
Solvent Refined Coal Studies: Effects and Characterization of Treated Solvent Refined Coal Effluent

Progress Report - FY 1977

**C. D. Becker
W. G. Woodfield
J. A. Strand**

July 1978

**Prepared for the U.S. Department of Energy
under Contract No. EY-76-C-06-1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by**



NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or 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.

The views, opinions and conclusions contained in this report are those of the contractor and do not necessarily represent those of the United States Government or the United States Department of Energy.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$____*; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.00
026-050	\$4.50
051-075	\$5.25
076-100	\$6.00
101-125	\$6.50
126-150	\$7.25
151-175	\$8.00
176-200	\$9.00
201-225	\$9.25
226-250	\$9.50
251-275	\$10.75
276-300	\$11.00

3 3679 00047 8984

PNL-2608

UC-11

**Solvent Refined Coal Studies:
Effects and Characterization of
Treated Solvent Refined Coal
Effluent**

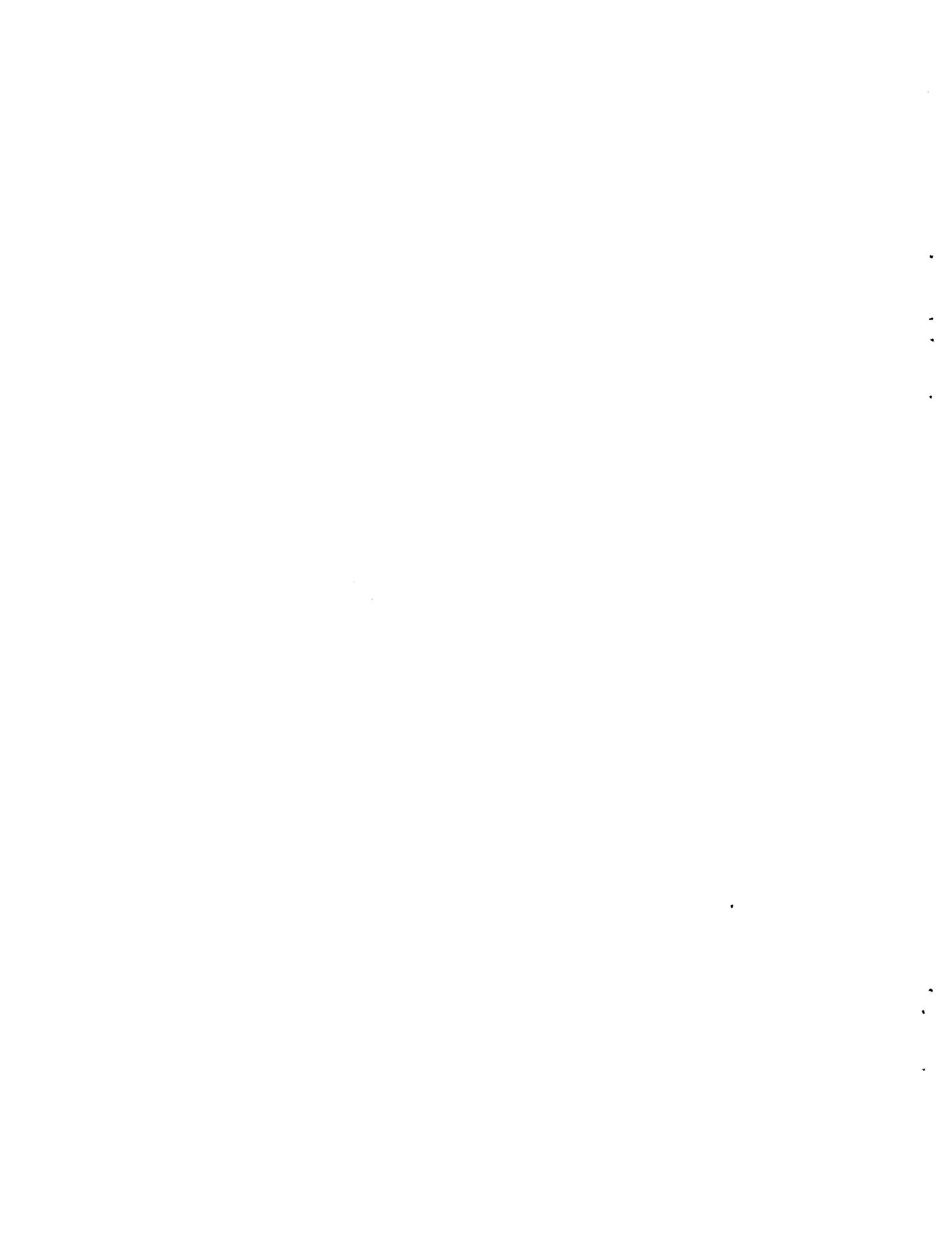
Progress Report - FY 1977

C. D. Becker
W. G. Woodfield
J. A. Strand

July 1978

Prepared for
the U.S. Department of Energy
under Contract No. EY-76-C-06-1830

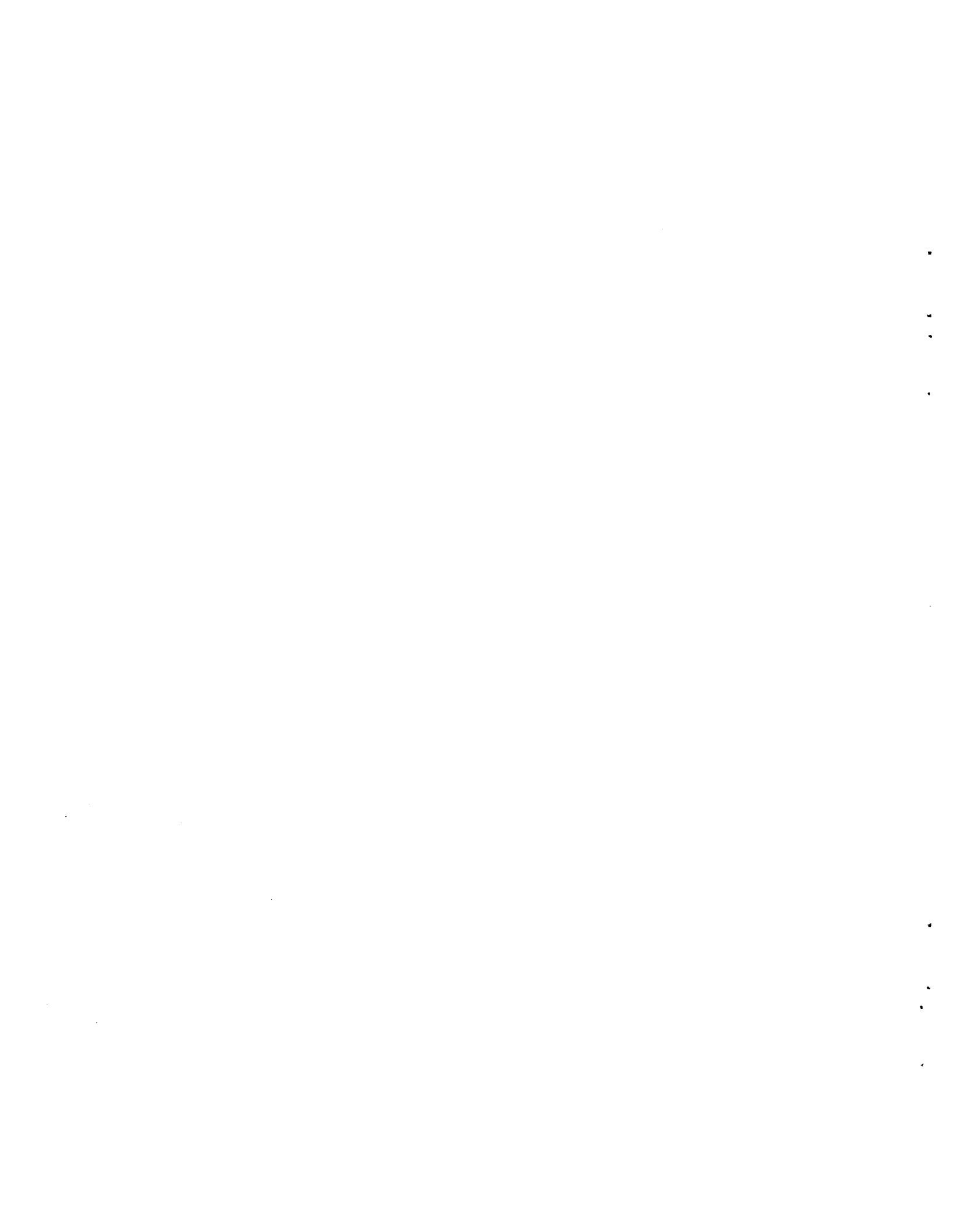
Pacific Northwest Laboratory
Richland, Washington 99352



SUMMARY

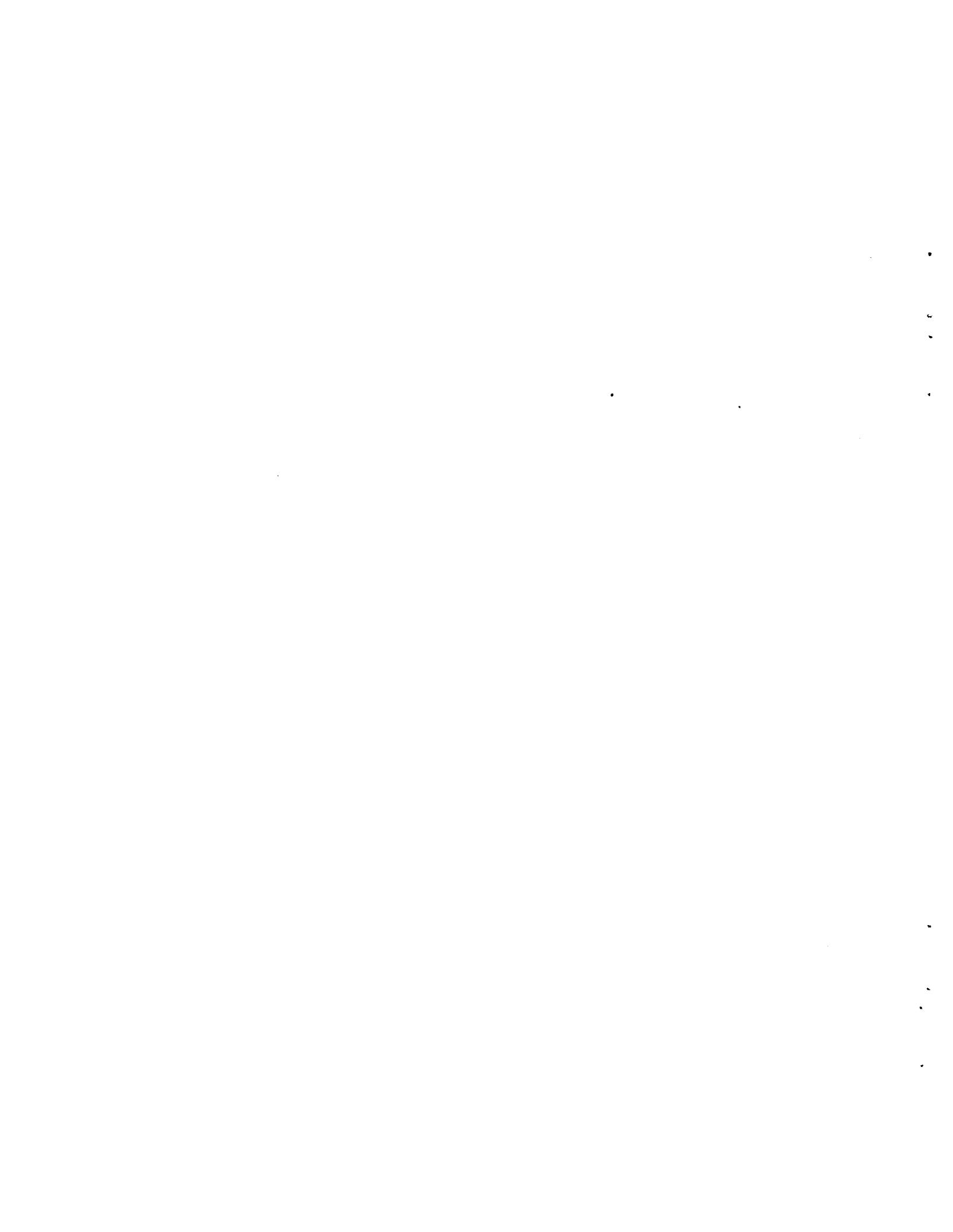
The Freshwater Sciences Section of PNL has initiated biologically oriented studies at the P&M solvent refined coal (SRC) pilot plant on the Fort Lewis Reservation in western Washington. Essentially, the study objectives are to identify residual components in the treated SRC process and assess potential for adverse impact on water quality and aquatic biota.

