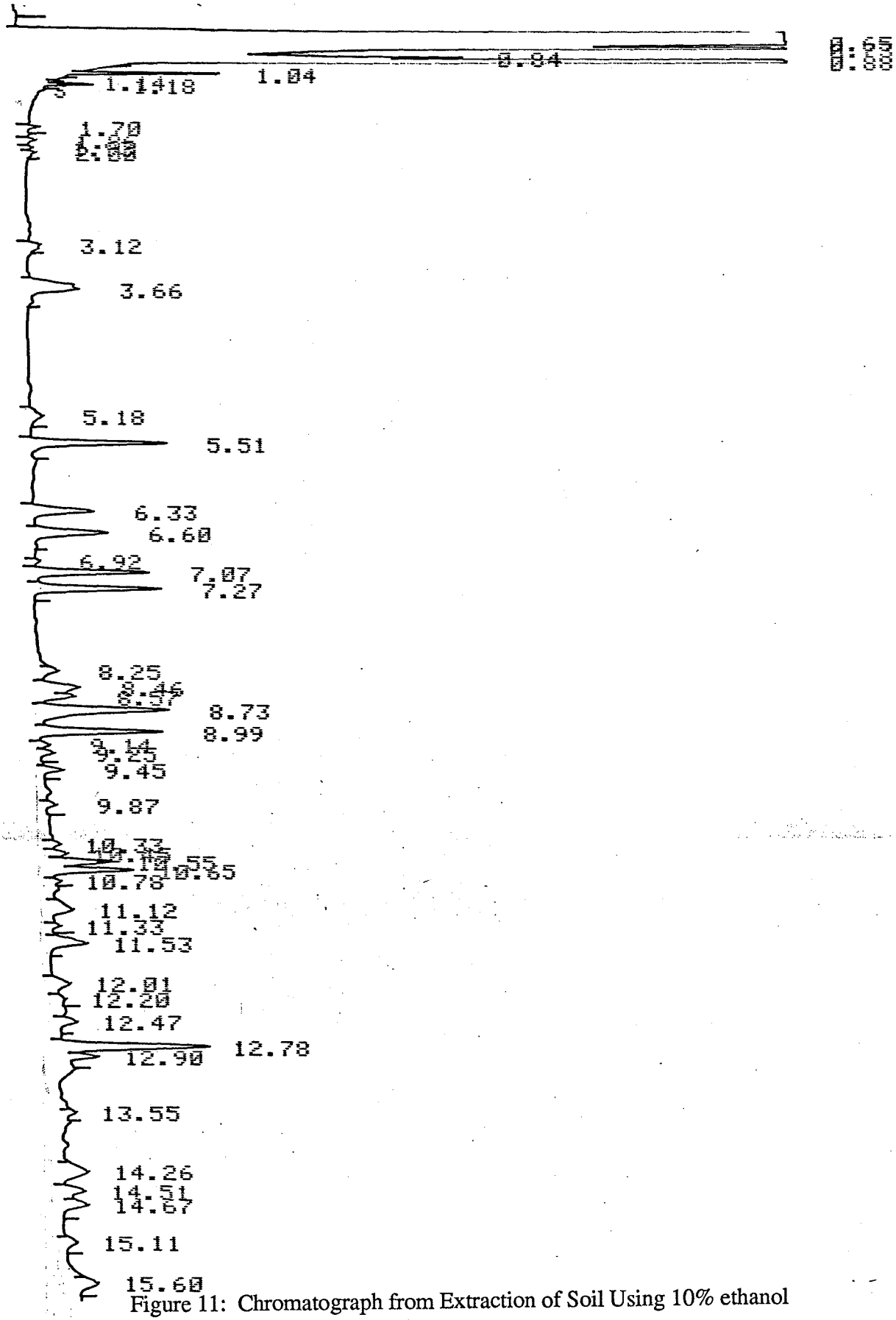

Figure 11: Chromatograph from Extraction of Soil Using 10% ethanol

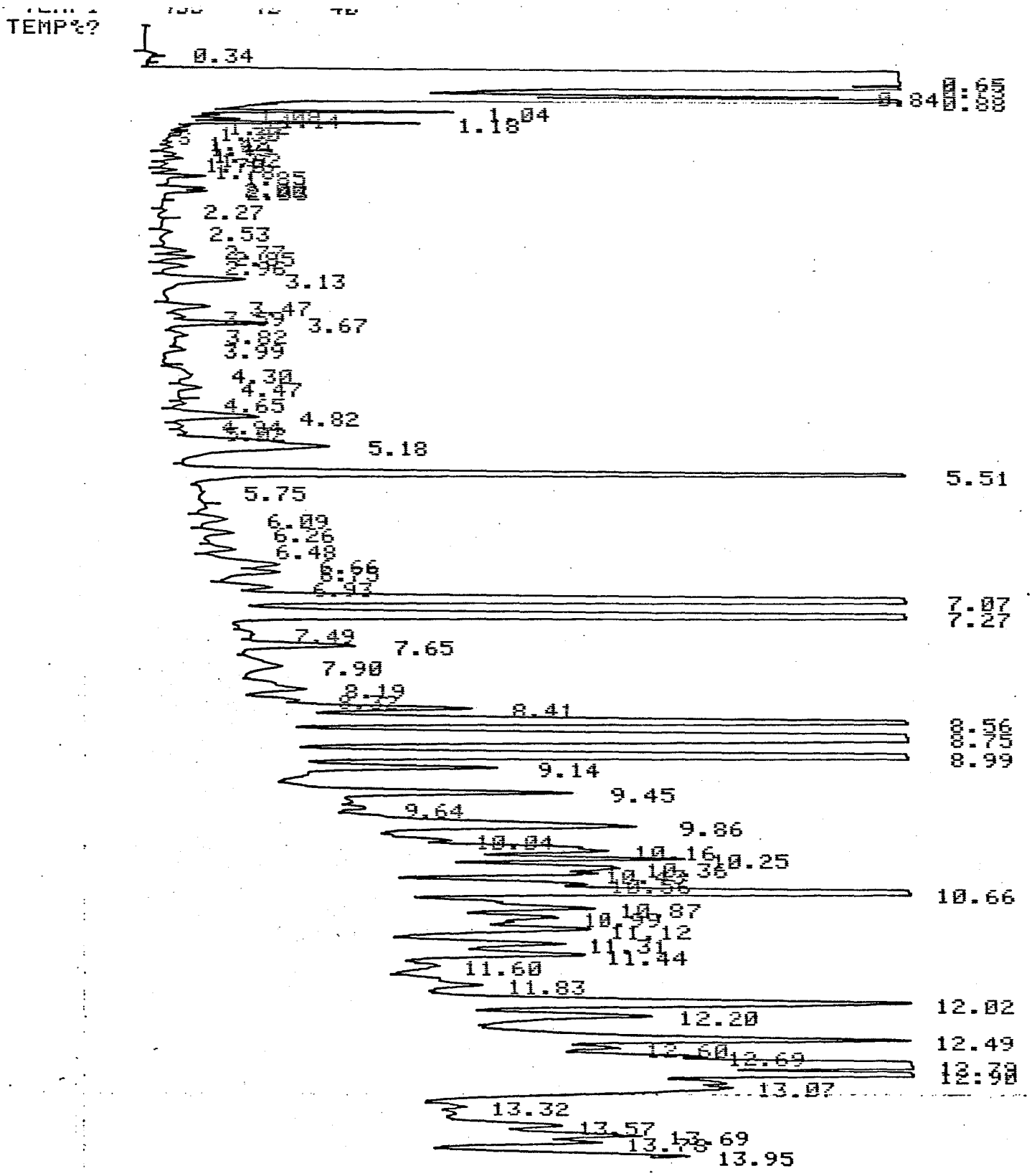

Figure 12: Chromatograph from Extraction of Soil Using 60% Ethanol

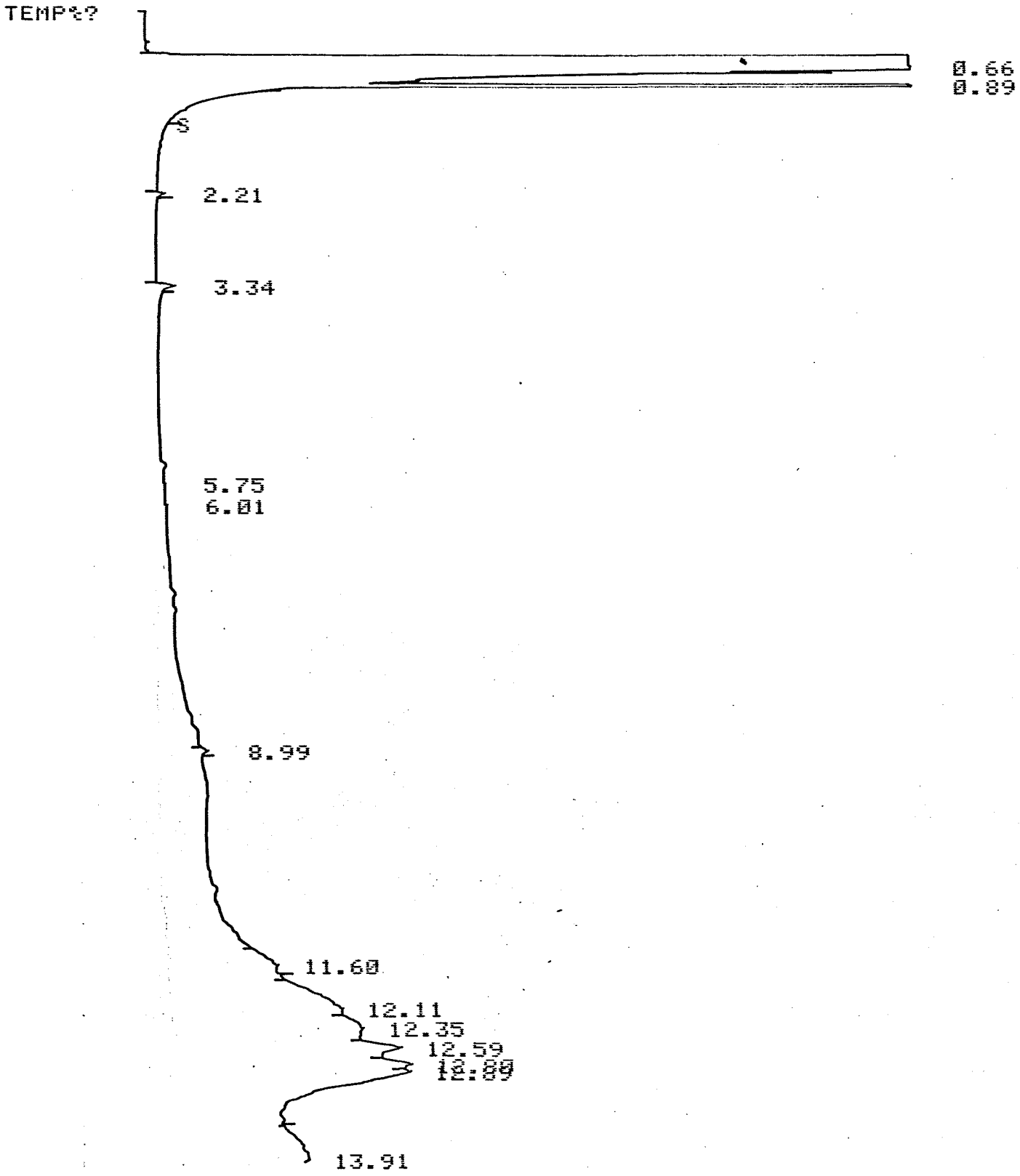

Figure 13: Chromatograph from Extraction of Soil Using Methylene Chloride

5. CONCLUSIONS

Results of this study were undermined by the lack of time available, which precluded the development of an analytical technique for quantitatively identifying compounds associated with the groundwater, column effluents, and soil extractions. Despite this, qualitative observations based on the results of these experiments can be used to assess areas for further research.

The expanded-bed anaerobic GAC reactors showed good removal of contaminants from Taylorville gasifier site groundwater, with only traces of 3-5 compounds remaining in the effluent. Whether removal was facilitated by biodegradation or adsorption is uncertain. The reactor