

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

ORGANIC COMPOUNDS IN COAL SLURRY PIPELINE WATERS. ANNUAL PROGRESS REPORT FOR PERIOD AUGUST 1 - SEPT. 30, 1979.

### Permalink

<https://escholarship.org/uc/item/0zn5b8mh>

### Authors

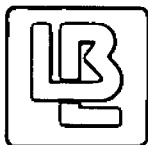
Newton, Amos S.

Pox, J.P.

Raval, Rajendra.

### Publication Date

1979-11-01



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## ENERGY & ENVIRONMENT DIVISION

ORGANIC COMPOUNDS IN COAL SLURRY PIPELINE WATERS

Annual Progress Report for period August 1 - September 30, 1979

Amos S. Newton, J. P. Fox, and Rajendra Raval

November 1979

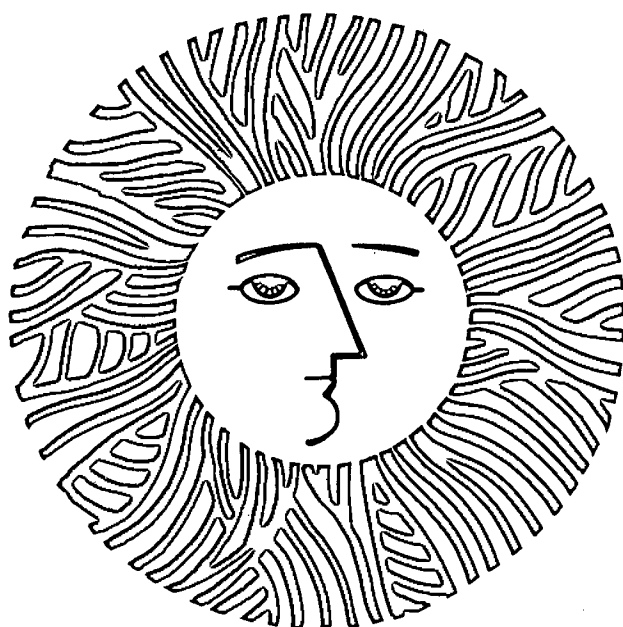
RECEIVED  
LAWRENCE  
BERKELEY LABORATORY

AUG 15 1979

LIBRARY AND  
DOCUMENTS SECTION

**For Reference**

**Not to be taken from this room**



## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

ORGANIC COMPOUNDS IN COAL SLURRY PIPELINE WATERS

Annual Progress Report  
for period  
August 1 - September 30, 1979

Prepared for the  
U. S. Department of Energy  
Division of Environmental Control Technology  
Contract No. W-7405-ENG-48  
Technical Program Officer: Charles Grua

by  
Amos S. Newton  
J. P. Fox •  
Rajendra Raval

November 1979

Energy and Environment Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, CA 94720

# ORGANIC COMPOUNDS IN COAL SLURRY PIPELINE WATER

Amos S. Newton, J. P. Fox, and Rajendra Raval

## ABSTRACT

The occurrence of organic contaminants in coal slurry pipeline water has been subjected to an initial investigation. A bibliography of papers related to this subject has been compiled. A laboratory model rodmill has been designed and constructed for batch preparation of coal slurries. Preliminary experiments have shown the presence of obvious contamination that was traceable to the laboratory de-ionized water. No non-polar compounds boiling between 200°C and 400°C were found in the coal slurry water at a concentration higher than approximately 0.1 ppb.

## INTRODUCTION

In order to meet the expected increase in use of coal, especially low-sulfur western coals, a large increase in transport capacity will be necessary. Much of this increased capacity will be met by the construction of coal slurry pipelines. At present only one coal slurry pipeline is in operation but several others are expected to be constructed soon.