Since inception of research in mid-1976, six static toxicity tests with treated SRC process effluent have been conducted. Toxic components, not yet specifically identified, sometimes occur in the effluent. It is believed these components involve organic hydrocarbons of the phenol and cresol groups. Analyses have been obtained on inorganic and organic constituents in partially-treated and treated process effluent. Concentrations of inorganics identified in the effluent did not differ greatly from their concentrations in Lake Sequalitchew or SRC plant tap water, but the low concentrations may be due primarily to dilution with freshwater before discharge. Organics identified in the effluent are similar to those found in samples contaminated with petroleum, and involve many complex hydrocarbons.



CONTENTS

SUMMARY	iii
INTRODUCTION	1
BACKGROUND INFORMATION	3
STATIC TOXICITY TESTS	7
METHODS	7
RESULTS	8
Test No. 1	9
Test No. 2	10
Test No. 3	11
Test No. 4	11
Test No. 5	11
Test No. 6	11
SAMPLE ANALYSES	13
METHODS	13
Sample Collection	13
Water Quality Analysis	13
Inorganic Analysis	13
Organic Analysis	14
RESULTS	14
Water Quality Analyses	14
Inorganic Analyses	14
Organic Analyses	18
RECOMMENDATIONS	25
REFERENCES	27
DISTRIBUTION	29



FIGURES

1	Physical Environs at the P&M SRC Pilot Plant, Fort Lewis, Washington	4
2	Diagram of the Waste Water-Oil Disposal System Flow at the P&M SRC Pilot Plant, Fort Lewis, Washington	5
3	Randomized Distribution of Aquaria and Effluent Concentrations as Used in Static Toxicity Tests with Treated SRC Process Effluent	8
4	Gas Chromatogram of Fraction 2 (Primarily Tetrалins and Naphthalenes) from Valve No. 9108 Taken 5/21/76	21
5	Gas Chromatogram of Fraction 2 (Primarily Tetrалins and Naphthalenes) from Treated Effluent Sample Taken 5/21/76	21
6	Gas Chromatogram of Fraction 3 (Primarily Fluorenes, Phenanthrenes, Pyrene and Oxygenates) from Valve No. 9105 Taken 5/21/76	22
7	Gas Chromatogram of Fraction 2 from Valve No. 9105 Taken 5/21/76 by Means of FID/FPD	22

TABLES

1	Basic "Water Quality" Parameters of the Liquid Effluent Stream Passing Through the Waste Water Oil Treatment System at the P&M SRC Pilot Plant	6
2	Summary of Results from 96-hr Static Laboratory Toxicity Tests with Treated SRC Process Effluent at 17-19°C	9
3	Results from Toxicity Test No. 1, Conducted August 3-7, 1976; 96-hr Static Test, No Aeration; Rainbow Trout Used as Test Organism, 10 Fish/Aquaria, Average Weight 6.4 gm/Fish; Temperature $18.5 \pm 0.5^\circ\text{C}$	10
4	Results from Toxicity Test No. 2, Conducted August 24-28, 1976; 96-hr Static Test, Aeration; Largemouth Bass (<i>Micropterus salmoides</i>) Used as Test Organism, 10 Fish/Aquaria, Average Weight 4.2 gm/Fish; Temperature $18.0 \pm 5^\circ\text{C}$	10
5	Results from Toxicity Test No. 3, Conducted October 12-16, 1976; 96-hr Static Test, Aeration; Rainbow Trout Used as Test Organism, 10 Fish/Aquaria, Average Weight 9.95 gm/Fish; Temperature $17.5 \pm 0.5^\circ\text{C}$	12

TABLES (Contd)

6	Results from Toxicity Test No. 4, Conducted November 16-20, 1976; 96-hr Static Test, Aeration; Rainbow Trout and Crayfish (<u>Pacifasticus leniusculus</u>) Used as Test Organisms, 10 Fish/Aquaria; Average Weight of Fish 15.4 gm, Length of Crayfish 25-46 mm; Temperature $17.5 \pm 0.5^{\circ}\text{C}$	12
7	Results from Toxicity Test No. 5, Conducted January 27-31, 1977; 96-hr Static Test, Nonaeration; Rainbow Trout Fry Used as Test Organism, 10 Fish/Aquaria, Average Weight 1.5 gm/Fish; Temperature $17.0 \pm 0.5^{\circ}\text{C}$	13
8	Results from Toxicity Test No. 6, Conducted June 21-25, 1977; 96-hr Static Test, Nonaeration; Rainbow Trout Fry Used as Test Organism, 10 Fish/Aquaria, Average Weight 1.9 gm/Fish; Temperature $17.7 - 19.7 \pm 0.5^{\circ}\text{C}$	13
9	Data on pH, Alkalinity and EDTA Hardness from Selected Liquid Samples at the P&M SRC Pilot Plant, Fort Lewis, Washington . . .	15
10	Summary of Inorganic Analyses, Untreated SRC Process Effluent from Valve #9105; Values Given in ppb ($\mu\text{g/l}$), X-ray Fluorescence Determinations	15
11	Summary of Inorganic Analyses, Partially Treated SRC Process Effluent from Valve #9108; Values Given in ppb ($\mu\text{g/l}$), X-ray Fluorescence Determinations	16
12	Summary of Inorganic Analyses, Treated SRC Process Effluent from Plant Discharge Pipe; Values Given in ppb ($\mu\text{g/l}$), X-ray Fluorescence Determinations	16
13	Summary of Inorganic Analyses, Tap Water from SRC Plant; Values Given in ppb ($\mu\text{g/l}$), X-ray Fluorescence Determinations	17
14	Summary of Inorganic Analyses, Lake Sequalitchew Water; Values in ppb ($\mu\text{g/l}$), X-ray Fluorescence Determinations	17
15	Characterization of Total Extractables from SRC Process Effluent Samples Taken 5-21-76 (SRC-I Process)	18
16	Characterization of Aromatic Components in SRC Process Effluent Samples Taken 5-21-76 (SRC-I Process)	20
17	Analysis of Phenol in Treated SRC Process Effluent at Various Dates, Determined by High Pressure Liquid Chromatography	23
18	Identification of Major Aromatic Components in Partially-Treated SRC Process Effluent Samples Taken on the Indicated Dates (SRC-II Process)	24

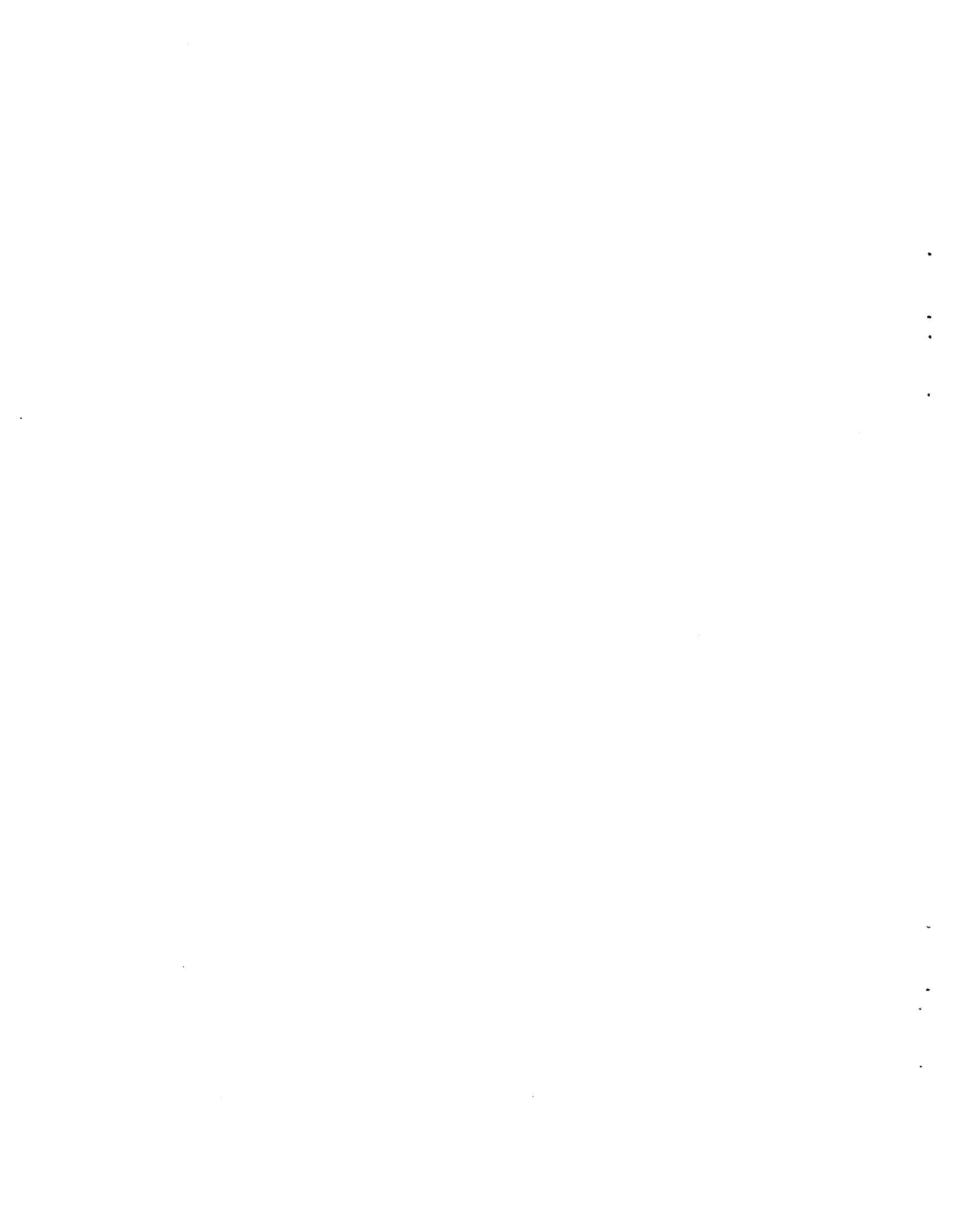
SOLVENT REFINED COAL STUDIES: EFFECTS AND CHARACTERIZATION OF TREATED SRC EFFLUENT

INTRODUCTION

Under DOE (formerly ERDA) contract, our research staff has collected liquid effluent samples at the solvent refined coal (SRC) pilot plant operated by the Pittsburg & Midway Coal Mining Co. (P&M) at the Fort Lewis, Washington, military reservation since May 1976. This report summarizes data obtained through September 30, 1977 in the following areas: 1) 96-hr static toxicity tests with treated SRC process effluent, 2) inorganic analyses of SRC process effluent, and 3) organic analysis of SRC process effluent.

Initial studies were designed to provide a cursory look at potential toxicity to fish of treated process effluent released from the SRC plant. Analyses of samples taken simultaneously were made to identify chemical components of the process effluent for correlation with fish mortality during bioassays. Thus, the first objectives were to: 1) determine direct, acute toxicity of treated effluent, if any, and 2) characterize the inorganic and organic constituents of the effluents.

Subsequent objectives of future studies based on initial work are to: 1) measure the accumulation and retention of key components occurring in treated SRC process effluent in selected freshwater organisms, and 2) assess the sublethal physiological and behavioral responses of freshwater organisms to key components occurring in treated SRC process effluent. Amended and/or additional objectives may result as the data base accumulates.



BACKGROUND INFORMATION

Solvent refining of coal is a promising new technology associated with the national effort to obtain fuller use of existing fossil fuel resources in the United States. P&M is currently producing solvent refined coal at a 50 ton/day pilot plant located on the Fort Lewis military reservation in western Washington. The refined product meets specific design specifications for reduced atmospheric emissions when burned. The plant was developed with support of an ERDA contract for study of the commercial feasibility of solvent refining of coal. The pilot plant includes all the major steps in the conceptual SRC process except the step required for production of hydrogen or synthesis gas from the process residue.

In the SRC process, crushed coal is mixed with a recycle solvent and heated to about 750-770°F in a preheater at a pressure of 1500 psi or more in the presence of hydrogen. The coal swells and then dissolves. The crude product slurry is filtered to remove insoluble inorganic residue and unconverted coal. The filtrate is distilled to recover the solvent for recycle, and the product resulting from solidification is solvent refined coal.

