Western Kentucky University
TopSCHOLAR®

Masters Theses & Specialist Projects

Graduate School

5-1984

Desulfurization of Coal Using Carboxylic Acids & Peracids

Dwight Watson
Western Kentucky University

Follow this and additional works at: https://digitalcommons.wku.edu/theses

Part of the Chemistry Commons

Recommended Citation

Watson, Dwight, "Desulfurization of Coal Using Carboxylic Acids & Peracids" (1984). *Masters Theses & Specialist Projects.* Paper 2955.
https://digitalcommons.wku.edu/theses/2955

This Thesis is brought to you for free and open access by TopSCHOLAR®. It has been accepted for inclusion in Masters Theses & Specialist Projects by an authorized administrator of TopSCHOLAR®. For more information, please contact topscholar@wku.edu.

DESULFURIZATION OF COAL USING CARBOXYLIC ACIDS AND PERACIDS

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Dwight D. Watson
May 1984

DESULFURIZATION OF COAL USING CARBOXYLIC ACIDS AND PERACIDS

Recommended April 5, 1984
(Date)

John T. Riley
Director of Thesis

John W Reasoner

Rita K. Hessley

Approved April 24, 1984
(Date)

Elmer Gray
Dean of the Graduate College

ACKNOWLEDGEMENTS

I would like to thank Dr. John Riley and Dr. Norman Holy for their guidance and cooperation. I would like to thank my parents for their support and love. I would especially like to thank Laura L. Ray for her patience and love without which this work could never have been completed.

BIOGRAPHICAL

Born on [redacted] in Murray, Kentucky, he attended Kirksey Elementary School and graduated from Calloway County High School in 1977. He received his B.S. degree in Chemistry from Murray State University, Murray, Kentucky in 1981. He taught high school for the school year 1981-82. He came to Western Kentucky University in the fall of 1982 seeking a Master of Science degree in Coal Chemistry. After graduation he plans to serve in the United States Navy as a surface warfare officer.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Tables (continued)

DESULFURIZATION OF COAL USING CARBOXYLIC ACIDS AND PERACIDS

Dwight Dan Watson May 1984 pages
Directed by: John T. Riley, John W. Reasoner, Rita K. Hessley
Department of Chemistry Western Kentucky University

Bituminous coals were desulfurized by leaching in a 325 ml, agitated, autoclave with hot, dilute solutions of carboxylic acids, buffered carboxylic acids, carboxylic salts, and carboxylic salt:alkali combinations. The partial pressure of oxygen was not increased as it was found not to increase the amount of organic sulfur removal. The effect of increasing carboxylic size and degree of desulfurization was studied. Among the carboxylic acids studied, formic acid removed the greatest amount of organic sulfur;and iso-valeric acid removed the greatest percentage of pyritic sulfur. It was found that there is a direct correlation between the amount of organic sulfur removal and the ASTM determined volatile matter of the coals.

INTRODUCTION

The intensity of the study of coal greatly increased when there seemed to be a shortage of oil in the late 1970's. Since that time, the oil shortage has subsided and the need for special utilizations of coal has been set aside. At this time the only economical way to utilize coal is to burn it to produce electricity. This open air combustion has presented many problems. They are not new problems, but with a greater public awareness of the environment, they have become more important. Of the minerals found in coal, sulfur is the most important single element impeding the utilization of coal as a clean fuel. It is very important that an economical method for desulfurization of coal prior to combustion be developed.

Sulfur in coal presents many problems, many are not related to its chemistry. Coal sulfur causes economical, political, and environmental problems. The economical problems of coal stem from its sale. Coal shippers are penalized a percentage of the amount of sale for selling a consumer coal that exceeds the contract specifications for sulfur percentage. A typical penalty is twenty-five cents per ton for each 0.1 percent over specifications. The charge can quickly become a substantial amount of money. In the political realm, coal combustion has caused strained relations among several states. The strained relations are caused by acid rain.

Acid rain is the result of the formation of sulfuric acid via the interaction of coal combustion emissions with moisture in the air. The sulfuric acid then mixes with rain and falls to the ground in raindrops. The acid then causes harm to lakes, streams, and even human water supplies. As an environmental problem, sulfur in combustion emissions causes damage to crops, plantlife, and animals. With all these problems, it would seem that coal would not be burned. Coal, however, is a very good fuel. It has a high heat content that is easily used. The United States needs coal as a supplement to oil consumption. It will not be too far in the future before coal will be the leading energy source. Therefore, the need for an economical desulfurization process is even more important.

HISTORICAL

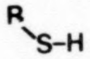
There are three different forms of sulfur in coal: metallic sulfides, metallic sulfates, and organic sulfur. Pyrite and marcasite are the two minerals that are collectively called pyritic sulfur. Both minerals have the same composition, FeS_2, but they have different crystalline formations. The crystalline structures are hard to distinguish and are therefore generally referred to as pyrites or iron pyrites.

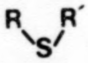
Pyrites are found in coal in many forms. They can be found in bands, nodules, cleats, and fine particles mixed in the coal. These forms dictate the amount of pyritic sulfur that can be removed by conventional cleaning techniques. The more finely divided and evenly distributed the pyrites are the harder it is to remove them from the coal.(1)

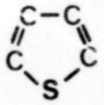
Sulfate sulfur is generally less than 0.05 percent of a coal. This amount increases as mined coal is exposed to oxygen. The pyrites oxidize to form sulfates,and an increase in sulfate is an indication that the coal has been weathered. Sulfate is readily leached from coal by water and because of its low overall percentage does not present problems for coal combustion.

Organic sulfur is chemically bonded to the coal matrix. It cannot be removed by washing techniques. Removal of organic sulfur can only be attained by chemical reactions. Organic sulfur is the principal form in low sulfur coals. As total sulfur increases with different coals, the organic and pyritic forms increase. There is no general ratio between organic and pyritic sulfur, as the ratio is different for different coals.(2) There is no information on the exact structures sulfur forms with the coal matrix, but there have been structures postulated. A list of structural evidence is given below:(3)

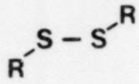
1. Bahtnager and Duti found mercaptans and disulfides in coal extracts. The majority of the sulfur remained in the residues of extraction.
2. Roy extracted coals with benzene and isolated mercaptans, sulfide, disulfides, and thiophenes. Oxidation of the coal led to removal of 30% of the organic sulfur and suggested that 70% of the organic portion was contained in the ring structure of the coal matrix.
3. Kavcic found also 70% of the organic sulfur to be a part of the heterocyclic ring structure.
4. In a coal molecule structure proposal, Hill and Lyon included organic sulfur structures which included







5. In the coal molecule proposed by Wiser, he included the sulfur structures of Hill and Lyon with the addition of



In both case 4 and 5, R and R' are considered part of the cyclic structure.

The ratios of mercaptans, sulfides, and thiophenes are not known. This information is critical in assessing the ability for a chemical desulfurization process to remove organic sulfur. The cyclic structures that contain sulfur are much harder to remove than the mercaptans of sulfides. It is generally accepted that 40-60% of organic sulfur in American coals has a cyclic structure.(4)

Coarse crushing of coal frees discrete mineral particles which most industrial coal cleaning methods can remove. Crushing to very fine particles is avoided for economic reasons. Application of fine coal cleaning technology is not as well developed as course parcile technology. Chemical extraction processes have not been developed into a commercial application state. The best currently available technology may only remove 43-80% of pyritic sulfur. In this discussion of coal cleaning methods, physical and chemical technology will be mentioned.

All physical methods of cleaning coal involve crushing the coal and separating the mineral matter from the organic part of the coal. Wet and dry methods of separation are used,but the wet methods are more common and are grouped in a broad category known as washing.

The density of the organic portion of coal is much less than that of the mineral matter of the coal. This enables a process called Float/Sink separation to be employed. The crushed coal is added to a liquid medium of intermediate density. The organic portion, being more bouyant,tends to float while the mineral matter sinks toward the bottom. This separation works well for mineral matter that is course and forms separate particles from the coal. The process is not efficient for mineral matter that is finely divided and is intimately mixed with the organic portion. The density separation of this situation is not sufficient for a good separation of minerals and organic portions.

Clean coal has a specific gravity of 1.3 - 1.7 and 2.5 - 5.0 for mineral matter. The solution medium must have a density of about 2.0. The medium usually consist of fine magnetite particles suspended in the water. The particles tend to settle,but with agitation and solution of clays from the coal the particles stay in suspension. The particles of organic that float must be separated by screening or cyclones. The best particle size for separation varies from 0.5 - 6 mm depending upon the type of screening process.(5)

A new medium for float/sink separation is Freon 11. Freon has a density of 1.48 and is less viscous than magnetite solutions which enables the coal particles to make a faster separation. The displacement of surface moisture by the nonpolar freon allows for a better separation as the hydrophillic mineral matter coagulates and falls to the bottom of the medium faster. The low vapor pressure of freon allows for quick drying of the coal and mineral matter.(6)

Hydraulic methods of coal cleaning rely upon the difference of settling rates of organic and mineral matter. Washing tables are an example of hydraulic techniques. The coal is passed over a set of riffles in a water suspension. The riffles catch and hold mineral matter that falls to the bottom faster. A series of tables is an efficient way of removing large portions of mineral matter.

Hydrocyclones remove mineral matter by centrifugal force. The mineral matter is forced outward from the vortex of the cyclone and falls to the bottom. The organic matter that stays suspended is forced up and out by the incoming new suspension.(7)

Some coal cleaning technology is based upon the surface nature of the coal constituents. Mineral matter tends to be hydrophillic, whereas the organic portion is hydrophobic. Froth flotation separation is based upon this principle. The coal is suspended in a water solution,and air is forced through the solution. The organic portion becomes attached to the air bubbles and are forced upward by the increase in buoyancy. The hydrophillic portions are left behind in the water suspension. The coal is removed from the surface with the froth. The organic portion is then screened and dried. Frothing agents such as methyl isobutyl carbinol or pine oil are added to increase the frothing of the water. Kerosene is also sometimes added to increase the hydrophobic nature of the organic portion of the coal.(8)

Oil agglomeration methods and solvent partioning methods rely upon the hydrophobicity of the organic components of the coal. In oil agglomeration, a small amount of oil is added to the water suspension of the coal. This oil attaches to the organic component and tends to coagulate the particles. The mineral matter stays in the water. The organic agglomerates can then be removed by selective screening.

Solvent partioning methods use large amounts of oil to form an immiscible layer on top of the coal/water suspension. The organic portion of the coal will migrate to the oil layer leaving the mineral matter in the aqueous layer causing the separation of the components.(9)

Chemical cleaning methods are needed to remove the finely disseminated pyritic sulfur and the organically bound sulfur. There are several methods in development that are designed to remove one or both of these forms of sulfur.

There are several chemical oxidants that are strong enough to remove pyritic sulfur and a portion of the organic sulfur. The removal of organic sulfur is harder to accomplish than pyrite removal. It is also questionable that organic sulfur is determined correctly in reacted coals. Organic sulfur is an analysis that is found by difference, and it is believed that a good comparison of an element that is not analyzed directly cannot be made.

There are four major processes under development that use air and aqueous media at elevated temperatures to remove pyrite and some organic sulfur. The first to be described is the Ledgemont Oxygen Leaching (LOL) Process.

The LOL process leaches ground coal in a solution containing dissolved oxygen. The reaction conditions are 10-20 atm. partial pressure of oxygen, 130 degrees celsius, 1-2 hours reaction time, and either slightly acidic or basic media. Using acidic solutions, 90% of the pyrite can be removed with little or no effect on organic sulfur. Pyrite is oxidized to ferric sulfate and sulfuric acid. The reaction is expressed in the following equation:

$$4\ FeS_2 + 15\ O_2 + 2\ H_2O = 2\ Fe_2(SO_4)_3 + 2\ H_2SO_4$$

Under alkaline conditions (1-3 M ammonium hydroxide), 80-85% of the pyrite is removed and 30-40% of the organic sulfur is removed. In alkali the oxidation of pyrite follows the following reaction;

$$FeS_2 + 4\ NH_3 + 7/2\ H_2O + 15/4\ O_2 = 2(NH_4)_2SO_4 + Fe(OH)_3$$

Oxygen is used at a rate of 0.1 kg/kg of coal. In alkali the coal looses 10% of its carbon content, but in acid conditions this loss is not seen.(10)

Similar to the LOL process is the promoted Oxydesulfurization Process. This leaching process uses oxygen at 20 atm partial pressure at 120 degrees celcius for one hour. The leaching is promoted by an iron-complexing agent such as oxalic acid or its salt. A second reaction follows the first leaching where the coal is heated to 350 degrees for one hour. Almost all of the pyrite is removed and about 35% of the organic sulfur is removed by the two-step process. Only about 5% of the heating value is lost.(11)

Higher temperatures are used in the PETC Oxydesulfurization Process. Temperature of 140-200 degrees celcius and oxygen partial pressures of 34-68 atm. are used. Leaching is very fast under these severe conditions. Reaction time is one hour with near 100% removal of pyrite. The general equation for the removal of pyrite is

$$2\ FeS_2 + 7\tfrac{1}{2}\ O_2 + H_2O = Fe_2(SO_4)_3 + H_2SO_4$$

$$Fe_2(SO_4)_3 + n\ H_2O = Fe_2O_3 \cdot (n-3)H_2O + 3\ H_2SO_4$$

Besides pyrite, up to 45% of the organic sulfur can be removed. Heating losses are usually in the order of 10%.(12)

The Ames Process uses basic solutions of sodium carbonate and 14 atm. partial pressures of oxygen to remove 95% of the pyrites and up to 50% of the organic sulfur. The time of reaction is one hour followed by a second leaching step at 240 degrees celcius in a nitrogen atmosphere. The pyrite is extracted as soluble sulfate and a residue of hematite. The general reaction of the process is

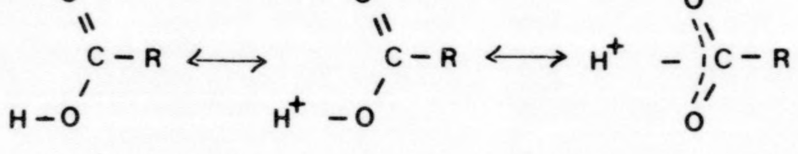
$$2\ FeS_2 + 7.5\ O_2 + 4\ H_2O = Fe_2O_3 + 4\ H_2SO_4$$

$$H_2SO_4 + 2\ Na_2CO_3 = Na_2SO_4 + 2\ NaHCO_3$$

The rate of pyrite removal is directly related to diffusion of oxygen through the hematite shell that forms around the pyrite crystals. The organic removal mechanism is not understood but is related to the availability of oxygen.(13)

These processes offer significant reductions in sulfur but are not very economical because of the severe reaction conditions and length of reaction. If a viable desulfurization process is to be developed, it must use mild conditions, short reaction times, and inexpensive reactants. Also, the process must not degrade the coal significantly.

This research began after the presentation of a seminar at Western Kentucky University, the seminar was entitled micelles. The seminar speaker discussed the type of molecules that form micelles. These molecules have a characteristic hydrophobic and hydrophillic part of the molecule. The carboxylic acids used in this research should penetrate the coal as a result of their hydrophobic nature and chelate soluble iron using their hydrophillic portion of the molecule. Given below is the resonance structure of a typical carboxylic acid:(14)



It was hoped that the chelation of iron would shift the solubility of pyrites and aid in pyritic sulfur removal.

EXPERIMENTAL

Materials

All reagents used in this research were of reagent grade. All reaction mixtures were prepared with water that had been deionized using an exchange column. The water used for rinsing had been deionized also. The air used to pressurize some of the reactions was designated breatheable quality.

Apparatus

The reactions were carried out in two types of reaction vessels. The majority of the preliminary reactions were carried out in a 325 ml. stainless steel autoclave, capable of maintaining a maximum pressure of 3000 psi. The autoclave was manufactured by American Instruments (Model 40 12150SP, Series G6 3129). The vessel is heated by a thermostat controlled sleeve and is agitated by a pivoting rocker cam. The second kind of vessel was a simple 250 ml roundbottom flask heated by a heating mantle and stirred by a magnetic stirrer.

Procedure

Seventy reactions were carried out using -8 mesh 82040. These reactions represent a systematic attempt to optimize reaction conditions and reagents for removing sulfur. Carboxylic and Peracids were reacted under varying conditions. The first nine reactions of the series of seventy were random in their quantities of reactants. After these initial nine reactions the decision was to be very systematic about reaction variables.

