COMBUSTION
OF HYDROTHERMALLY
TREATED COALS

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EPA REVIEW NOTICE

COMBUSTION
OF
HYDROTHERMALLY TREATED COALS

by

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ABSTRACT

This report presents the results of a study to evaluate (1) the combustion characteristics of hydrothermally treated (HTT) coals as they relate to environmental emissions, boiler design, and interchangeability of solid fuels produced by the Hydrothermal Coal Process (HCP) with raw coals currently being used as the source of energy and (2) conversion of solubilized coal to terephthalic acid.

Several HTT coals were prepared from raw Martinka and Westland coals by the Hydrothermal Coal Process using sodium hydroxide and a mixture of sodium hydroxide and calcium hydroxide as the leachants. The HTT coals and the corresponding raw coals were combusted in laboratory and Multifuel Furnace Combustion units and the general combustor behavior, pollutant emissions and ash properties were assessed to provide the necessary data for impact evaluation of HTT coals. Conversion of solubilized coal to terephthalic acid was examined by oxidation to benzene carboxylic acids.

Results indicate that the HTT coals prepared by the Hydrothermal Coal Process from selected coals are clean solid fuels that in many instances can be burned with little or no sulfur emissions. Sulfur oxide concentrations in the flue gases were well below Federal Sulfur Emission Standards for New Sources. Also, the HTT coal was found to burn as well or better than raw coal and trace metals emissions should be significantly reduced because of the lower concentrations in HTT coals. Therefore, the use of this clean, solid fuel in conventional boilers and furnaces ought to reduce environmental pollution resulting from the combustion of HTT coal. These HTT coals appear to be more suitable for firing in wet bottom furnaces than in dry-bottom furnaces because of potential slagging and fouling problems associated with the alkali content of the coals. However, it may be possible to alter the slagging and fouling characteristics by the use of additives.

The coal solubilized during the desulfurization step can be converted to terephthalic acid by the oxidation-Henkel reaction. However, low yields suggest that this approach may not be economical.

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EXECUTIVE SUMMARY

An alternative approach for converting our major source of coal-energy-to an environmentally acceptable solid fuel is to clean the raw coal by chemical benefication prior to combustion. One potential chemical beneficiation process is the Hydrothermal Coal Process. In order to confirm this, the program entitled "Study of the Battelle Hydrothermal Treatment of Coal Process" was conducted under the sponsorship of the U.S. Environmental Protection Agency, Contract No. 68-02-2119. The objectives of this program were to:

1. Evaluate the combustion characteristics of HTT coals as these relate to environmental emissions, boiler design and interchangeability of solid fuels, and

2. Examine the conversion of that portion of the coal solubilized during the hydrothermal treatment of the coal to organic chemicals, for example, terephthalic acid.

The objectives were achieved by

a. preparing several types of HTT coals in the HCP Miniplant facility

b. Conducting combustion studies on these coals in the 1 lb/hr laboratory combustion facility and in the Multifuel Furnace.

c. Evaluating the environmental impact of converting conventional boilers to hydrothermal treated coals

d. Assessing the interchangeability of hydrothermally treated coals in utility and industrial boilers, and

e. Assessing the conversion of solubilized coal to terephthalic acid by the oxidation-Henkel process.

Research results to date have confirmed the initial assessment that the Hydrothermal Coal Process is a potential method for producing environmentally acceptable solid fuel from certain coals. HTT coals prepared by this process from the Martinka and Westland coals are clean solid fuels that can potentially be burned with little or no sulfur emissions control. Sulfur oxide concentrations in the flue gases from the Laboratory Test Facility and the Multifuel Combustion Unit were well below Federal Sulfur Emission Standards For New Sources. Generally, the sulfur dioxide concentration in the flue gases were less than 500 ppm.

The low sulfur oxide concentrations resulted, in part, from (1) extraction of the sulfur from the raw coal by the Hydrothermal Coal Process and (2) in part, as the result of the sulfur capturing efficiency of the alkali contained in the HTT coals. Also the HTT coals were found to burn as well or better than the raw coals and trace metals emissions should be significantly reduced because of the lower concentrations in the HTT coals. Therefore, the use of HTT coals in conventional boilers and furnaces should reduce environmental pollution resulting from the combustion of coal.

Because of the low-ash-fluid temperatures of the ash in the HTT coals, firing of these coals in conventional dry-bottom furnaces could present slagging and fouling problems. It would probably be necessary to install additional slag blowers in the furnace and additional soot blowers in the convection tube banks to control slagging and fouling to an acceptable level. Some derating of the boiler may also be required. However, it may be possible to alter the slagging and fouling characteristics by the use of additives.

The HTT coals could be more suitable for firing in wet-bottom (slag-top or cyclone) furnaces because of the low-ash-fluid temperatures. Although firing in wet-bottom furnaces would avoid the slagging problem, boiler fouling would be a problem requiring adequate soot-blower capacity and, possibly, derating to lower gas temperatures in the convection section.

Conversion to HTT coals could have a significant effect on the atmospheric emissions from the combustion of coal. Preliminary results indicate that, of the 4 localities analyzed, St. Louis, Missouri and Detroit, Michigan could meet Federal Ambient Air Quality Standard of 80 $\mu g/m^3$ of SO_2 by simple substitution of HTT coals In all cases, significant decreases in SO_2 concentrations are predicted. Similarly, preliminary data show that emission of several of the trace metals to the atmosphere could also be reduced by hydrothermal treatment.

Analysis of the environmental problems associated with disposal of the combustion waste products revealed that direct disposal of the cooler ash from the NaOH treated coal would not be advisable because of the high degree of solubility. However, the sodium sulfate could be removed prior to disposal. With respect to trace metal values, the ashes from the HTT coals are less polluting than those from the raw coal.

Technically, the coal solubilized during the desulfurization operation can be oxidized to benzene carboxylic acids and subsequently converted to terephthalic acid. However, low yields suggest that approach may be economical.

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CONVERTING UNITS OF MEASURE

EPA policy is to express all measurements in meter units. When implementing this practice will result in undue cost or lack of clarity, conversion factors are provided for nonmetric units used in this report. Generally, this report used like English unit of measure. For conversion to the metric system, use the following conversion factors.

Table of Conversion Factors

Multiply English Unit	By Conversion	To Obtain Metric Unit
pound/hour	0.454	kilogram/hour
British thermal unit	0.252	kilogram - calories
British thermal unit/pound	0.555	kilogram - calories/ kilogram
ton (short)	0.907	metric ton (1000 kilograms)
pounds/square inch (gauge)	$(0.06805 \text{ psig} + 1)$ [a]	atmospheres (absolute)
inch	2.54	centimeters
feet	0.3048	meters
degree fahrenheit	$0.55 \ (^\circ F - 32)$ [a]	degree celcius
gallon	3.785	liters
ton/year	0.907	metric ton/year
pounds/million, British thermal unit	1.8×10^{-6}	kilogram/ kilogram- calories
pound	0.454	kilogram
square inches	6.452	square centimeters

(a) Actual conversion, not a multiplier.

STUDY OF THE BATTELLE HYDROTHERMAL
TREATMENT OF COAL PROCESS

by

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SECTION I.
INTRODUCTION

BACKGROUND

Coal is the major source of energy for the United States and will continue to be for many years. According to a recent survey, the United States has a coal reserve totalling 436 billion tons. At the present rate of consumption of about 620 million tons per year, the United States has enough coal to last for about 700 years.

However, much of this abundant source of energy contains high concentrations of sulfur, nitrogen, and mineral matter (ash)* which includes significant quantities of toxic metals. Examples of these metals are mercury, beryllium, and arsenic. During the combustion of coal, these materials are emitted into the environment and thus constitute a health hazard through atmospheric and food chain involvement. Consequently, the United States government has established requirements which necessitate controlling the effluent from coal combustion facilities by flue-gas scrubbing or by burning low-sulfur fuels.

Conceptually, the simplest option for meeting requirements for controlling the effluent from coal combustion would be to burn run-of-the-mine low sulfur coal. However, much of our coal supply has a sulfur content too high to permit direct combustion and remain within SO_2 regulations.

An alternative is to clean the coal prior to combustion by physical or chemical beneficiation. Physical beneficiation is not adequate for the removal of sulfur and other pollutant-forming constituents since, at the best, only a portion of the pyritic sulfur and the mineral matter is removed.

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* Mineral matter and ash are used interchangeably throughout the report.

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Furthermore, physical beneficiation cannot be applied to those coals having the pyritic sulfur distributed as microscopic particles throughout the coal particles.

Chemical beneficiation is an approach whereby pollutant-forming constituents are reduced to acceptable limits by treating the raw coal with a reagent or reagents that react with and liberate these constituents. This approach could increase significantly the quantity of our coal reserves which could be used directly as a solid fuel with minimal or no pollution control. One chemical beneficiation process for the production of a clean solid fuel from high sulfur coals is the Hydrothermal Coal Process. Basically, this process entails heating an aqueous slurry of coal and selected leachant in the autoclave at a temperature and corresponding steam pressure for a time sufficient to solubilize a significant portion of the sulfur and the ash. After which the product slurry is cooled and filtered. Then, the HTT coal is washed and dried for combustion or it may be deashed by treatment with dilute acid, for example H_2SO_4, to remove the majority of the mineral matter not extracted during the hydrothermal treatment. Research results to date have confirmed the initial assessment that this process is a potential means of producing an environmentally acceptable solid fuel from certain coals.

Consumption of these processed solid fuels as the source of energy for heat and power generation should reduce atmospheric emissions and, consequently, result in a healthier environment. In order to confirm this, the United States Environmental Protection Agency awarded Battelle's Columbus Laboratories the contract entitled "Study of the Battelle Hydrothermal Treatment of Coal Process". This report covers the results of the study from this contract.

OBJECTIVES

The first objective of this program was to evaluate the combustion characteristics of HTT coals as these relate to environmental emissions, boiler design, and interchangeability of solid fuels. Coal produced by the Hydrothermal Coal Process (HCP) were evaluated against raw (untreated) coals currently used

as the source of fuel. The second objective was to examine the conversion of solubilized coal, i.e., the humic acids leached from the coal during hydrothermal (desulfurization) treatment, to organic chemicals.

SCOPE OF WORK

The objective was achieved by

- Conducting combustion studies on hydrothermally treated coals and corresponding raw coals
- Evaluating the environmental impact of converting conventional boilers to burn hydrothermally treated coals as the source of fuel
- Assessing the interchangeability of hydrothermally treated coals in utility and industrial boilers
- Producing organic chemicals from solubilized coal.

SECTION II.
EXPERIMENTAL DETAILS

A research program was conducted which has resulted in a preliminary evaluation of the process for hydrothermal treatment of selected coals for the removal of pollutant-forming constituents. In order to achieve this, the research as discussed in the following paragraphs was conducted.

PHASE I. COMBUSTION CHARACTERISTICS
OF HYDROTHERMALLY TREATED COAL

In the initial evaluation of the combustion characteristics of hydrothermally treated coal, combustion studies were conducted in Battelle's 1-lb/hr combustion facility (LTF). Based on the results of these combustion studies, Battelle selected the raw and mixed leachant treated Westland coals for characterization in the Multifuel Furnace Facility (MFF) at a combustion rate of 30 lb/hr.

In carrying out this evaluation, the following tasks were conducted:

Task 1A. Selection of Coals

Candidate Coals. The criteria for selection of coals for this study were:

(1) Known Reserves. The coals were selected from seams of known large reserves from which adequate coal is avail-abel for commercial processing.

(2) Susceptibility to Hydrothermal Cleaning. The coals were known from prior research to be amenable to desulfurization by the hydrothermal process.

(3) Composition of Coals. These coals had sulfur contents too high for direct utilization by electric utilities without violating Federal New Source Sulfur Emissions Standards of 1.2 lb of $SO_2/10^6$ Btu.

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The two raw coals selected for this study were (1) Westland coal and (2) Martinka coal.[1] Westland coal is an Eastern bituminous coal from the Pittsburgh seam. The mine is located in Washington County, Pennsylvania. The coal represented by this mine is one of the major seams in Pennsylvania with estimated reserve of approximately 7 billion tons. As noted from the following analysis, this coal is a relatively high sulfur, high mineral matter content coal in the run-of-the-mine condition. However, it is subject to physical beneficiation to remove a portion of the sulfur and the mineral matter, but not to a level to permit direct firing without violating Federal Sulfur Emission Standards.

	Run-of-Mine Coal	Washed Coal**
H_2O (%)*	0	0.9
Mineral Matter (%)	30.1	8.4
Sodium (%)	--	0.023
Total Sulfur (%)(MAF)***	3.61	2.04
Pyritic (%) (MAF)	2.38	1.32
Sulfate (%) (MAF)	0.32	0.04
Organic (%) (MAF)	0.91	0.68

* Water content after drying at about 90°C for 24 hours.
** Coal washed in a preparation plant.
*** Moisture ash free basis.

Martinka coal is representative of the lower Kittanning Seam in West Virginia. This coal from the Martinka No. 1 Mine in Marion County is one of the major seams in West Virginia with an estimated reserve of 10.3 billion tons. The composition varies widely in the run-of-the-mine condition as noted below:

Mineral Matter (%)	18.6 to 22.7
H_2O (%)*	0.5
Total Sulfur (%) (MAF)**	1.32 to 2.92
Pyritic sulfur (%) (MAF)	0.6 to 1.93
Organic sulfur (%) (MAF)	0.25 to 0.71
Sulfate sulfur (%) (MAF)	0.01 to 0.05

* Water content after drying at about 90°C for 24 hours.
** Moisture ash free basis.

This coal, like the Westland coal, cannot be fired directly by electric utilities under new source standards without the implementation of some type of SO_2 pollution control.

From previous R&D at Battelle's Columbus Laboratories, each of these coals was found to be suitable for desulfurization and deashing by the Hydrothermal Coal Process (HCP)[2]. For example, hydrothermal treatment of Westland coal with the mixed leachant system produced a HTT coal with the following composition:

	Raw Coal	HTT Coal
H_2O, % (product basis)	0.87	0.41
Mineral matter, % (product basis)	8.37	15.2
Total Sulfur, % (MAF)	2.04	0.82
SO_2, lb/10^6 Btu	2.72	1.07

Similar results were attained with raw Martinka coal. In this case, the sulfur content of the HTT coal was lowered to a SO_2 equivalent (MAF) of 0.8 lbs/10^6 Btu from 3.92 lbs/10^6 Btu.

Also, the sodium hydroxide-prepared HTT coals selected for this study were susceptible to demineralizing with dilute sulfuric acid. For example, the mineral matter content of a HTT Westland coal hydrothermally treated with the sodium hydroxide leachant was lowered to 3.5 weight percent by leaching in dilute sulfuric acid solution. The HTT coal before demineralization contained 13.0 weight percent mineral matter.

From the above consideration, the following types of HTT coals were prepared in the HCP Miniplant (pre-pilot plant) Facility for combustion in the 1-lb/hr Laboratory Test Facility and the Multifuel Furnace.

| | Coal | | | | |
| | Westland | | | Martinka | |
Coal Treatment Prior to Combustion				Types of Coal Combusted	
Physically cleaned at Preparation Plant	x	x	x	x	x
Hydrothermally Treated (NaOH Leachant)	x		x	x	
Hydrothermally Treated (Mixed Leachant)		x			x
Hydrothermally Treated (NaOH Leachant)- Acid (H_2SO_4) Leached			x		

These coals were prepared from the two raw coals - Westland and Martinka - as discussed above.

Task 1B. Preparation of HTT Coals

Description of Hydrothermal Coal Process (HCP). Basically, the HCP entails heating an aqueous slurry of coal and selected leachant in the autoclave at a temperature and corresponding steam pressure for a time sufficient to solubilize a significant portion of the sulfur and the ash. After solubilization of the sulfur, the product slurry is cooled and filtered. Then, the HTT coal is washed and dried. (See Appendix A for a description of the Hydrothermal Coal Process.) In this study, the dried product was stored in a sealed container under a nitrogen atmosphere until burned.

Preparation of Various HTT Coals. The HTT coals evaluated in this program were prepared in the Miniplant Facility which is capable of hydrothermally cleaning coal on a continuous basis. (See Appendix B for a discussion of the Miniplant.) The overall process entails five basic operations:
  (a) coal preparation
  (b) hydrothermal desulfurization
  (c) product separation
  (d) product drying
  (e) leachant regeneration.

Only the first four operations were employed in this program.

In this study, no effort was made to optimize the processing conditions for preparation of the HTT coals. Instead, processing conditions which were known from previous work to produce the desired HTT coals were chosen.

Coal preparation entailed a crushing and milling operation. The raw coal which had been physically cleaned at a preparation plant to remove some of the mineral matter including a portion of the sulfur was air-dried to remove excess moisture. The air dried coal was then crushed in a Fitzmill to about 4-mesh. The crushed coal was then pulverized in a micro-pulverizer and screened in a Sweco 24-in. vibro-energy sieve to separate out the minus 200-mesh fraction. The oversize was returned to the Mikro-pulverizer and then rescreened. These operations were continued until the coal had been ground to at least 70 percent minus 200 mesh.

Hydrothermal treatment (desulfurization) entailed basically three operations. First, the ground coal was mixed with an aqueous alkaline leachant consisting of (1) either an 8 percent sodium hydroxide solution or (2) an 8 percent sodium hydroxide solution containing about 2.5 percent calcium hydroxide. Then, the slurry was pumped into the feed tank. From the feed tank, the raw coal slurry was pumped via high pressure pumps into and through the series of autoclaves, preheated to 275 C (pressure of about 1050 psig which included the steam pressure and an over pressure of nitrogen). In the autoclaves, the leachant reacted with the sulfur contained in the coal to form water-soluble sodium sulfur compounds. The product slurry was cooled by a water-cooled heat exchanger and exited from the hydrothermal treatment segment into a receiving tank through a pressure let-down valve. Residence time, the time the coal slurry was at 275 C, was 40 minutes.

The product slurry was then filtered to remove spent leachant. Residual leachant was removed from the clean coal product by a series of washing and filtration operations using water as the washing medium.

The wet, clean coal product containing 40 to 50 percent water was dried in a steam jacket drier under a flow of nitrogen. The nitrogen blanket was employed as a preventive measure to avoid any possible oxidation of the coal surface. The moisture content of the HTT coal was lowered to 1 percent or less by this drying operation.

Deashing of the HTT coals was accomplished by sulfuric acid leaching of the HTT prepared coal using sodium hydroxide as the leachant system.* This operation entailed slurrying the HTT coal in dilute acid, generally 10 percent, for approximately 30 minutes at ambient temperature. After which the slurry was filtered and the deashed HTT coal was washed free of sulfate using water as the washing medium. Then the deashed HTT coal was dried using the same drying procedure as used to dry the other HTT coals.

Three types of HTT coals were produced:

(1) Low sulfur, residual alkali**, residual ash in which the residual alkali was sodium. In this case, the leachant system was sodium hydroxide. Sodium content of the HTT coal was at a level attainable by water washing of the HTT coal. The sodium chemically bound to the coal and that associated with the ash was not removed by the water wash.

(2) Low sulfur, residual alkali, residual ash in which the residual alkali was primarily calcium. Sodium content was less than about 0.5 percent on a coal basis. In this case, the mixed leachant system composed of NaOH–Ca(OH)$_2$ was used to desulfurize the coal and to reduce the degree of sodium retention by the coal.

(3) Low sulfur, low ash, low alkali coal noted as deashed coal. This coal was prepared by leaching HTT coal type (1) in dilute sulfuric acid at ambient temperature. As discussed earlier, deashing of coal type (2) would have produced a product containing a high concentration of calcium sulfate formed from reaction of the calcium in the HTT coal with the sulfuric acid.

* Those HTT coals prepared using a mixture of sodium hydroxide and calcium hydroxide as the leachant system are not amenable to deashing with sulfuric acid. This is because the lime reacts with the sulfuric acid to form calcium sulfate which is not water soluble.

** Residual alkali is that which is not removed from the HTT coal by water washing. A portion of this alkali is chemically bound to the coal as the alkali salt of a carboxylic acid group. The remainder is present as the alkali inorganic salts such as complex aluminum silicates which are not are not water soluble.

For each combustion test in the 1-lb/hr Laboratory Test Facility, approximately 20 to 30 pounds (dried) HTT coal were prepared. Two hundred pounds were prepared for combustion testing in the Multifuel Furnace (MFF) Combustion unit.

Analyses of the Coals. Proximate and ultimate analyses of the HTT coals and the corresponding raw coals are shown in Table 1. Analysis of these data revealed:

(1) Environmentally acceptable solid fuel, with respect to sulfur content, can be produced by hydrothermal treatment of Martinka and Westland coals using either sodium hydroxide or a mixture of sodium hydroxide and calcium hydroxide as a leachant system. These clean coals contained a sulfur equivalent of 0.97 to 1.26 pound of $SO_2/10^6$ Btu.

(2) A small loss in heating value of these coals resulted from the hydrothermal treatment. Treatment of other coals under other programs has resulted in a gain in heating value. Normally, the heating value of the HTT coals (moisture ash free basis) will vary from $\pm$ 3 to 10 percent.

(3) Mineral matter content of the HTT coals was dependent on the leachant system. The mixed leachant resulted in an increase in the mineral matter content as the majority, if not all, of the calcium remained with the coal, whereas about 30 percent of the mineral matter was extracted from the Martinka coal by the sodium hydroxide leachant. Washing the sodium hydroxide leached HTT coal with sulfuric resulted in the extraction of 85.5 percent of the mineral matter to produce a product containing 2.25 percent mineral matter.

(4) Alkali retention by the coal was dependent on the leachant system, type of leachant, and mineral matter content of the

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TABLE 1.   ANALYSIS OF HTT COALS AND CORRESPONDING RAW COALS[a]

| | Martinka Coal | | |
	Raw	NaOH Leachant	Mixed Leachant
Proximate Analysis			
H_2O, %	0.41	3.05	0.40
Ash, %	19.7	13.4	28.0
Volatile	29.2(36.6)	28.5(34.1)	26.3(36.7)
Fixed Carbon	50.7(63.7)	35.0(65.8)	45.3(63.3)
Heat Value, Btu/lb(MAF)	(15,210)	(14,800)	(14,691)
SO_2, lb/10^6 Btu	2.94	0.97	1.16
Ultimate Analysis			
H_2O, %	0.41	3.05	0.4
Carbon, %	67.0(83.4)	71.4(85.5)	56.4(81.2)
Hydrogen, %	4.4(5.5)	4.5(5.4)	3.8(5.3)
Nitrogen, %	1.21(1.50)	1.3(1.56)	1.1(1.54)
Sulfur, %	1.79(2.24)	0.60(0.72)	0.61(0.85)
Ash, %	19.7	13.4	28.0
Oxygen, % by difference	5.5(6.9)	5.7(6.8)	7.7(10.75)
Sodium, %	0.02(0.03)	4.6(5.51)	1.4(1.96)
Calcium, %	0.13(0.16)	0.15(0.18)	6.6(9.2)

(a) Values in parenthesis denote moisture ash free basis; others are on a product basis.
(b) Heat value on coal containing 9.88% ash and 1.32% H_2O.
(c) Heat values on coal containing 16.48% ash and 9.18% water.
(d) Ash and moisture content of coal used to determine heat value were 1.82 and 7.02, respectively.
(e) Sulfur higher than usual because heater burned out during run. Normally sulfur content would be equal to or less than 1.2 lb $SO_2/10^6$ Btu.

Continued

	Westland Coal			
	Raw	NaOH Leachant	Mixed Leachant[b]	Acid (H_2SO_4) Leachant
Proximate Analysis				
H_2O, %	< 0.1	0.4	8.2	4.31
Ash, %	10.0	13.3	16.5	2.19
Volatile	36.9(41.0)	31.2(36.1)	30.4(40.4)	31.5(33.7)
Fixed Carbon	53.1(59.1)	55.1(63.8)	44.9(59.6)	62.0(66.3)
Heat Value, Btu/lb (MAF)	(14,950)	(14,320)	(14,100)[c]	13,079 (14,349)[d]
SO_2, lb/10^6 Btu	3.01	1.50[e]	1.50[e]	1.26
Ultimate Analysis				
H_2O, %	<0.1	0.4	8.2	4.31
Carbon, %	73.9(82.1)	70.3(81.5)	63.7(84.6)	76.0(81.3)
Hydrogen, %	5.1(5.7)	4.3(5.0)	4.3(5.7)	4.6(4.9)
Nitrogen, %	1.5(1.7)	1.5(1.7)	1.4(1.9)	1.5(1.6)
Sulfur, %	2.02(2.25)	0.93(1.07)	0.67(0.89)	1.05(1.12)[e]
Ash, %	10.0	13.3	16.5	2.19
Oxygen, % by difference	7.5(8.3)	4.3(10.8)	5.2(6.9)	
Sodium, %	0.02(0.02)	2.08(2.4)	0.19(0.25)	0.40(0.43)
Calcium, %	0.08(0.09)	0.20(0.23)	6.0(8.0)	0.84(0.09)

(a) Values in parenthesis denote moisture ash free basis; others are on a product basis.
(b) Heat value on coal containing 9.88% ash and 1.32% H_2O.
(c) Heat values on coal containing 16.48% ash and 9.18% water.
(d) Ash and moisture content of coal used to determine heat value were 1.82 and 7.02, respectively.
(e) Sulfur higher than usual because heater burned out during run. Normally sulfur content would be equal to or less than 1.2 lb $SO_2/10^6$ Btu.

TABLE 1. (Continued)

raw coal. Sodium hydroxide leachant produced HTT coals
containing 2.08 and 5.51 weight percent sodium (MAF),
whereas the mixed leachant produced HTT coals containing
0.25 to 1.96 weight percent sodium (MAF). The high sodium
values in both cases - 5.51 weight percent and 1.96 weight
percent - in the HTT Martinka coals resulted from the high
mineral matter content of the raw coal.

Task 2. Combustion Characterization Experiments

As part of the overall evaluation of the feasibility of hydro-
thermally treated coal utilization from an environmental point of view,
combustion studies were conducted in experimental laboratory combustion
units to characterize the burning of these coals.

Objective and Scope. The overall objectives of these combustion
studies were to characterize the combustion behavior and to evaluate the
pollutant emissions from the burning of the HTT coals relative to the corres-
ponding raw coals. Factors that were considered included:

● General combustion behavior

- Ignition
- Flame stability
- Carbon burnout

● Pollutant emissions

- SO_2
- NO
- CO
- Hydrocarbons
- Polycyclic organic matter (POM)
- Particulate (including size distribution)
- Trace elements

● Ash properties

- Fouling
- Slagging
- Disposal characteristics (leachability)
- Resistivity
- Particle size.

Ignition behavior and flame stability data were obtained on a qualitative basis by observing and comparing ignition behavior and flame stability of the HTT coals with those of the raw coals.

In addition, SO_2, NO_x, CO, and CO_2 concentrations in the flue gases were obtained by direct readout from meters which are part of the facilities. SO_2 concentrations on selected firings were obtained by collecting and analyzing samples of the flue gases. Likewise, the selected samples of the flue gases were collected and analyzed for hydrocarbons and POM concentrations. Carbon burnout data were obtained from analysis of the ash (particulate matter) and feed coal for carbon.

Analysis of the fly ash, with respect to composition and melting point, provided data from which the fouling and slagging properties of the various coals were predicted.

Disposal characteristics of the fly ash were assessed by chemical analysis of the ash and by conducting preliminary leaching studies followed by analysis of the leach liquor.

Combustion Plan. Because the quantity of HTT coals was limited, a small combustion facility was designed specifically to fire small quantities of coal (approximately one pound of coal per hour). This facility was used to characterize the candidate coals selected in Task 1. A larger combustion facility, with a firing rate of about thirty pounds per hour was used to verify the results of pound-per-hour unit for a selected HTT coal and the corresponding raw coal. Facility operating procedures were standardized to minimize day-to-day variations, while data collection and sample analyses were conducted utilizing standard procedures.

Combustion Facilities. Figure 1 is a schematic of the small pound-per-hour (1b/hr) Laboratory Test Facility (LTF). Figure 2 is a schematic of the larger Multifuel Furnace Facility (MFF). Specific details of the design and construction of these facilities are given in Appendix C while a brief description of each facility is given below.

The basic elements of the LTF are the combustion chamber and the cooler. The combustion chamber consists of an inner disposable alumina

Air Heater

Coal Feeder

Combustor

Cooler

Gas Line

Particulate Collection

NO_x, Thermoelectron, chemiluminescence

CO_2, Bechman, non-dispersed infra-red

CO, Beckman, non-dispersed infra-red

O_2, Taylor, paramagnetic analyzer

SO_2 Faristor, dry electrochemical analyzer
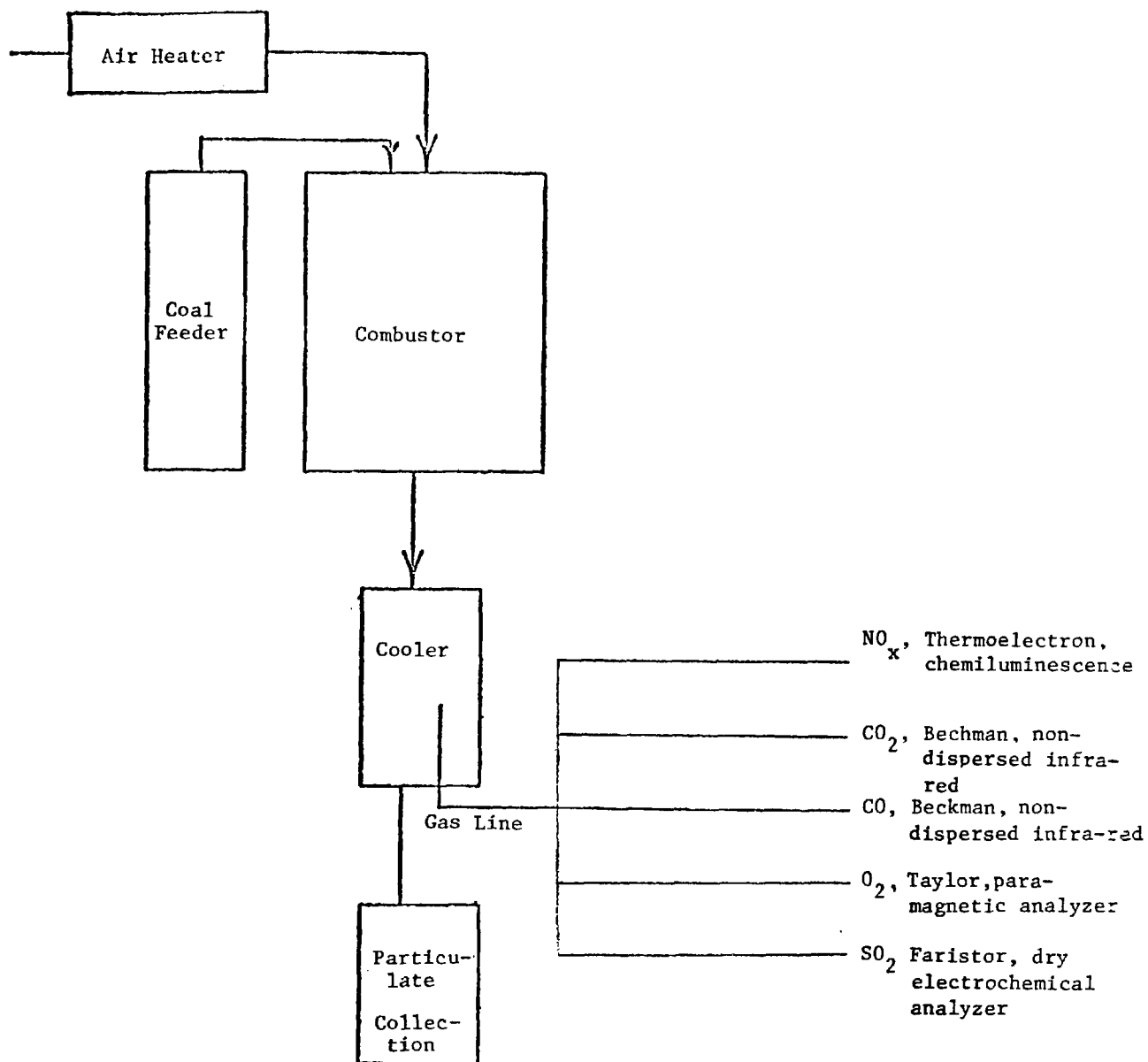
FIGURE 1.   SCHEMATIC OF 1 lb/hr LTF COMBUSTION UNIT
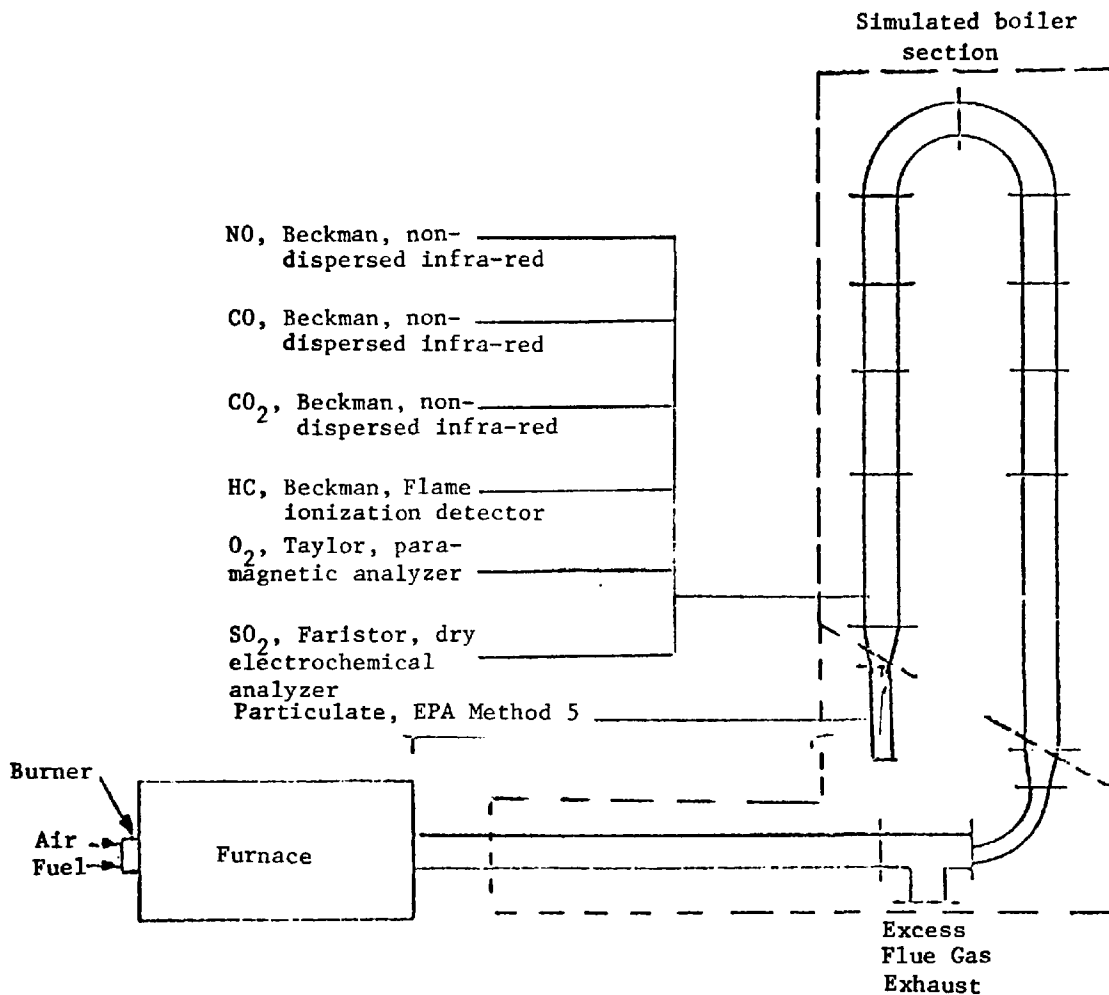
FIGURE 2. SCHEMATIC OF THE MULTIFUEL FURNACE FACILITY

tube, 2-1/2-in. I.D. and 18 inches long. (Initially, the combustion chamber was 12 inches. The chamber was lengthened after Run 18 to increase the residence time of the coal in the combustion chamber.) A second liner encases the inner liner. Insulation surrounds the outer liner to control furnace heat loss. Several platinum, platinum-rhodium thermocouples are imbedded along the inner tube to provide a measure of axial temperature distribution. The combustion gases pass from the combustion chamber to a cooler--a 3-in. I.D. x 5-ft. long air-cooled, counterflow stainless steel heat exchanger. Combustion gases are sampled in and or at the exit of the cooler as indicated in Figure 1.