The calorific value of solid SRC is about 16,000 BTU/lb, and its composition is uniform regardless of the type of coal processed. Ash contents of about 0.1% and removal of over 90% of the pyritic sulfur and about 50% of the organic sulfur from the coal are typical of SRC processing. As well as providing a low sulfur, very low ash, high calorific material for direct combustion, the SRC process can be used to produce high grade coke or further hydrogenated to produce a range of liquid fuels or refinery feedstocks (the SRC-II products). Thus, solvent refining of coal can produce either a solid product (the refined coal) or a liquid product. Further details on the SRC technology are available in the literature.^{1,2,3,4}

The SRC pilot plant operated by P&M is located in the U.S. Army military reservation at Fort Lewis, Washington, near Dupont and the site covers about 12 acres (Figure 1). Construction required about 2 years at an estimated cost near \$20 million. Plant facilities can be grouped into several areas including those for coal preparation and handling, coal liquefaction and filtration, gas cleaning and acid-gas removal, product handling and storage, solvent recovery, tank farm, hydrogen production, and auxiliary facilities such as steam generation, inert gas manufacture, a sulfur plant, and water treatment.⁵

The SRC plant is a pilot operation in which materials and operating conditions are frequently changed. Operational changes, for example, occur between SRC-I and SRC-II processes that presently utilize various eastern coals. Therefore, chemical components may vary substantially between various experimental runs and substantial monitoring is required for characterization.

Studies by the Freshwater Sciences Section of PNL were initiated in mid-1976 when permission was obtained from ERDA (DOE) and its contractor (P&M)

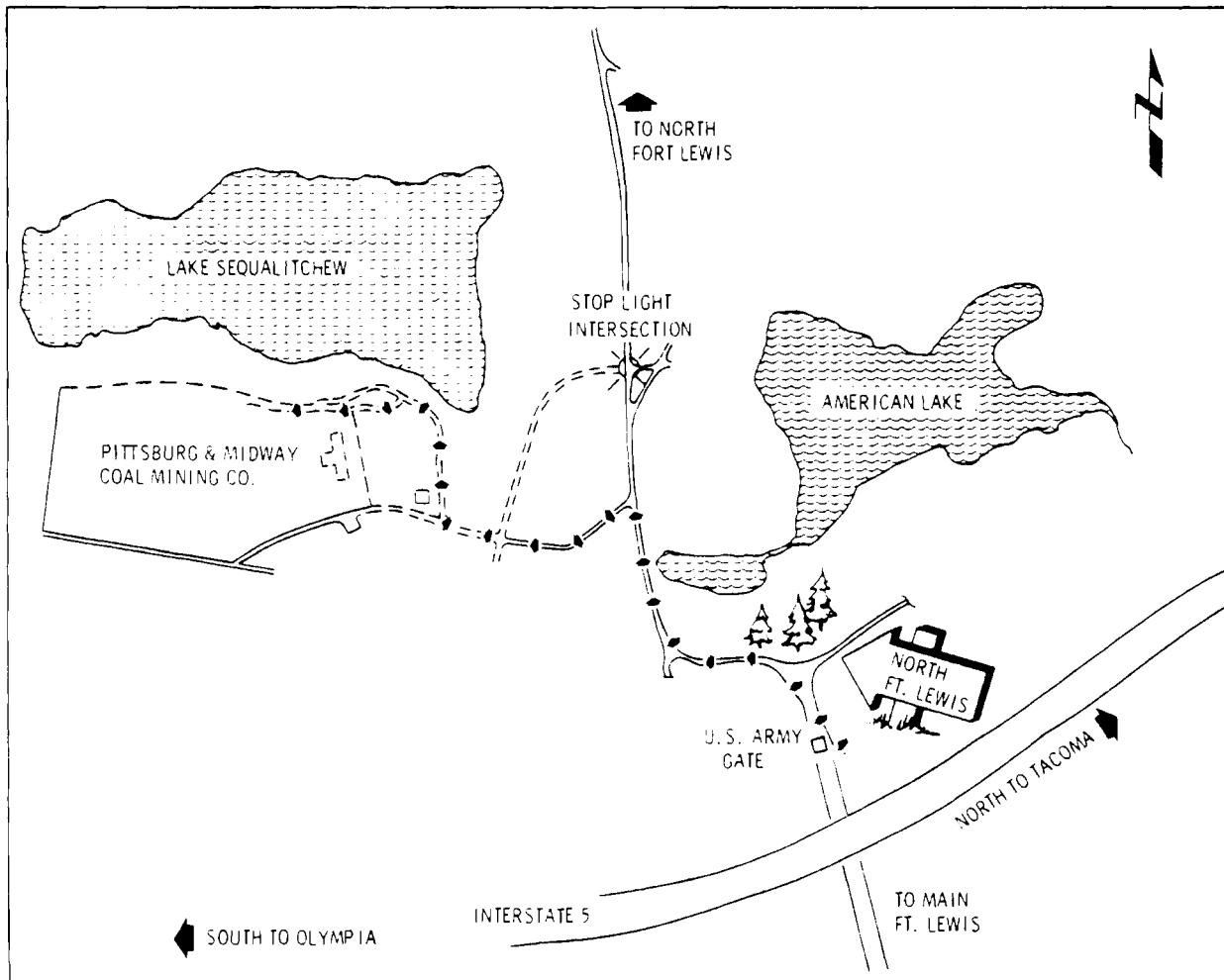


FIGURE 1. Physical Environs at the P&M SRC Pilot Plant, Fort Lewis, Washington. Water for plant use originates from Lake Sequaltchew, but first passes through a water treatment plant (unshown). The small discharge sump receiving treated process effluent is off the southwest corner of the plant enclosure.

to proceed with planned research at the SRC pilot plant. This research originated from environmental concerns regarding possible adverse impacts on water quality and aquatic biota. Consequently, our research focuses on byproducts or impurities of the SRC process that might reach aquatic habitats.

Our first research concern is focused on potential toxicants in treated process effluent. Liquid waste streams from the plant are combined and subjected to a waste treatment process consisting of clarification, biological treatment, sand filtration, and finally carbon filtration. The waste water - oil treatment system is diagrammed in Figure 2, and some basic "water quality" parameters of the liquid effluent stream passing through the treatment units are given in Table 1.

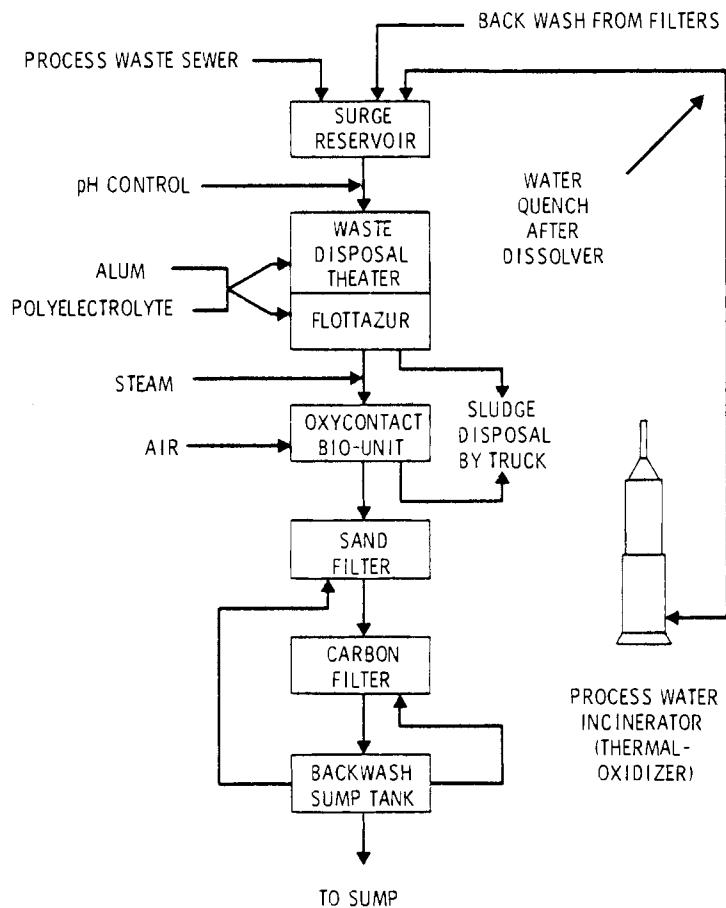


FIGURE 2. Diagram of the Waste Water-Oil Disposal System Flow at the P&M SRC Pilot Plant, Fort Lewis, Washington. The surge reservoir represents the major hydrocarbon emission point in the basic properties of the effluent at this point. Precipitation is accomplished by adding alum polyelectrolyte at different locations. The oxycontact bio-unit is an oxygenated sludge process incorporating phenol degrading micro-organisms. The sand filter removes particulates and the carbon filter removes residual hydrocarbons from the effluent before its discharge.

The treated process effluent is diluted with tap water and discharged into a small sump where any remaining chemical constituents are subject to biodegradation and/or bioaccumulation through natural processes. Potential toxicants or carcinogens present in minute or undetectable amounts in treated process effluent may concentrate in pond sediments and biota.

The P&M SRC pilot plant is an experimental facility with a mode of operation and operating conditions subject to change. The discharge of treated process effluent into an enclosed sump is an atypical process since

TABLE 1. Basic "Water Quality" Parameters of the Liquid Effluent Stream Passing Through the Waste Water Oil Treatment System at the P&M SRC Pilot Plant. The treated process effluent is diluted with tap water and discharged into a small sump. From Perrussel et al., 1977.⁵

	<u>Surge Reservoir</u>	<u>Waste Disposal Treater</u>	<u>Flottazur</u>	<u>Bio-Unit Effluent</u>	<u>Treated Plant Effluent</u>
pH	6.9-9.0	6.2-6.8	6.2-6.8	6.2-7.4	6.2-7.4
BOD, ppm			135-350	20-110	4-23
COD, ppm	1000-9600	650-5000	500-4000	40-400	5-75
TSS, ppm	90-400	50-300	30-200	20-300	0-20
Phenol, ppm	30-1500	25-1100	10-1000	0.1-3.0	0.0-0.6
Extractable Oil, ppm	10-250	6-150	4-30	0-4	0-3

other methods of effluent disposal may be used in a commercial operation. Moreover, an experimental facility is characteristically subject to sporadic perturbations in its waste disposal system.

STATIC TOXICITY TESTS

METHODS

Collections of treated process effluent were taken directly from the plant waste water flow as it discharged from 8 in. diameter pipeline. The effluent is diluted before discharge. After discharge, the effluent flows down a short ditch where it passes through an additional oil-filtration bed before entering the effluent sump. Arrangements must be made at the SRC plant to release diluted waste effluent for collection of effluent samples since discharge is periodic and not necessarily correlated with our sampling trips.

The treated process effluent was transported in glass carboys to our Richland laboratories for subsequent exposure of aquatic organisms (usually fish) in static bioassays. Carboys were thoroughly cleaned before use and were filled by means of metal bucket and metal funnel, plugged with a rubber stopper wrapped in teflon tape, and then sealed entirely with teflon tape for transportation.

Tests involved 96-hr exposures and were conducted in 54 l glass aquaria. All exposures were to static conditions, i.e., effluent was not replaced or changed over the duration of exposure. This procedure was necessary because sufficient volumes of treated effluent could not be transported to Richland to conduct a continuous-flow type assay where the exposure solution is continually replaced with fresh effluent.

Assay aquaria were arranged as 12 randomized replicates (Figure 3) at effluent concentrations of 100, 80, 60, 40, 20 and 0% (control). Dilution water was taken from the Columbia River and filtered before use. All exposures were at 17-19°C, the approximate temperature of the treated effluent when discharged from the SRC pilot plant. Temperature, pH, and dissolved oxygen were measured daily in each aquaria for quality control.

Initially, the test design was to conduct exposures without aeration to avoid possible loss of volatile compounds. The first assay indicated the need of aeration because of a decline of dissolved oxygen with exposure time, a function of organic matter and loading capacity of each aquaria. In assays, particularly of the static type, there is a maximum weight of organisms/liter of solution/aquaria/day for each 96-hr test.⁶ When the weight of test organisms exceeds acceptable volumetric limits for a static assay, test solutions must be aerated. We aerated the solutions only when required by excessive aquaria loading capacity.

The primary test organism was juvenile rainbow trout (Salmo gairdneri). This fish is commonly used in toxicity tests and its tolerance to various chemicals and trace elements is well documented. Since rainbow trout are raised in our experimental hatchery at PNL, their size, weight, disease state, temperature acclimation, and general history are controlled.