The carboxylic acids were the first reactants to be studied. The acids used were: formic, acetic, propionic, butyric, valeric, iso-butyric, iso-valeric, and trimethyl acetic acid. Each acid was reacted with ten grams of -8 mesh 82040. One hundred milliliters of 2.0 M acid was used in each case. The reaction mixture was placed in the autoclave and allowed to come to temperature. the reaction time for all the experiments was one hour, including a heat-up period of thirty minutes. The pressure in the reactor increased during the reaction because of reaction temperature. Reaction temperature of the autoclave was held at 150 degrees celcius. At the end of the reaction time, the pressure built up during the reaction was released. The reaction mixture was then immediately filtered.

The filtering procedure had to be standardized for all reactions. If there were changes in procedure, a discrepancy in ash removal might result. To prevent this, Schleicher & Schuell #588 prefolded filter paper was used. This paper is .008 inches in thickness and is considered a fast filter paper. After the reactor had been rinsed into the filter, 100 ml. of boiling water was poured over the coal.

After the coal had drained, the filter paper was scraped with a spatula to remove the coal from the paper.

The sample was then transferred to a beaker and placed in a vacuum oven. The temperature of the oven was 110 degrees celcius. The sample remained under vacuum for eighteen hours. After drying the sample was then pulverized in a high speed grinder. The sample had to be ground to a smaller particle size so that full analysis could be completed.

The reaction mixtures containing buffered solutions of the acids were prepared by adding sodium hydroxide pellets to the acid solution to neutralize one half of the available acid, resulting in a reaction mixture that was 1 M in the acid and the salt.

The reaction mixtures containing salt solutions were prepared by adding a stoichiometric amount of base to the acid to make a 2 M solution of the salt. The basic salt reaction mixture was made by adding one and one-half equivalents of base to the acid, producing a solution that was 2 M in the salt and 1 M in sodium hydroxide.

The peracids were prepared by adding hydrogen peroxide to the acid solution. One milliliter of sulfuric acid was added to catalize the formation of the peracids. The only peracids used were performic and peracetic. Reactions were carried out using the peracids, their buffered solutions, their salt solutions and their basic salt solutions. Sodium hydroxide was used to form these mixtures. The base was added one hour after the peracid mixture was made, thus preventing the base from reacting with the hydrogen peroxide and lowering the molarity of the peracids in solution. The base preapration was also cooled during the neutralization of the peracids to prevent decomposition of the peracids.

Formic and acetic acids were reacted under pressure. Air was used to pressurize the reactor to 600 psi. The acids were mixed in their respective acid, buffer, salt, and basic salt solutions. A combination of formic and acetic solution was also reacted under pressure. These reactions were 1 M in both formic and acetic acids. This combination was carried through the range of acid, buffer, salt, and basic salt conditions.

After examining the preliminary data, a decision was made to run a reaction combination of formic and trimethyl acetic acid salts. These reactions were carried out in the autoclave and an open air system. The open air reaction consisted of a solution boiling at 102 degrees celcius. The 82040 coal was added after boiling started and allowed to remain at temperature for thirty minutes. The reaction was stirred by a magnetic stirrer.

After evaluation of the preliminary experiments, it was decided to prepare a reaction mixtue containing formic and iso-valeric salts. This mixture was used in the final reactions with -60 mesh coals. The same reaction conditions were used during these experiments (150 degrees celsius, 2 M. solution in each salt, and one atm. initial pressure). The -60 mesh coals were filtered in the same way as the preliminary reactions. However, the coals were not dried in a vacuum oven. Instead they were dried at 110 degrees celcius with an air flow to prevent loss of volatile matter by the vacuum.

Analysis

The first analysis performed on the reacted coals was done by the LECO MAC-400. The MAC-400 is a microprocessor based unit that determines moisture, ash, volatile matter, and fixed carbon, by difference, of coal samples. A one gram sample is used for the analysis. Only one analysis was run for the preliminary reactions,and duplicates were performed on the -60 mesh reacted coals. The MAX-400 automatically tares and weighs the coal samples. It then ramps temperature according to a preprogrammed schedule. A determination is made when three consecutive weighings have less than 0.05 percent variance. The sensitivity of the instrument is 0.01 percent.(15)

All total sulfur determinations were made on the LECO SC-132, also a microprocessor based instrument for determining the sulfur content in coal, coke, and petroleum products. Samples are combusted in an oxygen atmosphere where the sulfur oxidizes to sulfur dioxide. Moisture and dust are removed,and sulfur dioxide gas in then measured by a solid state infrared detector. The sensitivity of the instrument is 0.001 percent. The instrument is calibrated using dry coals with standardized sulfur content.(16)

Carbon, hydrogen and nitrogen percentages were determined using the LECO CHN-600. The CHN-600 uses an infrared detector for determining carbon and hydrogen. A thermal conductivity detector is used to determine nitrogen. Sensitivity is 0.01 percent for carbon, hydrogen and nitrogen. Standardization of the instrument is accomplished using standarized dry coals.(17)

The calorific values of the -60 mesh coals were determined by the LECO AC-200 automatic bomb calorimeter. The AC-200 is a microprocessor based unit that uses an isothermal calorimeter to determine heating values to the nearest Btu per pound. The unit has a temperature resolution of 0.00025 degrees celcius.(18)

Forms of sulfur of all reacted coal samples was determined by ASTM procedure D 2492. A two to five gram sample is extracted with boiling hydrochloric acid (2:3 dilution). This removes sulfate sulfur and non-pyritic iron. The coal residue is filtered and ashed. The extracted sulfate sulfur is precipitated with barium chloride solution. Sulfate sulfur is then determined by gravimetric analysis of barium sulfate. The ashed coal residue is extracted with hydrochloric acid (2:3 dilution) and is diluted to a standard volume. The pyritic iron samples were then determined using a Varian atomic absorption spectrometer. After pyritic and sulfate sulfur is determined, their values are subtracted from the total sulfur percentage to give the organic sulfur percentage.(19)

RESULTS AND DISCUSSION

The samples of coal used in this research were picked from the available supply in the Western Kentucky University (WKU) Coal Laboratory. WKU coal #82040 was chosen for the preliminary experiments. This coal is a coal which has been subjected to washing techniques at the mine to remove ash and pyritic sulfur. Any subsequent removal of unwanted ash or sulfur by the system being developed would be a result of the reactions and not just leaching by water.

The 82040 samples were crushed to a -8 mesh size. The size of the coal particles in the reactions is directly related to the ability of a leaching process to remove sulfur. Successful use of -8 mesh coal will make this process attractive for commercial applications. Table 1 gives complete analysis information on coal #82040. This analysis was carried out in the WKU Coal Lab. and followed ASTM procedures. Table 2 gives a sieve analysis on the -8 mesh coal. The sieve analysis shows the percentages of large and small particles available in the -8 mesh coal. The majority of the coal fell between the -16 mesh sieve and the +60 mesh partition.

The first acid used was formic acid. Figure 1 presents the reductions or increases in organic, pyritic, and total sulfur for all the acid reactions. Notice that the pyritic

Table 1

```
                 ************************************
                 **  WESTERN KENTUCKY UNIVERSITY   **
                 ** COAL CHARACTERIZATION LIBRARY **
                 **          DATA SHEET            **
                 ************************************

                                                          NOV 25 1983
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

COAL # 82040

WKU COAL (PEABODY COAL CO.)

IL #6 - (WASHED) - ST. CLAIR CO., IL

ANALYSIS      AS RCVD   AS DETD   DRY BASIS  MOIST MMF   D M M F   D A F
--------      -------   -------   ---------  ---------   -------   -----

PROXIMATE ANALYSIS

MOISTURE       11.52      7.72      .....       8.72      .....    .....

ASH            10.26     10.71      11.6       .....      .....    .....

VOL. MATTER    39.26     40.95      44.37      46.3       48.47    50.2

  XED CARBON   38.94     40.62      44.01      44.96      51.52    49.79

BTU/POUND      11150     11630      12602      13239      14751    14257


ULTIMATE ANALYSIS


CARBON         59.95     62.53      67.76      70.7       79.31    76.65

HYDROGEN*       4.53      4.73       5.12       5.34       5.99     5.79

NITROGEN        1.07      1.12       1.21       1.26       1.42     1.37

SULFUR          3.26      3.41       3.69       3.85       4.32     4.18

OXYGEN*         9.37      9.78      10.59      10.09       8.93    11.98
(BY DIFF.)

*  As-determined basis excludes hydrogen and oxygen of moisture

ASTM RANK IS HIGH VOL BITUMINOUS - B

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
                        -- CONTINUED ON PAGE 2 --
```

Table 1 (continued)

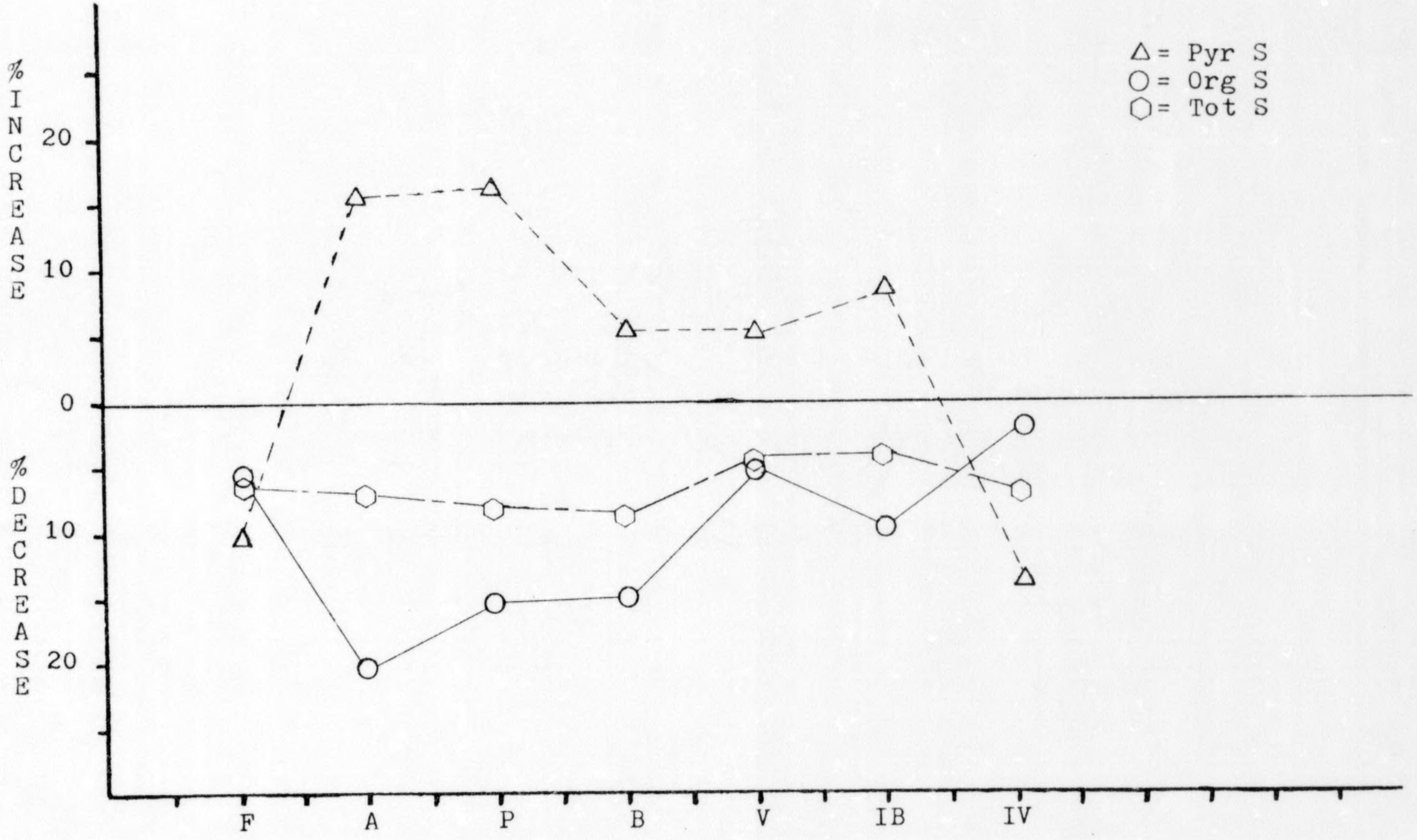
```
COAL  #  82040                                                    -- PAGE 2 --

ANALYSIS       AS RCVD   AS DETD    DRY BASIS  MOIST MMF   D M M F    D A F
--------       -------   -------    ---------  ---------   -------    -----

FORMS  OF  SULFUR

PYRITIC          1.14      1.19       1.28       1.34        1.5       1.45

SULFATE           .07       .08        .08        .09         .1        .09

ORGANIC          2.05      2.14       2.31       2.41       2.71       2.62

TOTAL S          3.26      3.41       3.69       3.85       4.32       4.18

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

MISCELLANEOUS  ANALYSIS

H/C ATOM RATIO (DAF) =  .9

O/C ATOM RATIO (DAF) =  .117

FREE-SWELLING-INDEX = 3.5

CHLORINE (PPM) =  413

HARDGROVE GRINDABILITY INDEX =

ASH FUSION TEMPERATURES (DEG FAHRENHEIT)
     INITIAL DEFORMATION TEMPERATURE, IT =  1986
     SOFTENING TEMPERATURE, ST           =  2054
     HEMISPHERICAL TEMPERATURE, HT       =  2135
     FLUID TEMPERATURE, FT               =  2365

MINERAL MATTER (DRY) =       (By oxygen plasma ashing)

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
```

Table 2

Sieve Analysis

On -8 Mesh #82040 Coal

U.S.A. Standard Sieve No.	Mesh Opening mm	Sieve Partition Percentage
+16	>1.18	4.44%
16-18	1.18-1.00	8.30%
18-35	1.00- .50	36.79%
35-60	0.5 -0.25	21.77%
60-100	0.25-0.15	9.67%
100-200	0.15-0.075	12.31%
-200	<0.075	6.72%



CARBOXYLIC ACID REDUCTIONS

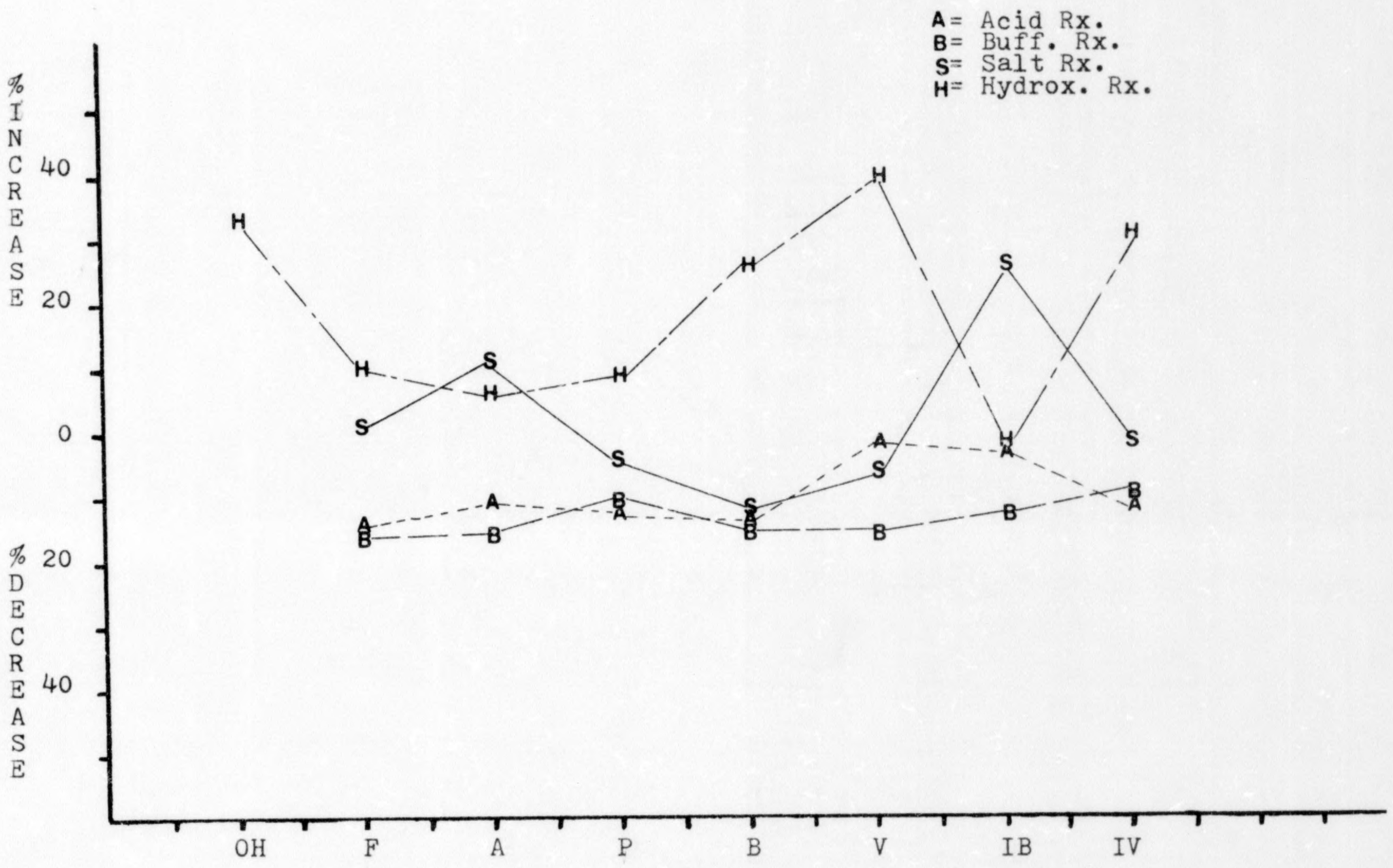
Figure 1

sulfur decreased for the formic acid reaction. The change is not understood, for in most cases there was an increase of pyritic sulfur for the smaller carbon content acids. Figure 2 illustrates the amount of ash removal or increase in all the reactions. As expected, the acid reactions remove ash. This removal is accomplished by the dissolving of basic mineral matter. Formic is the most acidic of the acids studied and does remove the most ash.

