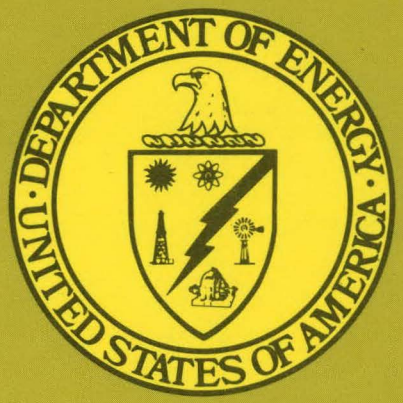

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AIR/WATER OXYDESULFURIZATION OF COAL - LABORATORY INVESTIGATION

by

R. P. Warzinski,[1/] S. Friedman,[2/] J. A. Ruether[3/] and R. B. LaCount[1/]

ABSTRACT

Air/water oxidative desulfurization has been demonstrated in autoclave experiments at the Pittsburgh Energy Technology Center for various coals representative of the major U.S. coal basins. This experimentation has shown that the reaction proceeds effectively for pulverized coals at temperatures of 150 to 200°C with air at a total system pressure of 500 to 1500 psig. Above 200°C, the loss of coal and product heating value increases due to oxidative consumption of carbon and hydrogen. The pyritic sulfur solubilization reactions are typically complete (95 percent removal) within 15 to 40 minutes at temperature; however, significant apparent organic sulfur removal requires residence times of up to 60 minutes at the higher temperatures. The principal products of the reaction are sulfuric acid, which can be neutralized with limestone, and iron oxide. Under certain conditions, especially for high pyritic sulfur coals, the precipitation of sulfur-containing compounds from the products of the pyrite reaction may cause anomalous variations in the sulfur form data. The influence of various parameters on the efficiency of sulfur removal from coal by air/water oxydesulfurization has been studied.

INTRODUCTION

The objective of this report is to detail the initial bench-scale experimental program conducted at the Pittsburgh Energy Technology Center of the Department of Energy, in which the air/water oxidative desulfurization (oxydesulfurization) of coal was investigated. The goal of this research is to develop an economically viable chemical desulfurization process capable of producing environmentally acceptable coal primarily for boiler fuel. Such a product would be attractive to industrial coal users who cannot afford to operate and maintain flue gas desulfurization systems (FGD). The utility industry, faced with more stringent emission standards, may realize a benefit by using chemically cleaned coal with partial flue gas scrubbing. A combination approach, when compared to full FGD, potentially could reduce capital and operating costs by increasing reliability and reducing the duplication of

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equipment needed to achieve present FGD requirements (3,8).[4/] Chemical coal cleaning could accomplish this by improving the feedstock uniformity and reducing trace elements and ash constituents responsible for deposits and corrosion. Also, the sludge disposal problem would be greatly reduced.

The cost of chemical coal cleaning is expected to fall between that of physical cleaning methods and processes for conversion to liquid or gaseous fuels (10). The unequivocal demonstration in the laboratory and initial pilot-plant stages of consistent and efficient organic sulfur removal is the most critical hurdle to be cleared before any chemical coal cleaning process can move towards commercial realization. No process as yet has demonstrated such ability.

This report presents the laboratory collected data on the efficiency of sulfur removal by air/water oxydesulfurization as governed by the variables: residence time, reaction temperature, air pressure (oxygen partial pressure), coal size, coal type, and slurry concentration. Data are also presented on the mixing efficiency of the bench-scale system as related to stirring rate and slurry loading. The illustrations throughout this report are all based on moisture-free data. Also the term "Btu loss" or "heating value loss" takes into account the weight-percent recovery of product.

BACKGROUND

Table 1 summarizes the various techniques being investigated for coal desulfurization. Physical cleaning is the only method used on a commercial scale. A more complete description of these coal cleaning methods can be found in the references contained in Table 1. It is evident that oxydesulfurization techniques form a significant portion of the coal cleaning spectrum. The term "oxydesulfurization" as used herein refers to processes using gaseous oxygen or air as the primary oxidant, in the presence of water, for coal desulfurization. Several patents exist which encompass the various oxydesulfurization approaches (1,4,7). Reference 28 attempts to compare on a conceptual level the cost of several of the processes in Table 1. The varying degrees of development of these processes, however, limit the utility of such comparisons. Also it is difficult to compare the applicability of these processes to our coal reserves since various coals were used for investigation.

The expected cost of any chemical coal cleaning process will undoubtedly be substantially greater than for physical cleaning. However, a combination approach using a chemical process to augment physical cleaning, primarily by removing organic sulfur, may be attractive (11). With the exception of Gravichem and Magnex, all of the chemical processes in Table 1 claim organic sulfur removal. It is difficult to quantify organic sulfur removal primarily because of its indirect determination. As will be demonstrated in this report, sulfur-containing compounds formed during the chemical cleaning process, but which are foreign to coal itself, may interfere in the sulfur form determination.

[4/] Numbers in parentheses refer to items in the list of references at the end of this report.

Table 1. Summary of Coal Beneficiation Technology

PROCESS	DESCRIPTION	ORGANIC SULFUR REMOVAL	REFERENCES
Physical Cleaning	Primarily Specific Gravity Separation	No	5
High Gradient Magnetic Separation (HGMS)	Wet Or Dry Magnetic Separation Of Pyrite And Ash From Coal	No	18
Gravichem (TRW) [1]	Specific Gravity Separation, Sink Fraction Subjected to Ferric Sulfate Leach	No	15, 26, 27, 28, 29
Magnex (Hazen)	Dry $Fe(CO)_5$ Treatment with Subsequent Magnetic Separation	No	19, 20, 21, 28
PETC Oxydesulfurization	Aqueous Air Oxidation	Yes	9, 10, 28, 36, 40
LOL Oxydesulfurization	Aqueous Oxygen Treatment in Acid, Neutral, or Basic Medium	Yes	1, 12, 28, 30
Ames Oxydesulfurization	Aqueous Oxygen Treatment in Na_2CO_3 Solution	Yes	25, 41
ARCO Oxydesulfurization	Aqueous Air Oxidation with Promoter	Yes	4
G.E. Microwave	Microwave Treatment of Aqueous Caustic Slurry	Yes	43
Battelle Hydrothermal	Caustic Leach	Yes	28, 32, 33
KVB	Dry Treatment with O_2, N_2, NO with Subsequent Caustic Leach	Yes	6, 13, 28
JPL Chlorinolysis	Oxidation with Chlorine in Appropriate Solvent with Subsequent Hydrolysis and Steam Distillation	Yes	16,17

1. References refer to the ferric sulfate leaching known as the Meyer's Process.

Although little is known of the organic sulfur reactions, the pyrite/air oxidation reaction in aqueous media has been studied extensively by Vracar and Vucurovic (37,38,39) in relation to producing sulfuric acid from pyrite for use in ore extraction. The following reactions were proposed for finely ground pyrite, based upon conditions similar to those used for coal treated by air/water oxydesulfurization (37).

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4 \quad (1)$$

$$2FeSO_4 + 1/2O_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O \quad (2)$$

$$Fe_2(SO_4)_3 + nH_2O \longrightarrow Fe_2O_3 \cdot (n-3)H_2O + 3H_2SO_4 \quad (3)$$

$$3Fe_2(SO_4)_3 + 14H_2O \longrightarrow 2Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O + 5H_2SO_4 \quad (4)$$

No elemental sulfur was observed above 140°C. Small amounts of the basic jarosite-like salt (reaction 4) were formed at lower pH and temperature. Vracar and Vucurovic (39) observed that for a 20 gm/l pyrite slurry under the conditions 200°C, 74 to 133 psi oxygen partial pressure, and 3-hour residence time, pyrite was completely converted to sulfuric acid and iron oxide. At temperatures below 200°C small amounts of unreacted pyrite, ferrous, and ferric sulfate were present. The pyrite reaction rate was found to be first order in unreacted pyrite with an activation energy of 51.0 kJ/mole (12.2 kcal/mole). In a more recent kinetic study by Slagle (31) in which an Upper Freeport coal was used under similar conditions, the pyritic sulfur reaction was found to be first order in unreacted pyrite with an activation energy of 46.7 kJ/mole (11.2 kcal/mole). The organic sulfur data were scattered, but were fitted to a zero order rate expression with an activation energy of 78.7 kJ/mole (18.8 kcal/mole). Broader reviews of pyrite oxidation and coal sulfur oxidation have been published by Meyers (26) and Yurovskii (42) covering reaction temperatures and pressures that are outside the ranges utilized for air/water oxydesulfurization.

APPARATUS, PROCEDURE, AND ANALYSIS

All of the air/water oxydesulfurization experiments in this report were made in an Autoclave Engineers[5/] 1-liter, magnetically stirred, 316 stainless steel autoclave. A diagram of this vessel is shown in Figure 1. Initially, an aqueous slurry of pulverized coal is prepared in a 316 stainless steel, glass, or teflon liner and inserted into the autoclave. Unless otherwise noted in the text or illustrations all coal samples were 200x0-mesh and prepared as a 26 weight-percent slurry with 100 ml distilled water. The glass liner has become the most frequently used due to the heat limitations of teflon and the corrosive nature of the acid product slurry on 316 stainless steel. The type of liner used and the specific slurry composition are noted, where pertinent, in the text.

[5/] Reference to specific brands is made for identification only and does not imply endorsement by the U.S. Department of Energy.

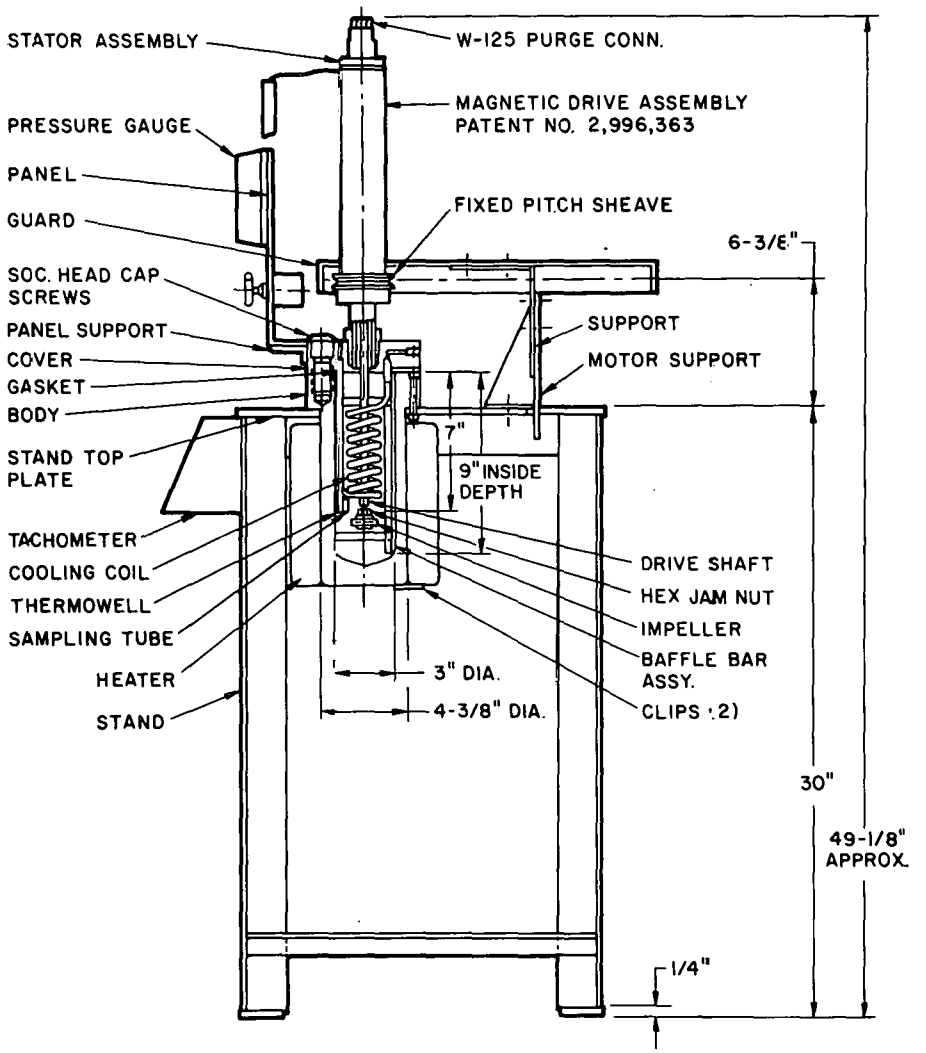

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FIGURE 1. DIAGRAM OF 1-LITER AUTOCLAVE (REPRINTED COURTESY OF AUTOCLAVE ENGINEERS).

The autoclave system can be operated in batch or semibatch (modified) modes. In the batch mode, the autoclave containing the coal slurry is pressurized with air at room temperature to the desired oxygen partial pressure, and subsequently heated by a jacket-type heater to reaction temperature at a rate of approximately 3°C/minute. The slurry is agitated with either a 3.175-cm-diameter stainless steel gas-dispersion-type impeller or a 3.8-cm-diameter 4-blade ceramic stirrer. Reaction temperature, once attained, is stabilized to within ±2°C by a proportioning temperature controller (a Variac power transformer was used in early experiments) and a manually operated internal water cooling coil. After the desired residence time at reaction temperature, the internal cooling coil is used to quench the reaction by lowering the temperature at an initial rate of 50 to 60°C/minute. A gas sample is normally taken when depressurizing after the autoclave reaches room temperature, and before the product slurry is removed.

A disadvantage of using the batch mode of operation is that the desulfurization reactions are likely to become "oxygen starved" since the partial pressure of oxygen is constantly decreasing. In some early experiments, to circumvent this problem, multiple batch charging of air was tried. This technique consists of venting the residual gas after a heating cycle and repressurizing the autoclave before reheating. A heating cycle consists of heating the reactor from ambient to reaction temperature and after the desired reaction time, cooling to room temperature. Gas samples are normally taken after each segment of the experiment.

Modifications of the autoclave system have permitted experiments to be made in what is referred to as a semibatch or modified mode. The coal slurry is prepared and reactor charged as in the batch mode; however, the reactor is then purged with inert gas (N_2 or He) at atmospheric pressure, closed off, and heated to reaction temperature. When this temperature is attained the autoclave is rapidly pressurized with air to the desired operating pressure, and a continuous air flow is maintained until the end of the reaction period. Because the air flow rates used are high in comparison to oxygen consumption, an oxygen partial pressure close to that calculated for water-saturated air at the conditions used is maintained. In order to minimize the evaporative loss of water from the slurry as a result of the air flow, approximately 70 ml of distilled water is placed between the reactor wall and the liner while charging the autoclave. The reaction is quenched by terminating the air flow and using the internal cooling coil. Gas samples are normally taken during and at completion of the experiment.

Product work-up consists basically of removing the soluble sulfates formed with distilled water and drying the sample before analysis. In early experiments the product was washed repeatedly with distilled water and vacuum filtered until little or no sulfate was detected in the washings with barium chloride. This procedure was simplified by the use of an aqueous soxhlet extraction following an initial wash with approximately 1-liter of distilled water on a vacuum filter. The product is removed from the soxhlet when the barium chloride test is negative. Analysis of the initial filtrate and the soxhlet washings for sulfur shows the amount of sulfates which are readily soluble in water as well as those which are not.

The washed product is dried for several hours at 100°C in vacuum and normally sieved through a 60-mesh screen before analysis. Routine analyses performed include moisture, ash, ultimate (C, H, N, S), sulfur forms, and calorific value. Other analyses are performed when necessary including determination of the free swelling index; and iron as iron oxide present in the ash. All of the aforementioned analytical procedures are described in detail in Bulletin 638 of the U.S. Bureau of Mines (34). These tests, however, are designed for coal and coke and may be less suitable for treated coals. This is especially true of the sulfur form analysis which differentiates the various forms of sulfur in coal by their solubility in acids. Sulfur occurring as sulfates (primarily calcium sulfate and iron sulfate) is extracted from a coal sample with hot, 25 volume percent hydrochloric acid. The pyritic sulfur (including marcasite) is calculated from the iron which subsequently is leached from the sample with 25 volume percent nitric acid. Finally, organic sulfur, the sulfur bonded to the coal, is determined as the difference between the total sulfur determined by the Eschka method and the sum of the sulfate and pyritic sulfur. It is probable that treating coal results in the formation of compounds foreign to coal, which are not properly accounted for in the sulfur and sulfur form analyses.

Air/water oxydesulfurization of coal produces primarily sulfuric acid and iron oxide with small amounts of ferrous and ferric sulfate. The iron sulfates are washed from the coal and the iron oxide is removed in the sulfate determination. Therefore, under normal operating conditions the sulfur and sulfur form analyses should be as accurate as with untreated coal. However, the corrosiveness of the dilute acid slurry on the stainless steel components, especially at temperatures approaching 200°C, results in additional iron and other metals, primarily chromium and nickel, being brought into solution. It is speculated that the increased metal concentration could result in the formation of various sulfur-containing compounds, similar to the basic iron salt proposed by Vracar and Vucurovic, precipitating on the product and interfering with the sulfur form determination. The thermal precipitation of basic sulfur-containing iron, chromium and nickel salts is well known in hydrometallurgy and has been reported in the literature (22).

An interesting effect observed with some coals under certain reaction conditions is an apparent increase in organic sulfur with oxidative desulfurization treatment. An example is shown in Figure 2 which illustrates four experiments made on a Lower Freeport coal according to the standard procedure for the continuous air feed mode and using the reaction conditions listed. Over 95 percent of the pyritic sulfur is removed in the initial 15 minutes, resulting in a total sulfur decrease of 60 percent. The organic sulfur registers an apparent increase, however, with the peak value at 15 minutes being 55 percent larger than the value for the untreated coal. With longer treatment time, the apparent organic sulfur decreases again, the value at one hour being close to the value for the untreated coal.

We do not believe that organic sulfur is created during processing, but rather that the anomalous results are an artifact arising from the analytical determination of organic sulfur by difference. As mentioned above, other solids can also be formed in our system, containing as it does ferrous, ferric, and sulfate ions, and smaller concentrations of other cations. Kwok and Robbins

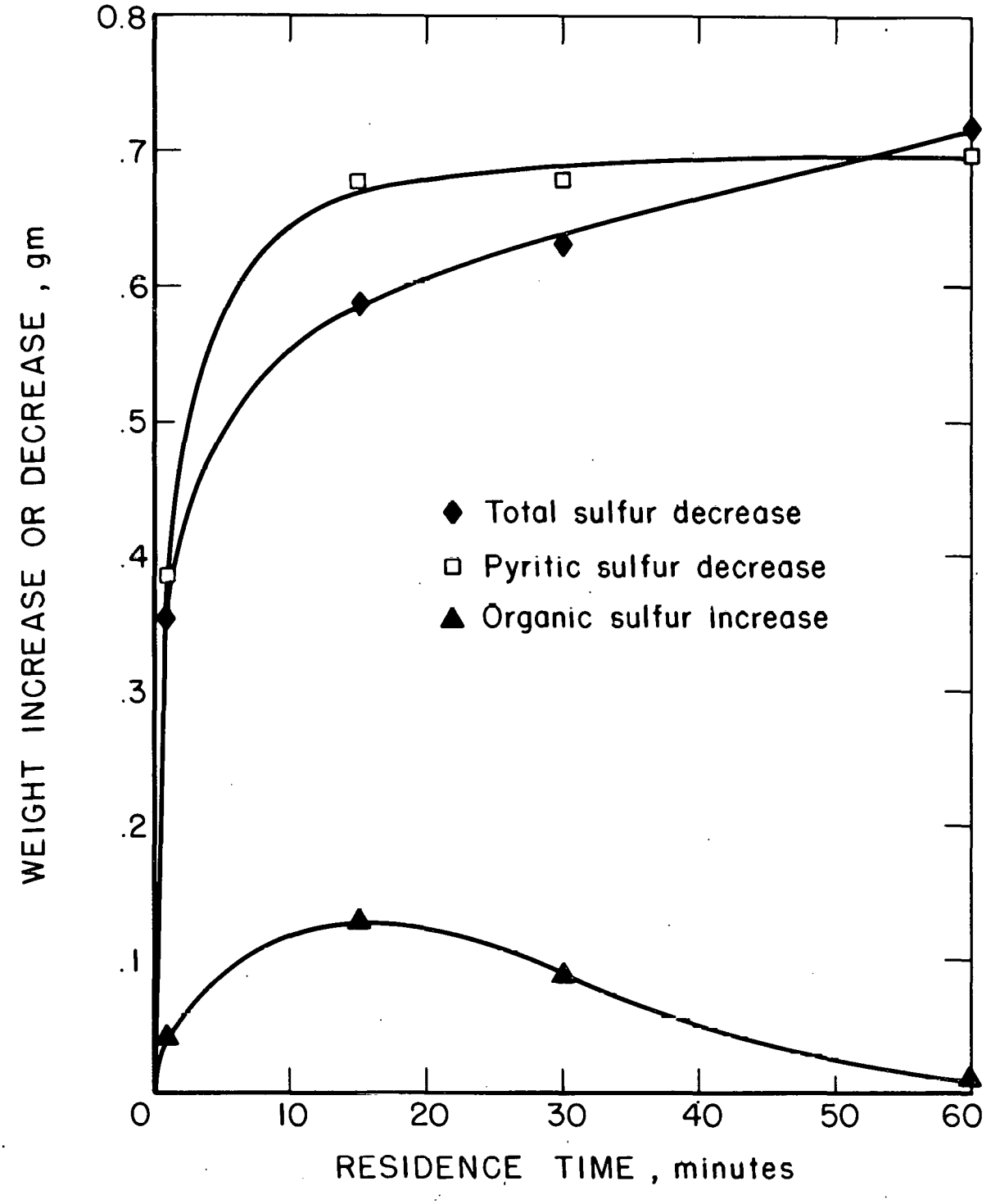

FIGURE 2. APPARENT INCREASE IN ORGANIC SULFUR WITH TREATMENT, LOWER FREEPORT HV/AB COAL, 180° C, 1000 PSIG.

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(22) have reviewed the formation of so-called thermal precipitates in aqueous solutions. Some of their data showing the formation of thermal precipitates in aqueous ferrous and ferric sulfate solutions are shown in Figure 3. For solutions with ferrous or ferric concentrations as indicated by a particular curve, a precipitate forms when the temperature and pH at 25°C place the system to the right of the curve. From calculated concentrations of ferrous/ferric ions and measured values of pH, it is determined that the formation of thermal precipitates is possible in our system. However, in order for a sulfur-containing species to report as apparent organic sulfur it must be amenable to the Eschka sulfur determination and resistant to the acid extractions used in the sulfur form analysis. Swaddle et al. report this type of behavior for the basic chromium sulfate, $Cr_3(SO_4)_2(OH)_5 \cdot H_2O$, which is practically insoluble in water and mineral acids, including aqua regia, even on heating, but dissolves in water after fusion with NaOH (35).

A possible explanation for the results shown in Figure 2 is that jarosite-like compounds are formed in the early stages of reaction in which the pyrite is almost completely consumed. The jarosites are not the most thermodynamically stable species at reaction conditions, but may form due to localized fluctuations in solution concentration in the vicinity of pyrite crystallites at the time they go into solution. Also, metals leached from the reactor components in contact with the acidic slurry are incorporated in these compounds which influence their solubility in the sulfur and sulfur form analyses. Kept in contact with the leachant solution, the jarosite-like compounds digest to more stable forms, metal oxides and sulfuric acid, which do not contain sulfur in the solid phase.

An iron-sulfur containing thermal precipitate was formed in an experiment in which a model sulfur compound was subjected to oxydesulfurization process conditions. The only source of iron was the stainless steel reactor components. X-ray diffraction analysis indicated that the precipitate was jarosite-like and could be detected when mixed with treated coal down to 0.3 weight-percent. X-ray flourescence showed the major components of the precipitate to be iron and sulfur. The compound contained 3 percent chromium as determined by atomic absorption; however, no sodium was detected by this method.

Therefore, the compound is not natrojarosite, for which the equilibrium precipitation temperature/acidity diagram is shown in Figure 3, but similar to the basic sulfate as proposed by Vracar and Vucurovic (37) in equation (4). Analysis of the precipitate by a Fisher sulfur analyzer indicated a sulfur content of 13.4 percent, which is close to the theoretical value of 13.34 percent for the basic sulfate, $Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O$.

To test the possibility that jarosite-like compounds could be responsible for apparent organic sulfur increase, a sample of an Upper Freeport seam coal was doped with the collected jarosite-like precipitate described above and submitted for analysis. All of the sulfur in the doped coal, including the jarosite sulfur, was determined by the ASTM Eschka method, but only 86 percent of jarosite sulfur was reported as sulfate sulfur. None was reported as pyrite and the 14 percent balance, therefore, was reported as organic sulfur. The organic sulfur in the doped sample, as a result, was 37 percent higher than normal. X-ray analysis of several treated coals, including those in Figure 2,

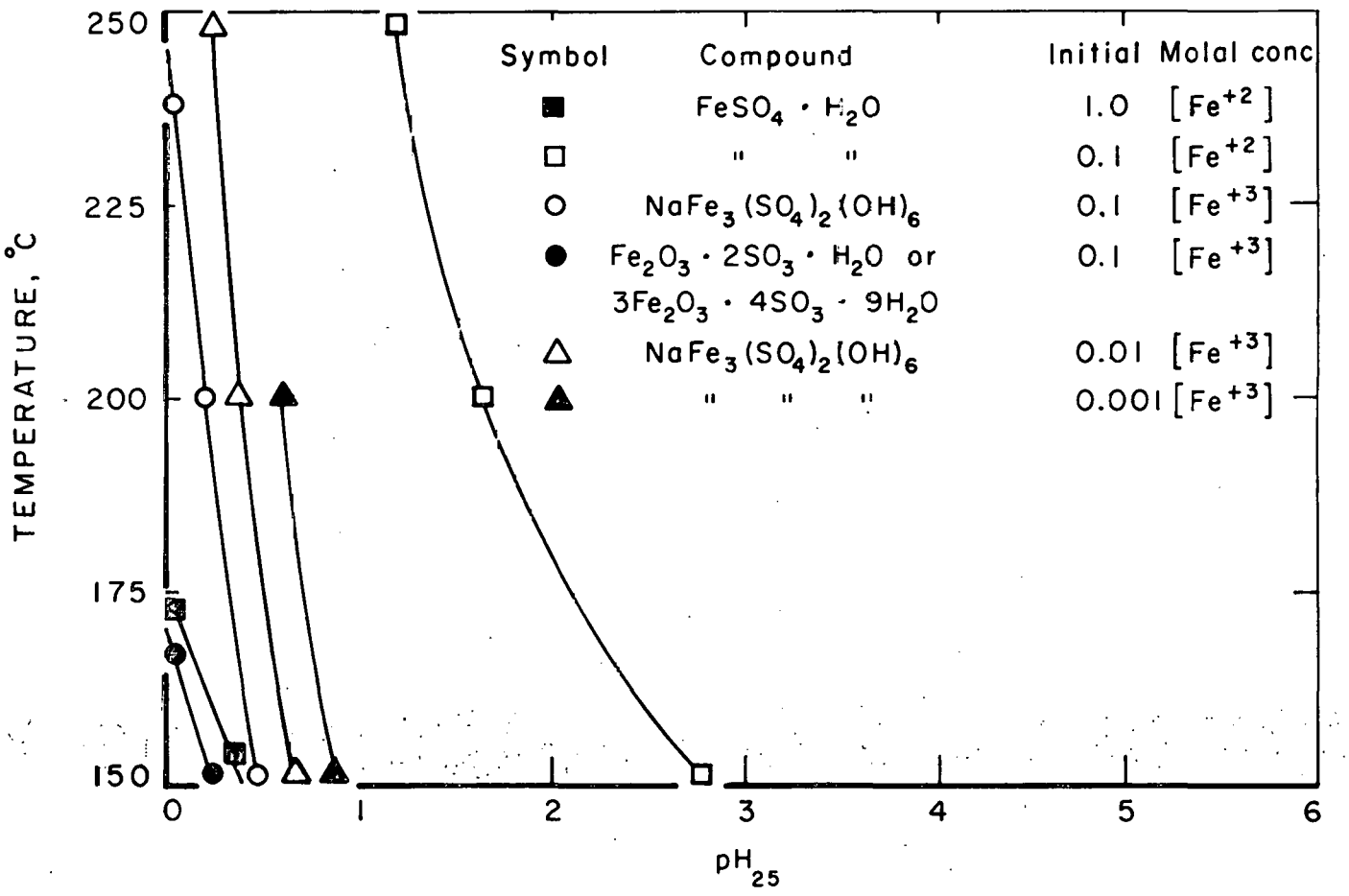

FIGURE 3. EQUILIBRIUM PRECIPITATION TEMPERATURE ACIDITY DIAGRAM FOR THE SYSTEMS $Fe(SO_4)$-H_2SO_4-H_2O, $Fe_2(SO_4)_3$-H_2O, AND $Fe_2(SO_4)_3$-Na_2SO_4-H_2SO_4-H_2O.

L-16225

has not provided any evidence for jarosite-like compound formation during oxydesulfurization of coal. It is likely that such species are amorphous when precipitated on the coal substrate and are, therefore, transparent to X-ray diffraction techniques. Preliminary Mössbauer data on the Lower Freeport coal treated for 15 minutes (Figure 2) indicate that approximately 10 percent of the iron in the sample is present as jarosite-like compounds. Additional Mössbauer data are being gathered to substantiate these results. The aforementioned anomaly and other instances where the analytical results appear to be influenced by the treatment used will be mentioned when necessary throughout this discussion.

DETERMINATION OF PREFERRED OPERATING CONDITIONS

The first experiment at the Pittsburgh Energy Technology Center utilizing the principle of air/water oxydesulfurization was made as part of a research program investigating the chemical removal of sulfur from coal primarily with various oxidation techniques. This was the ultimate experiment, using air as the oxidant in aqueous rather than in organic media. The operating parameters and results for this experiment (5L27) are shown in Appendix 1. The total sulfur content of the product was reduced 51 percent, with the pyritic and organic sulfur contents decreasing 91 and 27 percent, respectively. Under similar conditions in previous experiments (23), the organic sulfur content of the Indiana No. 5 seam coal had been reduced 40 percent in a benzene (80 ml)-cyclohexane (20 ml) slurry. In general, oxidation in organic media removes more organic sulfur from coal than in the air/water system; however, this is offset by the simplicity of the latter technique.

The remainder of the data in Appendix 1 summarizes the initial research exploring the practical range of the basic reaction parameters, temperature, pressure, and residence time. The results indicate the following: sufficient air must be present to prevent the reaction from becoming "oxygen starved"; the reaction temperature appears not only to influence the amount of sulfur removed but also its final distribution in the product; larger mesh-size coals (14x0) exhibit a slight resistance to sulfur reduction; and the pyritic sulfur solubilization rate appears to be faster than organic sulfur removal.

The incongruity of a few of the sulfur forms data in Appendix 1 cannot readily be explained. For example, the apparent incomplete pyritic sulfur reduction in experiments 5L41, 5L31, 6L11, and 6KW37 is inconsistent with the complete solubilization observed at 150°C (5L33). These experiments were all done in the batch mode; therefore, the slurry was exposed to air from room temperature up to reaction temperature in an environment of decreasing oxygen concentration. Experiments 1W39 and 2W11 on the Pittsburgh seam coal indicate that the pyritic sulfur solubilization is essentially complete in 30 minutes or less; therefore, the 20 to 30 minutes in which the slurry is between 140 and 200°C should be sufficient for most of the pyritic sulfur to react. An explanation for the abnormally high pyritic sulfur content is that the pyrite has undergone reaction, but due to thermal precipitation and the possible influence of excessive iron and other metals in solution as a result of increased corrosion at 200°C, other sulfur-containing compounds precipitate which ultimately interfere with the sulfur form analysis. However, these compounds, once formed, are not thermodynamically stable and decompose with continued

treatment as evidenced in 5L27. The corrosion at 200°C is noticeable both visibly as pitting of the liner and stirring assembly and in the HCl soluble iron determination (Appendix 1). At 150°C this problem is less severe.

The apparent organic sulfur contents of a few products (2W11 and 6L9) are significantly higher than in the original coal. This also is probably an artifact of the analytical determination being influenced by unexpected species in the treated coal, such as the jarosite-like compound formation problem previously discussed.

The difficulty in reproducibility of data in the batch system is shown by experiments 5L31, 6L11, and 6KW37 in Appendix 1. The variance observed is primarily a result of different heating durations. For example, the heat-up time for 6L11 was 30 minutes longer than in 5L31 and 6KW37 due to premature reduction in the external heat source as reaction temperature was approached. The slurry temperature over this period dropped to approximately 185°C before recovering and rising to 200°C.

In spite of the aforementioned problems the data in Appendix 1 provided sufficient information to define roughly a practical operating region. The use of relatively mild conditions, 150°C, 800 psig initial air charge, and a one-hour residence time, should effect removal of essentially all pyritic sulfur, and an increase in the operating temperature to 200°C should remove a portion of the organic sulfur from coal.

The data contained in Appendix 2 represent additional experimentation on the Indiana No. 5 seam coal, investigating the utility of air/water oxydesulfurization for organic sulfur removal. Most of these experiments were made with multiple batch charging of air since the system had not yet been modified to allow continuous air flow. The experiments were designed to exceed, in most cases, practical operating conditions to determine if a limit exists for organic sulfur removal. The results in Appendix 2 are arranged in order of decreasing organic sulfur content for treated coals. This generally parallels increases in treatment severity. Combining these data with those in Appendix 1 for the Indiana No. 5 seam coal allows plots to be made which illustrate various relationships between the elemental constituents and other properties of this coal resulting from treatment. In evaluating the data, the limitations unique to the batch air charging mode must be considered. Since the coal slurry is in contact with air from room to operating temperatures, the various reactions, i.e., pyrite and organic sulfur extraction, carbon and hydrogen oxidation and bond cleavage, etc., will proceed at different rates, which vary as the temperature increases and the oxygen partial pressure decreases.

An organic sulfur removal efficiency plot for the Indiana No. 5 seam coal is shown in Figure 4. This is defined as the ratio of the differential increase in organic sulfur removal to the differential increase in heating value loss. The slope of the line describing these data represents the organic sulfur removal efficiency. The slope of the line in Figure 4, calculated by the least squares method, is 1.23 with a correlation coefficient of 0.978. The abscissa intercept indicates that 6 to 7 percent of the heating value is lost before any organic sulfur is removed. This is not unexpected since the batch mode of operation may permit oxidation of the coal at temperatures that are insufficient for effecting organic sulfur removal. The impact of the initial

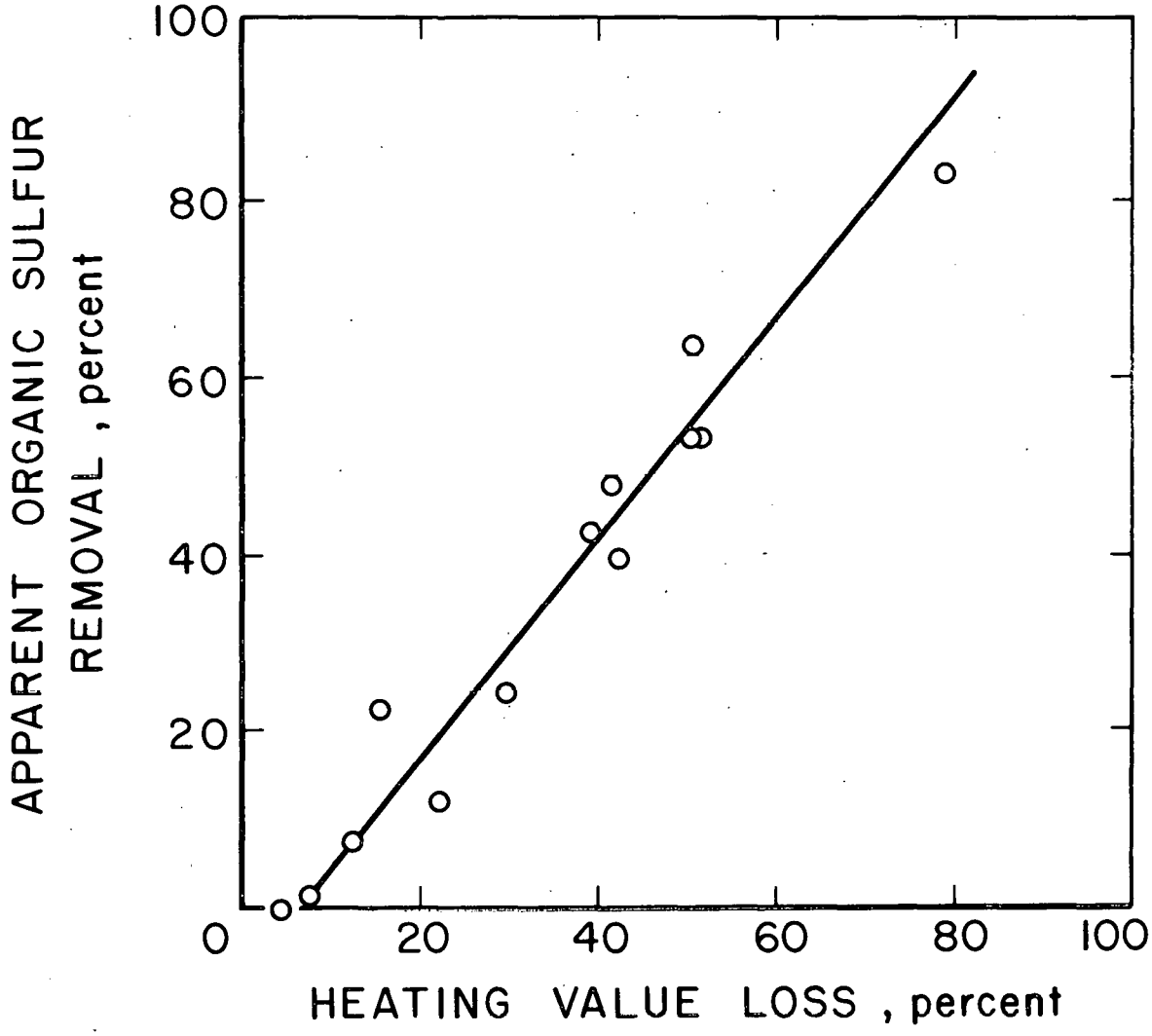

FIGURE 4. ORGANIC SULFUR REMOVAL EFFICIENCY FOR INDIANA NO. 5 HVBB COAL.

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heating value loss is clearly shown in Figure 5, which depicts the reduction in total and organic sulfur due to treatment as the lbs SO_2/MM Btu expected upon combustion. The initial lbs SO_2/MM Btu for the Indiana No. 5 seam coal is 5.30 with 3.21 due to the organic sulfur (indicated by the dashed line in Figure 5). Because of initial heating value loss, the lbs SO_2/MM Btu due to organic sulfur in the product is higher than 3.21 until approximately 35 percent of the organic sulfur is removed.