The MFF is capable of firing pulverized coal at rates from about 20 lb/hr to 80 lb/hr. The basic element of this facility is the refractory-lines furnace which is about 15 inches in diameter and 90 inches long. The furnace is lined with 4 layers of firebrick to minimize heat loss. Four observation ports are provided along the length of the furnace for flame observation and optical pyrometer readings at various distances from the burner. At the outlet, the diameter of the furnace is reduced to enclose the flame, provide for normal recirculation, and limit radiation loss. Combustion gases leave the furnace and enter the simulated boiler convection passes where they are cooled to 400 to 600 F. Combustion gases are sampled at the exit of this section as indicated in Figure 2.

Combustion air can be heated to temperatures of up to 800 F and can be introduced axially, tangentially, or a combination of both. In this study, air was admitted axially.

Operational Procedures. Both units were initially fired on gaseous fuels to a predetermined furnace temperature (about 1800 F for the LTF and 2200 F for the MFF units). Pulverized coal was then fired for one to two hours prior to data collection to establish the desired furnace operating conditions and furnace equilibrium.

Sampling and Analytical Procedures. Particulate and gaseous samples were collected and analyzed utilizing standard or presently acceptable procedures. Particulates were sampled during each run and the

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gaseous components listed in Figures 1 and 2 were continuously monitored throughout a run. Table 2 indicates the various analytical methods used for the samples collected. The procedures used in obtaining gaseous, particulate, and POM samples are described below.

The major gaseous components of interest, SO_2, NO, CO, CO_2, unburned hydrocarbons (monitored only on the MFF), and O_2 were monitored continuously throughout a given run. Figures 1 and 2 indicate the types of monitors used for each facility. For the LTF unit, gaseous samples were drawn from the cooler tube section about 1-1/2 feet from the exhaust end of the tube and at the center of the duct. For the MFF, samples were drawn in and near the simulated boiler convection pass section just upstream of the particulate sampling port.

For the LTF unit, particulate was collected by passing the entire flue gas stream through a Type A glass-fiber filter at a temperature of about 300 F. In addition to this filter catch, particulate samples were collected from the loose deposits on the wall of the cooler tube. The entire cooler tube was scraped clean after each run to obtain sufficient sample and to avoid contamination in subsequent runs. Both the filterable particulate and the cooler tube particulate were weighed, divided, and analyzed. Due to the nature of the combustor, a major portion of the particulate was retained in the combustion liner as slag. This slag was not representative of the particulate catch since it was subjected to high temperature and was highly oxidized.

For the MFF, a filterable particulate sample was collected and analyzed according to EPA Method 5.

POM samples were collected by a modified EPA Method 5 train with an adsorbent column located downstream of the filter. The probe wash, filter catch, an adsorbent column catch were all used to determine the POM levels utilizing gas chromatography/mass spectrometry computer quantification procedure (2).

TABLE 2. ANALYTICAL METHODS FOR SAMPLE ANALYSIS

Component	Analysis	Method[*]
Coal	C, H, N, O, S, SO_4, Ash, H_2O, Volatile Matter	ASTM D2492-68
	Fixed Carbon	ASTM D2492-68
	Na, Ca	AA
	Particle size	Coulter Counter, Sieve
	Trace elements	SSMS, OES
	Heating Value	Calorimeter/ASTM D2015
	Thermal Analysis	dTGA, DTA
Ash	C, H, N, O, S, SO_4, Ash, H_2O, Fixed Carbon	ASTM D2492-68
	Na, Ca	AA
	Trace elements	SSMS, OES
	Particle size	Coulter Counter
	Resistivity	Test Cell
	Leachability	--
Gases	CO, CO_2	NDIR
	SO_2	Coulimetric
	NO, NO_2	Chemiluminescence or NDIR
	O_2	Polarographic or paramagnetic
	POM	GC/MS
Particulates		Method 5

*AA - atomic absorption
 SSMS - spark source mass spectrometry
 OES - optical emission spectrometry
 dTGa - derivative thermogravemetric analysis
 DTA - differential thermal analysis
 NDIR - non-dispersed infra-red
 GC/MS - gas chromatography/mass spectrometry

Combustion Results

Combustion characterization experiments were conducted in the LTF and Multifuel Furnace units on a number of HTT coals and the corresponsing raw coals as noted in Table 3. The results of these experiments are summarized in Table 4, 5, and 6. (Run 8 was conducted for instrumentation checkout purposes, and therefore was not included in these tables.) As shown in Table 6, the results of the experiments in the LTF unit are consistent with those of the MFF based upon the firing of the raw and mixed leachant Westland coals in both facilities. The total capture of the SO_2 in the HTT firing in the MFF may be an artifact of the combustion facility as well as of the treated coal. The horizontal layout of the MFF allows more slag to collect beyond the combustion zone, thus aiding the capture of ash and product gases in the slag.

These results, supplemented by additional coal and ash analyses, determined the

    (1)   General combustion behavior

    (2)   Pollutant emissions

    (3)   Ash characteristics

of the HTT coals as compared to the corresponding raw coals. A discussion of the above three aspects of HTT coal utilization is presented in the following sections.

TABLE 3. COALS USED IN VARIOUS COMBUSTION EXPERIMENTS

	Run Numbers
A. Untreated (Raw)	
1. Westland (high ash) - run-of-mine	9, 19
2. Westland (low ash) - washed (Prep. Plant)	14, 15, 22, 30
3. Martinka (moderate ash) - washed (Prep. Plant)	1, 3, 16, 23
B. HTT, Low Sulfur, Residual Alkali, Residual Ash	
1. Martinka (NaOH) - Residual Na	2, 4, 5, 17, 21
2. Martinka (NaOH-CaO) - Low Na, Residual Ca	6, 7, 12, 25
3. Westland (low ash) - (NaOH) - Residual Na	10, 11, 13, 20
4. Westland (low ash) - (NaOH-CaO) - Low Na, Residual Ca	18, 29, 31
C. HTT, Low Sulfur, Low Alkali, Low Ash	
1. Westland - acid leached	24, 26, 27, 28

TABLE 4. COMBUSTION CONDITIONS AND RESULTS FROM LTF COMBUSTION UNIT

Run No. Coal Type	1 Raw Martinka	2 Martinka Batch D NaOH Leachant	3 Raw Martinka	4 Martinka NaOH Leachant	5 Martinka NaOH Leachant	6 Martinka Mixed Leachant	7 Martinka Mixed Leachant
Combustion Conditions							
Coal feed rate, lb/hr	1.9	1.5	2.2	2.25	1.1	0.84	1.85
Air feed rate, lb/hr	25.9	15.7	27.5	27.8	19.5	10.3	20.6
Sec: psi ratio	7.7	6.9	8.0	9.7	13.6	4.6	10.1
Furnace temp, $^\circ$F	2105(a)	2185(a)	2160(a)	2220(a)	1955(b)	1980(b)	2265(b)
Gas Analysis (as measured)							
CO_2, %	11.9	15.3	13.3	15.1	13.0	12.7	14.5
O_2, %	7.2	7.4	8.9	2.0	6.1	6.6	3.2
CO, ppm	345	135	265	750	160	115	90
NO_x, ppm	720	565	900	775	763	600	780
Theoretical NO_x, ppm	1803	2777	2146	2366	1634	2041	2254
SO_2, ppm	1240	210	1300	310	205	290	--
Theoretical SO_2, ppm	1184	590	1445	470	332	406	448
SO_2, lb/MM Btu (MAF)	2.9	0.97	2.97	1.06	1.06	1.16	--
Sulfur capture, %	--	64.4	10.0	34.04	38.25	28.57	--
Res. time, milli sec	47	76	44	45	71	137	61
Carbon burnout, %	--	--	99.3	--	--	97.7	--
Particulate loading, mg/Nm^3			818			4612	6544
POM loading, μg/Nm^3					23		

(a) Outer wall temperature at tube center
(b) Inside wall temperature at tube center

Continued

Run No.	9	10	11	12	13	14	15
Coal Type	Raw Westland High ash	Westland NaOH Leachant	Westland NaOH Leachant	Martinka Mixed Leachant	Westland NaOH Leachant	Raw Westland Low ash	Raw Westland Low ash

Combustion Conditions

	9	10	11	12	13	14	15
Coal feed rate, lb/hr	1.98	0.44	1.15	1.2	1.3	1.65	1.33
Air feed rate, lb/hr	20.1	8.1	17.0	13.2	16.6	19.65	16.25
Sec: psi ratio	8.8	7.2	10	7.6	9.1	10.00	8.00
Furnace temp, $^\circ$F	2100(b)	1855(b)	2140(b)	2080(b)	2060(b)	2320(b)	2270(b)

Gas Analysis (as measured)

	9	10	11	12	13	14	15
CO_2, %	12.8	6.7	14.5	12.9	13.2	14.7	14.5
O_2, %	11.5	12.4	3.5	3.5	2.0	2.0	2.0
CO, ppm	125	1200	95	90	67	150	135
NO_x, ppm	NA	215	625	605	695	660	715
Theoretical NO_x, ppm	2245	1701	2114	2254	2450	2608	2530
SO_2, ppm	2250	250	415	320	464	1725	1790
Theoretical SO_2, ppm	2312	458	570	448	660	1537	1498
SO_2, lb/MM Btu (MAF)	5.2	1.5	1.5	---	1.5	3.00	3.00
Sulfur capture, %	2.68	45.4	26.6	28.3	29.7	--	--
Res. time , milli sec	61	185	78	103	83	63	78
Carbon burnout, %	97.4	--	--	--	99.9	--	--
Particulate loading, mg/Nm^3	4471	--	--	--	233	--	2335
POM loading , μg/Nm^3			39	24		65	

(b) Inside wall temperature at tube center

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TABLE 4 (Continued)

Run No.	16	17	18	19	20	21	22
Coal Type	Raw Martinka	Martinka NaOH Leachant	Westland Mixed Leachant	Raw Westland High ash	Westland NaOH Leachant	Martinka NaOH Leachant	Raw Westland Low ash

Combustion Conditions

Coal feed rate, lb/hr	1.27	1.4	1.28	1.25	1.3	1.40	1.46
Air feed rate, lb/hr	12.26	16.75	14.6	16.53	16.28	16.46	16.6
Sec: psi ratio	4.0	8.4	7.8	4.4	4.4	4.3	4.3
Furnace temp, $^{\circ}F$	2095(b)	2080(b)	2090(b)	1656(c)	1760(c)	1740(c)	1873(c)

Gas Analysis (as measured)

CO_2, %	14.4	14.3	12.6	11.0	14.2	12.8	14.9
O_2, %	1.5	3.7	4.0	9.5	6.0	6.3	3.7
CO, ppm	705	100	55	76	77	72	70
NO_x, ppm	650	625	585	520	770	780	625
Theoretical NO_x, ppm	2789	2423	2779	1566	2142	2482	2734
SO_2, ppm	1910	380	250	1215	220	120	1115
Theoretical SO_2, ppm	1877	492	580	1741	651	493	1610
SO_2, lb/MM Btu (MAF)	2.97	1.06	1.27	5.04	1.46	1.03	3.00
Sulfur capture, %	--	22.7	56.9	30.2	66.2	75.67	30.7
Res. time, milli sec	110	81	93	174	168	168	157
Carbon burnout, %	--	--	--	98.7	99.4	99.3	95.4
Particulate loading, mg/Nm^3		4490	1514	2326	1952	4799	3857
POM loading, $\mu g/Nm^3$			46				

(b) Inside wall temperature at tube center
(c) Average of 5 thermosamples spaced equally along the tube length in the raw expanded combustor

TABLE 4 (Continued)

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TABLE 5. COAL-ASH ANALYSES

Run No.	1			2		3		
Analysis (MF)[1]	Coal	Ash / Cooler[2]	Ash / Slag[3]	Coal	Ash / Cooler	Coal	Ash / Filter[4]	Ash / Cooler
C	67.3			72.6	25.4	67.6	28.9	5.6
H	4.4			4.5	0.3	4.6	0.2	0.1
N	1.2			1.4	0.4	1.3	0.4	0.1
O	5.5			7.1		4.3	0.4	0.4
S	1.8	0.52	0.01	0.7	1.5	2.0	2.6	0.2
SO$_4$[5]	--	--	--	--	1.2	--	--	2.2
Ash	19.8	87.9	99.5	13.7	71.7	20.2	65.9	93.5
Na	0.03			1.9	10.1	0.03		
Ca	0.2			0.1	0.5	0.2		
V.M.	29.32			29.4		29.21		
Fixed C	50.9			56.8		50.8		
Heat value, Btu/lb (MAF)[6]	15,100			14,900		15,100		

Run No.	4		5			6		
Analysis (MF)	Coal	Ash / Cooler	Coal	Ash / Cooler	Slag	Coal	Ash / Filter	Ash / Cooler
C	69.6	8.0	70.1	11.4		59.9	22.5	13.3
H	4.3	0.1	4.5	0.1		3.9	0.2	0.1
N	1.4	0.1	1.4	0.1		1.2	0.4	0.2
O	7.0		6.6			5.7	3.8	0.2
S	0.6	2.4	0.6	2.3	0.4	0.6	0.7	1.6
SO$_4$[5]	--	2.2	--	1.8	--	--	--	--
Ash	17.1	90.6	17.4	86.9	100.0	28.3	71.0	86.3
Na	2.6	13.6	2.1	12.0	14.9	1.3	3.0	3.9
Ca	0.1	0.6	0.1	0.7	0.7	6.0	16.2	20.2
V.M.	27.4		27.4			26.4		
Fixed C	51.2		51.2			45.5		
Heat value, Btu/lb (MAF)	14,900		14,900			14,700		

(1) (MF)--moisture free
(2) Ash from cooler tube
(3) Slag from vicinity of burner
(4) Ash from filter
(5) Sulfate reported as percent sulfur
(6) (MAF)--mosture ash free

Continued

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Run No.	7			9			10		
		Ash			Ash			Ash	
Analysis (MF)	Coal	Filter	Cooler	Coal	Filter	Cooler	Coal	Cooler	Slag
C	59.9		6.6	55.6	29.3	22.2	70.6	29.4	
H	3.9		0.1	3.8	0.3	0.3	4.3	0.6	
N	1.2		0.1	1.1	0.4	0.4	1.5	0.7	
O	5.7		--	8.2	--	--	9.3	--	
S	0.6	1.2	2.3	2.6	1.7	0.72	0.9	4.8	2.7
SO_4 (*)	--	--	--	--	0.2	0.4	--	4.7	3.2
Ash	28.3	94.0	95.3	28.7	68.2	75.1	13.4	66.4	99.7
Na	1.3	4.1	4.7	0.08			2.1	11.5	14.3
Ca	6.0	22.5	22.5	0.4			0.2	1.2	1.2
V.M.	26.4			29.6			31.3		
Fixed C	45.5			41.7			55.3		
Heat value, Btu/lb (MAF)	14,700			14,100			14,400		

Run No.	11			12		13			
		Ash			Ash		Ash		
Analysis (MF)	Coal	Cooler	Slag	Coal	Cooler	Coal	Filter	Cooler	Slag
C	70.6	11.1		59.9	4.5	70.6	22.4	8.2	
H	4.3	0.2		3.9	0.1	4.3	0.3	0.1	
N	1.5	0.2		1.2	0.1	1.5	0.4	0.1	
O	9.3	--		5.7	--	9.3	--	--	
S	0.9	6.6	1.4	0.5	1.58	0.9	2.3	6.4	1.2
SO_4 (*)	--	5.6	1.6	--	1.5	--	2.0	7.0	1.3
Ash	13.4	88.6	99.7	28.3	95.0	13.4	79.2	92.8	100.1
Na	2.1	14.9	16.9	1.3	4.5	2.1	10.9	14.5	12.7
Ca	0.2	1.49	1.5	6.0	22.3	0.20	1.25	2.03	5.8
V.M.	31.3			26.4		31.3			
Fixed C	55.3			45.5		55.3			
Heat value, Btu/lb (MAF)	14,400			14,700		14,400			

(*) Sulfate reported as percent sulfur

TABLE 5. (Continued)

Run No.		14		15	Ash		16	Ash	
Analysis (MF)		Coal	Ash	Coal	Filter	Cooler	Coal	Filter	Cooler
	C	73.9	--	73.9	61.7	13.1	67.6	42.1	19.1
	H	5.1	--	5.1	0.4	0.1	4.6	0.3	0.2
	N	1.5	--	1.5	1.1	0.2	1.3	0.6	0.2
	O	7.5	--	7.5	7.5	--	4.3	--	--
	S	2.0	--	2.0	2.6	0.9	2.0	1.2	0.6
	SO_4 (*)	--	--	--	0.29	0.71	--	0.2	0.3
	Ash	10.0	--	10.0	34.9	84.9	20.2	55.2	79.4
	Na	0.02	--	0.2	0.03	0.5	--	0.04	0.19
	Ca	0.08	--	0.08	0.21	1.01	--	0.3	0.7
	V.M.	36.9	--	36.9	--	--	29.2	--	--
	Fixed C	53.1	--	53.1	--	--	50.8	--	--
Heat value, Btu/lb (MAF)		15,000	--	15,000	--	--	15,100	--	--

Run No.		17	Ash		18	Ash		
Analysis (MF)		Coal	Filter	Cooler	Coal	Filter	Cooler	Slag
	C	70.1	59.8	55.4	69.4	8.2	5.3	60.1
	H	4.5	2.8	2.4	4.7	0.1	0.1	60.1
	N	1.4	1.2	1.2	1.5	0.1	0.2	20.1
	O	6.6	--	--	5.7	--	--	--
	S	0.6	1.0	1.44	0.73	2.4	5.3	0.3
	SO_4 (*)	--	0.49	0.99	--	2.3	5.1	0.3
	Ash	17.4	31.8	36.6	18.0	91.2	94.0	100.0
	Na	2.1	4.8	5.40	0.2	1.13	1.3	0.5
	Ca	0.12	0.3	0.5	8.0	3.2	3.2	3.9
	V.M.	27.4			40.4			
	Fixed C	51.2			59.6			
Heat value, Btu/lb (MAF)		14,900			14,100			

(*) Sulfate reported as percent sulfur

TABLE 5. (Continued)

Run No.	19				20			
		Ash				Ash		
Analysis (MF)	Coal	Filter	Cooler	Slag	Coal	Filter	Cooler	Slag
C	55.5	19.8	16.3	1.3	70.36	12.8	11.8	
H	3.9	0.3	0.2	0.1	4.44	0.1	0.2	
N	1.0	0.3	0.2	<0.1	1.31	0.1	0.2	
O	8.4	--	--	--	9.68	--	--	
S	2.5	1.4	0.8	0.27	0.91	2.6	7.0	1.46
SO4 (*)	--	1.2	0.6	0.2	--	2.4	1.2	1.09
Ash	28.7	75.2	80.4	98.2	13.30	87.0	86.3	>100.0
Na	0.06	0.31	0.2	0.09	1.90	12.8	13.6	15.8
Ca	0.40	1.9	1.1	1.0	0.18	1.41	1.7	1.56
V.M.	29.6				31.33			
Fixed C	41.7				55.32			
Heat value, Btu/lb (MAF)	14,100				14,388			

Run No.	21				22			
		Ash				Ash		
Analysis (MF)	Coal	Filter	Cooler	Slag	Coal	Filter	Cooler	Slag
C	69.6	37.8	33.2	73.9	56.4	49.4		
H	4.32	0.5	0.3		5.1	0.7	0.6	
N	1.4	0.7	0.6		1.5	0.9	0.9	
O	7.0	--	--		7.5	1.3	0.2	
S	0.6	1.22	2.5	0.3	2.0	1.30	1.1	0.08
SO4 (*)	--	0.7	2.1	0.3	--	0.2	0.3	0.02
Ash	17.0	61.9	65.0	>100.0	10.0	38.7	46.0	100.0
Na	2.6	9.0	9.4	17.1	0.02	0.06	0.1	0.04
Ca	0.1	0.5	0.7	0.7	0.08	0.3	0.4	0.07
V.M.	27.4				36.9			
Fixed C	51.2				53.1			
Heat value, Btu/lb (MAF)	14,900				15,000			

(*)   Sulfate reported as percent sulfur

TABLE 5. (Continued)

Run No.	23		24		25	Ash	26	Ash	
Analysis (MF)	Coal	Ash	Coal	Ash	Coal	Filter	Coal	Filter	Cooler
C	67.6	--	76.0	--	60.0	13.2	76.0	62.2	41.8
H	4.6	--	4.6	--	3.9	0.1	4.6	--	--
N	1.3	--	1.5	--	1.2	0.2	1.5	--	--
O	4.3	--	10.3	--	5.7	--	10.3	--	--
S	2.0	--	1.0	--	0.6	0.6	1.0	0.9	2.1
SO$_4$(*)	--	--	--	--	--	0.5	--	0.6	1.8
Ash	20.2	--	2.2	--	28.3	85.8	2.2	45.4	54.3
Na	--	--	0.4	--	1.29	4.0	0.4	0.2	0.6
Ca	--	--	0.09	--	6.0	19.7	0.09	0.8	2.6
V.M.	29.2	--	31.5	--	26.4	--	31.5	--	--
Fixed C	50.8	--	62.0	--	45.5	--	62.0	--	--
Heat value, Btu/lb (MAF)	15,100	--	14,300	--	14,700	--	14,300	--	--

Run No.	27	Ash		28	Ash		29	Ash		
Analysis (MF)	Coal	Filter	Cooler	Coal	Filter	Cooler	Coal	Filter	Cooler	Slag
C	76.0	61.7	59.4	76.0	49.6	34.4	69.4	8.3	12.1	<0.1
H	4.6	--	--	4.6	0.3	0.3	4.67	0.1	0.2	<0.1
N	1.5	--	--	1.5	0.6	0.4	1.5	0.2	0.2	<0.1
O	10.3	--	--	10.3	--	--	--	--	--	--
S	1.0	--	--	1.0	--	--	5.7	--	--	--
SO$_4$ (*)	--	0.5	1.5	--	0.4	--		1.1	2.9	3.8
Ash	2.2	33.9	32.1	2.2	47.0	59.8	18.0	89.6	85.0	99.8
Na	0.4	0.2	0.5	0.4	0.2	2.0	0.21	1.4	1.4	1.20
Ca	0.09	0.8	1.4	0.09	1.0	1.01	8.0	34.7	34.2	34.9
V.M.	31.5	--	--	31.5	--	--	40.4	--	--	--
Fixed C	62.0	--	--	62.0	--	--	59.6	--	--	--
Heat value, Btu/lb (MAF)	14,300	--	--	14,300	--	--	14,100	--	--	--

(*) Sulfate reported as percent sulfur

TABLE 5. (Continued)

| Run No. | | 30 | | 31 | |
Analysis (MF)		Coal	Ash Filter	Coal	Ash Filter
	C	73.9	1.7	69.4	2.1
	H	5.1	.09	4.7	.08
	N	1.5	.1	1.5	<.1
	O	7.5	--	5.7	--
	S	2.0	6.5	.6	3.0
	SO_4 (*)	--	--	--	--
	Ash	10.0	65.2	18.0	85.9
	Na	.02	.31	.2	35.9
	Ca	.08	.07	8.0	1.45
	V.M.	36.9	--	40.4	--
	Fixed C	53.1	--	59.6	--
Heat value, Btu/lb (MAF)		15,000	--	14,100	--

(*) Sulfate reported as percent sulfur

TABLE 5. (Continued)

TABLE 6. COMPARISON OF RAW AND HTT WESTLAND COAL FIRINGS

	lb/hr		MFF	
	Raw [a]	Treated [b]	Raw [c]	Treated [d]
Firing Rate, lb/hr	1.6	1.3	30	30
Furnace Wall Temp, F	2270	2090	2550	2300
O_2, percent	2.0	4.0	5.0	5.0
CO_2, percent	14.7	12.6	14.4	14.4
CO, ppm	150	55	3	3
HC, ppm	NA	NA	0	0
NO, ppm	660	585	680	780
SO_2, ppm	1730	250	1230	0
SO_2-capture, percent	0	57	0	100
POM Loading, $\mu g/Nm^3$	65	46	0.12	0.12
Particulate Loading, mg/Nm^3	2335	1515	N.A.	7500

(a) Run 14
(b) Run 18
(c) Run 30
(d) Run 31

General Combustion Behavior. Certain general combustion characteristics of both the raw and treated coals, such as ignition temperature and reactivity, were determined quantitatively from the derivative thermogravimetric (dTGA) and the differential thermal (DTA) fuel analyses. The results of the dTGA and DTA are summarized in Tables 7 and 8, respectively.

From these analyses, the combustion characteristics of these coals, in terms of ignition, reactivity, and possibly flammability, may have been improved by the hydrothermal treatment. For example, the ignition temperature of Westland coal was reduced from 426 C to 344 C (Table 7), a reduction of 82 C, by treating the coal with sodium hydroxide and the mixed leachant systems. A similar effect was noted by hydrothermal treatment of the Martinka coal with these leachant systems.

This was expected in view of other hydrothermal work which has been conducted at Battelle-Columbus. In this work, hydrothermal treatment of coals resulted in alteration and modification of the coal structure to a more simplified structure. This is evidenced by the fact that the liquid products from the pyrolysis of HTT coals contained less asphaltenes than the liquid products from the corresponding raw coals[4]. These lower molecular weight organic liquids from the HTT coals should have a lower ignition temperature and a higher degree of flammability than the higher molecular weight liquids from the raw coals.

The increased reactivity is reflected in Table 8. For example, treatment of the Martinka and Westland coals with the mixed leachant system resulted in HTT coals which burned out at a maximum temperature of about 470 C, whereas the raw coals burned out at a temperature of about 585 to 600 C. A similar effect, but not to this degree, was observed with the sodium-hydroxide treated coals.

While there may not be a direct correlation between combustion and gasification, it has been observed that hydrothermal treatment of coal with the mixed leachant system results in an increase in the steam and hydrogasification rates by as much as 40 to 50 fold[4]. This has been attributed to (1) alteration and modification of the coal structure, and (2) impregnation of the coal particle with a catalyst, in this case, calcium and/or sodium. This work has also shown that the mixed leachant-treated coal is more reactive than the sodium-hydroxide treated coal.

TABLE 7. DIFFERENTIAL THERMAL ANALYSES OF RAW AND HTT COALS[a]

	Westland Raw Coal	Martinka Raw Coal[b]	Westland Coal NaOH Leachant[c]	Martinka Coal NaOH Leachant[d]	Westland Coal Mixed Leachant[e]	Martinka Coal Mixed Leachant[f]
Air						
Starting Exotherm, C	233	243	252	263	268	252
Ignition Point, C	426	432	344	360	344	376
Secondary Exotherm, C	--	--	488	508	494	493
End of Exotherm, C	615	622	564	578	555	553
Nitrogen						
Starting Endotherm, C	400	405	385	375	329	414
Peak No. 1, C	442	455	462	466	467	475
Peak No. 2, C	516	530	519	513	514	520
Peak No. 3, C	555	563	--	--	--	--
End of Endotherm, C	584	585	550	557	550	554
Peak No. 4, C	--	--	622	--	678	665

(a) DTA performed with Stone Model 202 at 15 C/min and dynamic gas flow of 94 ml/min.
(b) Sample 41167
(c) Sample 31731-53 + -60
(d) Run # 5, 41169
(e) Sample 32135-24
(f) Run # 7, 41171

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TABLE 8. THERMOGRAVIMETRIC ANALYSES OF RAW AND HTT COALS[a]

	Raw Westland Coal	Martinka Raw Coal, 41167	Westland Coal NaOH Leachant 31731-53 & 60	Martinka Coal NaOH Leachant Run #5, 41169	Westland Coal Mixed Leachant 32135-24	Martinka Coal Mixed Leachant Run #7, 41171
Ash, percent	10.3	19.7	13.4	17.0	17.4	28.4
Temperature Range[b],	220-585	250-600	230-570	240-510	240-465	270-470
Maximum Rate of Weight Loss, mg/min	17.5	19.0	21.5	27.5	23.0	27.0
Temperature at Maximum Rate of Weight Loss, C	320	275	305	275	285	310

(a) TGA performed with Cahn Electrobalance at 15 C/min and air flow of 800 ml/min.
(b) Temperature range over which most of the sample is lost.

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The results of the TGA and DTA analyses were not reflected in the actual combustion experiments. Combustion of the raw and treated coals in both the LTF and MFF facilities indicated no apparent (visible) difference in the combustion behavior (ease of ignition and flame stability) between the treated and corresponding raw coals. This is not surprising considering the relatively small (but definite) difference in the TGA and DTA of analyses of the raw and treated coals. However, qualitatively, the HTT coals burned as well or better than the raw coals. Thus, hydrothermal treatment did not have a detrimental effect on the combustion behavior of the coals evaluated.

Pollutant Emissions. Pollutant emissions levels were measured from the firing of the raw and treated coals in the LTF and MFF units under typical utility boiler conditions of about 15 to 20 percent excess air. Generally, from the analyses of the coal and knowing the type of combustion system, these emissions can be predicted as indicated by the emission factors contained in the literature[5]. Accordingly, the combustion studies were intended to verify these predictions and also to identify if there are any factors in the coal processing that alter the predicted emission levels.

SO_2 - Sulfur Capture. The SO_2 level in the exhaust gases of the burned coal was monitored continuously throughout a given run. In addition, for each run, SO_2 levels were calculated from the sulfur content of the coal and the amount of combustion air assuming total oxidation of the sulfur to SO_2. From the data, sulfur capture as defined by the equation

$$\text{Percent sulfur capture (SC)} = \frac{SO_2 \text{ (theoretical)} - SO_2 \text{ (measured)}}{SO_2 \text{ (theoretical)}} \times 100$$

was calculated. The measured and calculated SO_2 values and sulfur capture data, along with other pertinent data relating to composition of the coal are shown in Table 9.

TABLE 9. SULFUR CAPTURE IN RAW AND TREATED COALS[a]

| | Coal Analysis, weight percent (MF) | | | SO$_2$ in Flue Gas, ppm | | Percent |
Run No.	S	Na	Ca	Theor	Measured	Sulfur Capture
Martinka - raw						
1	1.80	0.03	0.16	1180	1240	--
3	2.00	0.03	0.16	1440	1300	10
16	2.00	0.03	0.16	0880	1910	--
Martinka - NaOH Leachant						
2	0.68	1.90	0.13	590	210	64
4	0.64	2.61	0.11	470	310	34
5	0.65	2.1	0.12	330	205	38
17	0.65	2.1	0.12	490	380	23
21	0.64	2.61	0.11	490	120	76
Martinka - mixed leachant						
6	0.55	1.29	5.95	410	290	29
7	0.55	1.29	5.95	450	--	--
12	0.55	1.29	5.95	450	320	28
Westland - raw						
14	2.02	0.02	0.08	1540	1725	--
15	2.02	0.02	0.08	1500	1790	--
19	2.54	0.06	0.40	1740	1220	30
22	2.02	0.02	0.08	1610	1170	31
30	2.0	0.02	0.08	1400	1250	11
Westland - NaOH Leachant						
10	0.93	2.09	0.20	460	250	45
11	0.93	2.09	0.20	570	420	27
13	0.93	2.09	0.20	660	465	30
20	0.91	1.90	0.18	650	220	66
Westland - mixed leachant						
18	0.73	0.21	8.0	580	250	57
29	0.73	0.21	8.0	540	125	77
31	0.61	0.21	8.0	450	0	100
Westland - acid leached						
24	1.05	0.43	0.09	630	560	11
26	1.05	0.43	0.09	660	510	14
27	1.05	0.43	0.09	660	520	20
28	1.05	0.43	0.09	660	500	24

(a) In laboratory combustion unit.