Acetic acid seems to remove the most organic sulfur in acid media. However, the pyritic percentage increases. This increase can be explained by removal of non-pyritic constituents in the coal. This removal would cause an overall increase in pyritic sulfur and thus not change total sulfur reductions.

The rest of the acids follow the same trends in sulfur and ash removal. There was a marked reduction in pyritic sulfur when iso-valeric was used. This could be explained as increase in the stability of an iron/iso-valeric ion complex as compared to the reast of the acid ions. Acid analysis results are given in Table 3, and reduction calculations are presented in Table 4.

The next set of reactions contained the buffered acid solutions. Figure 3 represents the sulfur reductions or increases for the acid buffer reactions. As one can see, the avriance of the removals in relation to the acid reactions is very eratic. There will be no attempt to explain individual trends except that there is an overall decrease in pyritic sulfur as compared to the acid reactions. As



ASH REDUCTIONS

Figure 2

Table 3

Acid Reaction Analysis

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	42.91	9.34	57.09	3.95	2.58	1.3
A	43.48	9.72	56.52	3.91	2.17	1.69
P	43.37	9.64	56.52	3.87	2.28	1.71
B	40.36	9.67	56.04	3.84	2.3	1.54
V	44.93	9.73	55.07	4.02	2.5	1.53
IB	43.36	10.60	56.64	4.04	2.46	1.58
IV	43.65	9.73	56.35	3.92	2.67	1.25

Analysis percentages are in dry ash free basis except ash which is in dry basis.

Table 4

Acid Reaction Reductions

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	-.43	14.39	.29	5.5	5.49	10.34
A	-1.76	10.9	1.29	6.45	20.51	-16.56
P	-1.5	11.64	1.11	7.41	16.48	-17.94
B	5.54	11.36	2.13	8.13	15.75	-6.21
V	-5.15	10.81	3.82	3.82	8.42	-5.52
IB	-1.48	2.84	1.08	3.34	9.89	-8.97
IV	-2.16	10.81	1.58	6.22	2.19	13.79

All reductions in percent of original analysis
Negative sign means increase

F = formic acid
A = acetic acid
P = propionic acid
B = butyric acid

V = valeric acid
IB = iso-butyric acid
IV = iso-valeric acid

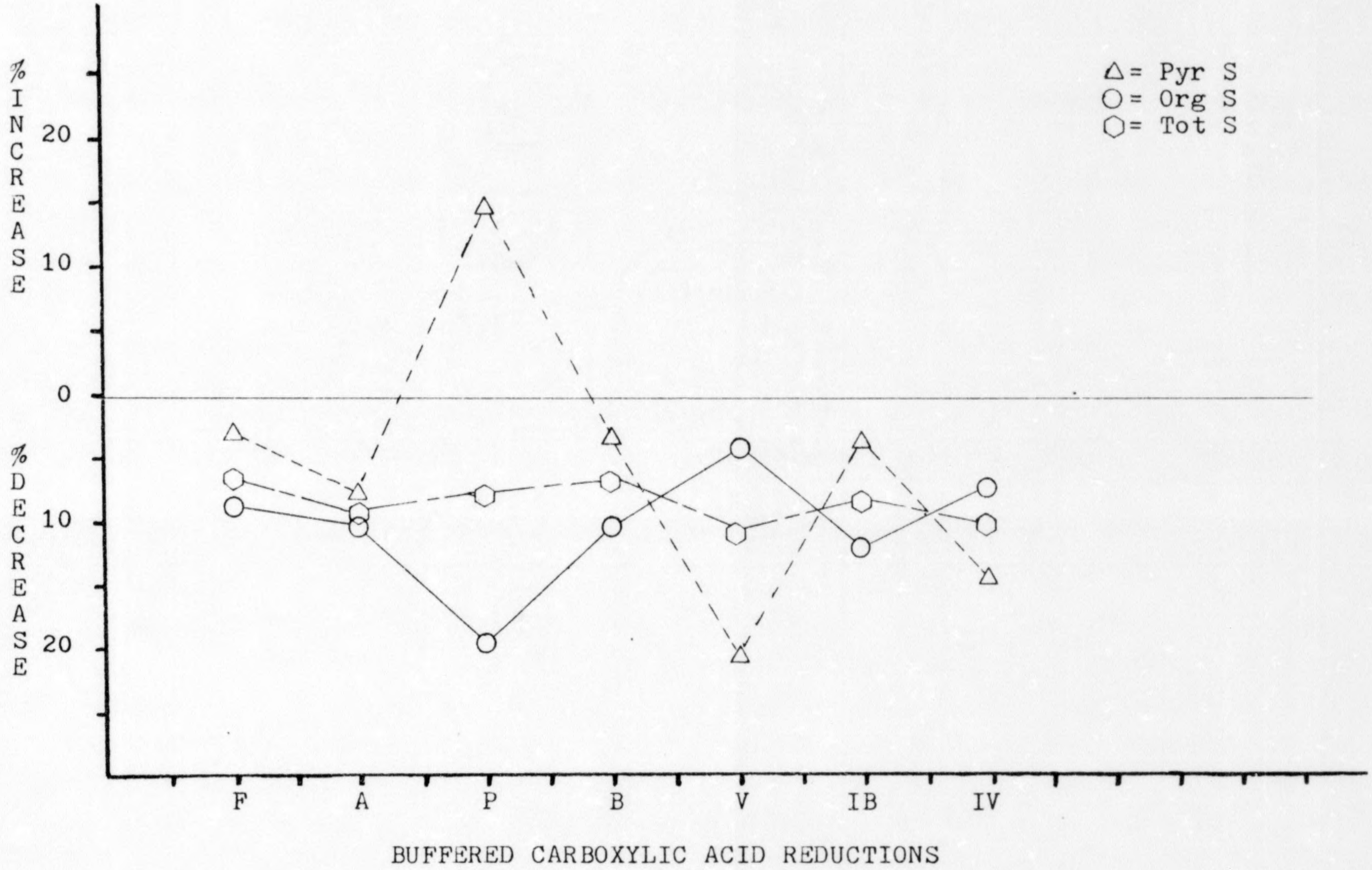
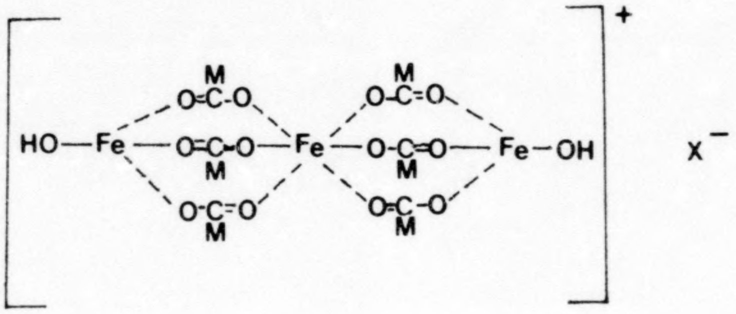

% INCREASE
20
10
0
% DECREASE
10
20
△= Pyr S
○= Org S
⬡= Tot S
F
A
P
B
V
IB
IV
BUFFERED CARBOXYLIC ACID REDUCTIONS

Figure 3

seen in Figure 1, ash removal does increase slightly for the buffered reactions. This possibly could have been a result of pyritic removal that occurred as the ash would contain a smaller amount of iron compounds. The analysis for the buffer reactions is given in Table 5 with reduction computations presented in Table 6.

Trends began to develop when analysis was finished on the reactions of the neutral salt solutions. The analysis results for the salt reactions are presented in Table 7. The percent reductions of the reactions in Table 8 were plotted in Figure 4. Pyritic reductions increase with increasing carbon structure. Iso-valeric salt removed the most pyritic sulfur. A study of iron being complexed with carboxylic ligands was made by D. D. Perrin in 1958.(20) He proposed that in high concentrations of ligands and iron, a 3:2:6 ferrichydroacid complex forms. The structure of the complex with the acetate ion is given below:



These complexes have high stability constants on the order of ten to the twentieth power. He also noticed that stability increased with carbon content of the acid. His studies showed that stability increased as pk's of the acids increased,but there was a marked increase of stability of

Table 5

Acid Buffer Reaction Analysis

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	43.11	9.22	56.89	3.92	2.49	1.41
A	43.16	9.22	56.84	3.79	2.46	1.34
P	43.29	9.78	56.71	3.86	2.20	1.67
B	42.88	9.52	57.12	3.91	2.50	1.41
V	44.08	9.33	55.92	3.74	2.6	1.14
IB	43.41	9.54	56.57	3.83	2.44	1.39
IV	43.67	9.85	56.33	3.77	2.53	1.24

Analysis percentages are in dry ash free basis except ash which is in dry basis.

Table 6

Acid Buffer Reaction Reductions

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	-.89	15.49	.64	6.22	8.79	2.75
A	-1.01	15.49	.73	9.33	9.89	7.58
P	-1.32	10.35	.96	7.65	19.41	-15.18
B	-.36	12.74	.24	6.45	8.42	2.75
V	-3.16	14.48	2.34	10.52	4.76	21.37
IB	-1.6	12.55	1.2	8.37	10.62	4.13
IV	-2.2	9.71	1.62	9.8	7.32	14.48

All reductions in percent of original analysis

Negative sign means increase

F = formic acid

A = acetic acid

P = propionic acid

B = butyric acid

V = valeric acid

IB = iso-butyric acid

IV = iso-valeric acid

Table 7

Acid Salt Reaction

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	42.55	11.12	57.45	3.89	2.1	1.79
A	41.52	12.17	58.48	3.99	2.28	1.71
P	43.15	10.57	56.85	4.02	21.8	1.84
B	42.45	9.72	57.55	3.94	2.4	1.54
V	43.94	10.35	56.05	4.01	2.55	1.46
IV	41.23	13.96	58.77	3.79	2.39	1.4
IB	43.15	9.97	56.85	3.81	2.57	1.24

Analysis percentages are in dry ash free basis except ash which is in dry basis.

Table 8

Acid Salt Reaction Reductions

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	.42	-1.93	-.34	6.93	23.07	-23.45
A	2.83	-11.55	-2.14	4.54	16.48	-17.94
P	-.99	3.11	.71	3.82	20.14	-26.9
B	.65	10.9	-.51	5.74	12.08	-6.21
V	-2.84	5.13	2.11	4.06	6.59	-.69
IB	3.51	-27.96	-2.64	9.33	12.45	3.44
IV	-.99	8.61	.71	8.85	5.86	14.48

All reductions in percent of original analysis

Negative sign means increase

F = formic acid

A = acetic acid

P = propionic acid

B = butyric acid

V = valeric acid

IB = iso-butyric acid

IV = iso-valeric acid

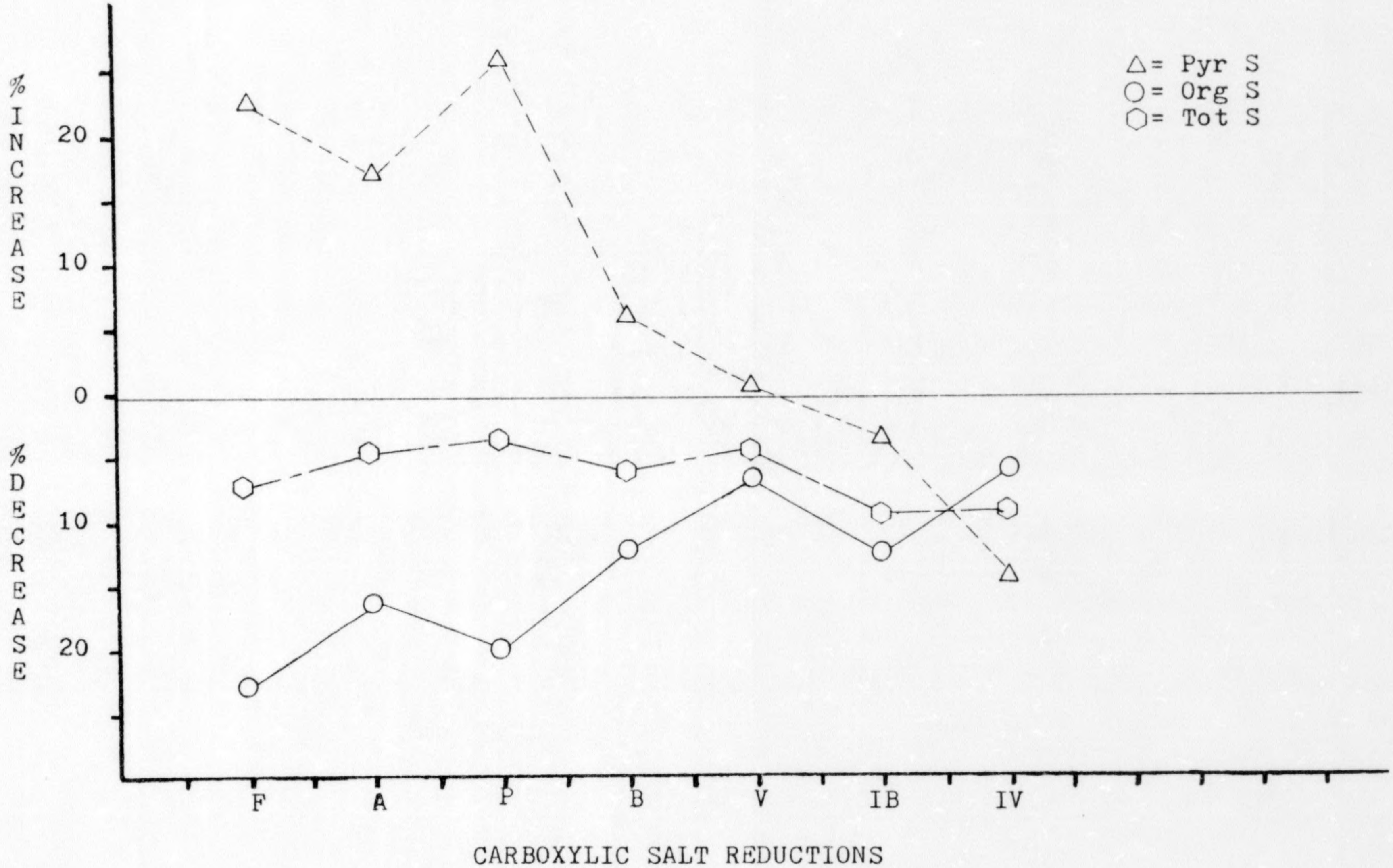

△= Pyr S
○= Org S
⬡= Tot S
% INCREASE
20
10
0
% DECREASE
10
20
F
A
P
B
V
IB
IV
CARBOXYLIC SALT REDUCTIONS

Figure 4

iso-butyric ligands. This increase was explained by the 3:2:6 complex above. Likewise the reduction of pyritic sulfur increases with increase of carbon content of the ligands. This could be explained by the stability of the iron complex.