The total lbs SO_2/MM Btu remaining after treatment appears to increase at first (Figure 5) with increased organic sulfur reduction, and as more severe treatment conditions are used (greater organic sulfur removal), this trend reverses. The shape of this curve is primarily influenced by the unusually high pyrite concentration after treatment in several experiments. Most of these experiments also have higher ash and HCl soluble-iron contents for the treated than for the feed coal, indicating the occurrence of reactor corrosion. The formation of sulfur-containing thermal precipitation products, which may be influenced by corrosion, may introduce some as yet undetermined factor into the sulfur form analysis. This has been partially substantiated by preliminary X-ray analysis of 5L31 and 5L41. The diffraction patterns indicate that significantly less pyrite is present than reported by chemical analysis. Additional discussion of this anomaly is contained in the section describing reaction temperature effects.

As illustrated in Figure 5, the loss in heating value has a significant effect on product quality. Most of this loss is a result of oxidation of the coal and the loss of carbon and hydrogen, as illustrated in Figure 6. The scatter observed for the oxygen data can be partially attributed to the indirect method used for its determination, which results in the summation of all errors incurred in the ash, carbon, hydrogen, nitrogen, and sulfur determinations. It is apparent in Figure 6 that the initial Btu reduction is largely due to the replacement of hydrogen by oxygen and to the oxidation of other susceptible sites on the coal. The loss of carbon, primarily as carbon dioxide, becomes prominent after approximately 20 percent of the original calorific content is lost. More severe conditions (higher heating value loss) cause the oxygen content of the product to decrease as the coal is consumed to the final oxidation products, carbon dioxide and water.

Another perspective of the data in Appendices 1 and 2 is presented in Figures 7 and 8, in which the changes in the various constituents of coal are related to the carbon reduction due to treatment. In Figure 7, hydrogen is observed to decrease initially at a faster rate than carbon. Nitrogen has the opposite relationship and also, there appears to be a 5 to 10 percent nitrogen loss before any carbon is removed. This suggests the presence of labile nitrogen moieties, such as amines; however, such groups have not yet been found to occur regularly in coal.

Figure 8 illustrates again the rapid uptake of oxygen by the coal with little carbon loss. The oxygen increases over 40 percent with only a 10 percent carbon decrease. Figure 8 also shows an interesting relationship between the organic sulfur and carbon reductions. Apparently for this coal, up to 20 percent of the organic sulfur is removed with little sensitivity to carbon loss. This indicates the organic sulfur in this coal exists in two environments,

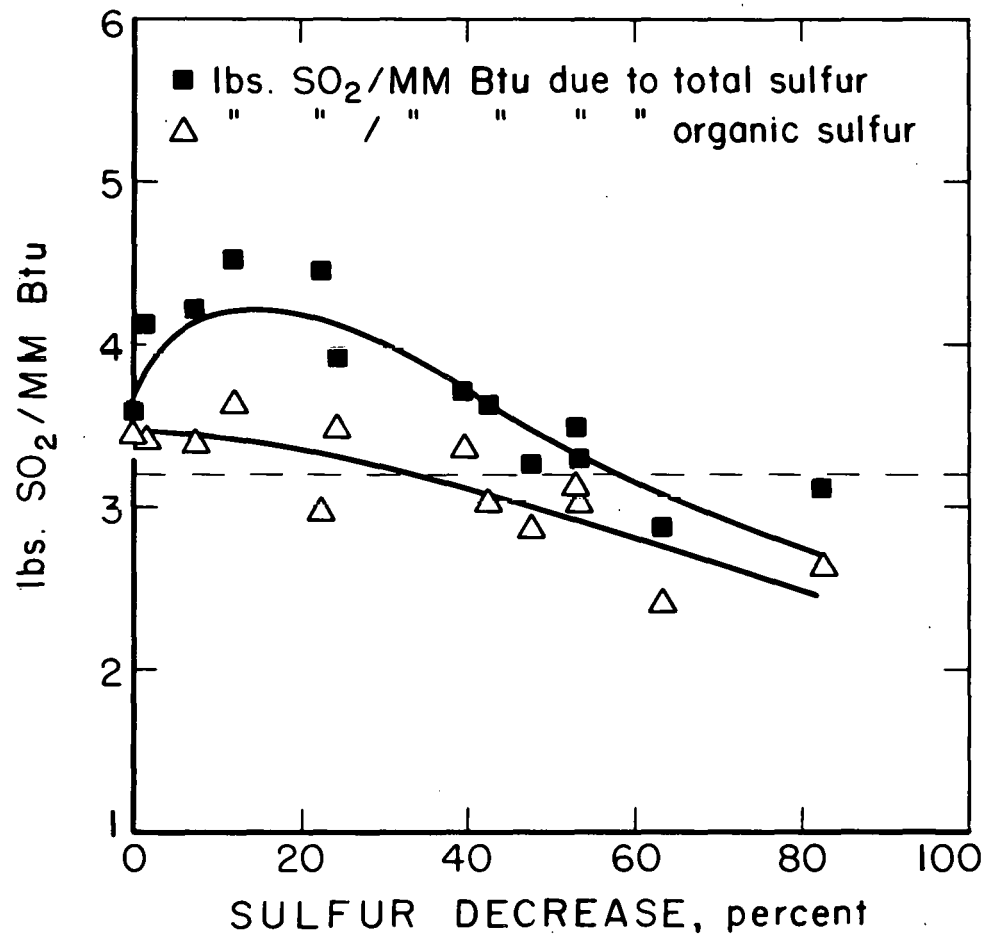

FIGURE 5. RELATIONSHIP OF PRODUCT QUALITY TO TOTAL SULFUR AND ORGANIC SULFUR REDUCTION FOR INDIANA NO. 5 HVBB COAL.

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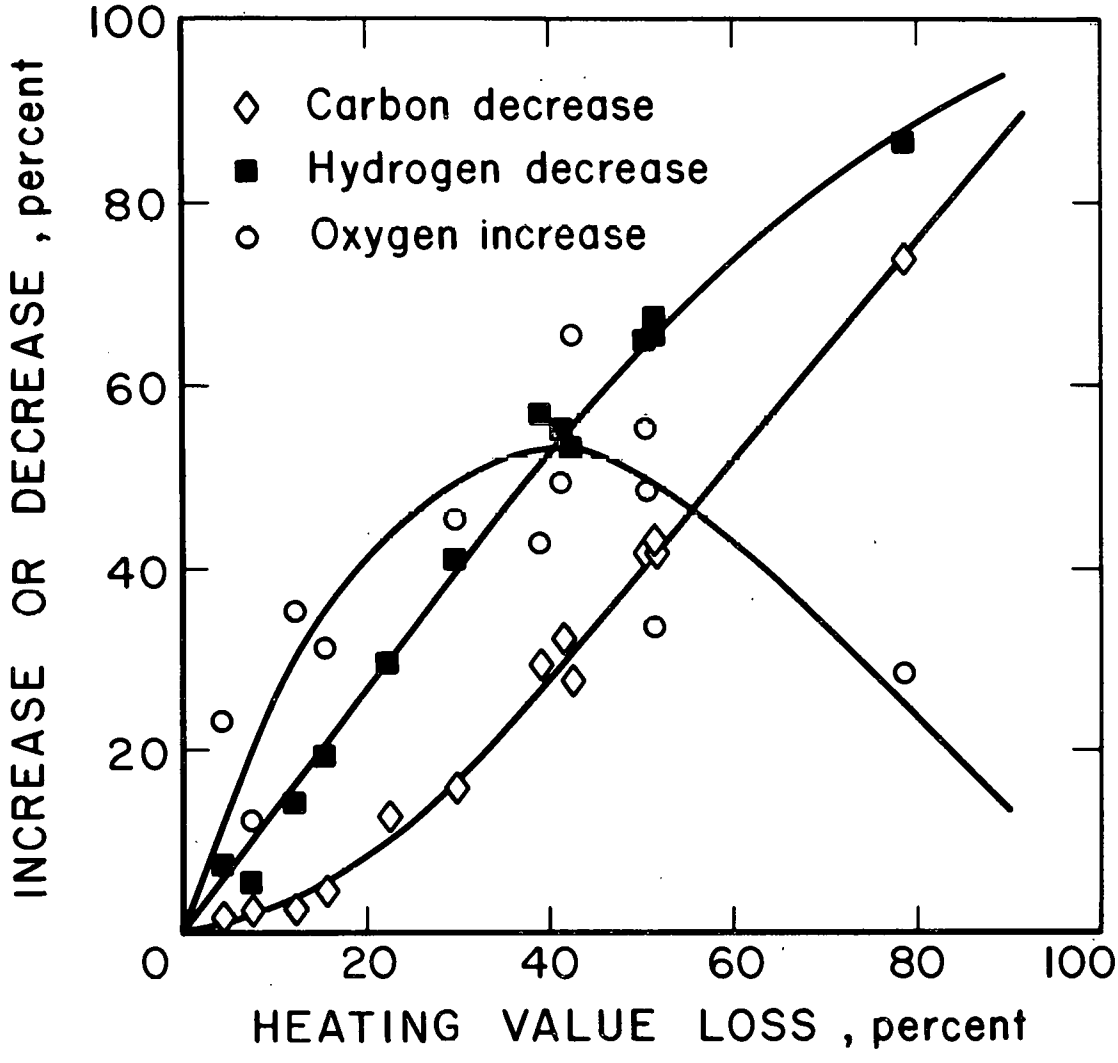

FIGURE 6. COMPARISON OF CARBON, HYDROGEN, AND OXYGEN VARIATIONS DUE TO TREATMENT TO HEATING VALUE LOSS FOR INDIANA NO. 5 HVBB COAL.

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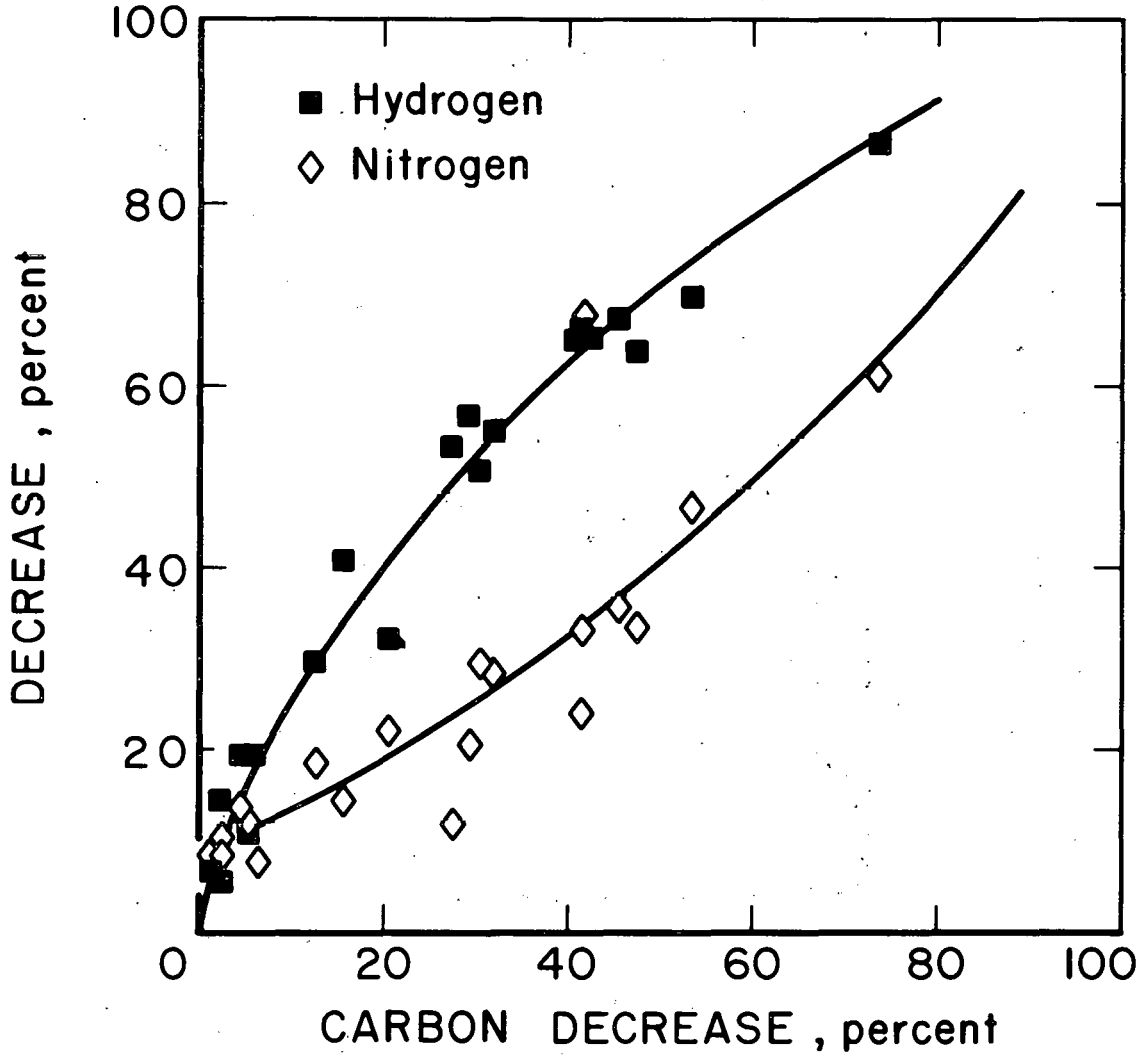

FIGURE 7. COMPARISON OF HYDROGEN AND NITROGEN REDUCTION TO CARBON DECREASE FOR TREATMENT OF INDIANA NO. 5 HVBB COAL.

3-29-79 L-16613

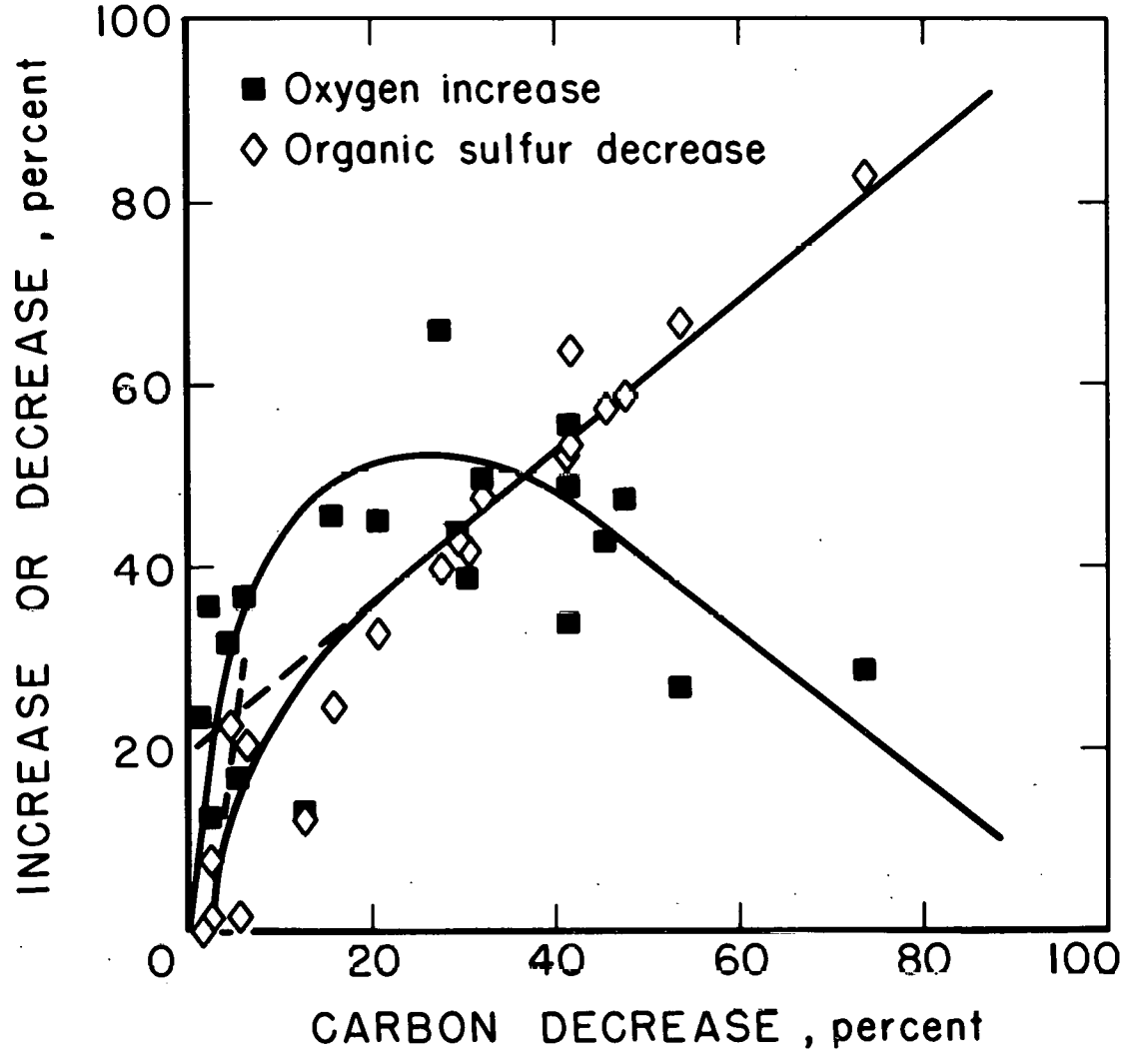

FIGURE 8. COMPARISON OF OXYGEN UPTAKE AND ORGANIC SULFUR DECREASE TO CARBON DECREASE FOR TREATMENT OF INDIANA NO. 5 HVBB COAL.

3-29-79 L-16627

one more reactive than the other. This hypothesis has been advanced by other investigators (2). We have shown that the nonreactive sulfur is likely in dibenzothiophenic type structures (9) and believe the labile sulfur exists as mercaptans, thiols, thioethers, and reactive thiophene groups. The ratio of the two types of sulfur activity would vary with different coals and, therefore, the amount of organic sulfur that can be readily removed by air/water oxydesulfurization and other similar processes would parallel this relationship.

With respect to the overall utility of air/water oxydesulfurization for organic sulfur reduction, there appears to be a limit to the amount that can be removed practically, dependent on the coal being used (Figure 8). Also, the initial heating value loss, which can possibly be reduced by not using batch air charging, must be considered when evaluating the performance of this process (Figure 5).

PARAMETRIC STUDIES

Several types of variables influence the air/water oxydesulfurization of coal. One group is the reactor configuration-dependent variables that include, agitation rate, slurry volume, and slurry concentration, all of which affect the concentration of dissolved oxygen in the slurry. Also important are factors controlling the reaction chemistry, such as temperature, residence time, oxygen partial pressure, and possibly the system total pressure and slurry concentration. The last group of variables concerns the coal itself. They are the type, or rank, and the size consist of the coal. The experimental program attempts, in a basic sense, to define the effects of the above variables on the properties of coal, especially pyritic and organic sulfur reduction and loss of calorific value. As previously mentioned, some of the sulfur species data, especially in the early research in which a stainless steel liner was used, are possibly influenced to varying degrees by thermal precipitation and corrosion products. This will be discussed as necessary to offer explanation for otherwise inexplicable results.

Mixing Efficiency

The data in Appendix 3 illustrate the variables for which the optimum values are fixed by the reactor geometry. The first set of data for the Indiana Minshall seam coal concerns the stirring rate and is plotted in Figure 9. It is evident that the 900 to 1000 RPM standard stirring speed used in most experiments is sufficient to avoid diffusion limitations for gas absorption with the reactor configuration used.

The experiments on the Pittsburgh seam coal, discussed in Appendix 3, show the effects of overloading the autoclave. A 26 weight-percent slurry was used in both experiments. In one the total charge was 580 gm; in the other it was the normal charge of 135 gm. The normal charge provides enough sample after treatment for complete analysis and any subsequent experimentation. This volume of slurry is also sufficient to adequately cover the stirring blade and thermowell while still providing maximum gas volume in the reactor. The large decrease in sulfur reactivity (50 percent removal in 4W99 to only 19 percent in 6W65) clearly shows the importance of slurry volume on gas absorption capacity.

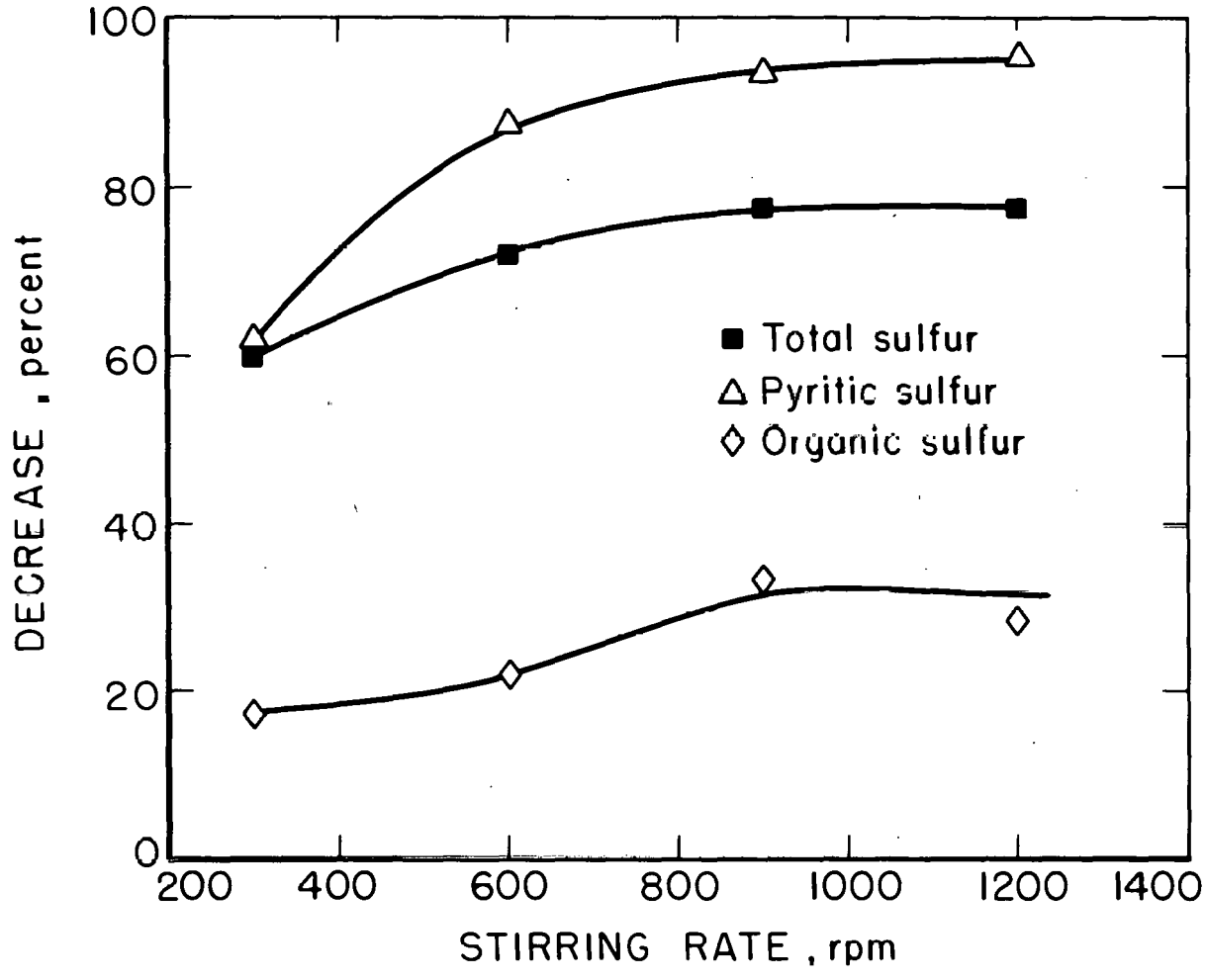

FIGURE 9. SULFUR REDUCTION AS A FUNCTION OF STIRRING SPEED, MINSHALL HVCB COAL, 180° C. 1000 PSIG, 7 SCFH AIR FLOW, 1 HOUR.

11-14-79 L-16614

Reaction Temperature

Initial experimentation showed that sulfur removal increased with temperature in the 150 to 200°C range, primarily due to organic sulfur extraction at the higher temperatures. However, higher reaction temperature also promotes greater heating value loss and corrosion of the stainless steel autoclave.

Appendix 4 contains several series of exploratory experiments on Indiana Minshall seam coal investigating the temperature influence on sulfur removal and heating value loss. The first two sets, 3W3 through 3W13 and 2W39 through 2W37, were made in the batch mode (stainless steel liner) with an 800 psig initial air charge. Experiments 3W3 through 3W13 were stabilized at the indicated temperatures for 5 minutes. The sulfur removal is shown in Figure 10. Due to the nature of batch mode operation, it is illogical to assume that less pyrite has reacted at or above 170°C than at lower temperatures. It is likely that thermal precipitation and/or corrosion products are interfering with the pyritic sulfur analysis. A similar explanation can be offered for the apparent organic sulfur increase. It is possible that more than one such foreign species is present due to the separate influences on the pyritic and organic sulfur results. Possible explanations for this are discussed below.

Figure 11 contains the sulfur removal data for the second set of experiments in Appendix 4. This series is identical to the above except for the use of 30-minute residence times. The amounts of total and pyritic sulfur are observed to decrease steadily as higher temperatures are used, and the extent of pyritic sulfur reduction appears to be independent of temperatures above 160°C. Also, the apparent organic sulfur increase now is inversely proportional to the reaction temperature. Therefore, if the precipitation of a foreign species is responsible for the increase in apparent organic sulfur, its rate of decomposition to soluble products increases with temperature.

It was later found that both of the above series of experiments were made with a synthetic air mixture that initially contained 30.6 percent oxygen. The extent of the influence of the higher oxygen content on the data is dependent on the sensitivity of the various reactions, e.g., pyritic and organic sulfur solubilization, coal oxidation, etc., to oxygen partial pressure. This will be discussed below. Also, note that 50 percent or more of the heating value lost in the 30-minute experiments is lost in the initial 5 minutes. This indicates that substantial heating value loss occurs during the heat-up period and/or during the initial part of the experiment at reaction temperature. The fact that the oxygen partial pressure is constantly decreasing also may limit the heating value loss at longer reaction times.

In the third set of experiments in Appendix 4 (5W33 through 5W45), the heat-up period took place under 1 atmosphere of nitrogen. Air was added at reaction temperature to increase the reactor pressure to 1000 psig. This technique results in lower oxygen partial pressure at the higher reaction temperatures. At 200°C the oxygen partial pressure was 161 psi, compared to 195 psi at 140°C, as a result of the different vapor pressures of water at these temperatures. Hopefully, the effects of these differences are reduced by limiting the reaction time to 5 minutes. The sulfur species variations are shown in Figure 12. The total sulfur is observed to decrease steadily up to

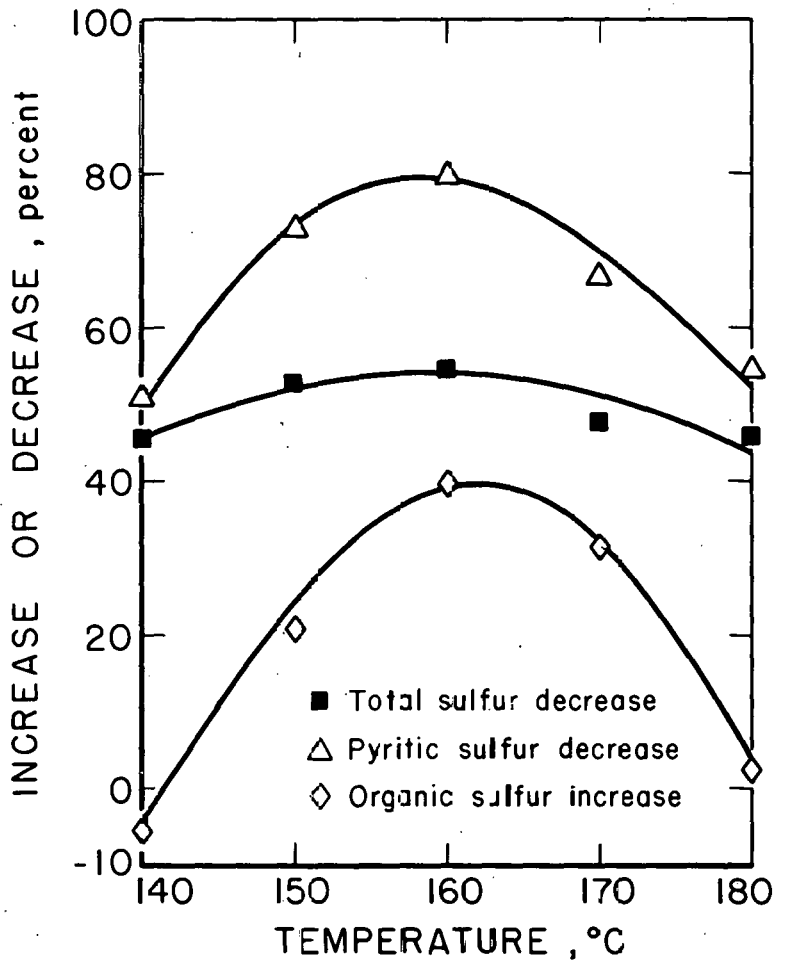

FIGURE 10. EFFECT OF TEMPERATURE ON DESULFURIZATION OF MINSHALL HvCb COAL, 5 MINUTE BATCH MODE TREATMENT, 800 PSIG INITIAL AIR CHARGE.

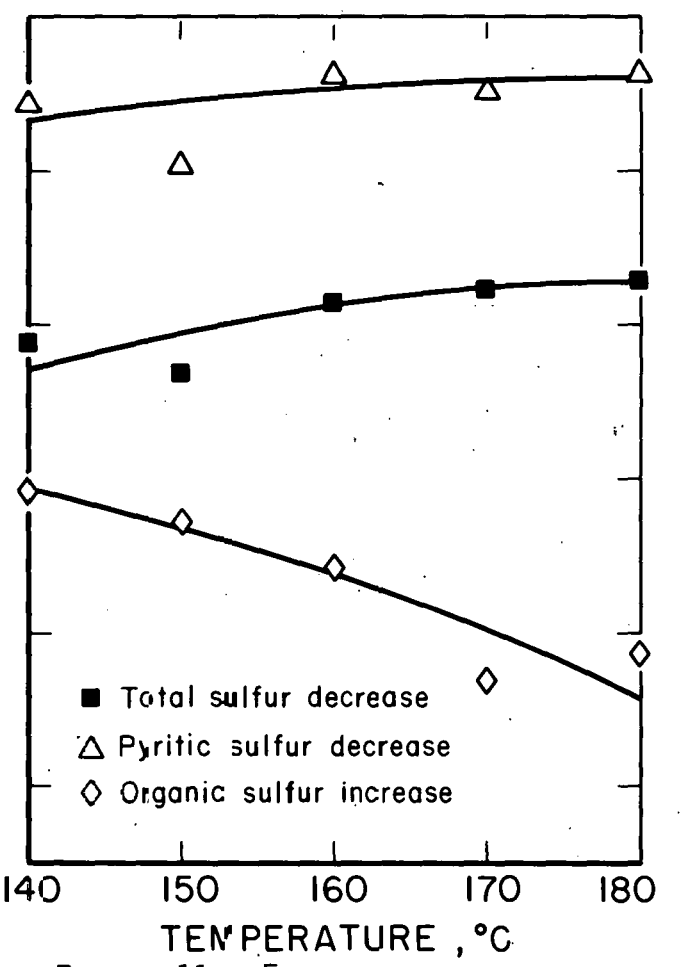

FIGURE 11. EFFECT OF TEMPERATURE ON DESULFURIZATION OF MINSHALL HvCb COAL, 30 MINUTE BATCH MODE TREATMENT, 800 PSIG INITIAL AIR CHARGE.

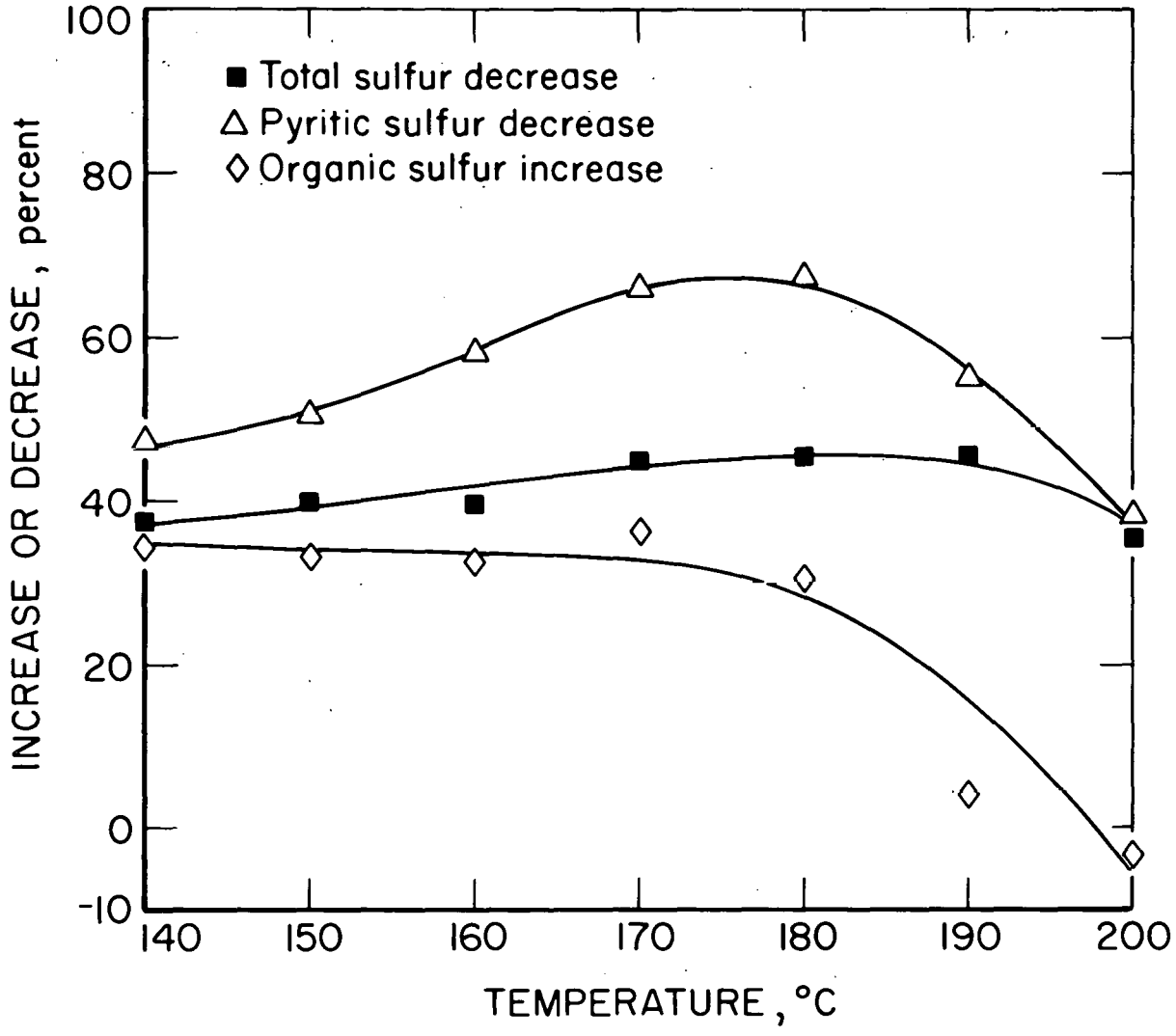

FIGURE 12. EFFECT OF TEMPERATURE ON DESULFURIZATION OF MINSHALL HVCB COAL, 5 MINUTE MODIFIED MODE TREATMENT, 1000 PSIG.

3-29-79 L-16616

approximately 190°C at which point the trend reverses. This is similar to that observed in Figure 3 for the 5-minute batch experiments with initial air charging, except for the temperature difference at which the trend occurs. Similarly, the apparent organic sulfur increase and the pyritic sulfur removal decrease at about the same rate after 180°C. If a foreign compound is interfering with the organic sulfur determination at the lower temperatures, it appears to be converted to one which interferes with the pyritic sulfur analysis at higher temperatures. Also, since the decrease in pyritic sulfur removal is not observed in the 30-minute experiments, this same species must eventually be solubilized.

The initial heating value loss as a function of reaction temperature is shown in Figure 13, illustrating the third set of data in Appendix 4. Little reduction is observed until higher temperatures are used, especially above 180°C. When compared to the previous results in Appendix 4 for the 5-minute experiments using an initial air charge (3W3 through 3W13), these data indicate that when air is present, 3 to 5 percent of the heating value is lost during the heat-up period.

Figure 14 and 15 show the changes in the elemental constituents of the coal due to treatment at the various temperatures. The heating value loss is obviously more dependent on the loss of carbon and hydrogen than on the uptake of oxygen. For example, at 180°C, only 2 percent of the original heating value is lost even though the oxygen content has increased 38 percent. Not until the higher temperatures, where increased oxidation causes cleavage of various groups from the coal, is the heating value greatly affected.

In summary, the data in Appendix 4 demonstrate the initial temperature dependence of the various oxidation reactions occurring for the Indiana Minshall seam coal. The pyrite solubilization was shown to be 45 to 65 percent complete in 5 minutes at 140 and 180°C, respectively. At higher temperatures the pyritic sulfur removal appears to decrease. However, based on the batch experiments with an initial air charge, the observed drop in reactivity is probably the result of the analytical determination of compounds, which precipitate at the higher temperatures, as pyritic sulfur. A similar problem appears to affect the organic sulfur results, except the interference occurs at the lower temperatures and then subsides as higher reaction temperatures are used. At reaction temperatures in excess of 180°C, the oxidative consumption of this coal becomes more intense as evidenced in Figures 13, 14, and 15. The last two experiments in Appendix 4 (1W35 and 4W25) evidence the aforementioned temperature effects on typical 1-hour treatments. The changes in the product are summarized in Table 2. The pyritic and total sulfur removals increase with temperature; however, the organic sulfur anomaly persists at the lower temperature, even after 1 hour. The dependence of the heating value loss on the carbon and hydrogen losses is also clearly shown. Overall, the higher reaction temperature provides a better quality product, as shown by the lbs SO_2/MM Btu.