receiving ethanol in the feed was able to metabolize the ethanol easily, showing no signs of biological inhibition due to the presence of the contaminants. The reactor receiving groundwater alone showed signs of biological activity, which may have been due to degradation of contaminants or to endogenous respiration of biomass previously in the reactor.

An adsorption isotherm conducted at room temperature indicated that most compounds in the water will not exhibit breakthrough at loadings of up to 32 liters of groundwater per gram of GAC. A few compounds, however, do not appear to be adsorbable on GAC. Because the proposed biological treatment is operated at 35°C to take advantage of faster metabolism in the mesophilic range, an isotherm should be run at this temperature to simulate adsorption conditions in the reactor.

Soil extractions using mixtures of ethanol and water clearly showed compounds from the soil that do not appear in the groundwater. Because the proposed treatment scheme consists of injection of ethanol into the contaminated soil at the site prior to removal of groundwater, it is the nature of these compounds which will ultimately dictate the applicability of the process to the site. The adsorptive properties of these extracts need to be determined by means of an isotherm, preferably at 35°C. Operation of an expanded-bed anaerobic GAC reactor on an actual soil extraction is needed to assess the ultimate applicability of the process.

Anaerobic biological treatment is a process which needs time to be analyzed properly due to the slow growth rates of the bacteria involved. This is especially true in a system where GAC adsorption/desorption is occurring, as these processes require time to equilibrate, and affect the biological phase of the treatment. The presence of the oily phase observed with this groundwater also illustrates the need for a longer study to assess the fate of these compounds in the reactor.

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