Another trend is also established by Figure 4. Organic sulfur is reduced more effectively by smaller carboxylic ions. Formate ion showed the highest potential for organic sulfur removal. The ash removal presented for the salt reactions in Figure 2 shows a variance around zero. This could possibly be expalined by the varying stabilities of the complexes formed from metal components of the ash.

The next group of experiments used a 1 M concentration of base along with the 2 M of acid salt. All of the reactions were marked by a breaking down of the coal matrix. This degradation was apparent in the very dark brown color of the washings during filtering. It was thought that the removal of sulfur would be greatest in a basic solution. This thought came from the ability of a base to remove an oxidized sulfur form from the matrix.(21) The base, however, removed so much of the matrix, the end product increased its ash content considerably. This increase in ash caused an overall increase of sulfur when analysis was determined on a dry ash free basis. Tables 9 and 10 give analysis and percent reductions,respectively,for the basic reactions. Figure 5 is a graphic representation of the percent reductions for the basic reductions.

Table 9

Basic Salt Reaction Analysis

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
OH	41.56	14.65	58.44	4.29	2.19	2.10
F	41.53	12.03	58.47	3.91	2.24	1.68
A	41.54	11.67	58.46	3.86	2.48	1.37
P	41.71	11.91	58.29	3.77	2.35	1.42
B	40.97	12.75	59.02	3.86	2.48	1.38
V	42.00	15.35	58.00	3.93	2.38	1.55
IB	42.62	10.78	57.38	3.87	2.68	1.19
IV	41.25	14.41	58.75	3.73	2.53	1.2

Analysis percentages are in dry ash free basis except ash which is in dry basis.

Table 10

Basic Salt Reaction Reductions

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
OH	2.73	-34.29	-2.07	-2.64	19.78	-44.83
F	2.8	-10.27	-2.12	6.45	17.94	-15.87
A	2.78	-6.97	-2.1	7.65	9.15	5.51
P	2.38	-9.17	-1.8	9.8	13.91	2.06
B	4.11	-16.87	-3.08	7.65	9.15	4.82
V	1.7	-40.7	-1.3	5.98	12.82	-6.9
IB	.25	1.19	-.21	7.41	1.83	17.93
IV	3.46	-32.09	-2.61	10.76	7.32	17.24

All reductions in percent of original analysis

Negative sign means increase

F = formic acid

A = acetic acid

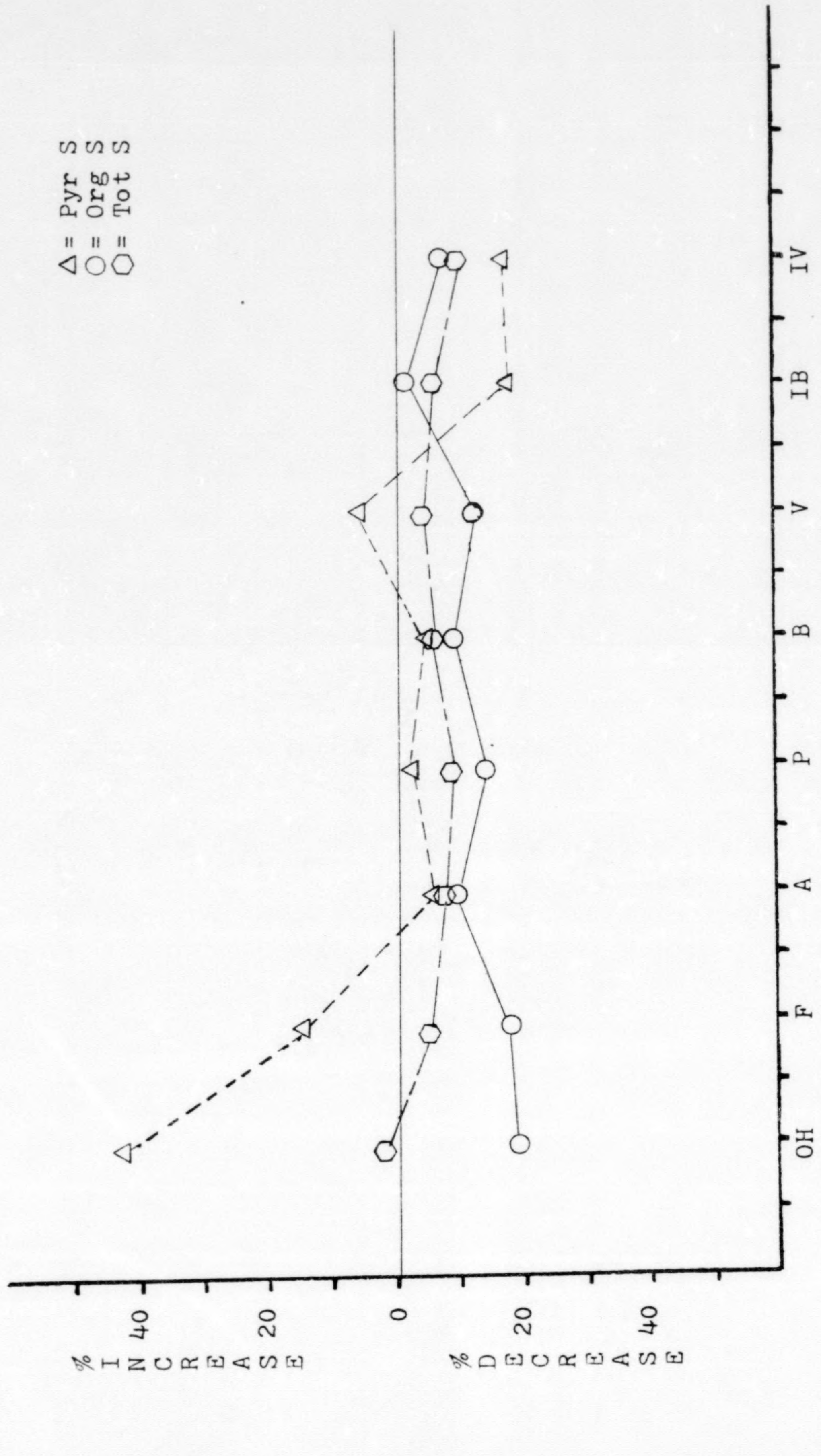
P = propionic acid

B = butyric acid

V - valeric acid

IB = iso-butyric acid

IV = iso-valeric acid



BASIC CARBOXYLIC SALT REDUCTIONS

Figure 5

There were a few trends set with the reactions that involved the various carboxylic acids in different acid media. First the ash reduction decreases going from acid to base conditions. Second, organic sulfur reductions decrease with increasing carboxylate ion size increases. Thirdly, pyritic sulfur removal increased with increasing carboxylic ion size.

The next set of reactions used peracids as the main reactant. The experimental portion of the paper described their preparation. Table 11 presents the analysis results for the peracid reactions. Only two peracids were prepared and used. Performic and Peracetic were chosen because of their solubility in aqueous systems. A blank reaction was done using only hydrogen peroxide. This reaction allowed a comparison of the peracids. The percent reductions of Table 12 are graphed in Figure 6. The total sulfur reductions are greatly increased by the peracids. This reduction is mostly due to the great decrease in pyritic sulfur. The high oxygen environment provided by the peracids allows for increased oxidations of pyritic sulfur. The organic reduction is similar to that found in the carboxylic reaction set. There is an increase in reduction of pyritic sulfur with peracetic where as performic does not increase the reduction of pyritic. Organic sulfur reductions decrease with performic, and there is no change in organic sulfur with performic. The peroxide blank removes the most organic sulfur.

The peracids were then taken to their respective buffered solutions and reacted. The peracid buffer analysis is given

Table 11

Peracid Analysis

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
H_2O_2	43.14	9.03	56.86	3.37	2.28	.77
F	43.28	8.91	56.72	3.41	2.32	.76
A	43.33	8.67	56.67	3.26	2.46	.46

Analysis percentages are in dry ash free basis except ash which is in dry basis.

Table 12

Peracid Reductions

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
H_2O_2	-.96	17.23	-52.61	19.37	16.48	46.89
F	-1.29	18.33	-52.23	18.42	15.01	47.58
A	-1.41	20.53	-52.1	22	9.89	68.27

All reductions in percent of original analysis
Negative sign means increase

F = formic acid

A = acetic acid

H_2O_2 = 1 M in H_2O_2

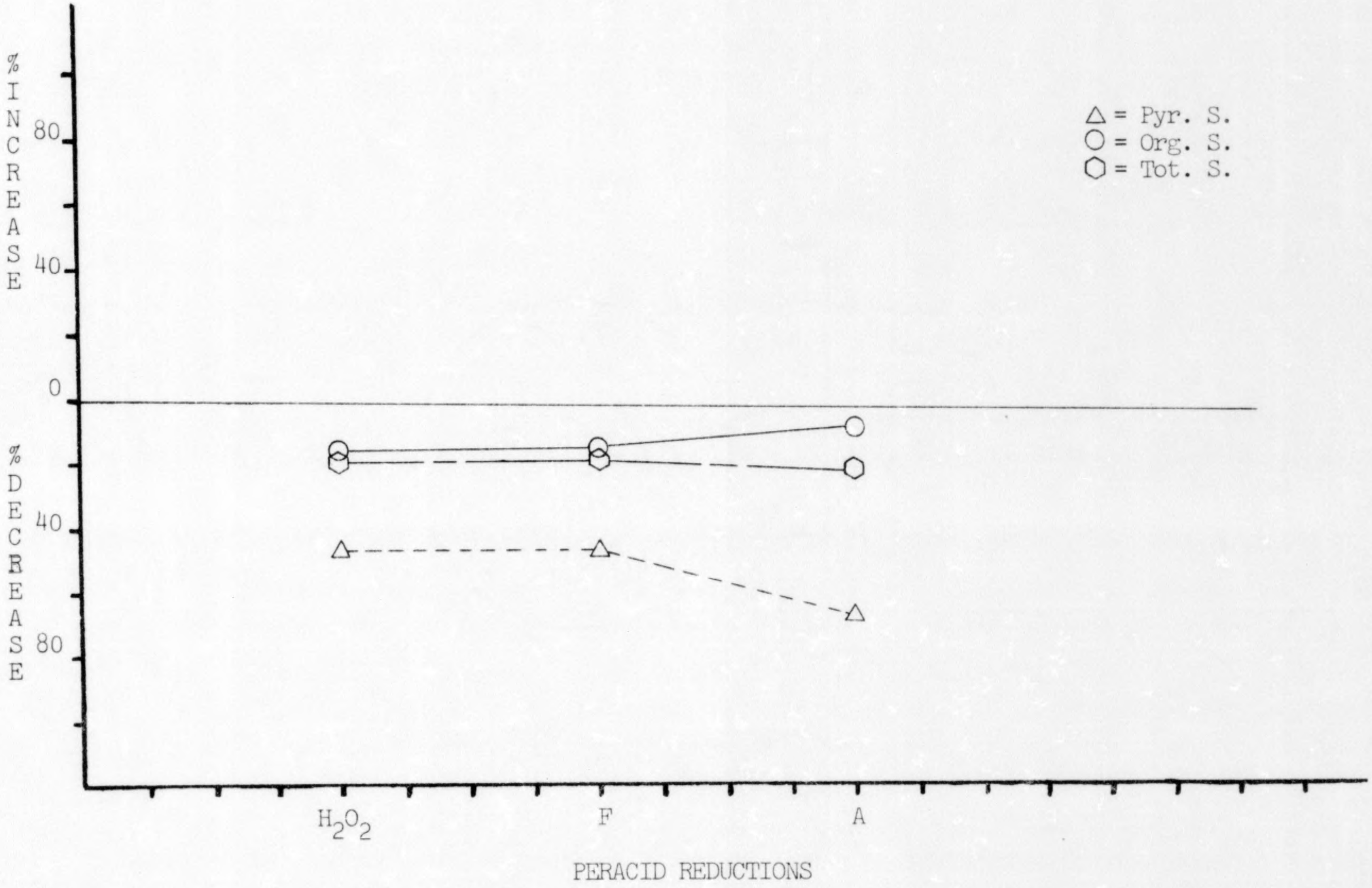

% INCREASE
80
40
0
% DECREASE
40
80
△ = Pyr. S.
○ = Org. S.
⬡ = Tot. S.
H_2O_2
F
A
PERACID REDUCTIONS

Figure 6

in Table 13. The sulfur reductions of Table 14 are plotted in Figure 7. In buffered solutions, the peracids do not reduce sulfur as well as the straight peracids. The trends of sulfur removal still remain. The peracetic buffer removes more pyrites while the performic buffer removes more organic sulfur. The ash removal for both the peracid and peracid buffer systems are similar. The two systems do remove more ash than do carboxylic reactions. This increased reduction must be a result of the high oxygen environment of the peracid reactions.

There was a discrepency in the neutral peracid reductions. The peracetic salt removed more organic sulfur than the performic salt. This change in characteristic is not understood. The peracetic salt did remove more pyritic sulfur. Tables 15 and 16 give the analysis and reductions, respectively, for the peracid salt reactions. The reductions in sulfur are graphed in Figure 8. There is a marked difference in ash removal between the two salts. Peracetic salt removed much more ash.

The trend in ash removal is also seen in the basic peracid salt reactions. Basic peracetic salt removed much more ash than the basic performic salt. Metals in the ash may be better chelated by the peracetate ion. The reductions shown in Table 18 are presented in Figure 9. The trend for performate to remove more organic sulfur is again established. Likewise, peracetate removes more pyritic sulfur.

The peracid reactions were not considered a viable desulfurization process. The cost of the peroxide needed

Table 13

Peracid Buffer Analysis

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	42.75	9.36	57.25	3.46	2.345	.77
A	42.87	9.59	57.13	3.52	2.80	.73

Analysis percentages are in dry ash free basis except ash which is in dry basis.

Table 14

Peracid Buffer Reductions

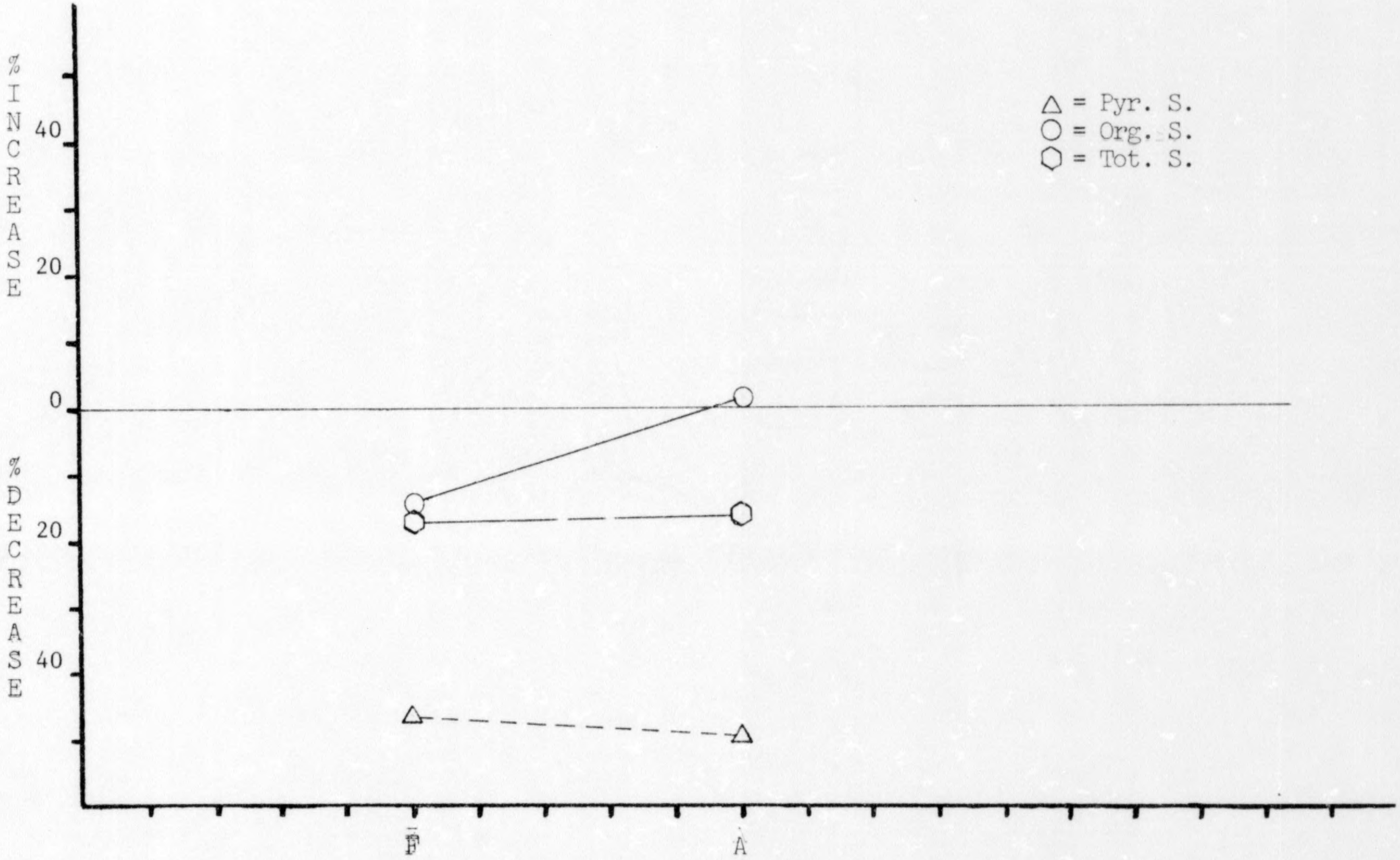
	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	-.05	14.2	.01	17.22	14.1	46.89
A	-.33	12.09	.22	15.78	-2.57	49.65

All reductions in percent of original analysis

Negative sign means increase

F = formic acid

A = acetic acid



PERACID BUFFER REDUCTIONS

Figure 7

Table 15

Peracid Salt Analysis

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	42.52	11.00	57.48	3.69	2.63	1.04
A	42.92	9.26	57.08	3.47	2.55	.90

Analysis percentages are in dry ash free basis except ash which is in dry basis.