From these data, it is evident that sulfur is being retained (captured by the ash), probably as sulfates. Additionally, the results indicate that the HTT coals with residual alkali are significantly more efficient in capturing sulfur oxides than are the raw coals. Analysis of the ash from the burned coals also tend to confirm the greater capture potential of the HTT coals as the ash from the combustion of the treated coals contained a higher percentage of sulfates than the ash from the raw coals.

Sulfur capture is attributed to the alkaline materials, sodium and calcium, contained in the HTT coals and also may be related to the ash composition. Corrosion studies at Battelle and elsewhere confirm that sulfur oxides in gas streams can lead to the production of sulfates and complex alkali-metal sulfates in caustic-containing systems[6]. It is likely that similar sulfur-containing compounds are formed in the alkaline systems derived from the HTT coals. Also, studies are being conducted which indicate that the relationship between the sodium, aluminum, and silicon content of lignite influence the degree of sulfur capture by the alkali in lignite[7]. For example, during the combustion of a lignite, the sodium may react with the sulfur to form sodium sulfate and/or with the aluminum and silicon values in the ash to form complex sodium aluminum silicates. This may be occurring in the combustion of HTT coals. If so, this may account for the variation in sulfur capture between the various HTT coals.

The degree of sulfur capture (Table 9) appears to be related to the concentration of alkali (sodium plus calcium) in the coal as noted below:

	Raw	HTT NaOH Leachant	HTT Mixed Leachant	HTT Deashed
Sulfur capture, wt % (av)	20.5	44.8	58.2	17
Range	10-30.7	22.7-75.0	28.3-100	10.8-24.2
Alkali (Na+Ca) wt % (av)	∿0.15	∿2.2	∿7.7	∿0.5 .

In general, coals low in alkali content, such as the raw and acid-leached, show a low potential for sulfur capture, whereas those containing higher concentrations of alkali showed a higher potential for sulfur capture.

One somewhat surprising result that deserves additional attention is the 100 percent sulfur capture in firing of the mixed leachant Westland coal in the MFF. The sulfur in the coal should be found in the products of combustion as SO_2 and/or as a sulfate. Accordingly, the 450 ppm of SO_2 (theoretical value) must appear in the particulate catch as a sulfate or gaseous SO_2. From the particulate loading of 7500 mg/Nm^3 (Table 7) and the weight percent of sulfur of 3.0 in the filterable particulate catch (Table 8) the sulfur concentration converts into an equivalent SO_2 level of 350 ppm or somewhat less than the predicted value of 450 ppm. This slight discrepancy appears reasonable in view of sensitivity of these values to the accuracy of the SO_2 determination (by the Faristor) and the analyses of the coal and the particulate catch for sulfur. Further confirmation of the observation of complete SO_2 removal is indicated by noting that the ratio of the sulfur to the mineral matter in coal (0.33) is nearly identical to the ratio of the sulfur to the ash in the filterable particulate sample (0.35). Thus, the 100 percent sulfur capture appears real.

In the lb/hr unit, sulfur captures of 57 percent with a 12-inch combustion chamber and 77 percent with an 18-inch chamber were observed for Runs 18 and 19, respectively. Apparently the longer residence time (700 milliseconds) and/or the slagging conditions in the MFF resulted in the higher sulfur capture.

NO_x Fuel-N-Conversion. In addition to the sulfur bearing compounds, coals generally have a measurable amount of nitrogen (N)-bearing materials. Although the HTT process has been shown to reduce significantly the sulfur materials in the coals, it has not been effective in reducing the N-bearing materials. The average NO_x levels observed in the seven different coals used in the lb/hr combustor are given in Table 10.

TABLE 10. NO$_x$ DATA FROM COAL FIRINGS IN THE LTF COMBUSTOR

| | Average NO$_x$, ppm | | | | Percent Conversion | |
| | Martinka | | Westland | | | |
Coal	Measured	Theore-tical	Measured	Theore-tical	Martinka	Westland
Raw	710	2330	630	2340	31	27
Caustic	660	2340	700	2230	28	31
Mix-leachant	670	2260	620	2700	30	23
Acid-leachant	--	--	700	2100	--	33
				Average	30	28

Most of the NO$_x$ measured in the flue gases was in the form of NO. The calculated NO$_x$ values in Table 10 are based on (1) complete conversion of the fuel-N to NO at the calculated excess air level used in the runs for each coal, and (2) no contribution of thermal NO.

The measured average NO$_x$ values are comparable for each coal burned, reflecting the inertness of the HTT process toward removing the fuel-N compounds. The measured NO$_x$ values, on the other hand, are lower than the corresponding calculated values. These NO$_x$ conversions are quite typical of results obtained in fuel-N conversion studies. Only at very low fuel-N levels (~100 ppm) is high conversion of fuel-N to NO$_x$ observed in combustion processes. As the fuel-N concentration increases in the fuel, the fraction of fuel-N converted to NO$_x$ decreases. In the present study, it appears that the overall average conversion efficiency is about 30 percent, which appears to be in line with results from other studies[8].

The NO emission levels measured during the two runs (Runs 30 and 31) in the MFF appear to be consistent with those measured in the LTF combustor. It should be noted that, for the MFF, NO levels from the combustion of the mixed-leachant coal were somewhat higher than those from the raw Westland coal even though the furnace wall temperatures were somewhat lower. These differences, however, appear to be within the data scatter of experimentation. They also suggest that the contribution of thermal NO is negligible.

$\underline{CO\text{-}CO_2\text{-}O_2}$. The CO, CO_2, and O_2 levels were used as indicators to establish the desired combustion operating conditions. These conditions were controlled by varying the excess air to maintain CO levels below 300 ppm. Fluctuations in the coal feed rate for the LTF produced excursions in the $CO\text{-}CO_2\text{-}O_2$ levels, but overall, the $O_2\text{-}CO$ levels were maintained at approximately the desired levels. However, CO levels on the order of 100 ppm were observed in the LTF unit indicating that carbon burnout was not as complete as desired. For the MFF, CO levels less than 5 ppm could be achieved at excess oxygen levels of about 5 percent.

Particulate Loading. For pulverized-coal-fired systems, particulate loadings are dependent upon the mineral matter content of the coal and the design of the combustion system*. Coal mineral matter will either be emitted as fly ash in the flue gases or retained in the combustion system. In utility power plants, approximately 50 to 80 percent of the coal mineral matter is retained in wet bottom or cyclone boilers while only 20 percent is retained in dry-bottom boilers. Both the LTF and MFF systems tend to operate as slagging units with the majority of ash being retained in the system. As a consequence, the particulate loading data gives an indication of the coal ash behavior (providing the carbon component is constant or negligible) rather than a realistic measure of the fly-ash emission.

In the LTF runs, particulate loadings were not determined according to Method 5 but were based on the fly-ash catch on a filter located at the exit of the cooler. The total combustion products passed through this filter. Because the furnace wall temperature (which should have a significant effect on ash retention in the system and thus on the particulate loading) was not constant from one run to another, the relative differences of the particulate loadings between the treated and raw coals could not be determined. However, it can be noted by comparing runs of the same coal type in Table 4 (for example, Runs 6, 7, and 25; Runs 11 and 13; Runs 15 and 22; Runs 18 and 29; and Runs 9 and 19) but with different furnace wall temperatures that higher particulate loadings were generally observed for those runs with lower furnace

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*Incomplete carbon burnout can contribute to the overall particulate levels but generally is small compared to the ash component.

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wall temperatures. Assuming that lower furnace wall temperatures are an indication of cooler ash particles, this observation suggests that the ash particles are not as "sticky" at lower temperatures and thus are emitted in higher levels as fly ash.

For the MFF runs, because the mixed leachant coal contains about 80 percent more ash than the raw Westland coal (Run 30), it was anticipated that the particulate loading from the combustion of the treated coal would be higher than that from the raw coal (Run 31). However, a significantly higher particulate loading was observed. The high particulate loading of the mixed-leachant coal is attributed to its relative narrow range of ash-fusion temperatures between the initial deformation and the fluid temperatures of the ash (about 100 F). Past experience indicates that for most coals fired in the Multifuel Furnace, over 90 percent of the ash is retained in the furnace system. This was the case for the raw Westland coal as the slag that formed in the furnace and the furnace exit duct* captured about 97 percent of the coal ash.

At the completion of the raw Westland run, the furnace exit duct was nearly plugged by the fused ash. This was not the case when firing the mixed-leachant coal as the furnace exit duct remained relatively "clean" as approximately 50 percent of the coal ash was retained in MFF system. The ash from the combustion of the mixed-leachant coal may have passed rapidly through the softening (plastic) region (and thus did not have the opportunity to collect in the furnace system) and exited as a dry dust.

The raw- and mixed-leachant Westland coals were fired in both the LTF and MFF systems. For these coals, the values of the particulate LTF unit are between those of the MFF. Because both the MFF and LTF retain the majority of coal ash within the system, it is not surprising to see a discrepancy between these values as the time-temperature history of the system becomes the controlling factor.

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*The temperature along this horizontal duct ranged from about 2400 F at
 the furnace exit to about 1800 F before passing into the vertical duct
 that simulates the convection passes of the boiler.

Carbon Burnout. For the LTF unit, solid samples from the burned coal were collected from three different regions of the combustion system. Samples were collected from at least one region for every run. Referring to Figure 1, these samples were designated as: slag (from the hot combustion chamber); cooler ash (from the cooler tube); and filter ash (from the filter placed in the gas stream). The carbon data from coal sample and the cooler and filter ashes analyses (where available) were used to generate carbon burnout data from the following equation:

$$\text{percent unburned carbon} = C_{ub} = \frac{C_{fa} + C_{ca}}{C_f}$$

and

$$\text{percent carbon burnout} = C_{bu} = (100 - C_{ub})$$

where

C_{fa} = weight of carbon remaining in filter ash

C_{ca} = weight of carbon remaining in cooler ash

C_f = weight of carbon fed to burner during ash collection period.

The weight of the carbon remaining in the slag was found to be negligible (as indicated in Runs 18 and 19 of Table 8) and therefore did not enter into the calculation.

Table 11 lists the C_{bu} determination and includes data on the weight percent of carbon remaining in the filter and cooler ash. Although the weight percent of carbon remaining in these ashes was often significant, the total weight of unburned carbon was not. Since the total weight of the filter and cooler ashes accounted for only about 10 percent of the coal ash, the other 90 percent remained on the combustion liner as slag. As seen from the data in Table 11, carbon burnout was high in all runs, ranging from 95.4 to 99.9 weight percent. Furthermore, there was no appreciable differences in carbon burnout between the raw and the treated coals. As previously discussed, the raw Martinka did exhibit a slightly higher carbon burnout than the Westland coals.

For the two runs in the MFF, analysis of the filterable particulate for carbon indicated that essentially all the carbon in both the raw and

TABLE 11. CARBON CONTENT OF FILTER AND COOLER ASH FROM LFT COMBUSTION UNIT

Type of Coal	Martinka Coal				Westland Coal			
	Run No.	Carbon Content, wt %		C_{bu}	Run No.	Carbon Content, wt %		C_{bu}
		Filter Ash	Cooler Ash			Filter Ash	Cooler Ash	
Raw	3	28.9	5.6	99.3	22	56.4	49.4	95.4
					30	1.7	--	--
NaOH Leached HTT	21	37.8	33.2	99.3	13	22.4	8.2	99.9
					20	12.8	11.8	99.4
Mixed Leached HTT	6	22.5	13.3	97.7	29	8.3	12.1	98.6
					31	2.1	--	--
De-Ashed HTT					26	62.2	41.8	97.9
					27	61.7	59.4	96.8
					28	49.6	34.4	98.1

mixed leachant Westland coals was burned completely. In comparison to the LFT burner, the MFF provided a relatively long residence time (approximately 0.7 sec as compared to 0.16 sec) at elevated temperatures which promoted the complete carbon burnout.

Trace Elements. Trace element analyses by spark-source mass spectrometry (SSMS) were obtained for 6 of the 7 coals burned. Trace element data were also obtained by optical emission spectroscopy (OES) for all 8 coals burned.

Analyses of the SSMS data in terms of element enrichment in the ashes are tabulated in Table 12 and Appendix D. With the Westland coal, hydrothermal treatment had no observable effect on enrichment of trace elements in the cooler and filter ashes during combustion. The same was true for enrichment of the trace elements in the ashes from combustion of the mix-leachant treated Martinka coal. However, enrichment of the trace element in the ashes from combustion of the caustic treated Martinka coal was observed.

TABLE 12. NUMBER OF ELEMENTS ENRICHED

	Martinka[a]			Westland[a]		
	(+)	(−)	(0)	(+)	(−)	(0)
Raw Coal Ash	25	28	10	57	6	2
Caustic Coal Ash	48	22	12	59	3	3
Mix-leachant coal ash	29	31	12	57	4	4

(a) + indicates an increase of element concentration going from coal ash to filter ash.

− indicates a decrease of element concentration going from coal ash to filter ash.

0 indicates no change of element concentration going from coal ash to filter ash.

The reason for this behavior has not been determined. However, it is possible that, during the hydrothermal treatment, the mineral matter (trace elements) in the Martinka coal reacts with the sodium hydroxide (caustic) leachant to form sodium salts which are nonvolatile. On the

other hand, the mineral matter (trace elements) in the Westland coal is not subject to attack by either the sodium hydroxide leachant or the mix-leachant. Likewise, the mineral matter in the Martinka coal is not attacked by the mix-leachant.

Element enrichment for the specific elements are shown in Table 13. Examination of this data indicates that hydrothermal treatment of these coals has little or no effect on the enrichment of these elements in the ashes during combustion. Element enrichment in the ashes appear to be a function of the coal rather than dependent on the hydrothermal treatment of the coal.

Polycyclic Organic Matter. Analyses of the polycyclic organic matter (POM) from the combustion products of Runs 5, 11, 12, 14, and 18 in the lb/hr unit and of Runs 30 and 31 in the MFF are presented in Table 14. Components found in measurable quantities in one or more of the samples analyzed are listed in the first column in the table. A starred component indicates carcinogenic potential[9] where 1 star indicates the lowest and 4 stars the highest carcinogenicity.

In addition to the POM noted in Table 14, the samples were also examined for the following other POM compounds:

Perylene	Dibenzo(a,h)anthracene
3-Methylcolanthrene	Dibenzo(c,g)carbazole
Indeno (1,2,3-cd) pyrene	Dibenz(ai and ah)pyrenes
Benzo(ghi)perylene	Coronene.

None of these components was found in any of the samples, within detection limits (∿10 ng/volume of gas analyzed which was normally that from about 4 pounds of coal).

The relative differences of the POM loadings among the LTF firings were quite small considering the differences in combustion conditions during these runs. The state-of-the-art of POM sampling and analysis being what it

TABLE 13.   ELEMENT ENRICHMENT OF SPECIFIC ELEMENTS

Source of Coal	Element [*]																			
	Li	Be	B	F	Al	P	Cl	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Cd	Sn	Sb	Pb
Martinka																				
Raw	−	−	0	−	+	−	−	0	+	−	0	−	+	+	0	+	−	+	+	−
Caustic HTT	−	−	0	+	+	−	0	−	+	0	+	+	+	+	+	+	0	+	+	+
Mixed Leachant HTT	+	−	−	−	+	−	+	−	−	−	−	−	+	−	−	+	0	+	+	+
Westland																				
Raw	NA	+	+	+	0	+	0	+	+	+	0	+	+	+	+	NA	+	+	+	+
Caustic HTT	NA	+	+	+	0	+	0	+	+	+	0	+	+	+	+	+	+	+	+	+
Mixed Leachant HTT	NA	+	+	+	−	+	0	+	+	+	0	+	+	+	+	NA	+	+	+	+

* + indicates an increase of element concentration going from coal ash to filter ash.

   − indicates a decrease of element concentration going from coal ash to filter ash.

   0 indicates no change of element concentration going from coal ash to filter ash.

TABLE 14. POM ANALYSES

Component	NAS* Notation	Micrograms/(Meter)^3			
		Run 5 NaOH Leachant Martinka	Run 11 NaOH Leachant Westland	Run 12 Mix-Leachant Martinka	Run 14 Raw Westland
Anthracene/Phenanthrene		9.1	18	11	23
Methyl Anthracene		3.4	19	12	37
Fluoranthene		4.0	.7	.5	.5
Pyrene		3.1	.8	.6	1.9
Methyl Pyrene/Fluoranthene		.6	.4	--	2.6
Benzo(c)phenanthrene	***	.6	--	--	--
Chrysene/Benz(a)anthracene	*	1.7	.3	--	.4
Methyl chrysenes	*	.2	--	--	.4
Benzo Fluoranthenes	**	.5	--	--	--
Benz(a)pyrene + Benz(c)pyrene	***	.1	--	--	--
Total POM Loading, $\mu g/m^3$		23	39	24	65
Percent Carcinogenic Material		14	.6	0	1.1

-- Below detection limits

 * Stars designated degree of hazard as discussed in "Particulate Polyclyic
   Organic Matter" published National Academy of Science (1972). The
   lower the number of stars, the lower the hazard associated with the
   material. No stars indicate material not reported as being carcinogenic.

Continued

Component	NAS Notation	Micrograms/(Meter)^3		
		Run 18 Mix-Leachant Westland	Run 30 Raw Westland	Run 31 Mix-Leachant Westland
Anthracene/Phenanthrene		18	.020	.066
Methyl Anthracene		26	.081	.028
Fluoranthene		.3	.0064	.010
Pyrene		.4	.0051	.0085
Methyl Pyrene/Fluoranthene		.9	.0044	.0054
Benzo(c)phenanthrene	***	.1	.0002	.0002
Chrysene/Benz(a)anthracene	*	.1	--	--
Methyl chrysenes	*	--	--	--
Benzo Fluoranthenes	**	--	--	--
Benz(a)pyrene + Benz(c)pyrene	***	--	--	--
Total POM Loading, u.g/m^3		45	.12	.12
Percent Carcinogenic Material		0.5	.2	.2

TABLE 14 (Continued)

is, however, one might not expect to see statistically different POM results from these firings.

The POM loadings appear low compared with the earlier work of Hangebrauck[10], yet we have no basis to feel that they are in error in any way. For firing rates of the order of 10^4 Btu/hr, Hangebrauck's results would call for POM (as BaP) on the order of 30-3000 $\mu g/m^3$; our results are at the low end of this spread, 23-45 $\mu g/m^3$. POM from the MFF firings was substantially lower, about 0.1 $\mu g/m^3$; this might be compared with values of 3-300 $\mu g/m^3$ for firing rates of 10^5 Btu/hr in Hangebrauck's earlier work. In essence, we observe similar trends to lower levels of POM at higher firing rates, but our data are an order of magnitude below that reported by Hangebrauck.

Ash Characteristics. Several properties of the coal ashes in addition to those already discussed were also considered and include (1) viscosity, (2) sodium content, (3) ash-fusion temperature, (4) resistivity, (5) particle size, and (6) leachability. These properties are important in the operation and the design of the overall boiler facilities, and accordingly, the implications of these data presented below will be discussed under the task on "Interchangeability of HTT Coals".

Viscosity. The viscosity of ash is used as a measure to estimate the fouling and slagging potential of a coal ash.[11] Generally, the lower the viscosity the greater is the potential for fouling and slagging. The weight percent of minor elements, Si, Al, Fe, Mg, and Na contained in the coal ash are used in this determination. Table 15 gives the ash composition based on these data, the reported values of these minor elements are converted to equivalent oxides because the ash constituents generally occur as oxides. The total oxides usually approach 100 percent, but as noted in Table 15, the total oxides in Runs 3 and 5 are somewhat low at 75 percent and 66 percent, respectively, while in Run 7 they total 93 percent. For comparison purposes, these values were normalized to total 100 percent. The "Silica Percentage", the ratio of SiO_2 to $SiO_2 + Fe_2O_3 + CaO + MgO$ was then calculated. This ratio is a measure of the viscosity in poises at 2600 F[11].

TABLE 15. ASH COMPOSITION AND FOULING POTENTIAL OF RAW AND TREATED MARTINKA

	Run 3 Raw Martinka		Run 5 Martinka NaOH Leachant		Run 7 Martinka Mixed Leachant	
Ash Composition (wt percent)						
Si	21.9		14.0		15.8	
Al	8.73		11.3		4.69	
Fe	7.30		4.63		5.53	
Cu	.45		0.29		25.7	
Mg	.09		0.21		0.54	
Na	.33		5.42		4.21	
Equivalent Oxide[a] (wt percent)						
SiO_2	46.9	(62.7)	30.0	(45.5)	33.8	(36.3)
Al_2O_3	16.5	(22.0)	21.4	(32.4)	8.9	(9.5)
Fe_2O_3	10.4	(13.9)	6.6	(10.0)	7.9	(8.5)
CaO	0.6	(0.8)	0.4	(0.6)	36.0	(38.6)
MgO	0.1	(0.1)	0.3	(0.4)	0.9	(1.0)
Na_2O	0.4	(0.5)	7.3	(11.1)	5.7	(6.1)
	74.9	(100)	66.0	(100)	93.2	(100)
Silica Percentage - $SiO_2/SiO_2+Fe_2O_3+CaO+MgO$	81 81		81		43	
μ, poises at 2600 F	550		< 550		< 4	
Base/acid Ratio = $SiO_2+Al_2O_3+Fe_2O_3/CaO+MgO+Na_2O$	.18		.28		1.19	
Fouling Factor = B/A x Na_2O	0.09		3.11		--	

(a) Values in parens were normalized to total 100 percent

The calculated data indicate that the hydrothermal processing of the coals lowers the viscosity of the ash, making it more fluid. The viscosity of the ash from the raw Martinka coal was calculated to be 550 poises (at 2600 F). The NaOH treatment lowers the viscosity to a value somewhat less than 550 poises but because of the high Na_2O content (11.1 percent on 100 percent basis) an accurate estimate of the viscosity cannot be determined from the ash composition.

For the mixed leachant system, the high CaO content lowers the silica percentage to only 43 indicating a viscosity of 4 poises (at 2600 F). In addition, the Na_2O is high at 6.1 percent, so that the actual viscosity would be less than 4 poises. Combustion of the mixed-leachant coal would produce a very fluid slag that could cause extreme fouling of heat-receiving surfaces.

Sodium Content. The sodium content of the ash can also be used as an indicator for slagging and fouling potential. Generally, for sodium contents of greater than 2.5 percent in the ash, severe fouling can be anticipated. Accordingly, the NaOH and mixed leachant treated coals would be expected to have a high potential to slag in boiler furnaces.

The fouling potential of an ash can be qualitatively related to its sodium content by the following analogy for usual ash compositions[10].

Percent Na_2O in Ash	Fouling
< 0.5	Low
0.5 - 1.0	Medium
1.0 - 2.5	High
> 2.5	Severe

For "lignitic" ash, where (CaO + MgO) is greater than Fe_2O_3 as found in the mixed leachant Martinka coal, the following quantitative relations apply

Percent Na$_2$O in Ash	Fouling
< 2.0	Low
2-6	Medium
6-8	High
> 8	Severe .

The Duzy "fouling factors" are not applicable to lignitic ash but they too show that sodium is the major source of problems. From Table 17 with

$$R_f = \frac{Base}{Acid} \times percent\ Na_2O\ (on\ ASTM\ ash),$$

the raw Martinka coal has an R_f of 0.09 and the caustic treated Martinka has an R_f of 3.11. "Low fouling" is less than 0.2 and "severe" is more than 1.0. On this basis, the raw Martinka is low fouling and the caustic treated Martinka is severely fouling.

Ash-Fusion. The ash-fusion temperature determination is an empirical laboratory procedure[12] that is used to predict the fusion characteristics of an ash as it is heated. A simple relation of these temperatures to actual combustion operating conditions is as follows:

- Initial Deformation Temperature (IDT). The IDT is used as an indication of the temperature at which the ash particles become "sticky" and have a tendency to agglomerate and slowly build up on heat adsorption surfaces.

- Softening Temperature. This temperature is related to that at which the fuel ash shows an accelerated tendency to mass together and stick in large quantities to heat absorbing surfaces.

● <u>Fluid Temperature</u>. This temperature is related to the
temperature at which the ash is expected to flow in
streams and drip from heat exchanger surfaces.

These temperatures are only used as a guide as the measurement of ash viscosity
has been found to be a more useful design tool to predict boiler fouling.

Table 16 summarizes the ash-fusion temperatures obtained for
the coal burned in this program. In general, the processing of the raw
coal significantly reduces the ash-fusion temperatures. This is attributed
to the addition of sodium and calcium during coal treatment. The one
exception was the Westland coal treated with mixed leachant which raised
the ash fusion temperatures by about 200 F. [This could be an anamoly
in the procedure due to large additions of calcium, or it may be, although
unlikely, that the mixed leachant processes alter this coal sufficiently
(by the addition of Ca and Na, and the reduction in Si, Fe, and Al) to
increase ash-fusion temperatures.] In addition, the ash-fusion data indi-
cate that processing of coal reduces the range between the initial deform-
ation and fluid temperatures.

<u>Resistivity</u>. Resistivity data are used to predict the behavior
of fly ash in electrostatic precipitators, which are designed for opera-
tion with ash resistivity in the range from 10^{10} to 10^{12} ohm-cm. Values of
resistivity below this range can result in operating problems, and values
above this range can result in reduced collection efficiency.

Table 17 summarizes resistivity data for 10 ash samples. It
will be noted that values are significantly below 10^{10} ohm-cm for three
samples, all of which contain considerable carbon. Resistivity values
approach the normal for all other samples. These results are somewhat
inconclusive because of the possible influence of carbon in the samples.
Any further evaluation of resistivity should examine the effects of fuel
sodium, potassium, iron, and sulfur content[13].

TABLE 16. FUSION TEMPERATURE OF ASH

Coal	Temperature °F							
	Initial Deformation		Softening (H = W)[a]		Softening (H = 1/2W)[a]		Fluid	
	Reducing	Oxidizing	Reducing	Oxidizing	Reducing	Oxidizing	Reducing	Oxidizing
Raw Martinka	1890	2110	2010	2400	2410	2490	2470	2520
NaOH Leachant Martinka	1800	2110	2030	2150	2210	2300	2230	2390
Mixed-Leachant Martinka	1850	2010	1970	2100	2000	2210	2020	2240
Raw Westland	1960	2070	2100	2260	2200	2370	2240	2400
NaOH Leachant Westland	1910	1940	2010	2020	2030	2050	2040	2070
Mixed-Leachant Westland	1890	2000	2300	2460	2400	2510	2440	2600
Deashed Westland	1790	1920	1850	2000	1870	2090	1890	2120

(a) H = cone height; W = cone width.

TABLE 17. RESISTIVITY OF COAL ASH SAMPLES AT 400 F

Coal Ash	Resistivity, (ohm-cm)	Applied voltage, (volts)	Carbon content, % in ash
Raw Martinka (Run 3)	1.5×10^{11}	500	12.0
(Run 3) [a]	4.7×10^{9}	500	0.0
NaOH Leachant Martinka sample (Run 4)	5.1×10^{8}	500	8.0
(Run 5)	5.7×10^{8}	500	11.4
(Run 5) [a]	1.8×10^{8}	500	0.0
Mixed leachant Martinka (Run 6)	5.9×10^{5}	150	13.7
(Run 7)	4.4×10^{5}	300	4.7
(Run 7)	3.0×10^{8}	500	0.0
Raw Westland (Run 15)	1.1×10^{5}	90	15.1
NaOH Leachant Westland (Run 13)	1.5×10^{9}	500	7.3

(a) These samples were completely ashed coals.

Particle Size. Particle-size distributions were determined by
Coulter Counter measurements of the particulate catch of the filter for
both the raw and treated coals. Figures 3 and 4 summarize the ash and
coal particle size distributions. In essence, the results show that the
size distribution of ashes from the LTF combustor are quite normal. The
mass median diameters of the Martinka and Westland ashes were 13 microns
for some Martinka firings and 25-50 microns for some Westland firings.
The Martinka ashes do not appear to have been effected by the treatment
process, whereas the Westland ashes appear to be smaller for the treated
coal than for the raw coal.

Task 3. Impact Evaluation of the Use of
Hydrothermally Treated Coal

From the analysis and evaluation of the results obtained from
Phase I, Task 2, the atmospheric impact which could result from the use
of hydrothermally treated coals in industrial and utility boilers and
environmental problems associated with disposal of the ash was assessed.
Also, problems which may be encountered in converting from raw coal to
hydrothermally treated coals in conventional boilers and the degree of
boiler modification which may be necessary were addressed.

Subtask 3A. Atmospheric Impact of HTT Coal. The atmospheric
impact of the utilization of hydrothermally-treated (HTT) coal on the air
quality has been investigated. This was accomplished by examining the
changes that would occur in sulfur dioxide (SO_2) and trace element levels
as a result of substituting HTT coal for the high sulfur-content coals that
are presently being used in many of the nation's large cities. Two high
sulfur-content coals, Martinka coal and Westland coal, were chosen for the
study. Four large cities that currently use considerable quantities of
these coals (Birmingham, Alabama; Peoria, Illinois; Detroit/Port Huron,
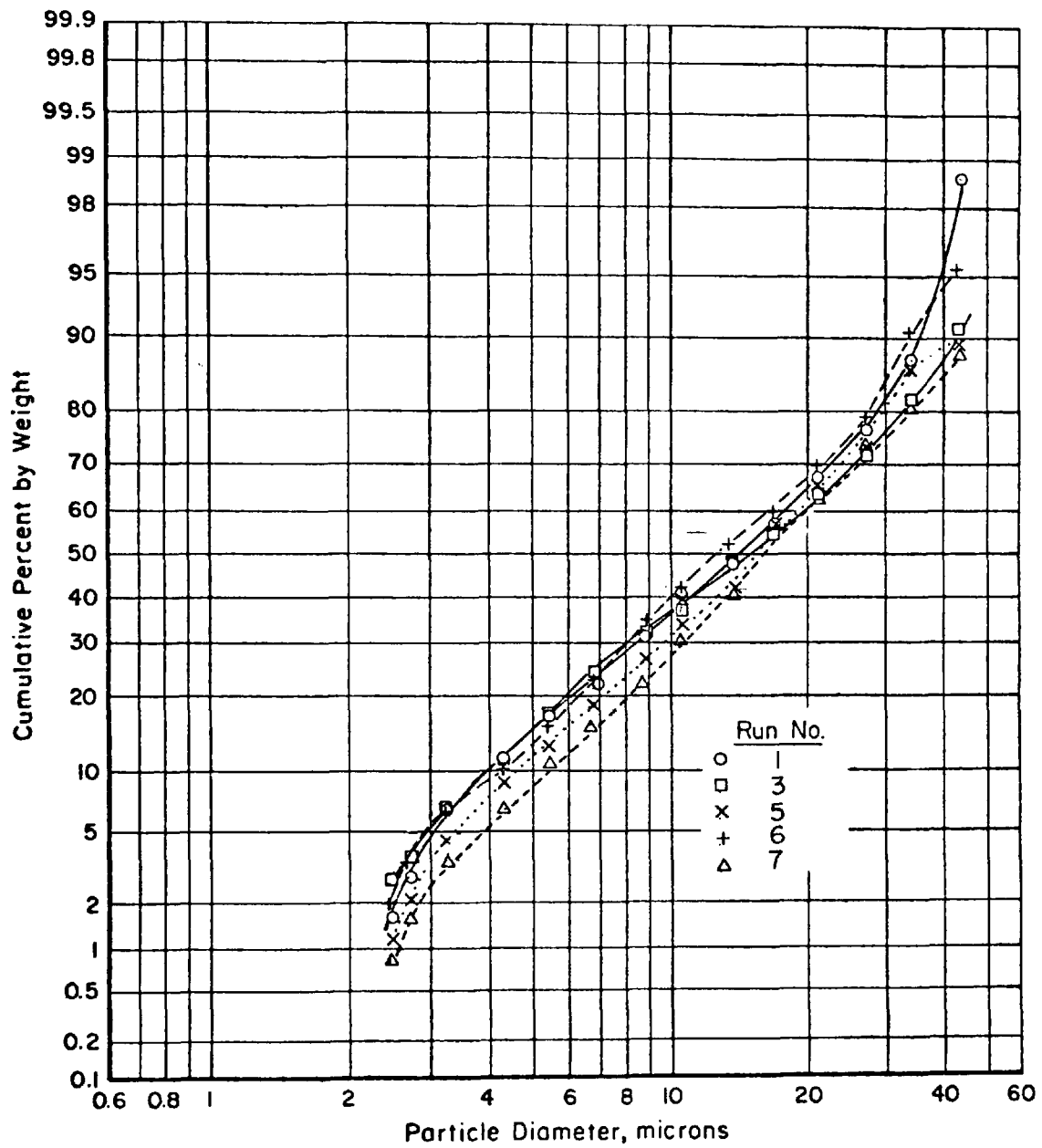
FIGURE 3. COULTER COUNTER ASH PARTICLE SIZE DISTRIBUTION --
MARTINKA FIRING

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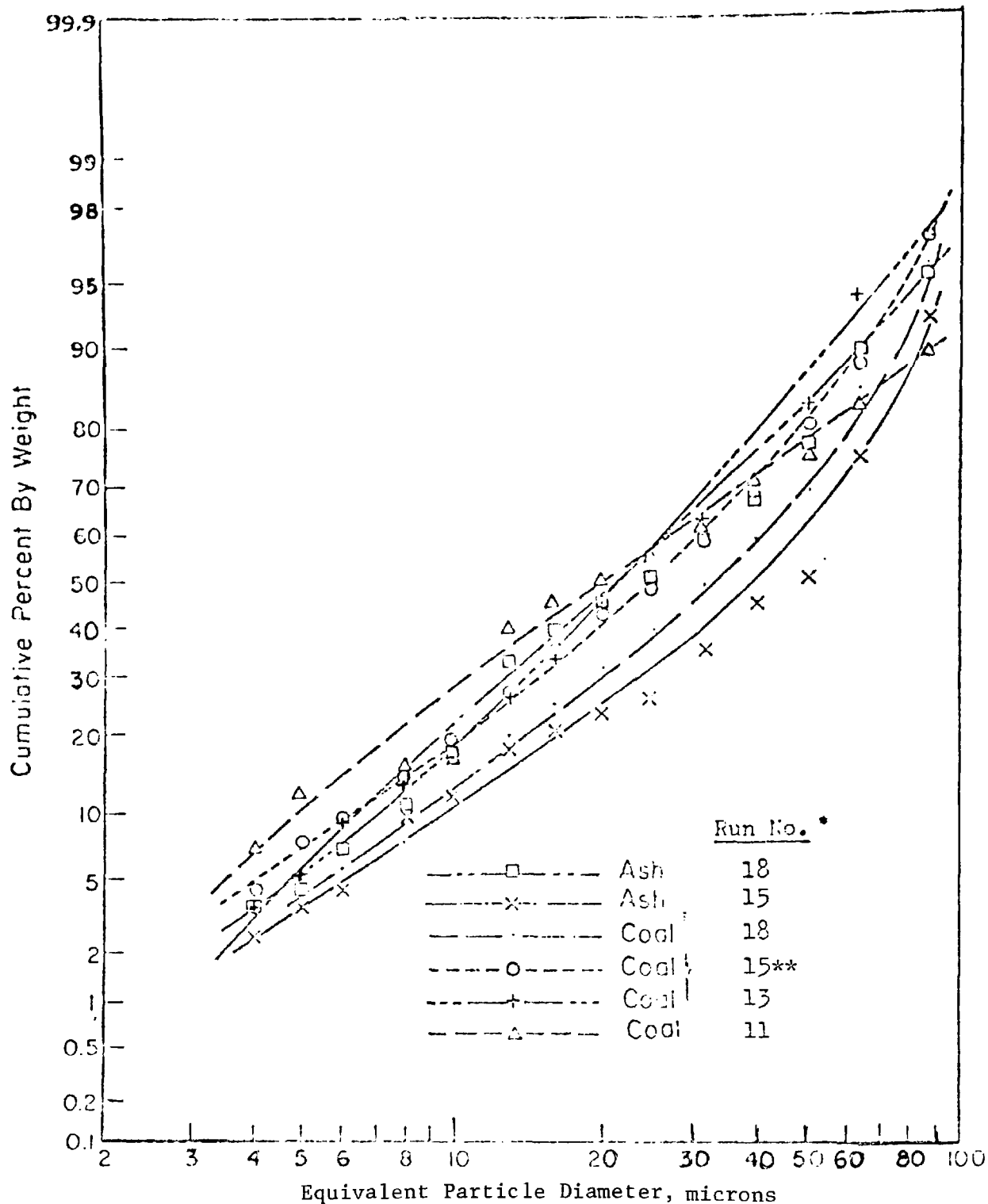
FIGURE 4. COULTER COUNTER PARTICLE SIZE DISTRIBUTION – WESTLAND COALS

 * Run 18 - mixed leachant; Run 15 - raw; Runs 13 and 11 - NaOH leachant
 ** Particle size of coal prior to combustion

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Michigan; St. Louis, Missouri) were chosen as representative cities for the study of sulfur dioxide emissions. Houston, Texas was chosen as a city representative of low coal consumption.