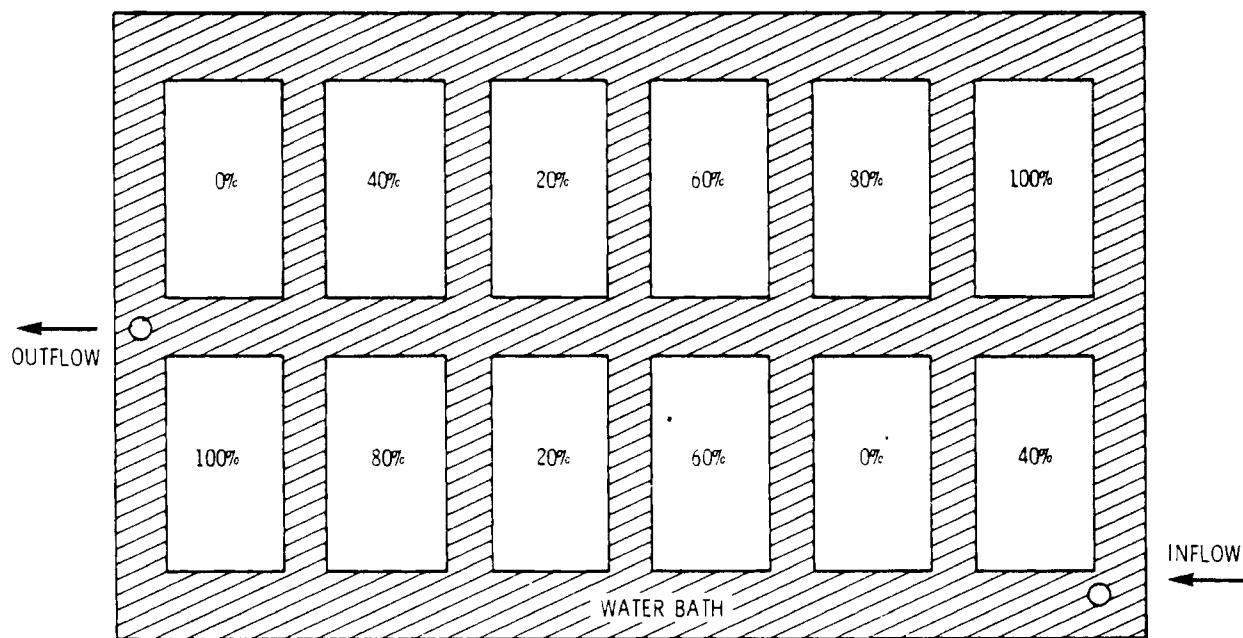


FIGURE 3. Randomized Distribution of Aquaria and Effluent Concentrations as Used in Static Toxicity Tests with Treated SRC Process Effluent. The aquaria are 54 liter capacity, and test temperatures are maintained at 17-19°C by the surrounding water bath. Each aquaria has a glass cover to restrict loss of volatiles.

Fingerling largemouth bass (*Micropterus salmoides*) and crayfish (*Pacifastacus leniusculus*) collected from the Columbia River and environs were also used as test organisms.

RESULTS

Toxicity tests provide only a general indication of the relative toxicity of treated SRC process effluent to fish, but are a fundamental building block of assessment research. Aquatic organisms such as fish are valuable indicators of toxic components in industrial waste discharges by exhibiting a variety of direct (lethal) and indirect (sublethal) responses. However, a biological response alone will not identify the particular toxicant or combination of toxicants evoking the response, but merely indicate that deleterious material is present.

The results of six static bioassays are summarized in Table 2. Treated process effluent exhibits varied effects. Mortality is sometimes apparent in exposed organisms, while at other times no effect is evident. Inconsistency in relative toxicity is influenced by factors that modify the organic and/or inorganic composition of the effluent such as the condition of the charcoal filter (effectiveness in sorbing low molecular weight, soluble organics), pH level in the biodigester that controls the effectiveness of microorganisms in breaking down organic material, and the point in the plant

TABLE 2. Summary of Results from 96-hr Static Laboratory Toxicity Tests with Treated SRC Process Effluent at 17-19°C. Effluent was collected at the P&M SRC pilot plant, Fort Lewis, Washington one day before start of each assay.

<u>Date Assay Conducted</u>	<u>Test Organisms</u>	<u>Test Conditions</u>	<u>Assessment</u>
Aug. 3-7, 1976	rainbow trout fingerlings	nonaerated	No relationship between mortality and effluent concentration. Losses due to low dissolved oxygen.
Aug. 24-28, 1976	largemouth bass fingerlings	aerated	No mortality attributable to effluent concentration. Some losses due to disease. Some stress display by fish.
Oct. 12-16, 1976	rainbow trout fingerlings	aerated	Significant mortality ($\geq 50\%$) at effluent concentrations of 80 and 100%.
Nov. 16-20, 1976	rainbow trout and crayfish	aerated	Significant mortality ($>50\%$) at effluent concentrations of 40, 60, 80 and 100% for rainbows, $>60\%$ for crayfish; narcosis evident among crayfish.
Jan. 27-31, 1977	rainbow trout fry	nonaerated	No mortality in 96 hr but some fish stressed at 80 and 100% effluent concentrations.
June 21-25, 1977	rainbow trout fingerlings	nonaerated	Limited mortality at higher effluent concentrations.

operational run at which the effluent sample is taken. There is also considerable evidence that organic compounds sorb to particulate matter in the treated process effluent.

A review of individual toxicity tests follows. Tests 1-5 were obtained when the plant was operating under the SRC-I process, Test 6 under the SRC-II process.

Test No. 1

Mortalities occurred in all aquaria throughout the 96-hr exposure, apparently in a random fashion (Table 3). Losses among fish exposed to undiluted (100%) SRC effluent were no greater than among the controls or among fish held in various effluent dilutions. Losses were attributed directly to low dissolved oxygen (DO) concentrations in the unaerated aquaria during the first and subsequent days. Aquaria having the highest losses of fish also accumulated organic matter, resulting in considerable biochemical oxygen demand (BOD) that contributed to critically low DO levels (<5.0 ppm).

That fish mortalities were actually due to low DO was illustrated by the fact that fish in 100% SRC effluent (Aquaria 6 and 7) had the highest survival.

TABLE 3. Results from Toxicity Test No. 1, Conducted August 3-7, 1976; 96-hr Static Test, No Aeration; Rainbow Trout Used as Test Organism, 10 Fish/Aquaria, Average Weight 6.4 gm/Fish; Temperature $18.5 \pm 0.5^{\circ}\text{C}$

<u>Aquarium</u>	Percent Effluent	Daily Mortality				Total Mortality	Percent Mortality
		1	2	3	4		
1	0	1	1	1	4	7	70
2	40	0	4	0	1	5	50
3	20	0	1	2	4	7	70
4	60	0	0	1	3	4	40
5	80	0	2	2	0	4	40
6	100	0	1	1	0	2	20
<hr/>							
7	100	2	0	0	1	3	30
8	80	0	7	0	0	7	70
9	20	1	1	0	2	4	40
10	60	0	6	1	0	7	70
11	0	1	1	0	2	4	40
12	40	0	1	1	1	3	30

Test No. 2

No mortalities were attributed to effluent toxicity (Table 4). All losses were due to Flexibacter columnaris, a bacterial pathogen of fish. Observation indicated that multistresses were apparent in aquaria with 60, 80, and 100% treated SRC effluent. Fish response indicated some toxification at a chronic rather than acute level. DO values ranged from 8.1 to 9.0 ppm during the exposure period, and pH from 6.8 to 7.8.

TABLE 4. Results from Toxicity Test No. 2, Conducted August 24-28, 1976; 96-hr Static Test, Aeration; Largemouth Bass (Micropterus salmoides) Used as Test Organism, 10 Fish/Aquaria, Average Weight 4.2 gm/Fish; Temperature $18.0 \pm 5^{\circ}\text{C}$

<u>Aquarium</u>	Percent Effluent	Daily Mortality				Total Mortality	Percent Mortality
		1	2	3	4		
1	100	0	0	0	0	0	0
2	40	0	0	0	0	0	0
3	0	0	0	0	0	0	0
4	60	0	0	2	4	6	60
5	20	0	0	0	0	0	0
6	80	0	0	0	0	0	0
<hr/>							
7	0	0	0	0	0	0	0
8	80	0	0	0	0	0	0
9	40	0	0	0	0	0	0
10	60	0	0	0	0	0	0
11	20	0	0	0	0	0	0
12	100	0	0	0	1	1	10

Test No. 3

Mortalities occurred in five aquaria, apparently from toxification associated with treated SRC effluent (Table 5). Fish showed no signs of disease, and deaths were largely restricted to effluent concentrations of 80% or more. Total mortalities occurred within 24 hr in 100% effluent, and within 48 hr in 80% effluent. DO values ranged from 7.5 - 9.5 ppm, and pH values from 6.8 - 7.7.

At the time of effluent collection, a "backflush" operation was said to be under way in the waste water treatment system, and that the effluent sample would consist of undiluted plant effluent used to "backflush" the charcoal filters. Thus, the concentration of waste products in the treated effluent was expected to be near maximum. The aquaria were aerated, most mortalities occurred in 24 hr, and effluent concentrations below 60% evoked no mortalities.

Test No. 4

Mortalities of 50% or above occurred among rainbow trout at effluent concentrations of 40% and above, with no losses during the first 24 hr of exposure (Table 6). Total mortality occurred among crayfish exposed to 60% effluent during the 4th day, but response at other dilutions was variable. Highest concentrations of effluent appeared to have a "narcotic" effect. Crayfish became sluggish and immobile, often appearing dead, but would respond to tactile stimulation and handling. At the end of 96-hr exposure, surviving organisms were removed and placed in freshwater. Over 80% remained alive after 48 hr.

Test No. 5

No mortality occurred during the standard 96-hr exposure period (Table 7). Although the aquaria were unaerated, DO values remained within acceptable limits for sustaining fish life because of the low load ratio obtained by using rainbow trout fry. For this reason, exposure duration was extended to 196 hr. DO values never became critically low, and the first mortality occurred in 100% effluent at 144 hr. At termination after 196 hr, mortality was 60% in 100% effluent, 10% in 80% effluent and zero in all other dilutions. The mortality pattern indicated chronic effects that accrued during long-term exposure to treated SRC effluent.

Test No. 6

Some mortalities occurred at the highest effluent concentrations (Table 8), but were influenced by low DO values associated with partially diluted or undiluted effluent. DO values ranged from 3.6 to 8.7 ppm. Aquaria containing effluent sustained a drop in DO to critical oxygen levels (<4 ppm) by termination. However, fish behavior indicated stress primarily during the first 2 days exposure while DO levels were still favorable.

Values for pH levels ranged from 6.8 - 7.6 with the largest spread on the 2nd day between 100% effluent (pH 6.8) and control water (pH 7.6). After 4 days, pH values had shifted to a point between 7.0 - 7.15. Precipitated "flock" appeared in all aquaria containing treated process effluent.

TABLE 5. Results from Toxicity Test No. 3, Conducted October 12-16, 1976; 96-hr Static Test, Aeration; Rainbow Trout Used as Test Organism, 10 Fish/Aquaria, Average Weight 9.95 gm/Fish; Temperature $17.5 \pm 0.5^{\circ}\text{C}$

<u>Aquarium</u>	<u>Percent Effluent</u>	<u>Daily Mortality</u>				<u>Total Mortality</u>	<u>Percent Mortality</u>
		1	2	3	4		
1	100	10	0	0	0	10	100
2	40	0	0	0	0	0	0
3	0	0	0	0	0	0	0
4	60	0	0	0	0	0	0
5	20	0	0	0	0	0	0
6	80	5	1	0	0	6	60
<hr/>							
7	0	0	0	0	0	0	0
8	80	9	1	0	0	10	100
9	40	0	0	0	0	0	0
10	60	2	0	0	0	2	20
11	20	0	0	0	0	0	0
12	100	10	0	0	0	10	100

TABLE 6. Results from Toxicity Test No. 4, Conducted November 16-20, 1976; 96-hr Static Test, Aeration; Rainbow Trout and Crayfish (Pacifasticus leniusculus) Used as Test Organisms, 10 Fish/Aquaria; Average Weight of Fish 15.4 gm, Length of Crayfish 25-46 mm; Temperature $17.5 \pm 0.5^{\circ}\text{C}$

<u>Aquaria (a)</u>	<u>Percent Effluent</u>	<u>Daily Mortality</u>				<u>Total Mortality</u>	<u>Percent Mortality</u>
		1	2	3	4		
1	100	0	4	2	3	9	90
2	40	0	0	1	4	5	50
3	20	1	0	0	0	1	10
4	0	0	0	0	0	0	0
5	80	0	0	1	4	5	50
6	60	0	0	1	5	6	60
<hr/>							
7	0	0	0	0	0	0	0
8	60	0	0	0	10	10	100
9	40	0	0	0	0	0	0
10	80	0	0	0	0	0	0
11	20	0	0	0	3	3	30
12	100	0	0	0	2	2	20

(a) Aquaria 1-6 contained rainbow trout only, aquaria 7-12 crayfish only.

