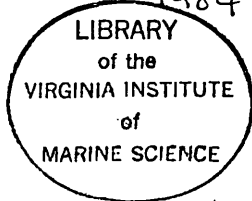


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**Trace Organic Analyses of Effluent  
Waters from a Model Slurry Pipeline  
Carrying Appalachian Bituminous Coal**

**Final Report to  
The State Water Control Board  
Richmond, Virginia**

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Trace Organic Analyses of Effluent Waters from a  
Model Slurry Pipeline Carrying Appalachian Bituminous Coal

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Abstract

Effluent waters from a model coal slurry pipeline have been analyzed for trace dissolved organic compounds. The model pipeline was operated under conditions simulating those proposed for a slurry pipeline from the region of Bristol to Hampton Roads, Virginia. Acidic, neutral and basic organic compounds in the separated waters were determined. Concentrations of individual compounds detected were generally less than 0.5 ppb and never exceeded 6 ppb. Adsorption experiments using coal slurry sorbents indicate that coal particles act as sorbing surfaces under coal slurry pipeline transport conditions.

Introduction

A coal slurry pipeline from western Virginia to the Port of Hampton Roads is presently under consideration. Yucel (1982) has presented a careful description of design and economic conditions for this pipeline. The final decision on pipeline construction will be based on financial, socio-political and environmental considerations. Work reported here relates to one environmental concern, the possible presence of water soluble organic compounds in effluent water from the coal slurry pipeline.

Low molecular weight organic compounds that occur in organic solvent extracts of bituminous coal have been identified by Radke et al. (1982) and White and Lee (1980). Many of these

compounds are soluble in water, but their partitioning between water and the bituminous matrix has not been determined. Organic compounds may be transferred from coal to water by leaching of water extractable material present in the interstices of the coal matrix (defined by Meyers, 1982) or by partial oxidative degradation of the coal matrix.

Water soluble organic compounds released from a bituminous coal may have several possible fates in a water-coal particle system.

1. Organic solutes may be sorbed on the surface of the partially degraded organic components (macerals) of the coal, leaving very low concentrations in solution.
2. Organic solutes may be sorbed on mineral matter such as clays, hydrous iron oxides and amorphous aluminosilicates that are ubiquitous constituents of coal seams.
3. If sorption of organic solutes is not important, the aqueous concentrations of these solutes in coal-water systems will increase regularly with time and eventually produce concentrations that may have adverse effects on receiving waters.

The present study was done because no prior information exists on the concentration of organic compounds in effluents similar to those which would be generated by the proposed coal slurry pipeline, and there are no predictive theoretical models which permit the fate of water soluble organic molecules in coal

to be calculated. An empirical approach was chosen to the question: Will the effluent from the Virginia coal slurry pipeline contain high levels of potentially toxic organic solutes?

In this approach, we simulated coal grinding, slurry production and storage, slurry pipeline transit, slurry terminal storage and slurry dewatering times and conditions applicable to the Virginia pipeline. Some approximations were required because the operation and construction engineering details of the proposed Virginia pipeline were not specified.

A similar approach was taken in studies of water soluble leachates from western lignitic (soft) coals in the proposed ETSI pipeline project (Sandhu and Gandhi, 1982; Peavy et al. 1981) but they did not analyze organic compounds in the effluent. In all prior work with coal slurry pipeline effluents, the effluents have been characterized only as to total organics in the water. Total organic concentrations may be appreciable in waters from western lignitic coals that release humic fragments, but the permissible total organic (or BOD) loading is quite high (Plummer and Jordan, 1982).

Analyses of organic compounds in aqueous leachates of Appalachian coals have not previously been done. There has been no prior study of a United States coal slurry transport system in which effluent water was analyzed for water soluble organic compounds present within the coal matrix. Davis and Boegly

(1978) have noted the deficiency, which still exists, in our knowledge of the organic composition of aqueous leachates of coal. There was no indication whether the proposed Virginia coal slurry pipeline would release harmful amounts of, for example, phenols, polynuclear aromatic hydrocarbons, and aromatic carboxylic acids to its receiving waters. The experiments reported here provide such information.