The coal consumption by sulfur category and by source type has been published by EPA for each of these regions. These data are in Table 18, together with SO_2 concentration data.

The goal of this subtask was to determine the change in these SO_2 concentrations, and of trace elements (for which little documentation exists). Several approaches were available, spanning a range of complexities and required supporting information.

The approach taken here offered a reasonable estimate of change of air quality to be determined with a minimal set of data. The quantities determined under this subtask are as follows:

(1) "Equivalent"* sulfur content of HTT coal

(2) Current mean SO_2 concentrations in the five urban areas

(3) Trace elements particulate levels

(4) Projected SO_2 levels as a result of substituting HTT coal.

Each of the four items will be discussed briefly and all results will be summarized in tabular form.

(1) Equivalent Sulfur Content of HTT Coal. The equivalent sulfur contents of HTT coal were determined for each of the following chemical treatments:

(a) NaOH leachant Martinka coal

(b) Mixed leachant Martinka coal

(c) NaOH leachant Westland coal

(d) Mixed leachant Westland coal.

---

*The sulfur content which, when applying EPA emission factors, produces the observed SO_2 emissions. This approach was chosen because the HTT ash traps significant fractions of the potential sulfur emissions, while EPA emissions factors presume only 5 percent trapping. The equivalent SO_2 content is found by multiplying the actual content by the fraction which leaves the stack, and dividing by 0.95.

TABLE 18. SO_2 PROFILE

Coal Utilization	% S in Coal	Coal Consumption 1000 ton/yr	SO_2 Emissions 1000 ton/yr	Contributions to Annual Average SO_2 Concentration, $\mu g/m^3$
City: Birmingham				
Utility	1.2	5,209	118.8	7.5
	2.45	1,209	57.2	3.6
Industrial	0.8	144	2.2	0.1
	1.2	361	8.2	1.5
	1.6	--	--	--
	2.45	217	10.1	1.5
Res/Comm	0.8	20	0.3	0
	1.2	18	0.4	0
	1.6	--	--	--
	2.45	--	--	--
Other			102.5	6.5
Total			299.7	19.0
City: Peoria				
Utility	1.2	--	--	--
	2.45	3,848	179.0	41.9
Industrial	0.8	--	--	--
	1.2	3	0.1	0
	1.6	--	--	--
	2.45	65	3.0	0.7
	3.0	202	11.5	2.7
Res/Comm	0.8	--	--	--
	1.2	1	0	0
	1.6	48	1.5	0.4
	2.45	51	2.4	0.5
Other			54.5	12.8
Total			252.4	59.0

Coal Utilization	% S in Coal	Coal Consumption 1000 ton/hr	SO_2 Emissions 1000 ton/yr	Contributions to Annual Average SO_2 Concentration, $\mu g/m^3$
City: St. Louis				
Utility	1.2	6,731	153.5	27.7
	2.45	5,191	241.6	43.0
Industrial	0.8	104	1.6	0.3
	1.2	--	--	--
	1.6	56	1.7	0.3
	2.45	370	17.2	3.0
	4.0	332	25.2	4.4
Res/Comm	0.8	--	--	--
	1.2	3	0.1	0
	1.6	38	1.2	0.2
	2.45	104	4.8	0.8
Other			214.0	38.2
Total			661.0	115.0
City: Detroit				
Utility	1.2	3,579	175.0	16.2
	2.45	6,619	415.0	38.4
Industrial	0.8	88	1.3	0.1
	1.2	921	21.0	1.9
	1.6	702	21.3	2.0
	2.45	2,501	116.4	10.8
	3.3	175	11.0	1.0
Res/Comm	0.8	20	0.3	0
	1.2	107	2.4	0.2
	1.6	99	3.0	0.3
	2.45	--	--	--
Other			119.6	11.1
Total			886.3	82.0

TABLE 18 (Continued)

Coal Utilization	% S in Coal	Coal Consumption 1000 ton/yr	SO_2 Emissions 1000 ton/yr	Contributions to Annual Average SO_2 Concentration, $\mu g/m^3$
City: Houston				
Utility	1.2	--	--	--
	2.45	--	--	--
Industrial	0.8	--	--	--
	1.2	--	--	--
	1.6	--	--	--
	2.45	--	--	--
Res/Comm	0.8	--	--	--
	1.2	--	--	--
	1.6	--	--	--
	2.45	--	--	--
Other			345.0	36.0
Total			345.0	36.0

TABLE 18 (Continued)

The average values of the sulfur content, in weight percent, were calculated and compared with the sulfur content of untreated coals. Table 19 summarizes the results from averages of sulfur emissions of Runs 1 through 22.

TABLE 19. EQUIVALENT SULFUR CONTENT OF COALS
(WEIGHT PERCENT)

Treatment	Martinka Coal		Westland Coal	
	Sulfur Content, %	Equivalent Sulfur, %	Sulfur Content, %	Equivalent Sulfur, %
NaOH treated	0.65	0.365	0.93	0.566
Mixed leachant-treated	0.55	0.469	0.74	0.331
Untreated	--	1.90	--	2.02

(2) Current Mean Sulfur Dioxide Concentrations. The annual arithmetic mean of the current sulfur dioxide emissions in five urban areas (Birmingham, Alabama; Peoria, Illinois; Detroit/Port Huron, Michigan; St Louis, Missouri; Houston/Galveston, Texas) were determined for ultimate comparison with SO_2 levels that would be projected from substitution to HTT coal. The current levels, listed in Table 20 were obtained from U.S.E.P.A.'s Air Quality Data - 1973 Annual Statistics.

TABLE 20. CURRENT MAXIMUM ANNUAL SO_2 LEVELS
IN FIVE URBAN AREAS

City	Concentration, $\mu g/m^3$
Birmingham, Alabama	19
Peoria, Illinois	59
Detroit/Port Huron, Michigan	45
St. Louis, Missouri	115
Houston/Galveston, Texas	36

(3) SO_2 Projected Concentrations. Using a roll-back procedure, it was possible to estimate for each city the ratio between emissions and

annual concentrations. By multiplying this ratio with an increment (decrement) in emissions, the resultant increment (decrement) in air quality can be estimated. These multipliers were used in the trace metal analyses of Section (4), as well as the SO_2 analyses of this section.

The sulfur dioxide emission levels that would result as a consequent of substituting HTT coal for untreated high sulfur-content coal were determined for three economic sectors: residential and commercial, industrial, electrical. The following determinations were carried out: (a) SO_2 levels that would be obtained by replacing all coals with greater than 1.2 percent* sulfur (weight basis) with HTT coal, for each of the economic sectors, (b) SO_2 levels resulting from substituting all coals with greater than 1.2 percent sulfur with HTT coal, for all three sectors combined, and (c) SO_3 levels resulting from replacing all coals with HTT coals, irrespective of the sulfur content of the coal. Table 21 summarizes all the results.

It is significant that St. Louis, Missouri, and Detroit, Michigan would meet the Federal Ambient Air Quality Standard of 80 $\mu g/m^3$ by simple fuel substitution. In all cases, significant decreases in SO_2 concentrations are predicted.

(4) Trace Metal Projected Concentrations. The process of producing HTT coal alters the trace element compositions and release rates for trace elements in the coal. For this reason, the impact of HTT coal substitution on the ambient air trace element contributions was estimated. Peoria, Illinois was chosen as the target city for trace metal studies because, of the five, it is the city most heavily impacted by coal combustion emissions.

A mass balance between the incoming coal and resultant ash concentrations allowed the estimate of the atmospheric release rate of the trace elements. When multiplied by the total coal consumption of Peoria, and the ratio between coal consumption and ambient concentration, the contribution of coal burning to the ambient concentration can be determined. Simple subtraction yields the incremental concentration due to HTT coal substitution.

---

*Coals with more than 1.2 percent S are generally considered high sulfur, and replacement of these coals with HTT coal should receive preferential consideration.

TABLE 21. PROJECTED SO_2 LEVELS WITH HTT COAL AMBIENT ANNUAL CONCENTRATION, $\mu g/m^3$ ANNUAL AVERAGE

	004 Birmingham, Alabama	065 Peoria, Illinois	123 Detroit, Michigan	070 St. Louis, Missouri
1. Current (untreated coal) level	19	59	82	115
2. Replacing all coal with > 1.2% sulfur[a]				
-Residential and Commercial	--	58.5	81.9	114.4
-Industrial	18.6	56.6	73.2	109.5
-Electrical	16.6	31.9	43.2	87.8
3. Replacing all coal with > 1.2% sulfur[b]				
-All sectors	16.2	29.0	34.3	
4. Replacing all coals irrespective of sulfur content with HTT coals[c]	5.0	26.6	31.8	44.9

(a) Coals in each sector containing greater than 1.2% sulfur replaced by HTT coal (average, all runs).

(b) Assuming all coals containing greater than 1.2% sulfur replaced with HTT coal (average, all runs).

(c) HTT sulfur emissions averaged from all runs.

Analysis for the concentrations of trace metals proceeds as in the case of sulfur dioxide: by determining emissions and multiplying by a predetermined constant, the annual average concentration (change) can be determined. The results as presented in Table 22 indicates some of the changes expected in trace element concentrations in Peoria providing all coal for this city was replaced by HTT coal and assuming the ash containing these elements were emitted to the atmosphere. However, most likely, the majority of the ash would be collected by electrostatic precipitators and/ or baghouses.

While this data are preliminary in nature, the data do indicate that the concentration of a number of the toxic elements -- beryllium, boron, fluorine, phosphorus, chlorine, potassium, vanadium, arsenic and bromine -- is lowered by the hydrothermal treatment. During the treatment, these elements are extracted from the coal by the solubilizing effect of the leachant. On the other hand, the concentration of some of the elements, for example, sodium and calcium, is increased. This results from reaction of the sodium and calcium contained in the leachant with the coal. During combustion, the sodium and calcium becomes part of the ash.

Subtask 3B.   Environmental Problems of Combustion Waste Products.
Solid waste products known as fly ash and bottom ash are formed in any com-
bustion operation. These ashes are generally disposed of in a landfill.
Problems associated with disposal of the ashes by this method if the land-
fill is not properly prepared will depend on the composition of the ashes.
For example, if the ashes contain a number of soluble components, these may
be leached from the landfill and subsequently contaminate our water system
by penetration of the underground water system or by runoff from the landfill
into the surface water.

It is expected that the chemical composition of the ashes from
HTT coals may be different from those of the corresponding raw coals. In
a gross manner, the HTT ashes will contain more alkali and more or less

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TABLE 22.   CHANGE IN TRACE ELEMENT CONCENTRATION IN ASH $(\mu g/m^3)$ FOR PEORIA, ILLINOIS, FROM COAL SUBSTITUTION

	Westland Coal		Martinka Coal	
	NaOH Leachant	Mixed Leachant	NaOH Leachant	Mixed Leachant
Be	.005	.003	.002	.003
B	.101	.101	.063	.069
F	.444	.128	.013	-.01
Na	N/A	-9.07	N/A	N/A
Mg	0	-3.16	-.790	-.7
Al	-6.909	-7.008	N/A	N/A
Si	-.395	-.721	N/A	N/A
P	0	.405	-.099	.395
Cl	-.099	.007	.194	.255
K	2.47	2.07	18.8	N/A
Ca	-5.43	-4.64	0	N/A
V	.041	.029	.147	.144
Cr	-.086	-.002	N/A	-.069
Fe	.296	.890	34.6	-4.25
Co	-.044	.011	.178	0
Ni	-.173	-.042	N/A	.484
Cu	-.034	-.066	N/A	0
Zn	-1.64	-.346	-.003	-.014
As	.004	.004	-.009	.007
Br	.046	.056	.008	.007

- Means higher concentration.
+ Means lower concentration

| | Westland Coal | | Martinka Coal | |
Element	NaOH Leachant	Mixed Leachant	NaOH Leachant	Mixed Leachant
Y	−.007	.014	.015	−.138
Zr	−.030	0	.190	−.158
Sn	−.061	.009	N/A	−.014
Ba	−.032	−.089	.286	−.432
Hf	−.002	−.002	.007	−.005
Pb	−.034	−.010	N/A	.087
Tb	−.003	−.003	N/A	−.021

TABLE 22 (Continued)

sulfate than the ashes from the untreated coals. Also, there will be lower concentrations of certain traces in the treated coals. Effects of these differences in chemical composition would be expected to be reflected in other important characteristics such as solubility. Therefore, the objective of this subtask was to evaluate the environmental problems associated with disposing of the ashes from the combustion of HTT coals.

This was achieved by conducting leachability studies on selected coal ashes and subsequent analysis of the leachates.

Leachability Tests. Leachability tests were conducted by a procedure provided to us by Dr. Robert Statnick for EPA. Essentially, this entailed leaching selected ashes with water at ambient temperature. For this study, a slurry of 4 parts water and 1 part ash (by weight) was prepared. This slurry was agitated for 3 days at ambient temperature, after which time the solids were separated from the liquid by centrifuging. Fresh water was added to the leached ash at the same ash/water ratio, the slurry was agitated for another 3 days, and the solid separated. This was repeated for an additional 8 times. The leachates were kept separate for subsequent analysis.

Analysis. The analysis consisted of:
(a) pH measurements on all leachates as a function of leaching time, and
(b) Determining the solids content of the leachates and composition of the solids in terms of trace metals, alkali (sodium and calcium), and sulfate contents.

Leaching Results. As shown in Table 23, pH of the leachates remained essentially constant throughout the leaching tests. In all cases, the final leachate from the various ashes were slightly basic (7.65) to strongly basic (about 11). The strongly basic solutions resulted from leaching of the ashes from the mixed-leachant coal ashes. Apparently, the calcium treatment is responsible for the higher pH solutions, possibly resulting from reaction of the calcium with sodium sulfate to form sodium hydroxide and calcium sulfate.

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TABLE 23. pH READING ON LEACHATES

Type of Coal/Ash	Run#1 pH	Run#2 pH	Run#3 pH	Run#4 pH	Run#5 pH	Run#6 pH	Run#7 pH	Run#8 pH	Run#9 pH	Run#10 pH
Raw Westland #22										
Cooler Ash (542144)	4.68	6.73	7.60	7.50	8.00	8.00	8.65	8.25	8.23	7.65
NaOH Leachant Westland #20										
Cooler Ash (541979)	8.68	9.18	8.48	8.03	7.83	8.08	8.75	8.63	8.95	8.05
N_2 Filter Ash (541978)	8.63	8.40	8.70	8.93	9.25	8.45	9.08	9.63	9.53	9.15
Mixed Leachant-Westland #18										
Cooler Ash (541713)	12.20	12.00	11.78	11.55	11.45	11.30	11.35	7.83	11.60	11.63
Slag (541715)	11.55	11.18	11.25	11.13	10.60	10.80	10.95	11.00	8.58	11.00
Raw Martinka #3										
Furnace Scraping (540117)	8.95	9.23	9.20	8.30	8.38	8.35	9.25	9.18	8.93	9.18
Cooler Ash (541168)	7.95	8.48	8.35	8.63	8.68	8.53	9.08	9.05	9.10	9.05
Filter Ash (540116)	6.05	6.60	6.90	7.13	7.78	7.70	7.98	8.73	7.95	8.50
NaOH Leachant Martinka #21										
Cooler Ash (542066)	7.98	8.10	8.20	8.18	8.45	8.60	8.73	9.00	8.68	8.30
Filter Ash (542065)	7.90	9.03	9.00	8.95	8.70	8.80	9.13	8.43	9.10	8.40
Mixed Leachant-Martinka										
Cooler Ash (541001)	11.85	10.93	10.85	10.50	7.93	8.40	10.60	8.18	10.70	10.45

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The degree of solubilization of the 3 selected cooler ashes from
Westland coals (1 raw and 2 HTT) and composition of the water soluble portion
in terms of sodium, calcium, and sulfate contents are shown in Table 24.
Trace metals content of this soluble portion is shown in Table 25.

The data show that the cooler ash from the NaOH leached West-
land coal is highly water soluble ($\sim$31 weight percent) with that from
the mixed leachant coal ranking second and that from the raw coal being
the least soluble. The high solubility of the cooler ash from the NaOH
leached coal is due, primarily, to the presence of sodium sulfate in the
cooler ash. Pure sodium sulfate (Na_2SO_4) contains 32.2 weight percent sodium
and 67.6 weight percent sulfate. The solubilized material was found to con-
tain 33 weight percent sodium and 81 weight percent sulfate. The difference
in sulfate content between 67.6 and 81 weight percent could be due to the
presence of $CaSO_4$ as the NaOH treated Westland coal contained 0.2 weight
percent calcium.

TABLE 24. LEACHABILITY OF COOLER ASH
(WESTLAND COALS)

Exper. No.	Type of Coal	Degree of Ash Solubilization, %	Composition of Solubiles, wt %*		
			$SO_4^=$	Na^-	$Ca^=$
22	Raw	1.73	0.06	NA	NA
20	NaOH Leachant HTT	30.6	0.81	0.33	NA
18	Mixed Leachant HTT	7.1	0.007	0.06	0.045

Similar reasoning is not applicable to that leached from the cooler
ash from the mixed leachant-treated Westland coal (Experiment No. 18). In
this case, the sulfate content of the solubilized solids is too low. There-
fore, the sodium and calcium may be present in the leachate as carbonates
which were not analyzed for.

Mass spectrographic analyses of the solubilized solids are shown
in Table 25. Of those trace metal values which are of major concern, the

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TABLE 25. ANALYSIS OF SOLIDS CONTENT OF COOLER ASH LEACHATES FROM WESTLAND COALS (ppm)

Element	Raw (Run 22)	Mixed Leachant HTT Coal (Run 18)	NaOH Leachant HTT Coal (Run 20)
Li	< 0.003	< 0.003	< 0.01
Be	< 0.005	< 0.005	< 0.01
B	< 0.03	< 0.03	< 0.05
F	30	10	1
Na	~ 2%	~ 2%	Major
Mg	~ 1%	100	500
Al	300	200	5
Si	3000	500	500
P	3	1	1
S	~ 2%	~ 1%	~ 5%
Cl	500	500	3000
K	2000	3000	~ 1%
Ca	5000	~ 3%	~ 1%
Sc	< 0.3	< 0.3	< 10
Ti	30	30	30
V	5	1	2
Cr	10	5	2
Mn	200	1	20
Fe	200	100	30
Co	20	< 2	< 10
Ni	50	5	100
Cu	5	1	≤ 20
Zn	200	10	30
Ga	< 0.1	< 1	< 2
Ge	50	1	1
As	3	2	10
Se[a]	< 5	< 5	< 10
Br	100	20	5
Rb	30	50	5
Sr	5000	3000	500
Y	- 0.2	- 0.5	- 1
Zr	< 0.2	< 0.2	< 0.2
Nb	< 0.1	< 0.1	0.1
Mo	3	10	< 0.5
Ru	< 0.3	< 0.3	< 2
Rh	< 0.3	< 0.5	< 2
Pd	< 2	< 2	< 1
Ag	< 1	< 3	< 0.5
Cd	< 1	< 1	< 0.5
In	< 1	< 1	< 1
Sn	0.2	2	0.5
Sb	1	0.1	< 0.5
Te	< 0.3	< 0.3	< 1
I	0.2	0.5	< 0.5

Continued

Element	Raw (Run 22)	Source of Solids Mixed Leachant HTT Coal (Run 18)	NaOH Leachant HTT Coal (Run 20)
Cs	< 0.5	< 1	< 2
Ba	200	50	20
La	< 0.1	< 0.1	< 0.5
Ce	< 0.1	< 0.1	< 0.3
Pr	< 0.1	< 0.1	< 0.5
Nd	< 0.5	< 0.5	< 2
Sm	< 0.5	< 0.3	< 1
Eu	< 0.3	< 0.2	< 0.5
Gd	< 0.5	< 0.3	< 1
Tb	< 0.1	< 0.1	< 1
Dy	< 0.3	< 0.3	< 1
Ho	< 0.1	< 0.1	< 2
Er	< 0.3	< 0.3	< 1
Tm	< 0.2	< 0.2	< 0.2
Yb	< 0.3	< 0.3	< 1
Lu	< 0.1	< 0.1	< 0.2
Hf	< 0.3	< 0.3	< 1
Ta	< 0.2	< 0.2	< 2
W	< 0.5	< 0.5	< 1
Re	< 0.2	< 0.2	< 0.3
Os	< 0.3	< 0.5	< 0.5
Ir	< 0.1	< 0.1	< 0.5
Pt[b]	300	3000	< 1
Au	< 0.1	< 0.2	< 0.3
Hg	< 0.3	< 0.3	< 1
Tl	< 0.1	< 0.1	< 0.3
Pb	10	3	< 0.5
Bi	< 0.1	< 0.1	< 0.3
Th	< 0.1	< 0.1	< 0.3
U	< 0.1	< 0.1	< 0.3

TABLE 25 (Continued)

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concentration of those shown in Table 26 in the leachate from the HTT coals were significantly lower than those in the leachate from raw coals.

Complete analyses of all ashes associated with the combustion of coal will need to be conducted before a definitive assessment can be made on the expected environmental problems to be associated with disposal of the combustion waste products (ashes). Preliminary assessment, based on the leaching studies conducted on selected cooler ashes from the 1 lb/hr combustor appears to indicate that direct disposal of the cooler ash from the NaOH treated coal would not be advisable because of the high degree of solubility. Most likely, the sodium sulfate would be removed from the ash before disposal.

Conversely as shown in Table 26, the ashes from the HTT coals are less polluting than those from the raw coal with respect to the trace metal values. Therefore, disposal would present less of a pollution problem.

Subtask 3C. Interchangeability of HTT Coal. HTT coal can be considered as a low sulfur substitute for conventional coal in utility boilers, industrial boilers, and industrial processes now fired by coal. It can also be considered as a potential substitute fuel for boilers and industrial processes designed for firing with oil or gas, although such substitution may require R&D. In these applications the low sulfur content and the optional low ash content of the HTT fuel offer the possibility of utilizing coal with minimum environmental impact and with minimum change in existing equipment. The feasibility of interchanging HTT coals with other fuels will be dependent on factors that include its burning characteristics, ash characteristics, and handling and storage properties. The importance of these factors that will affect the value or utility of HTT coal in various applications is somewhat dependent and different for different applications. Accordingly, it will be necessary to consider each application individually, but a general discussion of these factors will identify the important aspects of interchanging HTT coals.

Burning Characteristics. The combustion characteristics of importance in burning pulverized coal are good ignition at the burner to produce

TABLE 26.   TRACE METALS IN LEACHANTS

Trace Metal	Source and Concentration (PPM) *		
	Raw Coal (Run 22)	Mixed Leachant (Run 18)	NaOH Leachant (Run 20)
Al	300	200	5
Cu	5	1	20
F	30	10	1
Fe	200	100	30
Mn	200	1	≤20
Ni	50	5	100
Pb	10	3	<0.5
Sb	1	0.1	<0.5
V	5	1	2
Zn	200	10	30

* Cl concentrations were 10, 5 and 2 ppm, respectively.

a stable flame, and complete burnout of carbon within the furnace to minimize combustible loss. Most bituminous coals containing more than 20 percent volatile matter are interchangeable from the aspect of combustion characteristics. (Low-volatile coals, low-rank coals, and lignites may require special furnace or burner design for satisfactory combustion.) From the dTGA, DTA, and the proximate analysis of the raw and treated coals, the hydrothermal process does not significantly alter the burning characteristics of the treated coals. In fact, the process improves the overall burning characteristics.

Ash Properties. One of the more important ash properties to consider when interchanging coals is the potential for slagging and fouling. Of lesser importance are resistivity, particle size, and leachability characteristics.

Coals vary widely in their slagging and fouling characteristics, and less widely in their combustion characteristics. The slagging and fouling characteristics of the coal ash are the most important factors in sizing of boiler furnaces. When interchanging different coals in existing boilers, slagging and fouling characteristics determine the degree of derating needed for satisfactory operation without excessive slagging problems. In general, coals with high-ash-fusion temperatures can be burned in small furnaces having high furnace exit gas temperatures, and coals with low-ash-fusion temperatures must be burned in larger furnaces having lower exit gas temperatures. When a low-ash-fusion coal is fired in a furnace designed for a high-ash-fusion temperature coal, it is necessary to fire at a reduced rate such that the furnace exit gas temperature is below the ash softening temperature. It may also be necessary to modify the boiler by adding slag blowers in the furnace and soot blowers in superheater and boiler sections to control ash and slag accumulation. The sintering strength of ash deposits is another important variable that influences the difficulty of removing deposits after they have formed.

Table 27 summarizes some of the properties of coals affecting slagging and fouling performance in steam boilers. These include ash

TABLE 27. SUMMARY OF SLAGGING AND FOULING PROPERTIES

Coal and Treatment	Ash Fusion Temp. Oxidizing, F		Ash content, percent	Na_2O in ash, percent	Na in ash, percent	Fouling Indication
	IDT*	AFT*				
Martinka Coal						
Raw coal	2110	2520	20.2	0.4	0.15	Low
NaOH leachant	2110	2390	17.1	11.1	15.2	Severe
Mixed leachant	2010	2240	28.3	6.1	4.6	Severe
Westland Coal						
Raw coal	2070	2400	10.0	--	0.2	Low
NaOH leachant	1940	2070	13.3	--	15.6	Severe
Mixed leachant	2000	2600	18.0	--	1.1	Medium
Acid-leached	1920	2120	2.2	--	19.6	Severe

*IDT -- initial deformation temperature.

*AFT -- ash fluid temperature.

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fusion temperatures, ash content, sodium content of the ash, and an indication of boiler fouling characteristics based on sodium content.

A review of initial deformation temperatures (IDT) for the various coals shows that the IDT is unaffected in some cases and reduced in others. A reduction in IDT requires operation of a furnace at lower furnace-outlet gas temperature to avoid boiler fouling and, thus, may require some derating of the unit if it were satisfactory for the untreated coal.

A review of the ash fluid temperature (AFT) shows that, in almost every case, the AFT was reduced significantly by coal treatment. The one exception was Westland coal treated with mixed leachant, which raised AFT by 200 F. In general, when firing coal to a dry-ash removal furnace, a reduction in AFT would lead to an expectation of more severe furnace slagging problems. Ash deposits would have a greater tendency to fuse as liquid slag which is difficult to remove by furnace slag blowers. As furnace slagging progresses, furnace-outlet temperature will rise, leading to more severe fouling of convection surfaces. Thus, with HTT coal, it may be necessary to install additional slag blowers in the furnace, to operate slag blowers more frequently, and to derate the boiler to control slagging in a dry-ash furnace.

Fouling of boiler convection tube banks is related to the strength of sintered ash deposits on tubes, which may be very difficult to remove for ash of high fouling potential. The severity of fouling problems is closely related to the sodium content of the coal ash. As seen in Table 27 the sodium content of treated coals can be much higher than for raw coal, leading to indications of medium to severe boiler fouling. The NaOH leachant produces a high-sodium ash having severe fouling potential with both Martinka and Westland coals, while the mixed-leachant treatment results in an ash of lower sodium content and lower fouling potential. Although ash from the acid-leached Westland coal is high in sodium content, its small quantity, at about 2.2 percent of the coal, could result in a reduced rate of boiler fouling. However, the high sodium content of the ash could lead to severe fouling.

All of these characteristics suggest that the treated coals would be less suitable for firing in a dry-bottom furnace than were the raw coals. The reduction in ash fusion temperatures resulting from some treatments may require some boiler derating to avoid furnace slagging problems, and an even greater derating may be required to avoid boiler fouling problems. If treated coals were to be fired in existing dry-bottom furnaces, it would probably be advisable to install additional slag blowers in the furnace and additional soot blowers in the convection tube banks to control the slagging and fouling to an acceptable level.

The treated coals appear more suitable for firing in wet-bottom (slag-tap or cyclone) furnaces than for dry-bottom furnaces because of their low-ash-fluid temperatures. This would be especially true of the mixed leachant Martinka coal, for which the ash fluid temperature was reduced from 2520 F to 2240 F by treatment, and for both the acid leached Westland coal, which dropped ash fluid temperatures from 2400 to 2070 F and 2120 F, respectively. However, even when firing in wet-bottom furnaces, which would avoid furnace slagging problems, the potential for medium to severe boiler fouling would continue to be a problem requiring adequate soot-blower capacity and, possibly, boiler derating to lower gas temperatures in the convection region.

The HTT processing may affect fly-ash resistivity and dust loading somewhat, with the possibility of influencing operation or efficiency of electrostatic precipitators used for dust collection.

In comparison to the raw coals, the high sodium content of some of the HTT coals presents some added consideration in the handling and disposal problem. Depending on the type of system, the utilization of HTT coals may require a modification of the ash-handling system.

Coal Handling and Storage. Normally, for pulverized coal-fired boiler systems, crushed coal is delivered to the power plant and pulverized on site. This pulverized coal is then fed directly to the burners. In the past, some systems have stored the pulverized coal in bins from which the coal is eventually conveyed to the burners, but these systems are no longer used. Accordingly, some modifications in the coal handling and storage facilities will be required to utilize HTT coals as these systems were not designed to handle prepulverized coal. Two factors that need to be considered in storage and handling of HTT coals are the size consist and the moisture content of the coal.

HTT coal, as prepared, is in pulverized form with a size consist similar to that usually fired in pulverized coal-fired boilers. Coal of this fine consist is readily carried away by the wind, and clouds of dust are raised by any handling. Also, care must be exercised in handling of fine coal to prevent spontaneous combustion. This problem is not unique with HTT coal but applies to finely ground coal from any source. Thus, if used as a dry powder, it will be necessary to handle and store HTT coal in enclosed containers and handling systems, much like cement. Instead of shipping in hopper cars, it will be necessary to ship it in closed cars with provision for fluidization for unloading. Instead of storing coal in piles at the point of use, it must be stored in closed silos or bunkers designed for pulverized coal. The handling of fuel from a storage into the plant, and its feeding to burners, must be based on equipment suitable for pulverized fuel instead of crushed coal. Finally, it may be feasible to eliminate coal pulverization at the point of use. Thus, handling and storage of HTT coal in pulverized form will require modification in facilities and equipment to accomodate its pulverized form.

On the other hand, the HTT could be consolidated by briquetting or pelletizing which would reduce the problems associated with transportation and storage. The consolidated coal would be repulverized prior to combustion. Consolidation would also reduce the explosion hazards associated with handling of fine coal.

If HTT coal is to be used in smaller industiral boilers now fitted with coal stokers, two alternative approaches might be considered. The first is to modify the boiler for pulverized-coal firing, utilizing the HTT coal as manufactured. The second is to briquette the HTT coal into a form suitable for stoker firing. The first alternative would require replacement of coal storage and handling systems to accommodate pulverized coal. However, pulverized coal firing would be superior to stoker firing for many boilers, especially if furnace volume is sufficient that boiler derating would not be necessary. The alternative of briquetting would increase the cost of HTT coal, but would avoid the necessity of changes in the existing plant. Briquetting might also permit shipment in hopper cars, storage in open piles, and handling in conventional coal-handling equipment for crushed coal.

