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ENERGY & ENVIRONMENT DIVISION

COAL DESULFURIZATION PRIOR TO COMBUSTION

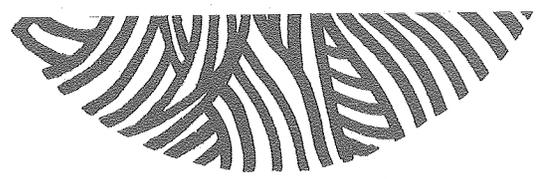
J. Wrathall, T. Vermeulen, and S. Ergun

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COAL DESULFURIZATION PRIOR TO COMBUSTION

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Energy and Environment Division
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J. Wrathall, T. Vermeulen, and S. Ergun

INTRODUCTION

Coal is most economically used as a direct boiler fuel. A combination of environmental and economic considerations dictates the amount of sulfur that can be emitted by coal-fired facilities. This, in turn, sets limits on the amount of sulfur in the coal to be burned. Other properties, such as free-swelling index, mineral matter composition, and volatility determine whether a particular coal can serve as a boiler fuel. Thus, both environmental and technical considerations enter into selection of boiler fuels.

The many coals of the United States were formed under a wide variety of conditions, and, as a result, display a wide range in all properties of interest. For example, pyrite weight-percent varies from nearly 0 to 20%, while organic sulfur varies from 0 to 10%. These two properties can be used to classify coals for optimum end use.

APPLICABILITY OF CLEANING PROCESSES TO U. S. COALS

Since current coal cleaning processes remove only a fraction of the total sulfur (1), the question arises as to what fraction of U. S. coals can be cleaned within current E.P.A. new source standards (1.2 lb. SO₂ per MMBTU). A number of studies has shown the fraction to be encouragingly large.

A report on the applicability of the Meyers process (2) estimates, on the basis of 35 coals sampled, that 40% of the samples could be burned cleanly after some combination of physical separation and chemical leaching (see Fig. 1).

A report by Ergun (3) on coal cleaning gives the higher estimate of cleanability of 56%, based on 455 samples properly weighted between Eastern and Western coals. Beyond this figure, Ergun estimates an additional 17% is cleanable if 30-40% of the organic sulfur is removed, bringing the total cleanable to 73%.

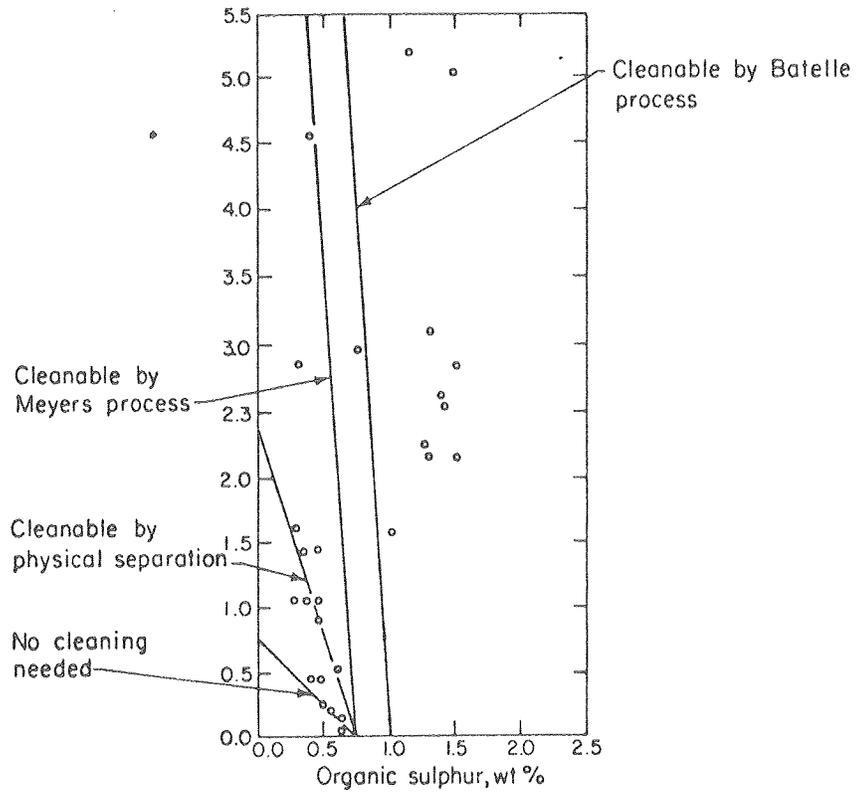
Data from a study by Cavallaro (4), with coal reserves taken from a study by Beekers (5), give an estimate in agreement with that of Ergun on the amount of coal cleanable by pyrite removal. The data are presented in Table 1.