The temperature sensitivity of several other coals to air/water oxydesulfurization treatment has been studied. The analyses of these coals prior to treatment are contained in Appendix 5. Two different size fractions were used for each coal. The 200x0-mesh samples were obtained by grinding the 14x0-mesh

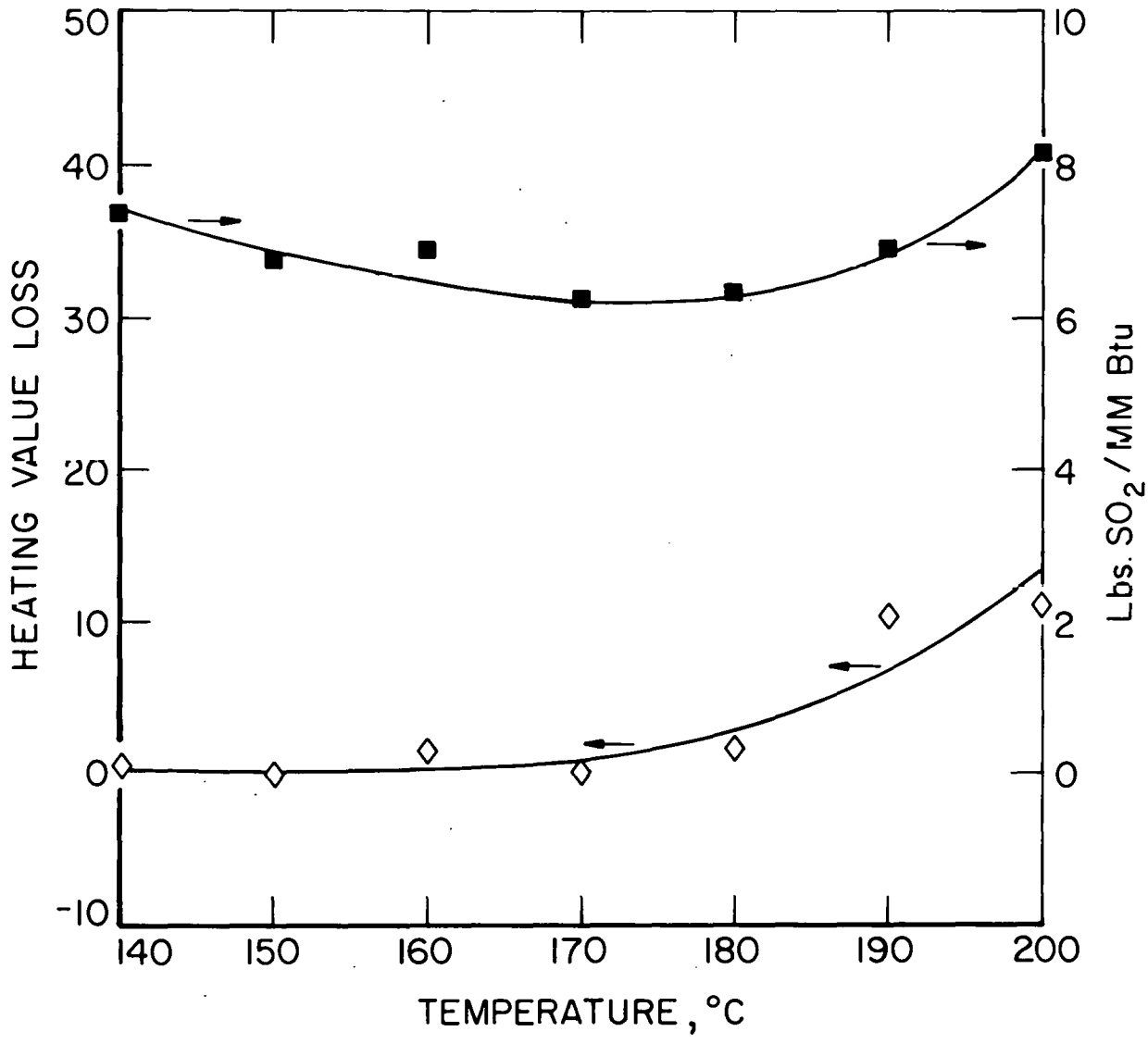

FIGURE 13. EFFECT OF TEMPERATURE ON HEATING VALUE AND PRODUCT QUALITY OF MINSHALL HVCB COAL, 5 MINUTE MODIFIED MODE TREATMENT, 1000 PSIG.

4-23-79 L-16643

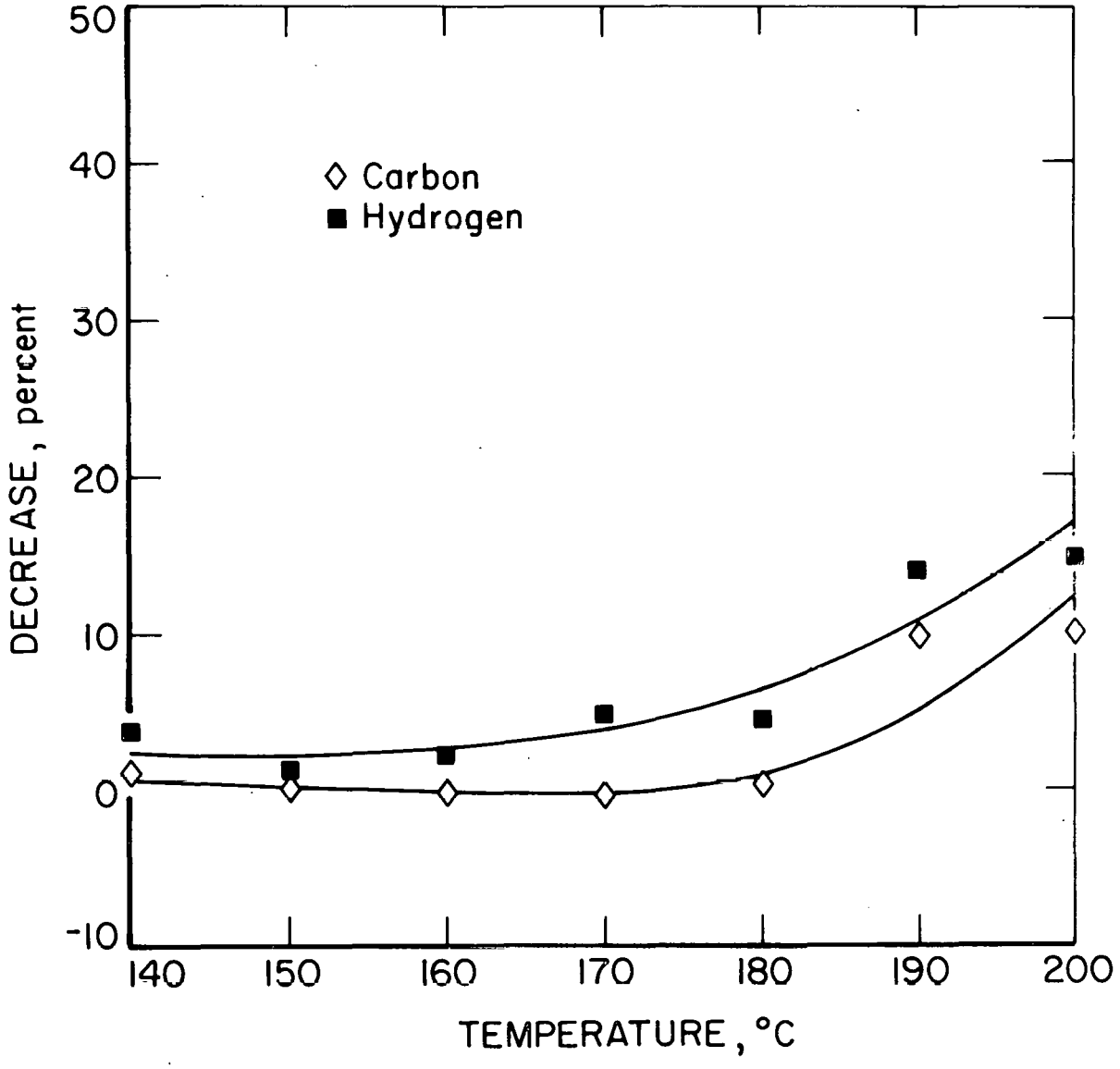

FIGURE 14. EFFECT OF TEMPERATURE ON CARBON AND HYDROGEN OF MINSHALL HVCB COAL, 5 MINUTE MODIFIED MODE TREATMENT, 1000 PSIG.

3-29-79 L-16611

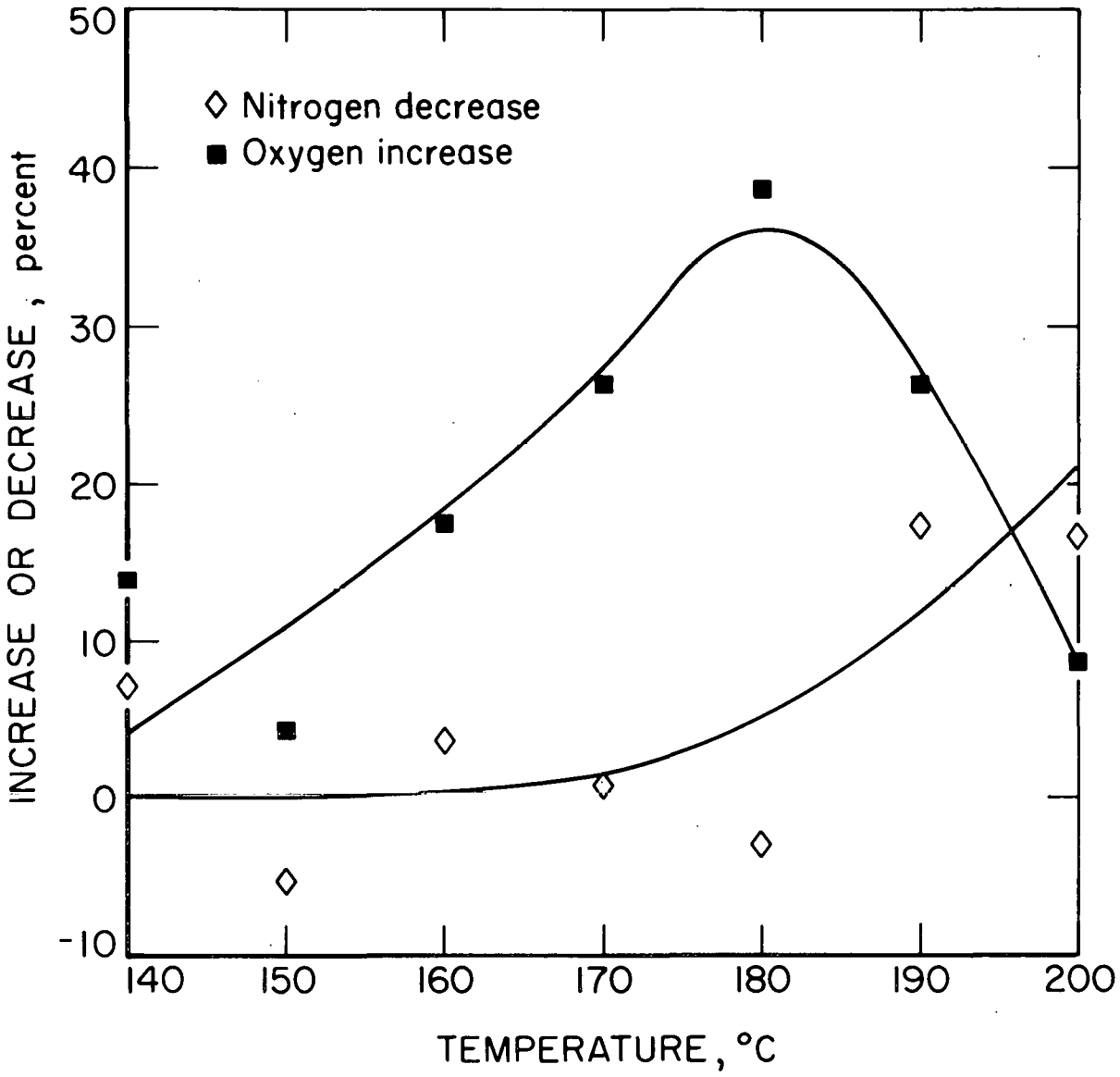

FIGURE 15. EFFECT OF TEMPERATURE ON NITROGEN AND OXYGEN OF MINSHALL HVCB COAL, 5 MINUTE MODIFIED MODE TREATMENT, 1000 PSIG.

3-29-79 L-16625

Table 2. Comparison of One–Hour Batch Mode Treatments at 150 and 200°C of Indiana Minshall (HvCb) Seam Coal

Experiment	1W35	4W25
Temperature (°C)	150	200
PERCENT CHANGE		
Sulfur	-63	-78
Pyritic Sulfur	-95	-97
Organic Sulfur	+32	-32
Carbon	- 6	-14
Hydrogen	-11	-38
Nitrogen	- 4	-12
Oxygen	+82	+70
Btu	- 9	-23
LBS. SO_2/MM BTU		
Sulfur	4.09	2.80
Pyritic Sulfur	0.39	0.20
Organic Sulfur	3.51	2.38

samples. What appear to be duplicate analyses are analyses of samples of the same coal taken from the same container at different times. Due to the deviations present, it is necessary when interpreting the results to use the correct untreated analysis. The coals in Appendix 5 contain less sulfur than the Minshall seam coal previously discussed, and therefore, have the potential for meeting the 1974 New Source Performance Standard (NSPS) for sulfur dioxide emissions from stationary power sources of 1.2 lbs SO_2/MM Btu after treatment. The lower sulfur contents of these coals also should reduce the severity of corrosion since less sulfuric acid will be produced. These coals also have various ASTM ranks. The correlations of coal reactivity to rank and to particle size, that are evident in the data to follow, will be discussed in a subsequent section.

The results due to oxydesulfurization treatment of the coals in Appendix 5, as well as the treatment conditions, are contained in Appendix 6. The reference code to Appendix 5 indicates the analysis used for calculations. In all cases a glass liner was used to contain the slurry of 35 gm coal in 100 ml distilled water. After heating under 1 atmosphere of nitrogen to the indicated temperature, the system was held for 1 hour at 1000 psig total pressure. An air flow of 6 to 8 SCFH (0°C, 1 atm) was utilized to maintain this pressure until the experiment was terminated. In addition to the ultimate analysis, Appendix 6 also contains the heating value, lbs SO_2/MM Btu, and heating value loss for the products. The influence of reaction temperature on heating value loss is immediately apparent. For the 200x0-mesh coals, the average loss at 150°C is 8.3 percent, 20.1 percent at 180°C, and 25.4 percent at 200°C. The heating value losses for the 14x0-mesh coals are slightly less, 15.1 and 19.8 percent at 180 and 200°C, respectively.

Figures 16 through 20 represent the changes in total, pyritic, and organic sulfur as a function of the reaction temperature for the coals in Appendix 6. The data for the Rosebud seam coal (Figure 20) and the coarser mesh coals will be discussed separately. However, the overall trends for the 200x0-mesh samples in Figures 16 through 19 are similar. The total sulfur reduction improves with increasing reaction temperature. This is primarily a result of the changes in the organic sulfur, since the pyritic sulfur is essentially removed at 150°C, with the final content in the products, in most cases, being 0.1 percent by weight or less. The apparent organic sulfur content appears to decrease steadily with increasing reaction temperature (Appendix 6) even though the Upper Freeport seam and Colorado coals exhibit an increase in apparent organic sulfur at 150°C (Figures 16 through 19). The two coals having this anomalous increase also initially contain more pyritic sulfur; therefore, the slurry becomes more acidic during the experiment, as indicated by the pH values in Appendix 6. The organic sulfur decreases at the higher temperatures, even though the final pH of the slurry is the same or lower. This concurs with the work of Vracar and Vucurovic previously cited (39), which states that the formation of the jarosite-like compound occurs when an acidity limit is exceeded, and the limit increases with temperature.

The reason for the unusual pyrite reactivity of the Rosebud seam coal (Figure 20) has not yet been ascertained. Further investigation is needed to determine if the precipitation of foreign species is causing the observed trend or if the nature or physical distribution of the pyrite in this low rank coal

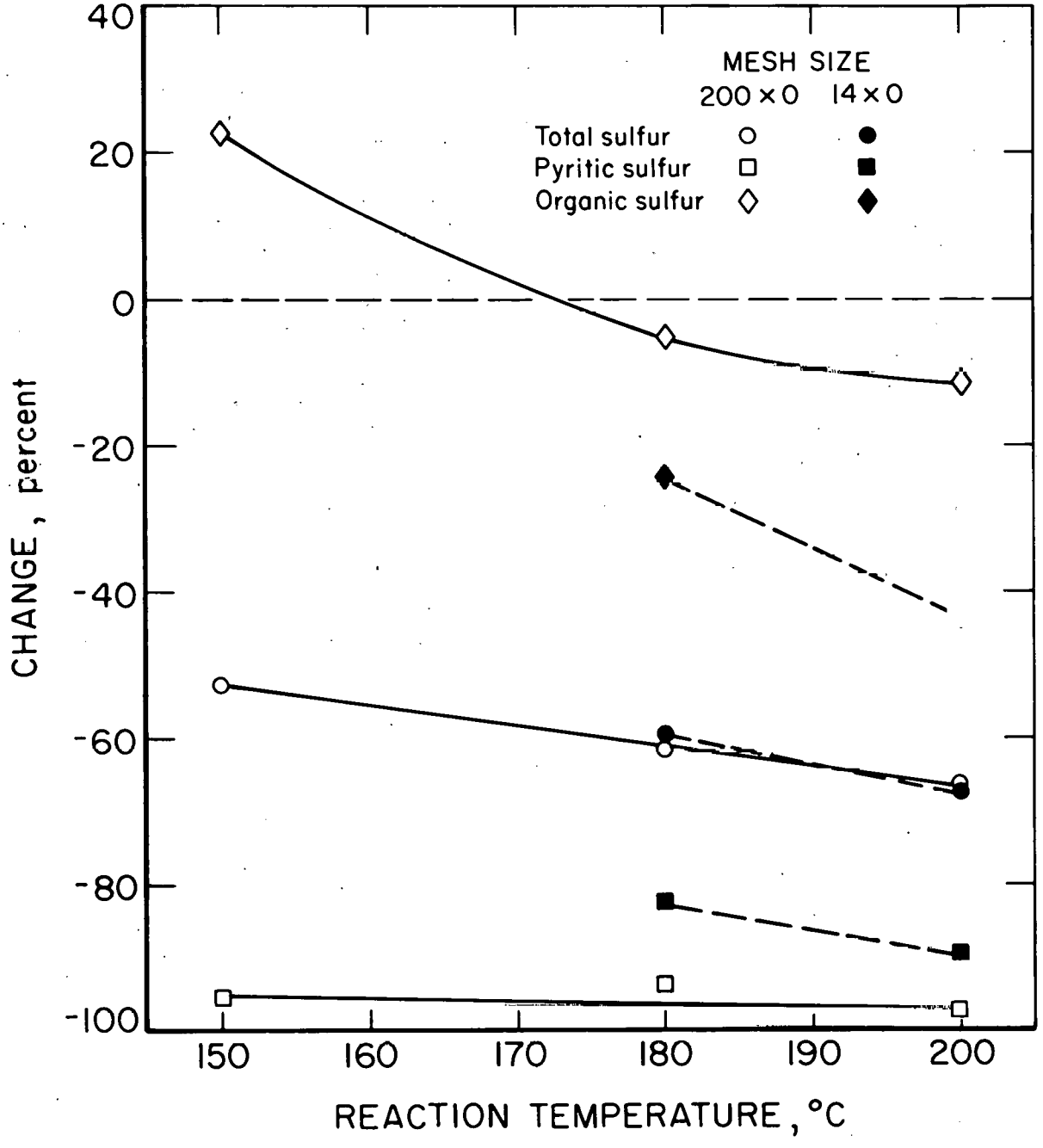

FIGURE 16. EFFECT OF TEMPERATURE ON DESULFURIZATION OF 14 x 0 AND 200 x 0 MESH SAMPLES OF UPPER FREEPORT MVB COAL, 1 HOUR, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-79 L-16620

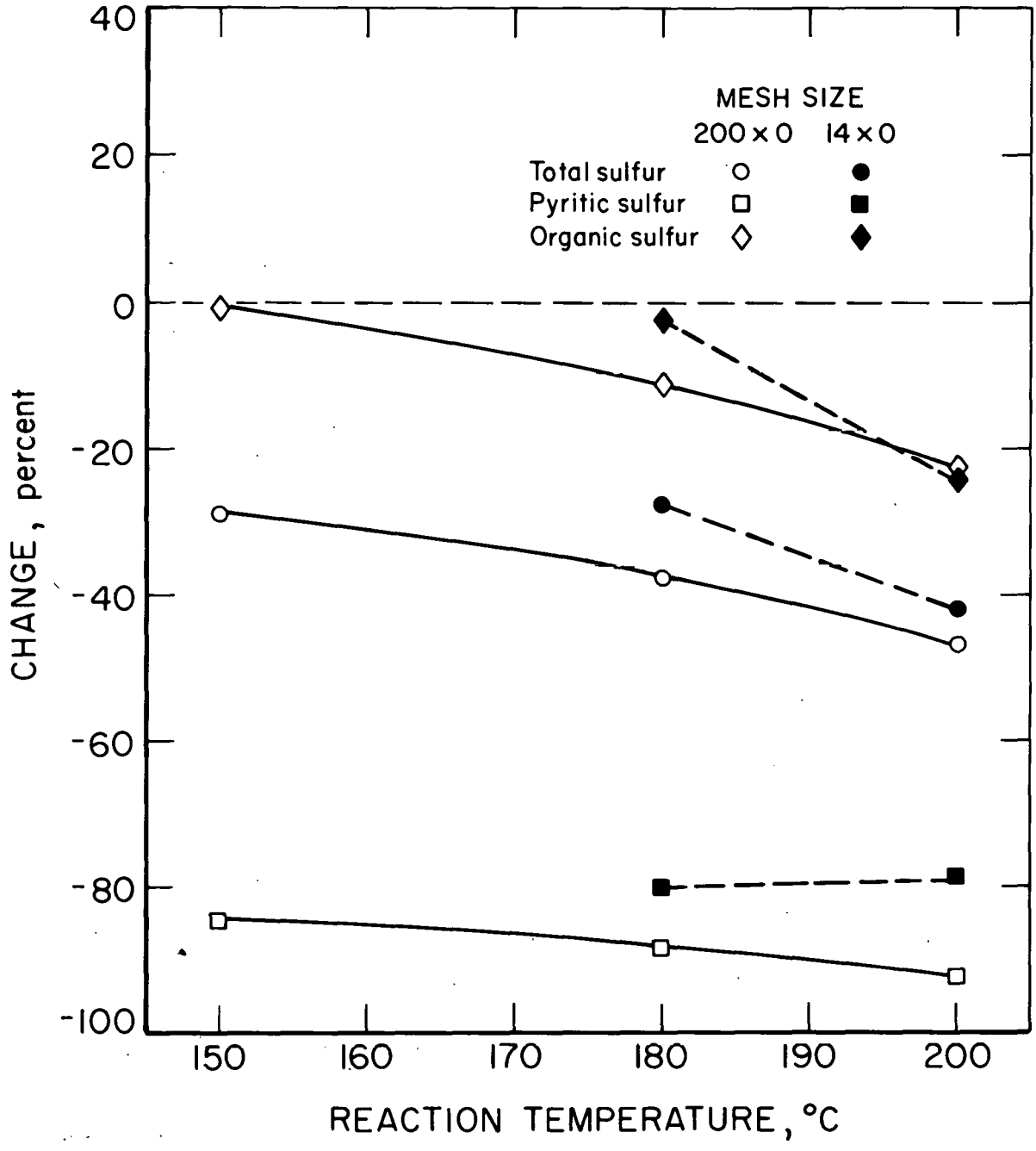

FIGURE 17. EFFECT OF TEMPERATURE ON DESULFURIZATION OF 14 x 0 AND 200 x 0 MESH SAMPLES OF IMBODEN HvAb COAL, 1 HOUR, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-79 L-16621

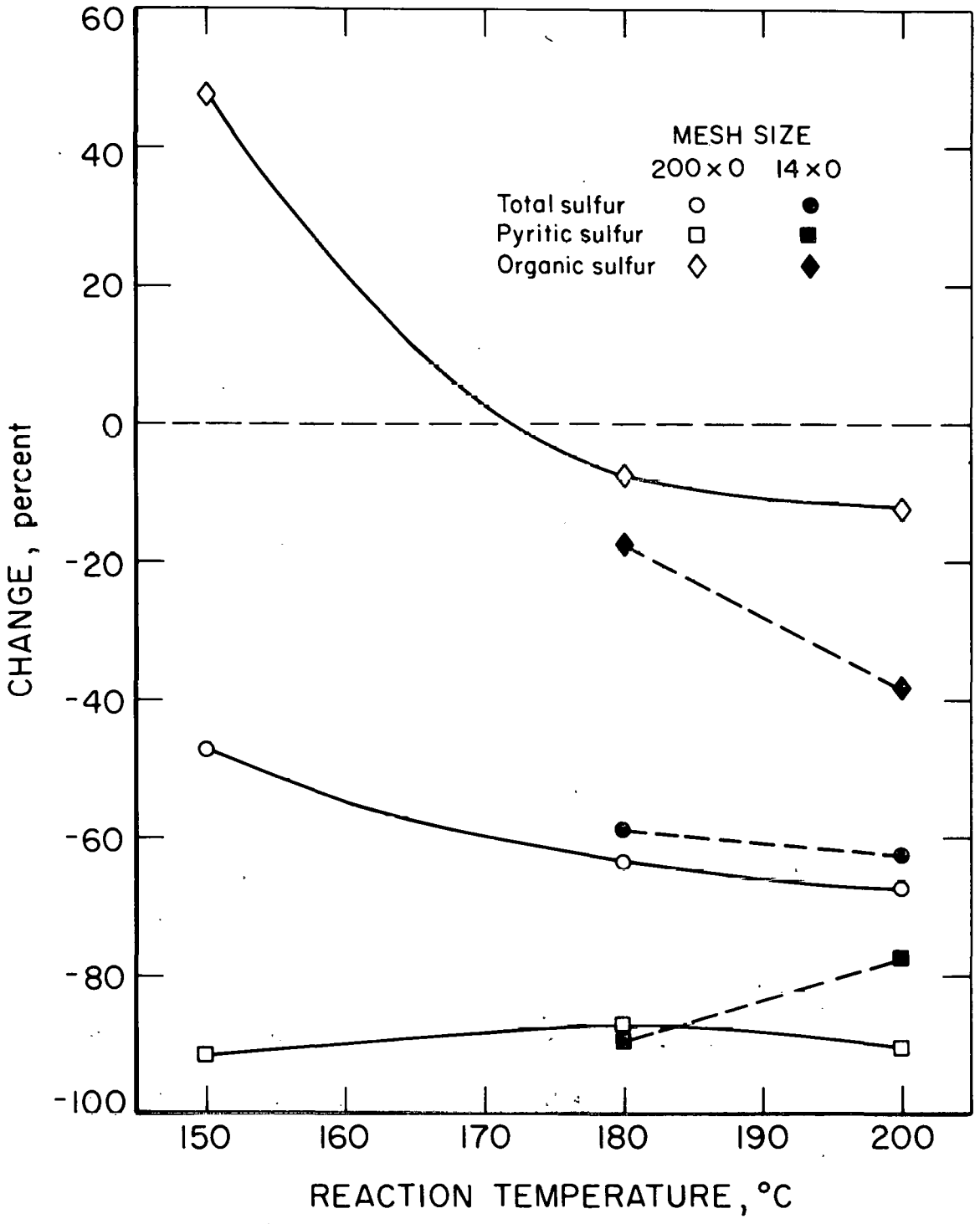

FIGURE 18. EFFECT OF TEMPERATURE ON DESULFURIZATION OF 14 x 0 AND 200 x 0 MESH SAMPLES OF COLORADO HvBb COAL, 1 HOUR, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-79 L-16622

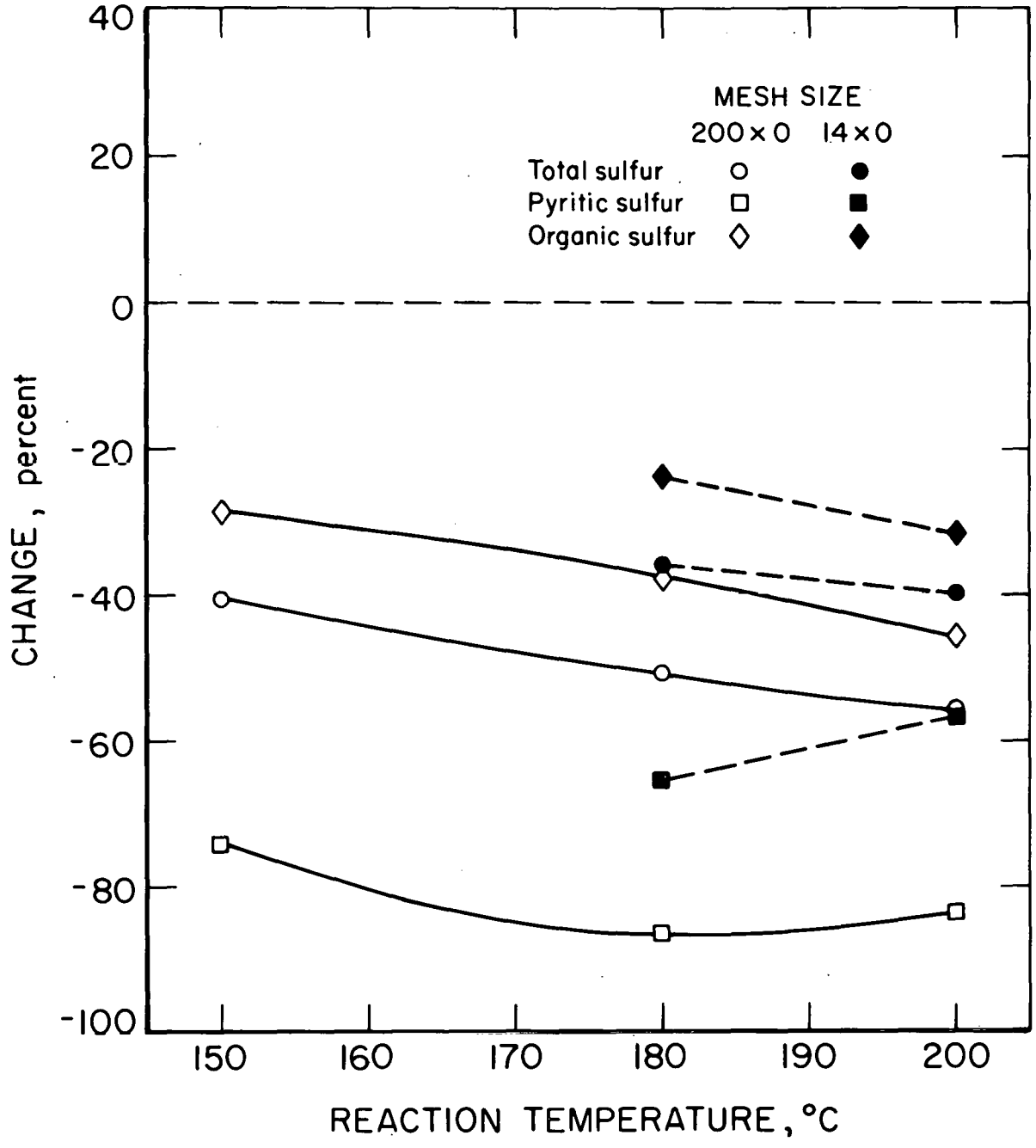

FIGURE 19. EFFECT OF TEMPERATURE ON DESULFURIZATION OF 14 x 0 AND 200 x 0 MESH SAMPLES OF MIDDLE KITTANNING HvCb COAL, 1 HOUR, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-79 L-16623

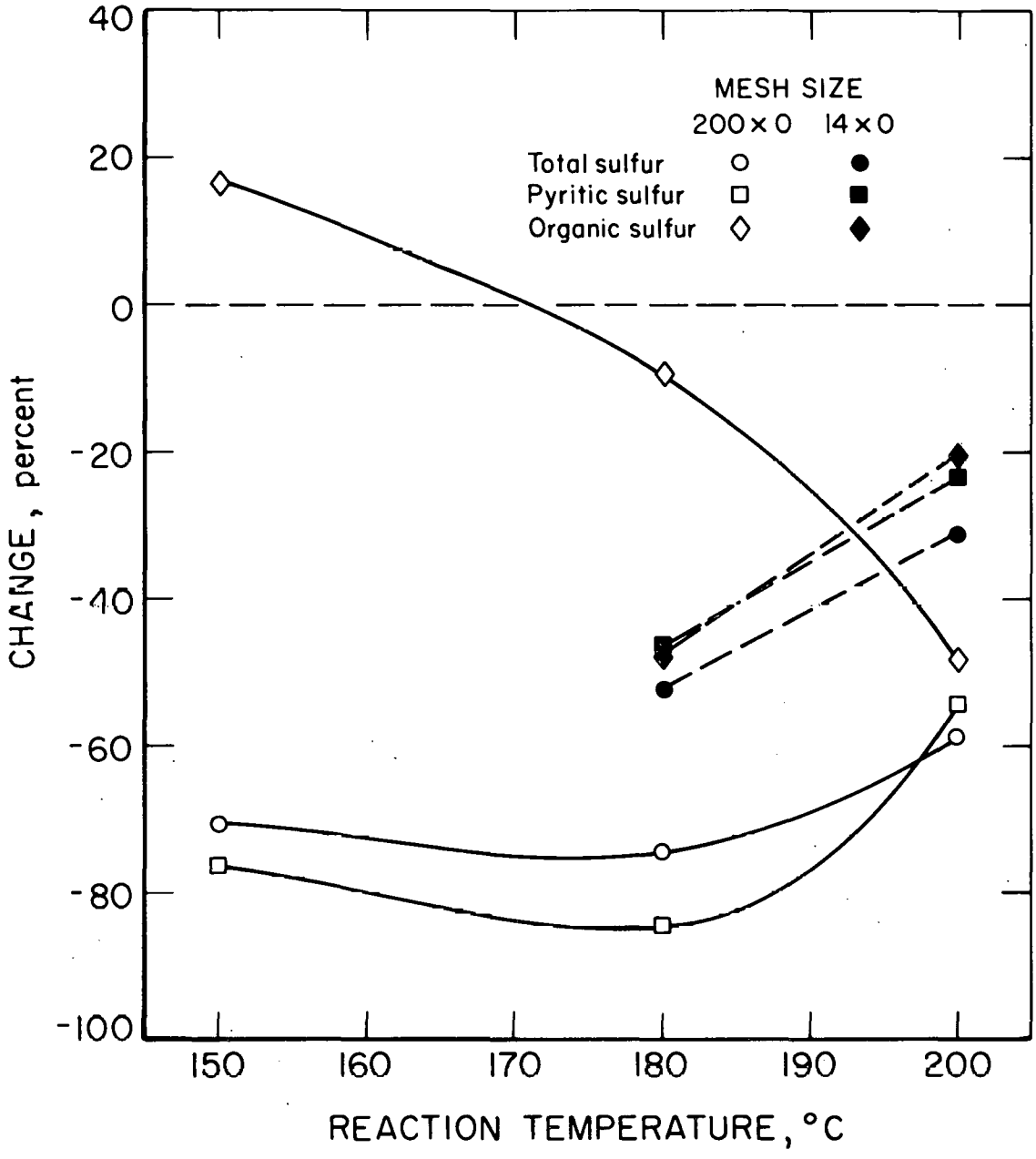

FIGURE 20. EFFECT OF TEMPERATURE ON DESULFURIZATION OF 14 X 0 AND 200 X 0 MESH SAMPLES OF ROSEBUD SBA COAL, 1 HOUR, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-79 16624

makes it unusually resistant to treatment. Also note the lower weight recovery of product indicated in Appendix 6 for this coal. The relatively higher susceptibility of this coal to oxidation may effectively decrease the oxygen available for pyrite reaction.

For most of the coals in Appendix 6 the product quality, as illustrated in Figure 21, improves with higher reaction temperatures. However, for the Middle Kittanning seam coal little if any advantage exists, and for the Rosebud seam coal the detrimental effect of increased temperature is quite severe. Even though the total sulfur removal increases with temperature for all but the Rosebud seam coal, the accompanying heating value loss may be restrictive with respect to final product quality.

Figure 22 depicts the dependence of the heating value loss on the reaction temperatures for the coals in Appendix 6. Figures 23, 24, and 25 are similar plots concerning the major factors influencing the heating value loss, i.e., carbon and hydrogen loss and oxygen uptake. Again, as with the Minshall seam coal the carbon and hydrogen loss appear to have the greatest effect on the reduction in heating value.

Figure 26 shows an organic sulfur removal efficiency plot (similar to Figure 4) for the 200x0-mesh coals in Appendix 6. A good linear correlation of the data, $r \geq 0.98$, is obtained for all of the coals except the Rosebud seam. The organic sulfur removal efficiencies for the Upper Freeport and Imboden seam coals are 1.06 and 1.12 respectively, while for the Colorado and Middle Kittanning seam coals the efficiency is less than one (0.63 and 0.72 respectively). Further consideration of the above data will be made in the discussion of coal rank and its influence on the product.

Coal Size Consist

The bulk of the laboratory experimentation used coal which was ground to pass through a 200-mesh sieve to reduce the possibility of diffusion limitations. The large-scale use of coal of this size is likely to be impracticable due to the energy requirements for grinding. Problems in handling such fine material would also be encountered. Power generating stations, however, typically use coal which is 60 to 70 percent minus 200-mesh, with a top size of approximately 30 to 60 mesh. Appendix 7 contains the size consist of the coarser coals which will be discussed below. Most of these coals were crushed in a hammermill to produce a coal with an approximate top size of 14-mesh and a minimum amount of minus 200-mesh material. A portion of this sample was further pulverized to completely pass through a 200-mesh sieve.