The handling and burning characteristics of briquettes made from HTT coal have not yet been investigated. Information appears necessary if conventional coal handling and stoker firing are to be evaluated.

Moisture Content. The handling of pulverized coal is affected adversely by moisture content above about 3 percent. With more moisture the coal will agglomerate and pack and will not flow freely in bins and feeders. Thus, if HTT coal is to be handled in dry form, it must be kept dry from the time of production to the time of firing. Alternatively, it may be dried just before firing.

If wetted by exposure to rain, pulverized coal can absorb far more moisture than crushed coal. If moisture concentration exceeds about 15 percent it can influence flame temperature, furnace heat absorption rate, and steam temperature, and may require boiler derating to keep steam temperature within design limits.

There appears to be some possibility that HTT coal could be handled as a slurry in water for pipeline shipment, followed by dewatering, or by firing as a slurry. Firing as a slurry containing about 1 lb water per lb coal would require some boiler modification for superheat control and would involve a moderate loss in boiler efficiency because of the increased moisture loss of the stack gas. It would be especially attractive as a means of firing coal to equipment designed for oil firing, but feasibility has not yet been demonstrated. The lower combustion temperature in firing a water slurry might also help reduce dry slagging problems.

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PHASE II.   TRACE METAL IDENTIFICATION AND
RECOVERY FROM HYDROTHERMALLY TREATED COALS

Hydrothermal treatment of coal results in the extraction of
certain trace metals from the coal and subsequent solubilization in the
leachant.   During regeneration of the leachant for recycle, the trace
metals may be removed from the leachant or, on the other hand, they may
build up in the regenerated leachant and contaminate the coal.   Thus,
the objective of Phase II was to determine the disposition of trace metals
in the selected raw coals and to assess the need for removal of the trace
metals from the spent leachant for recycle.

Task 1.   Trace Metal Analysis

Trace metal analyses were conducted on each raw coal and the
hydrothermally treated coals produced from these raw coals.   Originally,
optical emissions spectroscopy was employed; however, this technique was
not sensitive enough.   Consequently, mass spectroscopy was utilized.   In
addition to those elements listed below:

Aluminum	Chromium	Lead
Arsenic	Fluorine	Antimony
Boron	Iron	Selenium
Beryllium	Lithium	Tin
Cadmium	Manganese	Vanadium
Chlorine	Nickel	Zinc,
Copper	Phosphorus	

the coals were analyzed for a variety of other elements.   The analyses
are shown in Table 28 (Martinka coals) and Table 29 (Westland coals).

Examination of this preliminary data revealed that hydrothermal
treatment of coals is effective in extracting many of the trace metals.
Sodium hydroxide appears to be more effective than the mixed leachant.
Of the elements listed above, the concentration (ppmw) of the following in
the caustic leached Martinka HTT coal was lower than in the raw coal.

TABLE 28. MASS SPECTROGRAPHIC ANALYSIS OF MARTINKA RAW AND SELECTED HTT COALS

Element	Raw	Caustic HTT	Mixed Leachant HTT
Li	50	50	20
Be	5	3	1
B	100	20	10
F	20	10	30
Na	300	~ 3%	3000
Mg	3000	2000	2000
Al	~ 1%	~ 1%	~ 1%
Si	~ 5%	~ 3%	~ 5%
P	2000	2000	1500
Cl	300	100	50
K	~ 2%	5000	500
Ca	~ 2%	~ 2%	~ 5%
Sc	5	2	10
Ti	3000	3000	5000
V	300	100	100
Cr	200	100	200
Mn	300	200	300
Fe	~ 5%	~ 1%	~ 5%
Co	300	200	300
Ni	1000	300	500
Cu	10	5	10
Zn	< 30	< 30	< 30
Ga	< 10	< 10	< 10
Ge	< 2	< 2	< 2
As	20	< 10	< 10
Se	≤ 30	≤ 20	≤ 30
Br	10	3	3
Rb	200	30	50
Sr	1000	500	2000
Y	50	30	200
Zr	300	100	500
Nb	30	20	50
Mo	10	3	20
Ru	< 1	< 1	< 1
Rh	< 0.3	< 0.3	< 0.5
Pd	< 3	< 2	< 1
Ag	< 1	< 1	< 1
Cd	< 5	< 2	< 5
In	< 1	< 1	< 1
Sn	5	1	100
Sb	1	< 1	< 1
Te	< 1	< 1	< 1
I	3	< 1	< 1
Cs	0.5	< 1	< 1
Ba	500	< 1	1000
La	100	50	100
Ce	100	100	300
Pr	30	10	50
Nd	50	10	200
Sm	10	2	10
Eu	5	0.5	5
Gd	10	1	10
Tb	3	< 0.3	≤ 3
Dy	10	3	10
Ho	2	< 1	3
Er	5	< 2	5
Tm	< 3	< 3	< 10
Yb	< 5	< 2	< 10
Lu	< 2	< 0.5	< 2
Hf	< 5	< 3	< 10
Ta	< 10	< 3	< 3
W	≤ 5	< 3	< 3
Re	< 3	< 3	< 10
Os	< 5	< 5	< 5
Ir	< 3	< 3	< 3
Pt	< 5	< 5	< 5
Au	< 2	< 2	< 2
Hg	< 10	< 3	< 20
Tl	< 3	< 3	< 5
Pb	100	5	30
Bi	< 2	< 2	< 2
Th	5	< 2	30
U	20	< 2	20

TABLE 29. MASS SPECTROGRAPHIC ANALYSIS OF WESTLAND RAW AND SELECTED HTT COALS

Element	Raw	Caustic HTT	Mixed Leachant HTT
Li	50	50	20
Be	5	3	1
B	100	20	10
F	20	10	30
Na	300	~ 3%	3000
Mg	3000	2000	2000
Al	~ 1%	~ 1%	~ 1%
Si	~ 5%	~ 3%	~ 5%
P	2000	2000	1500
Cl	300	100	50
K	~ 2%	5000	500
Ca	~ 2%	~ 2%	~ 5%
Sc	5	2	10
Ti	3000	3000	5000
V	300	100	100
Cr	200	100	200
Mn	300	200	300
Fe	~ 5%	~ 1%	~ 5%
Co	300	200	300
Ni	1000	300	500
Cu	10	5	10
Zn	< 30	< 30	< 30
Ga	< 10	< 10	< 10
Ge	< 2	< 2	< 2
As	20	< 10	< 10
Se	≤ 30	≤ 20	≤ 30
Br	10	3	3
Rb	200	30	50
Sr	1000	500	2000
Y	50	30	200
Zr	300	100	500
Nb	30	20	50
Mo	10	3	20
Ru	< 1	< 1	< 1
Rh	< 0.3	< 0.3	< 0.5
Pd	< 3	< 2	< 1
Ag	< 1	< 1	< 1
Cd	< 5	< 2	< 5
In	< 1	< 1	< 1
Sn	5	1	100
Sb	1	< 1	< 1
Te	< 1	< 1	< 1
I	3	< 1	< 1
Cs	0.5	< 1	< 1
Ba	500	< 1	1000
La	100	50	100
Ce	100	100	300
Pr	30	10	50
Nd	50	10	200
Sm	10	2	10
Eu	5	0.5	5
Gd	10	1	10
Tb	3	< 0.3	≤ 3
Dy	10	3	10
Ho	2	< 1	3
Er	5	< 2	5
Tm	< 3	< 3	< 10
Yb	< 5	< 2	< 10
Lu	< 2	< 0.5	< 2
Hf	< 5	< 3	< 10
Ta	< 10	< 3	< 3
W	≤ 5	< 3	< 3
Re	< 3	< 3	< 10
Os	< 5	< 5	< 5
Ir	< 3	< 3	< 3
Pt	< 5	< 5	< 5
Au	< 2	< 2	< 2
Hg	< 10	< 3	< 20
Tl	< 3	< 3	< 5
Pb	100	5	30
Bi	< 2	< 2	< 2
Th	5	< 2	30
U	20	< 2	20

	Raw	Treated		Raw	Treated
Arsenic	20	< 10	Fluorine	20	10
Boron	100	20	Iron (possibly)	5%	~1%
Beryllium (possibly)	5	3	Nickel	1000	300
Chlorine	300	100	Lead	100	5
Copper	10	5	Tin	5	1
Chromium	200	100	Vanadium	300	100

*   Concentration in ppmw except where noted, same applies for all in this table and following tables.

In addition, other trace elements were extracted from the Martinka coal:

	Raw	Treated		Raw	Treated
Silicon (possibly)	5%	<3%	Zirconium	300	100
Cobalt (possibly)	300	200	Molybdenum	10	3
Bromine	10	3	Barium	500	< 1
Rubidum	200	30	Lanthanium and other elements of the Lanthanium series	Concentrations of a number reduced	
Strontium	1000	500	Uranium	20	< 2
Yittrium (possibly)	50	30	Thorium	5	< 2

Similar results were obtained in the treatment of Westland coal with sodium hydroxide. However, with this coal, chlorine, copper, fluorine, nickel, throium, and uranium were not extracted.

The mixed leachant was not as effective as sodium hydroxide in extracting the trace elements from Martinka and the Westland coals. Only those listed below were extracted from each coal:

	Martinka Coal			Westland Coal	
Metal	Raw	Treated	Metal	Raw	Treated
Lithium	50	20	Beryllium	0.4	0.2
Beryllium	5	1	Boron	25	<3.5
Boron	100	10	Potassium	~2800	280
Chlorine	300	50	Vanadium	37	7.0
Potassium	~2%	500	Chromium	37	13
Vanadium	300	100	Arsenic	6	1
Nickel	1000	500	Bromine	5	1
Arsenic	20	< 10	Rubidium	12	2.2
Lead	100	30	Molybdenum	2	0.1
Rubidium	200	50			

Further reduction in the overall mineral matter content and the concentration of other trace metals in an HTT coal was achieved by washing a sodium hydroxide treated Martinka coal with dilute (10 percent) sulfuric acid at ambient temperature as discussed under "Task 1B. Preparation of HTT Coals". Analysis for aluminum, boron, chlorine, fluorine, nickel, phosphorus, and zinc indicated that concentrations of these elements were significantly reduced by the deashing (acid leach) operation as noted below:

	Concentration (ppmw)		
Metal	NaOH-Treated	Raw Coal	Acid Leached
Aluminum	> 1%	> 1%	5000
Boron	4.7	25	<0.1
Chlorine	270	150	10
Fluorine	89	25	< 3
Nickel	33	14	10
Phosphorus	32	14	10
Zinc	16	7.3	5

On the other hand, acid leaching of the NaOH-HTT coal appeared to have increased the concentration of several of the trace metals in the coal. Examples of these are arsenic, copper, chromium, manganese, and possibly

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cadmium. However, total mass of elements in the HTT coal was significantly reduced by the acid leach as discussed below. The source of these particular trace metals could be the sulfuric acid used as the leachant. It may be that, under the conditions of this experiement, the coal acts as an ion exchange resin and absorbs the trace metals from the sulfuric acid. This observation may be in concurrence with some work which has been or is being conducted at the University of Melbourne by Professor Geoffrey Cullen. He has observed that brown coal is a very good ion exchange resin for extracting such metals as nickel, lead, copper, and cadmium from aqueous solutions.

The total mineral matter content of the NaOH leached coal was reduced from 13.4 weight percent to 2.2 weight percent by the deashing operation. The major mineral matter components remaining in the deashed HTT coal were silicon, aluminum, iron, calcium, and sodium in concentrations (metal basis) of 0.3, 0.03, 0.6, 0.03, and 0.43, wt percent, respectively.

One method for regeneration of the spent sodium hydroxide leachant for recycle entails sparging with carbon dioxide to liberate the sulfur as H_2S which, on a commercial scale, would be converted to elemental sulfur via the Claus or Stretford Process. During the sparging operation, the solubilized coal (humic acids) and, at least, a portion of the trace metals are precipitated. While additional work will need to be conducted in this area, it was established that a portion of the trace metals (Table 30) are removed from the spent leachant by this method of regeneration.

Thus, hydrothermal treatment of Martinka and Westland coals using either sodium hydroxide or a mixture of sodium hydroxide and calcium hydroxide as the leachant system resulted in the extraction of certain trace metal values along with a significant portion of the sulfur. Further reduction in the concentration of other trace metals in the HTT coal was achieved by leaching the HTT coal with a dilute sulfuric acid solution. The need for removal of these trace elements from the spent leachant for recycle was not established. This would require a series of regeneration-recycle experiments. However, it was determined that a significant portion of these metals may be removed from the spent leachant by treatment with carbon dioxide.

TABLE 30.   TRACE METALS CONTENT OF HUMIC ACIDS

Trace Metal	Concentration Weight Percent[*]
Iron	10-15
Silicon	10-20
Calcium	0.3
Sodium	3-6
Nickel	0.5
Molybdenium	0.2
Potassium	0.5
Magnesium	
Manganese	
Barium	
Cobalt	
Chromium	Were found at 0.1 percent or less level
Tin	
Vanadium	
Copper	
Titanum	
Strontium	

* On a metal basis.

PHASE III. ORGANIC CHEMICAL BY-PRODUCT RECOVERY
FROM HYDROTHERMAL TREATMENT OF COAL

Introduction

During hydrothermal treatment of coal, a portion of the coal is
solubilized or converted to a colloidal suspension of a fine solid in the
alkaline leachant. The solubilized coal commonly referred to as humic
acids can be precipitated from solution by neutralization.

Exact composition of the humic acids will depend probably on the
type of coal. While no effort was made to identify the composition of the
humic acids derived from the coal used in this program, a previous study
conducted at Battelle's Columbus Laboratories under the support of the
Battelle Energy Program on the characterization of humic acids derived
from a subbituminous coal revealed that they contained approximately 69
percent carbon, 4.5 percent hydrogen, 1.0 percent nitrogen, and 0.5 percent
sulfur. Studies by infrared spectroscopy and nuclear magnetic resonance
indicated that the humic acids contained fused ring structures substituted
in the ring with phenolic hydroxyl and carbonyl functionalities[14].
Molecular weight determination showed the average molecular weight of the
components to be about 770, covering the range of 100 to 3000. It is
expected that humic acid derived from the bituminous coal used in this
study would have a similar composition and average molecular weight.

The degree of coal solubilization is dependent on the processing
conditions such as temperature, time, leachant system and concentration of
leachant and on the rank of coal. For example, upwards of 90 percent of a
subbituminous Western coal has been solubilized in 10 percent aqueous sodium
hydroxide solution, whereas, in some instances, less than 5 percent of
Eastern bituminous coals was solubilized under similar conditions.

In the conceptualized HCP in which the spent leachant containing
the solubilized coal is regenerated by the carbonation-lime route, this
solubilized coal would precipitate during the carbonation step and would be
recovered at this point by filtration. The filter cake could either be used

as a source of process heat, mixed with the HTT coal product or possibly converted to coal chemicals. Terephthalic acid has been identified as one potential use for this solubilized coal.

Background Discussion

The concept of producing organic chemicals from coal is not new. Franz Fisher, et al.[11], studied the production of chemicals by direct oxidation of coal and related substances in the early 1900's. They reported the conversion of a number of carbonaceous materials to benzene carboxylic acids (BCAs) by wet oxidation with the following recoveries: cellulose, 1.2 percent; lignin, 5.4 percent; sugar, 2.9 percent; lignite, 0.3 percent; and coal, 1.0 percent. Later, studies at Carnegie Institute[16] compared BCA yields from several domestic coal products by wet-pressure oxidation. The following yields expressed as percent carbon converted were obtained: Illinois No. 6, 33 percent; Pittsburgh, 36 percent, High Splint, 37 percent; Pocahontas No. 3, 39 percent (equivalent to 69 percent BCA); anthracite, 38 percent; 500 C coke, 33 percent; 700 C coke, 22 percent; high-temperature coke, 7 percent; graphite, 2 percent; pitch, 30 percent. An average of 3.3 carboxylic acid groups per benzene ring was reported.

An extension of the Carnegie work[17] was carried out at Dow Chemical Company in a three-phase study with Pocahontas coal: first, in a 2-liter autoclave; second in a 96 ft x 0.25 I.D. tube; third, in a 5-gal autoclave. Yields similar to Carnegie's earlier work were obtained.

Numberous similar studies of the production of BCAs by the direct wet oxidation of coal and related materials have been made and are the subject of a thorough review by A. E. Bearse, et al[18].

In 1974, Battelle's Columbus Laboratories, as part of the on-going Battelle Energy programs in coal utilization, conducted a study directed toward conversion of coal to terephthalic acid via the oxidation - Henkel process. Preliminary results indicated that terephthalic acid could be produced by oxidation of a solubilized coal to BCAs and subsequent conversion of the

BCAs to terephthalic acid. In this case, all 12 BCAs were produced and rearranged to give terephthalic acid. However, the yield while not quantitatively measured appeared low and no effort was made to optimize the process conditions for production of either the BCAs or terephthalic acid.

As part of the combustion study, Battelle has conducted a program to investigate the potential for recovery of organic chemicals for the humic acids (solubilized coal) which are produced during the hydrothermal treatment of coal.

Experimental Procedure and Results

Recovery and utilization of the solubilized coal (humic acids) contained in the spent leachant entailed

(a) Recovery of solubilized coal (humic acid)

(b) Conversion of solubilized coal to BCAs.

Essentially the recovery and conversion of the humic acids to terephthalic acid would involve three reactions:

(a) Precipitation of Humic Acids

Na salts of humic acids (spent leachant) + CO_2 →

humic acids ↓ + Na_2CO_3 + $NaHCO_3$

(b) Preparation of BCAs
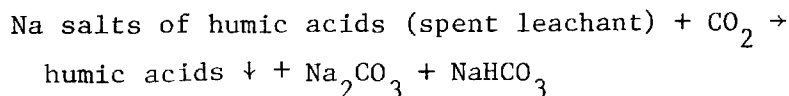
Humic acids + H_2O + O_2 → CO_2 + BCAs.
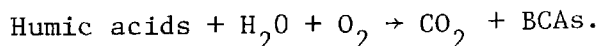
During the oxidation, humic acids of unknown composition are oxidized to a single benzene ring containing carboxylic acid groups (BCAs). Composition of this mixture may vary, but 12 benzene carboxylic acids as shown in Figure 5 are possible.

The BCAs would be converted to terephthalic acid by Reaction C:

(c) Preparation of Terephthalic Acid

(1) BCAs + K_2CO_3 $\xrightarrow{\text{heat}}$ potassium terephthalate + $H_2C_2O_3$

(2) Potassium terephthalate + HCl → terephthalic acid + KCl.

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Benzoic acid
(Benzenecarboxylic acid)

Phthalic acid
(1,2-Benzene-
dicarboxylic acid)

Isophthalic acid.
(1,3-Benzene-
dicarboxylic acid)

Terephthalic acid
(1,4-Benzene-
dicarboxylic acid)

Hemimellitic acid
(1,2,3-Benzene-
tricarboxylic acid)

Trimellitic acid
(1,2,4-Benzene-
tricarboxylic acid)

Trimesic acid
(1,3,5-Benzene-
tricarboxylic acid)

Pyromellitic acid
(1,2,4,5-Benzene-
tetracarboxylic acid)

Mellophanic acid
(1,2,3,4-Benzene-
tetracarboxylic acid)

Prehnitic acid
(1,2,3,5-Benzene-
tetracarboxylic acid)

Benzenepentacarboxylic acid

Mellitic acid
(Benzenehexacarboxylic acid)

FIGURE 5. NAMES AND STRUCTURAL FORMULAS OF BENZENECARBOXYLIC ACIDS

Terephthalic acid has the formula

$$\text{HOOC}-\langle\bigcirc\rangle-\text{COOH}$$

During this reaction, rearrangement of the carboxylic acid groups would occur and excess carboxylic acid groups would be converted or lost as carbon dioxide.

Recovery of Humic Acid from Spent Leachant. In order to develop a recovery process which was compatible with the overall HCP, the humic acid fraction of a sodium hydroxide spent leachant was precipitated by sparging the leachant at 60 C with carbon dioxide. Sparging was continued until the pH of the solution decreased to 8.5. The resulting mixture was vacuum-filtered. The filter cake was washed with water and vacuum dried.

The dried product was found to contain 33.9 percent organic carbon, 56.3 percent ash, 4.3 percent moisture and 0.7 percent sulfur. Carbon content of the spent leachant was lowered from 0.35 percent to 0.01 percent, while sulfur content was reduced to 0.06 percent from 0.19 percent.

Analysis of the ash component of the dried humic acid product revealed the presence of iron (10-15 percent); silicon (10 to 20 percent), calcium (0.3 percent), sodium (3 to 6 percent), aluminum (1 to 2 percent), nickel (0.5 percent), molybdenum (0.2 percent) and potassium (0.5 percent). Other metal values found at 0.1 percent or less level were: manganese, magnesium, barium, cobalt, chromium, tin, vanadium, copper, titanium, and strontium.

Conversion of Humic Acid to BCAs. The oxidative approach was employed to oxidize to the humic acids to BCAs. Typically, this entailed the following processing steps:

(1) The dried humic acid (2.75 g) was dispersed in 250 ml of water containing a small amount of wetting agent and, in some cases, other reagents such as K_2CO_3, oxalic acid, etc.

(2) The mixture from (1) was then heated in the autoclave at temperatures ranging from 250 C to 300 C under an oxygen

overpressure. Oxygen was added normally after the mixture had reached the desire temperature.

(3) Samples were withdrawn during the run as a function of time for analysis.

(4) The reaction products remaining in the autoclave at the termination of the experiment were cooled to room temperature, gas in the head space vented for analysis and contents of autoclave removed for analysis.

The results of these experiments are shown in Figure 6. Each point plotted for total BCA yield reflects a corresponding terephthalic yield since the total BCA yield could, by the Henkel reaction, be converted to terephthalic acid.

From comparison of these three curves, the data suggests that at 300 C the rate of conversion of humic acids to BCAs was rapid. However, the data further suggests that at this temperature BCAs are unstable, and after the first few minutes, the rate of decomposition was faster than the rate of formation. Thus, in order to obtain a high yield of BCAs at 300 C, a means of removing the BCAs from the reaction product must be developed.

At 250 C in the presence of water alone and K_2CO_3 plus water, the rate of conversion of humic acids to BCAs was higher than the rate of decomposition. The addition of K_2CO_3 which reacted with the BCAs as formed to produce the potassium and terephthalate carbonic acid (H_2CO_3) improved the yield significantly because the potassium salt of the BCAs was more stable than the BCAs.

The higher stability of the potassium salt of BCAs was evidenced by analysis of the gaseous products for carbon dioxide which was converted to carbon losses. For those experiments conducted in hot water, 60 to 85 percent of the carbon charged was converted to carbon dioxide. The addition of K_2CO_3 reduced the loss of carbon as carbon dioxide to 22 percent.

Interpretation of the gas chromatographic data from the K_2CO_3 experiment revealed that all 12 benzene carboxylic acids were formed by the oxidation of humic acids (Figure 7). The relative concentrations increased accordingly: mono < hexa < di < penta < tetra < tri with the concentration of mono-benzenecarboxylic acid being too low to plot. These results are in general agreement with those obtained by Germain[18] from the oxidation of a high volatile European coal in K_2CO_3.
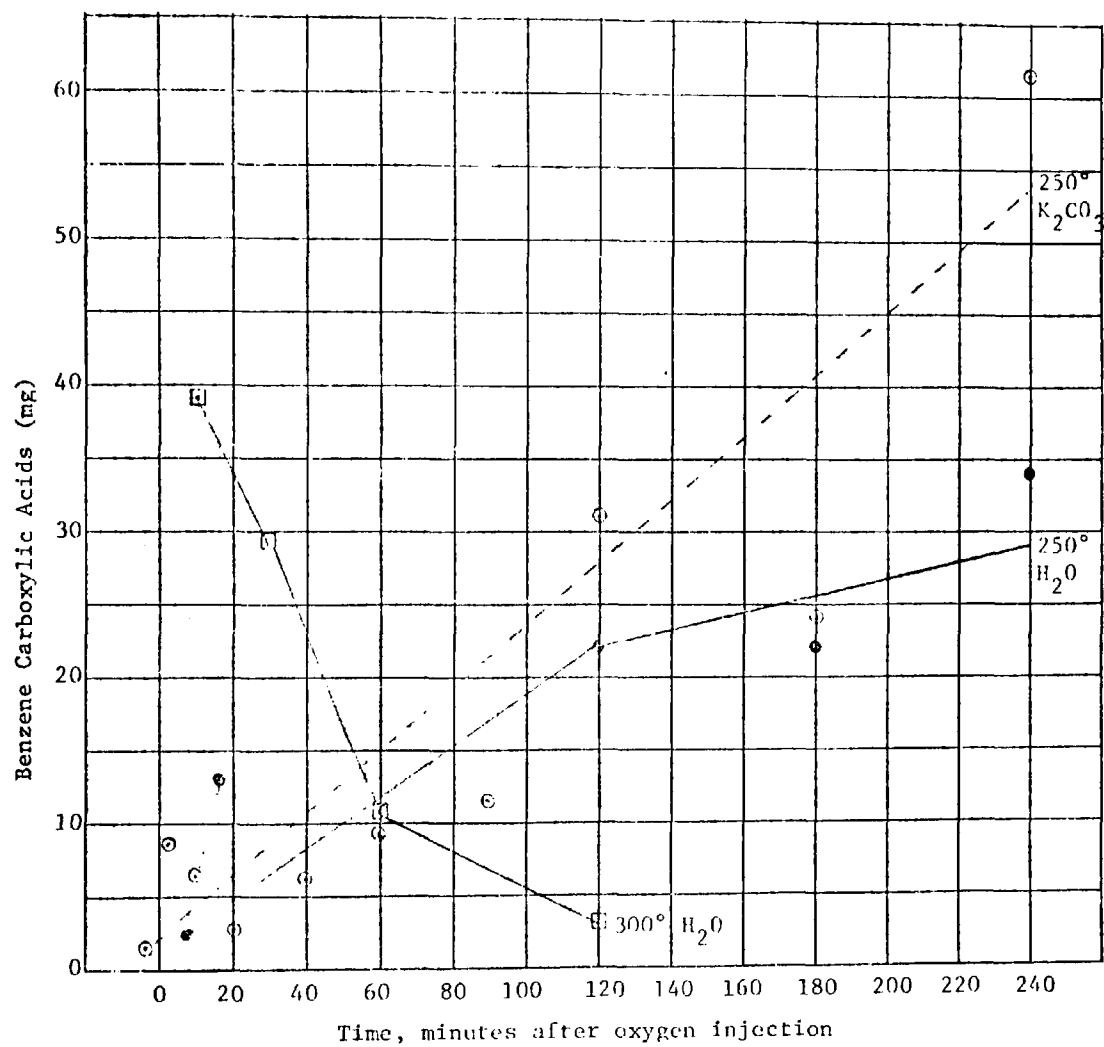
FIGURE 6. COMPARISON OF TOTAL BCA FORMATION RATES
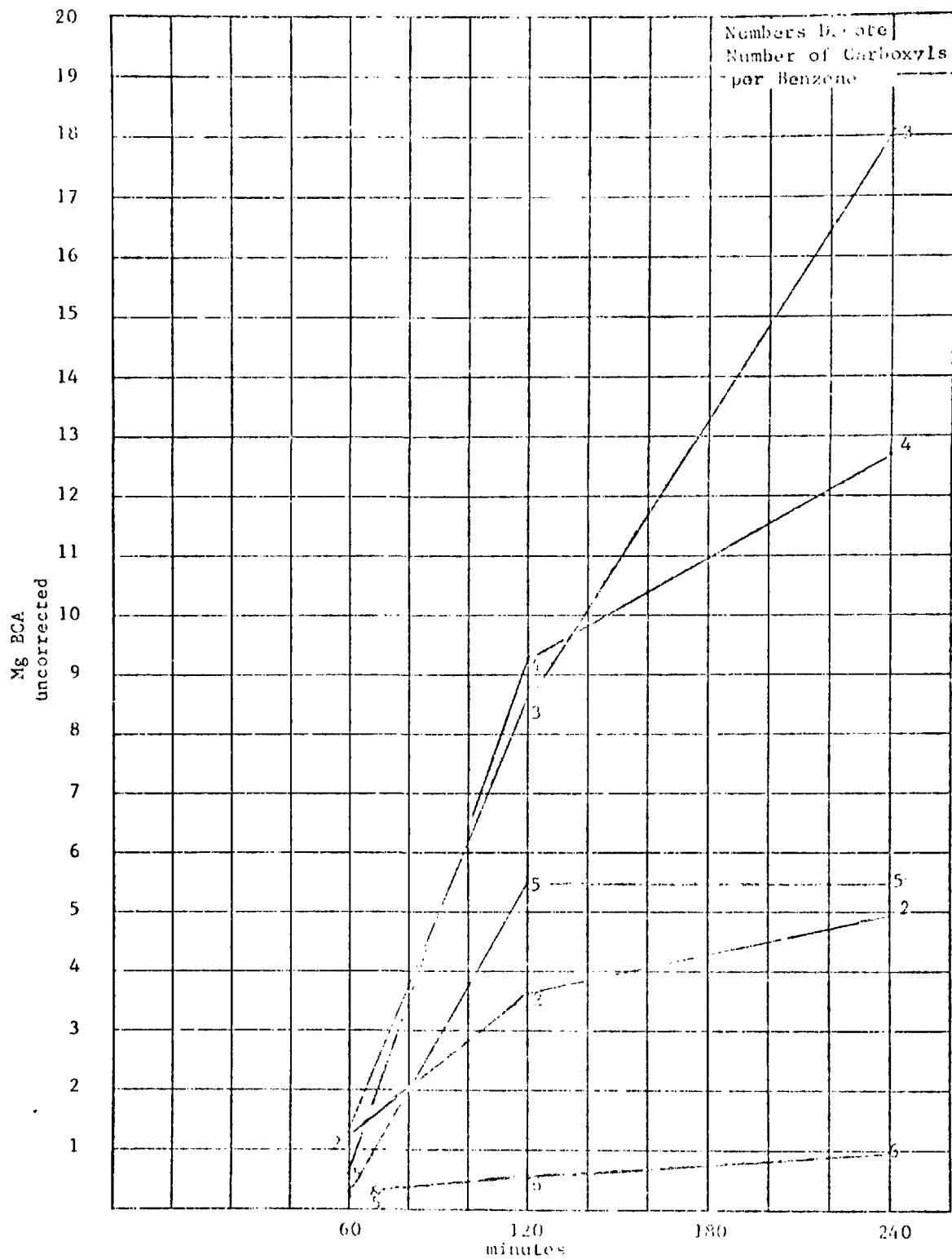UNDER VARIOUS CONDITIONS

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FIGURE 7. RELATIVE FORMATION RATES OF VARIOUS BCA's IN 7$\underline{N}$ K_2CO_3 AT 250 C

While the above data clearly illustrate the technical feasibility of converting humic acids to BCAs, the data also shows that at temperatures between 250 and 300 C the BCAs are unstable. In an effort to learn the fate of the BCAs, once generated by oxidation of humic acids, an experiment was conducted using a synthetic mixture of pure BCAs in water. The experiment was carried out at 250 C rather than at 300 C because of the rapid rate of decomposition of BCAs at the higher temperature. After attainment of temperature, samples were withdrawn prior to the injection of oxygen and at intervals thereafter. Gas chromatographic analyses were made on the samples. The results are summarized in Figure 8.

It appears that in water alone, the dicarboxylic acids are the most stable of the six different acids. In fact, the dicarboxylic acids present at zero time may have resulted in part from decarboxylation of the higher acids before oxidation was initiated. Also, the data shows that even at 250 C all of the benzenecarboxylic acids are unstable. Therefore, in order to obtain the best yield, pressure oxidation of humic acids must be carried out with rapid heating and cool down or quenching of the reaction mixture. Again, these results are in agreement with some work performed on alkaline oxidation of Pocahontas coal by Montgomery[14] who found that best yields were attained at a residence time of 1.5 minutes.
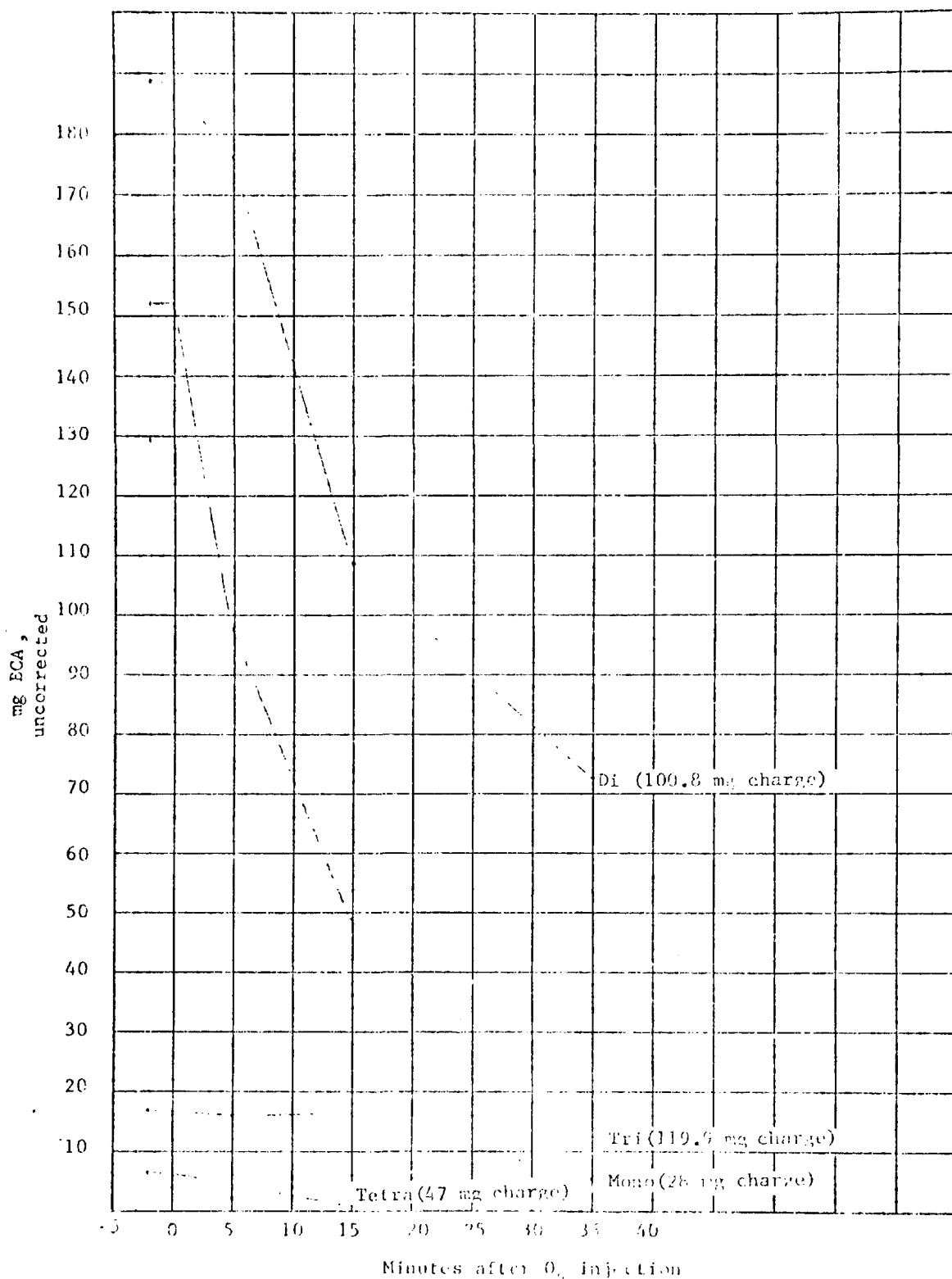
FIGURE 8. FATE OF PURE BENZENE CARBOXYLIC ACIDS IN PRESENT PROCESS

*BCA charge also included 51 mg penta carboxylic acid and 46 mg hexa carboxylic acid; neither was detected in product.

