FINAL REPORT

CHEMICAL REMOVAL OF NITROGEN AND ORGANIC SULFUR FROM COAL

CONTRACT NO. EHSD 71-7

17270-6007-R-00

14 MAY 1971

PREPARED FOR

THE AIR POLLUTION CONTROL OFFICE
DURHAM, NORTH CAROLINA 27701

TRW
SYSTEMS GROUP

PB 204-863

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Contract No. EHSD 71-7

by

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FOREWORD

This document constitutes the final report for the work accomplished between 27 August 1970 and 14 May 1971 by TRW Systems for the Air Pollution Control Office of the Environmental Protection Agency, under Contract EHSD 71-7 for "Chemical Removal of Nitrogen and Organic Sulfur from Coal".

This work was conducted under the technical direction of Messrs Lawrence Cramer and T. Kelly Janes of the Air Pollution Control Office, Durham, North Carolina.

The project was performed within the Applied Chemistry and Chemical Engineering Departments of the Chemistry and Chemical Engineering Laboratory, Applied Technology Division. Dr. E. A. Burns, Manager of the Applied Chemistry Department, provided line supervision and Dr. R. A. Meyers was Program Manager. Major technical contributions were provided by Drs. J. W. Hamersma, J. L. Blumenthal, C. A. Flegal and Messrs J. S. Land, M. L. Kraft and J. F. Clausen.

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1. INTRODUCTION AND SUMMARY

Approximately 30-million tons of sulfur oxides are emitted into the atmosphere yearly in the United States, and of this total, 60% of the oxides of sulfur come from coal-fired power plants. It is projected that sulfur oxide emissions will increase (in the absence of control processes) to 42-million tons in 1980 and 60-million tons in 1990, as more fossil-fuel-fired power plants are constructed to meet this country's power needs. Combustion of the sulfur content of coal (which is on the average present in equal portions as iron pyrite, FeS_2, and organic sulfur compounds) gives rise to the sulfur oxide emissions. Presently, about 4-million tons of NO_x are emitted annually from coal-fired power plants. It is generally agreed that organic nitrogen compounds contained within the coal matrix are a significant contributor to the oxides of nitrogen emission problem in coal-burning power plants.

Recently, TRW has discovered and demonstrated the principle of the basic feasibility of some exciting proprietary low-cost techniques for extracting organic sulfur and nitrogen compounds from coal without significantly altering the remainder of the coal matrix. Preliminary engineering cost analyses of the processes indicate that organic sulfur and nitrogen could be removed separately at a cost on the order of $1-1.50/ton of coal each (without byproduct credit). Further, in combining the processes, total costs could well be in the $1-1.50/ton range for organic sulfur and nitrogen removal. Under the present APCO contract, entitled "Chemical Removal of Nitrogen and Organic Sulfur from Coal", it has been demonstrated that up to 80% of the organic sulfur may be removed from coal, and it is indicated that significant quantities of nitrogen may be removed by simple liquid extraction. Heretofore, the organic sulfur and nitrogen compounds were thought to be unremovable.

The invention and laboratory investigation at TRW of processes for removing pollutants from coal was prompted by an assessment of the current technology for control of sulfur oxides, which indicated that a new approach to improve the economics of commission control was needed.

Sulfur oxide emissions from coal-fired power plants may be controlled, in theory, by one or more of the following methods:

- Burn low sulfur coal
- Remove sulfur oxides from flue gas, or
- Desulfurize coal.

The first of these options, that of burning low sulfur coal, is capable of solving only a small part of the problem, as low sulfur coal reserves are not available to utilities in sufficient quantities. Although considerable low sulfur (and low heat content) reserves are available in the western United States, it is generally agreed that transportation costs (ranging up to $20/ton) for utilizing these reserves in the east are excessive.

The second option, that of removing sulfur oxides from flue gas, is being actively investigated by the Environmental Protection Agency and the Tennessee Valley Authority. The results obtained thus far show that many problems remain to be resolved before these processes will find wide applicability for the control of sulfur oxide pollution. These include a) necessary major modifications to existing power plants, b) disposal of waste sorbents and c) high capital costs of the large size of reactors necessary for treating the dilute sulfur oxide gas streams.

The third method, that of desulfurizing coal, is under active investigation by the Environmental Protection Agency, as well as the Office of Coal Research. Three approaches are under consideration, a) deep cleaning of coal, b) solvent refining, and c) coal gasification. Deep cleaning (a physical separation), because of its low selectivity, results in a significant coal loss such that only 10-20 million tons annually out of a total United States production of 350-million tons can be economically deep cleaned. Solvent refining, a high pressure hydrogenative desulfurization and dissolution, suffers from the high capital costs of high pressure reactors and

catalyst fouling, as well as the necessity to consume hydrogen. In addition, the product (at present) still contains a significant organic sulfur content. Coal gasification (coal hydrogenative pyrolysis, under pressure, to form gaseous and liquid products and coke) is limited by high capital costs, as is the case for solvent refining. In addition, the coke or char, which often constitutes more than 50% of the original coal, contains about the same sulfur content as the starting coal. Hence, the char is not, at present, a low sulfur fuel source.

The TRW program, supported by APCO, for Chemical Removal of Nitrogen and Organic Sulfur from Coal was organized into three tasks, a) screening of solvents for removal of organic sulfur, b) screening of solvents for removal of nitrogen, and c) more detailed characterization of the extraction process and extracted coal. In addition, TRW supplemented (under its own funding) the effort for preliminary engineering analyses of processes based on the data obtained during the program, in order to direct the detailed characterization studies toward the evaluation of economically sensitive parameters.

The screening studies for the removal of organic sulfur were performed on four coals varying in total sulfur content from 1-5% and organic sulfur content from 0.6 to 2%. It was found (as determined by analyses of the coal sulfur before and after extraction) that organic sulfur could be extracted from the four coals. The solvents which were effective for removal of organic sulfur fall into two classes, a) weak organic acids, e.g. phenol, o-chlorophenol, cresol and nitrobenzene, and b) caustic solutions, e.g. aqueous or alcoholic sodium or potassium hydroxide. A summary of the screening results for these promising extraction solvents (in which the amount of removal is not optimized) is shown below.

Solvent	% Organic Sulfur Removed
Weak Organic Acids	
Phenols	17-48
Nitrobenzene	10-32
Caustic Solutions	0-28

The caustic solutions were effective on only two of the four coals which were investigated, while the weak organic acids were effective on all of the coals.

The screening studies for nitrogen removal indicate that weak organic acids and strong aqueous inorganic acids remove nitrogen from coal (according to analyses of the coals before and after extraction by the Dumas analytical procedure) as shown below.

Solvent	% Nitrogen Removal
p-cresol	39
20% HCl	32
Conc. H_3PO_4	27

The use of weak organic acids, e.g. p-cresol, to remove nitrogen is particularly attractive as nitrogen could then be removed essentially at no cost along with organic sulfur. However, analysis of the coal samples by the standard ASTM Kjeldahl analytical method for nitrogen indicated that no nitrogen had been removed from the coal samples. An assessment of these two analytical methods indicates that it is likely that nitrogen is being removed from the coal samples, and that these nitrogen compounds are probably coal-tar-base type materials which are not readily sensed by the standard Kjeldahl determination. Because of the importance of control of nitrogen oxides from fossil fuel combustion, it appears that the problem of nitrogen analysis of coal requires investigation.

The weak organic acid class of solvents was selected for detailed characterization of parameters for organic sulfur removal. In particular, the two representatives, p-cresol and nitrobenzene were chosen for their effectiveness, low cost, availability in large quantity, and resistance to attrition through oxidation or reaction. An engineering analysis indicated that organic sulfur could be removed from coal at an incremental cost of approximately $1/ton, and that important cost factors in the process were the following, a) coal particle size, b) retention volume of solvent, and c) ability to recycle solvent allowing a sulfur compound buildup in the liquid. The detailed characterization studies were then directed toward obtaining data for these parameters and also toward increasing the amount of organic sulfur removed by the solvents, as well as characterizing the extracted coal.

It was found that the amount of organic sulfur removed could be increased by the use of better solvent filtration from the coal and also by double extractions. These results are summarized below for Pittsburgh coal.

Solvent	No. of Extractions	% Organic Sulfur Removed
Nitrobenzene	1 X	77
p-Cresol	1 X	63
p-Cresol	2 X	80

It was found that coal particle size up to 1/2-inch (Pittsburgh seam) could be utilized in the process, and that the solvent (nitrobenzene) could be recycled at least three times.

These results were highly encouraging, as they indicate positive results for all of the process parameters which were investigated. However, a number of important factors remain to be investigated for accurate

assessment of the potential of the method for coal desulfurization. These factors include, a) recovery and identification of extracted organic sulfur compounds, b) regeneration of solvent by distillation, c) overall solvent losses, and d) maximum allowable sulfur compound buildup in the extraction solvent.

The detailed results of the program, conclusions and recommendations based on the results, descriptions of new technology developed in the project, and TRW supplemental engineering analyses are presented in the five sections to follow: Organic Sulfur Removal, Removal of Nitrogen, Conclusions and Recommendations, New Technology and Appendix.

2. ORGANIC SULFUR REMOVAL

This section provides the results of the laboratory effort for removal of organic sulfur from coal. The objectives were to, a) screen candidate liquids for ability to remove organic sulfur from coal, and b) characterize the process and extracted coals in more detail. In order to accomplish a more effective laboratory investigation, TRW performed a supplemental process engineering analysis prior to engaging in the process characterization phase of the program.

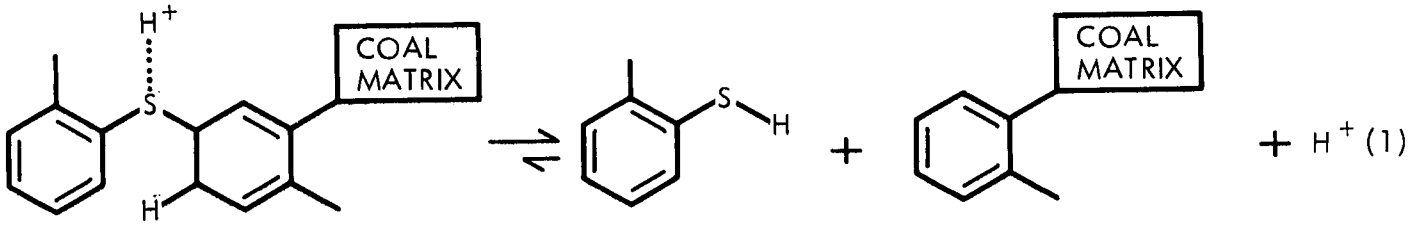
Discussions of, a) the theory associated with chemical removal of sulfur, b) the results of extraction solvent screening studies, c) an engineering analysis of a proposed process based on the experimental results, and d) the results of detailed extraction studies, are presented in the following sections.

2.1 CHEMISTRY OF ORGANIC SULFUR REMOVAL

For a number of years, chemists have studied the ability of solvents to extract compounds from coal. Hundreds of solvents have been investigated as to their dissolving power for coal (but not for removal of organic sulfur), these include mostly organics such as pyridine, tetralin, phenanthrene, anthracene oil and so on. Generally, the "solvent extractions" were run at elevated temperatures (400-800°F), extended reaction times, and very often under hydrogen pressure (400-5000 psi) which generally resulted in a total dissolution of the coal matrix. In the course of these processes, decomposition occured due to the high temperatures and in some cases due to hydrogenation of some of the bonds tying the coal polymer matrix together. In each case it was found that a nonselective "dissolution" of coal had taken place in which the main portion of coal which was extracted was actually present in the form of very fine particles, so that the composition of the extract was almost the same as the composition of the original coal.

The TRW approach to a process for removing organic sulfur from coal is based on low temperature, atmospheric pressure, acid catalyzed, depolymerization and subsequent dissolution of organic sulfur compounds from the coal matrix. The aim of this approach is to break down the coal

polymer matrix selectively at the points occupied by organic sulfur compounds without disturbing the bonding present in the major part of the coal material. Although the structure of coal has been the subject of numerous investigations, no truly concrete structural analysis is available at the present time. It is thought from pyrolysis studies that organic nitrogen heterocycles and amines, as well as sulfides, disulfides and sulfur heterocycles exist in coal. It may be postulated that the nitrogen and sulfur compounds occur in coal largely in the forms as stated above and that a part of the hydrocarbon structure of bituminous coal exists in a partially saturated or unaromatized form. Equation 1 shows a possible mechanism for the selective extraction involving an acid catalyzed decomposition of the coal matrix at the positions occupied by sulfur compounds, with aromatization shown as a possible driving force. Consequently, it is postulated that solvents which would promote the selective depolymerization and dissolution of organic sulfur compounds would be acidic in nature. It may be possible to utilize these acidic liquids in small amounts in a carrier solvent such as kerosene or gas oil.