The transport of coal by slurry pipeline involves the grinding of coal with water in a rodmill to a fineness such that the resulting slurry remains suspended during pipeline transport. A slurry of about 50% coal can be transported by pipeline. The coal user recovers the coal by centrifugation and/or filtration and

the recovered moist coal can be burned directly in a power plant. The recovered water must be disposed of in some manner if it is not used as make-up water in the power plant. In the Black Mesa pipeline system and Mohave power plant, the moist coal from the centrifuge is burned directly. The water from the centrifuge is further filtered and used as make-up cooling water. Washings from the filters are evaporated in watertight ponds and no water is released to the aquatic environment.

Because the disposal of pipeline water in a closed system may not be possible in all situations, it is important to have information on what contaminants might be present in the recovered water if proper treatment is to be made before disposal into the aquatic environment. A bibliography of coal-water interactions has been compiled. Several studies of coal-water interactions have been made, either in glass laboratory shaker bottles,<sup>1,2</sup> or in a closed-pipeline test loop.<sup>3</sup> The principal concern of these studies was the leaching into the water of inorganic constituents such as the elements As, Pb, Cr, Cd, Mn, Zn, and Hg, and the ions nitrate, sulfate, and carbonate. Little work has involved the study of organics in the water. Godwin and Manahan<sup>3</sup> found that leaching of lignites and sub-bituminous coals releases humic acids into water, and these authors were concerned about possible complexing of metals by the humic acids. Humic acids were estimated to be equal to the chemical oxygen demand (COD) of water.

Other studies on the drainage water from coal mines, water from washing coal, and drainage from open coal piles are related but are not exactly equivalent since in these cases the overall system is oxidizing owing to the presence of air. In wet grinding coal in a steel rodmill, hydrogen gas is produced and the system rapidly becomes reducing. Possible interactions of nascent hydrogen can result in the fragmentation of organic groups from the surface of the coal to produce organic compounds which may remain in the water. Because of the structure of coal, polynuclear aromatic hydrocarbons and phenolic compounds are expected products of this interaction.

Expected concentrations of organic compounds in slurry water are certainly limited to the respective solubility of each compound in water. For phenolic compounds this may be quite high, but for hydrocarbons such as phenanthrene, pyrene, etc., the solubility in water has been shown to vary from 2,700 ppb to less than 1 ppb (micrograms/liter) as shown in Table 1.<sup>4</sup> It is possible that the concentrations can exceed these solubility values if organic compounds are adsorbed onto colloidal material or very fine particulates in the water. It is also possible that the coal itself can act as an adsorbent for these organic compounds and that the concentrations in pipeline water may be well below the solubilities.

#### EXPERIMENTAL

An industrial rodmill for the preparation of coal slurries is approximately 4 meters in diameter and 5.5 meters long. The average residence time of coal in a continuous mill is only a few minutes. A laboratory batch mill cannot exactly duplicate all of these plant conditions, but a laboratory mill which does duplicate some of them is shown in Figs. 1 and 2. It is made from a 9-inch-long piece of 8 inch O.D. seamless steel pipe. Inside are welded 1/2 x 1/2 inch steel bars to carry the rods and provide a good grinding action. Five 1-inch diameter steel rods are adequate. The cover is sealed with an "O" ring, and it also contains a valve through which gas samples can be removed from the rodmill. The net volume of the mill for coal, water, and gas space is 5278 ml. The mill is driven on a jar mill drive, Fisher Scientific Co., Model 753 RM. The drive was modified to reduce the speed by adding an additional 4:1 reduction pulley system. With the modified drive the rodmill is rotated at 28 RPM.

The coals to be investigated are Black Mesa coal and Illinois No. 6 coal obtained from the Peabody Coal Company, and Wyodak Roland Seam Coal obtained from Wyodak Resources.