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CONCLUSIONS

(1) HTT coals prepared by the Hydrothermal Coal Process from Martinka and Westland coals burn as well as or better than the corresponding raw coals in the laboratory test facility and multifuel furnace combustion units.

(2) Sulfur dioxide concentrations in the flue gases were well below current Federal Sulfur Emission Standard for New Sources of 1.2 lb, ranging from about 125 to 500 ppm.

(3) The low sulfur dioxide and levels are attributed in part to the reduced sulfur concentration in the HTT coals, and in part to the sulfur capturing ability of the residual alkali in the HTT coals.

(4) Hydrothermal processing is effective in extracting trace metals such as beryllium, boron, vanadium, and arsenic from these coals. Alkali content -- sodium and/or calcium -- is increased as a result of the treatment.

(5) The potential slagging and fouling characteristics of the HTT coals suggest that these coals would be less suitable for firing in dry bottom furnaces than were the corresponding raw coals. The reduction in ash fusion temperature may in some cases require some boiler derating to avoid furnace slagging and boiler fouling problems. Firing of the HTT coals in existing dry-bottom furnaces may require the installation of additional soot blowers. Operation of the slag blowers more frequently and derating of the boilers would most likely be required. It may be possible to reduce the slagging and fouling characteristcis of the treated coals through the use of additives to raise the ash fusion temperature.

On the other hand, the low ash fusion temperature suggests that the HTT coals may be utilized directly in wet-bottom (slap tap or cyclone) furnaces. Firing in wet-bottom furnaces might avoid furnace slagging problems; however, boiler fouling may continue to be a problem, requiring adequate soot-blower capacity and, possibly, boiler derating to lower gas temperatures in the convection region.

(6) Data on the resistivity of the coal ash samples are inconclusive because of the possible influence of carbon in the samples. However, in general, the resistivity values of the ashes from the Martinka HTT coals were comparable to those from the raw coal.

(7) Preliminary assessment of the environmental problems associated with the combustion waste products indicate that direct disposal of the cooler ash from the NaOH treated coal would not be advisable because of high sodium sulfate content of the ash. However, the sodium sulfate could be removed prior to disposal. Removal of the sodium sulfate would produce an ash which would be less polluting with respect to trace metals than the ash from the corresponding raw coal since a significant portion of the trace metals would have been removed from the coal by the leaching process.

(8) Heating the solubilized coal (Humic acids) under oxidizing conditions in an aqueous medium resulted in the conversion of the humic acids to benzene carboxylic acids (BCAs), precursor to terephthalic acid. Yield of BCAs was low, less than about 10 percent. The majority of the coal was converted carbon dioxide. Therefore, this approach does not appear to be a viable process for conversion of the solubilized coal to terephthalic acid.

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APPENDIX A

DESCRIPTION OF THE HYDROTHERMAL COAL PROCESS

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DESCRIPTION OF THE HYDROTHERMAL COAL PROCESS

The Hydrothermal Coal Process (HCP) is a method for producing environmentally acceptable solid fuels (clean coal) from certain high-sulfur coals. Basically the process involves heating an aqueous slurry of coal and a chemical leachant at moderate temperatures and pressures to extract a significant portion of the sulfur and some of the ash, depending on the leachant, from the coal and subsequent regeneration of the leachant for recycle. The process, as depicted in Figure A-1, entails five major processing steps:

1. Coal preparation
2. Hydrothermal treatment (desulfurization)
3. Liquid/solid separation
4. Fuel drying
5. Chemical-leachant regeneration.

Coal preparation entails crushing or grinding of the raw coal, as received from the mine or after washing, to the particle size suitable for desulfurization, generally 70 percent minus 200 mesh.

Next, the coal goes to the slurry tank for mixing with the leachant, or, alternatively, the coal may be physically beneficiated to remove easily removable ash and pyritic sulfur and then pumped to the slurry tank.

After mixing with the leachant, the coal slurry is pumped continuously through the hydrothermal-treatment (desulfurization) segment where it is heated to a desired temperature whereupon sulfur and ash are extracted in amounts depending on the leachant.
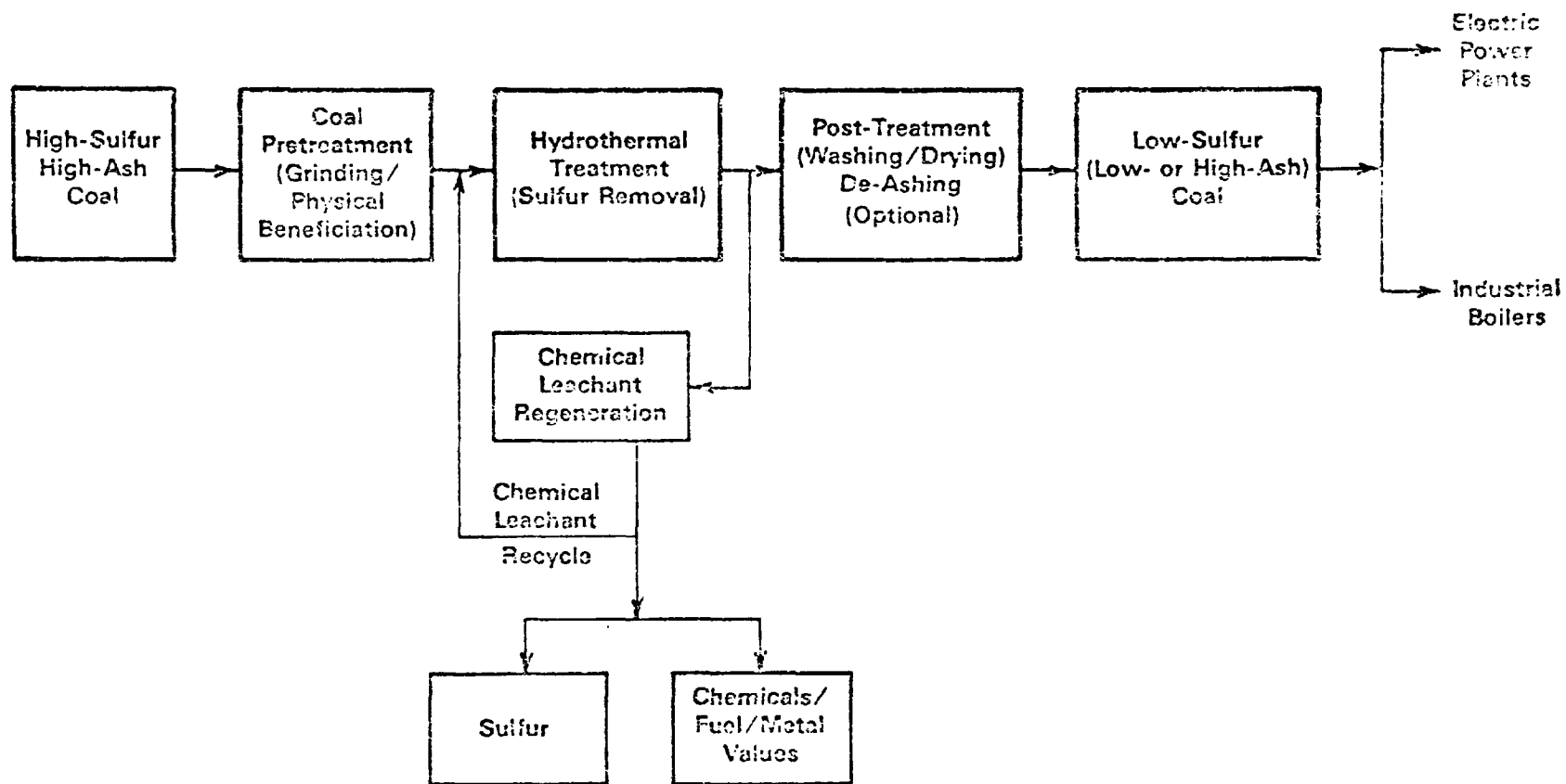
FIGURE A-1.   BATTELLE HYDROTHERMAL COAL PROCESS

The resulting coal-product slurry is passed through a heat exchanger into the product-separation (washing) segment where the desulfurized coal is separated from the spent leachant by a series of filtration and washing operations.

Next, the desulfurized coal is dried in, for example, a steam jacketed drier to remove residual water to produce a clean, solid fuel.

The spent leachant from the washing segment is regenerated in the leachant-regeneration segment where the sulfur is also removed as hydrogen sulfide by carbonation. The hydrogen sulfide on a commercial scale would be converted to elemental sulfur by a Claus or Stretford sulfur-recovery process. The carbonated liquor after filtering to remove solubilized coal and ash values is treated with lime and filtered to remove the calcium carbonate precipitate. The calcium carbonate is calcined to produce lime and carbon dioxide for recycle. The regenerated leachant is concentrated, composition adjusted, and returned to the process.

The miniplant was used to produce sufficient quantities of HTT coals for this combustion study. This facility encompasses the 5 process steps discussed above but for this study only the first 4 steps - coal preparation, desulfurization, liquid/solid separation, and product drying - were utilized. Maximum production rate is about 500 lbs per 24 hours.

APPENDIX B

MINIPLANT FACILITY

APPENDIX B

MINIPLANT FACILITY

The Miniplant is a small semi-continuous pilot plant with a pro-
duction capacity of about one-fourth ton per day (about 20 lb/hr) of HTT
coal. The facility consists of five major segments: Coal Preparation,
Hydrothermal Treatment, Coal Washing, Leachant Regeneration, and Coal
De-ashing Segment (Figure B-1). While the Miniplant was designed for con-
tinuous operation, sufficient storage tanks were installed so each segment
could be operated independently.

Coal Preparation Segment. Since most of the coals received are
water washed, each is dried before pulverization. After drying in the
steam jacketed dryer, the coals are ground in a two-stage process: (1)
to about 4-mesh size with a Fitzmill Model P comminuting machine and (2)
to the desired sizes with a Bantam Mikro-pulverizer (hammer-type). Various
sizes of coals are prepared by employing different sizes of screens in the
Mikro-pulverizer.

Classification of ground raw coals is conducted in large and small
scales. Large batches of raw coal are classified in a Sweco 24-inch vibro-
energy sieve. The oversize is reground in the Mikro-pulverizer. After
which the large batch of coal is mixed in a drum and a random sample is
taken to determine its size distribution. The technique employed for size
distribution determination in a mechanical Rotap is described in Appendix
A-1 of ASTM Designation: D-197-30 (Reapproved 1971).

Hydrothermal Treatment Segment. The Hydrothermal Treatment Segment
consists of four major units: coal slurry preparation, reactor system, pres-
sure let-down system, and product coal slurry separation. These four units
are connected and operated continuously. The Hydrothermal Treatment Segment
was designed to process 4 to 30 lb of coal per hour. However, its capacity
also depends on hydrothermal treatment conditions. Reactors were designed
for a maximum operating temperature of 275 C.

Coal Slurry Preparation. The schematic diagram of the coal slurry
preparation unit is shown in Figure B-2. The mix tank and the feed tank are
two 30-gal, conical bottomed, polyethylene tanks. The coal slurry is pre-