Alternatively, the organic sulfur compounds may be considered as bonded by strong hydrogen bonds to the coal matrix. Here again, acidic liquids or those with high polarity would tend to extract the sulfur compounds away from the coal matrix provided the liquids could effectively penetrate the organic structure of the coal.

2.2 SCREENING OF EXTRACTION SOLVENTS

Five classes of solvents have been assessed for their ability to remove sulfur from coal. These are: 1) organic acids, 2) organic bases, 3) neutral organic solvents, 4) aqueous inorganic acids, and 5) aqueous caustic solutions. Since the initiation of TRW's studies in this area (including both the present contract and previous company funded efforts), a significant amount of data has been generated utilizing the above classes of solvents on four coals: Illinois No. 6, Indiana No. V, Pittsburgh and Bevier. The analyses of those coals are shown in Table 1, together with an additional coal (Lower Freeport) the extraction of which will be described in Section 2.6. The coals vary in total sulfur content from 1% to nearly 5%, and in organic sulfur content from less than 1% to near 2%. Three of the coals utilized in the screening studies were pulverized in a hammer mill to pass 200 mesh, giving average particle sizes of 1.5 - 2.0 microns, which was comparable in size to the Illinois No. 6 coal, received as pulverized for use in an Illinois power plant (see Table 2, and Figure 1).

Table 3 presents the data obtained for extraction of the four coals with organic acids (see Appendix A for experimental method). The extraction durations were selected for sequential screening and should not be taken as indicative of required contact times. Extraction temperatures normally were chosen as the boiling point of the solvent. Extractions 1-12 show that phenols, a class of weak Bronsted acids ($k_a 10^{-9}$ to 10^{-10}), are effective in removing a significant portion of organic sulfur from the four coals, in extraction batch times as low as one hour. Interestingly, o-chlorophenol was ineffective on Illinois No. 6 but was highly effective on the Pittsburgh. This may indicate the dependence of the process on the chemical and/or physical structure of coal. More effective solvents for Illinois No. 6 are p-cresol or nitrobenzene (10 and 18). These may probably be improved in sulfur removal ability on Illinois No. 6 by adjustment of extraction temperature, retention time, and as we shall show later, filtration techniques. Experiments 13 and 14 show that dilution of o-chlorophenol with methanol or concentrated HCl destroys the sulfur removal properties of that solvent. Nitrobenzene (15-18), a weak Lewis acid, is also effective for the removal of sulfur. Conversely, the strong organic acids, acetic ($k_a 10^{-5}$) and formic ($k_a 10^{-4}$) acid, do not appear to remove sulfur.

A number of organic bases and neutral organics were evaluated (Table 4) and found to be totally ineffective for the removal of sulfur.

TABLE 1. TYPICAL ANALYSES OF COALS USED FOR SCREENING STUDIES

Coal		Ash	Volatile	Fixed Carbon		Sulfur* %		Weight, %				
Bed	Location	%	%	%	Btu/lb	Total	Organic	C	H	N	Cl	O
No. 6	Randolf, Ill.	12.84	40.05	47.11	12271	3.35	1.81	68.62	4.73	1.23	0.10	9.13
No. V	Hawthorne, Ind.	9.71	40.13	50.16	13064	3.28	1.57	72.52	4.92	1.20	0.04	8.33
Pittsburgh	Bruceton, Pa.	4.76	38.65	56.59	14442	1.23	0.61	80.84	5.37	1.35	0.06	6.39
Bevier	Macon, Mo.	8.74	42.01	49.25	12710	4.75	1.95	70.57	5.05	1.17	0.02	9.70
Lower Freeport	Lecontes Mills	14.36	24.72	60.92	13095	4.13	0.43	73.05	4.16	1.23	0.15	2.92

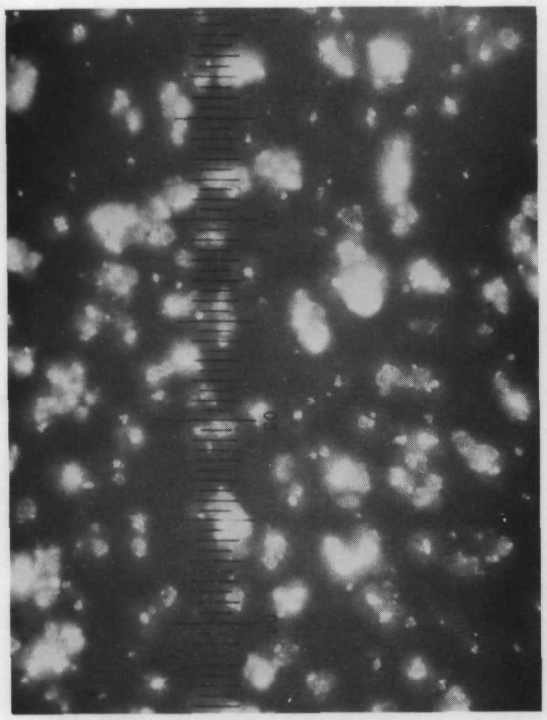
*These are typical values which varied from sample to sample.

TABLE 2. PARTICLE SIZE ANALYSIS*

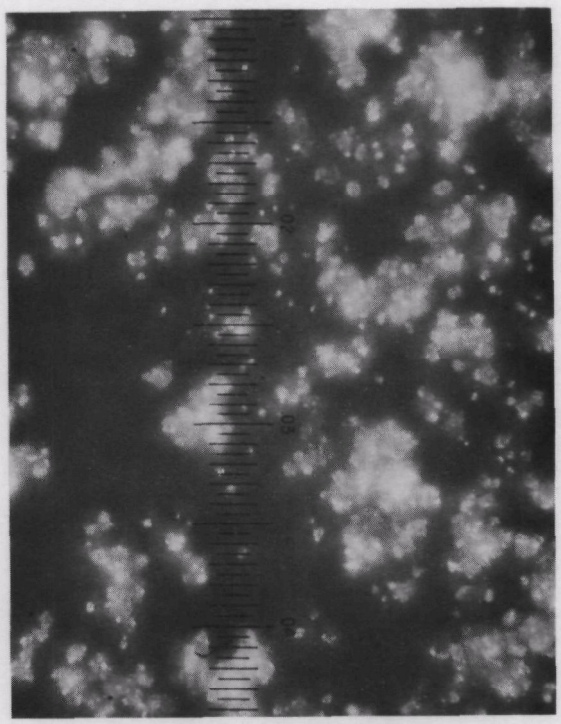
Coal Type	Average Particle Size (Microns)
Pittsburgh	2.0
Illinois No. 6	4.1
Bevier	1.5
Indiana No. V	2.0

*Average particle sizes were determined utilizing Fischer Sub-Sieve Analyzer

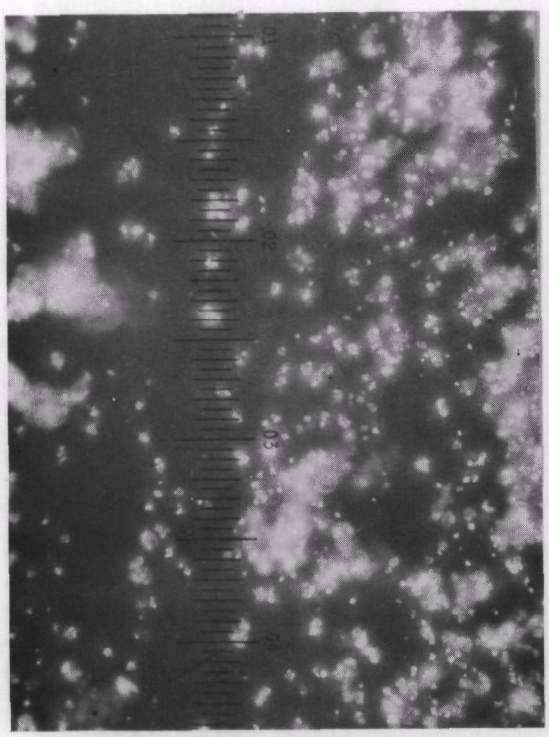
FIGURE 1. PHOTOMICROGRAPHS (400X, POLARIZED LIGHT) OF PULVERIZED COAL SAMPLES*



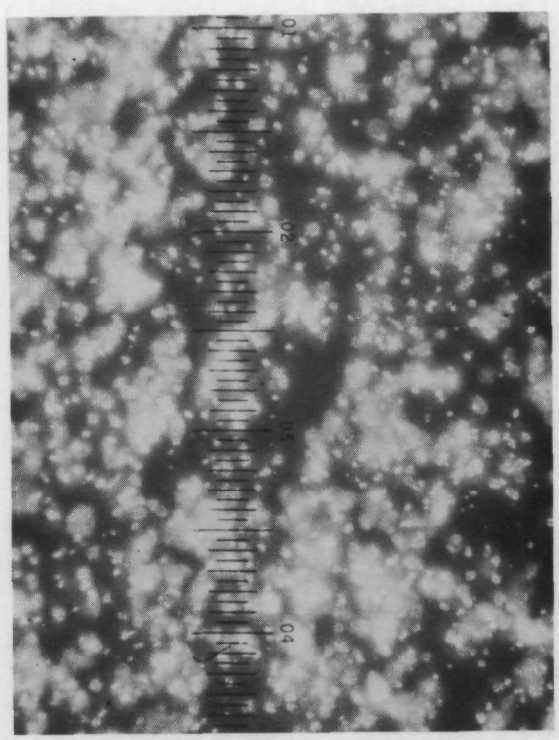
Illinois No. 6 Coal



Indiana No. V Coal



Pittsburgh Coal



Bevier Coal

*Least division = 3 microns

TABLE 3. SOLVENT SCREENING - ORGANIC ACIDS

Solvent[a,b]	Extraction Temperature °C	Extraction Duration hrs	Coal	% Sulfur After Extraction	% Sulfur[c,d] Removed	% Organic Sulfur Removed
1. o-chlorophenol	175	1	Pittsburgh	0.83	23	46
2. o-chlorophenol	175	3	Pittsburgh	0.82	24	48
3. o-chlorophenol	175	3	Indiana No. V	3.00	14	28
4. o-chlorophenol	175	3	Bevier	3.28	15	30
5. o-chlorophenol	175	1	Illinois No. 6	3.20	0	0
6. o-chlorophenol	175	0.5	Illinois No. 6	3.15	0	0
7. phenol	180	24	Bevier	3.17	18	29
8. phenol	180	3	Indiana No. V	3.12	10	20
9. p-cresol	200	3	Indiana No. V	2.76	21	47
10. p-cresol	200	1	Illinois No. 6	2.86	10	16
11. p-cresol	200	1	Bevier	3.42	11	17
12. p-cresol	200	1	Pittsburgh	0.88	19	38
13. 1:1 methanol:o-chlorophenol	65	3	Indiana No. V	3.53	0	0
14. 1:1 conc. HCl:o-chlorophenol	100	3	Indiana No. V	3.45	0	0
15. nitrobenzene	210	3	Indiana No. V	3.07	10	20
16. nitrobenzene	210	1	Bevier	3.36	13	20
17. nitrobenzene	210	1	Pittsburgh	0.91	16	32
18. nitrobenzene	210	1	Illinois No. 6	2.97	6	10
19. acetic acid	20	24	Bevier	3.82	0	0
20. formic acid	100	3	Indiana No. V	3.50	0	0

[a]Weight ratio of solvent to coal was 5:1

[b]Runs 1, 2, 7 and 19 were washed with hot water to remove adsorbed solvent, all others were washed with cold methanol. All were dried in oven to constant weight.

[c]Sulfur content was determined by the standard ASTM Eshka procedure for all samples except nos.: 2, 4, 7 and 19, which were analyzed by the Leco method.

[d]Calculations based on coal composition = organic sulfur content of 0.54% w/w and total sulfur content of 1.08% w/w for Pittsburgh coal; organic sulfur content of 1.73% w/w and total sulfur content of 3.48% w/w for Indiana No. V coal; organic sulfur content of 1.95% w/w and total sulfur content of 3.86% w/w for Bevier coal; organic sulfur content of 1.81% w/w and 3.17% w/w for Illinois No. 6 coal; all on dry basis, assuming sulfur removed is entirely organic.

TABLE 4. SOLVENT SCREENING - ORGANIC BASES AND NEUTRAL SOLVENTS

Solvent[a,b]	Extraction Temperature °C	Extraction Duration hrs	Coal	% Sulfur After Extraction	% Sulfur[d] Removed
1. pyridine	115	1	Pittsburgh	1.04	0
2. pyridine	115	24	Pittsburgh	1.07	0
3. pyridine	115	24	Bevier	3.90	0
4. pyridine	115	3	Indiana No. V	3.44	0
5. aniline	180	3	Indiana No. V	3.51	0
6. methanol	65	3	Indiana No. V	3.45	0
7. 1-methyl-2-pyrrolidone	200	3	Indiana No. V	3.44	0
8. dimethylformamide	150	3	Indiana No. V	3.45	0
9. triethylphosphite	240	1	Illinois No. 6	3.13	0
10. xylene	140	1	Illinois No. 6	3.20	0

[a]Weight ratio of solvent to coal was 5:1

[b]Runs 1-3 washed with hot water to remove adsorbed solvent, all others washed with cold methanol. All were dried in oven to constant weight.