### Experimental

Slurries used in this program were prepared from crushed and washed bituminous coal provided by Dr. Richard Wolfe of the United Coal Company, Bristol, Virginia. This coal grade and treatment would be typical of the feed material for a commercial coal slurry pipeline in Virginia. The coal was air dried at room temperature and dry ground in a laboratory-scale, all steel rod mill constructed for this project. Ground coal was then sieved on a set of steel screens, and coal particles that passed a 16 mesh (1.19 mm mesh size) screen were used for preparation of coal slurries. Slurries used in this study were a 1:1 by weight mixture of coal particles and deionized organic free water. A fresh slurry was prepared for each experiment.

#### A. Solvent extraction of coal

A portion (50g) of ground and air dried coal was soxhlet extracted with methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) for 24 hours.

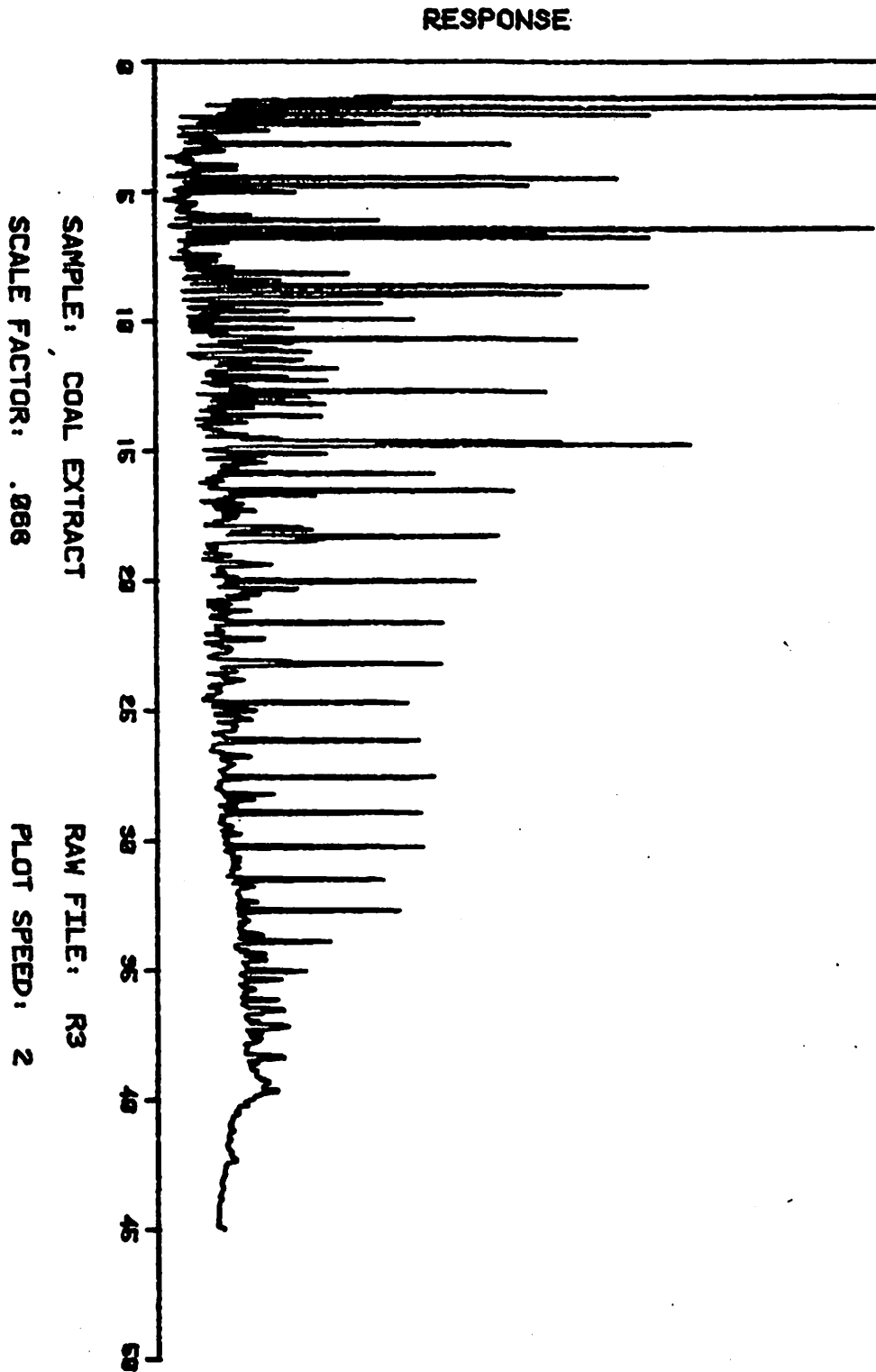
The  $\text{CH}_2\text{Cl}_2$  was then partially removed in a rotary evaporator and an aliquot of the concentrated extract was "cleaned" by gel permeation chromatography to remove large, non volatile molecules, and separated into nonpolar and polar-aromatic fractions by HPLC. Each fraction was analyzed by gas chromatography. Considerable amounts of low and medium molecular weight organic compounds were extracted. A gas chromatogram of the unfractionated coal extract is shown in figure 1. Large numbers of substituted naphthalenes and phenanthrenes were present, as were n-alkanes from  $\text{nC}_{10}$  to  $\text{nC}_{30}$ . This observation is in agreement with the work of Radke et al. (1982) on German bituminous coal. Extracted compounds were almost certainly removed from inclusions in the coal matrix, as  $\text{CH}_2\text{Cl}_2$  extraction under these conditions could not break covalent bonds of the coal matrix, and little  $\text{O}_2$  was available for coal matrix oxidation.