In summary, it can be seen that cleanable coal reserves increase by 33% if processes are used which can remove what are probably the more reactive organic sulfur species (6), such as aliphatic mercaptans, sulfides, and disulfides. A process which attacks the refractory thiophenic sulfur could conceivably increase the cleanable coal reserves by another 20 - 30%, assuming roughly equal distribution between reactive and refractory organic sulfur.

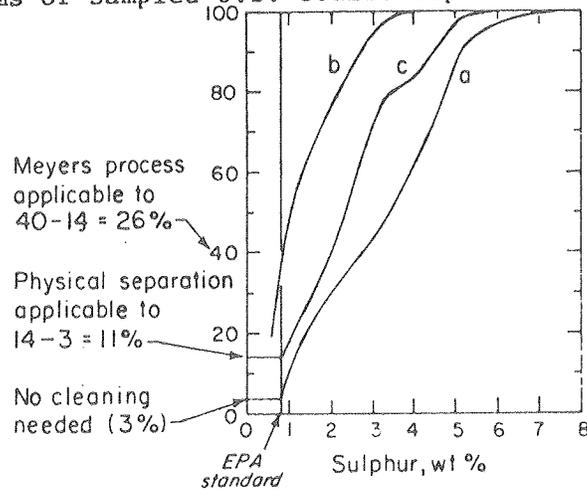
SCOPE AND ACCOMPLISHMENTS OF THE LBL RESEARCH

LBL is involved in four aspects of research in pretreatment of coal prior to combustion to decrease sulfur emissions. The first aspect is development of an acidic oxidative leach process involving H₂SO₄, (a cheap and readily available bulk chemical) in combination with Fe₂(SO)₃ and O₂ or possibly H₂O₂. Pyrite oxidation is complete under mild conditions. As yet, the effect of the acid solution on organic sulfur is minor.

The second aspect involves development of techniques for independent analysis of sulfur forms other than pyrite or sulfate. The first has been directed toward spectrophotometric identification of elemental sulfur, which may be an unwanted byproduct of pyrite oxidation, and also a component of raw coals.



Sulfur forms of sampled U.S. coals. Reproduced by permission of ACS, C 1977.



Sulfur content of survey run-of-mine coals (curve a) the same coals physically cleaned (curve c) and chemically desulfurized (curve b) Reproduced by permission of ACS, C 1977 XBL 795-1511

Fig. 1. U. S. Coal Cleanability

Table 1 - Coal Reserve Cleanability, B.O.M. Data*

Coal	MMBTU/ton, ROM	10 ⁶ ton res.	Quad res.	% clean, ROM + % cleanable
Northern Appalachian	22.34	72920	1629	12
Southern Appalachian	23.43	37349	875	50
Alabaman	24.10	2982	72	35
Eastern Midwest	21.45	88912	1907	2
Western Midwest	21.25	15720	334	4
Western	18.66	216065	4032	94
Total (Average)	(20.39)	433948	8849	(51)

1979 U. S. Coal Consumption (estimated) 14.89 quads.

1979 U. S. Energy Consumption (estimated) 68 quads.

*Based on proposed E.P.A., new source standards of 1.2 lb. SO₂/MMBTU.

Another study has dealt with direct identification of organic sulfur, using x-ray fluorescence. Hitherto, this component has been determined as a difference between inorganic sulfur (pyrite, sulfate, elemental) and total sulfur.

The third aspect considers the question of whether the organic sulfur species in coal can be effectively converted to water-soluble products without serious loss in the coal's calorific value.