[d]As in Table 3.

A variety of inorganic acids and bases were assessed for sulfur removal (Table 5). Caustic did not remove sulfur from the Bevier or Pittsburgh coals, but did remove sulfur from Indiana No. V (1-5). It would thus appear that the Indiana No. V and Illinois No. 6 coals may contain free organic thiols which are readily neutralized and dissolved by the caustic, while the Bevier and Pittsburgh coals contain none of these compounds. Concentrated hydrochloric acid removes sulfur from Indiana No. V, but not from Bevier (6-8). In the case of hydrochloric acid, it is possible that some of the sulfur removed is sulfate which was obtained by air oxidation of pyrites during the course of the extraction; however, it is also likely that the strong acid cleaves organic sulfides or disulfides from the coal matrix and dissolves them. Hydrobromic acid removes sulfur from Indiana No. V, Illinois No. 6 and Bevier coals (9-11), where again, a part of the sulfur removed may be inorganic in nature. Phosphoric acid appears to be ineffective for the removal of sulfur (12-14), except on long extraction time as in the case of the Illinois No. 6 coal (15). Hexafluorophosphoric acid removes sulfur (16) while sulfuric acid (17) dramatically increases the sulfur content by sulfonating the activated aromatic rings present in the coal matrix. Nitric acid, in varying concentrations, was evaluated for its ability to remove sulfur from the Bevier coal (18-22). As is well known, nitric acid removes all of the inorganic sulfur and in addition, on prolonged contact time, a small portion of the organic sulfur is also removed (18 and 19). Of course, at the same time the coal is oxidized and nitrated, hence the small amount of organic sulfur removal is not worth the price in consumption of nitric acid and modification of the coal matrix.

The type of sulfur which was removed by the two major candidate solvent types, weak organic acids and caustic from Indiana No. V coal, was determined by analysis of the total and inorganic sulfur content, before and after leaching of the coal (Table 6). For both solvents only organic sulfur is removed, as the pyrite content remained constant, while the sulfur content dropped appreciably.

The utilization of a continuous flow through method for the extraction of coal was briefly investigated using a TRW apparatus for continuously monitoring effluent sulfur content. However, it was found that coal particles tended to restrict solvent flow at extraction temperatures and this approach was discontinued (see Appendix for details).

TABLE 5. SOLVENT SCREENING - INORGANIC ACIDS AND BASES

Solvent[a,b]	Extraction Temperature °C	Extraction Duration Hrs	Coal	% Sulfur After Extraction	% Sulfur[c,d] Removed	% Organic Sulfur Removed
1. 20% Sodium Hydroxide	110	1	Bevier	3.82	0	0
2. 20% Sodium Hydroxide	110	1	Pittsburgh	1.10	0	0
3. 20% Sodium Hydroxide	115	3	Indiana No. V	2.95	15	30
4. 20% Methanolic Potassium Hydroxide	70	3	Indiana No. V	3.01	14	28
5. 20% Sodium Hydroxide	110	1	Illinois No. 6	2.98	6	10
6. 36% Hydrochloric Acid	120	24	Bevier	3.87	0	0
7. 36% Hydrochloric Acid	120	24	Indiana No. V	3.13	10	(20)
8. 36% Hydrochloric Acid	120	24	Indiana No. V	3.20	8	(16)
9. 48% Hydrobromic Acid	110	24	Bevier	3.44	11	(22)
10. 48% Hydrobromic Acid	110	3	Indiana No. V	2.72	22	(8)
11. 48% Hydrobromic Acid	110	1	Illinois No. 6	3.03	4	(10)
12. 85% Phosphoric Acid	150	20	Bevier	3.90	0	0
13. 85% Phosphoric Acid	150	3	Indiana No. V	3.45	0	0
14. 85% Phosphoric Acid	150	1	Illinois No. 6	3.21	0	0
15. 85% Phosphoric Acid	150	16	Illinois No. 6	2.92	8	(13)
16. 75% Hexafluorophosphoric Acid	20	24	Bevier	3.47	10	(20)
17. 98% Sulfuric Acid	20	1	Bevier	5.21	+35	-
18. 70% Nitric Acid	20	24	Bevier	1.43	63	(13)
19. 50% Nitric Acid	20	24	Bevier	1.47	62	(12)
20. 50% Nitric Acid	20	0.2	Bevier	1.73	55	(5)
21. 50% Nitric Acid	0	0.2	Bevier	1.74	55	(5)
22. 10% Nitric Acid	100	0.5	Bevier	1.93	50	-

[a]Weight ratio of solvent to coal was 5:1

[b]All runs were washed with water, neutralized, again washed with water and dried in oven to constant weight

[c]Sulfur content was determined by Leco procedure for all samples, except nos. 2-5, 7, 8, 10, 11, 13-15

[d](As in Table 3). Parentheses indicate that all or part of the sulfur removed may have been inorganic rather than organic. For nitric acid, the values in parentheses are the sulfur content removed in excess of the pyritic sulfur content.

TABLE 6. SULFUR FORMS IN EXTRACTED INDIANA NO. V COALS[a]

Extracted Sample	% Pyrite S Before	% Pyrite S After	% Organic S[b] Before	% Organic S[b] After	% Change in Organic S	% Change in Pyrite S
1. p-cresol-3 hr-200°C	1.73	1.78	1.75	1.00	-42	+2
2. 20% NaOH-3 hr-115°C	1.73	1.82	1.75	1.19	-31	+6

[a]Sulfate content is negligible

[b]Organic sulfur by difference

2.3 SELECTION OF EXTRACTION SOLVENTS FOR DETAILED CHARACTERIZATION

Nitrobenzene, phenols (o-chlorophenol, p-cresol and phenol), and caustic solutions all were found to remove significant quantities of organic sulfur, in short extraction times, as a result of the screening tests. Of these solvents, the phenols and nitrobenzene are more attractive candidates for the development of a process for the removal of organic sulfur from coal, as these liquids removed sulfur from all four coals which were investigated, while the caustic solutions removed sulfur from only two coals. p-Cresol appears to be the most attractive representative from among the phenol derivatives because of its effectiveness, moderate cost, availability in large quantities and thermal stability.

2.4 PRELIMINARY ENGINEERING AND ECONOMIC ANALYSIS OF A BASELINE PROCESSING SCHEME FOR ORGANIC SULFUR REMOVAL

In parallel with the current APCO Contract, TRW has funded a preliminary engineering and economic analysis of the new chemical extraction technique for selective removal of organic sulfur compounds from coal. This initial work was aimed at:

- Defining a baseline processing scheme which utilizes standard unit operations and conventional hardware.
- Determining those aspects of the baseline scheme which will have the greatest impact on the processing costs.
- Defining key laboratory experiments in the cost sensitive areas which will help to determine the processing economics better and point the direction to minimize processing costs.

Figure 2 presents a baseline processing scheme for extraction of the organic sulfur compounds from coal with p-cresol, although the treatment applies also to nitrobenzene (with minor modification, i.e. slight boiling point difference, lower cost). For purposes of calculation, 100 tons per hour of organic sulfur compounds (containing 1.2 tons/hour of sulfur)

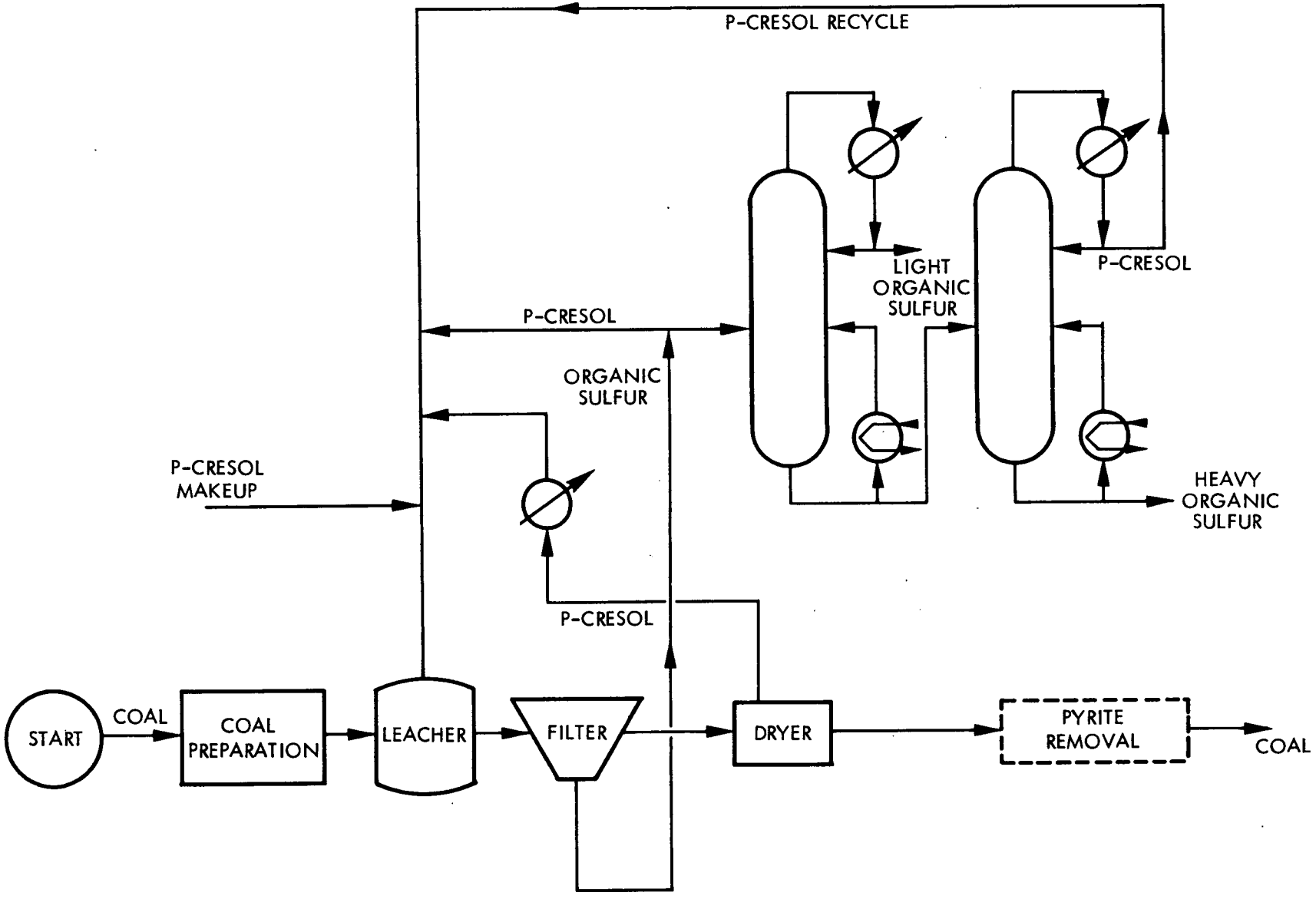


Figure 2. Process Diagram for Organic Sulfur Removal From Coal

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extracted from the coal. The baseline process can be divided into four primary sections or operations as follows:

- Leaching
- Filtering
- Coal drying and solvent recovery
- Distillation

In the leaching section makeup plus recycled cresol solvent is contracted with pulverized coal in 20,000 gallon stainless-steel stirred reactors (three to five units if retention time 0.5 hr and 5 tons solvent/ton coal) which are insulated and heated to 200°C. The leaching solution chemically separates the organic sulfur compounds from the coal matrix and dissolves them in the cresol solvent. Rotary vacuum disk filters are used to separate the bulk of the cresol solution from the coal. The cresol solution is recycled to the leacher, while the wet coal filter cake is transferred to a drying and solvent recovery unit.

Continuous, indirect heated, rotary, steam tube dryers are used to evaporate off the residual cresol which remains with the coal after filtering. Laboratory experimentation has shown that depending on particle size the coal entering the dryer may contain from 0.1 to 1.0 tons of absorbed cresol per ton of coal. This residual cresol solvent is evaporated from the coal and carried by a stream of nitrogen gas to a condenser where it is condensed and recycled to the leaching unit.

In order to remove the dissolved organic sulfur compounds from the leaching solvent, part of the cresol recycle stream is fed to the distillation section. In the distillation section, 4 tons per hour of organic sulfur compounds are separated from the cresol solvent. The fraction of the cresol recycle stream which must be fed to the distillation unit will depend upon the allowable buildup of dissolved sulfur compounds in the leaching solution. It is of course desirable to allow the sulfur compounds to buildup in the cresol recycle stream to the highest possible value (commensurate with not interfering with the extraction process) so that

the feed to the distillation section is minimized. For purposes of calculation, it was assumed that 50% of the organic sulfur compounds boil above p-cresol and 50% boil below p-cresol. Two distillation columns are used. The first column separates the light organic sulfur compounds from the p-cresol and heavy sulfur compounds and the second column separates the heavy organic sulfur compounds from the cresol. In sizing the distillation columns it was assumed that the heavy organic sulfur compounds were equivalent to thionaphthene (bp 220°C) and that the light organic compounds were equivalent to thiophene (bp 84°C).