#### B. Coal slurry transport simulation and analysis

As noted by Peavy et al. (1981), simulation of a full scale coal slurry pipeline by a small scale closed circuit pipe loop containing a slurry pump is not practical. Small pumps undergo bearing abrasion by the slurry and require introduction of large amounts of lubricants which would preclude trace organic analysis of coal slurry water. The unavailability of suitable slurry pumps was confirmed by contacting several pump manufacturers, and the loop scheme was immediately abandoned.

Figure 1

Gas Chromatogram of an Unfractionated  
Methylene Chloride Extract of Bituminous Coal



The bench scale reactor concept of Peavey et al. (1981) and Sandu and Gandhi (1982) was adopted with some modifications. Two steel reactor vessels were constructed from carbon steel of the type used in pipelines. A dimensioned drawing of a coal slurry reactor is shown in figure 2.

All joints and seams in this reactor were electric arc welded. A similar reactor was constructed without roughness strips. Coal slurry pipe simulation experiments were conducted with each reactor to provide a range of coal slurry transport turbulence conditions.

Slurry storage was simulated by placing the slurry in an open 14 cm diameter Pyrex cylinder which was allowed free contact with laboratory air. The slurry was then stirred either by a teflon coated magnetic stir bar or by a stainless steel vertical stirrer. Stirring by the latter method was more vigorous and provided more contact with air. The transparent storage cylinder permitted visual verification that the slurry was maintained without settling during the storage period. It is obvious that sufficient turbulence must be provided at all times during coal slurry transport to avoid settling of coal particles and consequent blockage of the transport system. This condition was met in the simulation studies reported here.