The fourth aspect is reductive desulfurization of primary conversion products from raw coal, for example high-sulfur forms of solvent-refined coal. The catalytic action of pyrite in hydrodesulfurization and the physical and chemical factors affecting that catalyses have been an area of study.

The fifth aspect is combustion of coal that has been treated with a "trapping agent," notably an alkali metal base or salt. Chemical costs for such treatment will probably be comparable to those for alkaline or neutral desulfurization, or lower if the cost of oxidizing agent (O_2 , air, H_2O_2) is included.

These activities are discussed in the following sections of this report.

I. OXIDATIVE DESULFURIZATION OF COAL, (D. Mixon , T. Vermeulen)

Oxidative desulfurization of coal is proposed as a method of coal cleaning that involves chemical conversion and extraction of coal sulfur. The optimal process requires that inorganic sulfur, mainly FeS_2 , and organic sulfur, such as mercaptans, sulfides, disulfides and thiophenic forms, be oxidized from formal oxidation states of -1 and -2 to the water-soluble +6 state. In this study, the oxidation of sulfur compounds will be carried out in a strong sulfuric acid medium using oxygen as the oxidant.

Previous workers have found that pyritic sulfur removed in neutral or slightly acid media cannot be fully oxidized to sulfate below $120^{\circ}C$. Instead, below $120^{\circ}C$ part of the coal sulfur is converted to insoluble elemental sulfur (S^0) that is difficult to remove. Stronger acid media are currently being studied to find a reaction path to eliminate the formation of elemental sulfur. This work requires a reliable method for determining elemental sulfur in coal, since there appears to be no published method for its direct determination. At present we are investigating the UV spectroscopy i.e. analysis of free sulfur dissolved in cyclohexane. This solution exhibits a UV spectrum obeying Beer's law, and has been used to measure the sulfur content of cyclohexane extracts of coal levels as low as 50-70 ppm.

Using this method, high-sulfur Illinois No. 6 was found to contain 850 ppm of S^o. Equipped now with the S^o analysis method, we seek the operating conditions for this process which will maximize the conversion of coal sulfur to soluble sulfates.

Pyrite conversions of up to 85% have now been achieved at 150°C with 420 psia of oxygen, in one hour's time. This method thus exceeds the performance of the well-known Meyers process. Attention is being turned to the possibility of simultaneous removal of the organic sulfur. Progress on this project is reviewed in more detail in the attached report LBL-9963.

II. QUANTITATIVE X-RAY ANALYSIS OF ORGANIC SULFUR IN COAL (J. Wrathall, M. E. Smith, S. Ergun)

Introduction

Energy-dispersive analysis of X-rays (EDAX) is a technique that has only recently found application in coal chemistry. Previously the time-consuming technique of transmission X-ray fluorescence has found application with good correlative results (Ref. 7). Electron probe microanalysis has been studied by Sutherland (8), and Solomon (9), Harris (10) and Raymond (11) but most of their techniques require painstaking petrographic work and questionable empirical correction factors, in addition to using standards of questionable relation to coal itself. The present work constitutes the first use of EDAX as a coal sulfur analytical tool.

Procedure

Coals with known organic sulfur are used for purposes of comparison. $\frac{1}{4}$ " grains are potted in epoxy, shaved, and polished to .05 μ size. A 1" metal disc, holding six potted grains, is lightly coated with gold or (preferably) carbon. The disc is placed in a scanning electron microscope and mineral-matter-free areas are selected using the CRT image. Electron beam energy is set at 20 KeV, magnification is set at 1000 X and the resulting X-rays of various energies are counted for 40 sec. The X-ray spectrum is checked for metal impurities and rejected if necessary. The scan area is 10 μ square. Fluorescence peak heights are plotted vs. ASTM organic sulfur analyses. An example of the EDAX theory and analysis is shown in Fig. 2.