Table 16

Peracid Salt Reductions

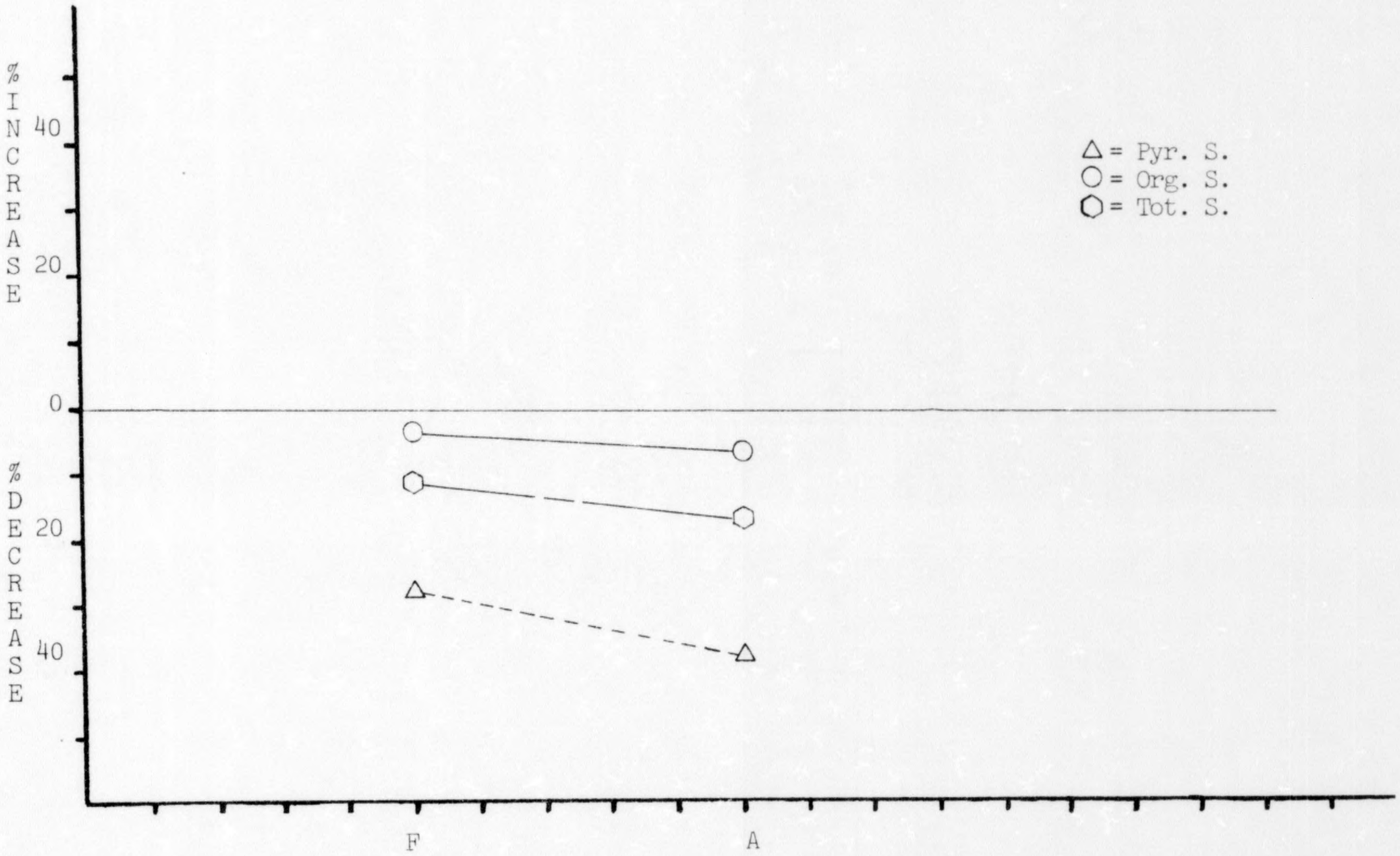
	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	.49	-.83	-.39	11.72	3.66	28.27
A	-.45	15.12	.31	16.98	6.59	37.93

All reductions in percent of original analysis

Negative sign means increase

F = formic acid

A = acetic acid



PERACID SALT REDUCTIONS

Figure 8

Table 17

Basic Peracid Salt

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	42.55	13.88	57.45	3.63	2.59	1.02
A	42.97	9.69	57.03	3.58	2.76	.81

Analysis percentages are in dry ash free basis except ash which is in dry basis.

Table 18

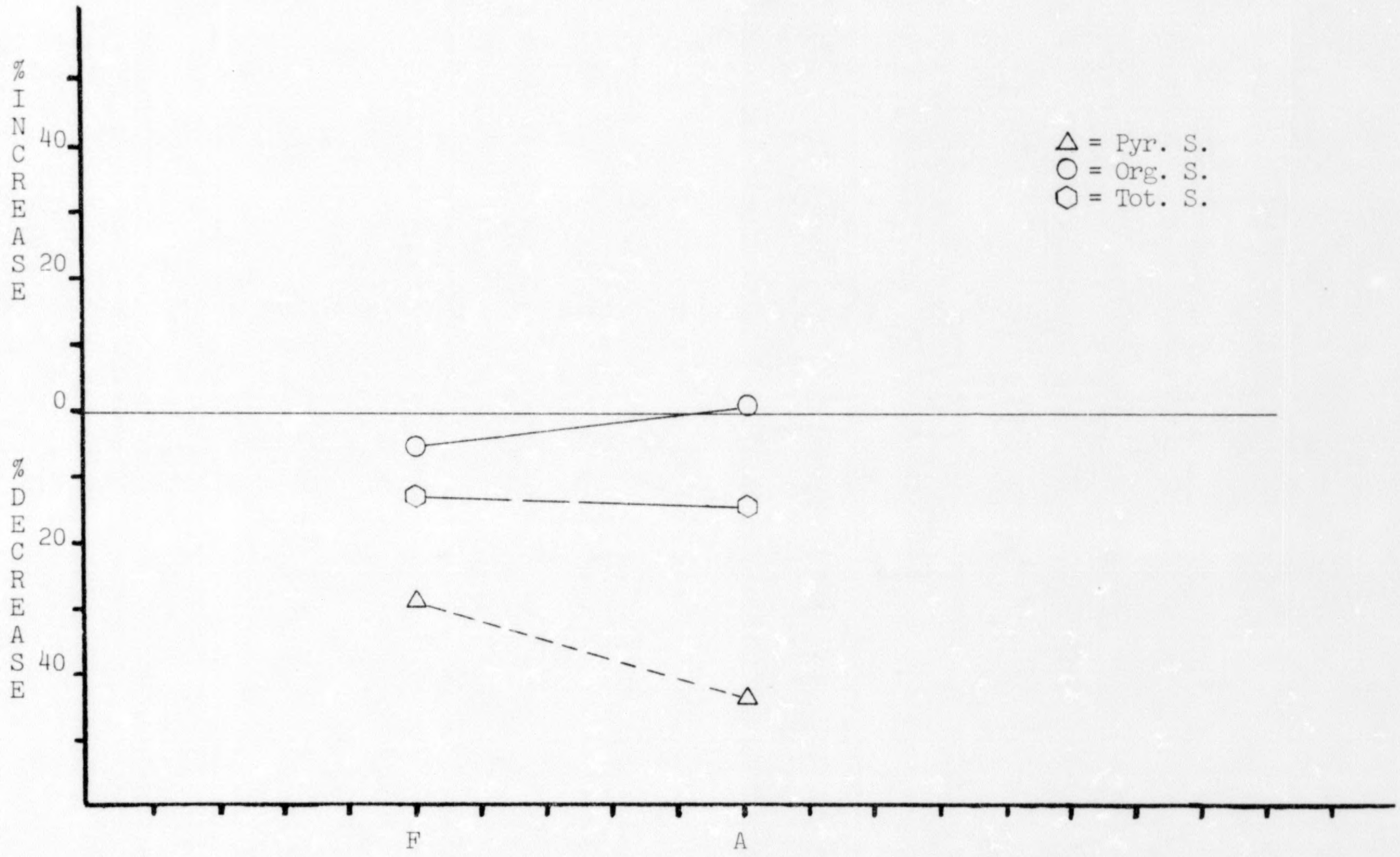
Basic Peracid Salt Reductions

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	.42	-27.23	-.34	13.15	5.12	29.65
A	-.57	11.18	.4	14.35	-1.1	44.13

All reductions in percent of original analysis
Negative sign means increase

F = formic acid

A = acetic acid



BASIC PERACID SALT REDUCTIONS

Figure 9

for the preparation of the solutions makes the process uneconomical. The reactions were conducted primarily as a point of interest. They do establish that organic sulfur reductions are better performed by a small attacking species such as the performate ion. Also pyritic sulfur removal is enhanced by increased organic size.

The amounts of sulfur removal attained by the peracidic reactions led to the next set of experiments. It was thought that a synthetic peracid system could be made by increasing the partial pressure of oxygen above the reactions mixture. Formic and acetic acids were reacted using 600 psi of air above the reactions. The acids were reacted using their acid, buffered, and neutral salt forms. Also a combination of the two was used to try to maximize total sulfur removal. It was thought that formate ion would attack the organic sulfur and acetate would help remove the pyritic sulfur.

Table 19 gives the analysis for the pressurized acid reactions. A water blank was employed for comparison. The reductions of Table 20 are graphed in Figure 10. The trends observed in sulfur form removal still hold for the pressurized acids. Organic sulfur is removed more readily by formic, while acetate removes more pyritic sulfur. The combination of formic and acetic acids did not increase the reductions. Ash removal was practically nonexistent for the reactions.

Buffered solutions were prepared for formic, acetic acid, and their combination. Organic sulfur removal was best accomplished by the acetic buffer. Pyritic sulfur removal was enhanced by the acetate buffer. The combination of

Table 19

Pressurized Acid Analysis

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
H_2O	42.73	10.68	57.27	3.87	2.64	1.19
F	42.69	9.84	57.31	3.81	2.63	1.16
A	42.75	9.46	57.25	3.85	2.85	.98
F+A	42.67	9.53	57.33	3.83	3.03	1.28

Analysis percentages are in dry ash free basis except ash which is in dry basis.

Table 20

Pressurized Acid Reductions

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
H_2O	0	2.1	-.02	7.41	3.29	17.93
F	.09	9.8	-.09	8.85	3.66	20
A	-.05	13.29	.01	7.89	-4.4	32.41
F+A	.14	12.64	-.13	8.37	-10.99	11.72

All reductions in percent of original analysis

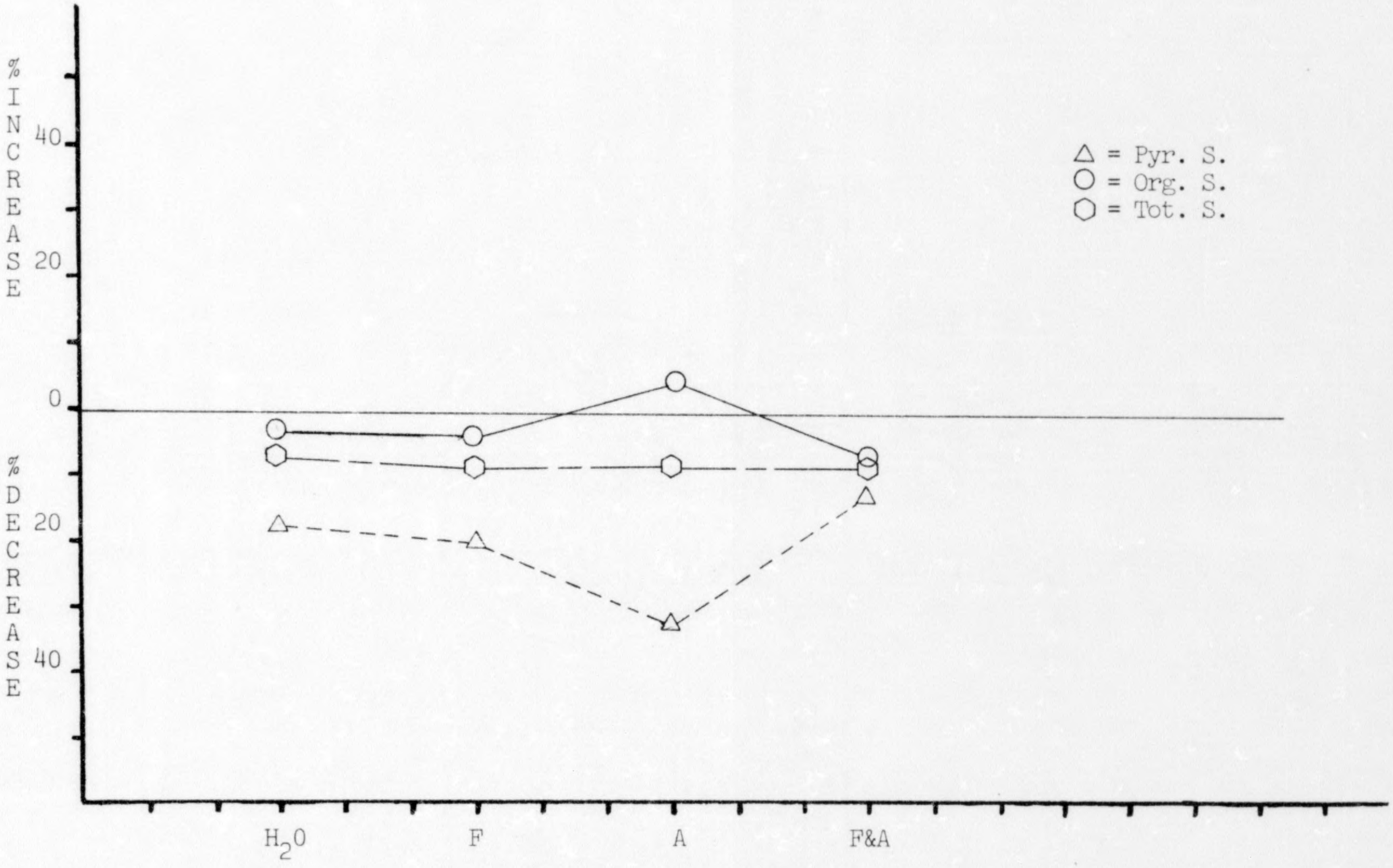
Negative sign means increase

H_2O = water blank reaction run

A = acetic acid

F = formic acid

F+A = formic and acetic acid combination



PRESSURIZED ACID REDUCTIONS

Figure 10

acids did not improve the reductions. Analysis and reduction data are given in Tables 21 and 22, respectively. The sulfur reductions are graphed in Figure 11. The ash content once again did not change dramatically.