Appendix 8 contains the results of experiments on several coals, comparing the reactivity of two size consists. For the coals in this table and the coals discussed in Appendix 6, there appear to be slight differences in the reactivity of 14x0- and 200x0-mesh samples. The sulfur removal data for the 14x0-mesh coals in Appendix 6 are plotted in Figures 16 through 20, which also show the respective results for the 200x0-mesh samples. The total sulfur reduction is generally less for the coarser coal samples. The pyritic sulfur reduction also follows the same trend; however, in most cases, the pyritic

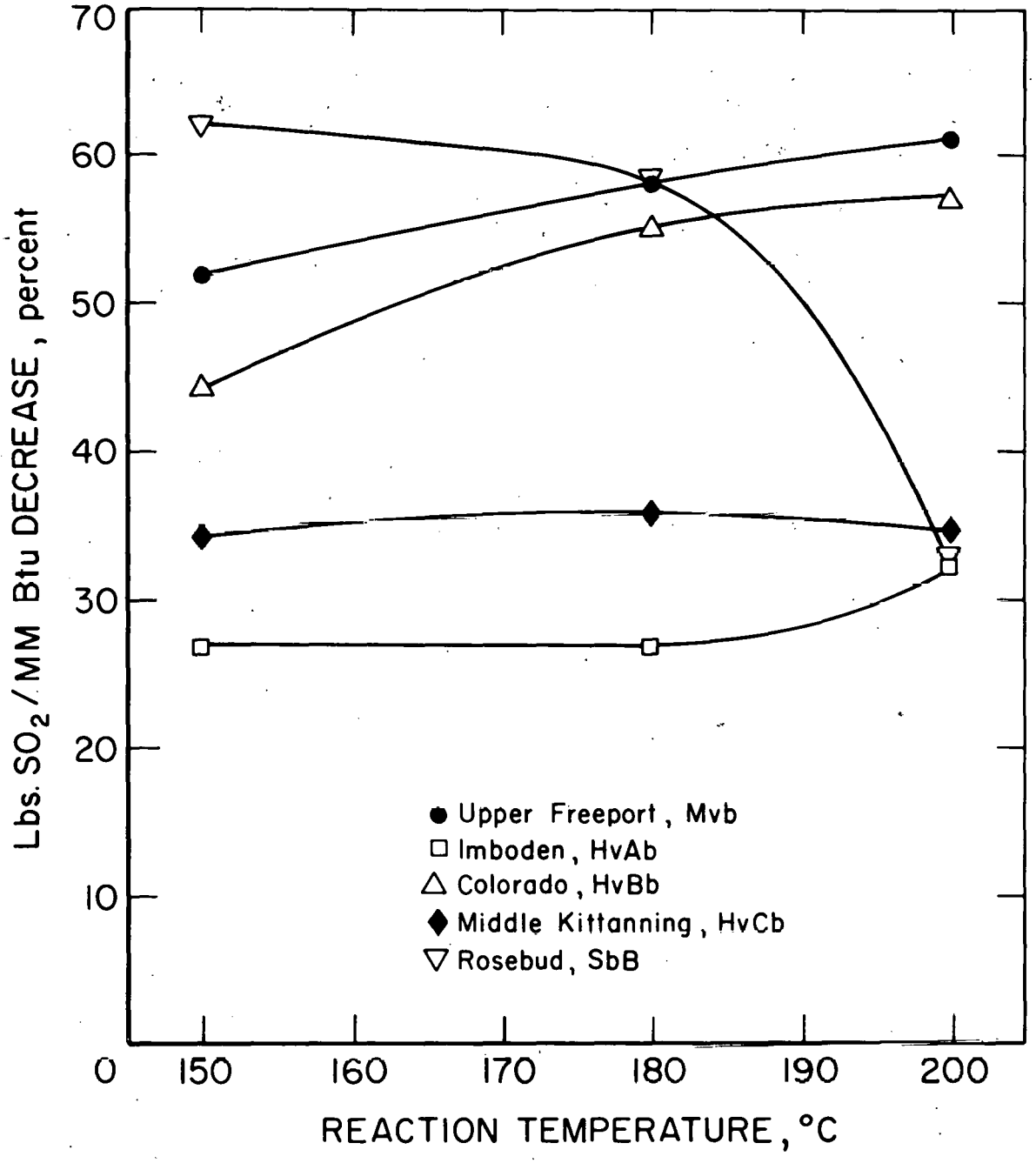

FIGURE 21. EFFECT OF TEMPERATURE ON PRODUCT QUALITY OF SEVERAL COALS, 1 HOUR, 1000 PSIG, 7-8 SCFH AIRFLOW.

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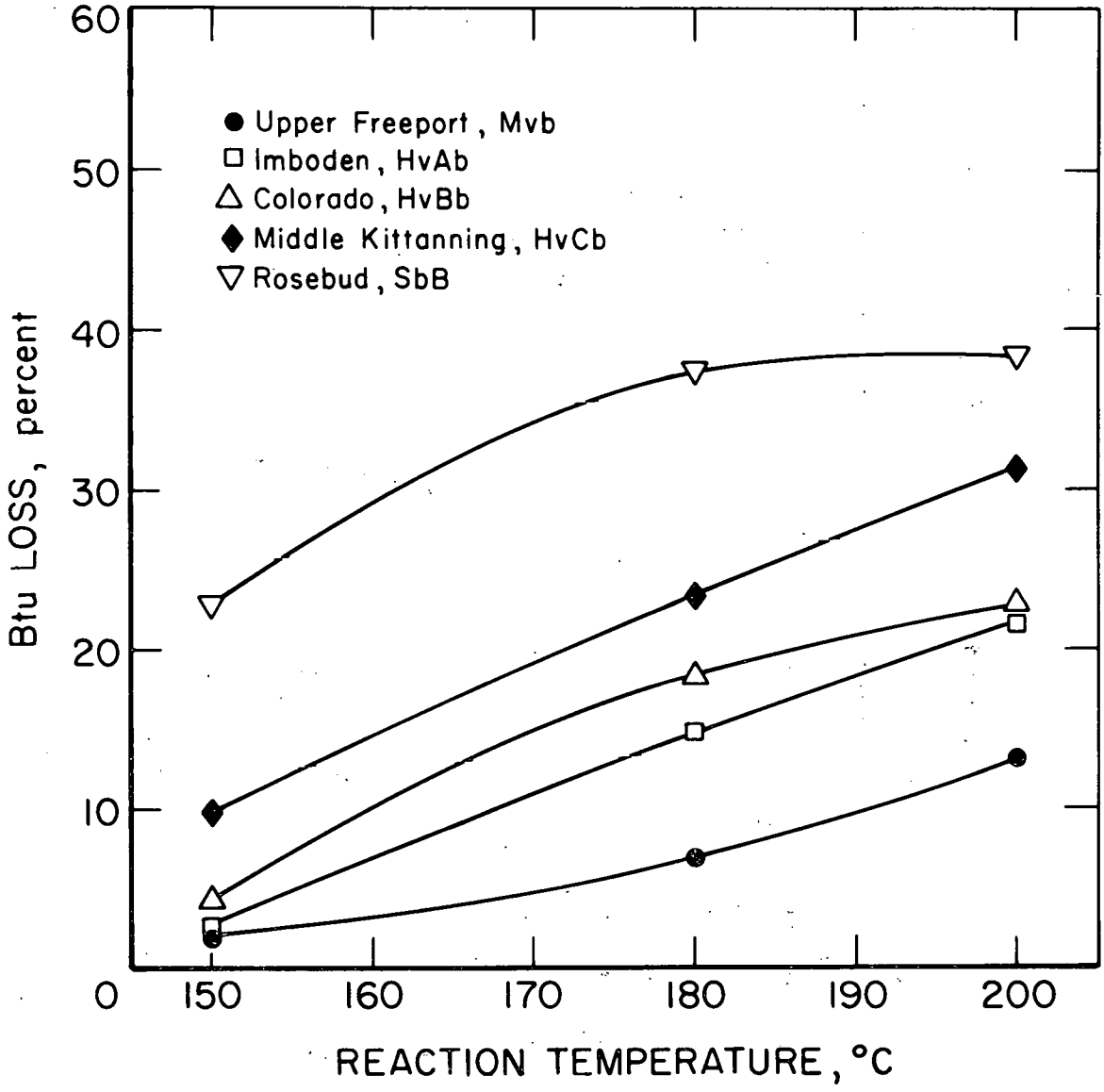

FIGURE 22. EFFECT OF TEMPERATURE ON HEATING VALUE LOSS OF SEVERAL COALS, 1 HOUR, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-79 L-16603

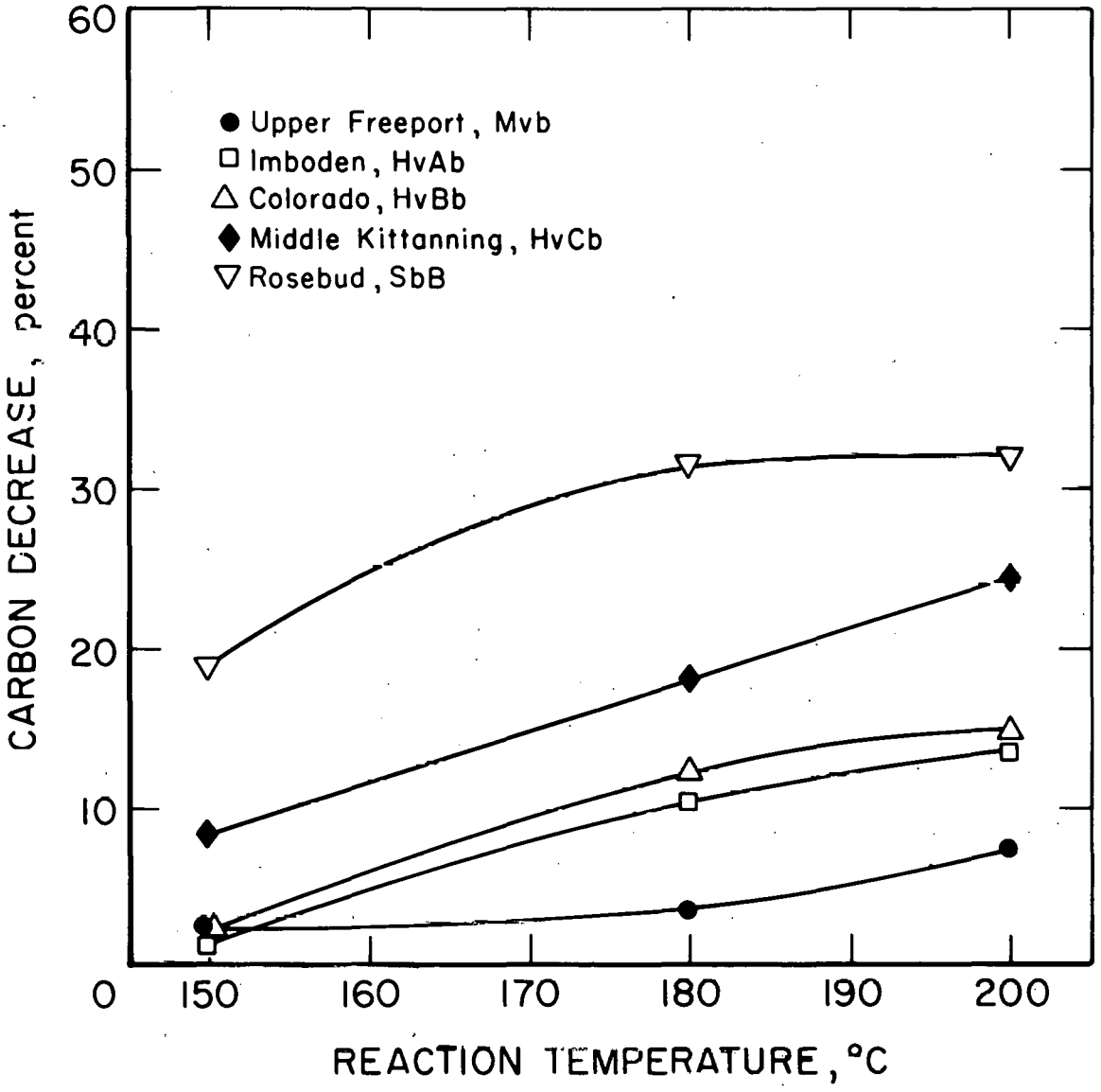

FIGURE 23. EFFECT OF TEMPERATURE ON CARBON LOSS OF SEVERAL COALS, 1 HOUR, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-79 L- 16604

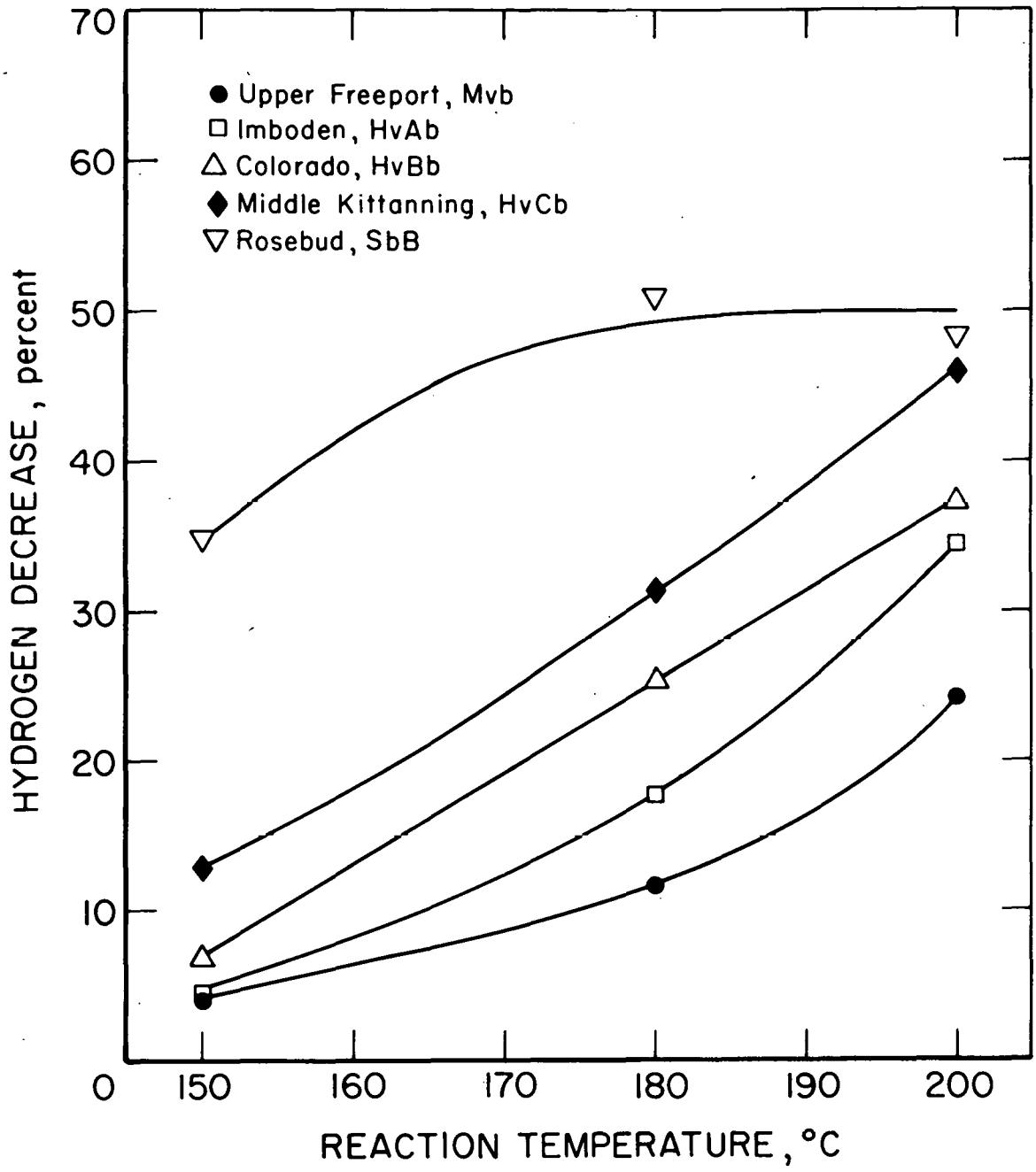

FIGURE 24. EFFECT OF TEMPERATURE ON HYDROGEN LOSS OF SEVERAL COALS, 1 HOUR, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-79 L-16601

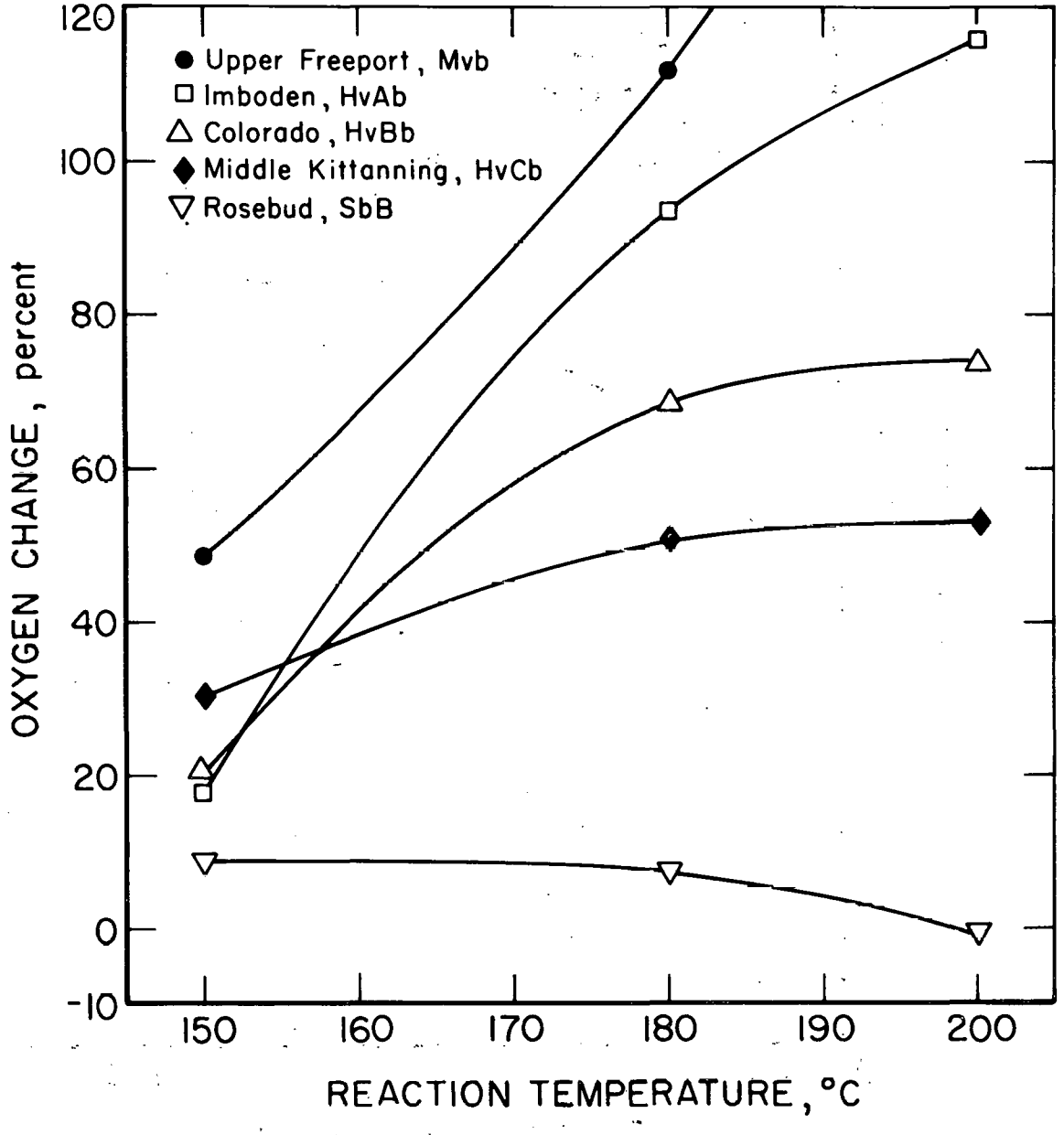

FIGURE 25. EFFECT OF TEMPERATURE ON OXYGEN UPTAKE OF SEVERAL COALS, 1 HOUR, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-79 L-16600

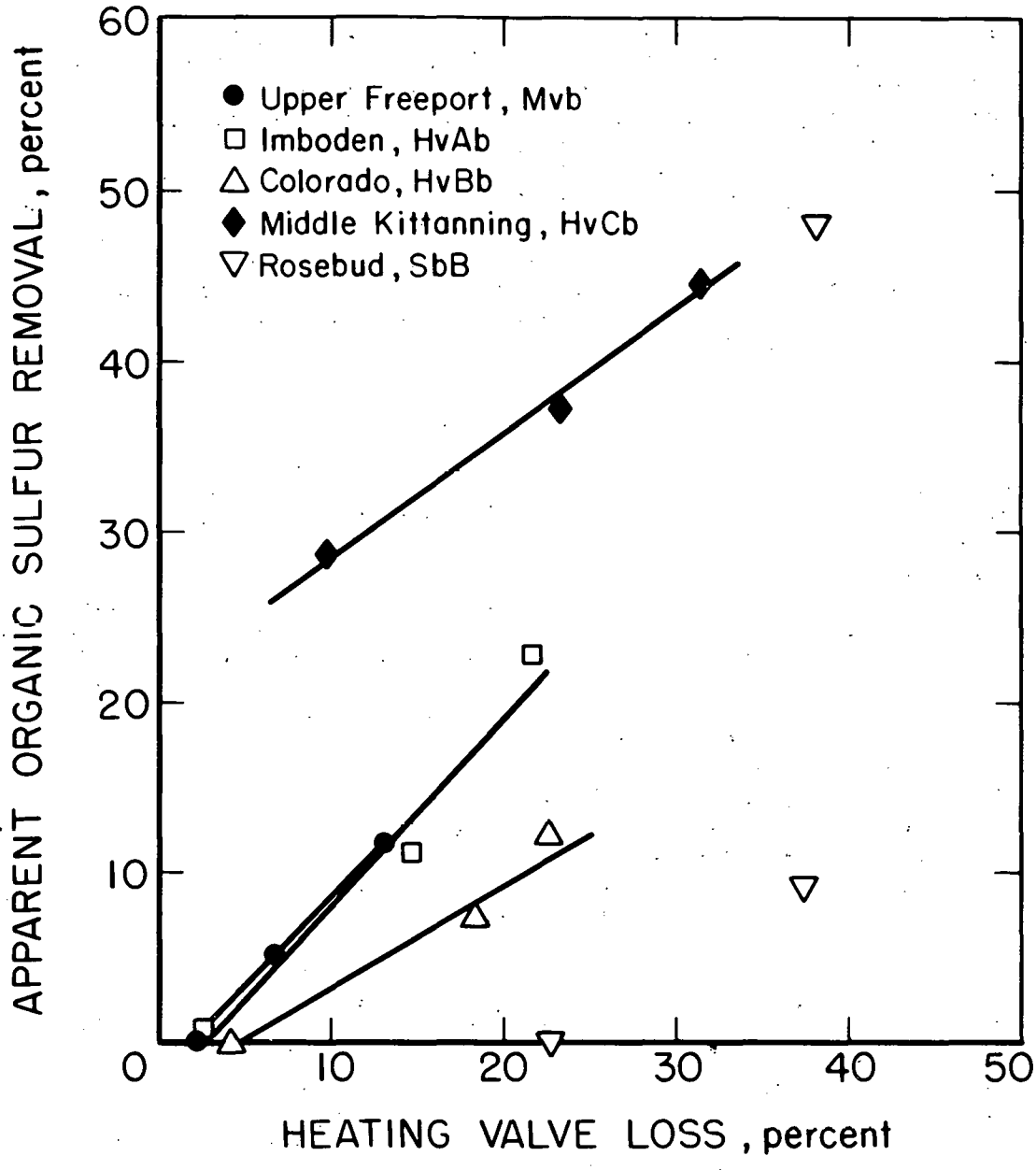

FIGURE 26. ORGANIC SULFUR REMOVAL EFFICIENCY PLOT FOR SEVERAL COALS, 1 HOUR, 1000 PSIG, 7-8 SCFH AIRFLOW.

11-1-79 L-17107

sulfur reduction is essentially complete, with the magnitude of the final results being near the limit of detection. The organic sulfur reduction varies from coal to coal and again represents the inability of the current analytical techniques to accurately determine this quantity; it is illogical to assume that more organic sulfur can be removed from coarser coals while the pyritic sulfur reduction is slightly less. Nevertheless, due to a better heating value recovery, the product quality of several of the coals in Appendices 6 and 8 is similar and most of the 200x0-mesh coals meeting the 1974 NSPS also meet this standard with less crushing. Since the 14x0-mesh samples treated here contain relatively few fines (<200-mesh), the results of treatment of plant grind (∿70 percent-200 mesh) coals would fall somewhere between the results of Appendices 6 and 8 and presumably closer to those for the 200x0-mesh samples.

Coal Rank

The ASTM system for classifying coals according to rank is based upon the degree of metamorphism or progressive alteration in the natural coalification series from lignite to anthracite (34). Structural differences and the resulting relative proportions of functionalities in coals of differing rank would be reflected in the oxidation susceptibility of the coal matrix with respect to air/water oxydesulfurization treatment. Some indication of this is apparent from the data in Appendix 6, especially for the 200x0-mesh samples. Note that the coals in Appendix 6 are listed in order of decreasing rank. The data from Appendix 6 plotted in Figures 16 through 20 show that the magnitude of total sulfur reduction is not related to coal rank, primarily because pyritic sulfur content has no relation to the rank. Other aspects of air/water oxydesulfurization treatment which are related to coal rank are shown in Figures 21 through 25. A negative temperature effect on product quality is observed for the subbituminous coal in Figure 21, in contrast to the other coals. The heating value, carbon, and hydrogen losses due to treatment, shown in Figures 22, 23, and 24, respectively, all have a similar response to coal rank, i.e., the lower rank coals exhibit greater losses, the relative magnitude of which increases with reaction temperature. The higher rank coals also appear to be able to withstand oxidative cleavage better than do the lower rank coals as evidenced in Figure 25. This, as with the carbon and hydrogen trends, is probably a result of the varying functionality of the different coals.

Figure 27 represents an approximation of the dependency of apparent organic sulfur reduction on coal rank. The data are from the 200x0-mesh coals in Appendix 6. The 200°C data have the best fit, with a correlation coefficient (r) of 0.86 from a least-squares fit. The observed trend is perhaps due to relatively more labile sulfur functional groups with respect to air/water oxydesulfurization in lower rank coals. The organic sulfur removal efficiency, as shown in Figure 26, is better for the higher rank coals, with the exception of the Rosebud seam coal. Obviously, more detailed information plus a definitive explanation for the observed increases in apparent organic sulfur after treatment is needed to fully explain these observations.

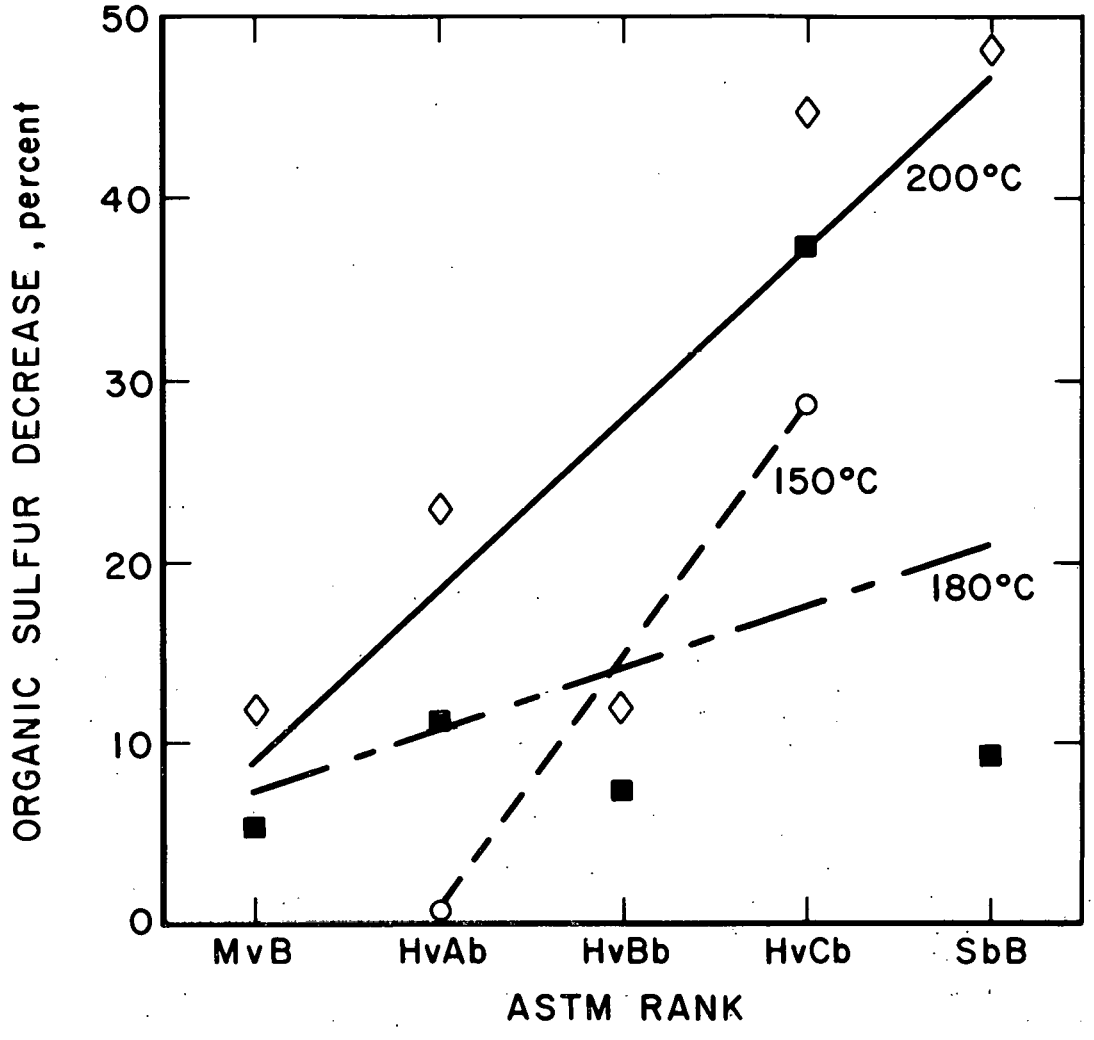

FIGURE 27. CORRELATION OF ORGANIC SULFUR REMOVAL WITH COAL RANK, 1 HOUR, 1000 PSIG, 7-8 SCFH AIRFLOW.

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Residence Time

The residence time is defined as the period of time the reactor is stabilized at a given set of operating conditions. The heating and quenching phases of the experiment are excluded. In general, the sulfur content decreases with time, the pyritic sulfur conversion being complete in a matter of minutes as observed in Figure 2. If thermal precipitation of insoluble sulfur species occurs (Figure 2), sufficient time must be provided to decompose the products formed. In the final analysis, the effect that residence time has on product quality, lbs SO_2/MM Btu, is the primary consideration for determining an optimum treatment time.

Appendix 9 contains a summary of batch mode data on the investigation of treatment time with Minshall seam coal. These experiments, especially the ones at 180°C, were made at various times in the experimental program. The differences in the compositions of untreated coal caused by pyrite oxidation during storage permit only qualitative observations. For this coal the principal concern is the apparent organic sulfur increase, which becomes more severe with increased treatment time. The equilibrium concentration of the species responsible for this anomaly appears to be attained in 30 minutes at 150°C, whereas at 180°C a longer time is necessary to attain the same level.

A clearer indication of the effects of residence time is gained by examining data from the modified mode of operation, which is contained in Appendix 10. The first two sets of data for the Lower and Upper Freeport coal seams show the variations in the product with treatment times up to 1 hour. The sulfur changes for the Lower Freeport coal were presented in Figure 2, to illustrate the evidence for an intermediate species causing the apparent organic sulfur increase. The same observation is evident for the Upper Freeport coal in Figure 28. For these coals at the conditions stated, the organic sulfur anomaly diminishes with longer treatment times and appears to require at least 1 hour to return to normal. This can either be due to actual organic sulfur reduction or to the decomposition of the intermediate formed. The results from the previous discussions concerning temperature and pressure effects indicate that the rate of decomposition of this proposed intermediate increases with reaction temperature and pressure. The pH of the slurry during reaction may also affect the rate of decomposition. Experiments 6W21 and 6W23 in Appendix 10, on the Lower and Upper Freeport seam coals respectively, evidence this supposition with respect to reaction temperature.

Figures 29 and 30 illustrate the changes in the major elemental constituents for the Lower and Upper Freeport seam coals respectively. The corresponding heating value loss and variation in product quality (lbs SO_2/MM Btu) are shown in Figures 31 and 32. For both coals the carbon and hydrogen exhibit a slow, steady decrease as does the heating value reduction. The oxygen content, however, increases at a much faster rate. The product quality steadily improves with time for both coals, primarily due to reduction in the apparent organic sulfur content. Both coals are brought close to compliance with the 1974 NSPS of 1.2 lbs SO_2/MM Btu.

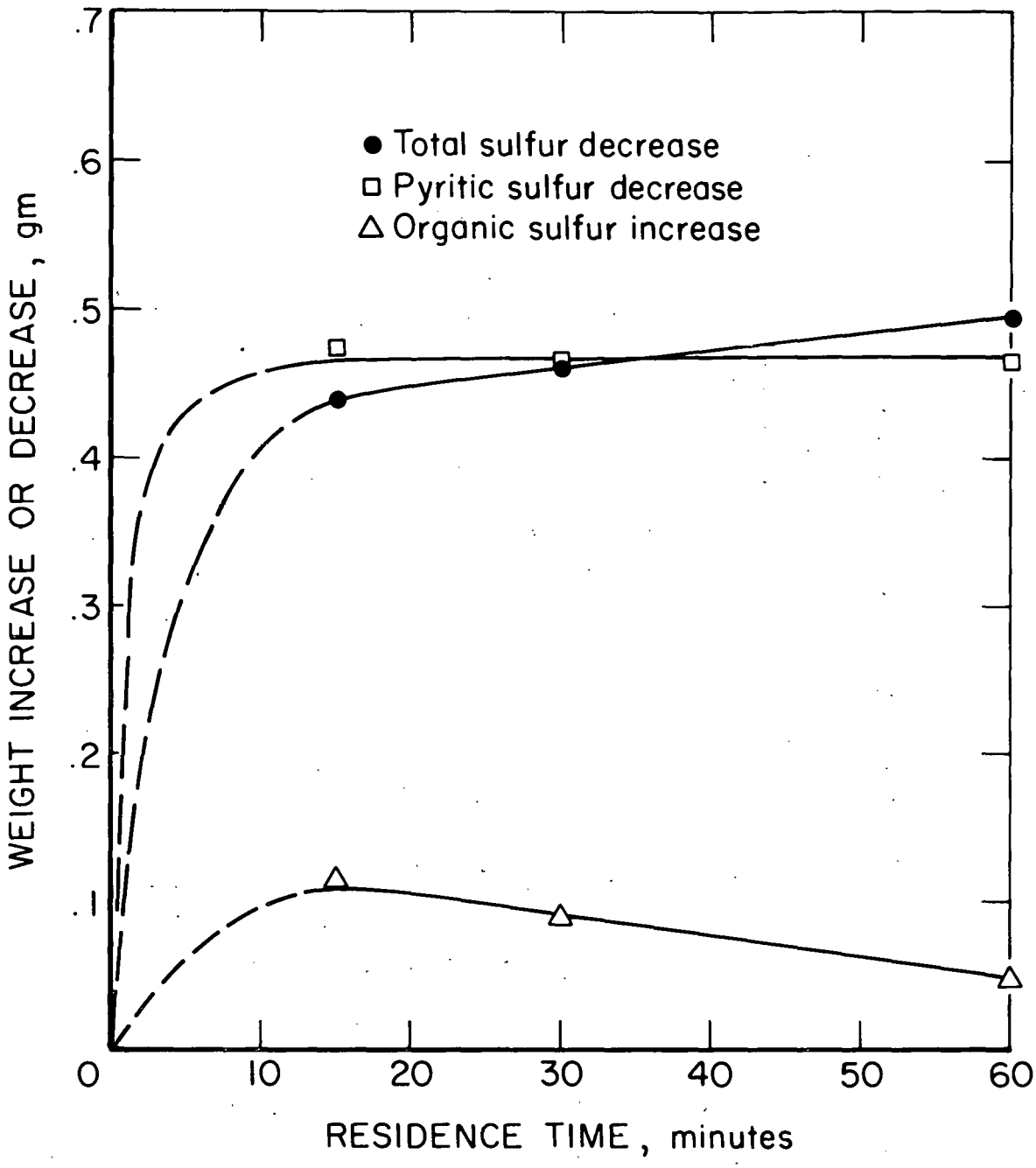


FIGURE 28. EFFECT OF TIME ON DESULFURIZATION OF UPPER FREEPORT MVB COAL, 180° C, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-79 L-16619

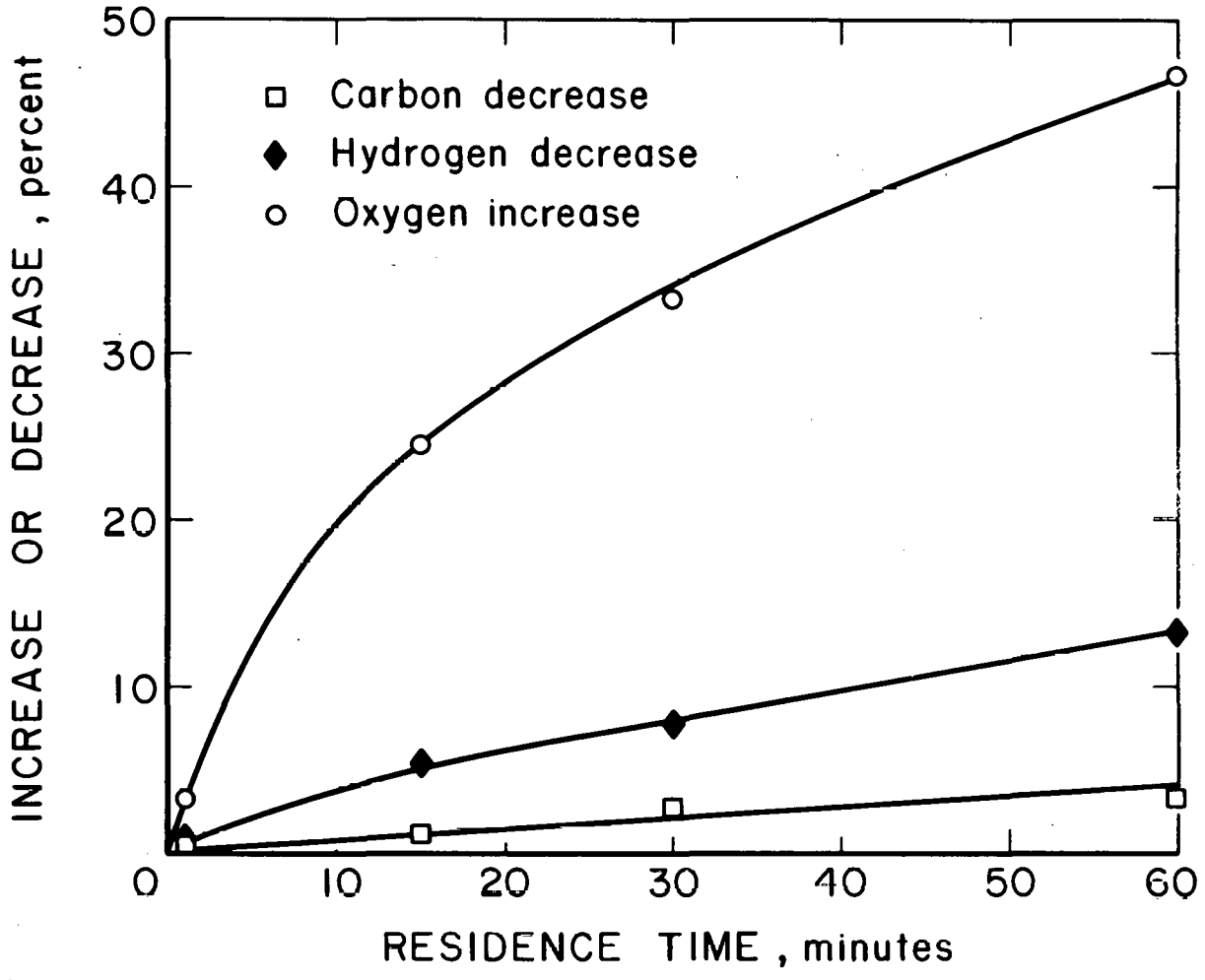


FIGURE 29. EFFECT OF TIME ON CARBON, HYDROGEN, AND OXYGEN OF LOWER FREEPORT HVAB COAL, 180° C, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-79 L-16610