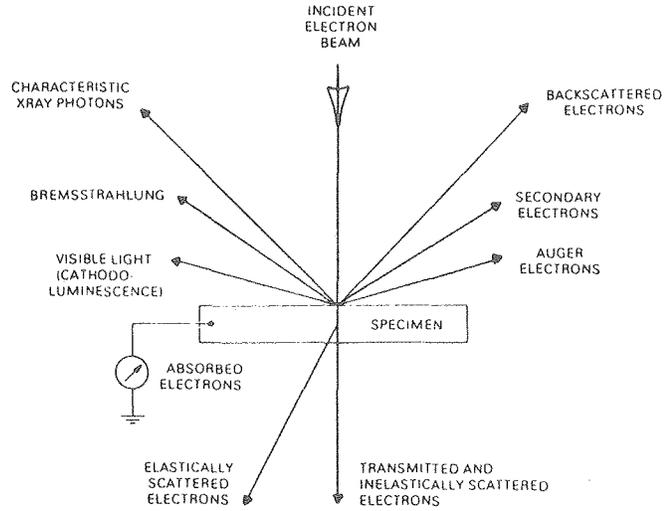


Fig. 2a. SEM Signal Generation (Ref 12)

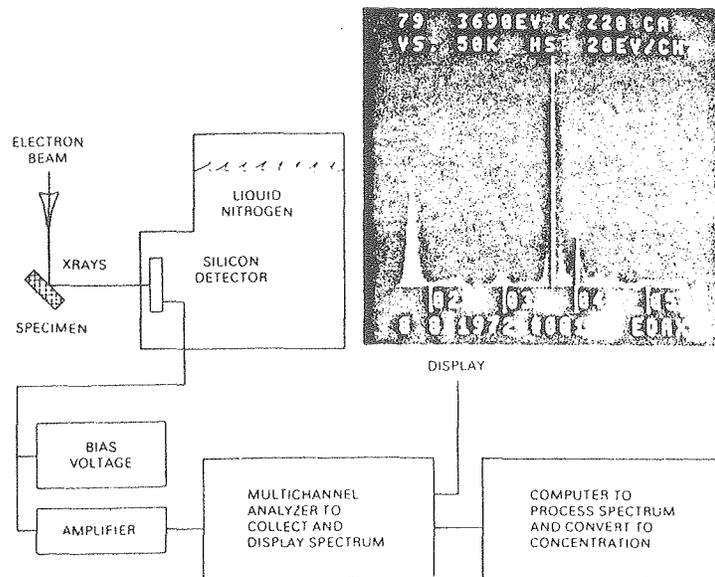


Fig. 2b. EDAX Analysis System (Ref 12)

Materials

For purposes of standardization, solutions of Dibenzothiophene (DBT) in Phenanthrene (PA) were prepared at 100°C to correspond to a range of sulfur contents from 1 to 17% organic sulfur. SRC from the Ft. Lewis plant was also studied. Coals with ASTM analyses were supplied from the Penn State Coal Data Base.

Results

The correlation between per cent organic sulfur and peak height holds moderately well for the standard, DBT in PA, which is plotted in Figure 3. The presence of mineral matter decreases the sulfur peak, presumably by decreasing sulfur fluorescence efficiency. ASTM analytical data for the 12 coals studied are shown in Table 2. EDAX K- α peak heights for the coals are shown in Table 3, while these data are plotted in Figure 4.

Only the points with no mineral matter or gold interference show any reasonable sort of correlation of the type shown in Figure 3. Unfortunately, the slope of Figure 3 is much less than that of Figure 4 indicating that the standard is not particularly representative of the coal matrix.

Further Work

1. We plan to develop a quick sample preparation technique that eliminates mineral matter interference.
2. We will set up and develop proficiency in carbon coating to eliminate gold interference.
3. We hope to develop computer capability to subtract background, noise, and interfering peaks.

Table 2

(DRY)

Sample	PSOC	% org.	% pyr.	% mm
1 - 1	287	0.71	6.17	20.10
2	287	1.09	8.81	27.69
3	319	0.08	10.98	21.12
4	408	2.62	1.09	14.75
5	591	2.23	1.68	12.94
6	719	1.63	1.38	6.61
3 - 1	752	1.70	0.84	10.23
2	753	2.19	1.80	5.06
3	757	2.63	1.33	6.09
4	759	2.62	20.09	44.94
5	765	1.79	1.20	6.37
6	799	0.92	8.83	15.10