The salt solutions of the three systems were reacted under pressure. Formate ion removed the most organic sulfur and formate removed the most pyritic sulfur. The analysis is presented in Table 23. The reductions of Table 24 are presented in Figure 12. The combination of salts did not remove sulfur as well as the independent salt forms.

The pressurized systems did not give the desired results. The increase in pressure would restrict the process in commercial applications. The slight increase in pyritic sulfur removal would not justify picking any one of these pressurized systems as the best system.

An open air system was investigated. Sodium formate, trimethyl acetate, and the combination of the two were reacted in an open roundbottom flask. The solutions were heated to reflux temperature. Trimethylacetic acid was used to try to maximize pyritic sulfur removal. Tables 25 and 26 give the analysis and reductions for the reactions. There was a removal of pyritic sulfur. This can be accounted for by a high availability of oxygen over the reactions. Organic sulfur increased, an indication that some pressure was needed by the ions to penetrate the coal structure. Sodium trimethylacetate and sodium trimethylacetate in combination with sodium formate were reacted in the autoclave as a control. The decrease in pyritic sulfur removal is consistent with the

Table 21

Pressurized Acid Buffer Analysis

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	42.75	9.88	57.25	3.94	2.65	1.28
A	42.03	10.15	57.99	3.80	2.58	1.2
F+A	42.46	10.38	57.54	4.08	2.77	1.31

Analysis percentages are in dry ash free basis except ash which is in dry basis.

Table 22

Pressurized Acid Buffer Reductions

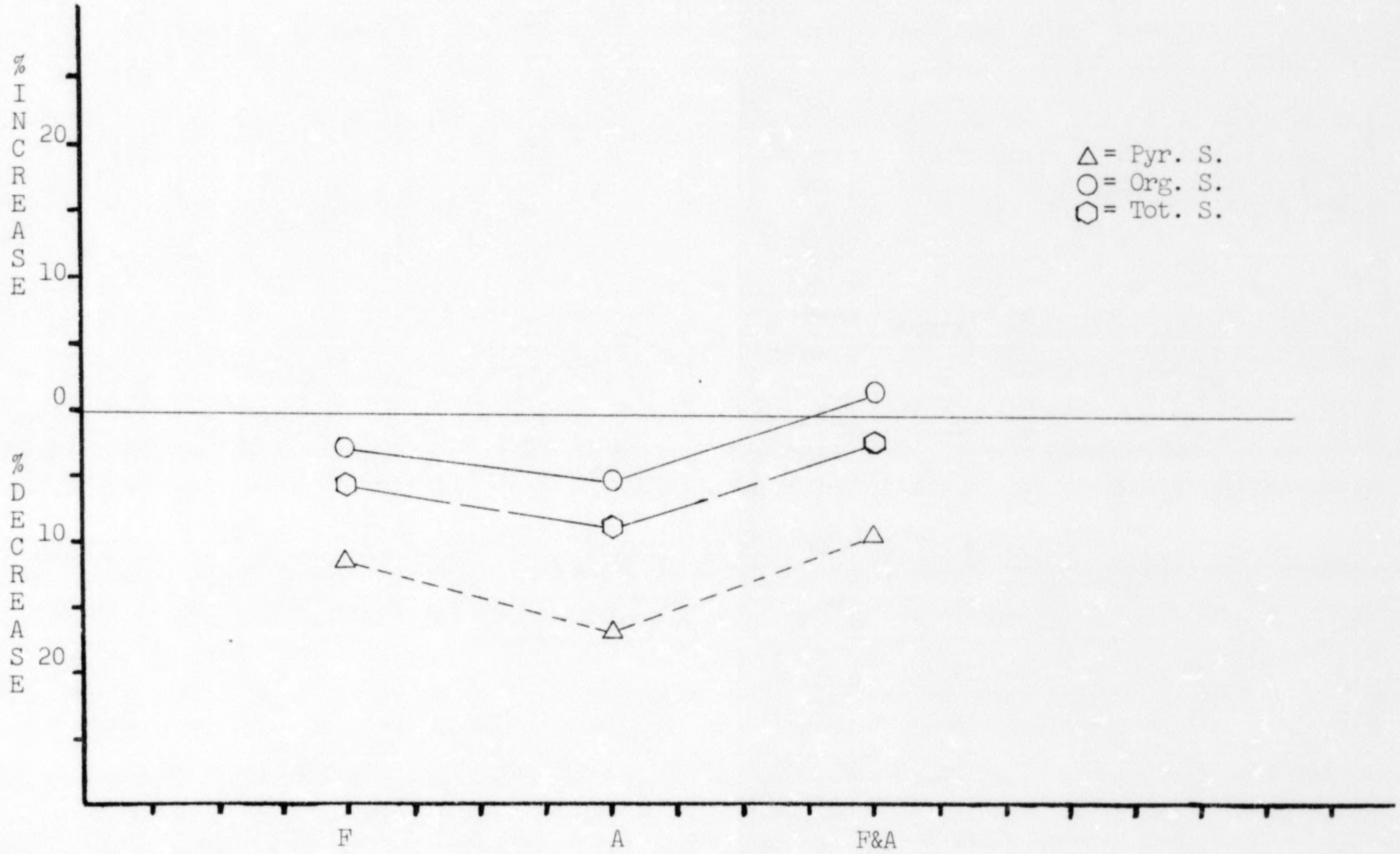
	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	-.08	9.44	.01	5.74	2.93	11.72
A	1.61	6.96	-1.28	9.09	5.49	17.24
F+A	.6	4.85	-.49	2.39	-1.47	9.65

All reductions in percent of original analysis
Negative sign means increase

F = formic acid

A = acetic acid

F+A = formic and acetic acid combination



PRESSURIZED ACID BUFFER REDUCTIONS

Figure 11

Table 23

Pressurized Acid Salt Analysis

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	41.84	11.25	57.51	3.89	2.45	1.45
A	42.32	10.89	57.68	3.86	2.52	1.32
F+A	42.72	11.82	57.28	4.1	2.71	1.38

Analysis percentages are in dry ash free basis except ash which is in dry basis.

Table 24

Pressurized Acid Salt Reductions

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	2.08	-3.12	-.44	6.93	10.25	0
A	.95	.18	-.74	7.65	7.69	8.96
F+A	.02	-8.35	-.04	1.91	.73	4.82

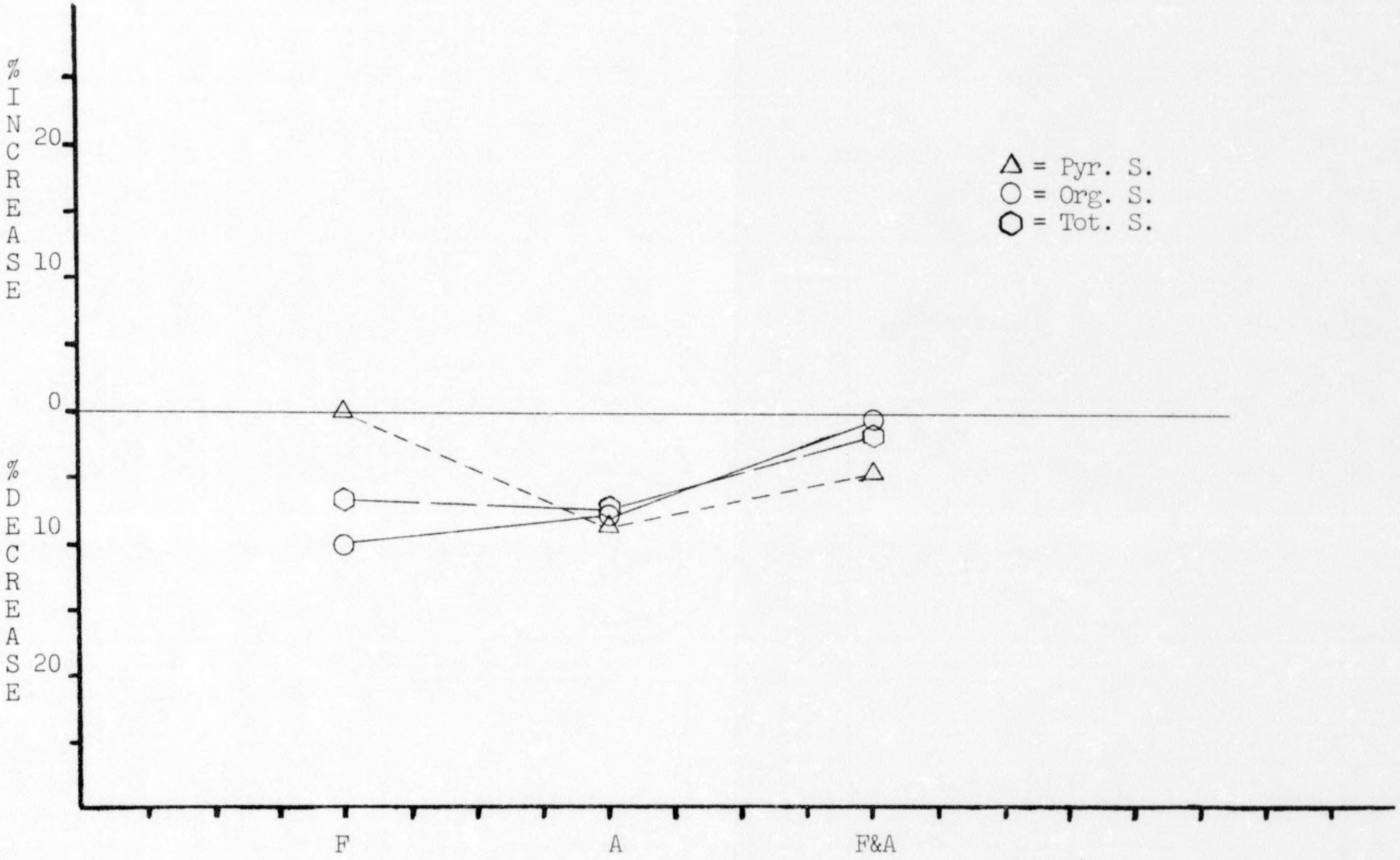
All reductions in percent of original analysis

Negative sign means increase

F = formic acid

A = acetic acid

F+A = formic and acetic acid combination



PRESSURIZED ACID SALT REDUCTIONS

Figure 12

Table 25

Open Air Analysis

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	42.71	11.88	57.29	4.46	3.14	1.31
T	43.14	11.39	56.86	4.19	2.98	1.21
F+T	43.39	10.98	56.60	4.25	2.86	1.39

Analysis percentages are in dry ash free basis except ash which is in dry basis.

Table 26

Open Air Reductions

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
F	.04	-8.9	-.06	-6.7	-15.02	9.65
T	-.96	-4.4	.69	-.24	-9.16	16.55
F+T	-1.55	-.65	1.15	-1.68	-4.77	4.13

All reductions in percent of original analysis
Negative sign means increase

F = formic acid
T = trimethylacetic acid
F+T = formic and trimethylacetic acid combination

idea that oxygen must be present for successful removal of this form of sulfur. The organic portion increased slightly in the control reactions. The organic portion increased slightly in the control reactions. The increase was much less than that of the open air systems, an indication that pressure is needed for successful organic sulfur removal. Analysis and reductions are presented in Table 27 and 28, respectively.

With the completion of the preliminary reactions, a "best system" had to be chosen for the reactions of the -60 mesh coals. In most all reactions, it was observed that organic sulfur was best reduced by formic acid derivatives. There seemed to be no variation in removal, of the organic sulfur, by varying acidic conditions. Sodium formate was chosen as one of the reactants. Pyritic sulfur was shown to be removed best by higher carbon content acids and salts. This led to the choice of iso-valeric acid to be used to reduce pyritic sulfur. It was decided that a combination of these two chemicals would be the system for the reactions of the -60 mesh coals. The question arose whether or not the two reactants would remove sulfur better together or separately. The decision was made to react one of the -60 mesh coals with the two reactants separately and together. The separate reactions of the coal were carried out on WKU coal #82040. Iso-valerate was reacted first, anticipating fracturing of the surface of the coal and opening more surface area to the attacking formate ion. It was thought that this breaking might possibly occur because

Table 27

Trimethyl and Formic Analysis

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
T	43.07	12.06	56.93	4.25	2.85	1.4
F+T	43.25	10.69	56.75	4.3	2.84	1.44

Analysis percentages are in dry ash free basis except ash which is in dry basis

Table 28

Trimethyl and Formic Reductions

	Vol. Matter	Ash	Fixed Carbon	Total Sulfur	Organic Sulfur	Pyritic Sulfur
T	-.8	-10.55	.57	-1.68	-4.4	3.44
F+T	-1.22	2.01	.89	-2.88	-4.03	.68

All reductions in percent of original analysis
Negative sign means increase

F = formic acid

T = trimethylacetic acid

F+T = formic and trimethylacetic acid combination pyrite is a non-matrix mineral. If the pyrite were to be attacked and removed, then there would be an increase in surface area. Tables 29-32 are a listing of the -60 mesh coals studied. The original analysis is given in different bases. Proximate, ultimate and forms of sulfur analysis are presented. The only -60 mesh coal not presented is #82040. Its analysis was presented in Table 1.

The -60 mesh coals were reacted in a combination of formate and iso-valeric ions. Only reaction #82040201 was done in two separate reactions. After the reactions were finished, complete analysis was carried out on the samples. The results of this analysis are presented as a group in Tables 33-38. The percent reductions are presented in Table 39. The coal numbers in Tables 1 and 29-32 correspond to the first five numbers in the reaction numbers of Tables 33-38.

There was little difference between the combination reaction of 82040202 and the in-tandum reactions run upon 82040201. There was a wide variance in the amounts of organic and pyritic sulfur removal of the different coals. This variance was expected because of the heterogeneous nature of coal. A relationship was found between the percentage volatile matter of each coal and the percent organic sulfur removed from the coal. This relationship is presented in Figure 13. The value of the combination run carried out on 82040202 was rejected. The remaining data were correlated comparing organic sulfur removal to percentage volatile matter (daf). The correlation coefficient

Table 29

```
*************************************
**  WESTERN KENTUCKY UNIVERSITY    **
** COAL CHARACTERIZATION LIBRARY  **
**           DATA SHEET            **
*************************************

                                                        NOV 23 1983
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

COAL # 82038

WKU COAL (DUNBAR COAL CO.)

CATES SEAM - BUTLER CO., KY

ANALYSIS      AS RCVD   AS DETD   DRY BASIS  MOIST MMF   D M M F   D A F
--------      -------   -------   ---------  ---------   -------   -----

PROXIMATE ANALYSIS

MOISTURE        8.19      5.07      .....       5.28      .....     .....

ASH             3.7       3.83       4.03      .....      .....     .....

VOL. MATTER    40.58     41.97      44.21      43.78      45.18     46.07

FIXED CARBON   47.51     49.13      51.75      50.93      54.81     53.92

BTU/POUND      12852     13290      13999      13922      14828     14588


ULTIMATE ANALYSIS

CARBON         71.84     74.29      78.25      77.49      82.89     81.54

HYDROG          5.13      5.31       5.59       5.53       5.92      5.82

NITROGEN        1.22      1.27       1.33       1.32       1.41      1.39

SULFUR          2.05      2.13       2.24       2.22       2.37      2.33

OXYGEN*         7.83      8.1        8.53       8.12       7.38      8.89
(BY DIFF.)

*  As-determined basis excludes hydrogen and oxygen of moisture

ASTM RANK IS HIGH VOL BITUMINOUS - B

  - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
```

Table 29 (continued)

COAL # 82038

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	MOIST MMF	D M M F	D A F
FORMS OF SULFUR						
PYRITIC	1.06	1.1	1.15	1.14	1.22	1.2
SULFATE	.04	.05	.05	.05	.05	.05
ORGANIC	.94	.98	1.03	1.02	1.09	1.07
TOTAL S	2.05	2.13	2.24	2.22	2.37	2.33

- -

MISCELLANEOUS ANALYSIS

H/C ATOM RATIO (DAF) = .85

O/C ATOM RATIO (DAF) = .081

FREE-SWELLING-INDEX = 3

CHLORINE (PPM) = 258

HARDGROVE GRINDABILITY INDEX =

ASH FUSION TEMPERATURES (DEG FAHRENHEIT)
INITIAL DEFORMATION TEMPERATURE, IT =
SOFTENING TEMPERATURE, ST =
HEMISPHERICAL TEMPERATURE, HT =
FLUID TEMPERATURE, FT =