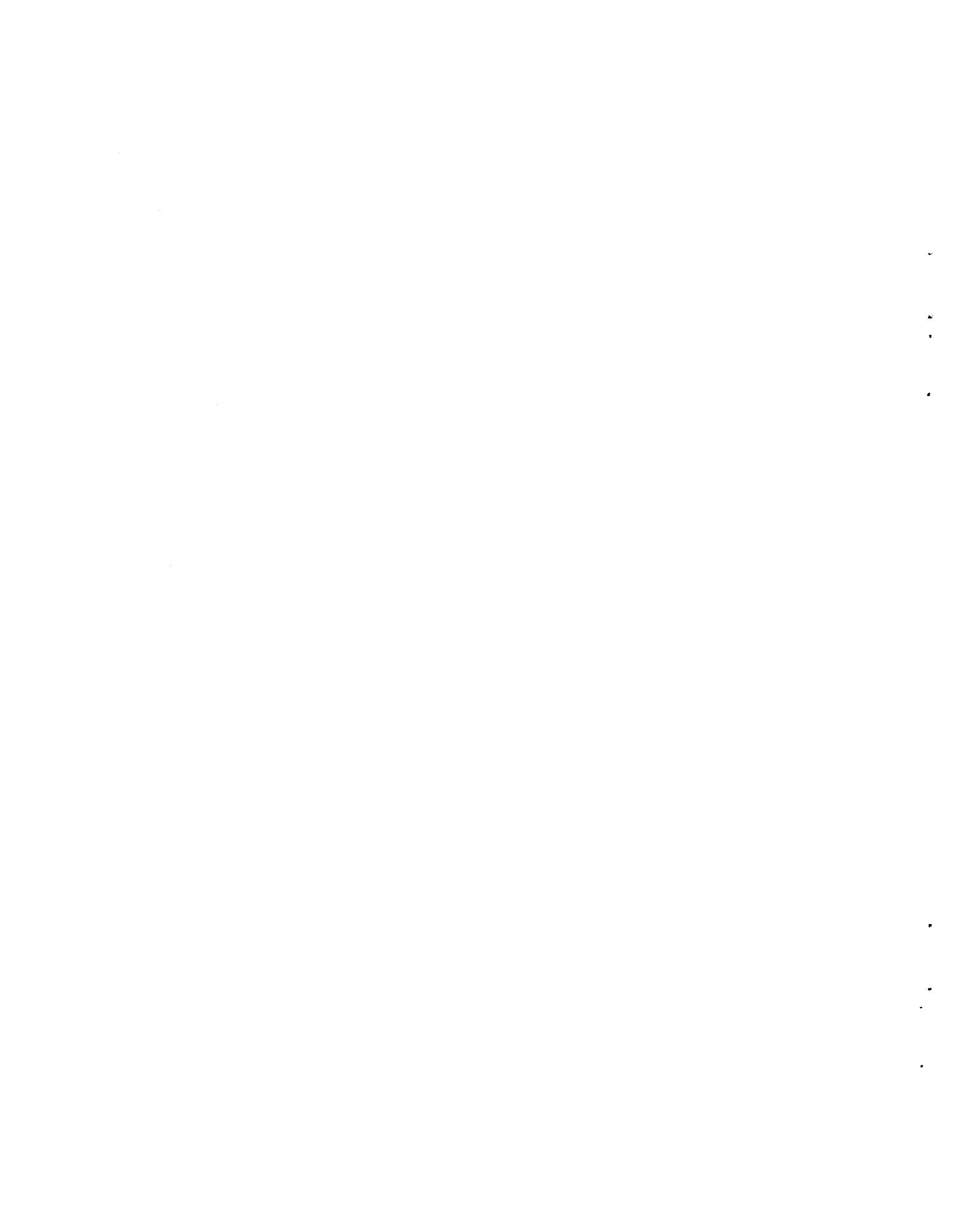
TABLE 7. Results from Toxicity Test No. 5, Conducted January 27-31, 1977; 96-hr Static Test, Nonaeration; Rainbow Trout Fry Used as Test Organism, 10 Fish/Aquaria, Average Weight 1.5 gm/Fish; Temperature $17.0 \pm 0.5^{\circ}\text{C}$

<u>Aquarium</u>	<u>Percent Effluent</u>	<u>Daily Mortality</u>				<u>Total Mortality</u>	<u>Percent Mortality</u>
		1	2	3	4		
1	100	0	0	0	0	0	0
2	40	0	0	0	0	0	0
3	20	0	0	0	0	0	0
4	0	0	0	0	0	0	0
5	80	0	0	0	0	0	0
6	60	0	0	0	0	0	0
<hr/>							
7	0	0	0	0	0	0	0
8	60	0	0	0	0	0	0
9	40	0	0	0	0	0	0
10	80	0	0	0	0	0	0
11	20	0	0	0	0	0	0
12	100	0	0	0	0	0	0

TABLE 8. Results from Toxicity Test No. 6, Conducted June 21-25, 1977; 96-hr Static Test, Nonaeration; Rainbow Trout Fry Used as Test Organism, 10 Fish/Aquaria, Average Weight 1.9 gm/Fish; Temperature $17.7 - 19.7 \pm 0.5^{\circ}\text{C}$

<u>Aquarium</u>	<u>Percent Effluent(a)</u>	<u>Daily Mortality</u>				<u>Total Mortality</u>	<u>Percent Mortality</u>
		1	2	3	4		
1	100	3	0	1	0	4	40
2	40	0	0	0	0	0	0
3	20	0	0	0	0	0	0
4	0	0	0	0	0	0	0
5	80	1	0	0	0	1	10
6	60	1	0	0	1	2	20
<hr/>							
7	0	0	0	0	0	0	0
8	60	0	1	0	0	1	10
9	40	0	0	0	0	0	0
10	80	0	1	0	0	1	10
11	20	0	0	0	0	0	0
12	100	1	0	0	0	1	10

(a) Plant converted to "SRC-II" process in period between Test No. 5 and Test No. 6.



SAMPLE ANALYSES

METHODS

Sample Collection

Samples of SRC process effluent for qualitative and/or quantitative analyses were taken from the following locations: a) Valve #9105, at the outlet of surge reservoir, a hydrocarbon emission point in the SRC plant (untreated effluent); b) Valve #9108, at the outlet of the flottazur unit following alum polyelectrolyte precipitation and clarification (partially treated effluent); c) completely treated process effluent leaving the bi-digester, passing through the oil filters, and exiting from the plant discharge pipe after dilution with sanitary water; d) SRC plant effluent pond, an enclosed sump open to dilution with rainwater; and e) either plant tap water and/or Lake Sequalitchew water as "standards" for reference. Tap water represents water from Lake Sequalitchew that has undergone processing at a nearby water treatment plant on the Fort Lewis Reservation. All samples for chemical analyses were collected in 500 ml polyethylene bottles.

Water Quality Analysis

Analyses of liquid samples for total alkalinity and EDTA hardness were performed onsite, using standard methods for titration to endpoint.

Inorganic Analysis

Inorganic determinations were done by X-ray fluorescence. The analytical process is well documented and accepted as suitable for both liquid and solid samples. The procedure for preparing a sample of liquid process effluent for analysis is as follows:

- 1) take a known volume of sample (200 ml);
- 2) adjust to pH 2 with HNO_3 ;
- 3) add X grams (amount dependent upon sample volume) ammonium 1 pyrrolidine carbodithioate (APDC), a chelating agent, and stir for 5 min;
- 4) filter sample on 0.4 μ nucleopore filter;
- 5) mount filter in 35 mm slide frame;
- 6) analyze.

A chelating agent (APDC) is necessary to measure total, particulate, and dissolved inorganic elements. One drawback with APDC, as with other chelating agents, is its specificity for only a certain group of inorganic elements. APDC chelates best with positive ion transition elements, thus giving a total inorganic measurement for arsenic (As), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni) and zinc (Zn). For elements not chelated by APDC, values obtained by X-ray analysis are essentially values of particle sizes greater than 0.4 μ , the pore size of the nucleopore filters used in sample filtration. Elements of

this nature are bromine (Br), calcium (Ca), chlorine (Cl), gallium (Ga), phosphorus (P), potassium (K), rubidium (Rb), selenium (Se), silicon (Si), titanium (Ti), and vanadium (V). Elemental analysis for aluminum (Al) and sulfur (S) can be obtained, but values must be discarded as the X-ray fluorescence chamber is made of aluminum and APDC is based on a sulfur compound, thus inducing error.

A unique property with X-ray fluorescence is the ability to obtain lower detection limits by exposing the sample longer. Samples from the SRC site were exposed for 1 hr each, giving the following detection limits.

<u>Element</u>	<u>Detection Limits ppb ($\mu\text{g/l}$)</u>
arsenic (As)	1.30
cobalt (Co)	0.75
copper (Cu)	0.64
iron (Fe)	1.50
manganese (Mn)	1.00
mercury (Hg)	1.30
nickel (Ni)	0.40
zinc (Zn)	0.93

Organic Analysis

Total organic analysis of the initial sample series (taken 5/21/76) was performed by the Organic and Structural Chemistry Section at Battelle Columbus Laboratories, Columbus, Ohio. Analyses of subsequent samples were performed by the Physical Sciences Department at PNL. Since the method of analysis is related to the results of that particular analysis, the methods are mentioned in the Results section, where appropriate.

RESULTS

Water Quality Analyses

Basic water quality parameters of liquid samples obtained on trips to the SRC pilot plant are listed in Table 9. In general, pH values decline from above neutral (pH 7.0) in Lake Sequalitchew to below neutral in the treated process effluent leaving the plant and in the discharge sump. Total alkalinity and EDTA hardness also slightly decline. Treated process effluent is diluted with water before discharge. Discharge sump water is subject to dilution by rainfall and runoff.

Inorganic Analyses

Concentrations of 21 inorganic elements in the process effluent are listed in Tables 10-14. Results are divided into total elemental analyses, based on elements that completely react with the chelating agent (APDC) used in analysis (number 1-10 in the tables) and particulate elemental analysis (numbered 11-21 in the tables).

TABLE 9. Data on pH, Alkalinity and EDTA Hardness from Selected Liquid Samples at the P&M SRC Pilot Plant, Fort Lewis, Washington

Date	Sample Location	pH	Alkalinity (mg/l as CaCO ₃)	EDTA Hardness (mg/l as CaCO ₃)
8-02-76	Plant tap water	7.1	43.3	204.7
	Treated effluent	6.5	13.8	50.5
8-23-76	Lake Sequalitchew	7.3	49.0	46.6
	Plant tap water	6.8	40.4	48.6
	Treated effluent	6.8	----	----
	Discharge sump	6.9	29.7	42.7
11-15-76	Lake Sequalitchew	----	43.0	51.5
	Plant tap water	----	50.0	56.3
	Treated effluent	7.05	----	----
	Discharge sump	----	34.0	42.7
1-26-77	Lake Sequalitchew	7.35	58.0	52.4
	Plant tap water	6.85	47.0	40.8
	Treated effluent	7.15	----	----
	Discharge sump	6.85	30.0	42.7
6-20-77	Lake Sequalitchew	----	78.0	----
	Treated effluent	----	----	----
	Discharge sump	----	77.0	----

TABLE 10. Summary of Inorganic Analyses, Untreated SRC Process Effluent from Valve #9105; Values Given in ppb (μg/l), X-ray Fluorescence Determinations