The experimental procedure in the first experiments has been to add the coal to water and agitate them for

Table 1

Solubilities of Some Polynuclear Aromatic Hydrocarbons in Water

Compound	Solubility in Micrograms/Liter @ 25°C	Solubility in Micrograms/Liter @ 20°C
Anthracene	75	89
Phenanthrene	1600	2700
Naphthalene	1.0	--
Chrysene	1.5	--
5-methyl chrysene	62	--
6-methyl chrysene	25	--
1,2 - Benzanthracene	11	--
Triphenylene	38	--
Pyrene	165	--
Perylene	<0.5	--
Picene	2.5	--
3,4 Benzpyrene	9.0	--



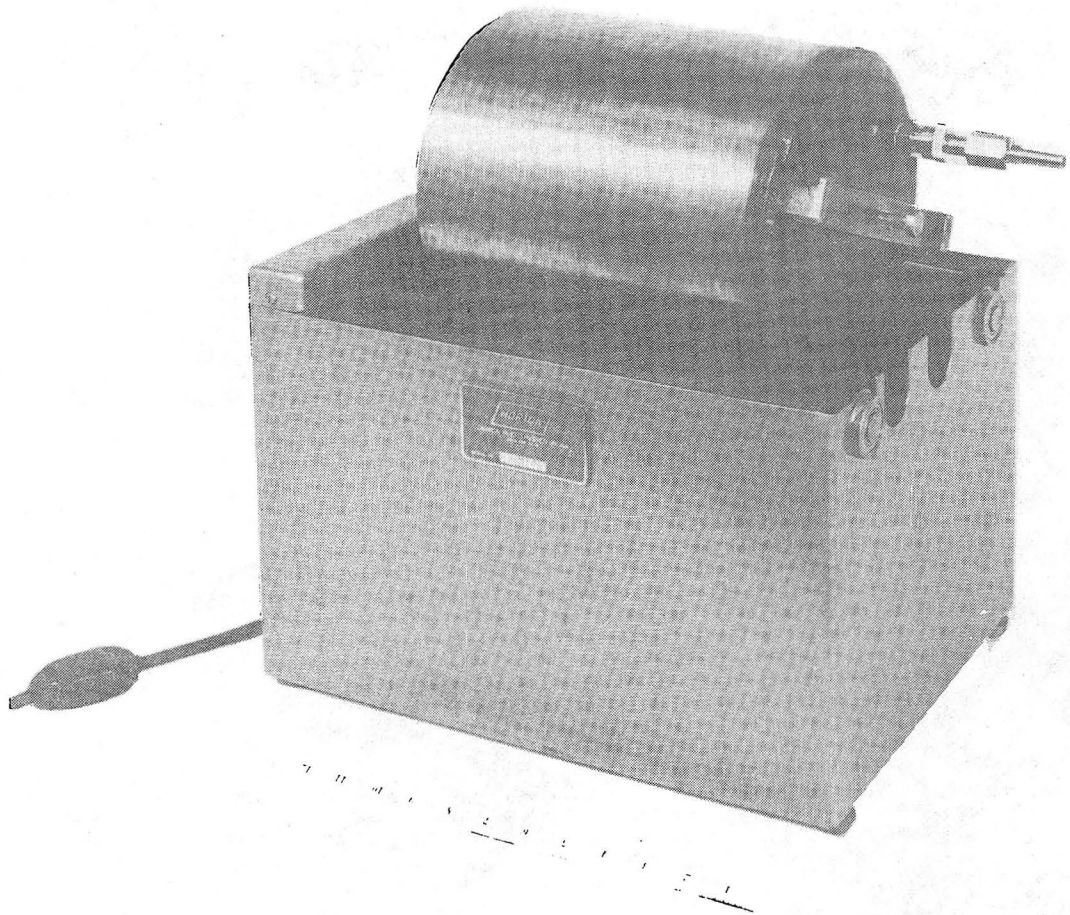


Figure 1.

XBB 790-15385

Photograph of laboratory rodmill and its  
drive for the preparation of coal slurries.  
(No. XBB-790-15385).