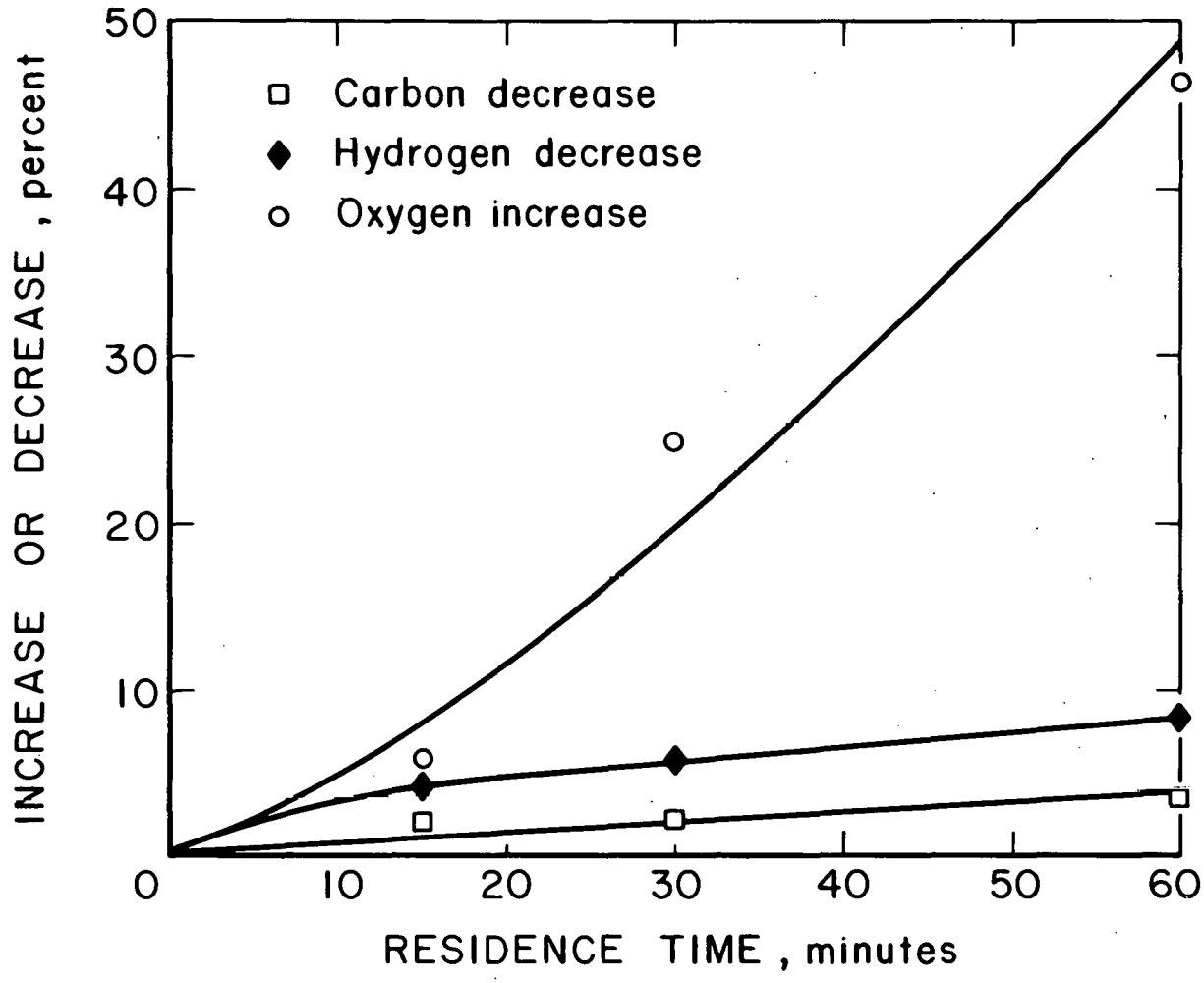


FIGURE 30. EFFECT OF TIME ON CARBON, HYDROGEN, AND OXYGEN OF UPPER FREEPORT MVB COAL, 180° C, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-79 L-16609

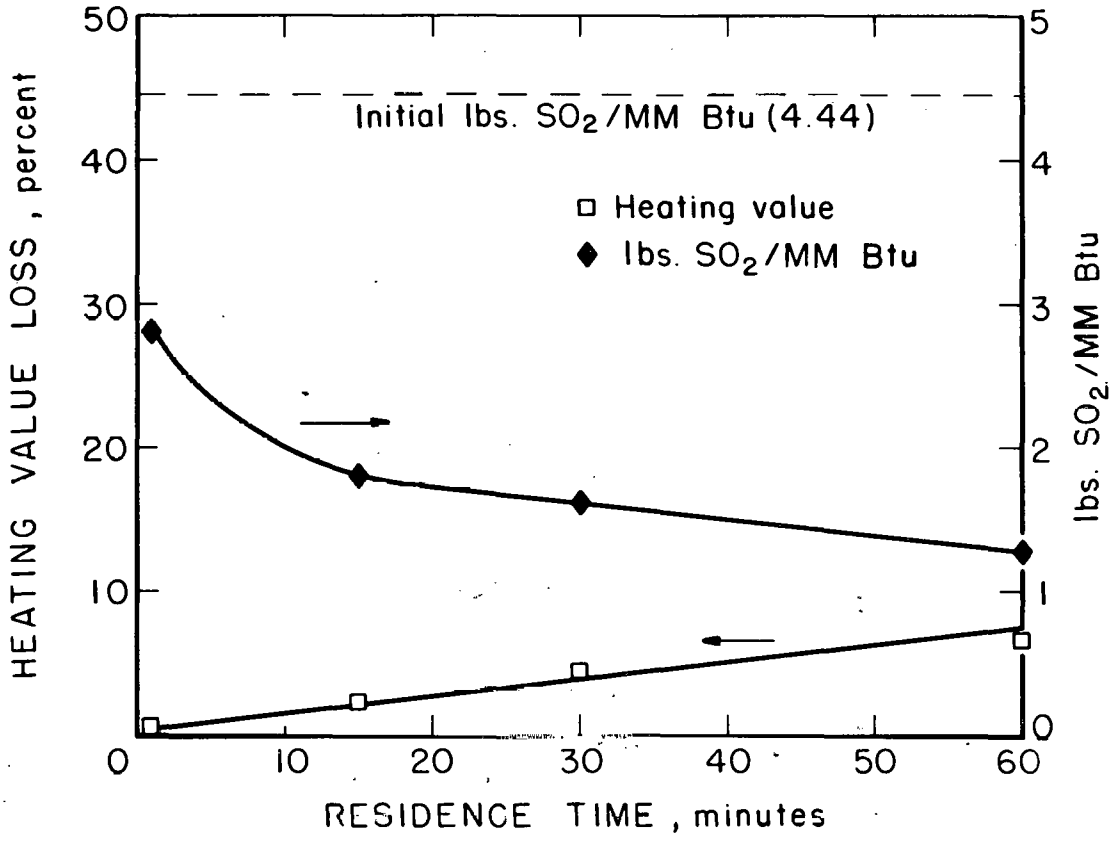


FIGURE 31. EFFECT OF TIME ON HEATING VALUE AND PRODUCT QUALITY OF LOWER FREEPORT HVAB COAL, 180° C, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-80 L-16630

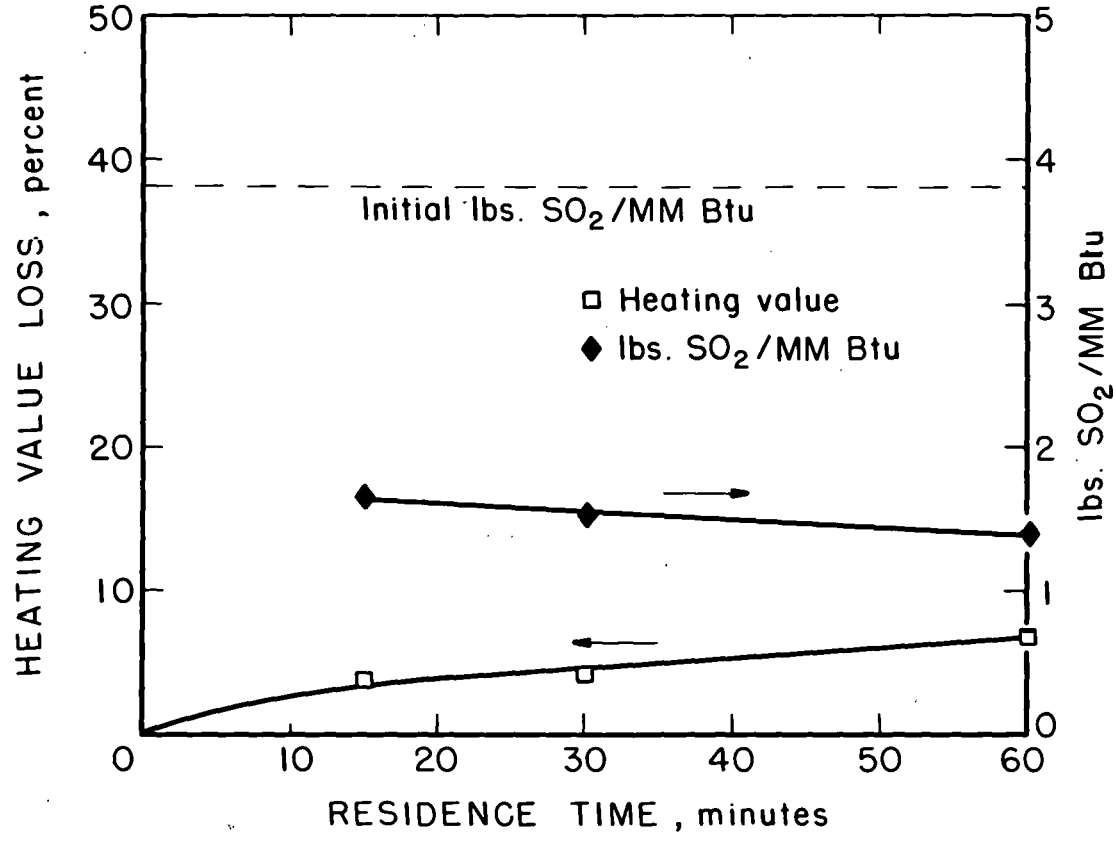


FIGURE 32. EFFECT OF TIME ON HEATING VALUE AND PRODUCT QUALITY OF UPPER FREEPORT MVB COAL, 180° C, 1000 PSIG, 7-8 SCFH AIRFLOW.

3-29-80 L-16631

The remaining data in Appendix 10 illustrate the results obtained by using residence times in excess of 1 hour in the modified mode of operation. The particle size distribution for the Lower Freeport seam coal ground to 14x0-mesh is given in Appendix 7. For the Minshall seam coal, the longer residence time results in a lower lbs SO_2/MM Btu, but at the expense of significantly greater heating value loss. The results for the coarser Lower Freeport coal indicate that a longer residence time at a lower temperature yields a better product due to less heating value loss than a 1-hour treatment at higher reaction temperature.

Air Pressure

In the discussion of results of experiments involving pressure variations, air pressure or, in the case of the modified operation mode, system pressure will be used to describe the experiments. The partial pressure of oxygen is certainly a limiting factor. In the batch mode the initial oxygen partial pressure is approximately 20 percent of the air charged to the reactor. During batch treatment, however, the oxygen partial pressure steadily drops and if sufficient oxygen is not initially present the system may become oxygen starved. Data illustrating oxygen consumption in the batch mode are discussed below. In the modified mode, if sufficient make-up air is added, the oxygen partial pressure is approximately 20 percent of the total system pressure after the steam pressure is accounted for. In most experiments, compressed air or synthetic breathing air cylinders containing between 19 and 23 percent oxygen were used. A cylinder used in some batch mode experiments contained 30.6 percent oxygen. The use of this cylinder is annotated in the text.

In Appendix 1 the importance of sufficient oxygen is first observed by the poor reactivity of experiment 5L37 in which a 400-psig initial air charge was used. The dependence of the air/water oxydesulfurization reaction on oxygen concentration is further illustrated by the data in Appendix 11. Experiments 1W35 and 1W41 indicate that pressures higher than the normal 800 psig initial air charge produce a significantly better product. This appears to be the result of a lower apparent organic sulfur increase. The same is observed for 2W29 and 3W39, which are 30-minute experiments using air containing 30.6 percent oxygen. Again, thermal precipitation of an insoluble sulfur-containing compound is probably responsible for the high apparent organic sulfur contents. It appears, however, that the decomposition of these species is faster at higher oxygen partial pressures. Additional supporting evidence is shown in Figure 33 which represents the variations in sulfur data for experiments 4W29 through 4W43 in Appendix 11. This figure also shows that up to 95 percent of the pyritic sulfur reacts during only a 5-minute hold time at temperature in the batch mode. Since the heating rate for these particular experiments was approximately 3.5°C per minute, the heat-up time was approximately 38 minutes.

Experiment 2W13 in Appendix 11 exemplifies the necessity of adequate oxygen partial pressure. Eight 100-psig batch repressurizations were used to effectively supply the same quantity of oxygen as a single experiment using an 800-psig initial air charge (1W35). The results show only a 62 percent decrease in pyritic sulfur for 2W13 compared to 95 percent for 1W35.

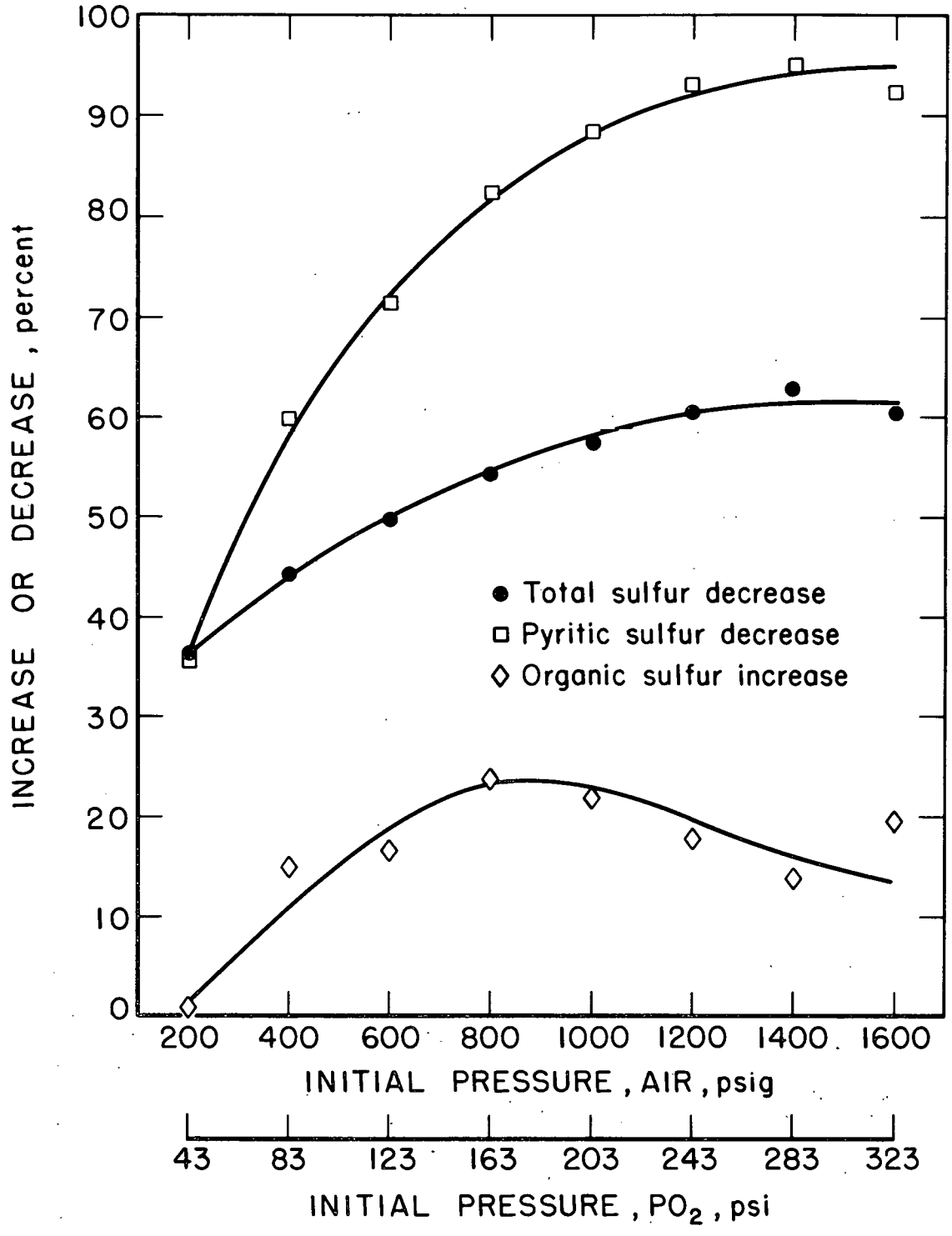


FIGURE 33. EFFECT OF PRESSURE ON DESULFURIZATION ON MINSHALL HvCb COAL, 5 MINUTES, 160° C, BATCH MODE.

3-29-79 L-16618

The above experiments were made prior to modification of the system to permit continuous air flow during treatment. Appendix 12 contains data comparing the batch and modified modes of treatment. These data, summarized in Table 3, show that modified mode treatment results in a comparable or improved product. In general, the modified as compared to the batch mode treatment yields improved sulfur removal but greater loss in heating value, especially at higher temperatures. The gas analysis data in Appendix 12 illustrates the principal disadvantage of the batch mode. The oxygen partial pressure of the residual gas is significantly below the level maintained by the air flow in the modified mode (except in 2W21, in which the cylinder containing 30.6 percent oxygen was used). Experiments 4W95, 5W5, and 7W9 in Appendix 12 indicate that a minimum air flow of approximately 6 SCFH is necessary to maintain the oxygen partial pressure at the theoretical value (114 psi at 25°C for 180°C treatment) for this coal. At these conditions, this is approximately a twenty-fold excess of oxygen for pyrite conversion based on the previously discussed stoichiometry and using 35 grams of a coal containing 4 weight-percent pyritic sulfur.

From an economic standpoint it is desirable to operate the oxydesulfurization reaction at the lowest possible pressure with minimal air throughput. Appendix 13 contains data from modified mode experiments investigating these requirements. The residence time in several of the experiments was increased to 2 hours, since the partial pressure of oxygen could be maintained at a relatively constant level with the flow of air through the reactor. The first series of experiments in Appendix 13 (5W3 through 5W7) indicates that longer residence time at intermediate pressure (5W9) is advantageous in terms of product quality for the Minshall seam coal. The primary reason is the improved apparent organic sulfur reduction at 2 hours. The last experiment on the Minshall seam coal (5W25) demonstrates the need for adequate oxygen pressure even when a faster flow rate and higher reaction temperature are used. The same conclusion is evident from the experiments in Appendix 13 on the Pittsburgh seam coal.

Slurry Concentration and Water Recycle

The results of experiments investigating the effect of stirrer speed on sulfur removal, discussed above, show that gas absorption resistance is potentially significant in the system studied. A stirring speed of 900 to 1000 RPM is necessary to maintain the dissolved oxygen content at nearly the saturation value for a 26 weight-percent coal slurry. The first set of data in Appendix 14 summarizes experiments in which the slurry concentration was increased from the normal 26 weight-percent to beyond the point where oxygen starvation occurs in the bulk liquid, resulting in slower sulfur removal. These data, as shown in Figure 34, indicate a severe decrease in reactivity between a 33 and 41 weight-percent coal slurry. Note also the data for experiment 2W31 in which no water was used. The heating value loss is much greater, obviously due to the coal being "burned" in the absence of water.

The data plotted in Figure 34 indicate that dilution of the coal slurry improves product quality. This is also apparent if the data for the Upper Freeport seam coal in Appendix 14 are compared to the data for experiment 6W15

Table 3. Comparison of Batch and Modified Modes of Treatment

COAL SEAM (STATE)	EXPERIMENT NO.	TEMP. (°C)	MODE[1]	PERCENT CHANGE			LBS. SO_2 / mm BTU
				TOTAL S	ORGANIC S	BTU	
MINSHALL (IN)	1W35	150	B	−63	+41	−10	4.09
	5W55	150	M	−65	+32	−4	4.10
	5W51	180	B	−66	+22	−8	4.13
	4W95	180	M	−75	−11	−17	3.50
Pittsburgh (WVA)	2W21	150	B	−37	+20	−6	3.84
	5W57	150	M	−41	+3	−6	3.62
	5W53	180	B	−47	−8	−10	3.43
	4W99	180	M	−50	−21	−16	3.41

1. B = Batch, M = Modified

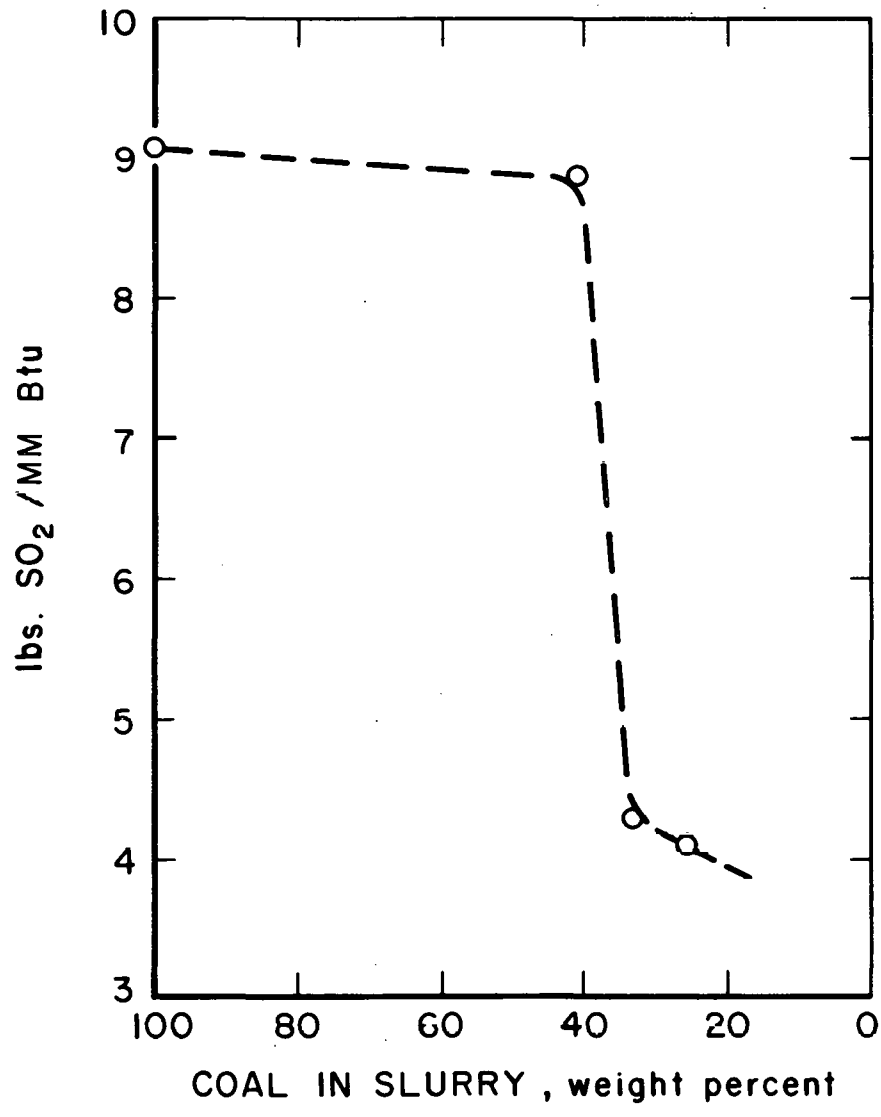
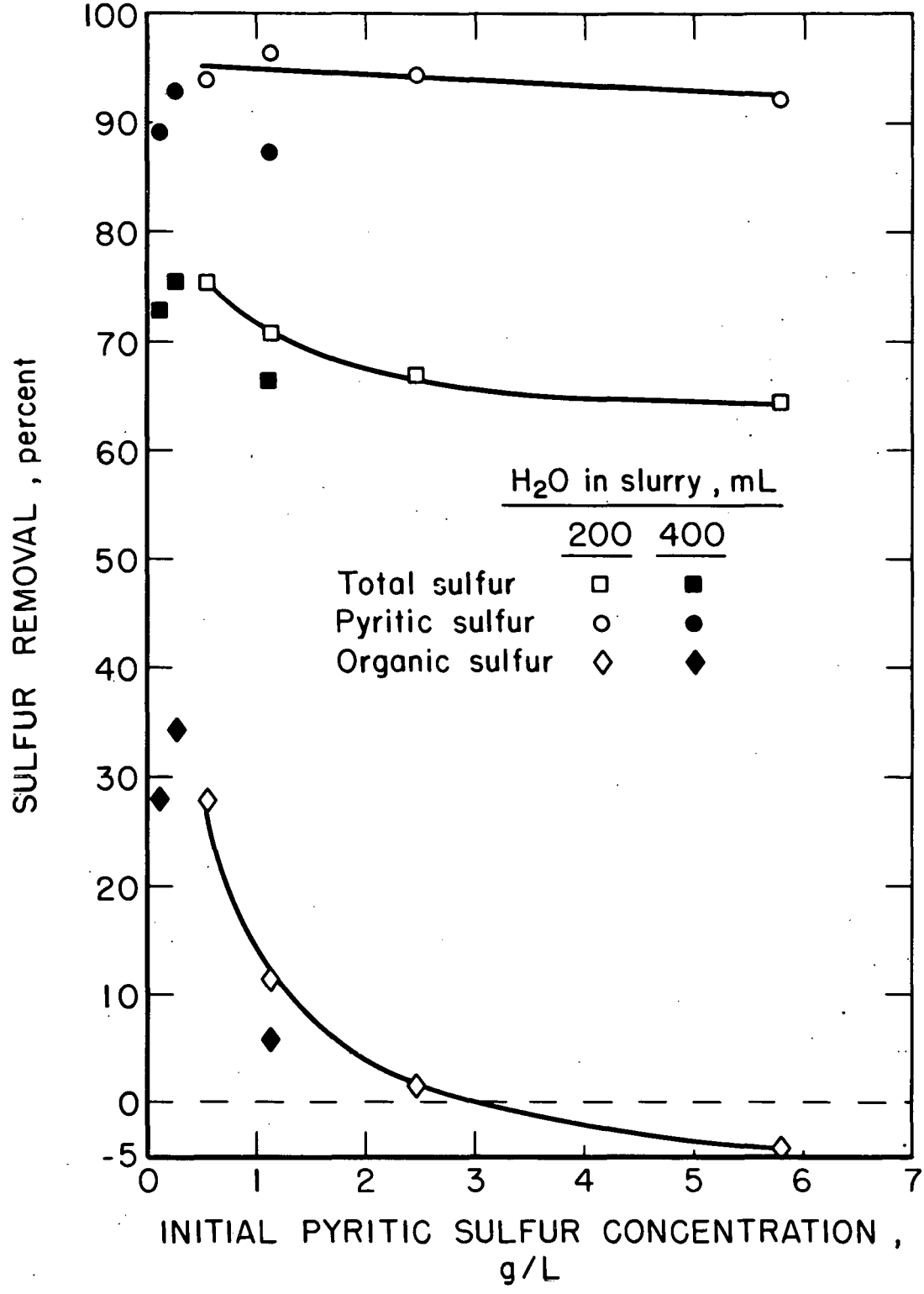


FIGURE 34. EFFECT OF SLURRY CONCENTRATION ON PRODUCT QUALITY OF MINSHALL HvCB COAL, 1 HOUR, 150° C, 800-1000 PSIG INITIAL AIRCHARGE.

3-29-80 L-16633A



IGURE 35. EFFECT OF INITIAL PYRITIC SULFUR CONCENTRATION IN THE SLURRY ON DESULFURIZATION OF MINSHALL HVCB COAL, 1 HOUR, 150° C, 1000 PSIG, 7-8 SCFH AIRFLOW.

8-21-79 L-16945

in Appendix 10. The product quality of 6W69, in which an 8 weight-percent coal slurry was used, is 1.24 lbs SO_2/MM Btu, whereas that of the 26 weight-percent slurry is 1.38. The difference is due to less heating value loss and a reduction in the apparent organic sulfur for the more dilute slurry, as compared to an apparent increase in 6W15. If thermal precipitation of insoluble sulfur-containing compounds is causing the anomalous increase in organic sulfur, it can therefore be avoided by using enough water to keep the pH of the slurry above the acidity limit for such precipitation.

The pH of the coal slurry is primarily determined by the quantity of pyritic sulfur solubilized during treatment. A series of experiments was therefore made to investigate the effect of pyritic sulfur concentration on sulfur removed, in particular organic sulfur reduction. The data are contained in Appendix 14, experiments 7W85 through 7W99. Indiana Minshall seam coal containing 1.71 and 2.00 weight-percent pyritic and organic sulfur respectively was used to prepare the various slurries. The weight-percent of coal in the slurries ranged from 26 to 0.8. The sulfur removal data are plotted in Figures 35 and 36. As indicated in the graphs, the amount of water had to be increased in the more dilute preparations to permit sufficient sample for analysis after treatment. A slight decrease in reactivity is observed for the larger volume (compare 7W89 and 7W99), however, the general trends in the data are similar. It is evident from these data that the apparent organic sulfur removal is indeed sensitive to the initial pyritic sulfur concentration. The logarithmic plot in Figure 36 indicates a maximum organic sulfur reduction for the Indiana Minshall seam coal of 30 to 35 percent under the conditions stated in Appendix 14.

Figure 37 depicts the relationship of the apparent organic sulfur decrease to the pH of the product slurry, measured after treatment, for the above experiments. The curved line indicates maximum apparent organic sulfur reduction occurring above pH 1.5 to 1.6. This same relationship is observed in the 150°C treatment of the coals in Appendix 6 (excluding the atypical Rosebud seam coal). Therefore, if thermal precipitation of insoluble sulfur-containing compounds is causing the anomalous increase in organic sulfur, it can be avoided by using enough water to keep the pH of the slurry above the acidity limit for precipitation.

The last series of experiments in Appendix 14 on the Pittsburgh seam coal summarizes the effects of slurry water recycle. The influence on the product quality is shown in Figure 38. The overall effect, shown by a least squares fit of the data, is a slight decrease in product quality as the slurry water is recycled. From examination of Appendix 14 this effect appears to be primarily due to decreasing organic sulfur reduction as the slurry water is reused.

Summary of Parametric Studies

The preceding parametric studies show that the efficiency of sulfur removal and the distribution of reaction products are primarily dependent upon the following variables; reaction temperature, treatment time, oxygen partial pressure, and slurry concentration. Obviously, the oxygen partial pressure must be sufficient to permit saturation of the desired reaction

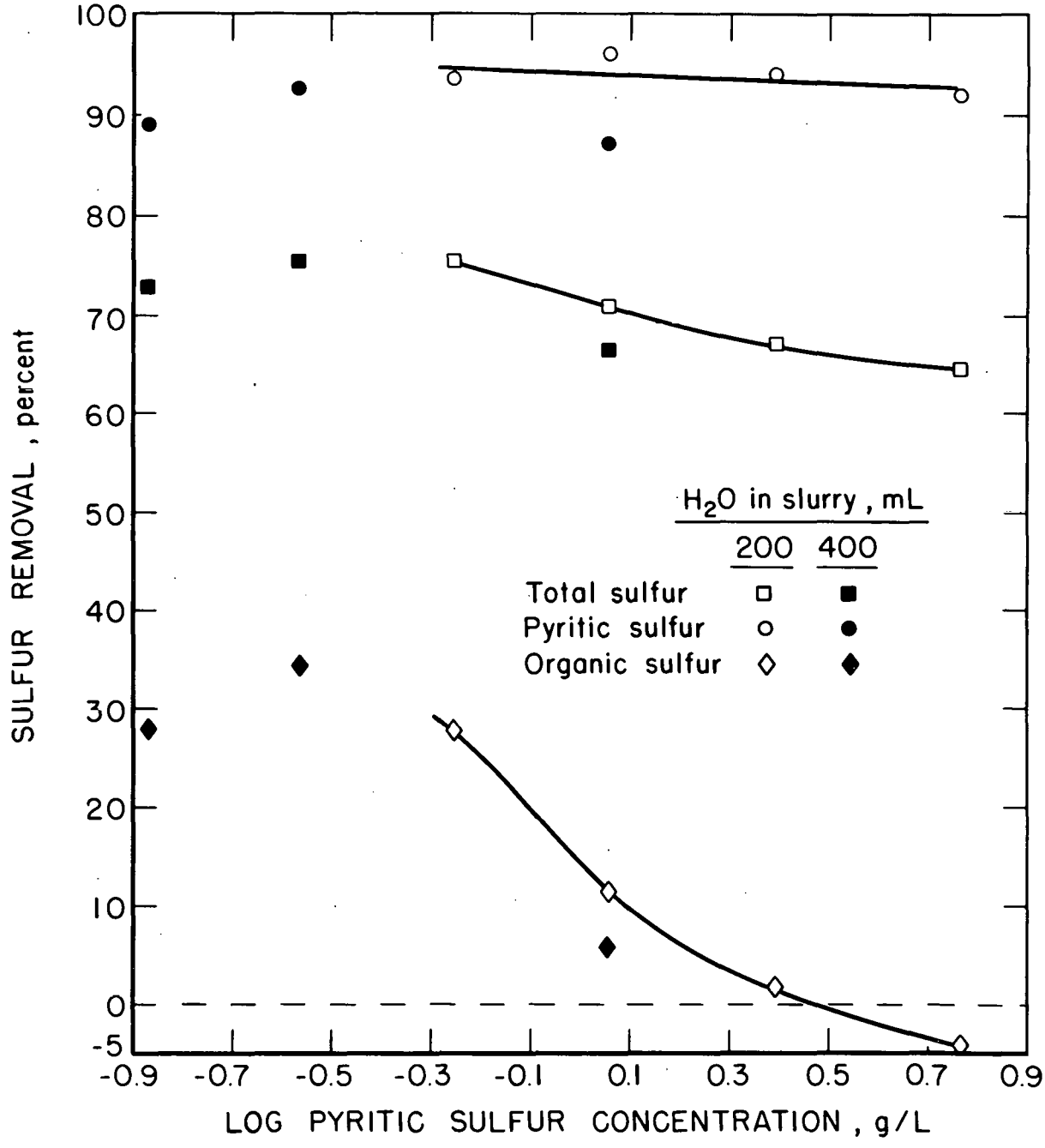


FIGURE 36. RELATIONSHIP OF THE LOG PYRITIC SULFUR CONCENTRATION IN THE SLURRY ON DESULFURIZATION OF MINSHALL HVCB COAL, 1 HOUR, 150° C, 1000 PSIG, 7-8 SCFH AIRFLOW.

8-21-79 L-16946

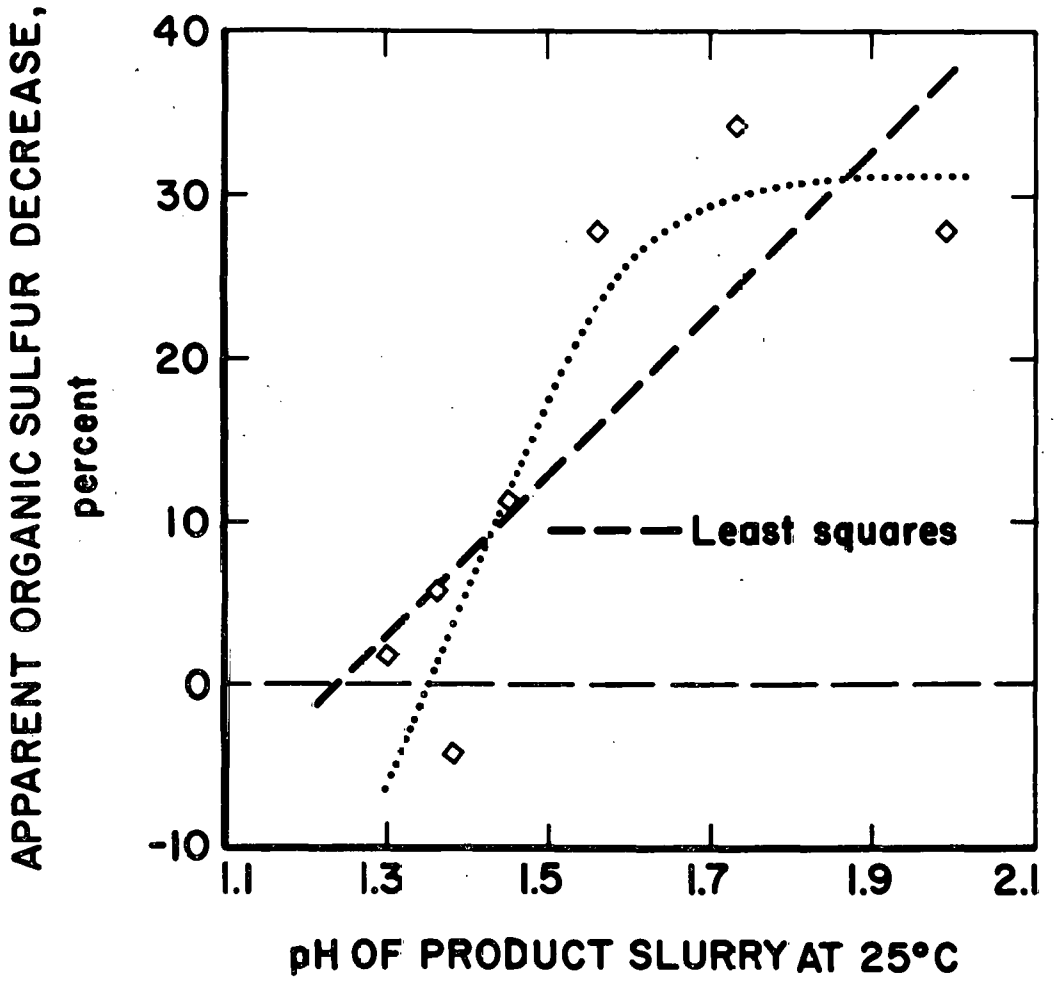
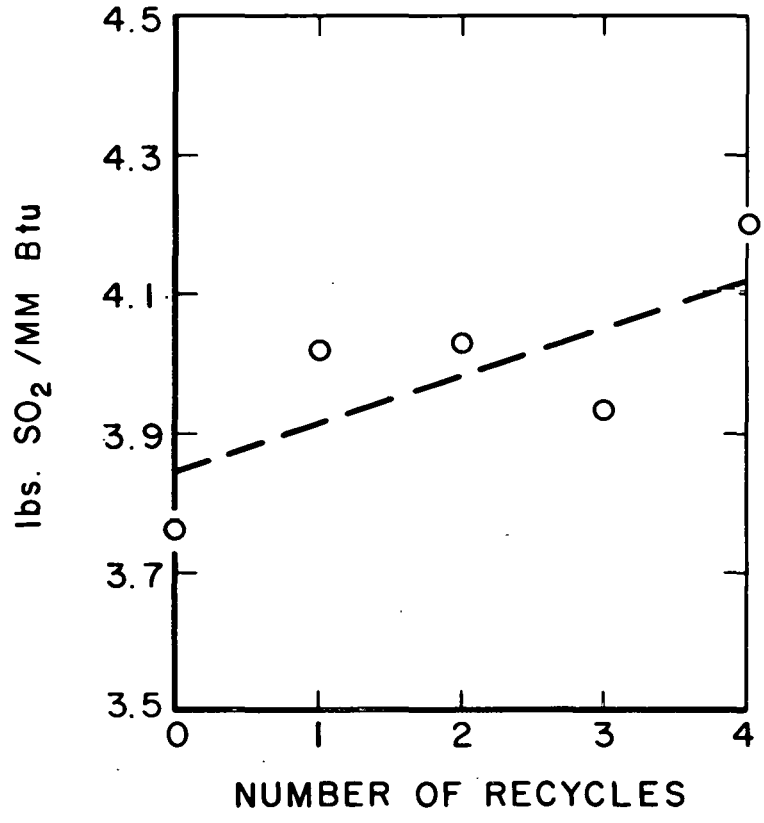


FIGURE 37. COMPARISON OF ORGANIC SULFUR REMOVAL TO THE pH OF THE PRODUCT SLURRY FOR TREATMENT OF MINSHALL HvCb COAL, 1 HOUR, 150° C, 1000 PSIG, 7-8 SCFH AIRFLOW.