To simulate coal slurry transit, the reactor was filled with slurry, capped and rotated by a motor driven roller friction

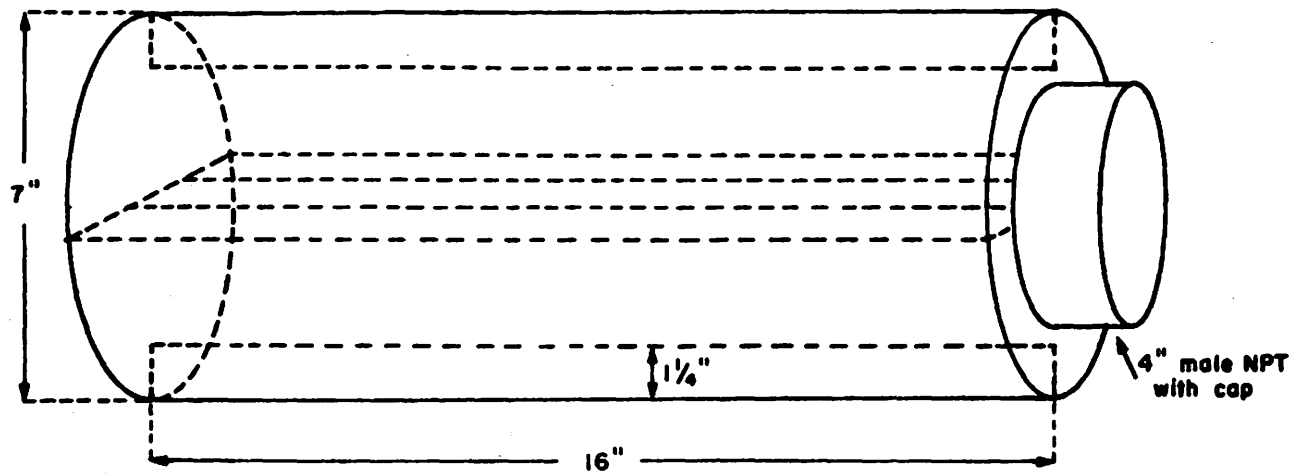


Figure 2

Coal Slurry Pipeline Simulation Reactor

(Dotted lines indicate internal roughness strips to insure turbulence)

drive system around the cylinder axis (horizontally oriented) at 48 rpm. Reactor temperature was room ambient (19°C-23°C).

Constant rotation of the reactor was maintained over an interval of approximately 4 days, the estimated time required for a slurry to pass from Bristol to Hampton Roads in a full scale pipeline. No effort was made to exclude air during loading and capping the reactor vessel, as Peavy et al. (1981) have shown that oxygen is depleted and pH decreases rapidly in the reactor vessel. This brief contact with oxygen is negligible in comparison with slurry contact with air during slurry storage simulation.

Slurry dewatering was simulated by simple gravitational settling in the storage cylinder at the end of each experiment with subsequent siphon removal of supernatant water for trace organic analysis. Chemical treatment, filtration and centrifugation were not investigated, as dewatering methods planned for the proposed Virginia coal slurry pipeline were not available. Gravitational settling was assumed to be the simplest, most economical, and the most likely used method of slurry dewatering.

Coal slurry transport was modeled in the sequence: slurry preparation, mine site storage, pipeline transit, shipping terminal storage, and dewatering. Methods for simulating each step are described above. Table 1 gives times and conditions for

the two coal slurry transport experiments. The second experiment was done under conditions of greater slurry turbulence with increased storage and settling time, and was intended to indicate the maximum abrasion and oxidation situation that could occur in pipeline transport.

A measured volume of water collected at the end of an experiment was transferred to a 2 liter separatory funnel and acidified to pH=2 by addition of 1N HCl. The water was then extracted three times with  $\text{CH}_2\text{Cl}_2$  and the extracts combined. This extract contains acidic and neutral organic molecules.

Water, which remained in the separatory funnel, was then brought to pH=10 by addition of 1N NaOH and extracted three times with  $\text{CH}_2\text{Cl}_2$  as above. This extract contains basic organic molecules. Acid-neutral and base extracts from each experiment were reduced in volume on a rotary evaporator and analyzed by G.C. under the same conditions as used for coal solvent extraction.