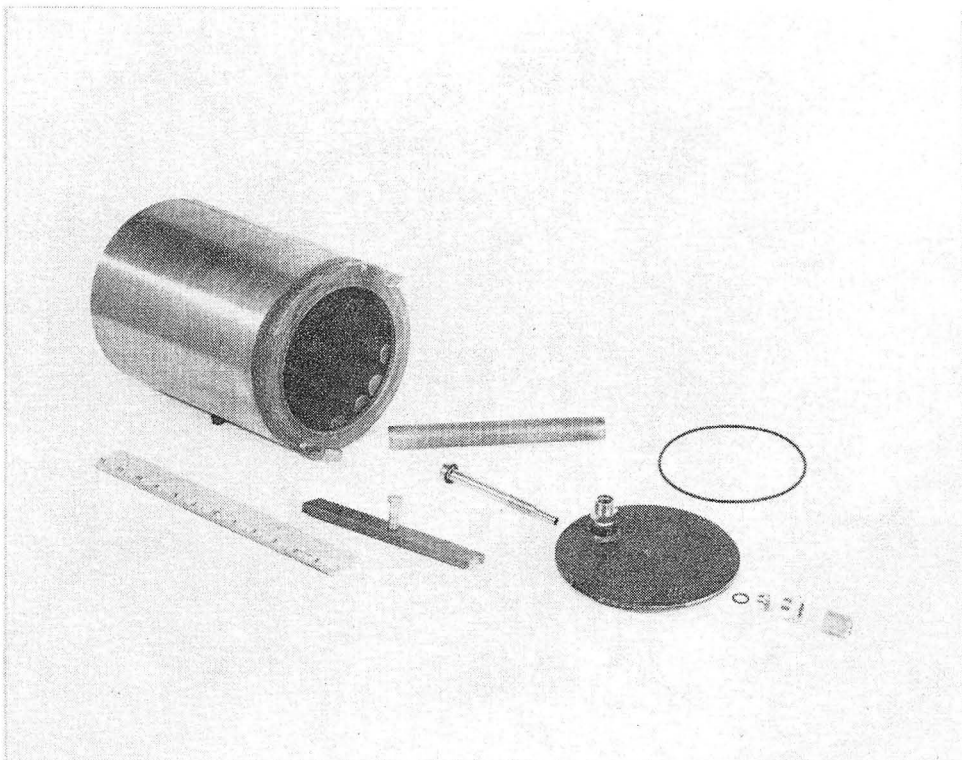


Figure 2.

XBB 790-15386

Photograph of laboratory rodmill in exploded view showing positioning of rods, cover, and valving system.

(No. XBB-790-15386)

16 - 18 hours. The slurry was centrifuged in glass bottles. The water was further filtered. The filtered water was extracted with nano-grade hexane and the hexane extract concentrated to a 1 - 2 ml volume in a vacuum evaporator. The sample volume was further reduced to less than 20 microliters by evaporation with a stream of nitrogen gas.

The concentrated sample was studied using a Finnigan Model 4023 GC/MS. A 30 Meter OV-101 capillary GC column was used with Grob injection. This system and method give excellent identification of many components, but only an approximate quantitative result can be cited.

#### RESULTS AND DISCUSSION

Three preliminary experiments, the results of which are shown in Table 2, have been performed. Samples Coal A and Coal C were made up with Wyodak coal and laboratory de-ionized water. The results show gross contamination with phthalate esters and squalene. As shown in Table 3, the phthalate esters are traceable to the de-ionized water which is in contact with polyvinyl chloride pipes. The squalene probably arises from fingerprints. These results illustrate the extreme care that must be taken in obtaining and analyzing samples.

The sample Rodmill-1 (Table 2) shows much less contamination than did the earlier samples made with de-ionized water. The low concentrations of hydrocarbons observed in sample Rodmill-1 may be residual contamination from traces of oil which were not removed in cleaning the rodmill. These should gradually be eliminated with use of the rodmill. Water must, however, be distilled from alkaline permanganate to eliminate all organic compounds from that source. No impurities were observed in the hexane.