10-16-79 L-16066

FIGURE 38. EFFECT OF SLURRY WATER RECYCLE ON PRODUCT QUALITY OF PITTSBURGH HVAB COAL, 1 HOUR, 150° C, 800 PSIG INITIAL AIRCHARGE, BATCH MODE.



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sites. This appears to be attained in our system by maintaining a system pressure of 1000 psig in the temperature range of 150 to 200°C. An air flow through the reactor of 6 SCFH is adequate for this purpose. The more extensively investigated parameters of reaction temperature and residence time show that the sulfur removal generally increases with reaction temperature with the pyritic sulfur removal essentially complete in 15 minutes and the organic sulfur removal requiring longer times and higher temperatures.

The formation of sulfur-containing jarosite-like species with unusual solubility properties is possible in our system and appears to occur if the solution conditions are favorable. The observed result is an increase above pretreatment levels in the apparent organic sulfur content, and in some instances in the pyritic sulfur content, of the product. Extended treatment time appears to solubilize the precipitates formed during the reaction, however, the best strategy is to prevent the occurrence of this phenomenon by maintaining the slurry pH above the limit for precipitation. At 150°C the acidity limit is a pH of 1.5 to 1.6 (measured after treatment at 25°C), however, at higher reaction temperatures the acidity limit occurs at a lower pH. The slurry acidity expected after treatment can be estimated from the pyritic sulfur concentration in the slurry prior to treatment. Sufficient water is used in the initial slurry to adequately dilute the sulfuric acid formed during treatment.

The optimum values of reaction temperature and residence time are influenced by the susceptibility of the particular coal used to oxidative degradation. This susceptibility can be correlated to coal rank. Higher rank coals yield a better product, in terms of lbs SO_2/MM Btu, at more severe treatment conditions than the lower rank coals which exhibit greater heating value loss at similar conditions. Therefore, at this time specific operating conditions for a coal can only be accurately determined by experimentation.

FRACTIONAL FACTORIAL EXPERIMENT

A fractional factorial experiment was conducted to observe simultaneously the effects of reaction temperature, residence time, and oxygen partial pressure. The previously discussed parametric studies assessed the individual effects of these variables. The fractional factorial experiment was designed not only to further investigate these parameters but also to highlight important interactions between them. The coal used in this series is a Lower Freeport seam, high-volatile A bituminous rank coal containing 2.39 percent total sulfur, of which 1.67 percent is pyritic sulfur and 0.66 percent is organic. The results of a particle size test on a riffled sample of this coal is given in Appendix 15. All of the samples used in this program were riffled to insure homogeneity.

The design of the program involves a series of data points taken on the exterior and interior surfaces of a three-dimensional spherical shell which has its origin at the center of the region of interest. This region of interest is a three-dimensional cube with sides delimited by the upper and lower bounds associated with three factors: time, temperature, and oxygen partial pressure. The interior surfaces of the spherical shell are inscribed exactly within this cuboidal region of interest. Figure 39 represents the three-dimensional spatial

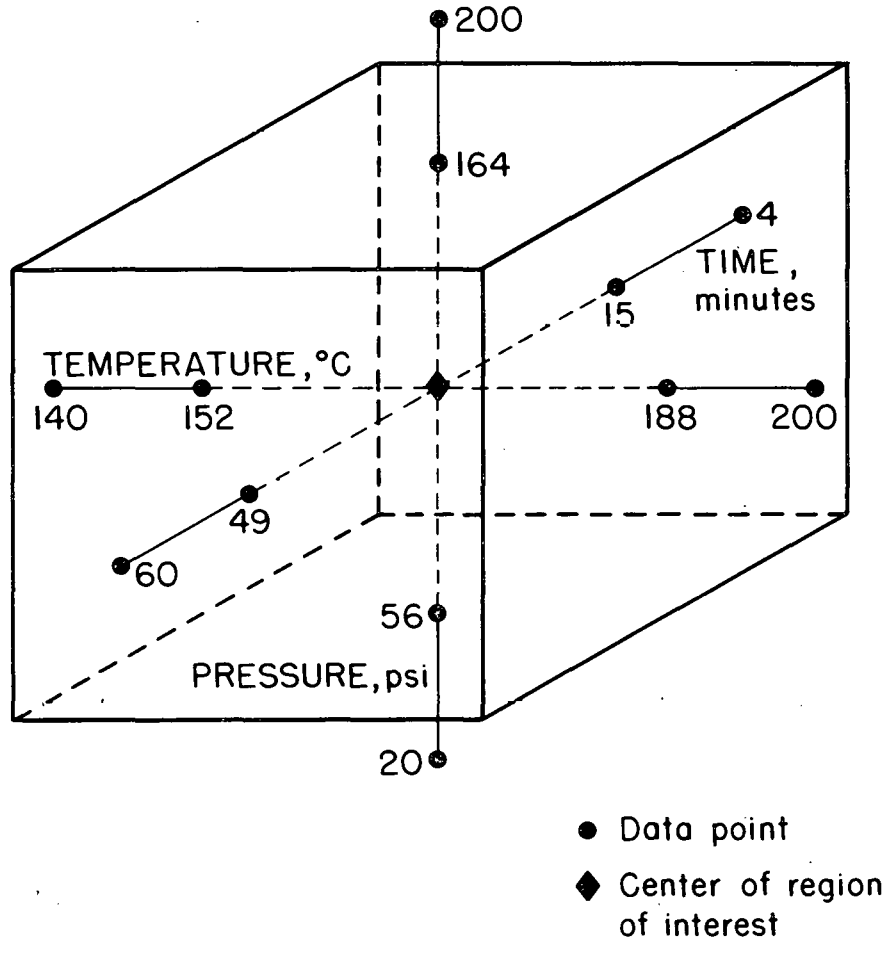

FIGURE 39. SPATIAL REPRESENTATION OF FRACTIONAL FACTORIAL DATA POINTS.

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arrangement of the data points. The large dots represent the location of the individual experiments, and the large dot at the center of the region of interest is the location in which a set of six replicate experiments was performed. The radius of the interior surface of the spherical shell is the distance from the midpoint to the end of an axis, or the limit of a factor, while the radius of the exterior surface is the distance from the midpoint to the experiments located in the corners of the cube shown.

Appendix 16 gives a complete summary of the data for the fractional factorial program. The untreated analysis and the variable settings for each experiment are also included. The order of the experiments in Appendix 16 form the sequence in which the experiments were performed, except for the last three replicate experiments which were made at the end of the program. This sequence is based on the pressure, starting with the highest total system pressure, to facilitate the use of the same air cylinders for the entire series. The reaction temperature was held to within ±2°C and to within ±1°C after the initial stabilization period which generally lasted 10 to 15 minutes. The only experiment in which this does not apply is 7W67, which is the lowest partial pressure investigated. In this case, the temperature was hard to control when air was added at 170°C, since the temperature dropped approximately 4°C after air addition. Upon air addition, the remaining experiments all exhibited some degree of exothermicity, which is easier to control by using the internal cooling coil to remove excess heat.

The work-up of these experiments is the same as previously described, except that no soxhlet extraction followed the 1-liter washing. The low sulfate levels shown in Appendix 16 demonstrate that for this coal, the 1-liter wash with distilled water is sufficient to effectively remove the acid product of the reaction.

A regression analysis computer program using the least squares criterion was modified to fit the factorial experiment data to second order polynomial equations and calculate the corresponding statistics. Any third order interactions are assumed to produce negligible differences in the reaction products. The general form of the polynomial is shown below:

$$Y = a_1 + a_2P + a_3T + a_4t + a_5P^2 + a_6PT + a_7Pt + a_8T^2 + a_9Tt + a_{10}t^2 \qquad (5)$$

where:

Y = dependent variable of interest

a_1, a_2,...a_{10} = regression coefficients

P = oxygen partial pressure (psi)

T = reaction temperature (°C)

t = reaction duration (minutes)

A summary of the statistical results and results of the regression analyses for several dependent variables are given in Table 4. As shown, the regression

analysis also can be used to search for and eliminate insignificant terms to produce the best data fit. The coefficient of multiple determination (r^2) indicates the percentage of the variability explained by the generated equation. If r^2 is less than 0.8, the experimental series and operational procedures should be re-evaluated to determine whether an unexplained factor is obscuring the results. The absolute correlation coefficient (r) indicates how well the data points correspond to the regression curve. A value near 1 indicates high correlation. The standard error of estimate represents the standard deviation expressing the uncertainty of the equation throughout the region enclosed by the experimental observation points. This uncertainty increases everywhere outside this region and is greatest at the regions where all the factor settings are at their upper or lower limits. The F-ratio test for lack of fit for the replicate experiments shows the degree of inability of the equation to accurately reproduce the measured experimental data. The lack of fit F-ratio computed for a good experiment should be less than the F-ratio tabulated, which is the maximum F-ratio, with 95 percent confidence, indicating the results can be explained by experimental error alone (24). The statistical results in Table 4 generally show that the regression equations adequately represent the actual experimental data. The sulfur, pyritic sulfur, oxygen, heating value, and lbs SO_2/MM Btu data in particular exhibit good correlation.

The results of the polynomial equations were used to prepare response surface contour maps for the characteristics in Table 4. Table 5 is the key to letters used in the various plots. As these plots are interpreted, it must be kept in mind that the statistical analysis applies only to the region of interest. Outside of this region the uncertainty increases and is not predictable. The plots are also edited slightly to remove any illogical results produced by the limitations of the computer program. This generally occurs as the extremes of one or more of the independent variables are approached.

Figures 40A through 40E are the complete set of contour maps for the lbs SO_2/MM Btu data. Each plot shows the variations of the data with reaction temperature and residence time at a specific pressure. The variations resulting from reaction pressure are apparent if the plots are overlaid to form a three-dimensional contour surface. It is apparent that by increasing the pressure, temperature and time, the product quality improves until a certain point is reached where increased time causes a slight decrease in the lbs SO_2/MM Btu. In Figure 40A this appears to be at about 50 minutes for this particular coal. Also, at the higher pressures an increase in the reaction temperature above 190°C has little or no effect on product quality. From the data, no significant advantage is apparent in using pressures greater than 164 psi O_2. The results at 110 psi O_2 show that this pressure may also be sufficient if higher times and temperatures are used. Below 110 psi O_2 the product quality is severely decreased.

The statistical analysis of the lbs SO_2/MM Btu results, part of which is contained in Table 4, show that the interaction terms in Equation 5 have a minor influence in correlation of the data. In fact, the three first-order terms, a_2P, a_3T, a_4t, alone account for 88 percent of the variability in the results. Including the squared terms, a_5P^2, a_8T^2, $a_{10}t^2$, the variability increases to 96 percent. The equation used to prepare Figures 40A through 40E includes only the a_7Pt interaction term, which results in explanation of 97 percent of the variability, which is only a 1 percent improvement.

Table 4. Statistical Summary of Fractional Factorial Results

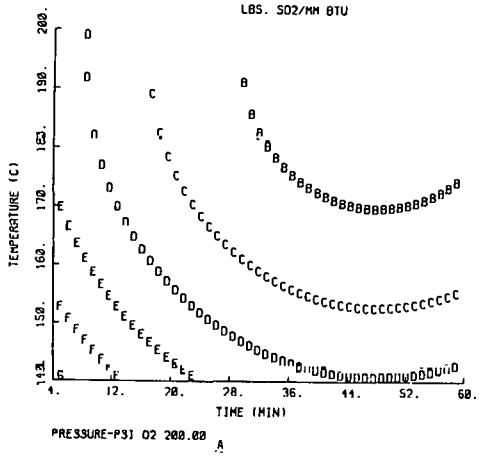
CHARACTERISTIC (Y)	VARIABLES[1] ELIMINATED	r^2[2]	r[3]	STANDARD ERROR OF ESTIMATE	F–RATIO, LACK OF FIT (0.95 Level)	
					COMPUTED	TABULATED
1) Sulfur Decrease, %	a_9Tt	0.972	0.986	3.257	3.27	4.95
2) Pyritic Sulfur Decrease, %	a_6PT, a_8T^2, a_9Tt	0.951	0.975	6.451	4.19	4.82
3) Organic Sulfur Increase, %	a_8T^2	0.834	0.913	7.880	4.86	4.95
4) Carbon Decrease, %	$a_{10}t^2$, a_5P2	0.881	0.939	4.224×10^{-1}	1.67	4.88
5) Hydrogen Decrease, %	$a_{10}t^2$	0.859	0.927	2.027	1.92	4.95
6) Oxygen Increase, %	—	0.969	0.985	9.920	2.59	5.05
7) Heating Value Decrease, %	—	0.964	0.982	5.624×10^{-1}	4.97	5.05
8) Lbs. SO_2/MM BTU	a_6PT, a_9Tt	0.968	0.984	6.258×10^{-2}	3.06	4.88

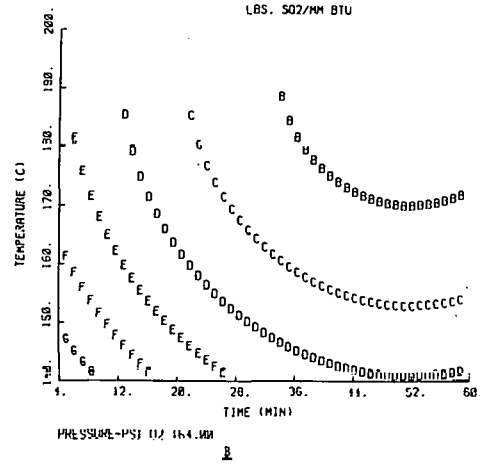
1. In order of elimination, refer to equation 5.
2. Coefficient of multiple determination.
3. Absolute correlation coefficient.

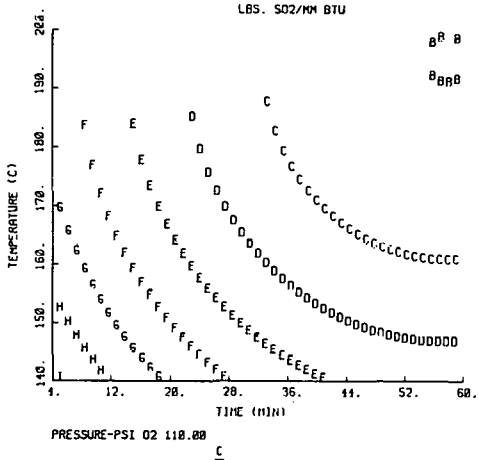
Table 5. Key to Fractional Factorial Contour Plots

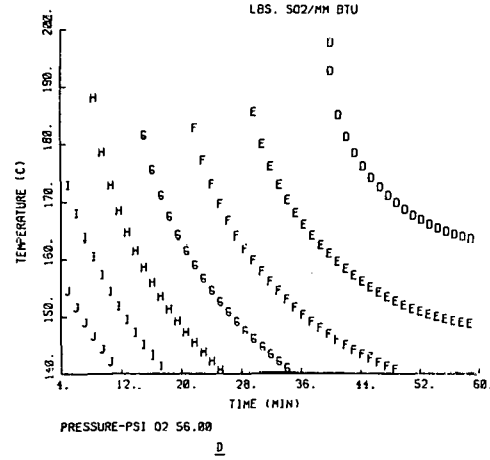
PLOT CODE	CHARACTERISTIC, Y[1]							
	1	2	3	4	5	6	7	8
A	5.0	25.0	-20.0	0.0	1.0	10.0	0.0	1.20
B	10.0	30.0	-15.0	0.5	3.0	25.0	1.0	1.50
C	15.0	35.0	-10.0	1.0	5.0	40.0	2.0	1.80
D	20.0	40.0	- 5.0	1.5	7.0	55.0	3.0	2.10
E	25.0	45.0	0.0	2.0	9.0	70.0	4.0	2.40
F	30.0	50.0	5.0	2.5	11.0	85.0	5.0	2.70
G	35.0	55.0	10.0	3.0	13.0	100.0	6.0	3.00
H	40.0	60.0	15.0	3.5	15.0	115.0	7.0	3.30
I	45.0	65.0	20.0	4.0	17.0	130.0	8.0	3.60
J	50.0	70.0	25.0	4.5	19.0	145.0	9.0	3.90
K	55.0	75.0	30.0	5.0	21.0	160.0	10.0	
L	60.0	80.0	35.0	5.5	23.0	175.0	11.0	
M	65.0	85.0	40.0	6.0	25.0	190.0	12.0	
N	70.0	90.0	45.0	6.5	27.0	205.0	13.0	
O	75.0	95.0	50.0	7.0	29.0	220.0	14.0	
P	80.0	100.0	55.0	7.5	31.0	235.0	15.0	

1. See Table 4.









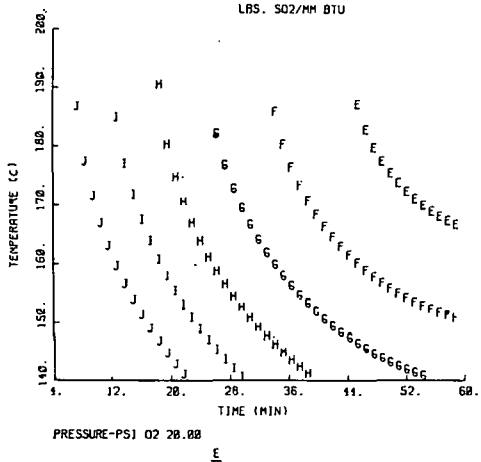


FIGURE 40. CONTOUR SURFACES REPRESENTING THE EFFECTS OF TIME, TEMPERATURE, AND PRESSURE ON PRODUCT QUALITY OF LOWER FREEPORT HvAb COAL, 7.1 SCFH AIRFLOW.

5-28-80 L-17686

The product quality is influenced by the sulfur and heating value content. Figures 41A through 41C contain contour plots for the total sulfur decrease at pressures of 110 psi O_2 and above. As expected, the curves have the same general contours as those for the lbs SO_2/MM Btu. Oxygen pressures lower than 110 psi are not shown since the product quality data indicated the impracticality of operating below this point. The temperature insensitivity noted above approximately 190°C in Figures 40A through 40E is not as prevalent in the sulfur data. The unusual decrease in the sulfur removal noticed at residence times approaching 60 minutes is likely an artifact of the computer modeling program. An increase in total sulfur with time has never been observed in previous experimentation.

For the sulfur removal data, the most important variable in Equation 5 is the pressure-temperature interaction term, a_6PT, which alone accounts for 42 percent of the variability over the region of interest. In conjunction with the a_4t term, 83 percent is explained.

The contour plots for the loss in heating value as a result of treatment are shown in Figures 42A through 42C. The results exhibit almost a linear correlation with reaction time and temperature. The rate of heating value loss appears to increase, though, as higher temperatures and longer residence times are used. The unusual hyperbolic contour evident at 110 psi is most probably a result of the limitations inherent to the computer modeling program.

The statistical analysis indicates the a_9Tt and a_6PT interaction terms in Equation 5 are the most significant. Along with the constant term, they alone account for 62 percent of the variability for loss in heating value.

The shape of the sulfur removal data in Figures 41A through 41C is a result of the pyritic and organic sulfur variations. The pyritic sulfur removal is shown in Figures 43A through 43C. The decreased removal at longer residence times observed for the sulfur data is even more pronounced in the pyritic sulfur removal results. The magnitude of this observation may be distorted somewhat by the regression analyses, since the uncertainty of prediction increases at the corners of the region of interest where the factor settings are at their upper and lower extremes. However, similar trends for pyritic sulfur removal have been observed in previous parametric studies (Appendix 1) and are, therefore, a possible occurrence. As postulated, the precipitation of interfering species may be the cause of the anomalous results.

The temperature independence of pyritic sulfur reduction is even more pronounced than for the sulfur removal. However, to achieve complete removal, temperatures of about 180°C appear to be necessary. Again, this may be due to precipitation products formed from the solubilized pyritic sulfur. The relative temperature independence is observed in Table 4. All but the first order term of Equation 5, a_3T, have been eliminated in the equation used. Other data show that the first order time, pressure, and constant terms account for 76 percent of the variability.

Of the 20 experiments in Appendix 16, only experiments 7W27 and 7W39 show a decrease in the organic sulfur. The other products exhibit varying degrees of increased apparent organic sulfur. As previously discussed, this is assumed to be the result of inorganic compound formation from solubilized sulfur and iron from the pyrite and other metals from corrosion of the reactor.

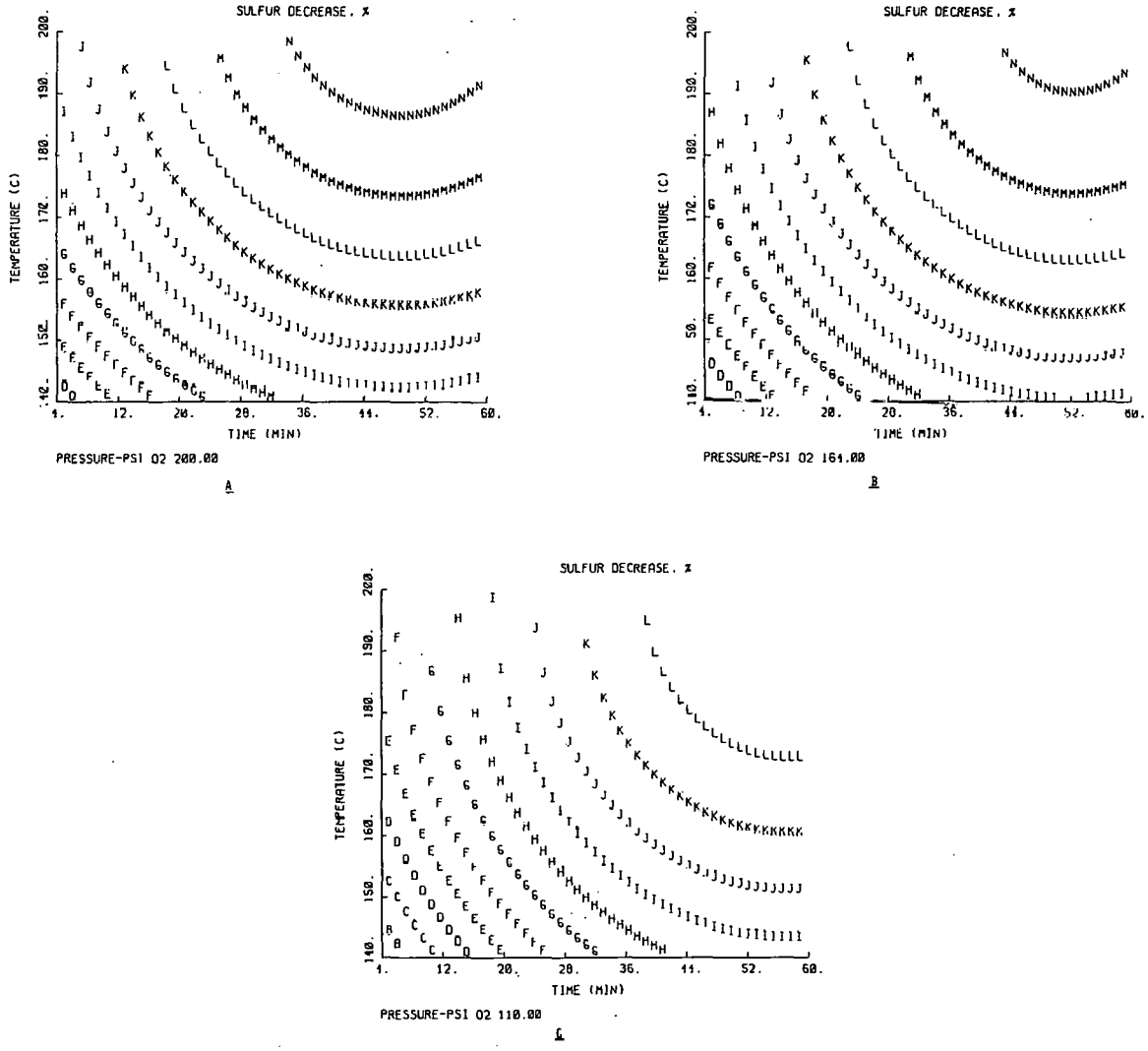


FIGURE 41. CONTOUR SURFACES REPRESENTING THE EFFECTS OF TIME, TEMPERATURE, AND PRESSURE ON TOTAL SULFUR OF LOWER FREEPORT HVAB COAL, 7.1 SCFH AIRFLOW.

5-28-80 L-17687

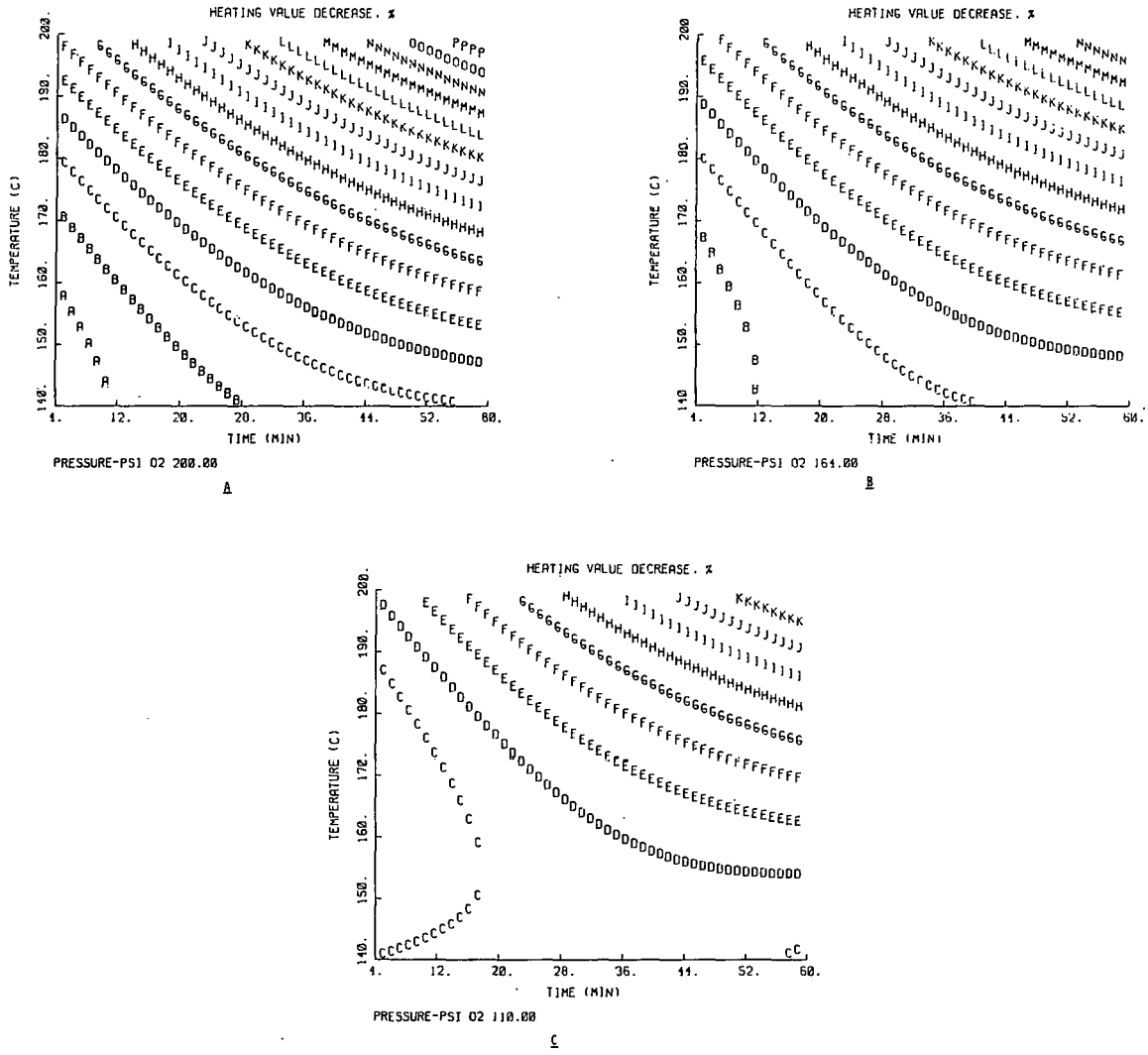


FIGURE 42. CONTOUR SURFACES REPRESENTING THE EFFECTS OF TIME, TEMPERATURE, AND PRESSURE ON HEATING VALUE OF LOWER FREEPORT HVAB COAL, 7.1 SCFH AIRFLOW.

5-28-80 L-17688

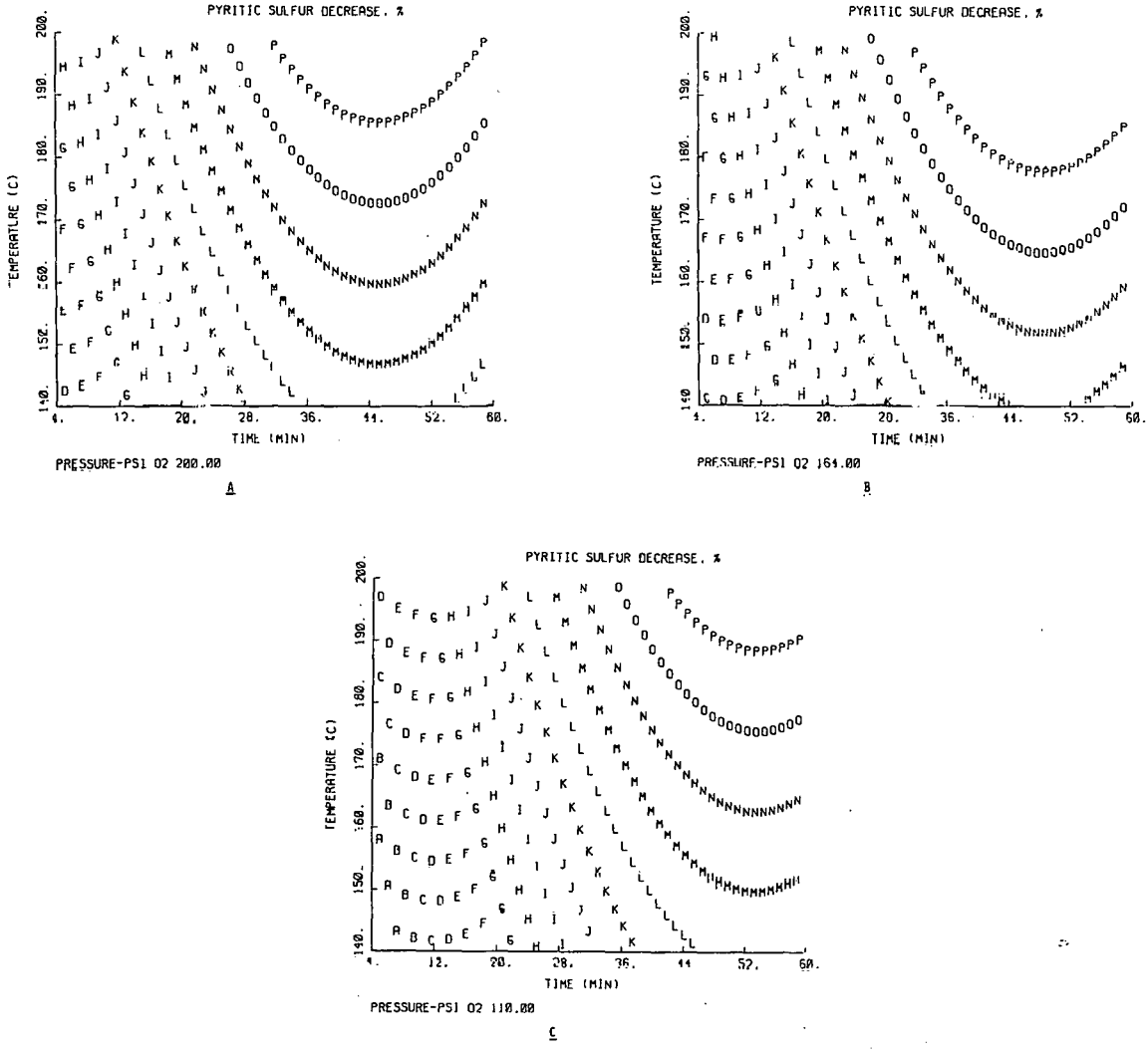


FIGURE 43. CONTOUR SURFACES REPRESENTING THE EFFECTS OF TIME, TEMPERATURE, AND PRESSURE ON PYRITIC SULFUR OF LOWER FREEPORT HVAB COAL, 7.1 SCFH AIRFLOW.

5-28-80 L-17689

The statistical analysis in Table 4 shows that the relative uncertainty in the organic sulfur data is greater than that for the total and pyritic sulfur results. The difficulty in accurately describing the data is partially a result of the fact that no direct analysis is used for organic sulfur. Therefore, the error associated with it would be the accumulation of errors in the sulfur and sulfur form analyses. Also the coal used contains 0.66 weight percent organic sulfur which is probably insufficient for accurate determinations of small variations.

Figures 44A through 44C are the contour plots for the apparent organic sulfur variations at and above 110 psi O_2. As shown in Table 5, letters before E represent an organic sulfur decrease while those after E indicate the apparent increase. From the graphs it appears that a significant reduction in the organic sulfur can only be achieved at high temperatures and pressures. None of the 20 experiments in Appendix 16, however, were made in this region. The apparent increase in organic sulfur occurs rapidly until a maximum value is reached. At the lower temperatures this maximum value occurs almost simultaneously with maximum pyritic sulfur solubilization (see Figures 43A through 43C). This is similar to the trends observed in Figure 4. As higher temperatures and pressures are attained, the apparent increases subside as if decomposition is enhanced. Further experimentation is planned to resolve the anomalous organic sulfur increase.

The carbon and hydrogen loss and oxygen uptake at 164 psi O_2 are represented in Figures 45, 46, and 47, respectively. As expected, the trends in all three are similar to the heating value contours observed in Figure 42B. The magnitude of the numbers involved indicates that the cleavage of carbon and hydrogen bonds has a greater effect on the heating value loss than does the addition of oxygen. This is similar to previous observations.

It is difficult to make absolute conclusions from the factorial data due to the limited number of experiments employed to explore the selected region of interest. Kinetic expressions can be derived but are of limited value due to the small number of data points. For example, Figure 48 represents a first-order rate plot for pyrite conversion at 170°C and 110 psi oxygen partial pressure. $[FeS_2]_o$ is the initial pyrite concentration expressed in weight-percent, and similarly $[FeS_2]_T$ is the concentration at time T. The first-order dependency agrees with kinetic results obtained by Vracar and Vucurovic for pyrite (38) and Slagle for an Upper Freeport seam coal (31). Conversion rates from the 32 minute experiments at 20, 110, and 200 psi oxygen partial pressure in Appendix 16 yield a 0.85-order dependence of the pyritic sulfur conversion on oxygen partial pressure. If this is valid, a plot of $\ln [([FeS_2]_o/[FeS_2]_T)/PO_2^{0.85})$ versus time should be linear. This is illustrated in Figure 49.

The data generated from the fractional factorial experiment are best used to illustrate the general relationships between the three major variables influencing the air/water oxydesulfurization reaction. The following conclusions can be made from the data presented:

1. Oxygen partial pressures above 110 psi are necessary to produce an acceptable product over the range of reaction temperatures and residence times investigated. Also, from the data obtained, the use

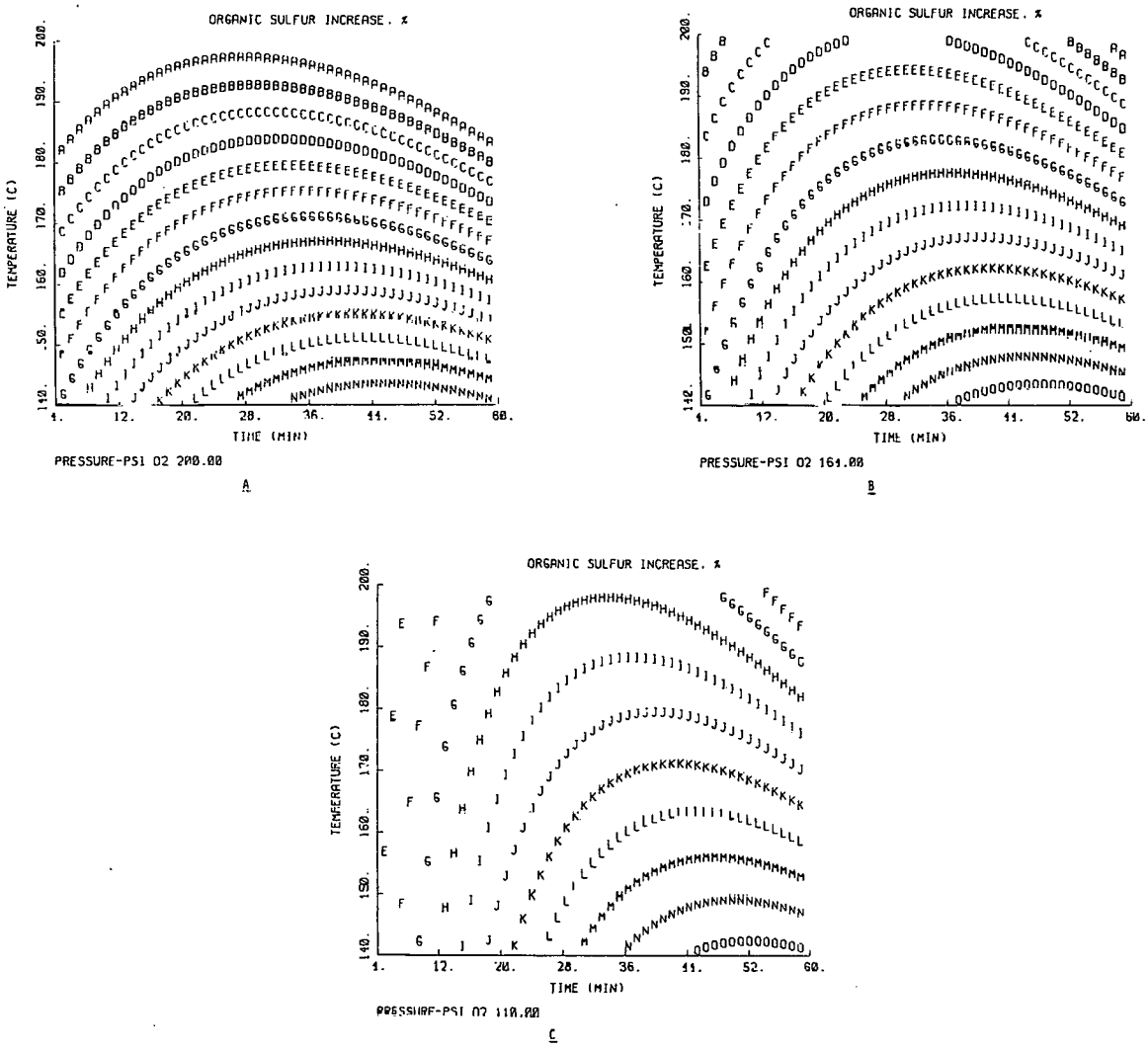


FIGURE 44. CONTOUR SURFACES REPRESENTING THE EFFECTS OF TIME, TEMPERATURE, AND PRESSURE ON ORGANIC SULFUR OF LOWER FREEPORT HVAB COAL, 7.1 SCFH AIRFLOW.