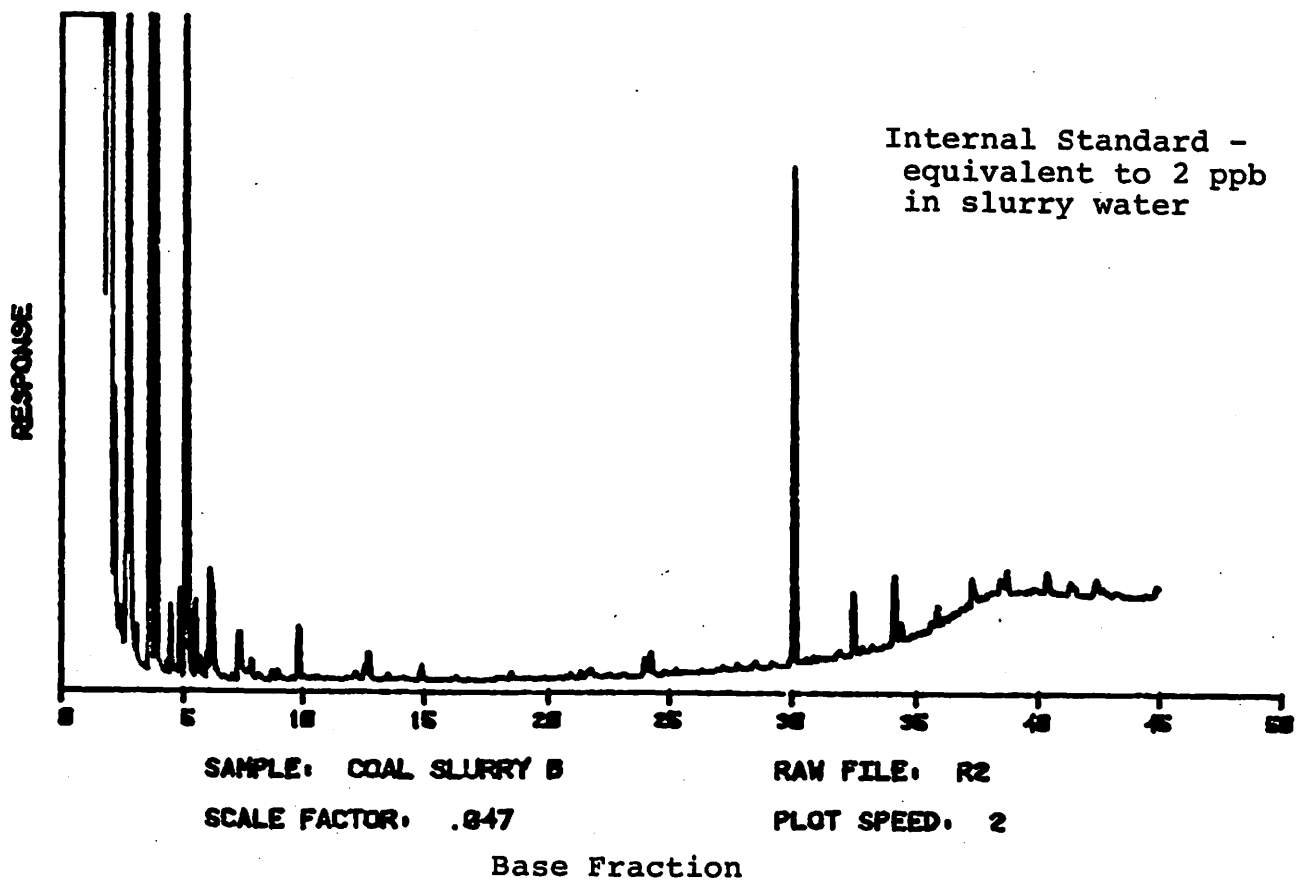
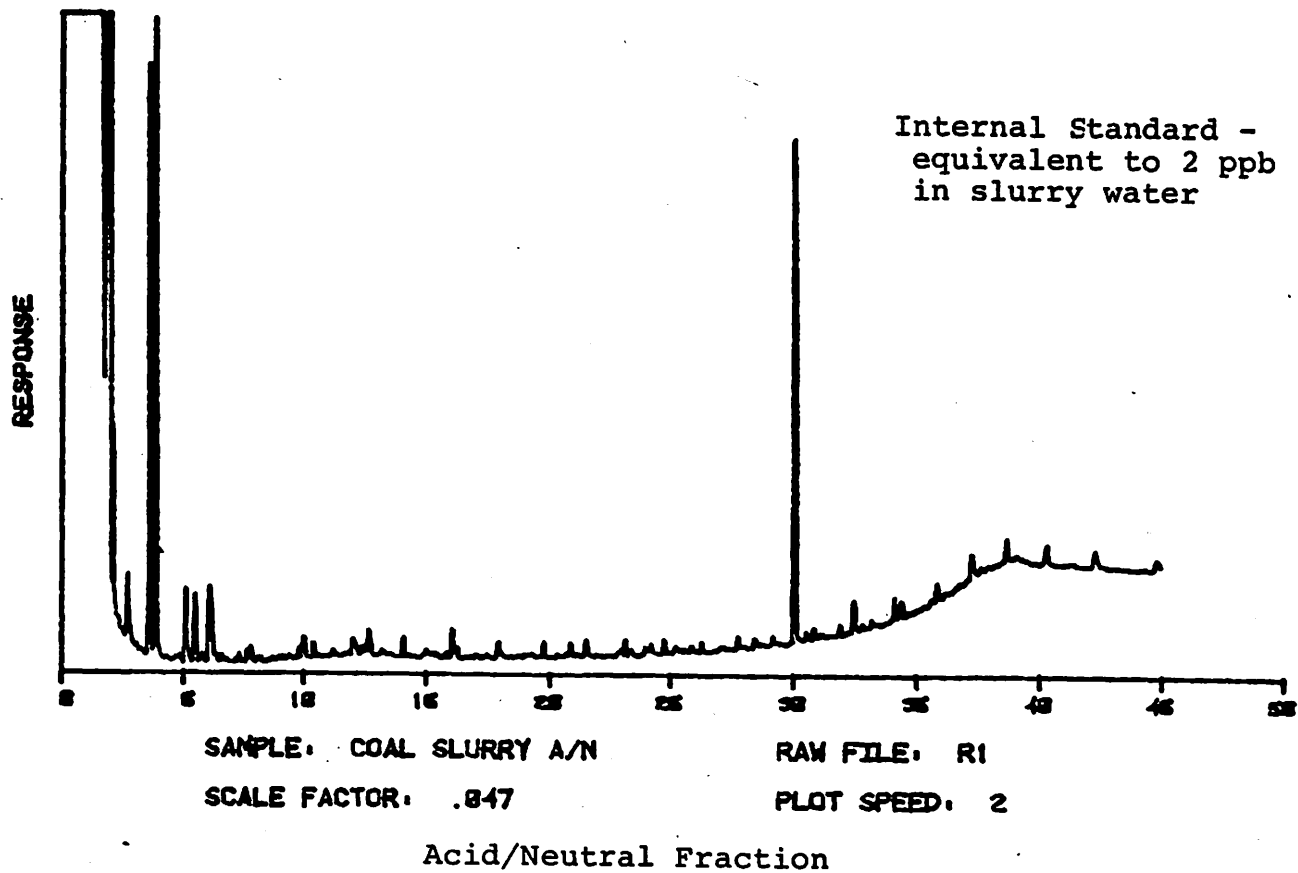
Chromatograms of the acid/neutral and basic fractions of the water extracts for the second pipeline simulation experiment are presented in figure 3.