Table 3

Sample	K α Peak Heights	Interference
1 - 1	295,290	N, N
2	300	N,
3	360,355	N, Y
4	140,160	Y, Y
5	320,340	N, N
6	200,200	Y, Y
3 - 1	130,125	N, N
2	175,170	N, N
3	195,190	N, N
4	225,205	N, N
5	150,130	N, N
6	80,80	Y, Y

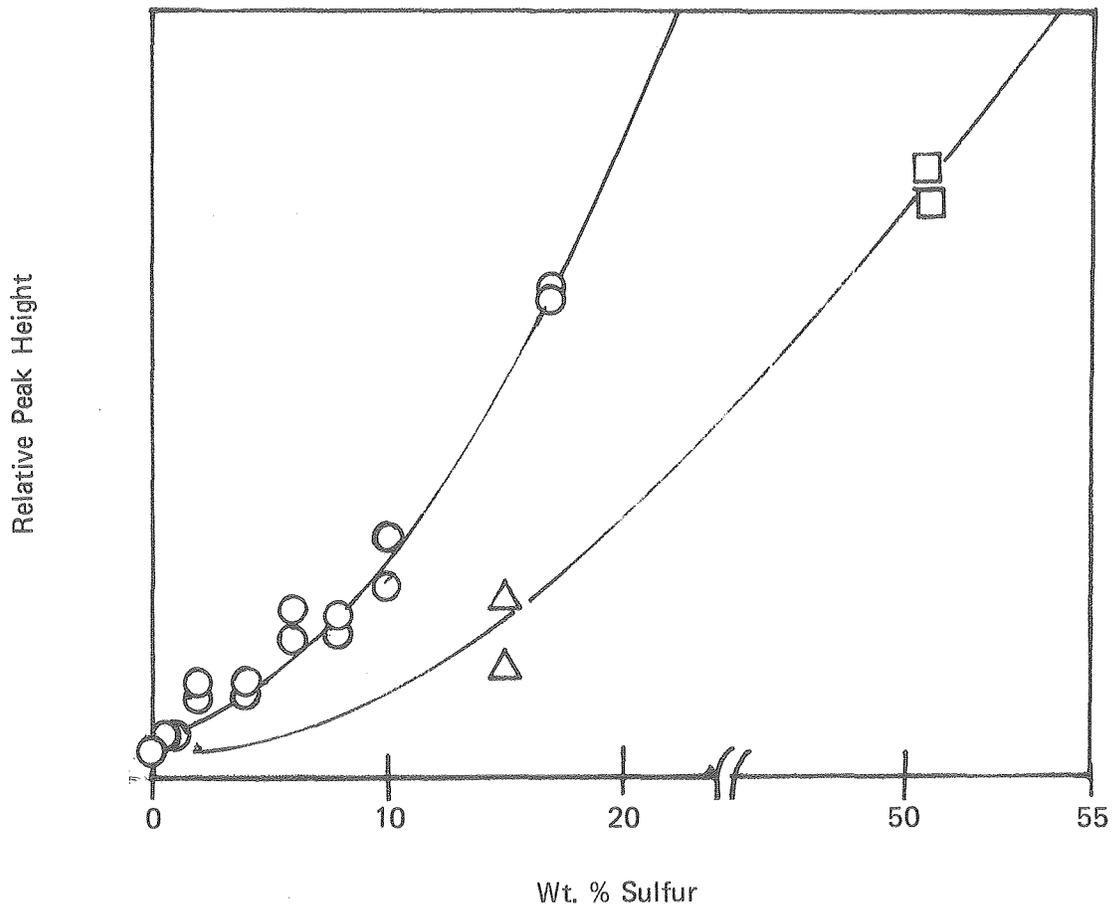


Fig. 3. EDAX Sulfur Response
(Dibenzothiophene standard)