5-28-80 L-17690

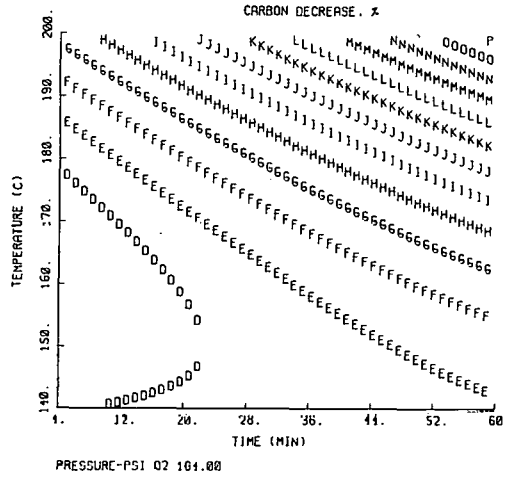


FIGURE 45. CONTOUR SURFACE REPRESENTING THE EFFECTS OF TIME AND TEMPERATURE AT 164 PSI PO_2 ON CARBON OF LOWER FREEPORT HvAb COAL, 7.1 SCFH AIRFLOW.

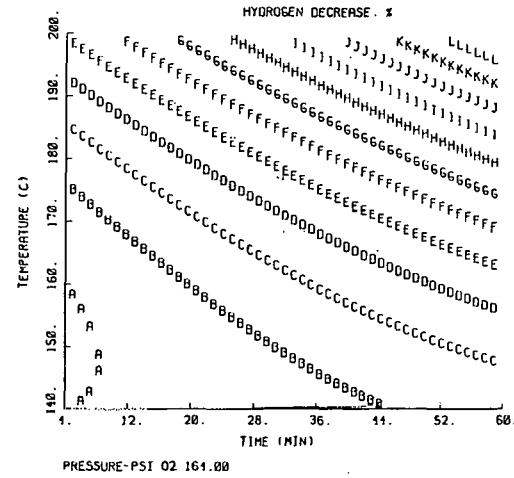


FIGURE 46. CONTOUR SURFACE REPRESENTING THE EFFECTS OF TIME AND TEMPERATURE AT 164 PSI PO_2 ON HYDROGEN OF LOWER FREEPORT HvAb COAL, 7.1 SCFH AIRFLOW.

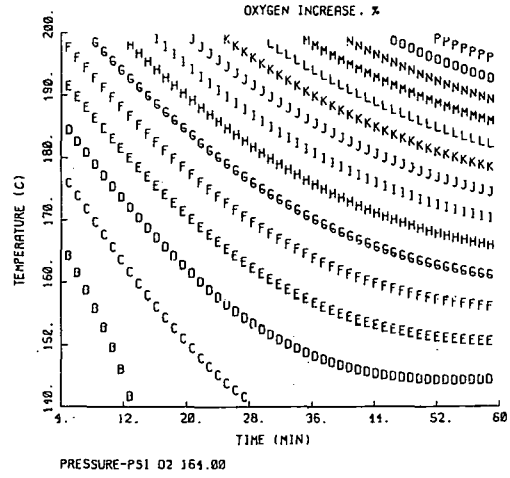


FIGURE 47. CONTOUR SURFACE REPRESENTING THE EFFECTS OF TIME AND TEMPERATURE AT 164 PSI PO_2 ON OXYGEN OF LOWER FREEPORT HvAb COAL, 7.1 SCFH AIRFLOW.

5-28-80 L-17691

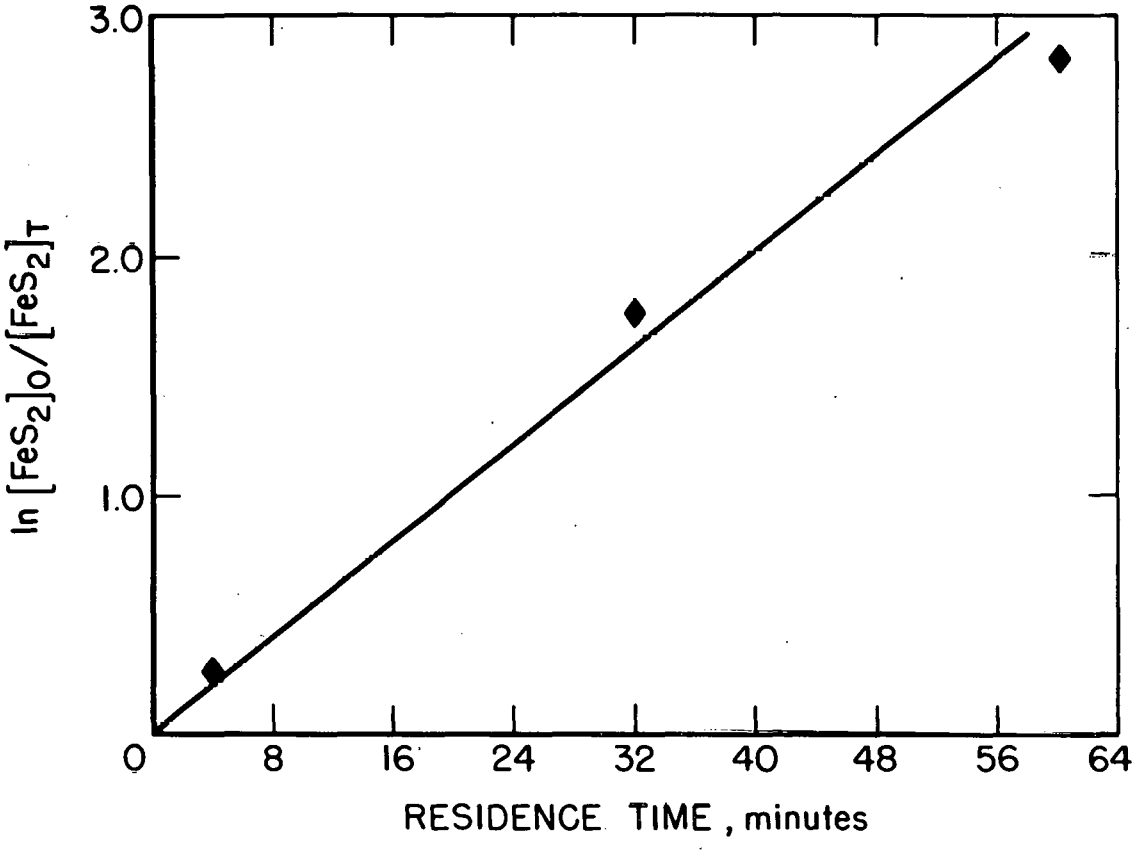


FIGURE 48. FIRST-ORDER RATE PLOT FOR PYRITE CONVERSION OF LOWER FREEPORT HVAB COAL, 170° C, 110 PSI, PO_2, 7.1 SCFH AIRFLOW.

10-25-79 L-17103

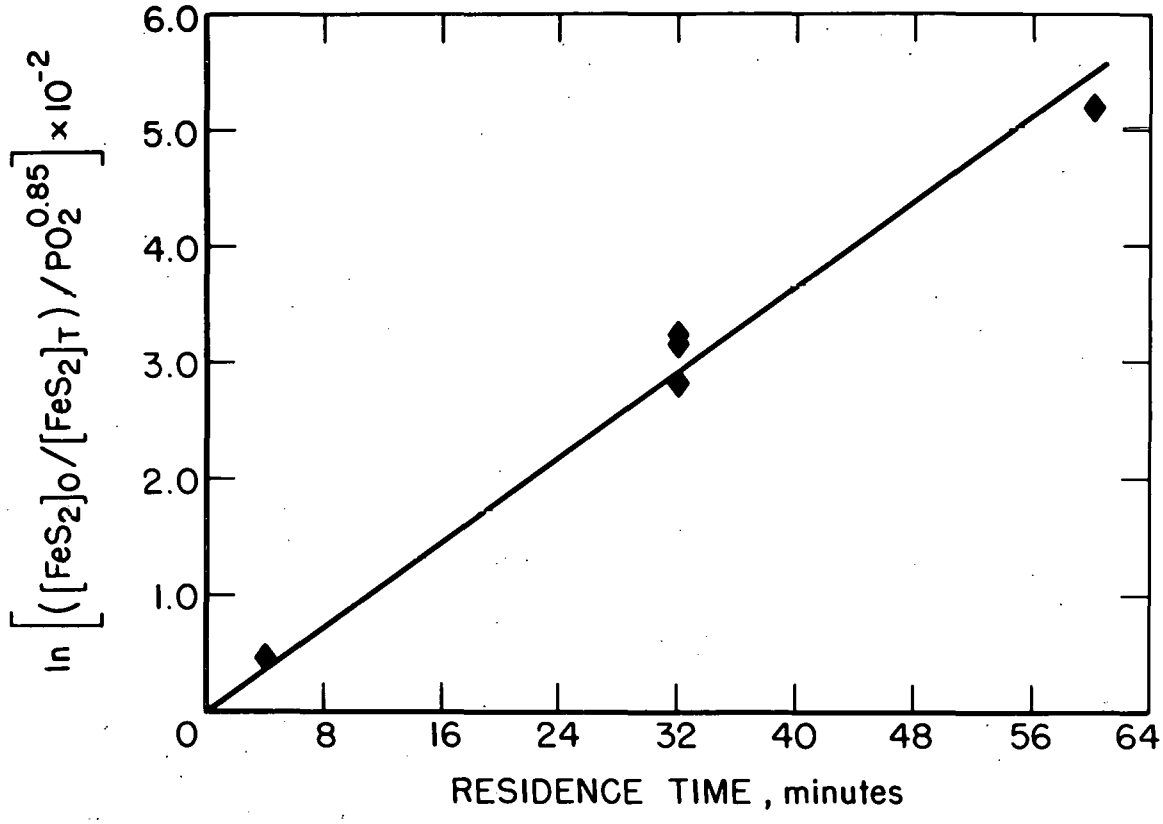


FIGURE 49. PLOT DEMONSTRATING THE 0.85 ORDER DEPENDENCE OF PYRITE CONVERSION ON OXYGEN PARTIAL PRESSURE FOR LOWER FREEPORT HVAB COAL, 170° C, 7.1 SCFH AIRFLOW.

10-25-79 L-17102

of oxygen partial pressures above 164 psi does not appear to be necessary in terms of product quality. Similar observations have been reported in the literature (38). These trends can be attributed to saturation of the pyrite surface with adsorbed oxygen which occurs at an oxygen partial pressure near 110 psi. Increasing the oxygen partial pressure above this level does not proportionally increase the rate of oxidation.

2. The sulfur removal remains essentially constant beyond a certain residence time which is dependent upon the oxygen partial pressure used (the a_6PT term is the most significant for total sulfur removal). Beyond this point the product quality is adversely affected due to the increasing heating value loss.

3. The relationship between the pyritic sulfur solubilization and the apparent organic sulfur increase again indicates the formation of an unusual intermediate species which perturbs the analytical results.

An experiment was made at the upper boundaries of the factorial parameter range to evaluate the predictive capabilities of the exercise. Most of the actual factorial experiments were made over the mid-range of the parameters, and as the upper or lower boundaries are approached, the statistical analysis becomes less valid. Table 6 contains the results of a recent analysis of the riffled sample of Lower Freeport coal used in this experiment and compares it to the average of the three untreated samples previously analyzed during the factorial experiment. Most of the recent determinations fall within 2σ of the previous analyses. Table 7 contains the results of the experiment at 200°C for 60 minutes under 200 psi oxygen partial pressure and compares them with the predicted values. Except for the organic sulfur removal the results are in excellent agreement with predicted values.

MATERIAL BALANCE

Sufficient data were collected in the factorial experiments to enable a material balance to be made around the system. Several approximations must still be made, which introduces some ambiguity in the results but the degree of uncertainty is less than in previous experiments. Experiment 7W27 in Appendix 16 was chosen for the example below since it yielded the best sulfur removal and is more typical of the air/water treatment than most of the other experiments in the factorial series. Table 8 contains data used in the calculations below.

The sulfur balance is straightforward since no gaseous sulfur products are formed. The sulfur balance is simply:

$$\frac{\text{S gm residue in product + S gm in wash water}}{\text{S gm in starting coal}} \times 100$$

Using the data in Table 8:

$$\frac{0.406 + 0.772}{1.184} \times 100 = 99.49 \text{ percent}$$

Table 6. Comparison of Untreated Sample of Lower Freeport (HvAb) Seam Coal with Three Previously Analyzed Samples

	PREDICTED[1] (σ)	OBSERVED[2]
Total Sulfur	2.39 (0.05)	2.34
Sulfate Sulfur	0.06 (0.03)	0.12
Pyritic Sulfur	1.67 (0.03)	1.62
Organic Sulfur	0.66 (0.06)	0.60
Carbon	69.70 (0.20)	70.30
Hydrogen	4.40 (0.00)	4.40
Nitrogen	1.20 (0.10)	1.10
Oxygen	4.40 (0.20)	3.90
Ash	17.90 (0.00)	17.90
Btu/Lb.	12398 (17.0)	12316
Lbs. SO_2/MM Btu	3.85 (0.09)	3.80

1. Average of 3 riffled samples used for factorial calculations, w/w moisture free.
2. 7W69S. Riffled sample, no treatment, w/w moisture free.

Table 7. Comparison of Experimental Results with Those Predicted by Fractional Factorial Data

	PREDICTED[1] (SEE)	OBSERVED[2]
Sulfur Decrease (%)	71.30 (3.26)	71.85
Pyritic Sulfur Decrease (%)	99.61 (6.45)	97.54
Organic Sulfur Decrease (%)	46.45 (7.88)	18.50
Carbon Decrease (%)	9.14 (0.42)	9.28
Hydrogen Decrease (%)	28.66 (2.03)	31.95
Oxygen Increase (%)	282.73 (9.92)	276.17
Heating Value Loss (%)	16.02 (0.56)	17.39
Lbs SO_2/MM Btu	1.40 (0.12)	1.30

1. Values are w/w on a dry basis. SEE is the standard error of estimate.
2. 200°C, 200 psi O_2, 60 minutes, w/w moisture free.

Table 8. Data Used in Material Balance Calculations

CONSTITUENT	DETERMINED AND CALCULATED QUANTITIES (gm)						
	INITIAL COAL CHARGE	PRODUCT COAL	PRODUCT WATER & WASHINGS	INITIAL AIR CHARGE[1]	RESIDUAL GAS[2]	INCOMING AIR FLOW[3]	TAIL GAS[4]
S	1.184	0.406	0.772	--	--	--	--
C	34.536	32.846	0.894[5]	--	0.192[6]	--	0.520
H	2.180	1.802	[7]	--	[7]	--	[7]
N	0.595	0.601	--	19.750	20.449	164.103	158.705
O	2.180	6.008	4.466[8]	6.328	5.796	52.590	45.692[9]
Fe	0.878	0.736	0.190	--	--	--	--

1. Reactor free space=0.67L
2. Reactor free space=0.72L
3. 7.10 SCFH air flow
4. 5.58 SCF
5. Dissolved as CO_2 in 117 ml slurry water plus 13 ml water remaining outside of liner.
6. 0.014 gm as CO, remainder CO_2.
7. H_2O loss from reactor unknown.
8. 1.444 gm used for sulfur oxidation, balance as dissolved CO_2.
9. 4.512 gm as CO_2.

Table 9. Gas Stream Compositions Used in Material Balance Calculations

COMPONENT[1]	INITIAL CHARGE[2]	RESIDUAL GAS[3]	AIR FEED[4]	TAIL GAS[5]
He	--	0.8	--	3.1
N_2	78.1	79.3	78.1	78.4
O_2	21.9	18.3	21.9	17.8
CO_2	--	1.5	--	0.6
CO	--	0.1	--	--

1. Reactor initially under 1 ATM He, water trap pressured to approximately 850 psig He. Results in volume percent.
2. 164 psi O_2 charge at 188°C in 0.67L volume. (749 psi air).
3. 565 psig remaining at 68°C in 0.72L volume.
4. 4.56 SCF used in 49 minutes.
5. 5.58 SCF measured at tail gas meter.

Similarly, the iron balance requires only the composition of the liquid and solid phases. For this experiment the iron balance is 105.47 percent. This indicates that the stainless steel components in contact with the slurry experienced corrosion.

The remaining material balances for C, H, N, and O must take into account the flow of gas through the reactor and, in some cases, the gaseous products formed under oxydesulfurization conditions, i.e., CO_2, CO, and H_2O. It is necessary, therefore, to approximate the composition of the gas stream exiting the reactor. A gas sample taken midway through the experiment will be used for this purpose. Table 9 represents the gas stream and residual gas compositions used in the calculations. Since the nitrogen in the air flow can be assumed to be unreactive under air/water oxydesulfurization conditions, the material balance can be made on the solid and gas phases separately and show the relative validity of the assumptions. The balance for the coal nitrogen is 101.01 percent and for the gas phase, 97.44 percent. This demonstrates the validity in assuming that the average gas composition of the tail gas is approximately that of the gas sampled midway through the experiment.

In determining the carbon balance, the amount of carbon as CO_2 and CO in the residual gas and the tail gas must be calculated as well as the amount dissolved as CO_2 in the final slurry. This latter figure was estimated assuming little variation due to the pH of the final slurry. The overall carbon balance is calculated as:

$$\frac{\text{C gm in Product + C gm in slurry + C gm in tail gas + C gm in residual gas}}{\text{C gm initial coal}} \times 100$$

This yields an accountability of 99.76 percent.

An oxygen balance is somewhat more difficult since an estimation of the oxygen content in the incoming gas and initial charge must be made, as well as for the oxygen used in sulfur oxidation. Some error is inherent in making the oxygen balance since no accurate measure was made of the water lost as a result of the air flow through the reactor. Initially, 143 ml of water was used to slurry the coal (0.9 percent moisture) and 70 ml of water was placed outside of the liner in the autoclave to limit evaporation of the water from the slurry. After the experiment, 117 ml of water was filtered from the product, 13 ml remained in the autoclave, and 23 ml was collected from a downstream trap. An additional 33 ml was removed from the product by vacuum drying. This accounts for 186 out of the 213 ml used, or 87.3 percent. A more efficient trap is necessary to enable an accurate water and subsequent oxygen balance to be made. Assuming that this error is relatively small in comparison to the oxygen in the gas phase, the oxygen balance can be expressed as:

$$\frac{\text{0 gm in product + 0 gm in slurry + 0 gm in residual gas + 0 gm in tail gas}}{\text{0 gm in initial coal + 0 gm in initial charge + 0 gm in air feed}} \times 100$$

From the data in Tables 8 and 9 the resulting oxygen accountability is 101.56 percent.

A hydrogen balance cannot be made because the magnitude of the numbers involved make it more sensitive than oxygen to the water balance. The above data show, however, that sulfur, carbon, oxygen, and nitrogen can adequately be accounted for in the reactor system.

THERMAL BALLISTIC EXPERIMENTS

The air/water oxydesulfurization treatment of coal results in the liberation of heat primarily due to the oxidation of sulfur, carbon, and hydrogen. The amount of coal heating value lost is proportional to the reaction temperature used. The modified mode of operation allows observation of the initial exotherm that occurs when air is added at reaction temperature. Appendix 17 contains a set of experiments designed to observe the magnitude of this initial temperature increase at various operating temperatures. In each case the autoclave under 1 atmosphere of nitrogen was stabilized at the temperature shown before air was added rapidly to increase the system pressure to approximately 1000 psig. The reactor was blocked off and the temperature of the slurry noted at 1-minute intervals. Figure 50 represents the exotherms that occurred at the temperatures investigated. The last three experiments in Appendix 17 represent blank experiments using nitrogen instead of air. The exotherms for these experiments are contained in Figure 51. The increase in heat content (Btu/lb) observed after treatment for some coals in Appendix 17 is due to reduction in ash before significant heating value (Btu) loss occurs. The heating value of the coal, however, decreases without exception after treatment.

The unusual results for the experiments using nitrogen cannot readily be explained. The products of 5W95 and 5W97 exhibit slightly greater carbon and hydrogen losses and oxygen uptakes than experiments 5W77 and 5W83 in which oxygen was present. The pyritic sulfur, however, was essentially not affected in the nitrogen experiments. Carbon dioxide was identified in the residual gas of the nitrogen experiments, although in lesser amounts than with oxygen present. It appears that the coal has reacted with the water in some as yet unknown manner resulting in coal oxidation comparable to air/water treatment.

Figure 52 contains the variation in sulfur and sulfur species as a function of the initial temperature at which air was introduced. Again an anomalous relationship appears to exist between the pyritic and organic sulfur reductions.

The temperature increase can be estimated from the heating value loss if the system is assumed to be adiabatic over the 15 minute duration of the experiment. The adiabatic temperature change is defined as:

$$\Delta T = \frac{\Delta H}{\sum m_i \; C_{pi}}$$

where:

ΔH = heat content

m_i = mass of i

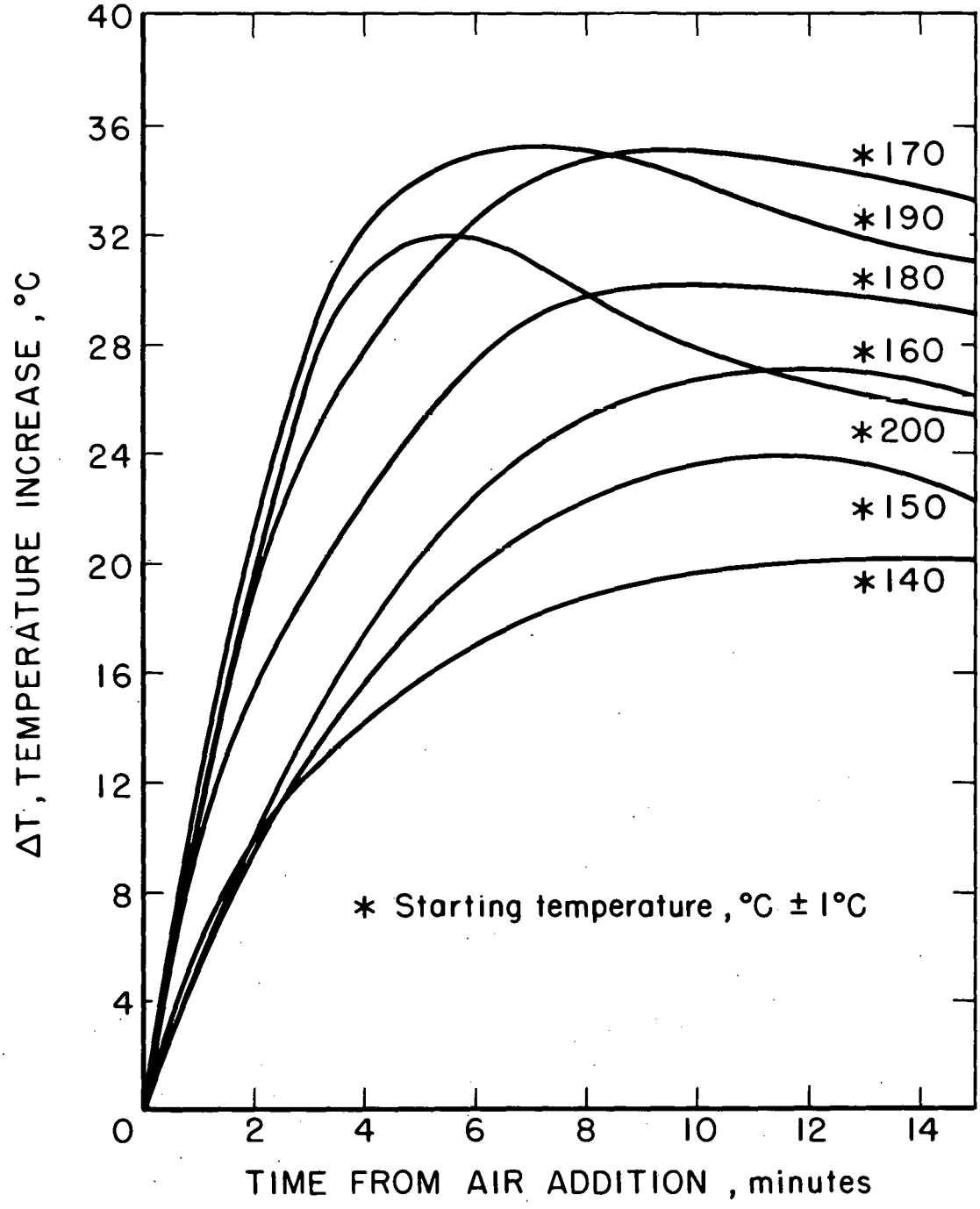


FIGURE 50. EXOTHERMS OBSERVED UPON AIR ADDITION AT REACTION TEMPERATURE FOR MINSHALL HVCB COAL, 15 MINUTES, MODIFIED MODE, 1000 PSIG.

3-29-79 L-16607

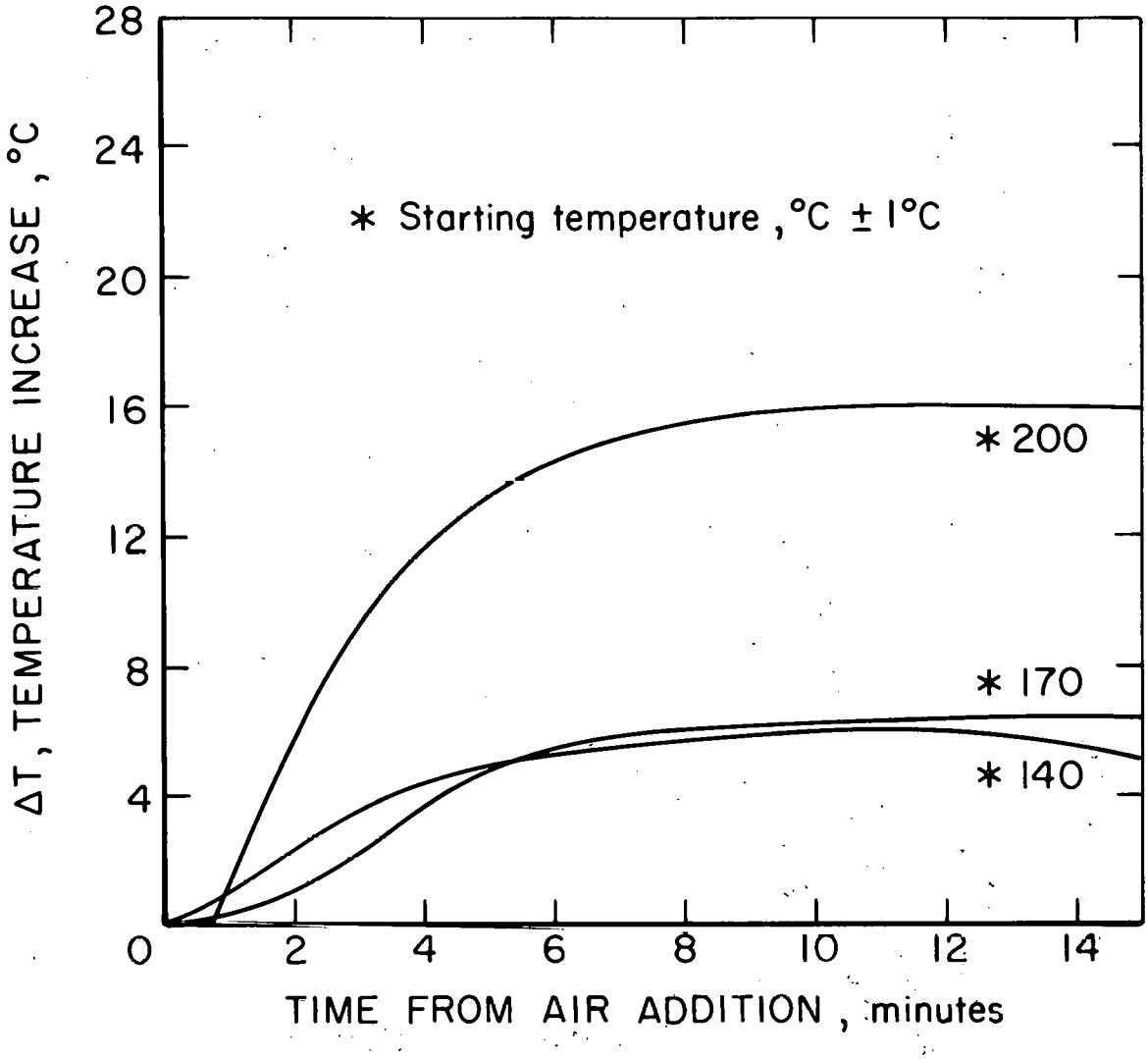


FIGURE 51. EXOTHERMS OBSERVED UPON NITROGEN ADDITION AT REACTION TEMPERATURE FOR MINSHALL HVCB COAL, 15 MINUTES, MODIFIED MODE, 1000 PSIG.

3-29-79 L-16608

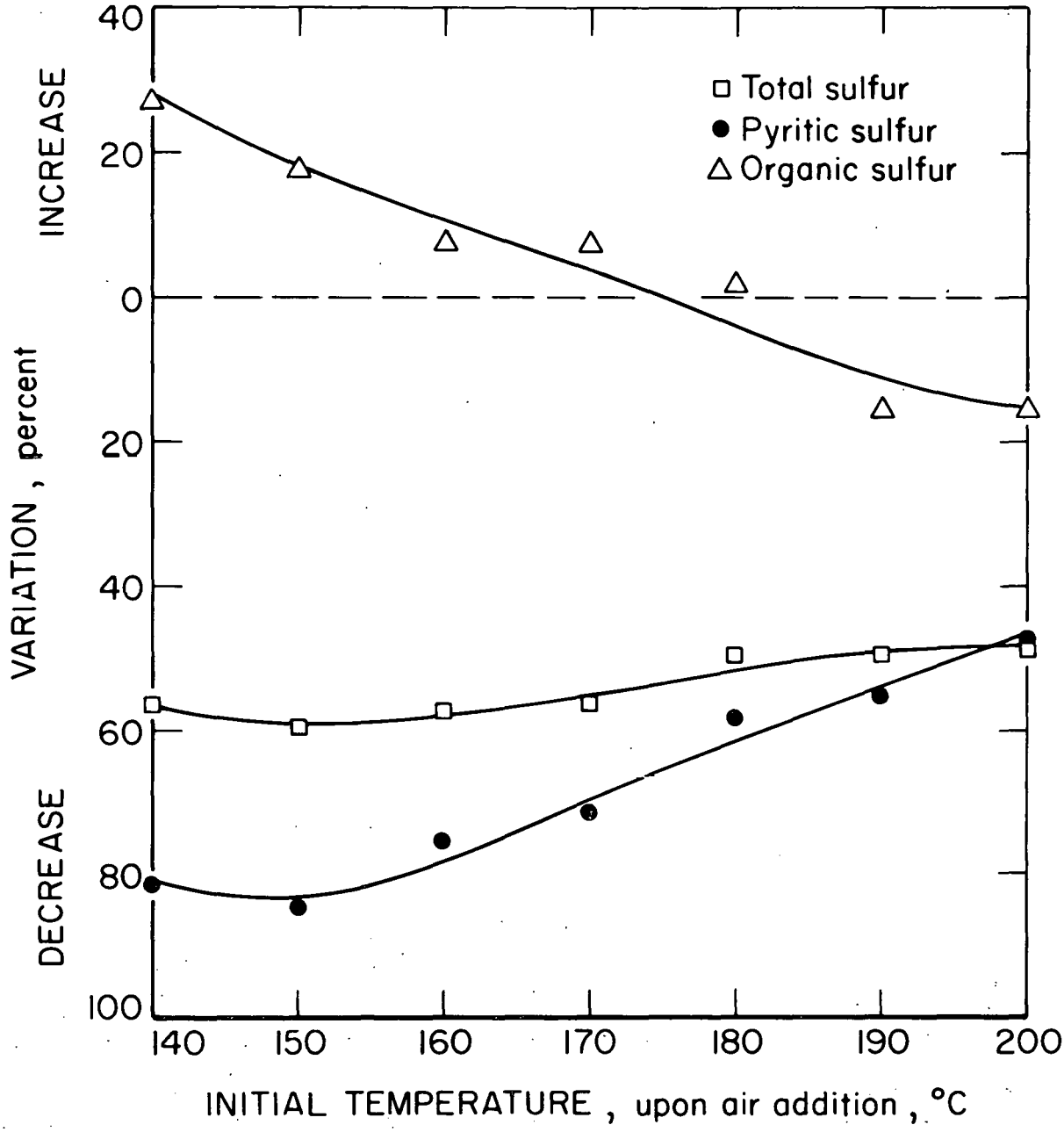


FIGURE 52. EFFECT OF INITIAL TEMPERATURE AT WHICH AIR IS ADDED ON DESULFURIZATION OF MINSHALL HVCB COAL, 15 MINUTES, MODIFIED MODE, 1000 PSIG.

3-29-79 L-16617

C_p = specific heat capacity of i

i = components of system

For example, the calculated temperature change for 5W83 at 170°C is:

$$\Delta T = \frac{\text{(weight of starting coal) (unit heating value loss)}}{\text{(weight of } H_2O)(C_p \text{ of } H_2O) + \text{(weight of coal)}(C_p \text{ of coal}) + \text{(weight of glass liner) } (C_p \text{ of pyrex})}$$

The following specific heat capacities were used:

C_p water, 170°C - 1.01

C_p coal - 0.29

C_p pyrex - 0.21

The heat capacity of the reactor will have a major effect on the calculation and this must be experimentally determined. Table 10 contains the observed and calculated temperature increases for the experiments in Appendix 17. The nitrogen experiments (5W95, 5W97, and 5W93) again exhibit unusual behavior. For the air/water treatments the calculated rises are consistently higher than observed, as we expected. A more accurate estimate could be made if the specific heat capacity of the reactor were known.

SUMMARY OF COALS TREATED

Twenty-four different coals have been treated by air/water oxidative desulfurization (40). Data for sulfur removal are given in Appendix 18, and the balance of the ultimate analyses are in Appendix 19. All 24 coals, unless noted in Appendix 18, were treated for 1 hour at the temperature indicated, under either 800 psig initial air pressure in the batch mode or 1000 psig total system pressure in the semibatch mode. An air flow of approximately 6 to 8 SCFH was used in the semibatch mode. The mode of operation is also indicated in Appendix 18. The first ten coals in the two tables would meet the 1974 EPA NSPS of 1.2 lb SO_2 per 10^6 Btu. Due to retention of sulfurous products in the ash during combustion, coals containing somewhat greater than 0.6 lb S per 10^6 Btu can be expected to meet NSPS. Reflecting the greater effectiveness of oxydesulfurization for removing more pyritic than organic sulfur, all ten of the untreated coals had less than 1 percent organic sulfur.

Coals 11 through 17 in the two tables had moderate amounts of organic sulfur, up to 1.5 percent. Depending on the sulfur-retention properties of the ash, some of these coals might meet NSPS. Relatively small improvements in oxydesulfurization processing could also bring these coals into compliance.

Coals 18 through 24 had high organic sulfur contents, greater than 1.5 percent. For these coals significant improvement in organic sulfur removal would be necessary to bring them into compliance. Consequently, due to their high organic sulfur contents, these coals have been used to investigate the removal of organic sulfur by air/water oxidative desulfurization.

Table 10. Observed Versus Calculated Temperature Increases

EXPERIMENT	ΔT	
	OBSERVED	CALCULATED
5W77	20	44
5W79	24	66
5W81	27	71
5W83	35	82
5W85	30	74
5W87	35	133
5W89	32	117
5W93	16	18
5W95	6	71
5W97	6	64

With increasing severity of operating conditions, increasing amounts of organic sulfur can be removed, but the removal is accompanied by heating value losses for the coal. This is not surprising, since one would expect oxidation of organic structures to proceed at a rate at least comparable to that for oxidation and cleavage of some C-S bonds. An organic sulfur removal efficiency plot, similar to Figure 4, is shown in Figure 53 for the coals in Appendix 18. The data exhibit considerable scatter but it should be remembered that besides temperature variations, the data also represent coals of six different ranks, ranging from hvAb to sbA.

The data in Appendix 19 show an increase in oxygen content of coal due to processing. This effect is shown graphically in Figure 54, where moles of oxygen taken up by the coal per mole of carbon in the product coal is seen to increase with loss of heating value. Hydrogen and carbon in the coal decrease due to processing. The data in Appendix 19 are plotted in Figure 55. It is seen for the range of heating value loss encountered, between 0 and 30 percent, that hydrogen is preferentially removed from the organic matrix. Apparently heating value is lost both by consumption of the coal to final oxidation products, carbon dioxide, and water, and by partial replacement of hydrogen by oxygen in the coal.

A beneficial side benefit of oxydesulfurization treatment is reduction in the ash content of the coal. Part of the ash probably is dissolved in the sulfuric acid formed during reaction. Inspection of Appendix 19 shows a maximum ash reduction of 41 percent and an average reduction for all coals treated of 20 percent. Oxydesulfurization treatment also completely destroys the caking properties of coal. This is desirable if the product is used as a feedstock for gasification or stoker fed boilers. The free swelling index, which is an approximate measure of the coking and caking characteristics of coal, for the coals in Appendix 18 is reduced in all cases to zero after treatment.