Capital and operating costs for each of the four major sections of the baseline processing scheme were investigated parametrically and the results are summarized in Figures 3-8.

Figure 3 shows the effect of coal residence time in the leaching section on the operating, capital, and labor costs (based on ¢/ton of coal). Although the total cost of operating the leaching section is a function of residence time, the cost differential between fifteen minute residence time in the leacher and two hour residence time is only about 10¢ per ton of coal.

Figure 4 shows the rate at which recycled cresol solution must be fed to the distillation unit as a function of the allowable buildup of sulfur compounds in the cresol recycle stream. Operating costs for the distillation unit are also plotted in Figure 4 as a function of feed rate to the distillation column. Capital costs of the distillation unit as a function of feed rate are presented in Figure 5. It is apparent from Figures 4 and 5 that the operating and capital costs in the distillation section are strongly dependent on the maximum allowable buildup of sulfur compounds in the cresol recycle stream. In order to keep the operating costs within reasonable bounds a sulfur compound buildup of 10% or more in the cresol recycle solution is required. Although experimental data for the actual extracted compounds is not yet available, the solubility in cresol of many of the compounds which are expected to be extracted from the coal is high and hence it appears likely that a sulfur compound buildup of 10% or greater is possible.

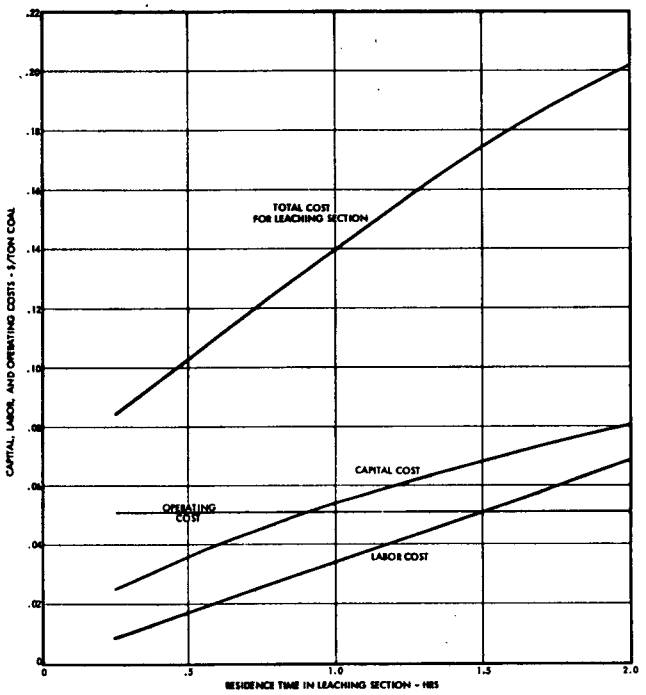


Figure 3. Leaching Section Costs vs Residence Time

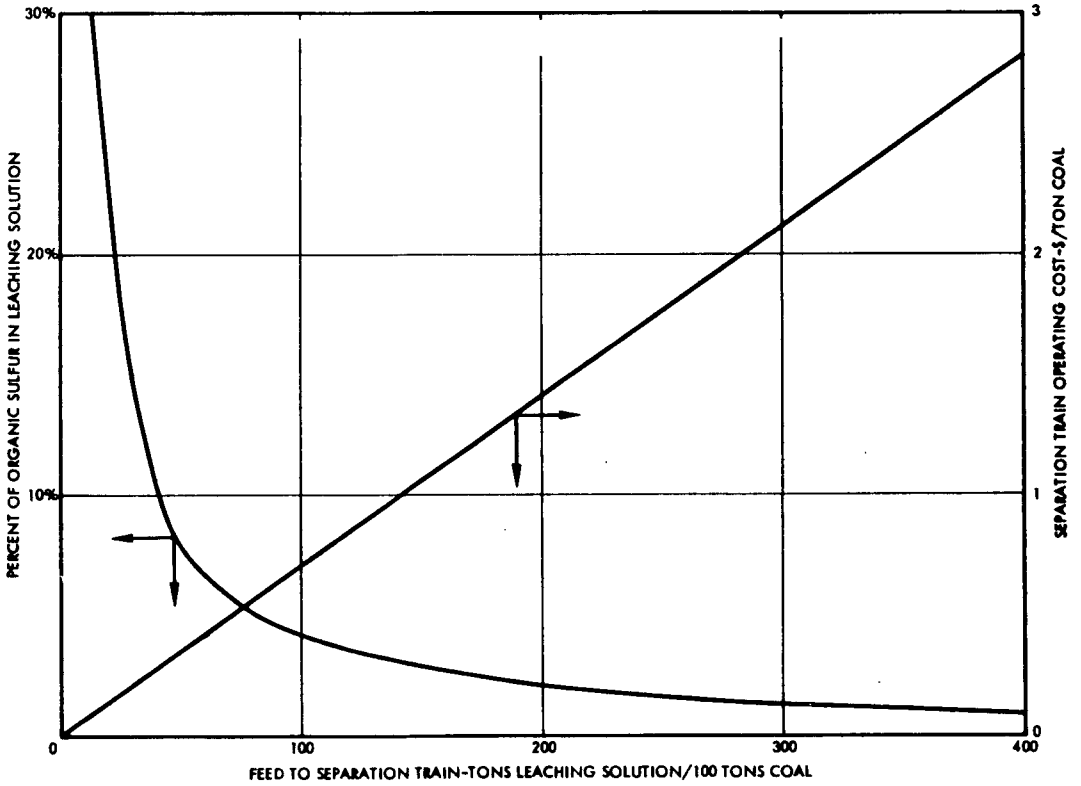


Figure 4. Separation Train Feed and Operating Costs as a Function of Allowable Sulfur Compound Buildup in the Leaching Solvent

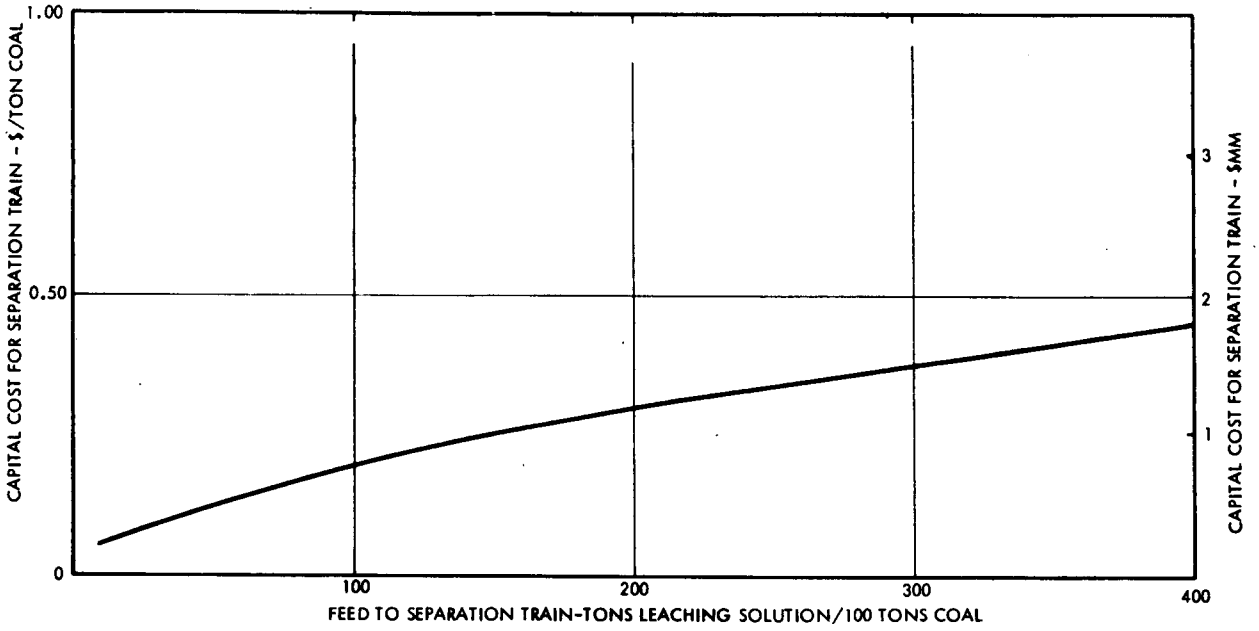


Figure 5. Capital Cost for Separation Train as a Function of Feed Rate to Distillation Units

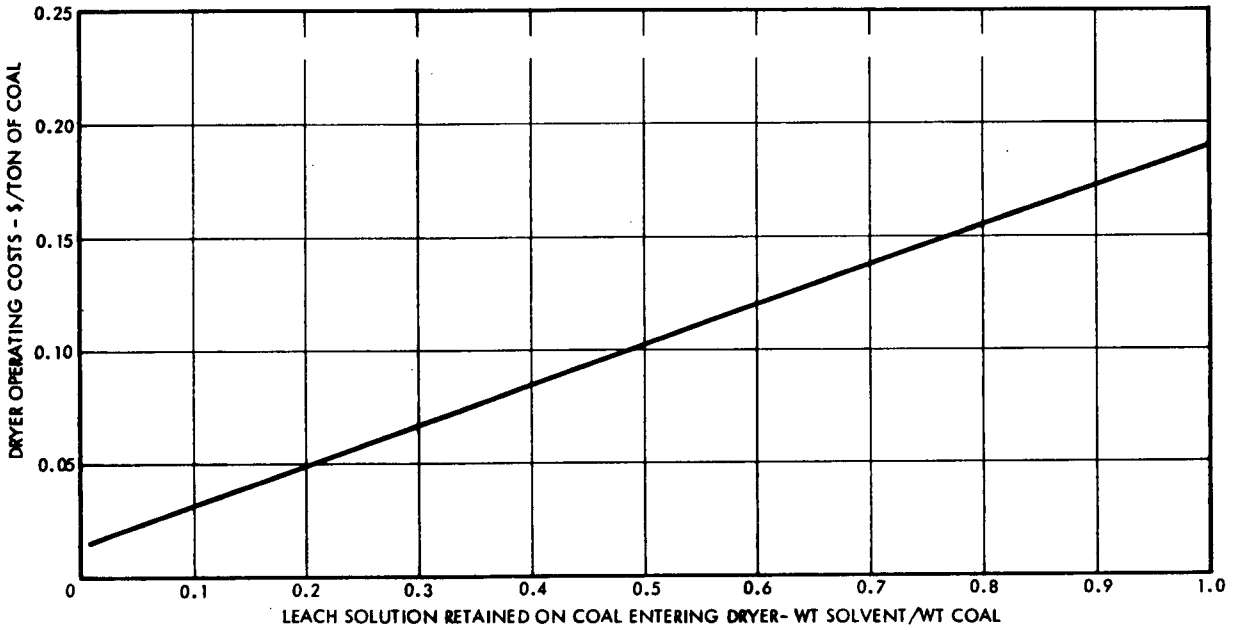


Figure 6. Dryer Operating Cost as a Function of Solvent Retained on Coal After Filtering

Operating and capital costs for the drying section are shown as a function of the cresol solution retained on the coal entering the dryer in Figures 6 and 7 respectively. It is apparent from Figures 6 and 7 that the drying costs will differ significantly depending on the amount of cresol retained on the coal after filtering. Laboratory tests have shown that cresol retention after filtering depends very strongly on particle size. -200 mesh coal was found to retain from 0.75 to 1.00 tons of solvent per ton of coal after filtering, while -14 mesh coal retained only 0.1 to 0.2 tons of solvent per ton of coal. Therefore, from the point of view of minimizing the costs in the drying section there is a great advantage to utilizing larger particle size coal. The question which remains to be answered, is how particle size effects the rate of leaching of the sulfur compounds from the coal. The best tradeoff must be established between maximizing sulfur removal and minimizing processing costs.

In Figure 8, the cresol solvent makeup cost is plotted as a function of the percentage of cresol recovery in the drying section. It is apparent from Figure 8, that a high degree of cresol recovery is required in order for the process to be economical. This is based on an expense of 10¢/lb for cresol solvent. It is possible that cresol acts as a catalyst in the separation of the sulfur compounds from the coal matrix and hence only small amounts may be required. Thus it could be possible to use a leaching solvent which consists of a small amount of expensive cresol dissolved in a large amount of very cheap carrier solvent such as kerosene or gas oil. The function of the carrier solvent would be to dissolve the organic sulfur compounds after they were severed from the coal matrix by the cresol. If this type of a low cost combination leaching solvent proves to be feasible, the requirement for a high degree of solvent recovery in the drying section would be considerably reduced.