Element	Sample Date			
	5-21-76 (Not Filtered)	8-23-76 (Filtered)	10-11-76 (Filtered)	11-15-76 (Filtered)
1) Arsenic (As)	<1.0	<1.0	<1.0	1.0
2) Chromium (Cr)	5.0	2.0	2.0	<1.0
3) Cobalt (Co)	6.0	<1.0	<1.0	<1.0
4) Copper (Cu)	3.0	3.5	2.0	2.0
5) Iron (Fe)	530.0	59.0	25.0	52.0
6) Lead (Pb)	10.0	<1.0	<1.0	<1.0
7) Manganese (Mn)	<1.0	<1.0	<1.0	<1.0
8) Mercury (Hg)	8.0	1.0	<1.0	<1.0
9) Nickel (Ni)	3.0	5.0	<1.0	3.0
10) Zinc (Zn)	130.0	<1.0	<1.0	14.0
-----	-----	-----	-----	-----
11) Bromine (Br)	<1.0	<1.0	<1.0	<1.0
12) Calcium (Ca)	16.0	4.0	5.0	7.0
13) Chlorine (Cl)	50.0	8.0	7.0	7.0
14) Gallium (Ga)	<1.0	<1.0	<1.0	<1.0
15) Phosphorus (P)	150.0	20.0	20.0	22.0
16) Potassium (K)	13.0	2.0	2.0	<1.0
17) Rubidium (Rb)	<1.0	<1.0	<1.0	<1.0
18) Selenium (Se)	<1.0	<1.0	<1.0	<1.0
19) Silicon (Si)	5.6 x 10 ³	70.0	77.0	70.0
20) Titanium (Ti)	7.0	5.0	2.0	1.0
21) Vanadium (V)	6.0	<1.0	<1.0	<1.0

TABLE 11. Summary of Inorganic Analyses, Partially Treated SRC Process Effluent from Valve #9108; Values Given in ppb ($\mu\text{g/l}$), X-ray Fluorescence Determinations

Element	Sample Date			
	5-21-76 (Not Filtered)	8-23-76 (Filtered)	10-11-76 (Filtered)	11-15-76 (Filtered)
1) Arsenic (As)	<1.0	<1.0	<1.0	<1.0
2) Chromium (Cr)	3.0	1.0	2.0	1.0
3) Cobalt (Co)	<1.0	<1.0	<1.0	<1.0
4) Copper (Cu)	<1.0	3.0	2.0	<1.0
5) Iron (Fe)	20.0	25.0	12.0	65.0
6) Lead (Pb)	<1.0	<1.0	<1.0	<1.0
7) Manganese (Mn)	<1.0	<1.0	<1.0	<1.0
8) Mercury (Hg)	10.0	3.0	<1.0	<1.0
9) Nickel (Ni)	1.0	3.0	<1.0	3.0
10) Zinc (Zn)	<1.0	<1.0	<1.0	<1.0

11) Bromine (Br)	<1.0	<1.0	<1.0	<1.0
12) Calcium (Ca)	<1.0	4.0	5.0	9.0
13) Chlorine (Cl)	30.0	6.0	16.0	8.0
14) Gallium (Ga)	<1.0	<1.0	<1.0	<1.0
15) Phosphorus (P)	100.0	15.0	15.0	25.0
16) Potassium (K)	3.0	4.0	6.0	1.0
17) Rubidium (Rb)	<1.0	<1.0	<1.0	<1.0
18) Selenium (Se)	<1.0	<1.0	<1.0	<1.0
19) Silicon (Si)	3.0	72.0	2.0	19.0
20) Titanium (Ti)	<1.0	1.0	3.0	<1.0
21) Vanadium (V)	<1.0	<1.0	<1.0	<1.0

TABLE 12. Summary of Inorganic Analyses, Treated SRC Process Effluent from Plant Discharge Pipe; Values Given in ppb ($\mu\text{g/l}$), X-ray Fluorescence Determinations

Element	Sample Date			
	5-21-76 (Not Filtered)	8-23-76 (Filtered)	10-11-76 (a)	11-15-76 (Filtered)
1) Arsenic (As)	<1.0	<1.0	<1.0	<1.0
2) Chromium (Cr)	2.0	2.0	2.0	1.0
3) Cobalt (Co)	<1.0	<1.0	<1.0	<1.0
4) Copper (Cu)	<1.0	3.0	2.0	2.0
5) Iron (Fe)	10.0	17.0	5.0	17.0
6) Lead (Pb)	<1.0	2.0	<1.0	<1.0
7) Manganese (Mn)	<1.0	<1.0	<1.0	<1.0
8) Mercury (Hg)	<1.0	3.0	<1.0	<1.0
9) Nickel (Ni)	<1.0	<1.0	<1.0	<1.0
10) Zinc (Zn)	<1.0	<1.0	<1.0	<1.0

11) Bromine (Br)	<1.0	<1.0	<1.0	<1.0
12) Calcium (Ca)	<1.0	3.0	5.0	3.0
13) Chlorine (Cl)	1.0	6.0	23.0	2.0
14) Gallium (Ga)	<1.0	<1.0	<1.0	<1.0
15) Phosphorus (P)	40.0	15.0	16.0	6.0
16) Potassium (K)	<1.0	2.0	2.0	<1.0
17) Rubidium (Rb)	<1.0	<1.0	<1.0	<1.0
18) Selenium (Se)	<1.0	<1.0	<1.0	<1.0
19) Silicon (Si)	2.5×10^3	130.0	192.0	37.0
20) Titanium (Ti)	<1.0	2.0	7.0	<1.0
21) Vanadium (V)	<1.0	<1.0	<1.0	<1.0

(a) Treated effluent taken during plant "backflush" operations.

TABLE 13. Summary of Inorganic Analyses, Tap Water from SRC Plant; Values Given in ppb ($\mu\text{g/l}$), X-ray Fluorescence Determinations

Element	Sample Date			
	5-21-76 (Not Filtered)	8-23-76 (Filtered)	10-11-76 (Filtered)	11-15-76 (Filtered)
1) Arsenic (As)	----	<1.0	<1.0	<1.0
2) Chromium (Cr)	----	2.0	1.0	<1.0
3) Cobalt (Co)	----	<1.0	<1.0	3.0
4) Copper (Cu)	----	16.0	5.0	1.0
5) Iron (Fe)	----	10.0	10.0	14.0
6) Lead (Pb)	----	2.0	2.0	2.0
7) Manganese (Mn)	----	<1.0	<1.0	<1.0
8) Mercury (Hg)	----	<1.0	<1.0	1.0
9) Nickel (Ni)	----	<1.0	<1.0	2.0
10) Zinc (Zn)	----	45.0	68.0	1.3×10^3
-----	-----	-----	-----	-----
11) Bromine (Br)	----	<1.0	<1.0	<1.0
12) Calcium (Ca)	----	8.0	8.0	8.0
13) Chlorine (Cl)	----	20.0	23.0	9.0
14) Gallium (Ga)	----	<1.0	<1.0	<1.0
15) Phosphorus (P)	----	20.0	17.0	28.0
16) Potassium (K)	----	2.0	2.0	1.0
17) Rubidium (Rb)	----	<1.0	<1.0	<1.0
18) Selenium (Se)	----	<1.0	<1.0	<1.0
19) Silicon (Si)	----	30.0	413.0	26.0
20) Titanium (Ti)	----	1.0	4.0	<1.0
21) Vanadium (V)	----	<1.0	<1.0	<1.0

TABLE 14. Summary of Inorganic Analyses, Lake Sequalitchew Water; Values in ppb ($\mu\text{g/l}$), X-ray Fluorescence Determinations

Element	Sample Date			
	5-21-76 (Not Filtered)	8-23-76 (Filtered)	10-11-76 (Filtered)	11-15-76 (Filtered)
1) Arsenic (As)	----	<1.0	<1.0	<1.0
2) Chromium (Cr)	----	2.0	1.0	<1.0
3) Cobalt (Co)	----	<1.0	<1.0	<1.0
4) Copper (Cu)	----	3.0	2.0	<1.0
5) Iron (Fe)	----	10.0	10.0	14.0
6) Lead (Pb)	----	<1.0	<1.0	<1.0
7) Manganese (Mn)	----	<1.0	<1.0	<1.0
8) Mercury (Hg)	----	1.0	1.0	<1.0
9) Nickel (Ni)	----	<1.0	<1.0	<1.0
10) Zinc (Zn)	----	<1.0	<1.0	<1.0
-----	-----	-----	-----	-----
11) Bromine (Br)	----	<1.0	<1.0	<1.0
12) Calcium (Ca)	----	20.0	10.0	1.0
13) Chlorine (Cl)	----	20.0	10.0	10.0
14) Gallium (Ga)	----	<1.0	<1.0	<1.0
15) Phosphorus (P)	----	20.0	20.0	10.0
16) Potassium (K)	----	10.0	2.0	1.0
17) Rubidium (Rb)	----	<1.0	<1.0	<1.0
18) Selenium (Se)	----	<1.0	<1.0	<1.0
19) Silicon (Si)	----	40.0	460.0	60.0
20) Titanium (Ti)	----	4.0	2.0	<1.0
21) Vanadium (V)	----	<1.0	<1.0	<1.0

Samples from SRC plant Valves No. 9105 and 9108, collecting trip 5/21/76, were not prefiltered for inorganic analysis prior to adding APDC. Due to heavy particulate load in samples from subsequent trips, these samples of incompletely treated effluent were filtered through a Watman 40 ashless filter to remove larger particles. In most cases, prefiltering yielded a decrease in elemental composition.

None of the elements quantified from treated process effluent differed greatly in concentration from levels in water from Lake Sequalitchew or the SRC plant tap. The process waste water - oil treatment system appears to efficiently remove most inorganic elements from the treated discharge. Dilution with freshwater before discharge may assure that inorganic levels in the treated process effluent are consistently minimal. However, dilution does not restrict accumulation of inorganic elements in the discharge sump, which has no outlet. Possible accumulation/transfer/degradation of inorganic compounds in the sump must be examined in future studies.

Organic Analyses

Organic analyses of SRC process effluent samples have been less than satisfactory to date due to difficulty in obtaining reliable qualitative and quantitative determinations among each sample series to correlate with bioassay results. Proper correlation of assays and analyses are important for future assessment work. All indications point to hydrocarbons as the unidentified components in treated process effluent that cause various sublethal and lethal effects among organisms exposed in 96-hr static toxicity tests.

The amount of total organic extractables in the initial sample collection (5/21/76) was determined gravimetrically and by infrared analysis (CCl₄ extracts only) at Battelle Columbus. Results are given in Table 15.

TABLE 15. Characterization of Total Extractables from SRC Process Effluent Samples Taken 5-21-76 (SRC-I Process)

Sample Location	Sample Volume, ml	Extraction Solvent	Amount of Extractables		
			Gravimetric (a)	Infrared (b)	Hydrocarbon Ratio(c)
Valve #9105	3960	CH ₂ Cl ₂	19.30	----	----
	3920	CCl ₄	29.90	12.10	0.09
	4075	CCl ₄	21.30	8.00	0.07
Valve #9108	3770	CCl ₄	16.10	5.60	0.15
	3735	CCl ₄	17.60	5.90	0.16
Treated Effluent	3788	CH ₂ Cl ₂	0.50	----	----
" "	3755	CH ₂ Cl ₂	0.19	----	----
" "	3660	CCl ₄	0.75	0.05	0.24
" "	3965	CCl ₄	0.58	0.06	0.47

(a) Determined by weighing the solvent-free residue from an aliquot.

(b) Determined from CH₂ absorption using API Reference Fuel Oil for calibration.

(c) $\frac{OD \text{ of } C=0}{OD \text{ of } CH_2}$ This ratio is used as an indication of the proportion of hydrocarbons. A ratio of 0.2 or less indicates that hydrocarbons probably represent a majority of the CCl₄ -extractable material.

In general, gravimetric values were two to three times greater than infrared values. This was because the extracts contained primarily aromatic components and a more highly saturated material, a fuel oil, was used for the infrared calibration curves. The gravimetric values are, therefore, considered more accurate.

Carbonyl/methylene absorption ratios are also listed in Table 15. They indicate the hydrocarbon nature of the extract. Hydrocarbons represent most of the CCl_4 - extractable material in process effluent at Valves #9105 and 9108, lesser amounts in the treated effluent that had passed through the oil filter and were discharged from the SRC plant.

Further processing of selected samples helped identify organic components in the effluent. The extracts were concentrated to 1 ml, the solvent was exchanged with heptane, fractionated by silica gel chromatography to give a saturated hydrocarbon and two aromatic hydrocarbon fractions, and these fractions were analyzed by gas chromatography. Representative samples of the aromatic fractions were analyzed by chemical ionization GC-MS with methane as the ionizing gas. The internal standard used for quantitation by gas chromatography was *n*-Dotriacontane. These procedures (GC and GC-MS) were carried out on four representative samples from the 11/21/76 collection. The results are given in Table 16 and Figures 4-7. Reference samples were run to confirm gas chromatography.

The identifications are based on molecular weight, determined by the mass spectrum and by GC retention indices. All components identified were highly aromatic, as indicated by a lack of fragmentation. The silica gel fraction in which the components were found provided some confirmatory evidence.