- O DBT
- △ Al_xS_y
- Fe S₂

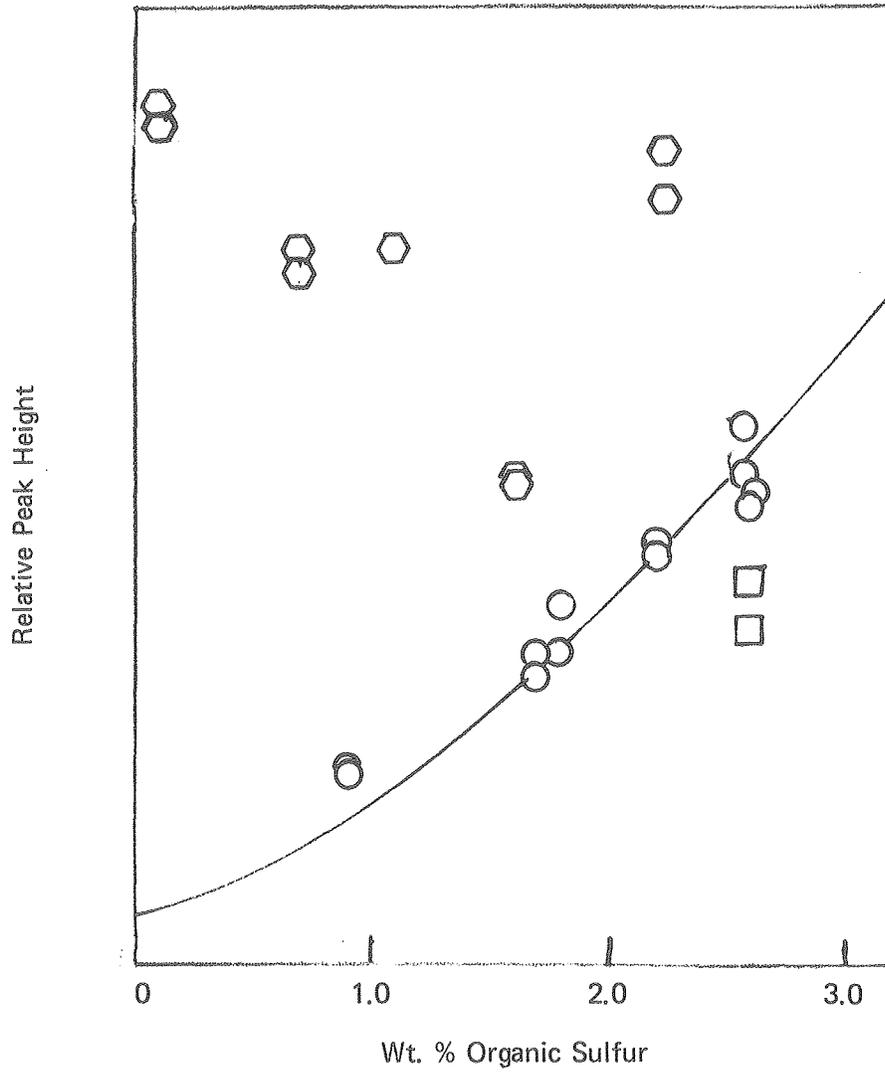


Fig. 4. EDAX Sulfur Response
(PSOC Coals)

- No interference
- ⬡ Gold interference
- Mineral matter interference

III. OXIDATIVE DESULFURIZATION OF MODEL COMPOUNDS (L. Clary, S. Lynn)

In this project, ferric sulfate is reacted with model organic sulfur molecules to learn whether it is an effective oxidant. Saturated solutions of $\text{Fe}_2(\text{SO}_4)_3$, H_2O , and H_2SO_4 are used to avoid the formation of Fe_2O_3 as a precipitate. The experiments are carried out in an inert atmosphere at temperatures up to 150°C in sealed bombs.

Dibenzothiophene is representative of the most difficult form of organic sulfur to remove from coal, and is therefore used as the primary model of study. Following reaction with Fe^{+++} , an analysis of Fe^{+++} and Fe^{++} will indicate oxidation of the model compound. Infrared absorption spectra will also be used to identify oxidized forms of the model compounds.

A bench-scale reactor has been constructed and tested. Tests with dibenzothiophene and other model compounds will be continued including alkyl sulfides and alkyl mercaptans. Subsequent work will depend on current results, but may include investigation of metal catalysts and the use of stronger oxidants such as peroxides. Experiments using coal will follow.