Table 7 summarizes the estimated capital, operating, and labor costs (based on ¢/ton of coal) for an example case together with the primary assumptions used in the cost estimate. No credit was taken for the sulfur compounds which were extracted from the coal nor was any credit taken for the energy released in the condensation of evaporated solvent. Three operating positions are assumed in calculating the labor costs. A value

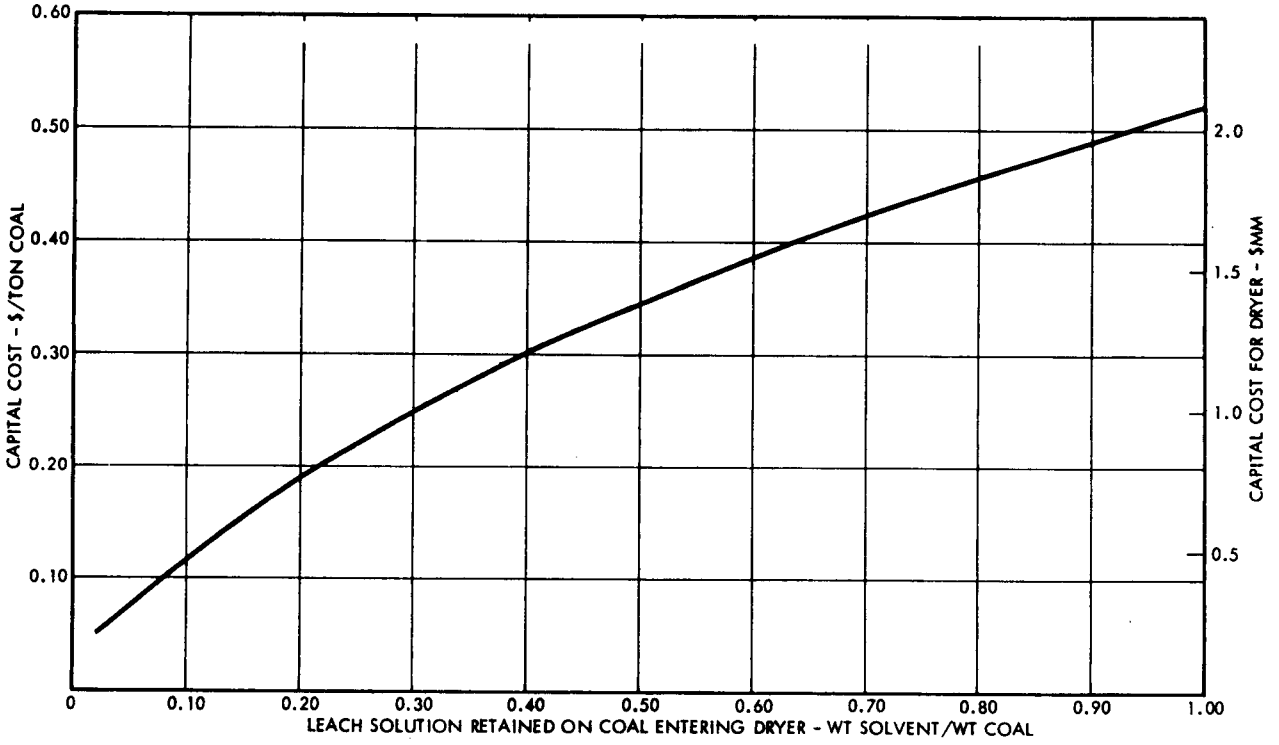


Figure 7. Dryer Capital Cost as a Function of Solvent Retained on Coal After Filtering

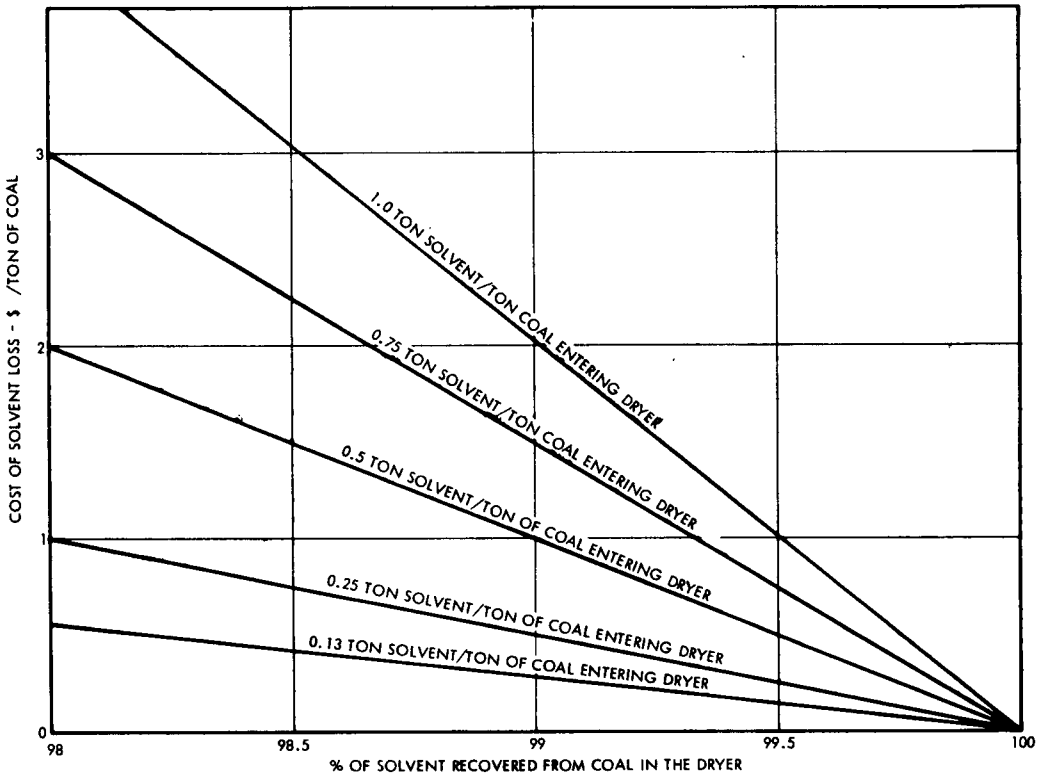


Figure 8. Solvent Makeup Cost vs % of Solvent Recovered from Coal in the Dryer

Table 7. Example Case for Organic Sulfur Removal Process

DESIGN BASIS: 100 TONS COAL/HR
1.2% WT ORGANIC SULFUR REMOVED FROM COAL (4 TON/HR OF ORGANIC SULFUR COMPOUNDS)

	¢/TON COAL		
	CAPITAL COST	OPERATING COST	LABOR
LEACHING SECTION	3.6	5.1	1.8
• 5:1 Wt Basis P-cresol to Coal			
• 0.5 Hr at 330°F			
• 30% Wt Solubility of Organic Sulfur Compounds in P-cresol			
FILTRATION SECTION	2.1	0.2	7.0
• 0.50 Tons of Leach Solution Retained Per Ton of Coal After Filtering			
DISTILLATION SECTION	6.0	10.0	8.7
• Two Distillation Units Required to Separate Light and Heavy Organic Sulfur Compounds from P-cresol			
• 0.14 Tons of Leaching Solution Fed to Separation Train per Ton of Coal			
COAL DRYING AND P-CRESOL RECOVERY SECTION			
DRYING	34.0	10.2	3.5
SOLVENT LOSS	-	29.0	-
• 99.7% of Solvent Recovered from Coal in Dryer			
SUBTOTAL	45.7	54.5	21.0

TOTAL COST FOR ORGANIC SULFUR REMOVAL: $1.21/TON COAL

of 0.5 tons of cresol solvent retained on the coal per ton of coal entering the dryer was assumed, although, laboratory data shows that 0.25 ton retention is the actual value for 1/2-inch coal. Capital costs were depreciated on a 10% per year basis with an additional 10% per year added for taxes, maintenance, etc.

From Table 7, it is seen that without byproduct credit, a conservative estimated cost of removing organic sulfur from a ton of coal is $1.21.

2.5 DETAILED CHARACTERIZATION

The screening studies indicated that it was technically feasible to remove varying amounts of organic sulfur compounds from all four coals which were investigated, utilizing p-cresol or nitrobenzene. It was the objective of the detailed characterization studies to, a) determine the maximum amount of organic sulfur which can be removed by the above two solvents, b) obtain preliminary data relating to important engineering cost parameters identified in Section 2.4, and c) characterize the extracted coal.

Studies for increasing the amount of organic sulfur removal were based on improving extraction techniques to maximize the amount of solvent filtered away from the coal, utilizing double extractions and adjustment of retention time.

The preliminary engineering and economic analysis for the removal of organic sulfur utilizing an organic solvent was performed in order to define clearly economically important process parameters for laboratory investigation. The process which was designed consists of (1) coal leaching, (2) coal-solvent filtration, (3) solvent distillation to remove sulfur compounds and (4) solvent recycle (see Figure 2).

The following were shown to be important cost factors: coal particle size, retention volume of solvent remaining in coal after filtration, and the ability to recycle the extraction solvent several times and allow a high sulfur compound buildup. It would be desirable to be able to utilize the largest possible coal particle size in a process for the removal of organic sulfur because, (1) fine mesh coal cannot be shipped by rail so that a coal desulfurization plant is limited to a location adjacent to a power plant

(note: -200 mesh is the size normally used for a pulverized coal-fired power plant), (2) fine mesh coal is difficult to filter on an industrial scale, and (3) the solvent retention on fine particles tends to be greater than on larger particles. The retention volume of solvent on coal must be minimized, as any solvent retained not only limits the amount of organic sulfur which may be removed by liquid-solid partition, but must be vaporized in the drying step of the process. Finally, it is critical to the economics of a process for the leaching of organic sulfur from coal, that the allowable buildup of organic sulfur compounds in the leach liquid be high (i.e., multiple recycle of solvent), so that only a minimum amount of extraction solvent need be sent to the distillation columns for separation on each pass.

The experimental results of the assessment of each of the above factors, as well as additional studies on heat content and coal analysis are presented in the following sections: Studies for Increase in Sulfur Removal, Assessment of Critical Engineering Economic Parameters and Extracted Coal Characterization.

2.5.1 Studies for Increase in Sulfur Removal

In contrast to the screening studies, the coal samples were not washed with water or methanol to remove residual solvent, but instead the residual solvent was vaporized from the coal (see Appendix for details). This procedure more closely approximates the envisioned process steps (Figure 2) and seems to lead to somewhat higher sulfur removal.

The effect of extracting coal twice with p-cresol is shown in Table 8. It can be seen that two extractions remove considerably more organic sulfur than was removed by one extraction alone. The removal of 80% of the organic sulfur from the Pittsburgh coal was particularly encouraging as this is far higher than has been obtained previously.

The effect of varying retention time from 0.5 to 3 hr. is shown in Table 9. The screening technique of water washing residual solvent was utilized for these runs, giving lower amounts of organic sulfur removal. No obvious change was observed in the amount of sulfur removed as a function of retention time. The apparent increase in sulfur removal for 0.5 hr extraction of Pittsburgh coal over 1.0 hr extraction is within experimental error for the

TABLE 8. SINGLE AND DOUBLE PASS EXTRACTIONS WITH P-CRESOL[a]

Coal[b]	No. of Extractions	% Sulfur After Extractions	% Organic Sulfur[c] Removed	% Total Sulfur[c] Removed
Bevier	1 X	2.69, 2.71	29	15
Bevier	2 X	2.32, 2.31	54	27
Pittsburgh	1 X	0.82, 0.86	63	32
Pittsburgh	2 X	0.73, 0.74	80	40

[a]Extraction with 5 vols/wt solvent to coal for 1 hr at 200°C, filtered, then dried to constant wt @ 150°C/20 min

[b]Particle size = -200 mesh

[c]Bevier: total sulfur = 3.10%, organic sulfur assumed = 1.6%
Pittsburgh: total sulfur = 1.23%, organic sulfur = 0.61%

TABLE 9. EFFECT OF RETENTION TIME ON REMOVAL OF SULFUR WITH p-CRESOL[a]

Coal[b,c]	Retention Time Hrs	% Sulfur After Extraction	% Organic Sulfur Removed	% Sulfur Total Removed
Indiana No. V	3	2.76	42	21
Indiana No. V	0.5	2.80, 2.78	39	20
Pittsburgh	1	0.99	39	19
Pittsburgh	0.5	0.87, 0.89	57	28

[a]Extraction with 5 vols/wt solvent/coal for 1 hr @ 200°C, filtered, washed several times with hot water on filter, then dried to constant wt @ 100°C/20 mm.

[b]Particle size = -200 mesh.

[c]Indiana No. V: total sulfur = 3.48%, organic sulfur = 1.95%.
Pittsburgh: total sulfur = 1.23%, organic sulfur = 0.61%.

Eshka sulfur analysis method*. Thus, it appears that p-cresol penetrates the coal organic matrix very rapidly (on a scale of minutes) and rapidly dissolves organic sulfur compounds. Similar results were obtained during the screening studies for the extraction of Pittsburgh coal with o-chlorophenol (at 1 hr, 46% removal, and at 3 hrs, 48% removal), in which there was no significant difference in organic sulfur removal (Table 3).