The amounts are reported as $\mu\text{g/l}$ of extracted process effluent sample. Total recovery of the extracts is assumed, but actual recovery may have been only 50% in some cases due to limitations in the method used.

In general, the components in the effluent were similar to those found in petroleum-contaminated samples. The major differences were the smaller amounts of alkylated compounds relative to the parent hydrocarbons, and the presence of two major oxygenates, phenyl ether and dibenzofuran.

Analyses of phenol content in several subsequent samples of treated process effluent taken from the discharge pipe and used in static toxicity tests are given in Table 17.

Analyses of these samples were by high-pressure liquid chromatography (Hupet Busch 1010B). HPLC columns were a PR-8 Lichrosorb 25 cm/10 micron and a uBondapak C-18 30 cm/10 micron. Both columns were kept isothermal and were gradient programmed for reverse phase, using water and methanol as the eluting solvents. The Lichrosorb has a flow of 0.5 ml/min and the uBondapack a flow of 2.0 ml/min. Sample injection was made by a 100 μl loop (Lichrosorb) and a 1 ml loop (uBondapack). A UV detector (Schaeffel SF 7700) was applied and set at 230 nm.

TABLE 16. Characterization of Aromatic Components in SRC Process Effluent Samples Taken 5-21-76 (SRC-I Process)

No.	Retention Index	M.W. (a)	Tentative Identification (b)	Amount Found in Sample $\mu\text{g/l}$ (d)			
				Valve #9105	Valve #9108	Valve #9108	Treated Effluent
1	1080	120	dimethylethylbenzene	54	10	2	e
2	1140	132	methylindan	28	16	21	e
3	1200	132	tetralin	130	37	68	e
4	1220	128	naphthalene	940	510	820	2
5	1220	134	benzothiophene	60	30	70	e
6	1250	146	methyltetralin	100	60	22	e
7	1260	146	"	49	27	10	e
8	1280	146	"	27	4	8	e
9	1300	146	"	160	34	56	0.5
10	1320	142	2-methylnaphthalene	800	330	510	2
11	1330	142	1-methylnaphthalene (c)	200	160	120	0.5
12	1330	148	methylbenzothiophene	70	30	70	e
13	1350	160	dimethyltetralin	30	11	6	e
14	1390	154	biphenyl	340	170	260	0.5
15	1410	156	ethylnaphthalene	210	64	62	0.5
16	1420	170	phenyl ether	390	240	260	4
17	1420	156	dimethylnaphthalene	130	35	32	0.5
18	1430	156	"	90	23	17	e
19	1450	156	"	33	7	8	e
20	1480	154	acenaphthene	62	35	55	0.5
21	1500	168	methylbiphenyl	170	47	44	1
22	1510	168	dibenzofuran	78	25	27	e
23	1570	166	fluorene	94	27	23	3
24	1580	168	methylacenaphthene (c)	59	15	8	2
25	1590	184	dibenzothiophene	25	8	8	e
26	1620	182	dimethylbiphenyl	34	3	2	e
27	1630	182	"	28	1	1	e
28	1660	180	methylfluorene	2	2	5	e
29	1680	180	"	2	1	2	e
30	1690	180	"	4	2	3	e
31	1740	182	dimethylacenaphthene	57	15	9	0.5
32	1760	178	phenanthrene	280	59	96	7
33	1880	192	methylphenanthrene	100	7	3	2
34	1900	192	"	37	4	2	1
35	2060	202	fluoranthene	76	4	6	0.5
36	2100	202	pyrene	38	3	3	3

(a) Determined by chemical ionization mass spectrometry using methane as the ionizing gas.

(b) Tentative identifications are based on the molecular weight, lack of fragmentation indicated by the mass spectra, and gas chromatographic retention times.

In some cases other isomers are equally likely, e.g., dimethylindan instead of methyltetralin or ethylbiphenyl instead of dimethylbiphenyl. Analyses were made by Battelle Columbus Laboratories.

(c) Sulfur-containing compounds were confirmed by flame photometric detection.

(d) The amounts are reported as $\mu\text{g/liter}$ of original water sample extracted.

(e) Not detected, $<0.5 \mu\text{g/l}$.

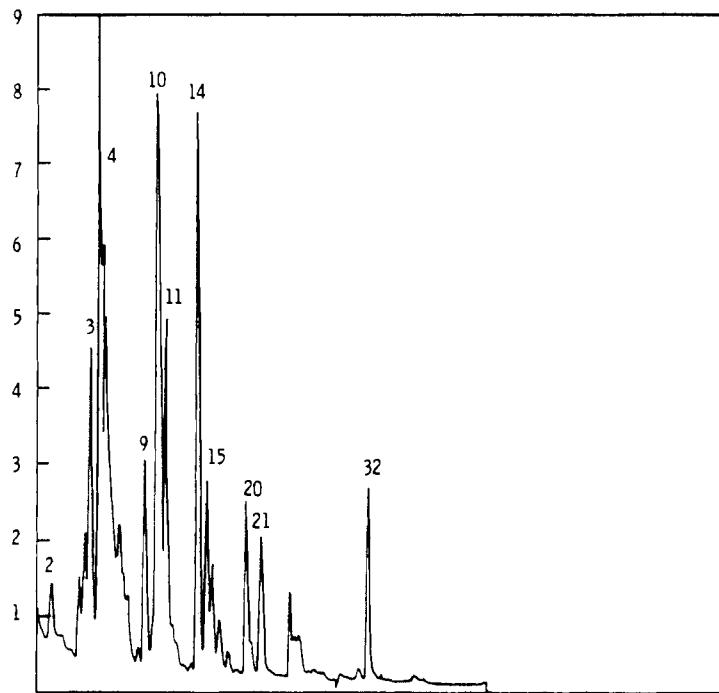


FIGURE 4. Gas Chromatogram of Fraction 2 (Primarily Tetralins and Naphthalenes) from Valve No. 9108 Taken 5/21/76. The numbers assigned to major peaks refer to compounds identified in Table 16.

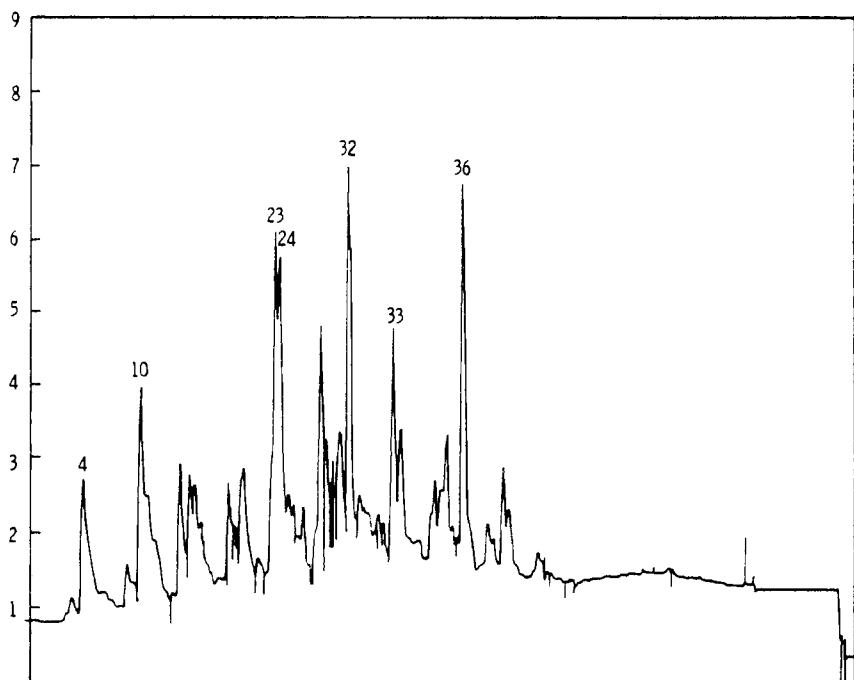


FIGURE 5. Gas Chromatogram of Fraction 2 (Primarily Tetralins and Naphthalenes) from Treated Effluent Sample Taken 5/21/76. The numbers assigned to major peaks refer to compounds identified in Table 16.

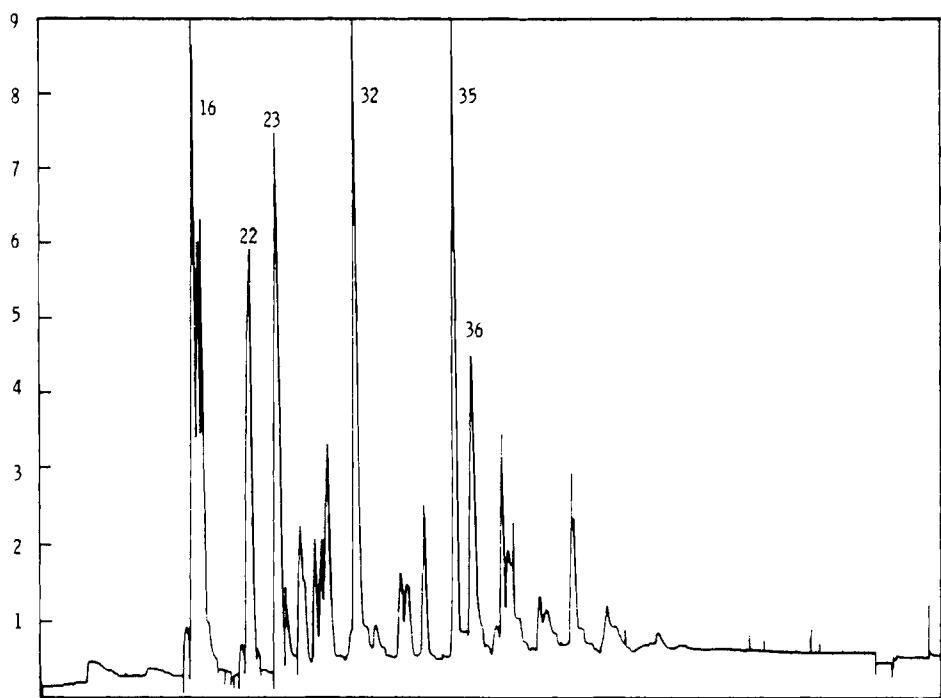


FIGURE 6. Gas Chromatogram of Fraction 3 (Primarily Fluorenes, Phenanthrenes, Pyrene and Oxygenates) from Valve No. 9105 Taken 5/21/76. The numbers assigned to major peaks refer to compounds identified in Table 16.

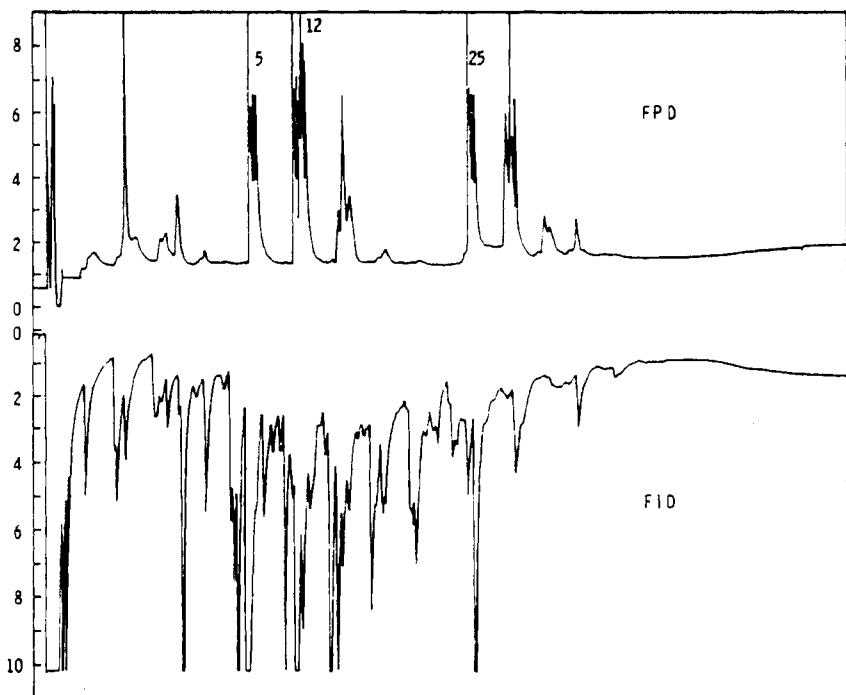


FIGURE 7. Gas Chromatogram of Fraction 2 from Valve No. 9105 Taken 5/21/76 by Means of FID/FPD. The numbers assigned to major peaks refer to compounds identified in Table 16.