MINERAL MATTER (DRY) = (By oxygen plasma ashing)

* *

Table 30

```
***********************************
**  WESTERN KENTUCKY UNIVERSITY  **
** COAL CHARACTERIZATION LIBRARY **
**          DATA SHEET           **
***********************************
```

JAN 4 1984

* *

COAL # 83013

EAST KY COAL FROM JIM HOWER - IMMR

MASON SEAM - BAILEY HILL #4

ANALYSIS		AS RCVD	AS DETD	DRY BASIS	MOIST MMF	D M M F	D A F
PROXIMATE ANALYSIS							
MOISTURE	..	1.59	.....	1.87	.....	.....	
ASH	..	14.05	14.27	.....	.....	.....	
VOL. MATTER	..	32.61	33.13	38.44	37.19	38.65	
FIXED CARBON	..	51.75	52.58	59.68	62.8	61.34	
BTU/POUND	..	12715	12920	15048	15430	15072	
ULTIMATE ANALYSIS							
CARBON	..	69.94	71.07	82.45	84.87	82.9	
HYDROGEN*	..	4.77	4.34	5.62	5.78	5.65	
NITROGEN	..	1.87	1.9	2.2	2.26	2.21	
SULFUR	..	1.52	1.34	1.79	1.84	1.8	
OXYGEN* (BY DIFF.)	..	6.26	6.36	6.05	5.21	7.42	

* As-determined basis excludes hydrogen and oxygen of moisture

ASTM RANK IS HIGH VOL BITUMINOUS - A

- -

Table 30 (continued)

```
:OAL # 83013                                                 -- PAGE 2 --

ANALYSIS        AS RCVD   AS DETD   DRY BASIS  MOIST MMF   D M M F   D A F
--------        -------   -------   ---------  ---------   -------   -----

FORMS OF SULFUR

PYRITIC           ..        .62        .63        .73        .75       .73

SULFATE           ..        0          0          0          0         0

ORGANIC           ..        .9         .91        1.06       1.09      1.06

TOTAL S           ..        1.52       1.54       1.79       1.84      1.8

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

MISCÉLLANEOUS ANALYSIS

H/C ATOM RATIO (DAF) =  .812

O/C ATOM RATIO (DAF) =  .067

 REE-SWELLING-INDEX = 7.5

CHLORINE (PPM) =

HARDGROVE GRINDABILITY INDEX =  41

ASH FUSION TEMPERATURES (DEG FAHRENHEIT)
     INITIAL DEFORMATION TEMPERATURE, IT =
     SOFTENING TEMPERATURE, ST           =
     HEMISPHERICAL TEMPERATURE, HT       =
     FLUID TEMPERATURE, FT               =

MINERAL MATTER (DRY) =         (By oxygen plasma ashing)

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
```

Table 31

```
                    ***********************************
                    **  WESTERN KENTUCKY UNIVERSITY  **
                    ** COAL CHARACTERIZATION LIBRARY **
                    **          DATA SHEET           **
                    ***********************************

                                                              JAN 4 1984
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

COAL # 83022

DOT COAL #3


ANALYSIS       AS RCVD    AS DETD    DRY BASIS  MOIST MMF    D M M F    D A F
--------       -------    -------    ---------  ---------    -------    -----

PROXIMATE ANALYSIS

MOISTURE        11.47      10.43       .....      11.55       .....      .....

ASH              8.88       8.99       10.03      .....       .....      .....

VOL. MATTER     32.3       32.69       36.49      36.2        38.81      40.55

FIXED CARBON    47.33      47.9        53.46      52.24       61.18      59.44

BTU/POUND       11351      11486       12823      12785       14672      14254


ULTIMATE ANALYSIS

CARBON          63.62      64.38       71.87      71.3        82.24      79.89

HYDROGEN*        4.27       4.33        4.83       4.79        5.53       5.37

NITROGEN         1.27       1.29        1.44       1.42        1.64       1.6

SULFUR           2.83       2.87        3.2        3.17        3.66       3.56

OXYGEN*          7.61       7.71        8.6        7.74        6.91       9.56
(BY DIFF.)

*  As-determined basis excludes hydrogen and oxygen of moisture

ASTM RANK IS HIGH VOL BITUMINOUS - C
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
```

Table 31 (continued)

```
COAL # 83022                                                  -- PAGE 2 --

ANALYSIS       AS RCVD    AS DETD    DRY BASIS  MOIST MMF    D M M F    D A F
--------       -------    -------    ---------  ---------    -------    -----

FORMS OF SULFUR

PYRITIC           .72        .73         .81         .8          .93       .9

SULFATE           .03        .04         .04         .04         .05       .04

ORGANIC          2.08       2.11        2.35        2.33        2.69      2.61

TOTAL S          2.83       2.87        3.2         3.17        3.66      3.56
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

MISCELLANEOUS ANALYSIS

H/C ATOM RATIO (DAF) =  .8

O/C ATOM RATIO (DAF) =  .089

FREE-SWELLING-INDEX = 4.5

CHLORINE (PPM) =

HARDGROVE GRINDABILITY INDEX =  43

ASH FUSION TEMPERATURES (DEG FAHRENHEIT)
     INITIAL DEFORMATION TEMPERATURE, IT =
     SOFTENING TEMPERATURE, ST           =
     HEMISPHERICAL TEMPERATURE, HT       =
     FLUID TEMPERATURE, FT               =

MINERAL MATTER (DRY) =       (By oxygen plasma ashing)

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
```

Table 32

****
** WESTERN KENTUCKY UNIVERSITY **
** COAL CHARACTERIZATION LIBRARY **
** DATA SHEET **
****

1 19 1984

* *

COAL # 83039

KCER #7953

AMOS COMPOSITE, JOB #4 – BUTLER CO., KY

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	MOIST MMF	D M M F	D A F
PROXIMATE ANALYSIS						
MOISTURE	..	4.48	.....	5.13	.....	.....
ASH	..	11.77	12.32	.....	.....	.....
VOL. MATTER	..	35.31	36.96	40.45	40.51	42.16
FIXED CARBON	..	48.44	50.71	54.41	59.48	57.83
BTU/POUND	..	12417	12999	14307	15248	14826
ULTIMATE ANALYSIS						
CARBON	..	68.25	71.45	78.18	83.81	81.49
HYDROGEN*	..	4.82	5.04	5.52	5.91	5.75
NITROGEN	..	1.55	1.62	1.77	1.9	1.85
SULFUR	..	2.5	2.61	2.86	3.06	2.98
OXYGEN* (BY DIFF.)	..	6.63	6.94	6.51	5.29	7.91

* As-determined basis excludes hydrogen and oxygen of moisture

ASTM RANK IS HIGH VOL BITUMINOUS – A

- -

Table 32 (continued)

COAL # 83039 -- PAGE 2 --

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	MOIST MMF	D M M F	D A F
FORMS OF SULFUR						
PYRITIC	..	1.81	1.89	2.07	2.22	2.16
SULFATE	..	.01	.01	.01	.01	.01
ORGANIC	..	.68	.71	.77	.83	.81
TOTAL S	..	2.5	2.61	2.86	3.06	2.98

- -

MISCELLANEOUS ANALYSIS

H/C ATOM RATIO (DAF) = .84

O/C ATOM RATIO (DAF) = .072

FREE-SWELLING-INDEX =

CHLORINE (PPM) =

HARDGROVE GRINDABILITY INDEX =

ASH FUSION TEMPERATURES (DEG FAHRENHEIT)
INITIAL DEFORMATION TEMPERATURE, IT =
SOFTENING TEMPERATURE, ST =
HEMISPHERICAL TEMPERATURE, HT =
FLUID TEMPERATURE, FT =

MINERAL MATTER (DRY) = (By oxygen plasma ashing)

* *

Table 33

```
***********************************
**  WESTERN KENTUCKY UNIVERSITY  **
** COAL CHARACTERIZATION LIBRARY **
**          DATA SHEET           **
***********************************
```

MAR 31 1984

* *

COAL # 82040201

DESULFURIZATION PROJ.

FORMATE AND ISO-VALERIC SALTS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	MOIST MMF	D M M F	D A F
PROXIMATE ANALYSIS						
MOISTURE	..	.09	.....	.1	.....	.....
ASH	..	10.56	10.56	.....	.....	.....
VOL. MATTER	..	36.55	36.58	41.25	39.14	40.89
FIXED CARBON	..	52.81	52.84	58.64	60.85	59.1
BTU/POUND	..	12467	12478	14170	14366	13952
ULTIMATE ANALYSIS						
CARBON	..	69.28	69.34	78.19	79.83	77.53
HYDROGEN*	..	4.7	4.7	5.3	5.41	5.26
NITROGEN	..	1.31	1.31	1.47	1.5	1.46
SULFUR	..	3.14	3.14	3.54	3.61	3.51
OXYGEN* (BY DIFF.)	..	10.92	10.92	11.37	9.62	12.22

* As-determined basis excludes hydrogen and oxygen of moisture

ASTM RANK IS HIGH VOL BITUMINOUS - A

- -

Table 33 (continued)

COAL # 82040201

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	MOIST MMF	D M M F	D A F
FORMS OF SULFUR						
PYRITIC	..	.76	.76	.85	.87	.85
SULFATE	..	.23	.23	.25	.26	.25
ORGANIC	..	2.15	2.15	2.42	2.47	2.4
TOTAL S	..	3.14	3.14	3.54	3.61	3.51

- -

MISCELLANEOUS ANALYSIS

H/C ATOM RATIO (DAF) = .808

O/C ATOM RATIO (DAF) = .118

FREE-SWELLING-INDEX = 0

CHLORINE (PPM) =

HARDGROVE GRINDABILITY INDEX =

ASH FUSION TEMPERATURES (DEG FAHRENHEIT)
INITIAL DEFORMATION TEMPERATURE, IT =
SOFTENING TEMPERATURE, ST =
HEMISPHERICAL TEMPERATURE, HT =
FLUID TEMPERATURE, FT =

MINERAL MATTER (DRY) = (By oxygen plasma ashing)

* *

Table 34

```
**************************************
**  WESTERN KENTUCKY UNIVERSITY     **
** COAL CHARACTERIZATION LIBRARY    **
**           DATA SHEET             **
**************************************
```

MAR 31 1984

* *

COAL # 82040202

DESULFURIZATION PROJ.

FORMATE AND ISO-VALERIC SALTS

ANALYSIS		AS RCVD	AS DETD	DRY BASIS	MOIST MMF	D M M F	D A F
PROXIMATE ANALYSIS							
MOISTURE	..	1.27	.....	1.42	.....	.....	
ASH	..	10.2	10.33	.....	.....	.....	
VOL. MATTER	..	37.59	38.07	42.24	40.73	42.44	
FIXED CARBON	..	50.95	51.59	56.32	59.26	57.55	
BTU/POUND	..	12390	12549	14020	14411	13995	
ULTIMATE ANALYSIS							
CARBON	..	68.28	69.15	76.73	79.42	77.12	
HYDROGEN*	..	4.92	4.98	5.52	5.72	5.55	
NITROGEN	..	1.23	1.24	1.38	1.43	1.38	
SULFUR	..	3.17	3.21	3.56	3.68	3.58	
OXYGEN* (BY DIFF.)	..	10.92	11.07	11.36	9.73	12.34	

* As-determined basis excludes hydrogen and oxygen of moisture

ASTM RANK IS HIGH VOL BITUMINOUS - A

- -

Table 34 (continued)

COAL # 82040202

-- PAGE 2 -

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	MOIST MMF	D M M F	D A F
FORMS OF SULFUR						
PYRITIC	..	.65	.65	.73	.75	.73
SULFATE	..	.32	.32	.35	.37	.36
ORGANIC	..	2.2	2.22	2.47	2.55	2.48
TOTAL S	..	3.17	3.21	3.56	3.68	3.58

MISCELLANEOUS ANALYSIS

H/C ATOM RATIO (DAF) = .857

O/C ATOM RATIO (DAF) = .12

FREE-SWELLING-INDEX = 0

CHLORINE (PPM) =

HARDGROVE GRINDABILITY INDEX =

ASH FUSION TEMPERATURES (DEG FAHRENHEIT)
INITIAL DEFORMATION TEMPERATURE, IT =
SOFTENING TEMPERATURE, ST =
HEMISPHERICAL TEMPERATURE, HT =
FLUID TEMPERATURE, FT =

MINERAL MATTER (DRY) = (By oxygen plasma ashing)

* *

Table 35 .

```
***********************************
**  WESTERN KENTUCKY UNIVERSITY  **
** COAL CHARACTERIZATION LIBRARY **
**          DATA SHEET           **
***********************************
```

MAR 31 1984

* *

COAL # 82038208

DESULFURIZATION PROJ.

FORMATE AND ISO-VALERIC SALTS

ANALYSIS		AS RCVD	AS DETD	DRY BASIS	MOIST MMF	D M M F	D A F
PROXIMATE ANALYSIS							
MOISTURE	..	.21	.....	.21	.....	.....	
ASH	..	4	4	.....	.....	.....	
VOL. MATTER	..	39.27	39.35	41.04	40.19	40.98	
FIXED CARBON	..	56.53	56.63	58.73	59.8	59.01	
BTU/POUND	..	14072	14101	14763	14887	14690	
ULTIMATE ANALYSIS							
CARBON	..	76.85	77.01	80.31	81.3	80.22	
HYDROGEN*	..	5.23	5.24	5.46	5.53	5.45	
NITROGEN	..	1.52	1.52	1.58	1.6	1.58	
SULFUR	..	1.72	1.72	1.79	1.81	1.79	
OXYGEN* (BY DIFF.)	..	10.46	10.49	10.6	9.73	10.93	

* As-determined basis excludes hydrogen and oxygen of moisture

ASTM RANK IS HIGH VOL BITUMINOUS - A

\- -

Table 35 (continued)

```
COAL # 82038208                                          -- PAGE 2 -
-

ANALYSIS      AS RCVD   AS DETD   DRY BASIS  MOIST MMF    D M M F   D A F
--------      -------   -------   ---------  ---------    -------   -----

FORMS  OF  SULFUR

PYRITIC          ..      1.41       1.41       1.47        1.49     1.47

SULFATE          ..       .09        .09        .09         .09      .09

ORGANIC          ..       .22        .22        .22         .23      .22

TOTAL S          ..      1.72       1.72       1.79        1.81     1.79

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

MISCELLANEOUS  ANALYSIS

H/C ATOM RATIO (DAF) =  .809

O/C ATOM RATIO (DAF) =  .102

FREE-SWELLING-INDEX = 0

CHLORINE (PPM) =

HARDGROVE GRINDABILITY INDEX =

ASH FUSION TEMPERATURES (DEG FAHRENHEIT)
      INITIAL DEFORMATION TEMPERATURE, IT =
      SOFTENING TEMPERATURE, ST           =
      HEMISPHERICAL TEMPERATURE, HT       =
      FLUID TEMPERATURE, FT               =

MINERAL MATTER (DRY) =        (By oxygen plasma ashing)

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
```

Table 36

```
**************************************
**  WESTERN KENTUCKY UNIVERSITY     **
** COAL CHARACTERIZATION LIBRARY **
**           DATA SHEET                **
**************************************
```

MAR 31 1984

* *

COAL # 83013205

DESULFURIZATION PROJ.