TABLE 1

## Conditions of Pipeline Simulation Experiments

<u>STAGE</u>	<u>Experiment 1</u>		<u>Experiment 2</u>	
	<u>TIME (hrs)</u>	<u>CONDITION</u>	<u>TIME (hrs)</u>	<u>CONDITION</u>
Slurry Preparation	0.5	mixing in pyrex cylinder	0.5	mixing in pyrex cylinder
Mine Site Storage	8	magnetic stirring in pyrex cylinder	38	mixer stirring in pyrex cylinder
Pipeline Transit	88	rotation in smooth internal surface reactor	103	rotation in reactor with internal roughness strips
Terminal Storage	22	magnetic stirring in pyrex cylinder	40	mixer stirring in pyrex cylinder
Dewatering	25	gravitational settling	100	gravitational settling

Figure 3



### C. Batch Adsorption of Dissolved Organics by a Coal Slurry

The coal slurry from experiment #2 above was transferred to a cleaned glass reagent bottle with teflon lined cap. Distilled organic free water was added to replace that removed in the previous experiment, restoring the ratio of 2 kg coal to 2 kg water. A control was prepared using a similar reagent bottle containing 4 kg of distilled organic free water.

Organic compounds that were found in solvent extracts of bituminous coal were added to each bottle at less than saturation concentrations. The object of these experiments was to determine whether coal in a slurry acts as a self-adsorbent for organic compounds that might be locally leached from the coal matrix in a batch process which simulates to the conditions of coal slurry pipeline transport.

Compounds tested were 1-methylnaphthalene and phenol. Initial concentrations were 18 mg/l 1-methylnaphthalene and 25 mg/l phenol. After addition of a compound each bottle was immediately capped, shaken for 10 minutes, allowed to rest for 12 hours, shaken again and left for 6 more hours. Supernatant water from the settled coal slurry and water from the control bottle were analyzed. 1-methylnaphthalene concentration was reduced by almost 100% (complete removal to detection limit  $<.005$  mg/liter) in water contacting coal particles. Similarly, phenol concentration was reduced by 99%.

## Discussion

Solvent extracts from the source coal contain large amounts of low molecular weight organic compounds, whereas the effluent water from the coal slurry pipeline contains only very small amounts of similar compounds. Most peaks corresponded to concentrations less than 0.5 ppb and no peak concentrations exceeded 6 ppb. With the exception of a xylene isomer none of the detected compounds could be identified due to their low concentrations. There is obviously little low molecular organic matter in the effluent water. Even the low concentrations of compounds detected may not have been in true solution in water, but may have resulted from solvent extraction of the few coal particles remaining in the water after the simulated dewatering. Total concentration of organic compounds detected in the acid/neutral fraction was 8.8 ppb and in the base fraction, 30 ppb. It should be noted that these total concentrations are much lower than those detected in municipal sewage effluents. Barrick (1982) determined total extractable organics of Seattle effluent water at the 10 ppm level with concentrations of individual compounds at least an order of magnitude higher than detected here. Eganhouse and Kaplan (1982) made similar observations for sewage from several sources, reporting, for example, up to 1,250 ppb of polycyclic aromatics in these effluents.

The batch adsorption experiments were conducted to test the hypothesis that leaching of organic compounds from coal under the conditions of slurry storage and transport is limited because coal slurry particles act as adsorbents for organic compounds released. Zubkova et al. (1974) have provided support for this hypothesis using Russian coals in contact with aqueous solution of phenol. Coal slurry particles may be good adsorbents for dissolved organic compounds of the types found in coal, and sorption is a probable reason that very little dissolved organic matter is found in the model slurry pipeline effluent. Isaacson and Frink (1984) have shown that recent sediment organic matter is an efficient sorbent for phenols, which are in part irreversibly sorbed. Since "coal" contains small portions of clays and other materials which cannot be completely separated, it cannot be determined whether the sorbent surfaces are clay minerals, amorphous oxides or organic maceral components of coal. Therefore the sorption process cannot be more closely defined.

The results obtained here indicated that a bituminous coal slurry is an efficient sorbent for low molecular weight dissolved organic molecules leachable from coal. It is proposed that this sorption capability limits the concentration of dissolved organic molecules leached under coal slurry pipeline conditions.

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