TABLE 17. Analysis of Phenol in Treated SRC Process Effluent at Various Dates, Determined by High Pressure Liquid Chromatography. No cresols or xylenols were detected.

Sample Date	Source/Treatment	Phenol (ppb)	Remarks
10-11-76	Plant discharge pipe	$6.6+0.6$ ^(a)	2 days later at start of toxicity test
10-11-76	Plant discharge pipe	$5.2+0.5$	
10-13-76	Plant discharge pipe	$8.2+0.7$	after 4 days aeration during toxicity test
1-26-77	Plant discharge pipe	$6.6+0.6$	
4-12-77	Plant discharge pipe	$39.0+4.0$	
4-12-77	East end discharge pond	$7.9+0.7$	
4-12-77	West end discharge pond	$13.1+1.2$	

(a) Samples on 10-11-76 consisted of treated effluent at "undiluted" strength, taken during backflush and/or cleansing operations.

Organic components of four subsequent samples were identified and in some cases quantified. Analyses were made from methylene chloride extracts of 1 liter liquid samples by means of GC-MS. This information is listed in Table 18. Interfering compounds in the GC peaks restricted the amount of quantitative data obtained. No correction was made for possible loss of the more volatile compounds during the analysis. Precision in most cases was at least 30%. However, it is clear that many complex hydrocarbons occur in partially treated SRC process effluent.

Radiological Sciences Department of PNL has obtained qualitative data on certain other emissions from the pilot SRC plant.³⁹

TABLE 18. Identification of Major Aromatic Components in Partially-Treated SRC Process Effluent Samples Taken on the Indicated Dates (SRC-II Process)

Tentative Identification	Amount Found in Sample, ppm ^(a)			
	6-21-77		7-26-77	
	Valve #9105	Valve #9108	Valve #9105	Valve #9108
indane	+	+	+	
phenol	44.4	41.6	13.2	0.7
C ₂ -pyridine			+	
tetralin		+	+++	+
tetrahydronaphthalene	++			
naphthalene	2.9	2.2	2.0	0.08
methylnaphthalene			+	
2-methylindane	+	+		
C ₂ -phenol		++		2.6
cresol	86.8	78.1	31.3	1.6
C ₁ -naphthalene		+		+
2-methylindane-xylenol	++			
dimethylphenol		15.7	17.0	
1-methylnaphthalene	+++		+	
xylenol	57.2			
C ₃ -phenol	+	+	5.2	0.2
C ₂ -naphthalenebiphenol	++			
C ₂ -naphthalene + biphenylether	+++			
methylethylphenol		4.1		
C ₂ -naphthalene	++			+
teraphthaldehyde		+		
acenaphthylene	++			
C ₃ -naphthalene	++	+	+	+++
1-thiatetralin		+	+	
dibenzofuran	+	+	+	+
C ₄ -phenol			+	++
C ₄ -tetrahydronaphthalene	+			
fluorene	++		+	+
methylfluorene	++			
methylbenzothiophene		+		
C ₄ -naphthalene	++		+	+
C ₅ -phenol		+	+	+
xanthene	+	+		
C ₆ -phenol			+	+
phenanthrene	10.2	+	0.22	0.01
methylphenanthrene	+			
C ₆ -xanthene			+	
fluoranthene	+		+	
carbazole		+	+	++
pyrene	+			
chrysene	+			

(a) A rough estimate of relative abundance based on height and area of gas chromatograph peaks is given by +, ++, +++, and ++++. Ppm values are usually for the abundant organic compounds in the ++++ category. Analyses were made by PNL Radiological Sciences Department.

RECOMMENDATIONS

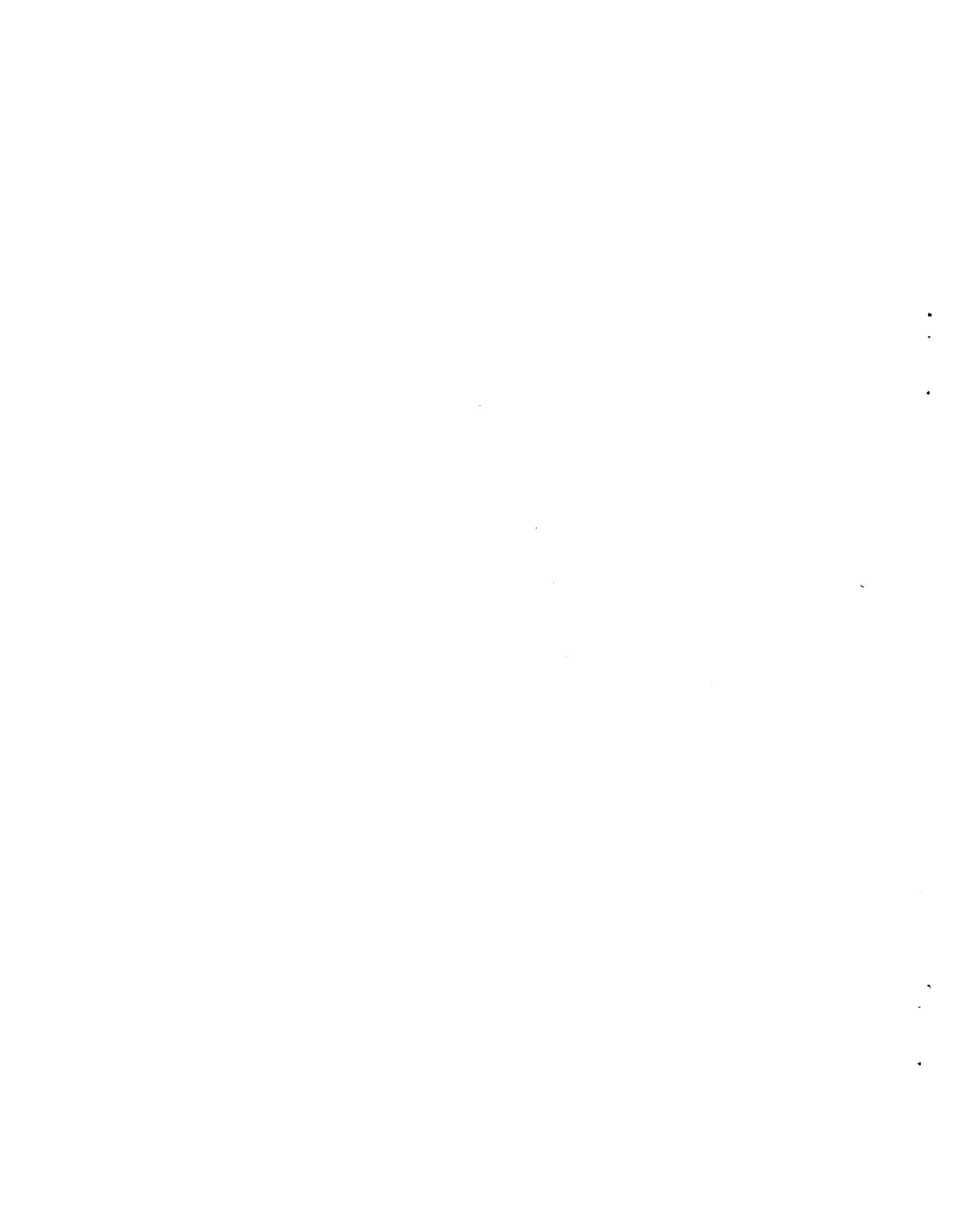
Studies at the SRC pilot plant discharge sump involve "risk analysis." Introducing any chemical wastes into an ecosystem incurs an element of risk because the material is alien to the ecosystem. A necessary part of risk analysis is ecological monitoring, which consists of gathering and interpreting biological, chemical and physical data. Ecological monitoring can only be accomplished onsite. The obtained data provide the information required for rational planning decisions and implementing technological changes as the new process develops.

We believe ecological monitoring is required in the effluent sump (or pond) adjacent to the Fort Lewis SRC pilot plant and now receiving treated process effluent. Assessment of potential impact or "risk" is impractical or extremely difficult via monitoring after process effluent is discharged into large bodies of standing or flowing water, as may occur in future commercial application of SRC technology. The effluent sump at the pilot plant does not portray the disposal method expected of a commercial operation. But it does represent a miniature outdoor microcosm where natural chemical and biological processes can be efficiently monitored, and extrapolation of the detected phenomena can be undertaken.

Environmental assessment studies at the Fort Lewis SRC pilot plant would be facilitated by establishment of a PNL mobile aquatic laboratory at the site. Part of the need involves logistics, because PNL laboratories at Richland are about 200 miles away. But close monitoring of the SRC plant is required for environmental assessment needs because, as a pilot facility, operating conditions are subject to change. The two refining processes under development, SRC-I and SRC-II, involve different procedures. Analytical samples must be properly timed to represent the waste products produced under the different conditions. Other sampling and surveillance requirements must be efficiently met. The ability of the environmental scientist to monitor plant operational changes is served most efficiently by an onsite laboratory.

REFERENCES

1. Howard-Smith, I. and G. J. Werner. 1976. Coal Conversion Technology. Chemical Technology Review No. 66, Noyes Data Corporation, Park Ridge, NJ, 133 pp.
2. Kloepper, D. L., T. F. Rogers, C. H. Wright, and W. C. Bull. 1965. Solvent Processing of Coal to Produce a De-Ashed Product. R&D Report No. 9, Office of Coal Research, U.S. Dept. Interior, Washington, DC.
3. Anonymous. Development of a Process for Producing an Ashless, Low-Sulfur Fuel from Coal. Vol. III - Pilot Plant Development Work, Part 1 - Design of Pilot Plant. R&D Report. No. 53, Interim Report. No. 2. Office of Coal Research, U.S. Dept. Interior, Washington, DC. 1969.
4. Hinderliter, C. R. 1974. Environmental Aspects of the SRC Process. Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, Report EPA-650/1-74-118. Office of Research and Development, U.S. Environmental Protection Agency, pp. 159-169.
5. Perrussel, R. E., W. Hubis, and J. L. Reavis. Environmental Aspects of the SRC Process. In: Symposium Proceedings: Environmental Aspects of Fuel Concession Technology, II. Environmental Protection Technology Series, EPA-600/2-76-149, NTIS, Springfield, VA, 1976, pp. 183-190.
6. National Water Quality Laboratory. 1975. Methods for Acute Toxicity Tests with Fish, Macroinvertebrates, and Amphibians. Ecological Research Series, EPA-660/3-75-009, NTIS, Springfield, VA, 61 pp.
7. Anonymous. Development of a Process for Producing an Ashless, Low-sulfur Fuel from Coal. Vol. III - Pilot Plant Development Work, Part 3 - Startup and Operation of the SRC Pilot Plant. R&D Report No. 53, Interim Report No. 22. Office of Coal Research, U.S. Dept. Interior, Washington, DC, pp. 165-188.
8. Petersen, M. R. 1976. Progress Report. Organic Constituents in Process Streams of a Solvent-Refining Coal Plant. BNWL-B-470, Battelle, Pacific Northwest Laboratories, Richland, WA, 8 pp.
9. Petersen, M. R., J. S. Fruchter and J. C. Laul. 1976. Quarterly Report. Characterization of Substances in Products, Effluents and Wastes from Synthetic Fuel Production Tests. BNWL-2131, UC-48, Battelle, Pacific Northwest Laboratories, Richland, WA, 20 pp.



DISTRIBUTION

<u>No. of Copies</u>	<u>No. of Copies</u>
<u>OFFSITE</u>	
1	<u>DOE Chicago Patent Group</u> 9800 South Cass Avenue Argonne, IL 60439
	H. E. Ransom M. W. Tiernan J. D. White
10	<u>DOE Division of Biomedical and Environmental Research</u>
	C. W. Edington C. W. Fischer W. O. Forster R. E. Franklin R. A. Lewis J. L. Liverman D. H. Slade J. Swinebroad R. Watters
27	<u>DOE Technical Information Center</u> P.O. Box 62 Oak Ridge, TN 37830
	R. M. Bean C. E. Becker (10) D. B. Gearlock C. E. Cushing, Jr. G. W. Dawson H. Drucker D. W. Felix R. F. Foster C. I. Gibson S. Goldsmith S. Marks T. L. Page M. R. Petersen M. J. Schneider J. B. States J. A. Strand W. L. Templeton B. E. Vaughan D. G. Watson R. E. Wildung W. G. Woodfield Technical Information (5) Publishing Coordination (2)
<u>ONSITE</u>	
	P. F. X. Dunnigan, Jr. J. L. Landon
	Freshwater Sciences Section (25)