FORMATE AND ISO-VALERIC SALTS

ANALYSIS		AS RCVD	AS DETD	DRY BASIS	MOIST MMF	D M M F	D A F
PROXIMATE ANALYSIS							
MOISTURE	..	.18	.....	.21	.....	.....	
ASH	..	13.65	13.67	.....	.....	.....	
VOL. MATTER	..	33.47	33.53	39.25	37.43	38.83	
FIXED CARBON	..	52.71	52.79	60.53	62.56	61.16	
BTU/POUND	..	12986	13009	15291	15413	15070	
ULTIMATE ANALYSIS							
CARBON	..	70.83	70.95	83.07	84.06	82.19	
HYDROGEN*	..	4.8	4.8	5.62	5.69	5.57	
NITROGEN	..	1.87	1.87	2.19	2.21	2.17	
SULFUR	..	1.5	1.5	1.75	1.78	1.74	
OXYGEN* (BY DIFF.)	..	7.17	7.18	7.12	6.23	8.32	

* As-determined basis excludes hydrogen and oxygen of moisture

ASTM RANK IS HIGH VOL BITUMINOUS - A

\- -

Table 36 (continued)

```
COAL # 83013205                                                    -- PAGE 2 -

ANALYSIS      AS RCVD   AS DETD    DRY BASIS  MOIST MMF    D M M F   D A F

FORMS OF SULFUR

PYRITIC           ..        .75        .75        .87         .89       .87

SULFATE           ..        .01        .01        .01         .01       .01

ORGANIC           ..        .74        .74        .86         .87       .85

TOTAL S           ..       1.5        1.5        1.75        1.78      1.74
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

MISCELLANEOUS ANALYSIS

H/C ATOM RATIO (DAF) =  .807

O/C ATOM RATIO (DAF) =  .075

FREE-SWELLING-INDEX = 0

CHLORINE (PPM) =

HARDGROVE GRINDABILITY INDEX =

ASH FUSION TEMPERATURES (DEG FAHRENHEIT)
     INITIAL DEFORMATION TEMPERATURE, IT =
     SOFTENING TEMPERATURE, ST           =
     HEMISPHERICAL TEMPERATURE, HT       =
     FLUID TEMPERATURE, FT               =

MINERAL MATTER (DRY) =        (By oxygen plasma ashing)

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
```

Table 37

****
** WESTERN KENTUCKY UNIVERSITY **
** COAL CHARACTERIZATION LIBRARY **
** DATA SHEET **
****

MAR 31 1984

* *

COAL # 83022206

DESULFURIZATION PROJ.

FORMATE AND ISO-VALERIC SALTS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	MOIST MMF	D M M F	D A F
PROXIMATE ANALYSIS						
MOISTURE	..	.08	.....	.08	.....	.....
ASH	..	9.64	9.64	.....	.....	.....
VOL. MATTER	..	35.9	35.92	40.07	38.08	39.76
FIXED CARBON	..	54.38	54.42	59.83	61.91	60.23
BTU/POUND	..	12871	12881	14467	14654	14256
ULTIMATE ANALYSIS						
CARBON	..	71.34	71.39	79.63	81.22	79.02
HYDROGEN*	..	4.74	4.74	5.29	5.39	5.25
NITROGEN	..	1.38	1.38	1.54	1.57	1.52
SULFUR	..	3.05	3.05	3.4	3.47	3.37
OXYGEN* (BY DIFF.)	..	9.76	9.77	10.04	8.33	10.82

* As-determined basis excludes hydrogen and oxygen of moisture

ASTM RANK IS HIGH VOL BITUMINOUS - A

- -

-- CONTINUED ON PAGE 2 --

Table 37 (continued)

```
COAL # 83022206                                                -- PAGE 2 -


ANALYSIS       AS RCVD    AS DETD     DRY BASIS  MOIST MMF    D M M F    D A F

FORMS OF SULFUR

PYRITIC             ..       1.32        1.32       1.47        1.5       1.46

SULFATE             ..        .04         .04        .04        .04        .04

ORGANIC             ..       1.69        1.69       1.88       1.92       1.67

TOTAL S             ..       3.05        3.05       3.4        3.47       3.37

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

MISCELLANEOUS ANALYSIS

H/C ATOM RATIO (DAF) =  .791

O/C ATOM RATIO (DAF) =  .102

FREE-SWELLING-INDEX = 0

CHLORINE (PPM) =

HARDGROVE GRINDABILITY INDEX =

ASH FUSION TEMPERATURES (DEG FAHRENHEIT)
     INITIAL DEFORMATION TEMPERATURE. IT =
     SOFTENING TEMPERATURE, ST           =
     HEMISPHERICAL TEMPERATURE, HT       =
     FLUID TEMPERATURE, FT               =

MINERAL MATTER (DRY) =        (By oxygen plasma ashing)

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
```

Table 38

```
*************************************
**  WESTERN KENTUCKY UNIVERSITY   **
** COAL CHARACTERIZATION LIBRARY **
**          DATA SHEET            **
*************************************
```

MAR 31 1984

* *

COAL # 83039207

DESULFURIZATION PROJ.

FORMATE AND ISO-VALERIC SALTS

ANALYSIS		AS RCVD	AS DETD	DRY BASIS	MOIST MMF	D M M F	D A F
PROXIMATE ANALYSIS							
MOISTURE	..	.08	.....	.09	.....	.....	
ASH	..	12.6	12.61	.....	.....	.....	
VOL. MATTER	..	37.02	37.04	42.85	40.93	42.38	
FIXED CARBON	..	50.31	50.34	57.05	59.06	57.61	
BTU/POUND	..	12774	12784	14861	14996	14628	
ULTIMATE ANALYSIS							
CARBON	..	69.52	69.57	80.47	81.61	79.61	
HYDROGEN*	..	4.98	4.98	5.76	5.84	5.7	
NITROGEN	..	1.52	1.52	1.75	1.78	1.74	
SULFUR	..	2.06	2.06	2.38	2.41	2.35	
OXYGEN* (BY DIFF.)	..	9.23	9.24	9.52	8.33	10.58	

* As-determined basis excludes hydrogen and oxygen of moisture

ASTM RANK IS HIGH VOL BITUMINOUS - A

\- -

Table 38 (continued)

COAL # 83039207

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	MOIST MMF	D M M F	D A F
FORMS OF SULFUR						
PYRITIC	..	1.65	1.65	1.9	1.93	1.88
SULFATE	..	.02	.02	.02	.02	.02
ORGANIC	..	.39	.39	.45	.45	.44
TOTAL S	..	2.06	2.06	2.38	2.41	2.35

- -

MISCELLANEOUS ANALYSIS

H/C ATOM RATIO (DAF) = .853

O/C ATOM RATIO (DAF) = .099

FREE-SWELLING-INDEX = 0

CHLORINE (PPM) =

HARDGROVE GRINDABILITY INDEX =

ASH FUSION TEMPERATURES (DEG FAHRENHEIT)
INITIAL DEFORMATION TEMPERATURE, IT =
SOFTENING TEMPERATURE, ST =
HEMISPHERICAL TEMPERATURE, HT =
FLUID TEMPERATURE, FT =

MINERAL MATTER (DRY) = (By oxygen plasma ashing)

* *

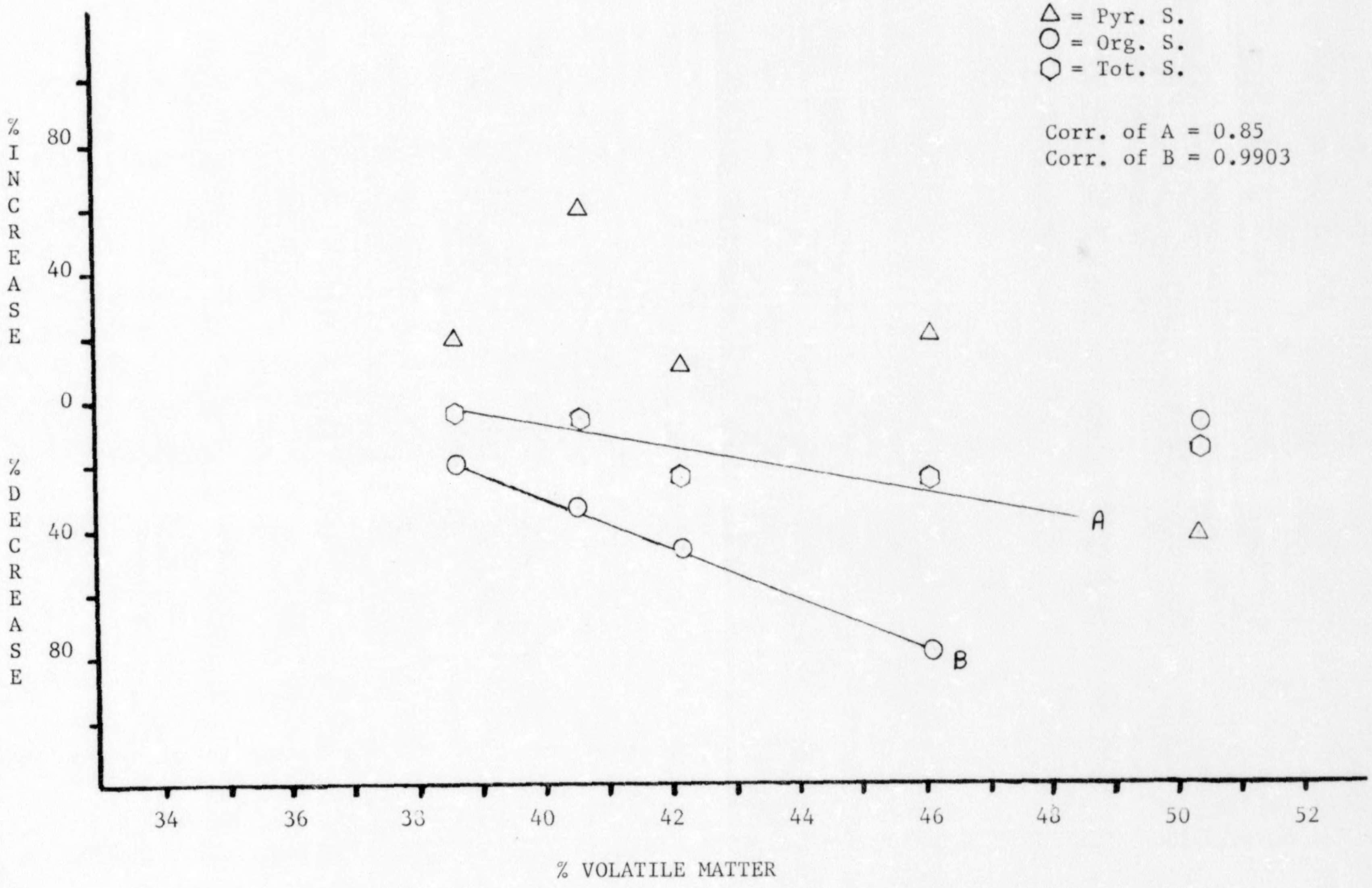
Table 39

Sulfur Reductions of Reacted -60 Mesh Coals

Coal Reaction No.	Total Sulfur	Organic Sulfur	Pyritic Sulfur	Sulfate Sulfur
82040201	16.03	8.40	41.38	-177.8
82040202	14.35	5.34	49.66	-300.0
82038208	24.03	79.44	-22.5	-80.00
83013205	3.33	19.80	-19.18	-100.00
83022206	5.34	28.35	-62.22	0.00
83039207	23.51	46.99	12.96	-100.00

All reductions in percent of original analysis

Negative sign means increase



Correlation of Volatile Matter with Sulfur Reductions

Figure 13

was 0.9903 for these values. The total sulfur of these four values was correlated with volatile matter and produced a correlation coefficient of 0.85. These results may indicate that a major portion of the organic sulfur is found in the pore structure of the coal. It is believed that pyritic removal is a competing reaction with organic removal. The mechanism for pyritic sulfur removal follows the shrinking core mechanism put forward by Joshi and co-workers.(21) The mechanism assumes that the pyrite is in an easily removable form, that is to say, the pyrite is not intimately mixed into the coal matrix. The obvious crystalline structure of pyrite suggests that this would be so. The rate of attack of the crystal would be related to the surface area of the crystal. When the shrinking core of the crystal becomes very small the rate of removal decreases. The variance of the pyritic removal shown in Figure 13 suggests that there were different forms of pyritic structure in the coals. The decrease in removal of pyrite in some of the coals suggests that these coals have an intimate mixture of pyrites. It is thought that the removal of pyrite in reaction 82040202 competed for available oxygen and reduced the amount of organic removal.

Joshi and Shah reported in 1981 that oxydesulfurization of organic sulfur was independent of the partial pressure of oxygen over the reaction solution.(22) They stated that although the kinetics were zero order in the partial pressure of oxygen, the intraparticle diffusion of oxygen played an important role. They also proved that significant organic sulfur removal could only be accomplished in neutral to basic media.

SUMMARY

The reactions of carboxylic acid with bituminous coals developed many trends that were worth mentioning. First, it was shown that desulfurization occurs in solutions of varying pH. There were solutions that removed large portions of sulfur, but overall, desulfurization occurred in all reaction mixtures.

The second trend developed was the ability of large carboxylic acids to remove large portions of pyritic sulfur. The trend was sustained in all solutions of varying pH. The stability of the complexes formed by iron and the carboxylic ligands increases as the carbon structure increases or branching occurs. The increase in stability of these iron complexes is shown by the greater removal using isovaleric acid in comparison to reactions using valeric acid.

Lastly, a trend developed showing that organic sulfur is more easily removed by smaller carboxylic species. Formic acid derivatives made the largest reductions in organic sulfur. The experimental evidence reflects the ability of formic acid and its derivatives to penetrate the coal structure more effectively.

Although there is not enough evidence to support a relation between volatile matter and the organic sulfur reduction potentials of various coals, this area looks promising and should be studied further. The goal of this research was to find an alternative desulfurization process. It is believed that this goal was met. The potential for this desulfurization process becoming commercial is very high.

BIBLIOGRAPHY

1. J. D. McClung, M. R. Greer, and H. J. Gluskoter, in Coal Preparation, 4th ed., J. W. Leonard, ed., (AIME New York, 1979), Chap. 1, pp. 53-79.

2. E. Mendizabel, Low Temperature Processes for Coal Desulfurization, Lawrence Berkeley Laboratory of Univ. of Ca., for the U.S. Energy Research and Development Administration, August 1976, p. 41.

3. Ibid., p. 43.

4. D. D. Whitehurst, in Organic Chemistry of Coal, J. W. Larsen, Ed., ACS Symp. Series No. 71, (Am. Chem. Soc., Washington, D.C., 1978) pp. 1-35.

5. R. T. Greer, in Coal Desulfurization: Chemical and Physical Methods, T. D. Wheelock, ed., ACS Symp. Series No. 64 (Am. Chem. Soc., Washington, D.C., 1977), pp. 1-15.

6. D. V. Keller, Jr., in New Physical Methods for Cleaning Coal, Y. A. Liu, Ed., (Marcel Dekker, Inc., New York, in press).

7. M. Sokaski, M. R. Geer, and W. L. McMorris III, in Coal Preparation, 4th ed., J. W. Leonard, ed., (AIME, New York, 1979), Chap. 10, pp. 1-39.

8. S. C. Sun, Mining Eng. 6(4), 396-401 (1954).

9. T. D. Wheelock and R. Markuszeuski, in Chemistry and Physics of Coal Utilization - 1980 (APS, Morgantown) AIP Conf. Proceedings No. 70, ed. by B. R. Cooper and L. Petrakis, American Institute of Physics, New York, 1981, pp. 357-387.

10. J. C. Agarwal, R. Al Giberti, P. F. Irminger, L. J. Petrovic, and S. S. Sareen, Mining Congr. J. 61(3) 40-3 (1975).

11. E. H. Burk, J. S. Yoo, and J. A. Karch, U. S. Pat. 4,097,244 (June 27, 1978).

12. S. Friedman and R. P. Warzinski, J. Eng. Power 99(3) 361-4 (1977).

13. C. Y. Tai, G. V. Graves, and T. D. Wheelock, in Coal Desulfurization: Chemical & Physical Methods, T. D. Wheelock, ed., ACS Symp. Series 64 (Am. Chem. Soc., Washington, D.C. 1977), pp. 182-197.

14. R. Boyd and R. Morrison, Organic Chemistry, 4th ed. Allyn & Bacon, Inc., Boston, 1983 p 779.

15. LECO MAC 400, Instrumentation Manual, Leco Corp., p.4.

16. LECO SC 132, Instruction Manual, Leco Corp., p.5.

17. LECO CHN 600, Instruction Manual, Leco Corp., p.4.

18. LECO AC-200, Instruction Manual, Leco Corp., p.5.

19. Annual Book of ASTM Standards, part 26, 1982, D2492, p. 345.

20. Perrin, D. D., Stability of Iron Complexes: Part IV. Verric Complexes with Aliphatic Acids, Journal of the Chem. Society, 1710, 1959.

21. Joshi, J. B. "Particle Size Effects in the Oxidation of Pyrite in Air/Water Chemical Coal Cleaning, AICHE, 73rd Annual Meeting Chicago, 1980.

22. Joshi, J. B., Kinetics of Organic Sulfur Removal from Coal by Oxydesulphurization.