IV. REDUCTIVE COAL DESULFURIZATION (J. Wrathall, S. Ergun)

Studies at Sandia Labs (12) and elsewhere (13 - 16) have shown that spiking of coals with iron sulfide causes significant increases in liquid yields in SRC processes. Pyrite shows a greater catalytic effect than that of the completely reduced form, indicating that an intermediate phase is most effective for catalysis.

Other studies (17) have shown that, at liquefaction temperatures, cubic pyrite is converted to hexagonal pyrrhotite under mild reducing conditions with no significant sulfur loss. This implies that the iron sulfide most effective in liquefaction catalysis is a sulfur-rich pyrrhotite.

The mechanism given below can be used to explain the catalytic effect of iron sulfide. The first step is thermal conversion of the cubic lattice to hexagonal form. The next step is adsorption of H_2 on adjacent sulfur sites of the crystal. Then two competing reactions can occur. The first is cleavage of H_2 and abstraction by coal fragments to cap thermally cleaved methylene, ethylene, or ether bonds. The second reaction uses the cleaved H_2 to form H_2S , which then reversibly enters the gas phase. Eventually the pyrrhotite becomes so depleted in sulfur that no proper H_2 cleavage sites remain on the crystal surface. This is confirmed by the finding that recycled SRC pyrrhotite has negligible catalytic effect (18).

If the reaction $H_2 + FeS_2 \rightarrow H_2S + FeS$ is reversible, then an SRC process involving H_2S recycle becomes attractive. Since the SRC product residue has to be recycled anyway, it makes sense to sulfide the residue to reactivate the pyrrhotite contained therein.

Experimental Study

Our SRC conditions consist of 100 g coal (12 PSOC coals of varying pyritic and organic sulfur content), 200 g tetralin, 2000 psig H_2 and tetralin pressure and 400°C for 2 hr in a magnedrive - stirred Autoclave Engineers 1 liter vessel of 316SS. The vessel is heated, as described elsewhere (19), by a combination of external and internal heating of equal wattage. At the end of the reaction, the liquids are flashed to a 2 gal stainless drum and gases are sampled and passed through a dry ice trap. The gases are then passed through ammoniacal $CdCl_2$ to absorb H_2S . The system is described in Figure 5. The yield is defined as per cent gas and liquid accumulated in the flash drum.

Of the approaches assembled for this purpose, the H_2S absorber, autoclave, and heat-exchange system have been tested successfully, but the flash system has not yet been assembled. Two desulfurization experiments have been done to date; the chemical analyses are still in progress.