In Table 4 the gases present in sample Rodmill-1 are shown. Hydrogen, some CO<sub>2</sub>, and the oxygen-depleted air initially present in the samples were found. In this sample some gas was lost owing to excessive pressure build-up. No methane was detected.

Table 2

Organic Compounds Found in Coal Slurry Water

Compound	Concentration in ppb in Water		
	Coal A <sup>a</sup>	Coal C <sup>b</sup>	Rodmill-1 <sup>c</sup>
Diethyl Phthalate	5.0	.15	≤0.005
Dibutyl Phthalate	15	2.8	0.15
Hexanedioic Acid ester unidentified (not a phthalate)	--	--	0.15
Diisooctyl Phthalate	3.0	0.25	0.05
Squalene	0.3	0.007	0.10
Hydrocarbons C <sub>15</sub> -C <sub>30</sub> (each)	≤0.1	<0.015	<0.005

<sup>a</sup> Coal A sample was 250 g Wyodak Coal (<100 mesh) shaken with laboratory de-ionized water in a 500 ml glass bottle. Hexane extract of water analyzed.

<sup>b</sup> Coal C sample was like Coal A except 500 g lump coal used with 500 ml water and 100 g 1-cm steel ball bearings added. Hexane extract of water analyzed.

<sup>c</sup> Rodmill-1 sample was 2300 g of Wyodak coal ground with 2500 ml LBL tap water (EBMUD water) for 16 hours. Hexane extract of water analyzed.

Table 3

Blank Determinations of Water and Hexane Used

Compound	ppb Impurities In:			
	De-ionized Water		Tap Water	Hexane
	A	B		
Diethyl phthalate	--	--	--	--
Dibutyl phthalate	0.1	0.6	0.001	<0.001 <sup>a</sup>
Hexanedioic acid ester	--	1.6	--	--
Diisooctyl phthalate	14	12	0.004	<0.001 <sup>a</sup>
Squalene	0.3	10	--	<0.001 <sup>a</sup>
Hydrocarbons	--	--	--	--

<sup>a</sup> No contamination observed at this sensitivity level.

Table 4

Analysis of Gases From Sample Rodmill - 1

Compound	% Compound	Amount of Gas, Millimoles
H <sub>2</sub>	78.9	97
N <sub>2</sub>	19.3	24
O <sub>2</sub>	0.0	(-6) <sup>a</sup>
Ar	0.24	0.3
CO <sub>2</sub>	1.51	1.8

<sup>a</sup> This amount of O<sub>2</sub> was depleted from the air initially present.

The results presented here show that water from a slurry with Wyodak sub-bituminous coal contains no hexane-extractable contaminants attributable to the coal in amounts larger than 0.1 ppb. In the present experiments, phenols and other polar compounds were not determined and volatile compounds such as benzene and toluene would have been lost in the hexane concentration step.

REFERENCES

- 1) Moore, J. W., "Water Quality Aspects of Coal Transportation by Slurry Pipeline," Proc. 4th Int. Tech. Conf. on Slurry Transportation, Las Vegas, Nev., Mar. 28-30, 1979, p.157.
- 2) Anderson, O. L., Rogozen, M. B., Margler, W. L., Mankiewicz, P., and Axelrod, M. H., "Water Pollution Control for Coal Slurry Pipelines," Institute of Geophysics, UCLA and Science Applications, Inc. Report SA 1-068-79-516, June 30, 1978.
- 3) Godwin, J. and Manahan, S. E., "Interchange of Metals and Organic Matter Between Water and Sub-bituminous Coal or Lignite Under Simulated Coal Slurry Pipeline Conditions," Environmental Science and Technology, 13 1100 (1979).
- 4) Seidell, H. and Linke, W. F., "Solubilities of Inorganic and Organic Compounds," Supp. to 3rd Ed., D. Van Nostrand Co., N.Y. 1952, p. 758.



This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720