Coal

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            Coal                Hydrothermal              Coal
         Preparation     →       Treatment        →      Washing
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           Sulfur              Leachant                   Coal           Low-Sulfur
                              Regeneration              Treatment   →
      Soluble                                                            Low-Ash Coal
      Organic
      Fraction
```
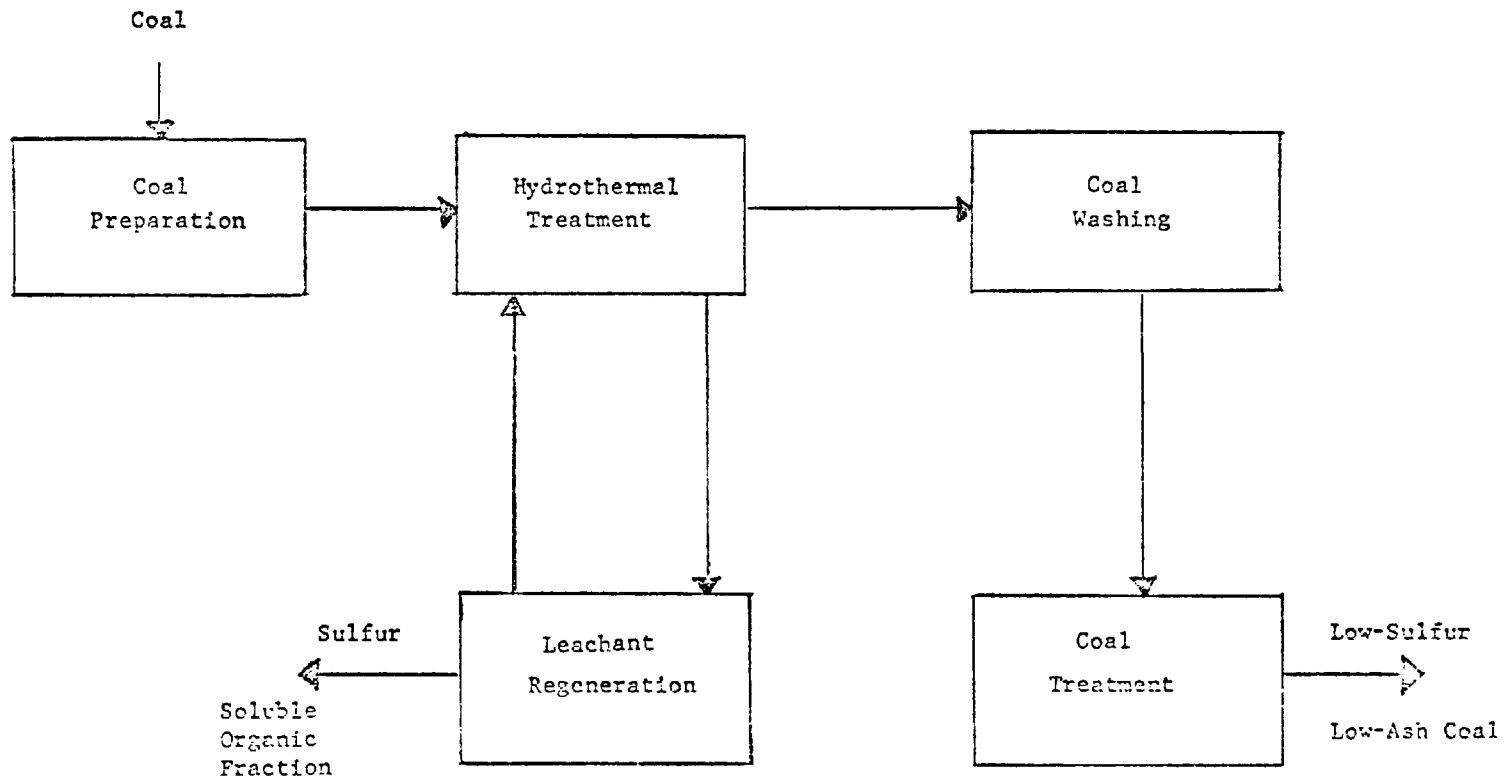
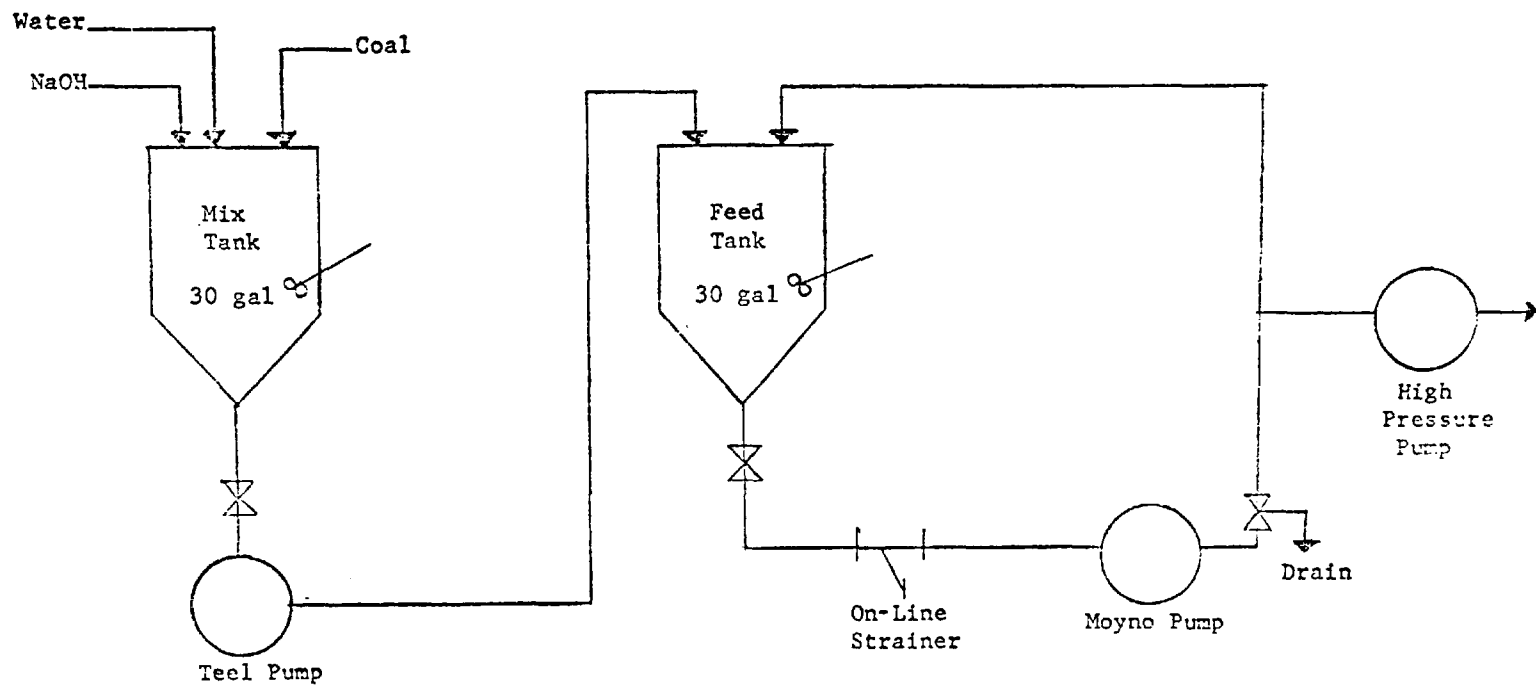FIGURE B-1. BLOCK DIAGRAM OF THE BHCP MINIPLANT

FIGURE B-2. COAL SLURRY PREPARATION

pared in the mix tank and transferred into the feed tank installed on an electronic scale equipped with a digital readout. The slurry is transferred from the mix tank to the feed tank with a Teel pump. A Moyno pump is used to recirculate the coal slurry around the feed tank. Recirculation is necessary to prevent coal from settling in the pipe. An in-line pipe strainer installed in front of the recirculating pump (Moyno Pump) acts as a safety device to trap foreign particles in the coal slurry.

Reactor System. The reactor system is constructed inside a steel safety barricade. Major equipment in this system are high-pressure pumps, preheaters, reactors, and cooler (Figures 23,24, and 25).

The high-pressure pumps are two Millroyal reciprocating pumps; a 6-gph low-flow equipped with maximum delivery pressure of 2100 psi and a 25-gph high-flow pump with a maximum delivery pressure of 1555 psi. The flow rate on each pump is adjustable and the pumps are operated at a minimum flow of 1/3 of its capacity. Actual feed rate is measured by weighing the feed tank mounted on an electronic scale.

To prevent vapor locking of the pumps by air pockets check valves and bleed valves were installed to bleed off the air without interrupting an experiment. A rupture disc was installed between the check valve and the pump discharge to protect the high-pressure pump.

Figure B-3 shows the heating system of the Hydrothermal Treatment Segment. The heaters are short lengths of 1/4-inch nickel pipe. The first heater is a double pipe heat exchanger, 3 feet long, with 60 psig steam used to heat the slurry. The next four heaters are 2-foot lengths of 1/4-inch pipe silver soldered into a 2-inch square copper bar. The copper is heated with Chromalox strip heaters capable of up to 4 kw on each heater. Each heater is insulated with pipe insulation. The final heater is an autoclave with a 1-gal nickel-lined body and a 3.5 kw tubular furnace. The autoclave heater is installed to reduce plugging problems in the tube heaters.

The temperature of the electrical tube heaters is measured in the copper block near the fluid outlet. The temperature in the autoclave heater is measured by a thermocouple inserted into a thermowell in the autoclave. The temperature in the steam heater is controlled by an off-on valve.

The power to the electrical heaters is controlled by Chromalox electronic proportional temperature controllers. The temperature is measured
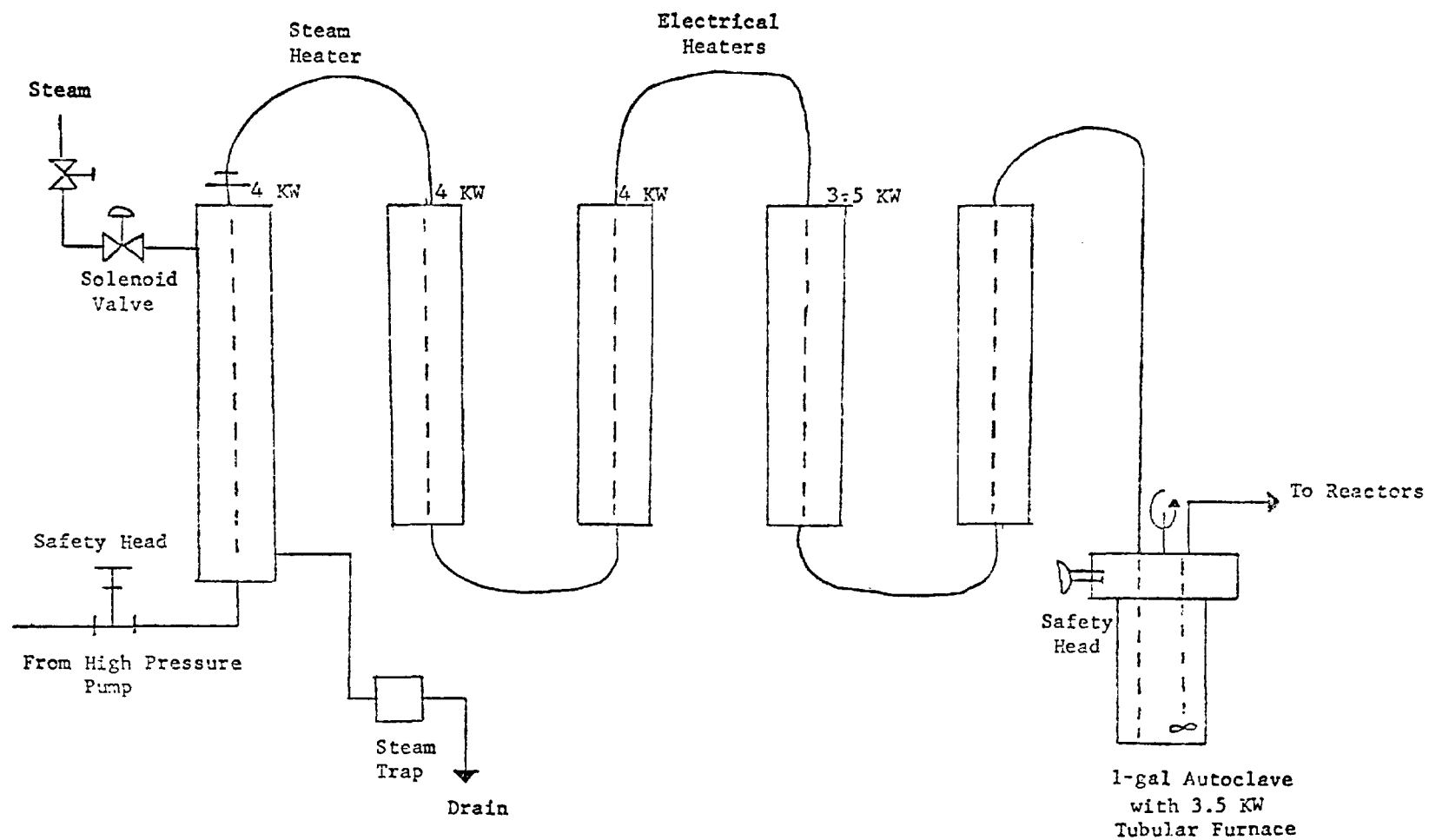
FIGURE B-3.   PREHATERS

by thermocouples which are installed inside the copper bars of the outlet ends of the electrical heaters and on the U-tubes between the heaters.

The autoclave system was designed as shown in Figure B-4. However, the second 1-gal autoclave is replaceable with a 2-gal body to provide additional capacity of the reactor system. The autoclave bodies are nickel-lined.

Each autoclave is stirred magnetically. The first autoclave has a 2-gal nickel-lined body, and the second autoclave has a 1-gal nickel-lined body (Figure B-4). The 2-gal autoclave and the 1-gal autoclave is equipped with two and one 3.5 kw furnaces, respectively. The temperature is measured with a thermocouple inserted in a well extending into the coal slurry and controlled by a Chromalox electronic proportional temperature controller.

The product cooler is a tubular water-cooled heat exchanger as indicated in Figure B-5. Water is used in the shell-side as a coolant.

Pressure Let-Down System. A schematic diagram of the pressure let-down system is shown in Figure B-6. The product slurry flows from the product cooler into a 5-gal autoclave rated at 1150 psi. The autoclave is mounted on an electronic scale which measured the amount of slurry in the autoclave. Adjustable high- and low-limit switches are built into the scale. Switches on the scale are arranged to open the valve to drain the autoclave and to open a valve to admit nitrogen into the autoclave to maintain the desired nitrogen overpressure between a high and a low limit. The switch opens the valves at the high limit to drain product and close at the low limit when a selected quantity of product has been removed. Normally, about four points differential is set between the high and the low limit. The low limit is set to prevent gas from venting through the liquid outlet.

Larger differentials causes an excessive pressure drop in the system. To eliminate this effect, a second 5-gal autoclave was installed in the system and connected to the gas space at the top of the receiver autoclave. With this arrangement, the pressure drop in the system is about three percent of the system pressure. As first installed, vibrations, electrical transients, etc., caused the scale to indicate the high level had been reached before the three pounds of slurry was added to the autoclave. A 2 second time delay relay in the high-limit circuit prevents such indications.

From Heater

To Product
Cooler

2-gal Autoclave
with two furnaces,
3.5 KW Each

1-gal Autoclave
with one furnace,
3.5 KW
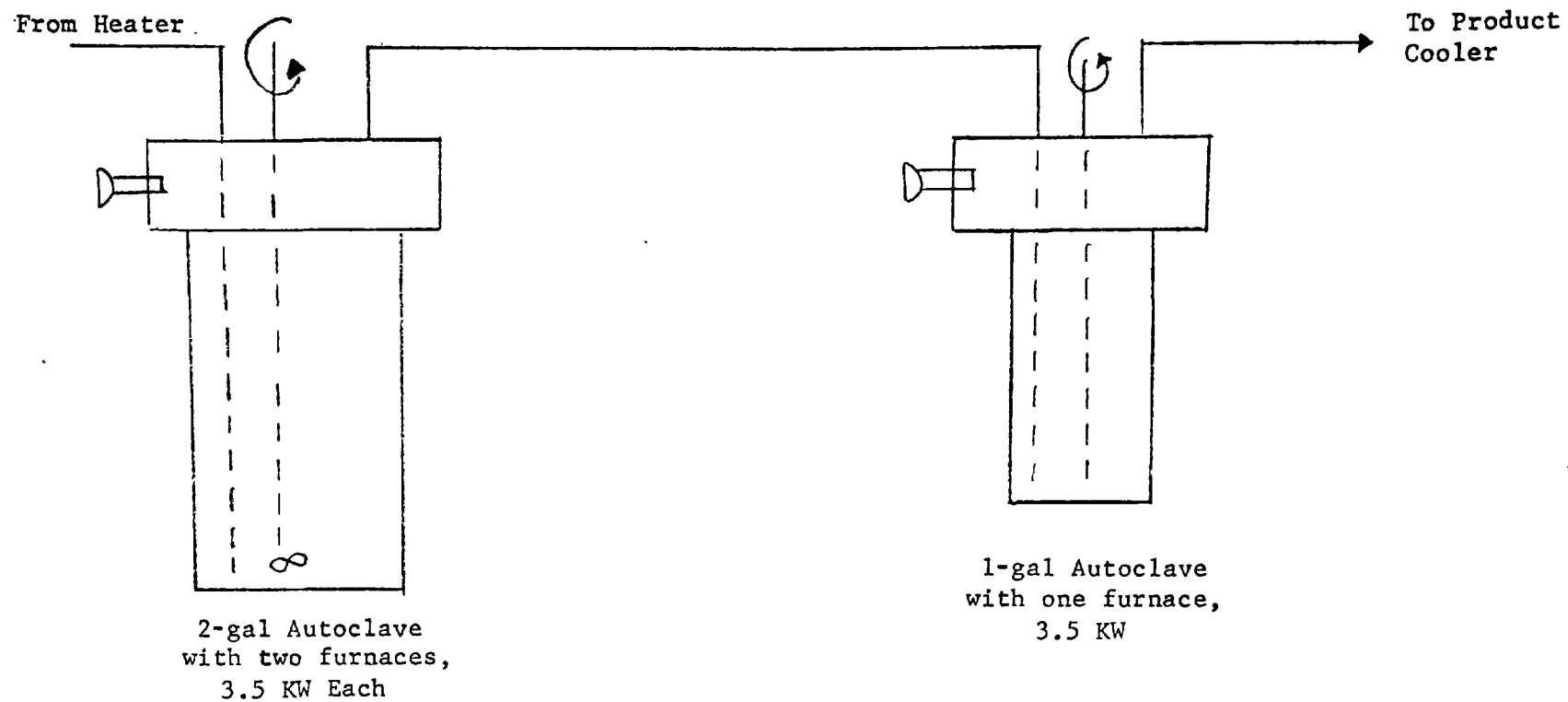
FIGURE B-4. REACTORS
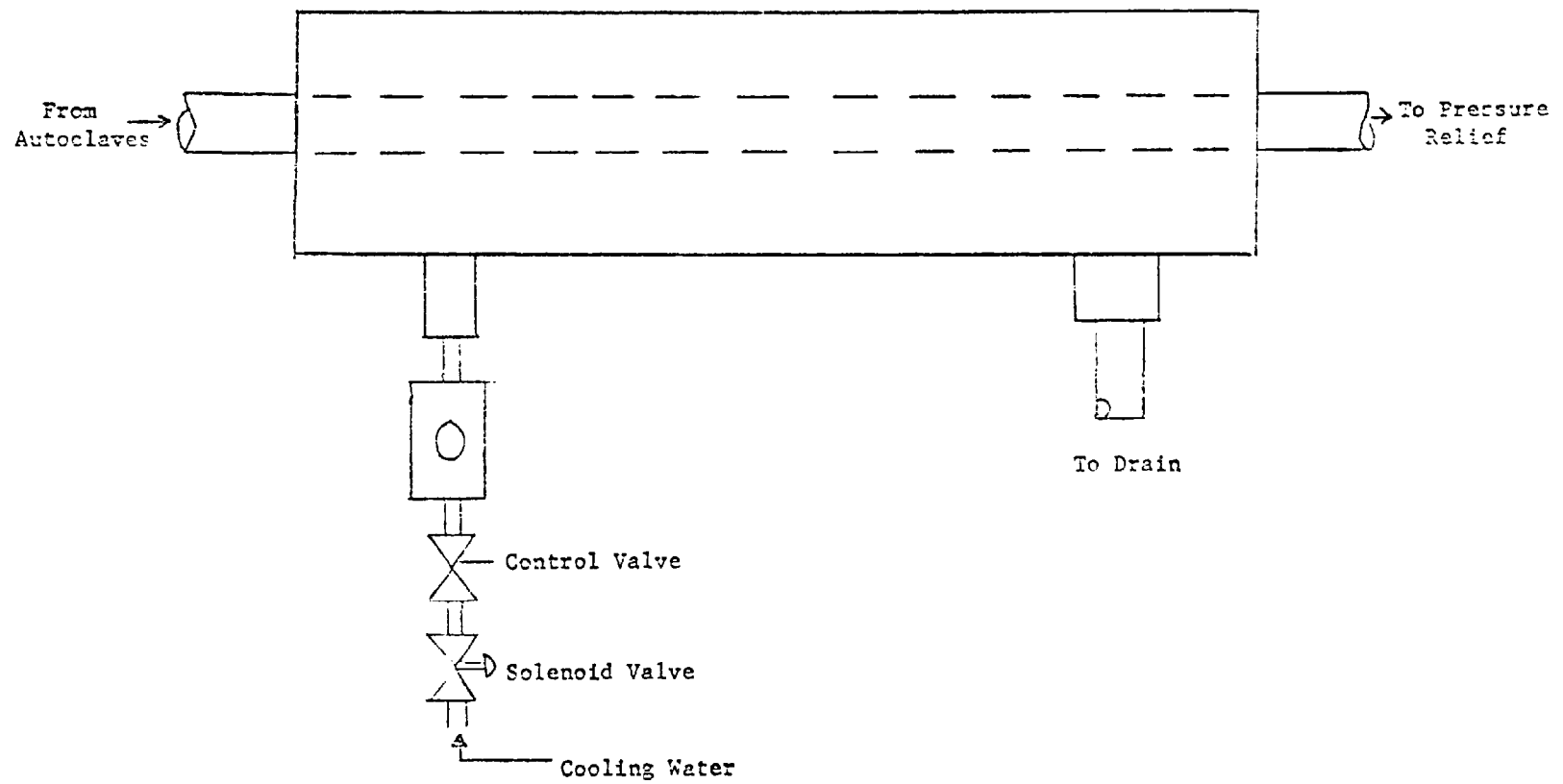
FIGURE B-5.   PRODUCT COOLER

Regulator Valve

Product Slurry
From Cooler

Bleed
Valve

5-gal.
Autoclave

5-gal.
Autoclave

Nitrogen
Cylinders

Scale

Pressure
Controller

To Centrifuge

Scale
Controller

100-gal.
Tank
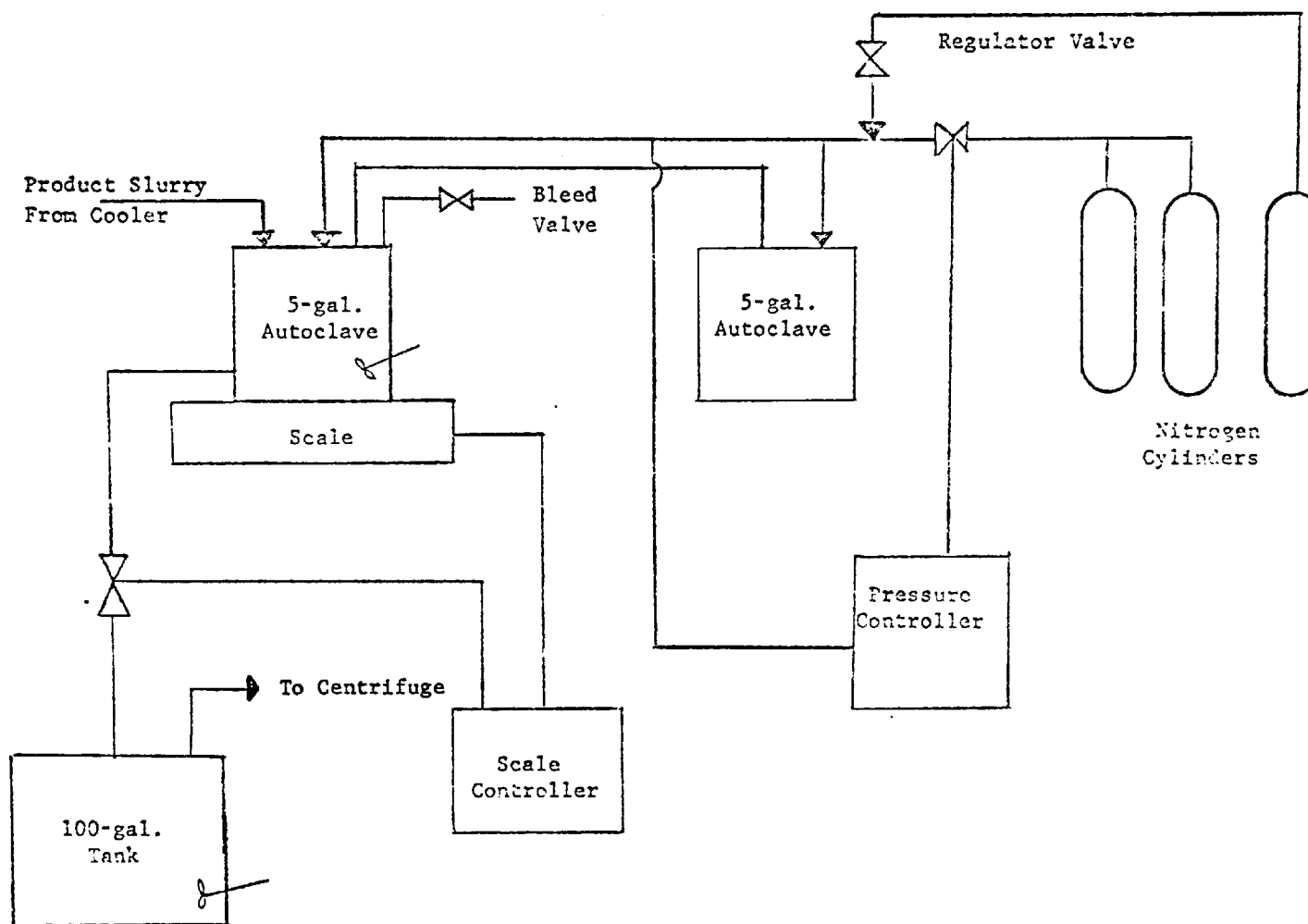
FIGURE B-6.   PRESSURE LET-DOWN SYSTEM

The pressure controller prevents overpressure in the system by venting nitrogen when the pressure exceeded its set point. The controller is a Fischer proportional controller and the control valve is a Badger Meter 1/4-inch air-actuated valve with size M trim (Cv = 0.0004 - 0.01). The regulator valve on the nitrogen cyclinder is a high-pressure regulator valve set at 1400 psi.

Product Slurry Separation. The solid fuel product is separated from the spent leachant in the Product Slurry Separation Segment. The slurry from the HTT Segment discharges into a 100-gal tank from which the slurry is pumped into a centrifugal filter. The centrifugal filter is a Bock basket centrifugal, 17 inches in diameter and 14 inches deep separating at about 1725 rpm. Polypropylene is used as the filter cloth.

APPENDIX C

DESCRIPTION OF THE COMBUSTION
FACILITIES

APPENDIX C

DESCRIPTION OF THE COMBUSTION
FACILITIES

Two laboratory-scale combustion facilities, a small one lb/hr labora-
tory test facility (LTF) and a larger Multifuel Furnace (MFF), were used during
the program and are described below.

ONE LB/HR LABORATORY TEST FACILITY

This facility consists of a coal feeder, a burner, a combustion
chamber, and a cooler as shown in the schematic of Figure C-1.

Feeder

The coal feeder, shown in Figure C-2, consists of a tubular reservoir
for coal, a double tube to supply air to the feed and remove the coal-air
suspension, a pulley and motor to slowly lift the reservoir from the air tube,
and lid mounted on the air tube. In operation, high pressure air is admitted
into the outer part of the double tube at the bottom and leaves at high velocity
through small holes near the top of the tube. This high velocity air suspends
coal particles that flow through the inner part of the double tube into
a line leading to the combustor. The motor and pulley combination lifts the
coal in the reservoir into the high velocity air jets. The lid on the dust
chamber confines the coal-air suspension to a definite volume and is necessary
for uniform feeding.

Several types of screw feeders were tried and found to be unsatis-
factory because the uniformity and control of coal feed rate was inadequate.
Screw feeders probably cannot be improved to the degree necessary for these
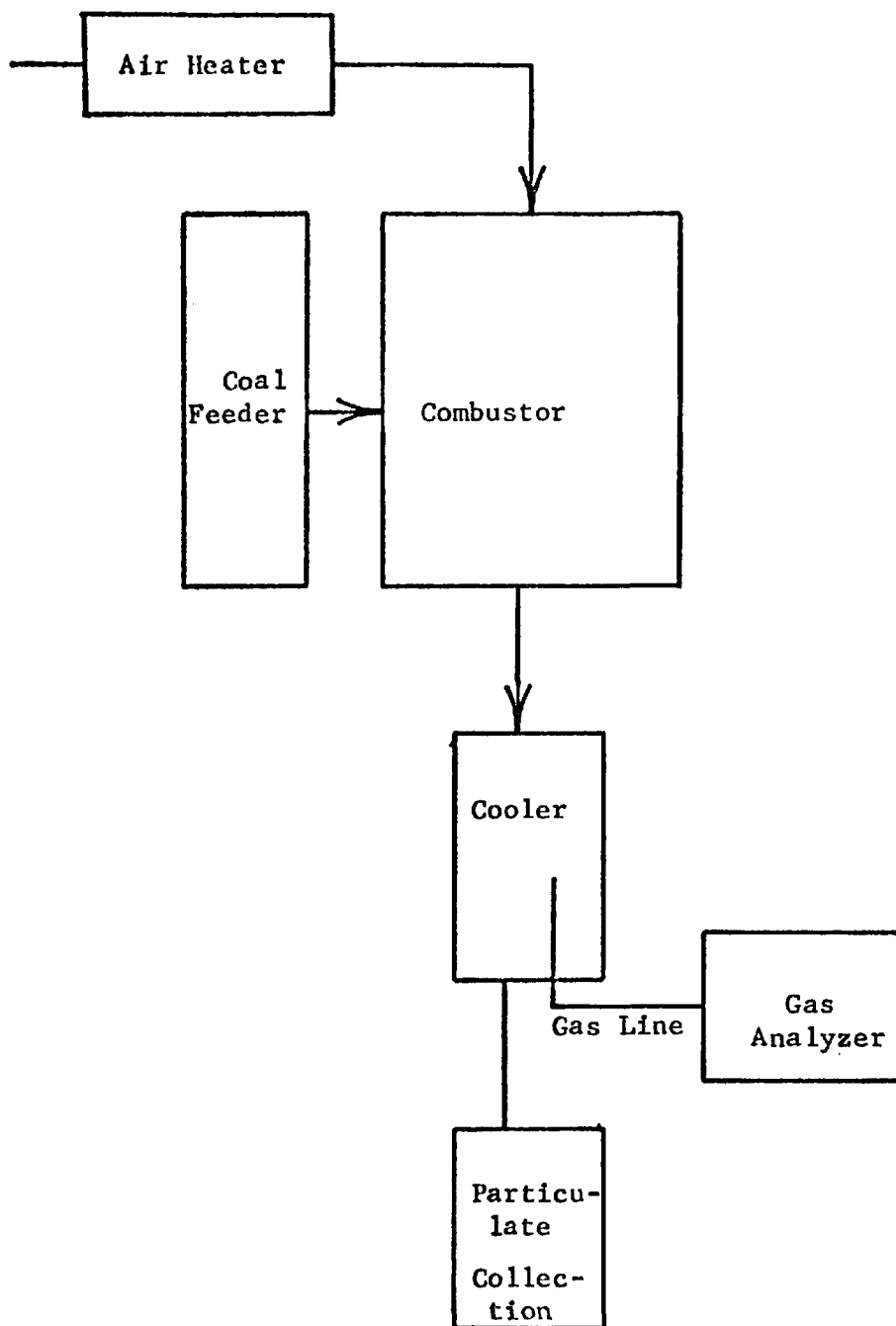
FIGURE C-1. SKETCH OF EXPERIMENTAL APPARATUS

C-3
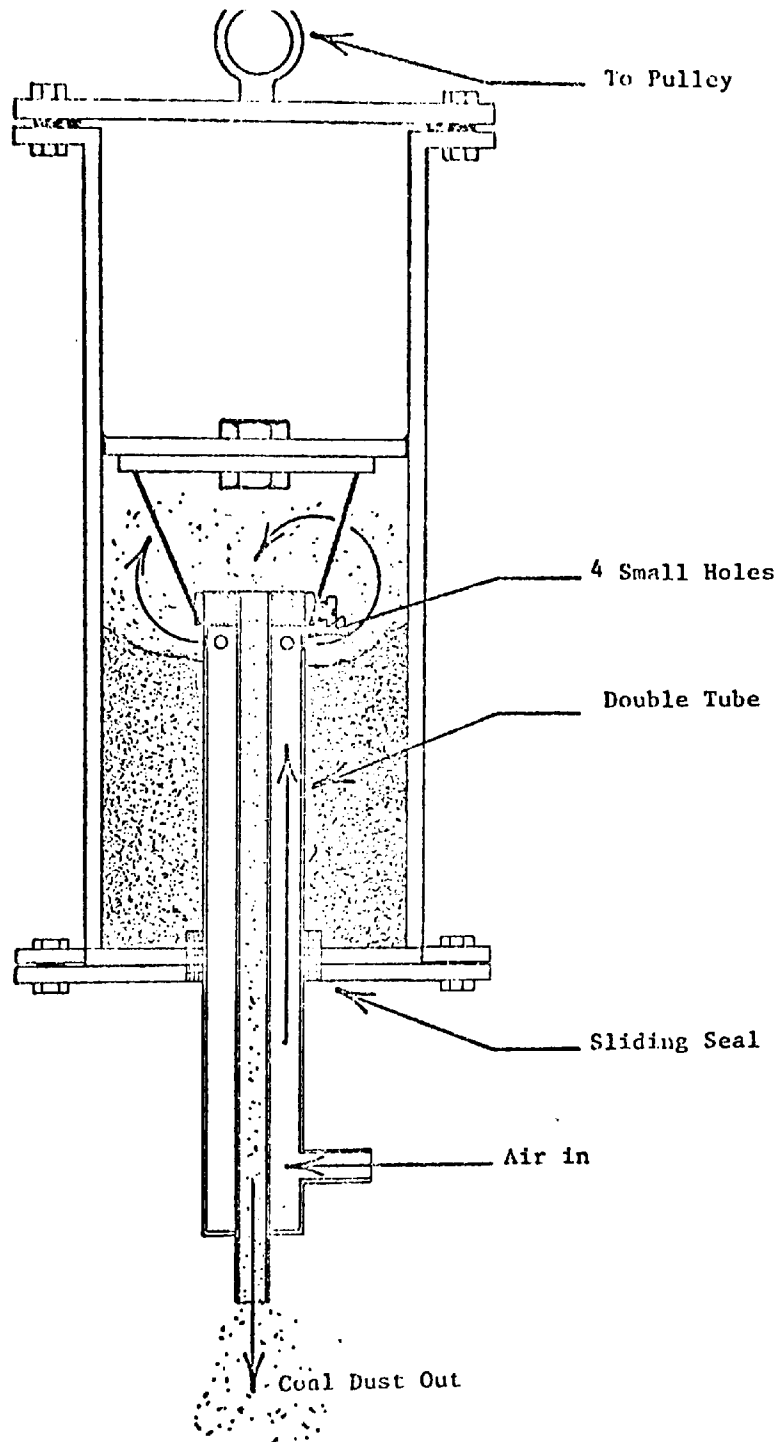
FIGURE C-2. COAL FEEDER

small-scale combustion experiments without an unreasonable amount of research. However, the new type of feeder is adequate for purposes of this program.

Burner

Figure C-3 shows a sketch of the burner. The brass burner construction is mounted on top of the combustion chamber so that when in place the tip of the burner emerges slightly into the combustion chamber.

The burner is designed to provide a tangential entry for hot secondary air which mixes with the primary air and fuel emerging from the central feed tube. The burner is cooled by air or water in a circular cooling chamber. Modifications in swirl pattern and flame can be made by adjusting the entry port of the secondary air and velocity of the mixture at the burner throat, thus giving flexibility in operation to the system. Propane was used for system warm-up prior to coal combustion.

Combustion Chamber

Figure C-4 shows a sketch of the combustion chamber. The chamber consists of inner disposable alumina tube, 2-1/2 in. I.D. and 10-in. long, which contains the flame. A wire-wound furnace tube which in turn is insulated with Fiberfrax insulation surrounds the alumina tube. The entire assembly is encased in a stainless steel housing. The tubes are supported at the ends by a piece of insulating firebricks. A platinum, platinum-rhodium thermocouple is imbedded in the furnace tube for monitoring the system temperature at all times.

During operation, the furnace is heated electrically to 1500 F; then to approximately 1750 F with propane.

Cooler

The hot combustion gases emerging from the combustor enter the cooler section. Figure C-5 shows details of the cooler and

Primary Air
& Coal Entry

Secondary
Air Entry

Cooling Air
Jacket

Swirl Chamber

Burner Throat

FIGURE C-3. BURNER

Primary Air and Coal

Secondary
Air

Burner

Furnace Tube

Enclosing Cylinder

K-30 Bricks
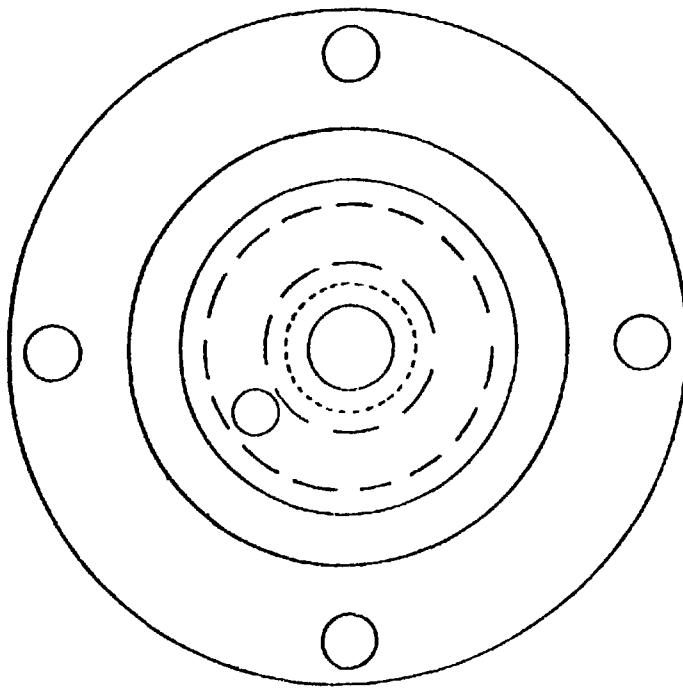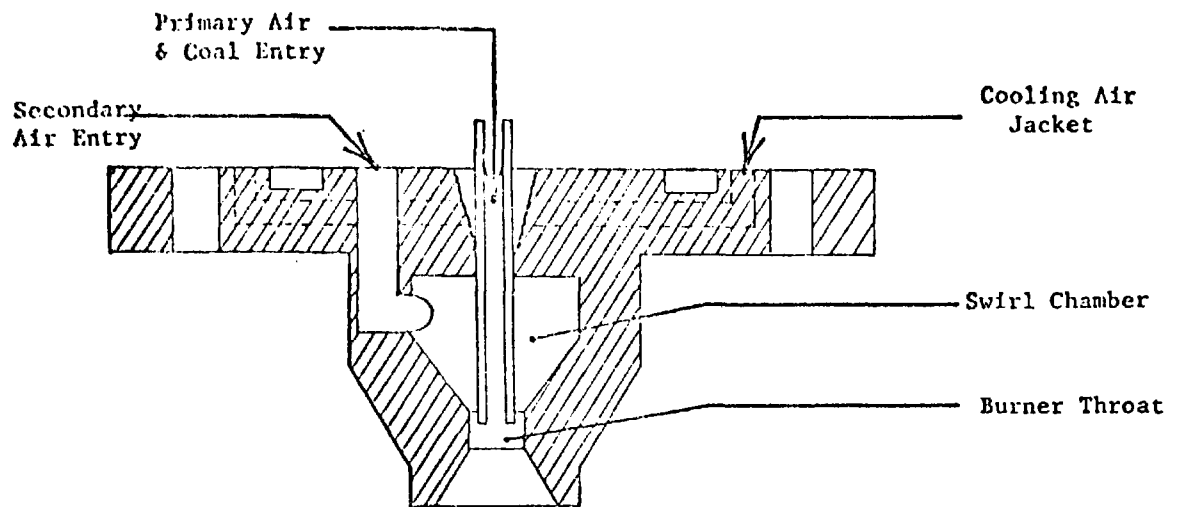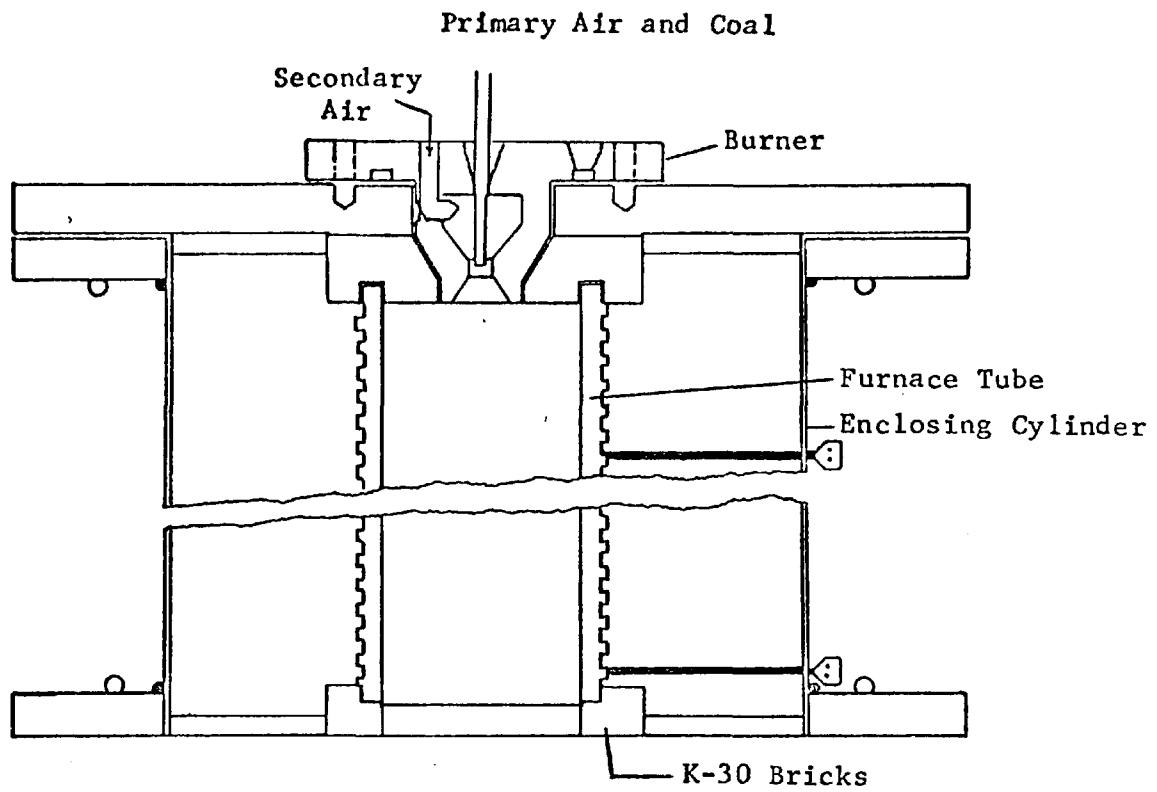
FIGURE C-4. COMBUSTION CHAMBER

Hot Gases From Combustion Chamber

Cooling Air
Entry
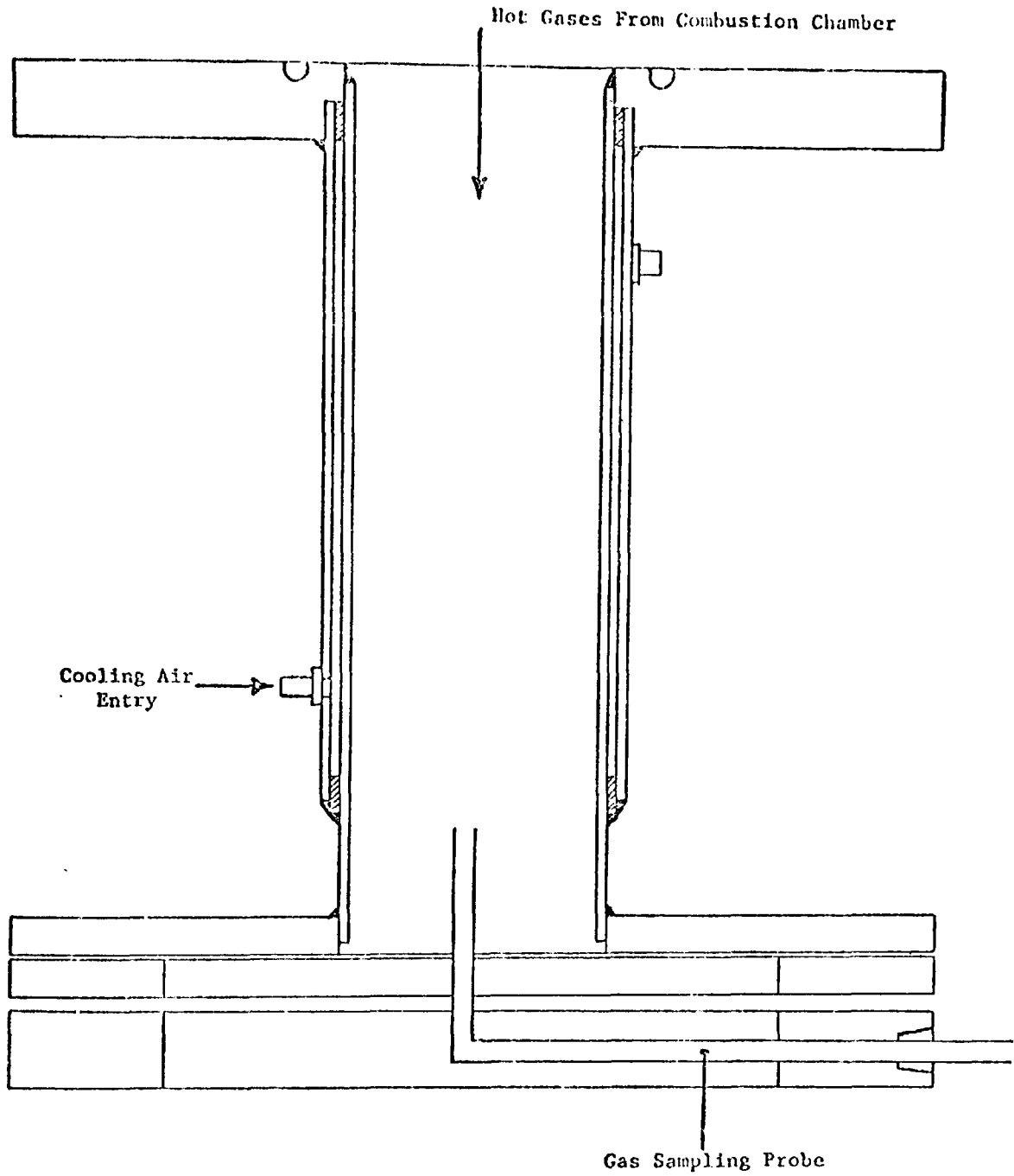
Gas Sampling Probe

FIGURE C-5. COOLER

sampling process. The cooler is a 3-in. I.D. and 5-ft long counter-current, externally air-cooled stainless steel heat exchanger. Cooling air flows upward through an annulus between 4-in. I.D. and 3-1/2-in. O.D. tube. Hot gases flow downward through the inner tube and are cooled to approximately 300 F before being sampled and exhausted to the atmosphere.

MULTIFUEL FURNACE FACILITY

The Multifuel Furnace Facility was designed to generate flue gas and fly ash under conditions closely simulating those of a power-generation station. This implies combustion at a high enough temperature with a proper cooling schedule to produce flue gas and fly ash having physicohemical properties similar to those of a typical central-station boiler and its associated stack and plume. In addition, the laboratory-scale system is flexible enough to permit firing with either pulverized coal, residual or distillate oil, or gas.

The Multifuel Furnace Facility is usually operated with an electrostatic precipitator for coal firing but without the electrostatic precipitator in firing oils. However, in this program the electrostatic precipitator was not used.

Figure C-6 is a schematic of the gas-combustion and flue-gas conditioning system with major sections indicated. The major sections of the facility are discussed below.

The Multifuel Furnace

Figure C-7 is a photograph of the Battelle-Columbus Multifuel Furnace to be used on this program. This small-scale furnace consists of a cylindrical combustion chamber approximately 17 inches in diameter by 90 inches in length. The furnace is lined with three layers of firebrick and insulation to accommodate surface temperatures up to 2900 F. At the outlet, the diameter of the
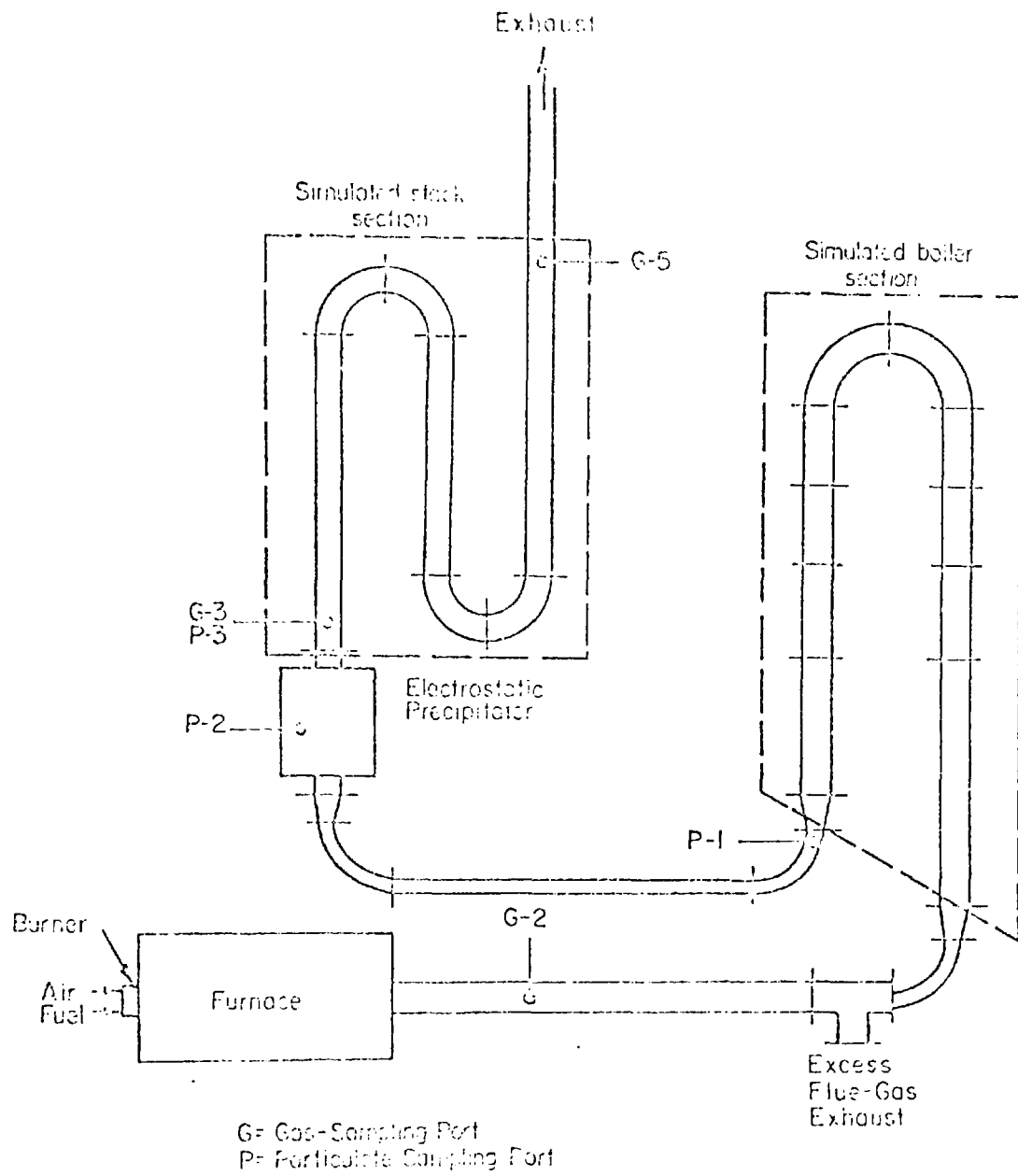
FIGURE C-6. SCHEMATIC OF LABORATORY FLUE-GAS
CONDITIONING SYSTEM
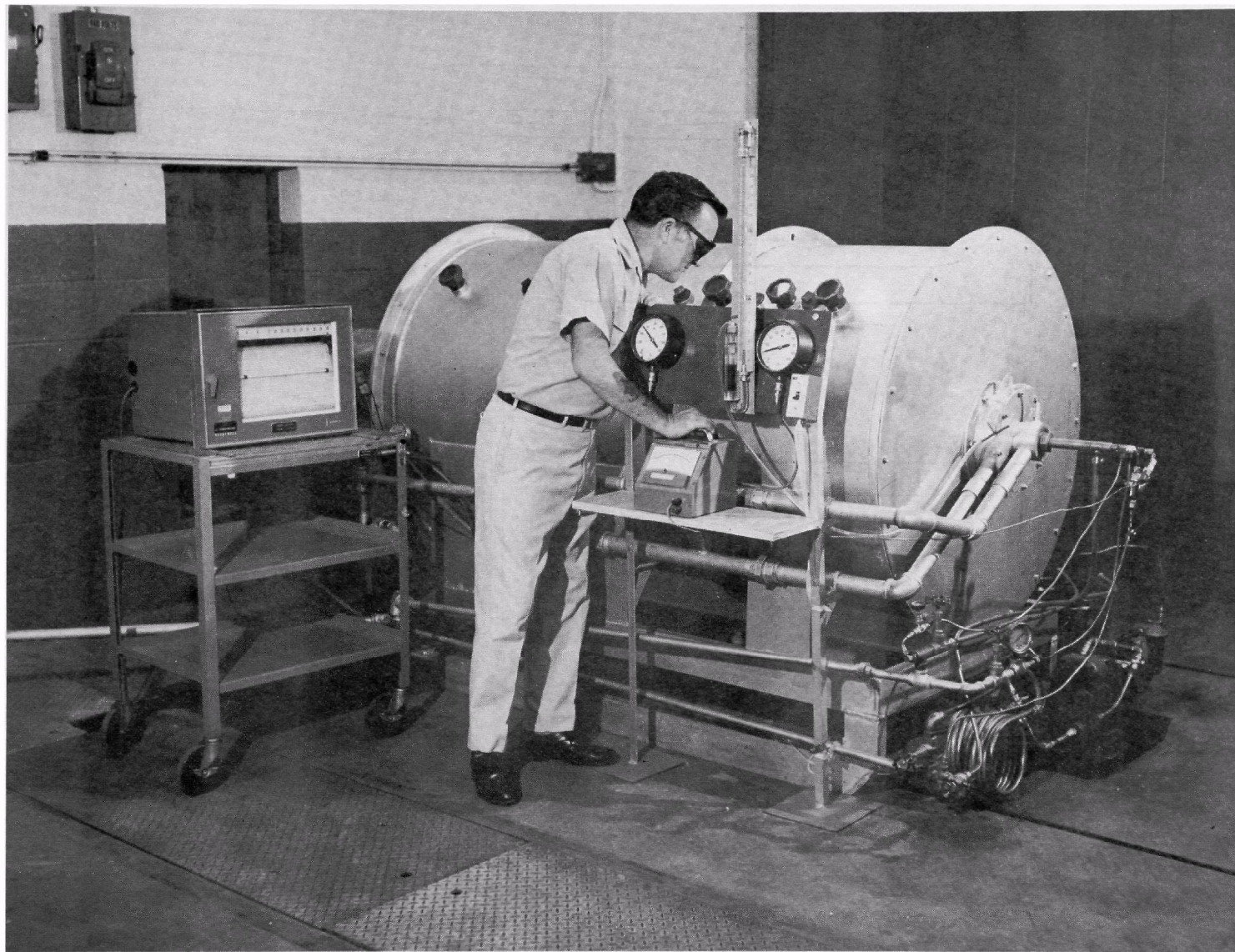
FIGURE C-7. BATTELLE MULTIFUEL FURNACE

furnace is reduced to 5 inches to enclose the flame, provide for normal re-circulation, limit radiation losses, and provide sufficient gas velocity to keept fly ash suspended in the gas stream. Viewpoints along the axial dimension of the furnace provide for visual access during periods of adjustment of firing conditions.

In normal operation of the furnace, natural gas is fired to maintain system temperatures at approximately the desired levels on a more or less continuous basis while runs are not being made. Upon switching to either coal or oil firing, the entire system is allowed to equilibrate for several hours before any data are taken.

An adjustable-flow, positive-displacement pump that was precalibrated is used to regulate the supply of residual oil to the furnace at about 3 gal/hr, and the oil is preheated to insure the desired viscosity at the burner nozzle. With coal firing, a dispersion of the fuel in air is fed to the burner (at a rate of 20 to 80 lb/hr) via a screw feeder mounted within a pressurized coal hopper.

Furnace temperatures can be controlled by varying the firing rate. However, when the firing rate is varied, the residence time varies also. If it is ever determined to be necessary, a minor modification could be made to the furnace to permit cooling surface (water-cooled loops) to be inserted into the furnace to absorb heat and, thus, permit independent control of firing rate and furnace wall (and combustion) temperatures. This approach has been successful in previous studies with an early furnace of similar design.

Burner Design

To meet the special requirements of the furnace, it was important that the burner be flexible enough to permit operation over a range of conditions.

Figure C-8 is a cross-section drawing of the burner that was designed for this furnace.

Mounting plate

Coal Nozzle

Coal nozzle is adjusting axially

Air-tight seal

3-1/2"

2-7/8" ID x 0.3-1/2" OD plug

Cast refractory

9"

Axial air

Swirl air

(24) holes, 1/4" diam

2-3/4

12 vanes 2-/4" x 3/4" opening 0.5" or less
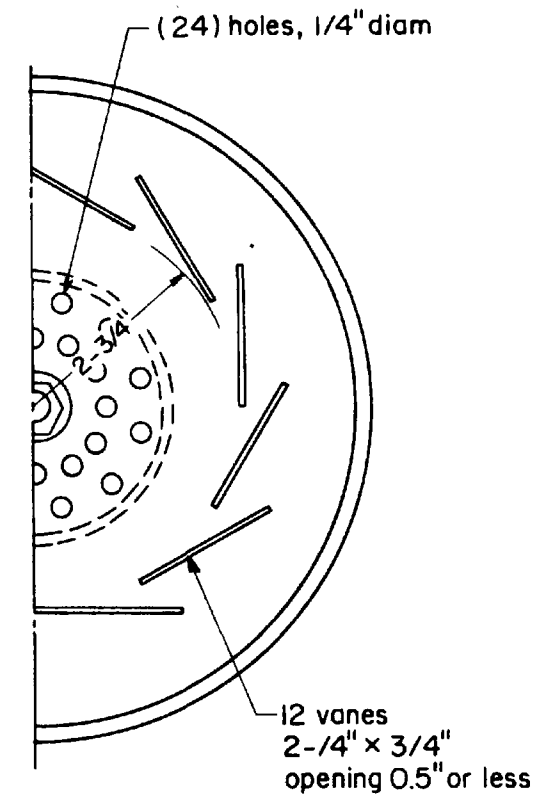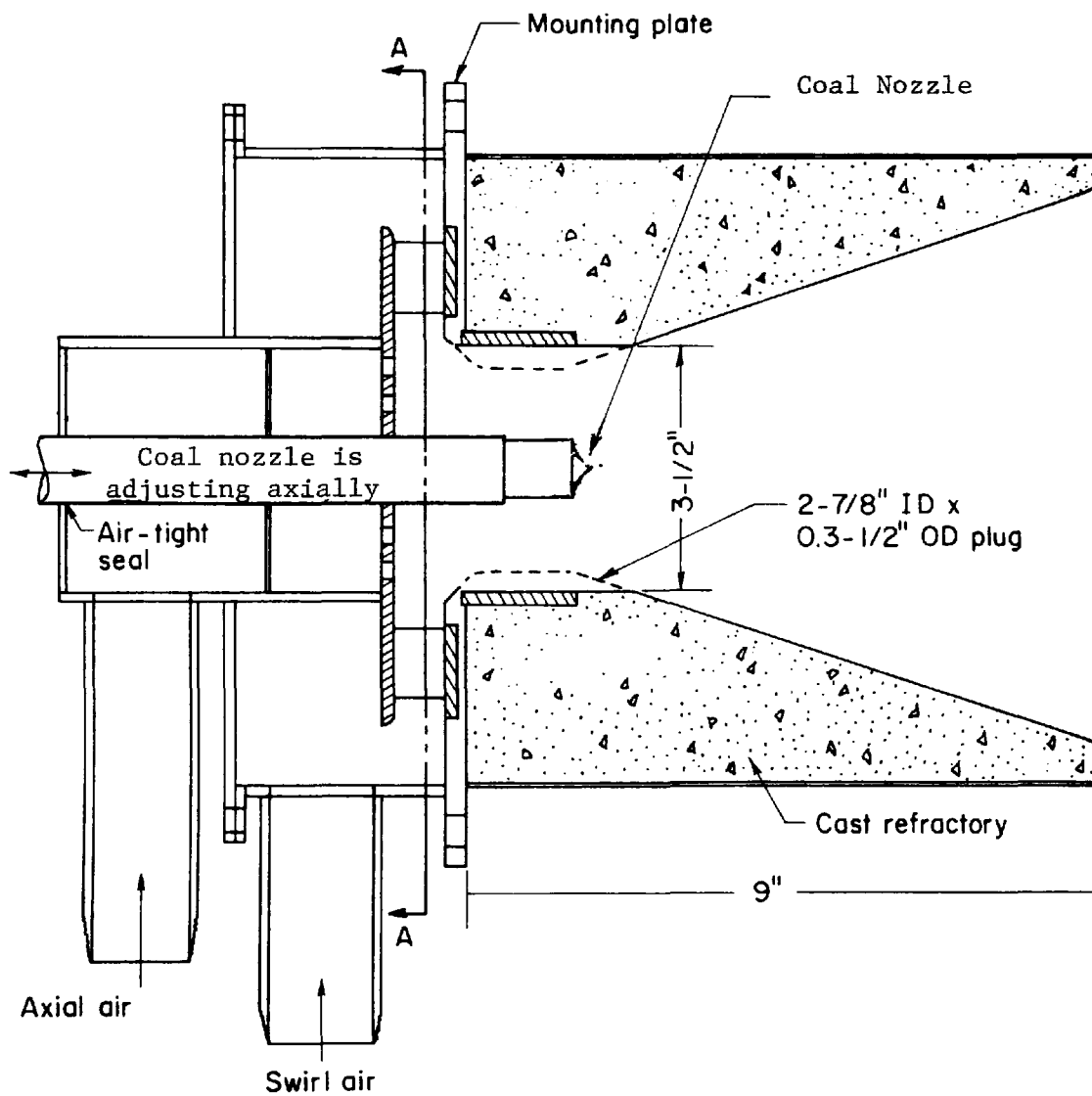
View A-A
Detail of swirl vanes

FIGURE C-8.   BURNER FOR BATTELLE MULTIFUEL FURNACE

This burner design permits varying the firing rate, flame velocity, swirl angle, type of fuel burner, atomizer type and size, and atomizer location relative to the air-admission path. Combustion air may be admitted through openings between 12 vanes positioned to give the air a high degree of swirl, it may be admitted through axial holes in the plate behind the burner throat (see Figure C-8) to provide axial flow, or a combination of swirl and axial air may be used. In the latter case, adjustment of the proportion of air flow to the swirl vanes and to the axial holes varies the percentage of swirl in the burner throat. Air flows to the swirl-air plenum and the axial-air plenum are separately manifolded, controlled, and measured. For coal firing, all axial air is used.