A series of experiments were performed on the Lower Freeport coal in order to assess the ability of p-cresol and nitrobenzene to remove organic sulfur in retention times as short as 15 minutes (Table 10). Normally, the Lower Freeport coal analyzed 4-4.1% total sulfur with approximately 0.4% organic sulfur (Table 1). However, during the course of these experiments it was found that the analyses performed by Commercial Testing Company began to give highly variable sulfur content for each unextracted sample sent for analysis and, in addition, where replicates were run, the variance was greatly above that normally obtained with the ASTM method. Thus, although the sulfur analyses of the extracted Freeport coals were lower than those for most of the unextracted samples, which were run by Commercial Test Company, no firm interpretation can be made.

This variance may be due to a sampling problem, or difficulty in the sulfur analysis method for this particular coal. This type of problem is of great importance in assessing the results obtained for the treatment of coal by any process for the removal of sulfur, and should be investigated further.

2.5.2 Assessment of Critical Engineering Parameters

The effect of varying the particle size of Pittsburgh coal is shown in Table 11. The organic sulfur removed decreased somewhat for nitrobenzene extracted coal, in going from -200 mesh pulverized coal to 1/2-inch pieces, while the solvent remaining sorbed on the coal decreased dramatically in

*Duplicate determinations on the same sample with same operator should not differ by more than 0.05% for sulfur contents of 2% or less. For different samples, the difference is 0.1%. Hence, for a 1.2% Pittsburgh coal, there is no significant difference between the 1.0 and 0.5 hr samples.

TABLE 10. EXTRACTION OF -14 MESH LOWER FREEPORT COAL[a]

Solvent[b]	Retention Time Hrs	% Sulfur After Extraction
p-Cresol	0.25	3.00
p-Cresol	0.25	2.83
p-Cresol	0.50	2.96
Nitrobenzene	0.25	2.97
Nitrobenzene	0.50	3.01, 3.03
Nitrobenzene	1	2.75, 2.77

[a]Starting Lower Freeport coal analysis had changed from a normal 4.13% sulfur to give the following chronological results on separate samples from the same container: 4.00, 3.37, 3.40 (2.97 on repeat) 3.13, 3.00, 3.04 (the average of all of these being 3.27).

[b]Extraction with 5 vols/wt solvent/coal @ 200° and 210°C, respectively for p-cresol and nitrobenzene filtered, then dried to constant wt @ 150°C/20 torr.

TABLE 11. EFFECT OF PARTICLE SIZE ON EXTRACTION OF SULFUR FROM PITTSBURGH COAL

Solvent[a]	Particle Size	Solvent % by wt on Coal Before Drying	% Sulfur After Extraction	% Organic Sulfur Removed	% Total Sulfur Removed
Nitrobenzene	-200 Mesh[b]	200	0.78	72	36
Nitrobenzene	-14 mesh[c]	85	1.29	31	13
Nitrobenzene	1/2 inch[c]	25	1.17	48	20
p-Cresol	-200 mesh[b]	90	0.84	63	32
p-Cresol	-14 mesh[c]	85	1.44	0	0
p-Cresol	1/2 inch[c]	60	1.43	0	0

[a]Extraction with 5 vols/wt solvent/coal for 1 hr @ 200° and 210°C, respectively for p-cresol and nitrobenzene, filtered, then dried to constant wt @ 150°C/20 torr

[b]Pittsburgh coal sample : total sulfur = 1.23%, organic sulfur = 0.61%

[c]Pittsburgh coal sample: total sulfur = 1.48%, organic sulfur = 0.63%

going to larger size coal*. In the case of p-cresol, it appears that organic sulfur may be removed only when the coal is pulverized to the -200 mesh range, at least for Pittsburgh coal. It should be noted that the analyzed sulfur content of the unextracted Pittsburgh coal increased from 1.23 to 1.48% during the latter part of these experiments (one sample analyzed 1.60%). It would be very desirable to design a process based on the extraction of half-inch range coal, as the plant could be set up either at a mine face or at a power plant, filtration is extremely facile and it would be necessary to vaporize a relatively small amount of solvent from the coal in the drying step. The engineering analysis (Section 2.4, Figures 5, 6, and 7) shows that the results obtained for nitrobenzene leach of 1/2-inch coal, 0.25 ton solvent/ton coal, would reduce process operating costs (e.g., $0.06/ton of coal operating costs, $0.23/ton of coal capital costs for the dryer section). By contrast, the example case (Table 7) assumed 0.50 tons solvent/ton coal leading to a higher dryer section cost than may be the case. It should be noted that extraction of the 1/2-inch coal resulted in fragmentation (as a result of the swelling action of the nitrobenzene) so that the dried coal was approximately 1/8-inch particle size.

It is important for the economic utility of the process (Figure 4) that the leach solvent be capable of multiple recycling so that the organic sulfur buildup in the solution may reach at least 10% without necessity of sending the liquid to the separation train. In order to get a first cut in the evaluation of this factor, a sample of nitrobenzene was utilized three times for extraction of fresh Pittsburgh coal (Table 12). It was found that the organic sulfur removal decreased after the first cycle but remained constant into the third cycle indicating that organic sulfur buildup may be allowed to continue to some reasonable concentration. A calculation based on the measured amount of organic sulfur removal, assuming that the sulfur compounds are modeled after benzothiophene, indicates a roughly 1% buildup of organic sulfur compounds in the nitrobenzene after the third cycle. This

*The apparent increase in sulfur removal in going from -14 mesh to 1/2-inch is within experimental error for the Eshka procedure.

TABLE 12. EFFECT OF MULTIPLE RECYCLES OF NITROBENZENE SOLVENT ON SULFUR REMOVAL FROM PITTSBURGH COAL[a,b]

Solvent Cycle	% Sulfur After Extraction	% Organic Sulfur Removal[c]	% Total Sulfur Removed[c]
1	0.76	77	38
2	0.97	43	21
3	0.95	46	23

[a]Extraction with 5 vols/wt solvent to coal for 1 hr @ 210°C, filtered, then dried to constant wt @ 150°C/20 min

[b]Particle size = -200 mesh

[c]Total sulfur = 1.23%, organic sulfur = 0.61%

is, of course, far short of that which will need to be measured during the course of process development studies, e.g. about 10 times this number of recycles will have to be obtained.

2.5.3 Characterization of Extracted Coals

The heat content of the coals should not appreciably change as a result of extraction of organic sulfur compounds. Typically, where 0.5% of the total sulfur is removed, and this sulfur is borne on molecules of the type of benzothiophene (about 2.5% of the organic matrix is removed), the ash to organic ratio would remain about constant and hence, the heat content should not change. A number of heat contents were determined before and after extraction and these are shown in Table 13. The Bevier and Lower Freeport coals showed no measurable heat content change, while the Illinois No. 6 decreased slightly and the Pittsburgh had a mean decrease of 5%. These heat losses are probably due to a small amount of coal oxidation during drying.

Detailed analyses of some extracted coals were obtained for cresol, nitrobenzene and o-chlorophenol extraction (Table 14). It is difficult to interpret the slight changes which can be noted in these analyses compared with those in Table 1 for unextracted samples, as it has been shown that the sulfur content of the Pittsburgh and Lower Freeport coals tends to vary significantly according to the sample, hence it can be anticipated that the ultimate and proximate analyses of the starting coals also vary according to the particular sample. As the analyses reported in Table 1 (which were obtained near the beginning of the program) cannot be definitely assigned as those of the unextracted coals for the particular extractions reported in Table 14 (obtained near the end of the program), no meaningful treatment of data can be made at this time.

TABLE 13. EFFECT OF SOLVENT TREATMENT ON HEAT CONTENT OF COALS

Coal	Solvent[a]	Retention Time Hrs	Heat Content Before Btu	Heat Content After Btu	% Heat Content Change
Illinois No. 6	Nitrobenzene	1	12271	11961	-2
Bevier	p-Cresol	1	12710	12670	0
Bevier	Nitrobenzene	1	12710	12660	0
Pittsburgh	p-Cresol	1	14354	13662	-5
Pittsburgh	o-Chlorophenol	1	14165	12416	-12
Pittsburgh	Nitrobenzene	1	14165	13654	-4
Pittsburgh	Nitrobenzene	1	14442	13711	-5
Pittsburgh	Nitrobenzene	1	14442	13745	-5
Pittsburgh	Nitrobenzene	1	14442	12000	-16
Lower Freeport	p-Cresol	0.25	13460	13560	0
Lower Freeport	p-Cresol	0.50	13460	13488	0
Lower Freeport	Nitrobenzene	1	13460	13512	0

[a]Extraction with 5 vols/wt solvent/coal @ 200° and 210°C, respectively for p-cresol and nitrobenzene, filtered, then dried to constant wt @ 150°C/20 torr.

TABLE 14. ULTIMATE AND PROXIMATE ANALYSES OF EXTRACTED COALS

Coal	Treatment	Ash %	Volatile %	Fixed Carbon %	Btu/lb	Sulfur,%	Weight, %				
							C	H	N	Cl	O
Lower Freeport	Cresol-1 hr	11.42	27.37	61.21	13560	3.00	77.04	4.43	1.12	0.12	2.87
Pittsburgh	Nitrobenzene-1 hr	4.96	32.50	62.54	12000	0.76	73.53	2.28	3.19	0.02	15.26
Pittsburgh	Chlorophenol-1 hr	4.49	36.31	59.20	12416	0.83					

3. REMOVAL OF NITROGEN

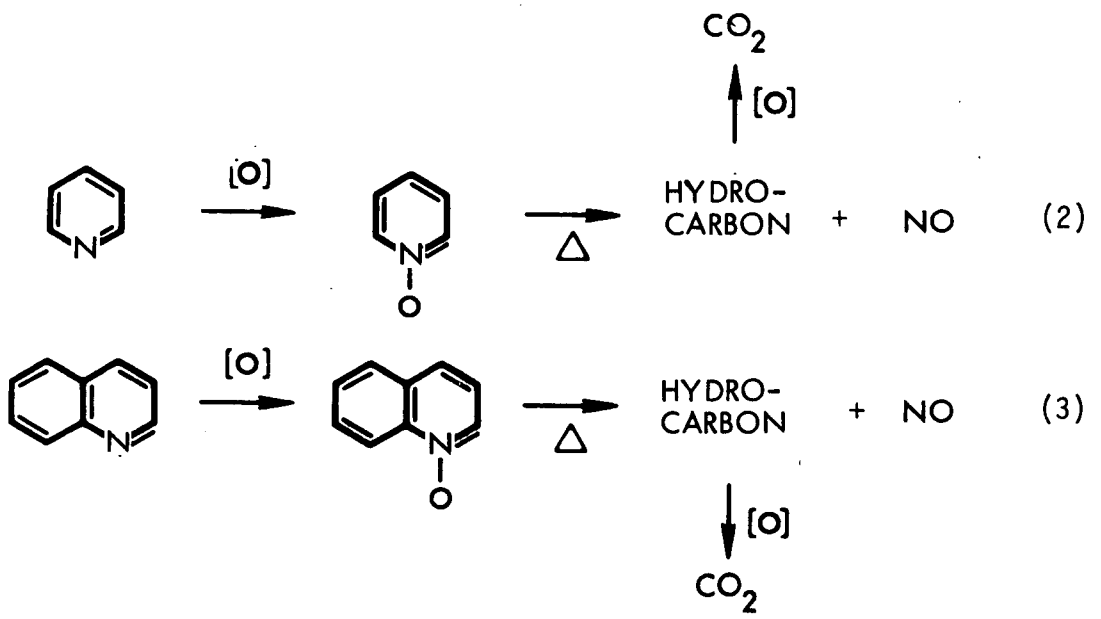
This section provides the results of the laboratory effort for removal of nitrogen from coal. The objectives of the effort were to determine the ability of selected solvents to remove nitrogen from coals. In addition, TRW performed a process engineering analysis for the use of one of the candidate solvents to leach nitrogen compounds in a cyclic batch-mode process.

Discussions of, a) the need for removal of nitrogen from coal, b) the theory associated with chemical removal of nitrogen, c) experimental results, and d) and engineering analysis (TRW funded) of a proposed process based on the experimental results are presented in the following sections.

3.1 NEED FOR REMOVAL OF NITROGEN

Approximately 14-million tons of nitrogen oxides are emitted into the atmosphere yearly and of this total, 25-30% come from coal fired power plants.