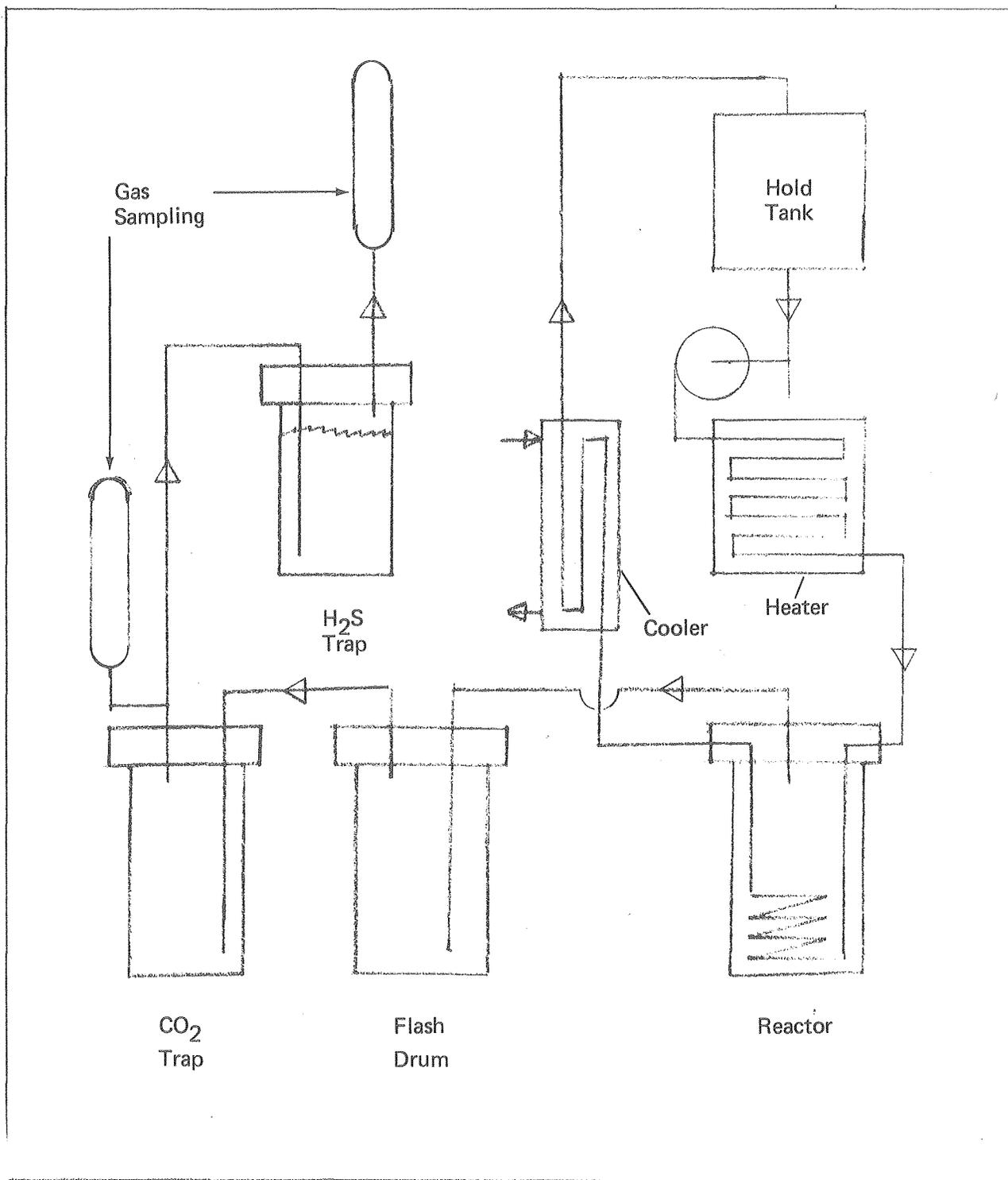


Fig. 5. Reductive Coal Desulfurization Reactor Flow System.

V. SULFUR FIXATION DURING COMBUSTION (M.C. Smith, E. Petersen)

This work is concerned with the desulfurization of coal during combustion. The process involves the addition of alkali metals to the coal so that sulfur dioxide formed in the burning is absorbed by the alkali, forming alkali sulfates which remain in the ash. This method may provide an alternative to other methods of desulfurization and can be applied to furnaces already in operation.

The work over the past months has centered on the development of a computer model for the combustion of a coal particle containing alkali-absorbing agents. The object of the model is to calculate how sulfur dioxide is released as the particle burns. It is hoped that the results of the model will indicate important areas for research experiments needed to understand the process. Initially the coal particle is modeled by two asymptotic limits: as a solid reacting with increasing porosity and constant radius, and as a solid reacting with constant porosity and decreasing radius. The latter leads to the intuitive result that the amount of sulfur dioxide released is proportional both to radius cubed, (or to the amount of sulfur initially present) and to a factor involving the ratio of the rate of SO_2 absorption and the rate of SO_2 production by combustion. The greatest difficulties in writing the model are the estimation of the rate of SO_2 uptake and the characterization of the distribution of alkali within the coal particle.

The use of alkali within coal is not without problems. Research into the fouling of coal burning furnaces has shown that the alkali content of the coal is an important factor in the build-up of ash deposits on the boiler tubes. Considerable work has been done in characterization of the deposits, and much less work has been done with the ash itself. Because the project involves the addition of alkali to coal, the implication of the alkali additives on furnace operation should be carefully examined.

Experimental work is just beginning. Samples containing the alkali additives will be burned in a high-temperature furnace, and the ash analyzed for sulfur retained as alkali sulfate. Variables to be examined are the effectiveness of various alkali additives, the mode of addition of the additives, the temperature of the furnace, the residence time of the ash in the furnace, and the amount of additive. The kinetics of SO_2 absorption by unaltered coal ash and by pure coal minerals are other possible areas for experimental investigation.

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