The burner throat of a 3.5 in. diameter is designed for an axial velocity of 15 fps, tp produce a large flame that will fill the furnace. This flame should simulate residence times in the flame region that are comparable to residence times in the flames of boiler furnaces.

A variety of fuel nozzles of the air-atomizing, steam-atomixing, or pressure-atomizing types may be fitted to the nozzle holder. It is possible to fire natural gas in this burner by replacing the fuel nozzle assembly with a gas injector. Pulverized coal is fired by substituting a coal nozzle for the oil atomizer. The coal nozzle requires a central cone to form a conical coal dispersion much like an oil spray.

Simulated Boiler-Economizer Section

The simulated boiler-economizer section of the rig is constructed of stainless steel pipe lined with a castable refractory material and insulated on the outside. Gas velocities in horizontal portions of this section are typically 60 ft/sec, and velocities in vertical portions are about 5 ft/sec. Temperatures drop from about 2600 F at the inlet to about 600 F or less at the outlet.

APPENDIX D

OPTICAL EMISSION AND MASS SPECTROGRAPHIC ANALYSIS

APPENDIX D

OPTICAL EMISSION AND MASS SPECTROGRAPHIC ANALYSIS

Optical emission analysis of the eight coals burned are shown in Table D-1. Mass spectrographic analysis of coal and coal ashes are shown in Table D-2 and D-3.

TABLE D-1.   OPTICAL EMISSION ANALYSIS OF THE EIGHT COALS BURNED

Run No. Element	1. Raw Martinka Coal			Wt % as Metal in Sample 2. Na-Treated Martinka			3. Raw Martinka Coal					4. Na-Treated Martinka		5. Na-Treated Martinka			6. Mix-Leach. Martinka		
	Coal	Ash	Slag	Coal	Ash	Slag	Coal	C.Ash	F.Ash	F.AshB.	Slag	Coal	C.Ash	Coal	C.Ash	Slag	Coal	Ash	Slag
Si	1-3	5-10	5-10	1	4-8	5-10	1-3	5-10	5-10	5-10	5-10	1-2	5-10	1-2	5-1-	5-10	5-10	5-10	5-10
Al	1-2	10-20	10-20	1-2	10-20	10-20	1-2	10-20	10-20	10-20	10-20	1-2	10-20	1-2	10-20	10-20	2-4	2-4	4-7
Fe	1	7-12	7-12	0-5	5-10	5-10	1	7-12	7-12	7-12	7-12	1	4-7	1	4-7	4-7	3-6	3-6	3-6
Ca	0.1	1	1	0.05	0.07	1	0.1	1	0.7	0.7	0.7	0.1	1	0.1	0.7	1	15-25	15-25	15-25
Mg	0.1	0.3	0.4	0.05	0.3	0.3	0.1	0.3	0.3	0.3	0.3	0.05	0.4	0.05	0.4	0.4	0.4	0.4	0.6
Na	0.1	0.3	0.3	0.5	5-10	10-20	0.1	0.3	0.2	0.2	0.3	0.5	5-10	0.5	5-10	8-15	2-4	2-4	3-5
K	0-5	1-2	1-2	0.1	0.5	0.5	0.5	1-2	1-2	1-2	1-2	0.1	1	0.1	0.75	0.7	<0.1	<0.1	<0.1
Ti	0.1	0.5	0.5	0.02	0.3	0.3	0.1	0.5	0.2	0.3	0.5	0.1	0.3	0.1	0.3	0.3	0.2	0.2	0.2
Zr	<0.01	0.02	0.02	<0.01	0.02	0.03	<0.1	0.02	0.02	0.02	0.03	<0.01	0.02	<0.01	0.02	0.02	0.02	0.02	0.02
Pb	<0.01	0.02	0.02	<0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	<0.01	0.02	<0.01	0.02	<0.01	0.01	<0.01	<0.01
Mn	<0.005	0.02	0.02	<0.005	0.02	0.02	<0.005	0.02	0.02	0.02	0.02	<0.005	0.02	<0.005	0.01	0.01	0.01	0.01	0.02
Ba	0.01	0.05	0.08	0.01	0.02	0.04	0.01	0.08	0.03	0.05	0.01	0.01	0.05	0.01	0.03	0.05	0.02	0.02	0.04
B	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.05	<0.01	-	-	-	-	-	-	-	--
Cr	0.01	0.1	<0.03	0.01	0.1	0.03	0.01	0.1	0.01	0.02	0.03	≤0.01	0.02	≤0.01	0.1	0.03	0.03	0.01	0.02
V	<0.01	0.02	0.02	<0.01	0.01	0.02	<0.01	0.02	0.01	0.02	0.02	<0.01	0.01	0.01	0.01	0.01	<0.01	<0.01	<0.01
Cu	0.003	0.01	0.01	0.003	0.01	0.01	0.003	0.01	0.01	0.01	0.01	<0.003	0.01	<0.003	0.01	0.007	0.005	0.005	0.01
Ni	<0.005	0.04	0.01	<0.005	0.04	0.02	<0.005	0.05	0.01	0.01	0.01	<0.005	0.05	<0.005	0.05	0.03	0.03	0.01	0.02
Co	<0.01	0.01	0.01	<0.01	0.01	0.02	<0.01	0.01	0.01	0.01	0.02	<0.01	0.01	<0.01	0.01	0.01	<0.01	<0.01	<0.01
Sr	0.01	0.03	0.05	<0.01	0.03	0.05	0.01	0.05	0.03	0.03	0.04	0.01	0.03	0.01	0.02	0.03	0.03	0.02	0.03
Sn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

TABLE D-1. (Continued)

Run No. / Element	7. Mix-Leach. Martinka F.Ash	C.Ash	9. Raw Westland (high-ash) F.Ash	C.Ash	10. Na-Treated Westland C.Ash	11. Na-Treated Westland C.Ash	12. Mix-Leach Martinka C.Ash	13. Na-Treated Westland F.Ash	C.Ash	Slag
Si	5-10	2-4	5-10	5-10	3-5	5-10	5-10	1-2	5-10	4-8
Al	4-7	1	3-6	3-6	3-6	5-10	3-5	1	5-10	2-4
Fe	3-6	1-2	3-6	3-6	3-6	3-6	4-6	1	7-12	5-10
Ca	15-25	4-7	1	1	1	1-2	15-25	0.1	1	0.2
Mg	0.6	0.1	0.4	0.4	0.4	0.5	0.5	0.03	0..	0.08
Na	3-5	1	0.3	0.3	8-12	10-15	3-6	<0.1	0.5	<0.1
K	0.3	0.1	1	1	0.5	1	0.1	<0.1	0.1	0.2
Ti	0.3	0.1	0.3	0.3	0.2	0.3	0.3	0.03	0.3	0.1
Zr	0.02	<0.01	0.02	0.02	0.01	0.02	0.01	<0.01	0.02	0.01
Pb	0.01	<0.01	<0.01	0.01	0.01	0.02	0.01	<0.01	0.01	<0.01
Mn	0.002	<0.005	0.01	0.01	0.01	0.02	0.02	<0.005	0.02	0.005
Ba	0.04	0.01	0.04	0.04	0.02	0.04	0.03	<0.01	0.03	0.01
Cr	0.02	<0.01	0.01	0.02	0.03	0.03	0.01	<0.01	0.03	0.01
V	<0.01	<0.01	0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01
Cu	0.05	0.02	0.005	0.01	0.005	0.01	0.005	<0.003	0.03	0.005
Ni	0.02	0.005	0.01	0.02	0.03	0.03	0.01	<0.005	0.02	0.005
Co	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sr	0.03	0.01	0.03	0.03	0.03	0.04	0.04	<0.01	0.02	0.01
Sn	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
B			0.03	0.03	<0.01	<0.01	<0.01	<0.01	0.03	0.03

Run No. Element	15. Raw Westland Low Ash			16. Raw Martinka		17. Na-Treated Martinka		18. Mix-Leach. Westland			20. Na-Treated Westland			22. Raw Westland low Ash			
	Coal	C.Ash	F.Ash	F.Ash	C.Ash	F.Ash	C.Ash	Slag	C.Ash	F.Ash	Coal	C.Ash	F.Ash	Raw Coal	Slag	C.Ash	F.Ash
Si	1-2	5-10	4-8	5-10	5-10	4-6	4-6	5-10	5-10	5-10	1	5-10	5-10	1	10-15	4-6	4-6
Al	1	5-10	2-4	5-10	5-10	2-4	3-5	2-4	2-4	2-4	0.7	3-6	4-7	0.7	10-20	3-5	3-5
Fe	1	7-12	5-10	4-8	5-10	1	1	5-10	4-6	5-10	1	5-10	5-10	1-2	10-20	3-5	3-5
Ca	0.1	1	0.2	0.3	0.4	0.2	0.3	20-40	20-40	20-40	0.3	2-3	1-2	0.05	1.2	0.3	0.3
Mg	0.03	0.1	0.08	0.1	0.2	0.1	0.1	0.3	0.3	0.3	0.03	0.3	0.3	0.03	0.3	0.1	0.1
Na	<0.1	0.5	<0.1	<0.1	0.1	1-3	1-3	<0.1	0.5	0.5	1	5-8	3-6	≤0.1	0.3	0.1	0.1
K	<0.1	0.1	0.2	0.1	0.5	0.3	0.3	0.1	0.3	0.1	0.1	1	1	0.1	2-3	1	1
Ti	0.03	0.3	0.1	0.2	0.3	0.1	0.1	0.1	0.1	0.1	0.03	0.3	0.3	0.03	0.3	0.1	0.1
Zr	<0.01	0.02	0.01	0.01	0.02	<0.01	<0.01	0.01	0.01	0.01	<0.01	0.02	0.02	<0.01	0.03	<0.01	≤0.01
Pb	<0.01	0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	0.01	<0.01	<0.01	<0.01	<0.01
Mn	<0.005	0.02	0.005	0.005	0.01	0.005	0.005	0.01	0.01	0.01	<0.005	0.01	0.01	<0.005	0.01	<0.005	<0.005
Ba	<0.01	0.03	0.01	0.03	0.04	0.01	0.01	0.02	0.02	0.02	<0.01	0.03	0.03	<0.01	0.06	0.03	0.02
Cr	<0.01	0.03	<0.01	<0.01	0.02	0.01	0.01	<0.01	0.01	<0.01	<0.01	0.03	0.01	<0.01	0.01	0.01	<0.01
V	<0101	0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01
Cu	<0.003	0.03	0.005	0.005	0.01	0.003	0.003	0.005	0.005	0.005	<0.003	0.01	0.02	<0.003	0.01	0.005	0.01
Ni	<0.005	0.02	0.005	0.005	0.01	0.005	0.005	0.01	0.01	0.01	<0.005	0.02	0.02	<0.005	0.01	0.005	<0.005
Co	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sr	<0.01	0.02	0.01	0.02	0.03	0.01	0.01	0.02	0.02	0.02	0.01	0.03	0.03	<0.01	0.04	0.02	0.01
Sn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
B	<0.01	0.03	0.03	0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.02	0.02

TABLE D-1. (Continued)

Run No. Element	23. Raw Martinka			24.Acid-Leach. Westland			25. Mix-Leach. Martinka			Repeat	26. Acid-Leach. Westland		27. Acid-Leach. Westland		28. Acid-Leach Westland		29. Mix-Leach. Westland (dehydrated lime)		
	Slag	C.Ash	F.Ash	Coal	C.Ash	C.Ash	Coal	C. Ash	F. Ash	P. Ash	C.Ash	F.Ash	C.Ash	F.Asn	C.Ash	F.Ash	Slag	C.Ash	F.Ash
Si	10-15	5-10	5-10	0.3	2-3	1-2	2-4	5-10	5-10	5-10	5-10	4-6	4-6	4-6	4-6	4-6	4-6	4-6	4-6
Al	5-10	4-6	3-5	0.03	0.7	0.3	1	3-6	2-4	4-6	1	0.5	0.5	0.7	1-2	1	2-3	1-2	2-3
Fe	5-10	4-6	3-5	0.6	5-10	4-6	1	5-10	5-10	4-6	10-15	10-15	5-10	10-15	10-15	15-25	5-10	3-5	5-10
Ca	0.5	0.4	0.3	0.003	1	0.2	5-10	20-40	20-40	20-40	3-5	0.5	1	0.8	4-6	1	20-40	20-40	20-40
Mg	0.3	0.2	0.2	0.02	0.2	0.1	0.1	1	1	0.3	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.3	0.4
Na	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3	2-3	1-2	1-2	0.3	0.2	0.2	0.2	0.5	0.2	1-2	1	1
K	1	0.5	0.5	-	0.1	0.1	-	0.5	0.3	0.2	0.2	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2
Ti	0.3	0.3	0.2	0.03	0.2	0.2	0.06	0.2	0.2	0.3	0.2	0.2	0.2	0.3	0.3	0.4	0.2	0.1	0.2
Zr	0.02	0.01	<0.01	-	0.01	0.01	-	0.01	0.01	0.01	0.0e	0.02	0.02	0.03	0.002	0.04	0.01	<0.01	0.01
Pb	<0.01	<0.01	<0.01	-	0.01	<0.01	-	0.01	0.01	<0.01	0.02	0.01	0.01	0.01	0.01	0.01	<0.01	<0.01	<0.01
Mn	0.01	0.005	0.005	<0.005	0.005	<0.005	<0.005	0.01	0.01	<0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.02
Ba	0.06	0.04	0.03	<0.01	0.02	0.02	0.01	0.04	0.04	0.03	0.03	0.03	0.02	0.03	0.03	0.1	0.01	0.01	0.01
Cr	0.01	0.01	<0.01	-	0.03	0.01	-	0.01	0.01	0.01	0.1	0.01	0.03	0.01	0.1	0.03	0.01	0.01	0.01
V	0.01	0.01	<0.01	-	-	-	-	-	-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	0.005	0.005	0.02	-	0.006	0.003	-	0.006	0.006	0.01	0.1	0.03	0.03	0.02	0.03	0.03	0.01	0.01	0.01
Ni	0.005	0.005	0.005	-	0.01	0.005	-	0.01	0.01	<0.01	0.04	0.01	0.02	0.01	0.05	0.02	<0.01	<0.01	<0.01
Co	<0.01	<0.01	<0.01	-	<0.01	<0.01	-	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	0.01	<0.01	<0.01	<0.01
Sr	0.05	0.03	0.02	-	<0.01	<0.01	-	0.03	0.03	0.02	0.02	0.01	0.01	0.01	0.01	<0.01	0.02	0.01	0.02
Sn	<0.01	<0.01	<0.01	-	-	-	-	-	-	-	<0.01	<0.01	<0.01	<0.01	-	-	-	-	-
B	<0.01	0.01	0.01	-	-	-	-	-	-	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
Zn										<0.1	0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1

TABLE D-2. MASS SPECTROGRAPHIC ANALYSIS OF COAL AND ASH (ppmw)
MARTINKA COALS

Element	Raw		Caustic HTT		Mixed Leachant HTT	
	Run #1 Coal	Run #3 Ash	Run #5 Coal	Run #5 Ash	Run #7 Coal	Run #7 Ash
Li	50	30	50	20	20	30
Be	5	3	3	1	1	0.5
B	100	100	20	20	10	3
F	20	10	10	20	30	5
Na	300	2000	~3%	~10%	3000	~3%
Mg	3000	~1%	2000	1000	2000	1000
Al	~1%	Major	~1%	~20%	~1%	~3%
Si	~5%	Major	~3%	~20%	~5%	~10%
P	2000	1000	2000	500	1500	200
S	~3%	1000	~5%	~2%	~1%	3000
Cl	300	100	100	100	50	100
K	~2%	2000	5000	3000	500	3000
Ca	~2%	5000	~2%	5000	~5%	~20%
Sc	5	50	2	20	10	30
Ti	3000	5000	3000	2000	5000	3000
V	300	300	100	50	100	20
Cr	200	500	100	1000	200	100
Mn	300	200	200	200	300	100
Fe	~5%	~5%	~1%	~3%	~5%	~2%
Co	300	50	200	50	300	20
Ni	1000	500	300	2000	500	300
Cu	10	30	5	30	10	20
Zn	<30	<100	<30	100	<30	10
Ga	<10	100	<10	50	<10	20
Ge	<2	<10	<2	<10	<2	<10
As	20	20	<10	20	<10	5
Se	≤30	100	≤20	30	≤30	50
Br	10	5	3	10	3	3
Rb	200	100	30	200	50	200
Sr	1000	1000	500	1000	2000	2000
Y	50	50	30	30	200	50
Zr	300	100	100	100	500	200
Nb	30	10	20	20	50	10
Mo	10	20	3	30	20	10
Ru	<1	<1	<1	<1	<1	<2
Rh	<0.3	<0.5	<0.3	<0.5	<0.5	<0.2
Pd	<3	<5	<2	<5	<3	<5
Ag	<1	2	<1	10	<1	<1
Cd	<5	<2	<2	≤2	<5	<2
In	<1	<1	<1	<1	<1	<3
Sn	5	20	1	50	100	300
Sb	1	5	<1	3	<1	2
Te	<1	<1	<1	<1	<1	<1
I	3	2	<1	2	<1	0.2

Continued

TABLE D-2 (Continued)

Element	Raw		Caustic HTT		Mixed leachant HTT	
	Run #1 Coal	Run #3 Ash	Run #5 Coal	Run #5 Ash	Run #7 Coal	Run #7 Ash
Cs	0.5	5	<1	20	<1	10
Ba	500	500	200	500	1000	1000
La	100	30	50	50	100	50
Ce	100	50	100	100	300	200
Pr	30	10	10	20	50	20
Nd	50	50	10	50	200	100
Sm	10	20	2	30	10	20
Eu	5	10	0.5	10	5	10
Gd	10	10	1	20	10	20
Tb	3	3	<0.3	3	≤3	3
Dy	10	10	3	10	10	10
Ho	2	.1	<1	2	3	0.5
Er	5	5	<2	5	5	3
Tm	<3	1	<3	0.5	<10	0.5
Yb	<5	10	<2	10	<10	10
Lu	<2	0.3	<0.5	<0.1	<2	0.3
Hf	<5	·2	<3	<0.5	<10	1
Ta	<10	≤1	<3	≤1	<3	<0.5
W	≤5	10	<3	20	<3	2
Re	<3	<0.2	<3	<0.2	<10	<0.2
Os	<5	<0.3	<5	<0.3	<5	<0.3
Ir	<3	<0.2	<3	<0.2	<3	<0.2
Pt	<5	<0.5	<5	<0.5	<5	<0.5
Au	<2	<0.5	<2	<0.5	<2	<0.3
Hg	<10	<1	<3	<1	<20	<1
Tl	<3	5	<3	20	<5	10
Pb	100	50	5	200	30	100
Bi	<2	1	<2	1	<2	0.3
Th	5	10	<2	20	30	20
U	20	10	<2	10	20	100

Elemental Enrichment

24+	38+	29+
28-	22-	31-
10 0	12 0	12 0

(+ increase in ash, - decrease in ash, 0 no change)

TABLE D-3. MASS SPECTROGRAPHIC ANALYSIS OF COAL AND ASH (ppmw)
WESTLAND COALS

Element	Caustic HTT Run #13A Ash	Caustic HTT Run #13C Coal	Raw Run #15A Ash	Raw Run #15C Coal	Mixed Leachant HTT Run #18A Ash	Mixed Leachant HTT Run #18C Coal
Li	12		220	0.13	86	
Be	0.6	0.15	6.0	0.35	2.6	0.17
B	59	4.7	170	25	59	3.5
F	250	89	290	53	170	110
Na	>0.5	4100	640	210	>1%	890
Mg	~1800	400	~1800	710	>0.5%	710
Al	>1%	>1%	~3000	>1%	>1%	>0.5%
Si	>1%	>1%	>1%	>1%	>1%	>1%
P	720	32	720	14	310	14
S	>1%	~2300	>0.5%	~2300	>0.5%	~2300
Cl	240	270	120	150	120	150
K	~2400	~1200	>0.5%	~2800	~2700	280
Ca	>1%	~3800	>0.5%	~1100	>1%	>1%
Sc	6.1	3.7	7.3	3.7	3.7	3.7
Ti	~1700	400	~1300	400	~1700	400
V	25	3.7	70	37	38	7.3
Cr	190	20	87	37	87	13
Mn	26	17	26	17	26	17
Fe	>1%	>1%	>1%	>1%	>1%	>1%
Co	70	8.0	25	4.0	14	8.0
Ni	230	33	46	14	99	67
Cu	78	3.9	44	3.9	120	9.0
Zn	~1700	16	40	7.3	400	73
Ga	11	0.4	5.3	1.7	2.3	0.8
Ge	1.4		3.0	0.47	3.0	0.93
As	4.1	0.46	8.7	5.9	4.1	1.4
Se	4.4		4.4	0.48	0.94	
Br	12	0.93	60	4.7	2.6	0.70
Rb	22	6.0	20	12	7.3	2.2
Sr	470	80	160	80	250	160
Y	36	9.4	29	9.4	17	16
Zr	150	10	120	24	120	24
Nb	16	1.5	9.6	3.1	6.9	6.6
Mo	3.3	0.11	3.3	2.2	1.4	0.11
Ag	0.3		0.3		0.15	
Cd	6.7	0.10	1.4	0.16	1.4	0.10
Sn	83	0.28	21	0.56	12.0	2.8
Sb	2.9	0.39	1.2	0.56	0.83	<0.39
Te	—	<0.37	--	<0.37	—	<0.37
I	8.7		5.8		0.58	

Continued

TABLE D-3 (Continued)

Element	Caustic		Raw		Mixed Leachant HTT	
	Run #13A Ash	Run #13C Coal	Run #15A Ash	Run #15C Coal	Run #18A Ash	Run #18C Coal
Cs	8.7	0.14	4.3	0.65	1.9	0.33
Ba	490	35	180	76	270	76
La	45	2.5	15	5	30	11
Ce	80	8.4	44	8.4	52	8.4
Pr	20	1.0	4.0	5.0	8.6	5.0
Nd	50	3.1	10	15	21	31
Sm	8.3	0.36	3.6	0.36	8.3	0.31
Eu	1.9		0.5		1.1	
Gd	1.6	0.70	0.69	0.40	1.4	0.35
Tb	0.95		0.54		0.54	
Dy	4.7	0.60	2.0	0.70	4.70	0.60
Ho	1.2		0.54		0.61	
Er	1.2	0.39	0.42	0.44	1.2	0.44
Tm	0.3				0.14	
Yb	7.0	<0.21	1.6	0.23	3.3	0.21
Lu	1.0		0.38		1.0	
Hf	3.7	0.2	1.8	0.20	3.7	0.16
Ta	1.3		1.9		1.4	
W	3.2	0.22	1.8	0.22	0.46	0.22
Tl	4.0		1.1	0.25	1.0	0.18
Pb	43	0.22	8.7	1.1	19	0.22
Bi	1.3		0.80		0.80	
Th	5.7	0.50	2.4	1.0	5.7	1.0
U	4.0	0.23	0.8	0.23	1.7	0.22

Elemental Enrichment

	Caustic	Raw	Mixed
-	3	6	3
+	58	55	55
0	3 0	2 0	6 0

(+ increase in ash, - decrease in ash, 0 no change)

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16. ABSTRACT The report gives results of an evaluation of: (1) the relationship of the combustion characteristics of hydrothermally treated (HTT) coals to environmental emissions, boiler design, and interchangeability of solid fuels produced by the Hydrothermal Coal Process (HCP) with raw coals currently being used as the source of energy; and (2) the conversion of solubilized coal to terephthalic acid. Results indicate that the HTT coals are clean solid fuels that, in many instances, can be burned with little or no sulfur emissions. Flue gas SO2 concentrations were well below Federal Sulfur Emission Standards for New Sources. The HTT coal was found to burn as well as or better than raw coal. Trace metals emissions should be significantly reduced because of the lower concentrations in HTT coals. Therefore, the use of HTT coal in conventional boilers and furnaces should reduce environmental pollution. HTT coals appear to be more suitable for firing in wet-bottom than in dry-bottom furnaces because of potential fouling and slagging associated with their alkali content. However, additives may possibly be used to reduce fouling and slagging. The coal solubilized during desulfurization can be converted to terephthalic acid by the oxidation-Henkel reaction. However, low yields suggest that this approach may not be economical.

17.	KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
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