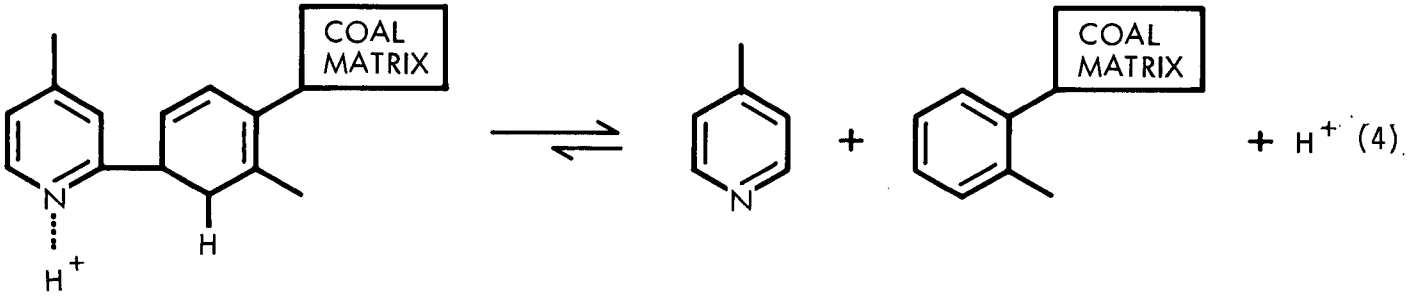
The potential requirement for removal of nitrogen from coal has only recently been recognized. Heretofore, it has been assumed that nitrogen fixation during combustion is the only significant source of nitrogen oxides emitted from utility stacks. However, it is likely that a portion of the organic heterocyclic components of coal are converted during the combustion process to their N-oxides which then decompose directly to nitric oxide (the major component of NO_x emission), as shown in Equations 2 and 3 below.



3.2 CHEMISTRY OF NITROGEN REMOVAL

Nitrogen occurs in coal in an organic form. It is thought that nitrogen compounds in coal may be categorized in three compound classes, a) nitrogen heterocycles, also known as coal tar bases, b) aromatic amines and c) aromatic amides. Of these three classes, the first is thought to be the major structural form in which nitrogen is found in coals and other fossil fuels. The experimental basis for the assignment of the heterocyclic structure to nitrogen in the coal is via destructive distillation or pyrolysis investigations, not direct determination. These compounds are thought to be bonded to the coal polymer matrix by covalent bonds, although a more likely interpretation of the bonding structure may actually be simple hydrogen bonding. Up to the present time, no method has been available for removing these compounds from coal.

The TRW approach to removing nitrogen from coal is similar to that advanced in Section 2.1 for removal of organic sulfur, that is, low temperature, atmospheric pressure, acid catalyzed, depolymerization and subsequent dissolution of organic nitrogen compounds from the coal matrix. As before, the aim of this approach is to break down the coal matrix polymer selectively at the points occupied by organic nitrogen compounds without disturbing the bonding present in the major part of the coal material. Equation 4 shows a possible mechanism for the selective extraction involving acid catalyzed decomposition of the coal matrix at the positions occupied by the nitrogen compounds, with aromatization shown as a possible driving force. Here again, it appears that solvents which would be effective would be acidic in nature.



3.3 EXPERIMENTAL RESULTS

The initial screening studies (Table 15) were performed on a rather unusual Bevier coal containing 0.5% nitrogen, as determined by the Kjeldahl method. The nitrogen removal results (Kjeldahl analysis) showed that hydrochloric acid and phosphoric acid were effective at removing organic nitrogen from the coal, while sulfonic acid type liquids were ineffective. Multiple leach experiments were performed with the phosphoric acid and found to give increasing removal of organic nitrogen compounds.

Subsequently, the screening studies were continued on the APCO program for Chemical Removal of Nitrogen and Organic Sulfur from Coal. In these studies, some more widely used coals (see Appendix for extraction experimental methods) were investigated (Table 16), with some of the same acids utilized in the previous study but also including p-cresol, the liquid of choice for removal of organic sulfur compounds from coal. It was found that p-cresol, 20% aqueous hydrochloric acid and concentrated phosphoric acid remove significant amounts of nitrogen from two coals according to the Dumas analytical technique, while the Kjeldahl method indicates that nitrogen is not removed from the coal samples. It should be noted that the starting coals showed a higher nitrogen content by the Dumas method than by the Kjeldahl. Consequently, it is apparent that the analytical techniques utilized for analysis of coal nitrogen require further evaluation.

The Kjeldahl method is the most widely used for determining nitrogen in coal. The method consists of boiling pulverized coal with concentrated sulfuric acid which contains potassium sulfate and a catalyst such as mercury or selenium, until the mixture reaches a straw-colored stage. The method depends on complete reduction of the organic nitrogen compounds to ammonium salts by treatment with the above solution. Following the digestion, the solution is made alkaline and the resulting free ammonia is distilled into a trap and determined titrimetrically. However, it has long been known that nitrogen contained in the form of pyridine rings is highly resistant to this type of treatment, and may not be totally reduced in the first step. Because nitrogen compounds in coal are believed to consist partially of pyridine derivatives (e.g. coal tar bases) and partially of amino type compounds, it

Table 15. Initial Nitrogen Removal Screening Tests[a]

Liquid	Extraction Temperature °C	Extraction Duration Mins	Nitrogen Removed %
Methane Sulfonic Acid	100	1200	0
Benzene Sulfonic Acid	100	1200	0
98% Sulfuric Acid	0	60	0[b]
85% Phosphoric Acid	20	1200	56
85% Phosphoric Acid (1X)	150	1200	60
85% Phosphoric Acid (2X)	150	1200	84
85% Phosphoric Acid (3X)	150	1200	91
36% Hydrochloric Acid	100	150	48

[a]Untreated dry Bevier coal nitrogen content: 0.52%, Kjeldahl method (TRW)

[b]Extracted sample showed an increase in sulfur content arising from sulfonation

TABLE 16. NITROGEN REMOVAL SCREENING TESTS

Liquid	Extraction Temperature °C	Extraction Duration Mins	Coal[a,b]	Nitrogen Content Dumas Analysis Method %	Change in Nitrogen Composition		Kjeldahl Analysis Method %
					Dumas Analysis Method %	Kjeldahl Analysis Method %	
P-cresol	200	60	Illinois No. 6	1.16	-39	0	1.24
20% HCl	100	60	Illinois No. 6	1.28	-32	+9	1.39
Conc. H_3PO_4 (1X)	150	900	Illinois No. 6	1.55	-18	+13	1.44
Conc. H_3PO_4 (2X)	150	900	Illinois No. 6	1.39	-27	+9	1.38
P-cresol	200	60	Pittsburgh	2.28	-20	-	-
Conc. H_3PO_4	150	60	Pittsburgh	2.43	-25	-	-

[a]Untreated dry Illinois coal nitrogen content: 1.90%, Dumas method (Elek Microanalytical Laboratories, Torrance, California); 1.23%, Kjeldahl method (Commercial Test Laboratory, Chicago, Illinois); 1.27%, Kjeldahl method (TRW).

[b]Untreated dry Pittsburgh coal nitrogen content: 3.03%, Dumas method (Elek Microanalytical Laboratories, Torrance, California); 1.35%, Kjeldahl method (Commercial Test Laboratory, Chicago, Illinois).

appears that special digestion treatment may be necessary to ensure determination of the former compounds by the Kjeldahl method.

The Dumas nitrogen determination method analyzes the total nitrogen content of coal by a completely different approach. In this method, pulverized coal mixed with copper oxide is heated in a stream of carbon dioxide and oxygen at 950-1000°C in contact with platinum. All nitrogen present in the sample is converted to nitrogen gas which is measured volumetrically after sorption of oxygen gas on hot metallic copper and carbon dioxide in an aqueous sodium hydroxide scrubbing media.

Thus, it is apparent that further work is required in the area of evaluating the effectiveness of the various nitrogen analysis methods so that precise information can be obtained as to the effectiveness of the various leaching liquids for removal of organic nitrogen from coal.

3.4 ENGINEERING ANALYSIS OF A PROCESS SCHEME

From the initial feasibility experiments it would appear that both p-cresol and concentrated inorganic acids such as phosphoric acid or hydrochloric acid are candidates for selectively removing organic nitrogen compounds from coal. Of the two approaches, p-cresol extraction is by far the more attractive from a cost standpoint since the organic nitrogen compounds would be removed (essentially for free) along with the organic sulfur compounds. The only question with the p-cresol approach is whether or not sufficient nitrogen is removed from the coal. Additional nitrogen may be removed from some coals, if required, by the phosphoric acid leaching approach. In order to obtain a preliminary estimate of the costs associated with a phosphoric acid leaching process, a preliminary analysis of one possible processing scheme was made and is described below.

Figure 9 presents a processing scheme for removal of nitrogen compounds by phosphoric acid leaching. The plant is sized to process 100 tons/hr of coal and it is assumed that 3.5 tons/hr of coal tar bases (nitrogen compounds) are extracted from the coal. The process can be divided into 6 major sections, as follows:

- Leaching

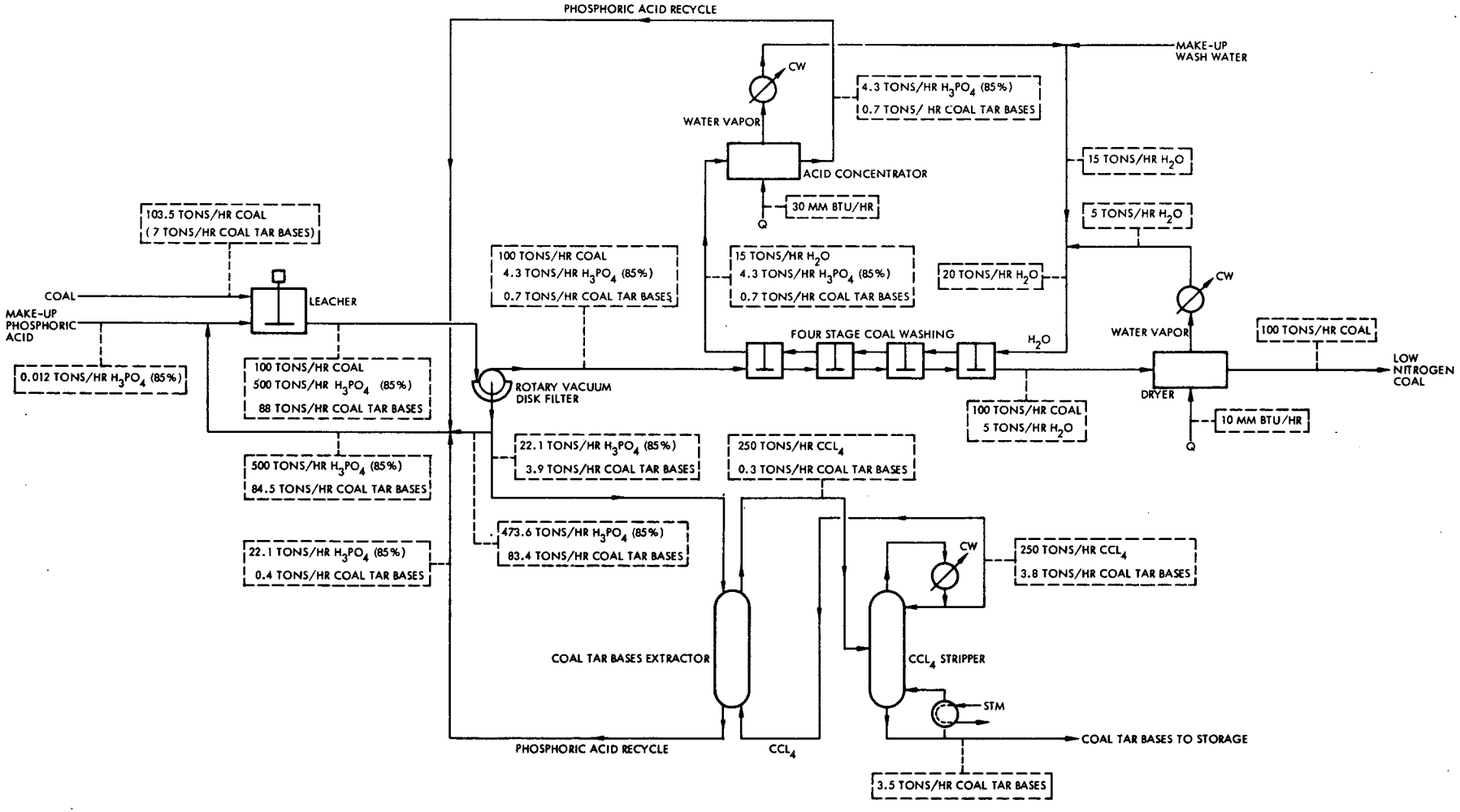


Figure 9. Processing Scheme for Removal of Nitrogen Compounds by Phosphoric Acid Leaching

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- Filtering
- Coal washing
- Acid concentration
- Extraction
- Distillation

In the leaching section 100 tons/hr of pulverized coal are slurried with 500 tons/hr of concentrated phosphoric acid and stirred at 300°F. Residence time of the coal in the leaching section is 30 minutes. Insulated, atmospheric pressure, stainless steel tanks are used for the leaching operation.

Rotary vacuum disc filters separate the bulk of the concentrated phosphoric acid from the coal. It is assumed that 0.05 tons of acid solution are retained on the coal filter cake per ton of coal after filtering. The concentrated phosphoric acid is recycled to the leaching unit while the coal filter cake is transferred to the washing section.

Four stages of counter current washing with intermediate filtration are used to remove the residual phosphoric acid from the coal. After washing the coal contains less than 100 ppm of phosphorous impurity.

After washing, the extracted coal is fed to a drying unit where the residual wash water is evaporated from the coal, condensed and recycled to the washing unit.

The dilute phosphoric acid solution leaving the washing unit is concentrated in an evaporator or acid concentrator and the concentrated phosphoric acid recycled to the leaching unit. The water evaporated from the acid solution is condensed and recycled to the washing unit.

Part of the phosphoric acid recycle stream is fed to a liquid-liquid extractor where the coal tar bases are extracted from the phosphoric acid with carbon tetrachloride. It is assumed that the coal tar bases can be allowed to buildup in the phosphoric acid leaching solution to approximately 20% without significantly affecting the leaching capability of the acid.

In the distillation section the coal-tar bases are separated from the carbon tetrachloride solution. The CCl_4 is recycled to the liquid-liquid extractor and the coal tar bases are collected and sold as a by-product of the process.

Table 17 summarizes the estimated capital, operating, and labor cost, for the phosphoric acid extraction process. No credit is taken for the coal-tar bases. Capital costs are depreciated as a 10% per year basis with an additional ten percent of the capital costs taken for taxes, maintenance, etc. Based on the assumptions described above and in Table 12 the cost of processing the coal is $1.18 per ton.

It is interesting to note that if a $40 per ton credit is taken for the coal tar bases the phosphoric acid leaching process more than pays for for itself. For comparison purposes, the selling prices* of coal tar and some of the chemicals present in coal tar bases are presented below:

Crude coal tar - $40/ton (tank cars, works)
Refined coal tar - $48/ton (tank cars, works)
Pyridine - $680/ton (denatured, drums)
Quinoline - $1000/ton (tank cars)
Aniline - $280/ton (tank cars)

* Oil paint and drug reporter, 1969

Table 17. Example Case for Organic Nitrogen Removal Process

DESIGN BASIS: 100 TONS/HOUR OF LOW NITROGEN COAL
3.5 TONS/HOUR COAL TAR BASES REMOVED FROM COAL

	¢/TON COAL		
	CAPITAL COST	OPERATING COST	LABOR
LEACHING SECTION	3.6	5.4	1.8
• 5:1 Wt Basis Phosphoric Acid (85%) to Coal			
• 0.5 Hr at 300°F and 1 Atm			
• 15% Wt Solubility of Coal Tar Bases in Phosphoric Acid Leaching Solution			
COAL FILTRATION AND WASHING SECTION	13.2	1.0	7.0
• Four Stage Washing with Intermediate Filtering			
• 0.05 Ton Solution/Ton Coal Retained After Each Filtering			
• 20 Tons/Hr Wash Water Entering Counter Current Washing Sections			
COAL TAR BASES EXTRACTION AND DISTILLATION	26.2	31.8	8.7
• 0.26 Tons of Coal Leaching Solution and 2.5 Tons of CCl_4 Fed to Coal Tar Bases Extractor per Ton Coal			
• 2.54 Tons of Extract Solution Fed to Distillation Column Per Ton Coal			
COAL DRYING AND H_3PO_4 CONCENTRATION SECTION	3.2	10.8	3.5
• 20 Tons/Hr Wash Water Evaporated from Phosphoric Acid Recycle			
PHOSPHORIC ACID MAKEUP		2.0	
• Four Stage Washing			
• 0.01 TONS/Hr of Phosphoric Acid (85%) Remains with Washed Coal			
SUBTOTAL	46.2	51.0	21.0

TOTAL COST FOR ORGANIC NITROGEN REMOVAL: $1.18

4. CONCLUSIONS AND RECOMMENDATIONS

Laboratory results of the Chemical Removal of Nitrogen and Organic Sulfur from Coal Program show that the following preliminary conclusions can be drawn:

1. The concept for chemical removal of organic sulfur and nitrogen is feasible.

2. Weak organic acids remove 45-80% of the organic sulfur from the coals investigated in this program depending on process conditions and the specific coal leached.

3. Nitrobenzene appears to be the most efficient solvent for the removal of organic sulfur.

4. Aqueous caustic removes small amounts of organic sulfur from some coals, but none from others.

5. Particle size (-200 mesh to 1/2-inch) has no discernable effect on the removal of organic sulfur by nitrobenzene.

6. The leaching solvent, nitrobenzene, may be recycled at least three times to remove organic sulfur from coal.

7. Weak organic acids and strong inorganic acids appear to remove nitrogen from the coals tested in this program according to the Dumas analytical method, but no nitrogen is removed according to the Kjeldahl method.

The engineering analysis results show that:

1. Weak organic acids for removal of organic sulfur from coal may be readily adapted to engineering process schemes.

2. The cost of the process for removal of organic sulfur from coal is highly dependent on, a) the degree of solvent loss, and b) the ability to recycle solvent and allow high sulfur compound buildup.

3. Utilizing the laboratory data and assuming reasonable values for undetermined parameters, the process cost for removal for organic sulfur is approximately $1.00-$1.50/ton of coal.

Based on the above laboratory results and conclusions, it is recommended that:

1. Information should be developed to support a pilot plant effort.

2. The process for utilization of weak organic acids to remove organic sulfur from coal should be investigated on a bench scale to assess important engineering parameters such as,

a) recovery and identification of extracted organic sulfur compounds, b) regeneration of solvent by distillation, c) overall solvent loss, d) maximum allowable sulfur compound buildup in the extraction solvent and e) coal sampling factors.

2. Nitrogen removal screening studies should be continued in order to determine, a) the correct analytical method for determining the nitrogen content of extracted and unextracted coal, and b) the amount of nitrogen removed from coal by the various leaching liquids.

3. If nitrogen removal appears promising, bench scale evaluation of the process should be performed.

5. NEW TECHNOLOGY

An Invention Disclosure based on information developed under APCO funding was submitted to the TRW Patent Office for filing entitled, "The Removal of Organic Sulfur from Coal with Caustic Solutions". A summary of the disclosure is presented below.

The Removal of Organic Sulfur from Coal Utilizing Caustic Solutions - Aqueous or alcoholic sodium or potassium hydroxide removes organic sulfur from certain coals. Coal is pulverized and treated with aqueous caustic for 1-3 hrs at reflux. The caustic is filtered from the coal, the coal is washed to neutrality and dried in a vacuum oven to constant weight. The extracted coal has a decreased sulfur content. The aqueous solutions containing organic sulfur compounds may be regenerated by air oxidation and separation of the organic phase.

APPENDIX A

EXTRACTION PROCEDURE

Organic Solvents. - The organic solvent (typically 350 ml) was added to a three-neck round bottom flask fitted with a reflux condenser and an overhead stirrer. For the screening studies, magnetic stirring was used. The flask was heated to bring the well stirred solvent to near reflux, then the coal (typically 70 g) was added. The mixture was maintained at mild reflux for the specified retention time (typically 1 hr), then immediately the dark brown liquid phase was separated from the coal while still hot on a sintered glass or Whatman No. 4 filter. In some cases, the coal was then washed with water or methanol to remove the remaining solvent. The coal was dried in a vacuum oven at 100-150°C/20 torr to a constant weight (typically for 16-24 hrs).

Aqueous Acids or Bases. - The aqueous solution (typically 100 ml) and coal (typically 20 g) were added to a single-neck round bottom flask fitted with a reflux condenser and a magnetic stirrer. The flask was heated to mild reflux for the specified retention time, then the aqueous phase was separated from the coal on a sintered glass filter. The coal was washed several times with water, neutralized and rewashed, then dried in a vacuum oven to constant weight at 100°C/20 torr.

FLOW THROUGH EXTRACTION OF COAL

It was anticipated that if pulverized coal beds were amenable to continuous extraction with a solvent, and an extraction device could be constructed in which a moving front of liquid would pass through a stationary pulverized coal bed and then into a device for continuously monitoring the sulfur content of the effluent, such a device would be particularly useful for measuring the rate of sulfur compound extraction. This could be done as a function of residence time and solvent volume. The data thus obtained, would be particularly useful if the eventual design of the process for the removal of organic sulfur from coal was to operate in this process mode.

A continuous extractor apparatus with a sulfur detection system, capable of continuously monitoring effluent sulfur in a solvent carrier, was constructed (Figure 10). The apparatus was constructed under TRW funds, as

both the extractor element and the sulfur detection system (the combustor and Faristor) would be generally useful for a wide range of general process studies. The equipment consists of: (1) a pump capable of pumping up to 290 ml/hr of liquid at pressures up to 1000 psi (an adjustable spring type relief valve is used to protect against over pressurizing the system and Bourdon type gauges are used before and after the packed column to monitor pressure, (2) a heat exchanger consisting of a six-foot length of 1/4-inch stainless-steel tubing, (3) a packed (pulverized coal) column contained in a thermostatic air circulating oven capable of maintaining temperatures up to 200°C, (4) an automated fraction collector, (5) an oxygen combustor system based on a quartz glass combustion tube Fedvia 1/16-inch capillary tube, and (6) a Faristor sulfur detector with recorder output.

An initial assessment of the usefulness of the apparatus was performed utilizing weak organic acid solvents with pulverized Pittsburgh coal (-200 mesh) at temperatures of 100°C. It was found that the solvent flow was quickly reduced to zero even at maximum pressure due to the pulverized coal forming an impenetrable mass. This problem was overcome by utilizing pulverized coal with no fines of less than -20 mesh and the recorder output indicated some sulfur content in the effluent. However, when the column temperature was adjusted to the typical extraction temperatures of 150-200°C which had been found to be favorable for removal of organic sulfur compounds from coal in a batch mode, the column again became inpenetrable probably due to agglomeration, swelling, or plastic deformation of the coal material, so that solvent could not pass.

Due to the operating problems encountered with this mode of coal extraction and to the choice of a batch mode for the large scale process for removal of organic sulfur from coal, experiments utilizing the continuous extractor with sulfur detector where discontinued.

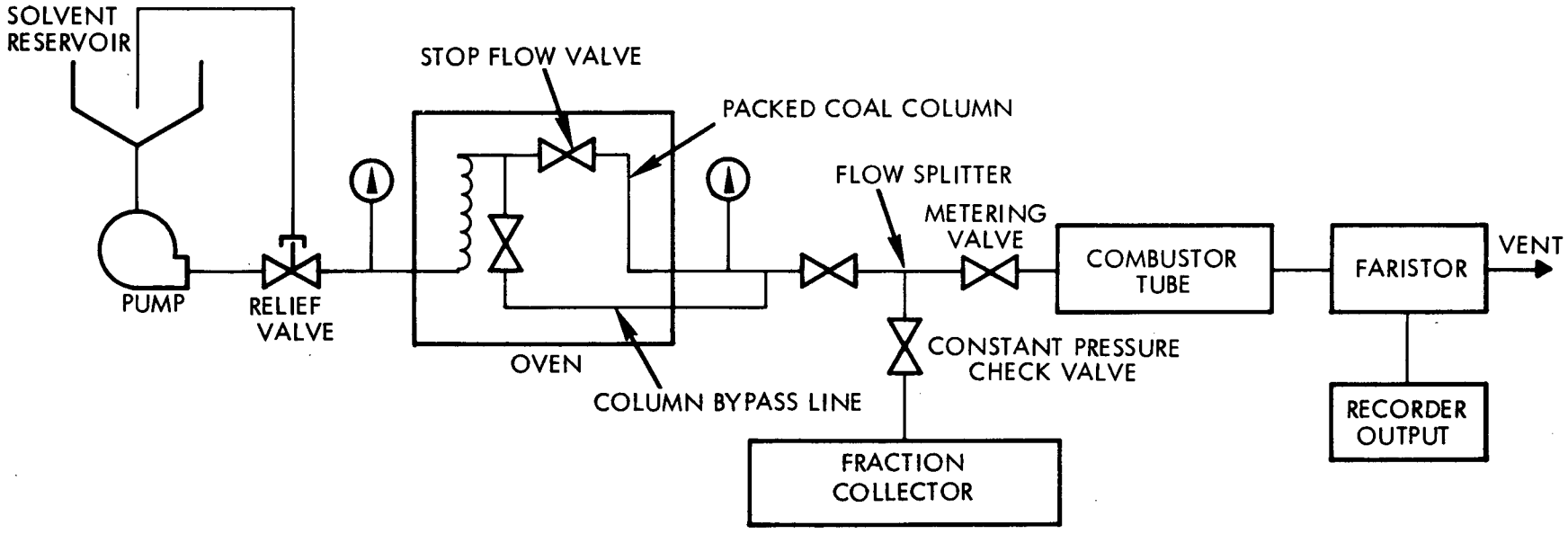

Figure 10. Continuous Extractor with Sulfur Detector