CONCLUSIONS

Laboratory experimentation has shown that air/water oxydesulfurization is an effective means of removing the pyritic and a portion of the organic sulfur from coal. The reaction proceeds favorably in the range of 150 to 200°C under an oxygen partial pressure of 100 to 200 psi O_2. Optimum operating conditions, however, are dependent on the type of coal used. Higher rank coals generally yield a better product in terms of lbs SO_2/MM Btu after treatment at more severe operating parameters than lower rank coals which suffer excessive heating value losses at similar conditions. The pyrite solubilization is essentially complete in 15 minutes; however, longer treatment times and higher temperatures are necessary to effect reduction in the apparent organic sulfur.

The formation of sulfur bearing precipitates from the solubilized pyrite appears to present a problem in interpreting the actual pyritic and organic sulfur data for some coals. The factors surrounding this phenomenon are complex and not yet well understood. The interference generally occurs for higher sulfur coals which produce a more acidic slurry during treatment. The incorporation in the thermal precipitates of metal cations leached from the

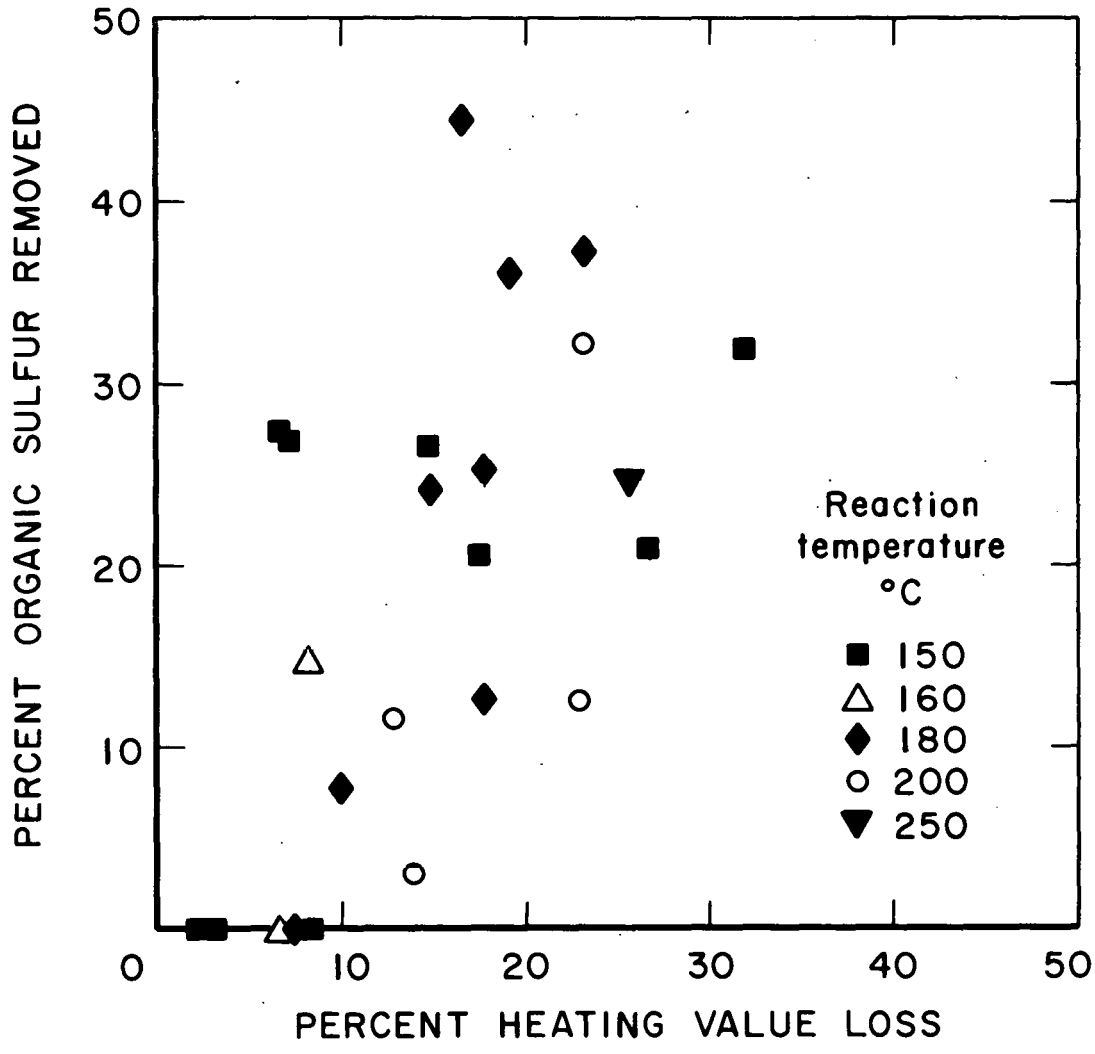


FIGURE 53. ORGANIC SULFUR REMOVAL EFFICIENCY PLOT FOR SELECTED TREATMENTS OF VARIOUS COALS.

2-8-80 L-16208

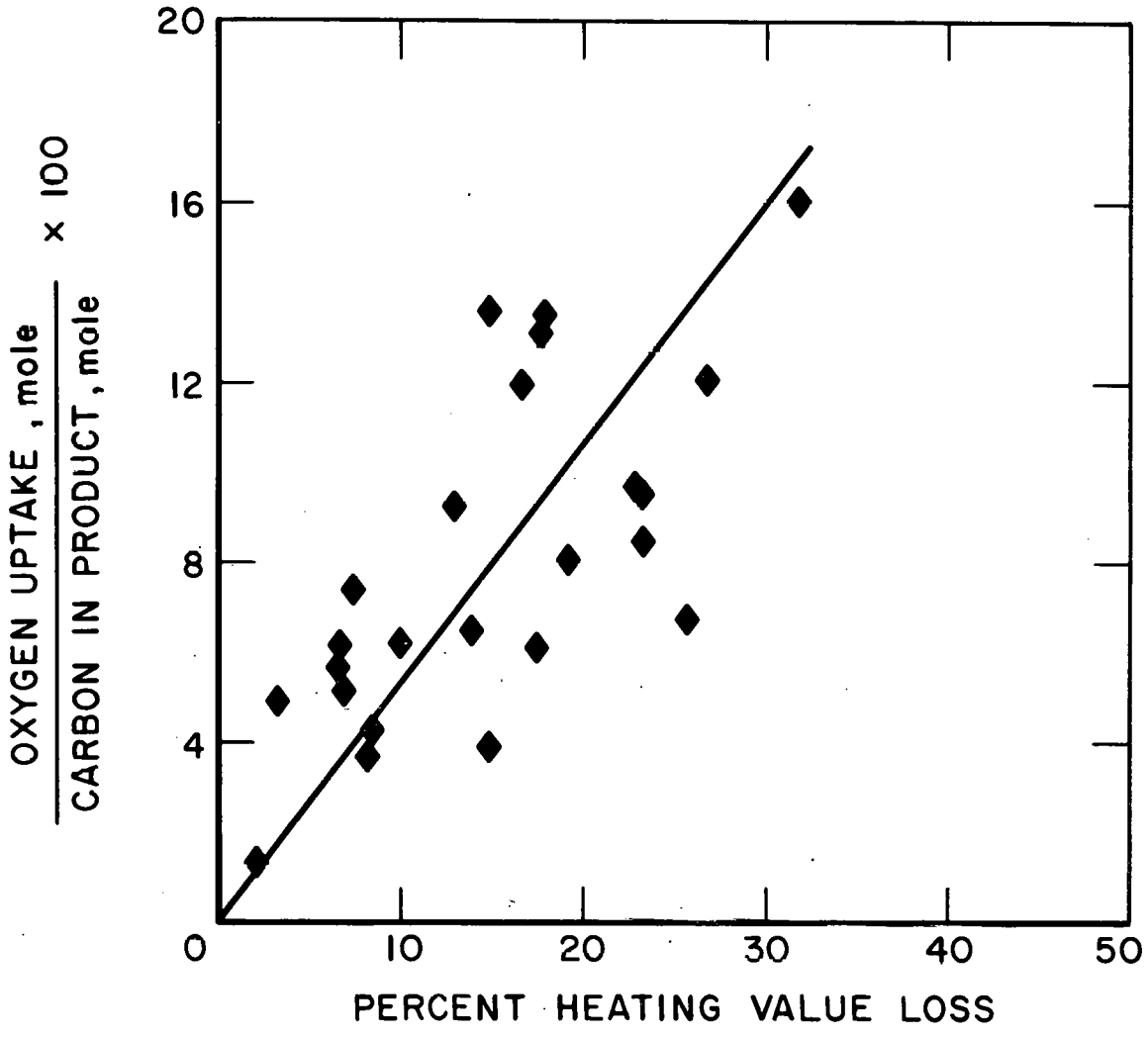


FIGURE 54. RELATIONSHIP OF OXYGEN UPTAKE TO HEATING VALUE LOSS FOR VARIOUS COALS TREATED.

8-29-78 L-16226

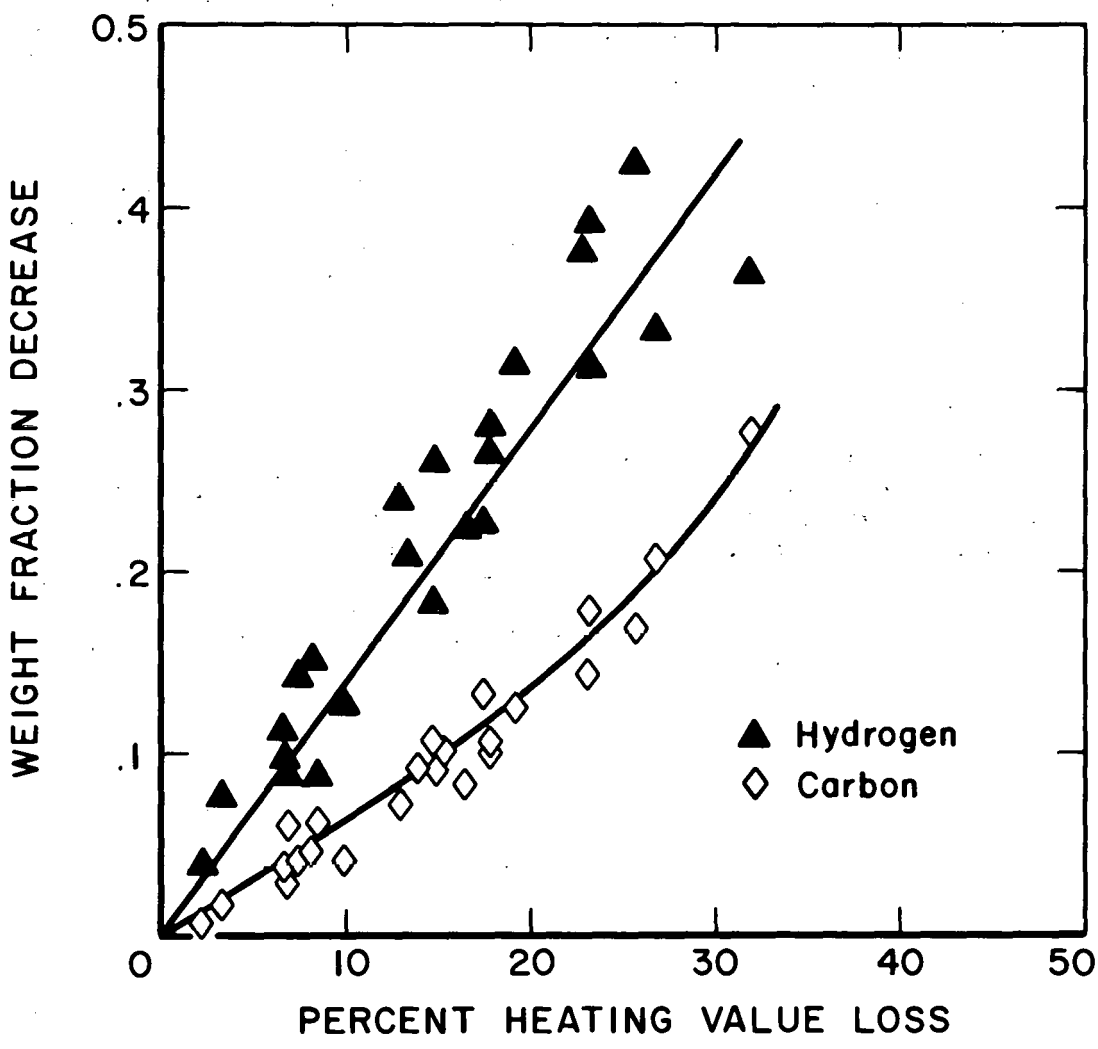


FIGURE 55. RELATIONSHIP OF CARBON AND HYDROGEN DECREASES TO HEATING VALUE LOSS FOR VARIOUS COALS TREATED.

8-24-78 L-16209

reactor components in contact with the acidic slurry may impact the acid solubility characteristics necessary for such compounds to cause the anomalies observed in the sulfur form analysis. The use of a sufficiently dilute slurry appears to alleviate this problem.

The data presented in this report were used in the design of a continuous slurry flow unit which is currently being operated to further define the potential commercial applications of this technology. Additional laboratory experiments are being conducted to resolve the precipitation phenomenon and its influence on the observed organic sulfur variations. An investigation is also underway to ascertain the nature of organic sulfur in coal and the chemistry involved in its removal by oxydesulfurization and other methods.

ACKNOWLEDGMENTS

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Appendix 1. Initial Exploratory Results

COAL SEAM	ASTM RANK	EXPERIMENT NO.	TREATMENT[1]			MOISTURE FREE WEIGHT PERCENT										BTU/ LB.	HCl[7] SOLUBLE Fe (%)
			TIME (HR.)	TEMP. (°C)	AIR[2] PRESSURE (PSIG)	RECOVERY[3]	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S		
Indiana No. 5	HvBb	5LHS	NO TREATMENT				9.10	69.37	4.86	1.58	11.82	3.27	0.59	0.70	1.98	12340	0.79
		5L27	2	200	800	[4]											
			2	200	800	[4]											
			2	200	800	[4]											
			2	200	800	83	10.08	60.51	2.75	1.49	23.58	1.59	0.09	0.06	1.44	8590	0.71
		5L41	2	200	800	104	14.11	63.65	3.77	1.31	14.93	2.23	0.09	0.66	1.48	10016	3.28
		5L31	1	200	800	107	14.46	63.20	3.90	1.35	14.96	2.13	0.01	0.40	1.71	10127	2.77
		6L11	1	200	800	88	8.38	68.70	3.88	1.46	15.12	2.46	0.09	0.39	1.98	[5]	0.61
		6KW37	1	200	800	102	12.85	63.77	3.84	1.43	15.82	2.29	0.19	0.55	1.55	10896	2.83
		5L33	1	150	810	99	8.28	68.89	4.54	1.44	14.71	2.14	0.03	0.05	2.06	11930	0.86
		5L37	1	150	400	97	8.16	69.56	4.73	1.46	13.67	2.42	0.10	0.31	2.01	11738	0.46
		6L7	1	130	1500	95	8.28	68.97	4.55	1.46	14.52	2.22	0.06	0.11	2.05	[5]	0.64
Illinois No. 6	HvCb	11R1531[6]	NO TREATMENT				11.70	69.27	4.92	1.31	9.15	3.65	0.24	1.15	2.25	[5]	0.36
		5L39[6]	1	150	800	97	9.23	66.74	4.59	1.26	15.44	2.74	0.03	0.35	2.35	11188	0.51
		1W37S	NO TREATMENT				11.55	65.99	4.80	1.18	13.32	3.65	0.31	1.13	2.25	12190	0.42
		1W37	1	150	800	94	9.77	65.68	4.34	0.95	16.84	2.42	0.03	0.10	2.29	11290	0.86
		1W43	1	150	1500	91	11.04	61.03	3.43	1.13	21.25	2.12	0.01	0.11	2.00	10030	1.61
Pittsburgh	HvAb	1D6[6]	NO TREATMENT				5.54	79.40	5.26	1.50	6.99	1.31	0.01	0.61	0.68	14170	0.18
		5L35	1	150	800	104	4.65	76.49	4.82	1.52	11.72	0.80	0.04	0.05	0.71	13430	0.44
		1W39	0.5	150	800	100	4.62	76.31	4.80	1.54	11.89	0.82	0.01	0.06	0.75	13370	0.59
		2W11	0.08	150	800	101	4.92	77.97	5.13	1.63	9.24	1.11	0.01	0.23	0.87	13960	0.35
		1W47[6]	1	150	800	99	4.88	76.74	5.00	1.56	10.97	0.85	0.01	0.12	0.72	13570	0.39
Lower Kitanning	Lvb	1D83	NO TREATMENT				7.10	83.47	4.45	1.41	2.61	0.96	0.03	0.53	0.39	14590	0.10
		6L9	1	150	800	98	6.97	79.77	4.09	1.36	7.24	0.57	0.02	0.08	0.47	13630	0.78

1. 35 gm, 200 x 0 mesh coal in 100 ml H_2O. Stainless steel liner. Stirring Rate 900 to 1000 RPM.
2. Initial charge at Room temperature.
3. On a dry basis.
4. Autoclave vented and repressurized, no sample taken
5. Value not obtained
6. 14 x 0 mesh
7. As received

Appendix 2. Experimentation Investigating Limits Of Organic sulfur Removal for Indiana No. 5 (HvBb) Seam Coal

EXPERIMENT NO.	NO. OF[2] CYCLES	TREATMENT[1]			MOISTURE FREE											HCl[4] SOLUBLE FE (%)
		TIME (HR.)	TEMP. (°C)	AIR[3] PRESSURE (PSIG)	WEIGHT PERCENT										BTU/ LB.	
					RECOVERY	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S		
5LHS	NO TREATMENT					9.10	69.37	4.86	1.58	11.82	3.27	0.59	0.70	1.98	12340	0.71
1W11	1	1	250	1500	92	11.49	63.42	3.12	1.47	18.66	1.84	0.01	0.20	1.63	9400	1.39
6FW49	4	1	150	1000	85	8.10	64.62	3.89	1.45	20.15	1.79	0.03	0.17	1.58	[7]	0.92
6FK31	2	1	150	1000												
	2	1	200	1000	77	9.83	62.50	3.11	1.45	21.28	1.83	0.18	0.16	1.50	[7]	0.98
1W13[5]	1	1	150	800												
	1	1	250	1500	80	11.61	61.37	2.63	1.57	21.12	1.70	0.10	0.18	1.42	9400	1.52
1W1	1	1	150	300												
	2	1	200	1000	76	8.80	62.06	2.88	1.48	23.23	1.55	0.07	0.12	1.36	9550	0.58
1W9	1	1	150	800												
	1	1	200	1500												
	1	1	250	1500	69	12.81	58.69	2.32	1.74	22.93	1.51	0.11	0.05	1.35	8680	0.15
6FW45	4	1	200	1000	65	10.37	58.23	2.47	1.56	25.92	1.45	0.08	0.05	1.31	[7]	
1W5[6]	1	2	130	1500												
	2	1	200	1500	72	12.85	56.45	2.37	1.47	25.46	1.40	0.08	0.04	1.28	8510	2.49
6FK33	1	2	200	1000												
	1	1	200	1000												
	1	2	200	1000												
	1	1	200	1000	68	14.96	53.71	2.61	1.55	25.57	1.60	0.31	0.06	1.22	[7]	2.75
6FK35	4	1	200	1000	57	11.52	56.83	2.60	1.48	26.21	1.36	0.10	0.09	1.17	[7]	0.13
1W3	1	1	150	800												
	2	1	200	1500	68	9.99	59.69	2.47	0.75	25.84	1.26	0.01	0.18	1.07	8920	1.20
1W7	1	1	150	800												
	2	1	200	1500												
	1	1	250	1500	35	19.11	51.88	1.91	1.76	24.18	1.16	0.13	0.05	0.98	7480	1.53

1. 35 gm, 200 x 0 mesh coal in 100 ml H_2O, stainless steel liner, 900 to 1000 RPM st rring rate.
2. Number of repressurizations at conditions listed
3. Initial charge at or near room temperature
4. As received
5. 29.1 gm coal
6. 36.0 gm coal
7. Value not obtained.

Appendix 3. Experimentation Investigating Aggitation Efficiency and Reactor Loading

COAL SEAM (STATE)	EXPERIMENT NO.	TREATMENT[1]				MOISTURE FREE											
						WEIGHT PERCENT										BTU/ LB.	BTU LOSS (%)
		TEMP. (°C)	PRESSURE (psig)	AIR FLOW (SCFH)	STIRRING RATE (RPM)	RECOVERY	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S		
Indiana Minshall (IN)	[2]	NO TREATMENT				--	14.7	61.7	4.4	1.2	11.6	6.53	2.07	2.61	1.85	11065	--
	7W7	180	1000	7.0	1200	80	8.6	65.3	3.6	1.2	19.5	1.82	0.02	0.15	1.65	10717	22
	7W9	180	1000	7.0	900	82	9.6	64.6	3.5	1.3	19.2	1.78	0.07	0.20	1.51	10647	21
	7W11	180	1000	6.9	600	88	10.7	66.4	3.9	1.3	15.5	2.38	0.07	0.37	1.64	11263	10
	7W13	180	1000	7.1	300	88	11.0	67.6	4.3	1.3	12.8	2.37	0.09	1.14	1.74	11843	6
Pittsburgh (WVA)	4W85S	NO TREATMENT				--	8.4	74.1	5.1	1.4	7.1	3.80	0.31	1.38	2.22	13560	--
	4W99	180	1000	2.2	950	99	7.0	69.2	4.0	1.2	16.6	1.96	0.04	0.15	1.77	11510	16
	6W65S	NO TREATMENT				--	7.9	71.7	5.1	1.3	10.0	3.91	0.47	1.16	2.28	13199	--
	6W65[3]	150	1000	3.6	950	93	7.4	71.6	5.1	1.2	11.3	3.42	0.12	1.03	2.27	13348	6

1. One hour in modified mode, 200 x 0 mesh coal, 35 gm coal to 100 ml H_2O in glass liner.
2. Average of two samples. All samples for stirring rate experiments were riffled.
3. 150 gm coal to 430 ml H_2O.

Appendix 4. Temperature Effects at Various Residence Times

EXPERIMENT NO.	TREATMENT[1]			MOISTURE FREE											BTU LOSS (%)
	TIME (MIN.)	TEMP. (°C)	PRESSURE (PSIG)	WEIGHT PERCENT										BTU/ LB.	
				RECOVERY	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S		
[2]	NO TREATMENT			—	16.28	63.70	4.46	1.16	8.74	5.65	0.79	3.61	1.26	11475	--
3W3	5	140	800[3]	93	13.39	66.75	4.70	1.27	10.55	3.34	0.14	1.92	1.28	11960	3
3W5	5	150	800[3]	94	13.08	67.29	4.65	1.28	10.83	2.87	0.19	1.05	1.62	11890	3
3W9	5	160	800[3]	93	12.83	66.29	4.66	1.27	12.16	2.79	0.11	0.79	1.89	11770	5
3W11	5	170	800[3]	93	13.43	65.83	4.65	1.26	11.63	3.20	0.10	1.31	1.78	11760	5
3W13	5	180	800[3]	94	13.60	65.24	4.58	1.25	12.06	3.27	0.14	1.76	1.37	11650	4
2W29S	NO TREATMENT			—	16.49	64.63	4.51	1.22	7.34	5.81	0.56	3.85	1.40	11650	--
2W39[4]	30	140	800[3]	96	11.85	67 08	4.54	1.26	12.71	2.56	0.08	0.46	2.02	11830	2
2W1	30	150	800[3]	95	12.68	66.48	4.51	1.34	12.15	2.84	0.08	0.78	1.98	11760	5
2W29[4]	30	160	800[3]	95	12.58	65.28	4.30	1.26	14.28	2.30	0.10	0.31	1.89	11305	8
2W35[4]	30	170	800[3]	96	12.08	65.21	4.16	1.25	15.14	2.16	0.10	0.40	1.66	11205	8
2W37[4]	30	180	800[3]	97	12.09	64.92	4.07	1.24	15.60	2.08	0.08	0.31	1.69	11080	8
5W49S	NO TREATMENT			--	14.85	64.35	4.53	1.17	8.59	5.51	1.19	3.78	1.53	11540	--
5W33	5	140	1000[5]	93.6	11.38	68.00	4.66	1.16	10.45	4.35	0.02	2.12	2.20	12270	0
5W35	5	150	1000[5]	94.0	11.91	68.33	4.76	1.31	9.53	4.16	0.01	1.98	2.17	12280	0
5W37	5	160	1000[5]	95.4	11.91	67.56	4.65	1.18	10.58	4.12	0.32	1.66	2.13	11960	1
5W39	5	170	1000[5]	95.6	11.65	67.52	4.52	1.21	11.35	3.75	0.22	1.34	2.18	12030	0
5W41	5	180	1000[5]	96.3	11.64	66.53	4.50	1.25	12.37	3.71	0.34	1.29	2.07	11750	2
5W43	5	190	1000[5]	97.9	12.10	65.96	4.44	1.10	12.34	4.06	0.33	1.91	1.81	11760	10
5W45	5	200	1000[5]	97.8	13.05	66.03	4.41	1.11	10.62	4.78	0.44	2.66	1.68	11680	11
1W35[6]	60	150	800[3]	93.0	12.08	65.63	4.32	1.26	14.39	2.32	0.10	0.22	1.99	11350	9
4W25S	NO TREATMENT				15.93	62.79	4.55	1.24	9.84	5.65	1.11	3.01	1.53	11320	--
4W25	60	200	800[3]	85.0	11.07	63.19	3.32	1.28	19.71	1.43	0.10	0.10	1.22	10230	23

1. Indiana Minshall (HvCb) seam coal, 200 x 0 mesh, 26 wt % slurry (35 gm coal: 100 ml H_2O), 900 to 1000 rpm.
2. Average of two separate analyses.
3. Initial air charge at room temperature, batch mode.
4. Average of two analyses.
5. Heated to temperature under 1 atm. N_2, this is total system pressure at beginning of experiment.
6. W1074 in Appendix 14 used as reference analysis.

Appendix 5. Analyses of Several Coals Used in Parametric Studies

COAL SEAM (STATE)	CODE[1]	EXPERIMENT NO.	MESH SIZE	ASTM RANK	WT. % MOISTURE	MOISTURE FREE										
						WEIGHT PERCENT									BTU/ LB.	LBS. SO_2/ MM BTU
						ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S		
Upper Freeport (MD)	A	6W71S	200 x 0	Mvb	0.1	16.2	72.3	4.3	1.3	4.3	1.58	0.20	0.82	0.56	12642	2.50
	B	6W57S	14 x 0	Mvb	0.7	14.8	74.3	4.4	1.2	3.7	1.55	0.06	0.86	0.63	12981	2.39
	C	7W3S	14 x 0	Mvb	0.5	16.0	72.5	4.3	1.3	4.3	1.62	0.00	0.84	0.78	12743	2.54
Imboden (VA)	D	6W75S	200 x 0	HvAb	0.1	3.7	80.2	5.1	1.5	8.4	1.19	0.15	0.26	0.78	14273	1.67
	E	6W61S	14 x 0	HvAb	1.2	3.5	81.1	5.2	1.5	7.6	1.13	0.11	0.25	0.77	14470	1.56
	F	7W15S	14 x 0	HvAb	0.7	3.5	81.2	5.1	1.5	7.5	1.25	0.14	0.23	0.88	14414	1.73
Colorado[2] (CO)	G	6W77S	200 x 0	HvBb	0.5	6.5	73.7	5.3	1.6	10.9	1.88	0.33	0.95	0.60	13123	2.86
	H	6W63S	14 x 0	HvBb	2.6	6.9	74.7	5.3	1.6	9.6	1.90	0.34	0.74	0.82	13237	2.87
	I	7W17S	14 x 0	HvBb	1.2	6.3	74.3	5.2	1.7	10.9	1.69	0.28	0.64	0.77	13378	2.53
Middle Kittanning (OH)	J	6W67S	200 x 0	HvCb	1.6	16.9	64.6	4.4	1.2	11.8	1.08	0.04	0.26	0.78	11184	1.93
	K	6W55S	14 x 0	HvCb	3.1	15.5	65.9	4.6	1.2	11.9	1.00	0.07	0.22	0.71	11517	1.74
	L	7W1S	14 x 0	HvCb	1.2	15.8	65.3	4.6	1.3	12.1	0.96	0.08	0.16	0.72	11465	1.67
Rosebud (MT)	M	6W73S	200 x 0	Subbit. B	1.5	13.3	61.1	4.4	0.9	17.2	3.09	0.30	2.32	0.47	10301	6.00
	N	6W95S	200 x 0	Subbit. B	3.1	12.9	62.3	4.1	0.9	17.0	2.79	0.38	1.74	0.67	10693	5.22
	O	6W59S	14 x 0	Subbit. B	8.9	12.0	63.2	4.2	1.0	17.1	2.45	0.24	1.49	0.72	10844	4.52
	P	7W5S	14 x 0	Subbit. B	3.8	12.2	63.3	4.1	1.0	17.2	2.24	0.25	1.42	0.57	10750	4.17

1. Codes are referred to in Appendix 6
2. Uncorrelated Seam

Appendix 6. Effect of Reaction Temperature and Coal Top Size on Several Coals Treated by Air/Water Oxydesulfurization

COAL SEAM (STATE)	UNTREATED ANALYSIS CODE[2]	EXPERIMENT NO.	MESH SIZE	TREATMENT[1] TEMP. (°C)	TREATMENT[1] AIR FLOW (SCFH)	MOISTURE FREE WEIGHT PERCENT RECOVERY	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S	BTU/LB.	LBS. SO_2/MM BTU	BTU LOSS (%)	PH OF PRODUCT SLURRY
Upper Freeport (MD)	A	6W81	200 x 0	150	7.8	98.2	15.3	72.0	4.2	1.3	6.5	0.76	0.02	0.04	0.70	12615	1.20	2.0	1.24
	A	6W71	200 x 0	180	7.6	100.1	15.4	69.7	3.8	1.3	9.1	0.61	0.03	0.05	0.53	11765	1.04	6.8	1.39
	A	6W93	200 x 0	200	7.7	98.9	14.6	67.7	3.3	1.2	12.7	0.54	0.02	0.02	0.50	11117	0.97	13.0	1.28
	B	5W57	14 x 0	180	6.9	99.4	16.2	71.0	4.0	1.3	7.0	0.63	0.00	0.15	0.48	12241	1.03	6.3	—
	C	7W3	14 x 0	200	7.4	85.0	14.0	69.9	3.6	1.3	10.6	0.63	0.01	0.10	0.52	11705	1.08	21.9	1.35
Imboden (VA)	D	6W85	200 x 0	150	7.3	99.5	3.4	79.6	4.9	1.4	9.9	0.85	0.02	0.04	0.79	13977	1.22	2.6	1.64
	D	6W75	200 x 0	180	7.6	97.7	3.2	73.8	4.3	1.4	16.5	0.76	0.02	0.03	0.71	12473	1.22	14.6	1.54
	D	6W97	200 x 0	200	7.7	95.6	3.0	72.6	3.5	1.4	18.9	0.66	0.01	0.02	0.63	11705	1.13	21.6	1.55
	E	6W61	14 x 0	180	6.5	99.5	2.7	78.5	4.5	1.4	12.0	0.82	0.02	0.05	0.75	13523	1.21	6.6	—
	F	7W15	14 x 0	200	7.2	96.7	2.8	77.6	4.3	1.3	13.3	0.75	0.01	0.05	0.69	13163	1.14	11.7	1.73
Colorado[3] (CO)	G	6W87	200 x 0	150	7.8	98.6	5.9	73.2	5.0	1.6	13.3	1.03	0.03	0.08	0.90	12731	1.59	4.3	1.17
	G	6W77	200 x 0	180	7.9	94.2	5.4	68.7	4.2	1.6	19.5	0.72	0.01	0.13	0.59	11360	1.28	18.5	1.20
	G	6W99	200 x 0	200	7.7	92.4	5.2	68.0	3.6	1.9	20.5	0.67	0.00	0.10	0.57	11001	1.22	22.5	1.19
	H	6W63	14 x 0	180	6.8	97.7	4.9	71.8	4.6	1.9	16.3	0.84	0.03	0.08	0.69	12209	1.31	9.9	—
	I	7W17	14 x 0	200	7.2	89.8	4.9	70.6	4.2	1.7	17.9	0.71	0.02	0.16	0.53	11892	1.19	20.2	1.31
Middle Kittanning (OH)	J	6W79	200 x 0	150	7.4	95.9	16.2	61.9	4.0	1.1	16.0	0.67	0.02	0.07	0.58	10530	1.27	9.7	1.97
	J	6W67	200 x 0	180	6.7	88.9	15.3	59.6	3.4	1.1	20.0	0.60	0.01	0.04	0.55	9648	1.24	23.3	—
	J	6W91	200 x 0	200	7.7	84.8	16.5	57.6	2.8	1.2	21.2	0.57	0.01	0.05	0.51	9040	1.26	31.5	1.78
	K	6W55	14 x 0	180	6.4	94.2	14.5	63.1	3.9	1.2	15.5	0.68	0.00	0.08	0.60	10508	1.29	14.0	—
	L	7W1	14 x 0	200	7.7	88.3	15.9	61.5	3.5	1.3	17.2	0.66	0.02	0.08	0.56	10061	1.31	22.5	1.95
Rosebud (MT)	M	6W83	200 x 0	150	7.9	81.9	11.0	60.7	3.5	1.0	22.8	1.00	0.03	0.40	0.67	9720	2.26	22.7	1.69
	M	6W73	200 x 0	180	7.5	72.3	11.4	57.9	3.0	1.0	25.5	1.10	0.01	0.50	0.59	8911	2.47	37.5	1.35
	N	6W95	200 x 0	200	7.7	71.0	11.0	59.8	3.0	0.9	23.8	1.52	0.01	1.12	0.49	9306	3.48	38.2	1.60
	O	6W59	14 x 0	180	6.6	68.1	11.8	60.9	3.4	1.0	21.2	1.72	0.00	1.16	0.56	9803	3.51	38.4	—
	P	7W5	14 x 0	200	7.4	79.2	10.4	63.4	3.7	1.0	19.5	1.95	0.01	1.37	0.57	10454	3.73	23.0	2.12

1. One hour residence time, 1000 psig total pressure, stirring rate 900 to 1000 RPM, glass liner, heat-up under 1 ATM. N_2.
2. Refer to Table 6.
3. Uncorrelated Seam.

Appendix 7. Size Consist of Various Coals Used in Parametric Studies

COAL SEAM (STATE)	ASTM RANK	SIZE FRACTIONS[1] PERCENT					
		+10	-10+30	-30+50	-50+100	-100+200	-200
Pittsburgh (PA)	HvAb	0.0	20.2	32.0	23.9	12.4	11.5
Illinois No. 6 (IL)	HvCb	0.2	44.9	23.0	15.3	8.1	8.5
Black Creek (AL)	Mvb	0.2	39.4	23.2	16.3	9.1	11.8
Upper Freeport (MD)	Mvb	0.2	31.8	24.0	19.3	11.0	13.7
Imboden (VA)	HvAb	0.3	40.6	23.4	16.8	9.2	9.7
Colorado[2] (CO)	HvBb	0.1	26.8	29.0	21.6	11.4	11.0
Middle Kittanning (OH)	HvCb	0.1	45.6	22.6	14.2	7.5	10.0
Rosebud (MT)	SbB	1.3	48.2	22.9	15.4	7.5	4.7
Lower Freeport (PA)	HvAb	0.0	2.8	18.9	30.2	20.7	27.4

1. U.S. Standard mesh sizes
2. Uncorrelated seam

Appendix 3. Additional Experimental Results Comparing 14 x 0 and 200 x 0 Mesh Coals Treated by Air/Water Oxydesulfurization.

COAL SEAM (STATE)	ASTM RANK	EXPERIMENT NO.	MESH SIZE[5]	TREATMENT[1]		MOISTURE FREE										BTU/LB.	LBS. SO_2/MM BTU	BTU LOSS (%)
				TEMP. (°C)	INITIAL AIR PRESSURE (PSIG)	WEIGHT PERCENT												
						RECOVERY	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S			
Pittsburgh (PA)	HvAb	1D6	14 x 0	NO TREATMENT		--	5.54	79.40	5.26	1.50	6.99	1.31	0.01	0.61	0.68	14170	1.85	--
		1W47	14 x 0	150	800	99	4.88	76.74	5.00	1.56	10.97	0.85	0.01	0.12	0.72	13570	1.25	5
		5L35	200 x 0	150	800	104	4.65	76.49	4.82	1.52	11.72	0.80	0.04	0.05	0.71	13430	1.19	1
Illinois No. 6 (IL)	HvCb	11R1531	14 x 0	NO TREATMENT		--	11.70	69.27	4.92	1.31	9.15	3.65	0.24	1.15	2.25	[2]	--	--
		5L39	14 x 0	150	800	97	9.23	66.74	4.59	1.26	15.48	2.74	0.03	0.35	2.35	11188	4.90	--
		1W37S	200 x 0	NO TREATMENT		--	11.55	68.37	4.57	1.22	10.60	3.69	0.31	1.13	2.25	12190	6.05	--
		1W37	200 x 0	150	800	94	9.77	65.68	4.34	0.95	16.84	2.42	0.03	0.10	2.29	11290	4.29	13
Black Creek (AL)[3]	Mvb	6W51S	14 x 0	NO TREATMENT		--	3.90	76.70	5.20	1.70	11.40	1.23	0.11	0.41	0.71	13699	1.80	--
		6W51	14 x 0	180	1000[4]	97	3.00	74.40	4.40	1.50	15.90	0.77	0.01	0.20	0.56	12568	1.22	11
		6W49S	200 x 0	NO TREATMENT		--	3.70	76.90	5.20	1.60	11.40	1.22	0.11	0.42	0.69	13595	1.79	--
		6W49	200 x 0	180	1000[4]	94	2.60	71.60	3.80	1.60	19.80	0.65	0.02	0.16	0.47	11694	1.11	19

1. Initial air pressure at room temperature, stainless steel liner, 1 hour residence time, 900 to 1000 RPM.
2. Data not available, 1W37S data used for calculation
3. Glass liner used for all experiments.
4. Modified mode, heatup under 1 ATM N_2, 1000 psig total pressure at 180°C, approximately 6.7 SCFH air flow.
5. Refer to Appendix 7.

Appendix 9. Effect of Residence Time on Indiana Minshall (HvCb) Seam Coal Treated at 150 and 180°C in the Batch Mode

EXPERIMENT NO.	UNTREATED ANALYSIS REFERENCE	TREATMENT[1]		MOISTURE FREE										BTU/LB.	LBS. SO_2/MM BTU	BTU LOSS (%)
		TIME (MIN)	TEMP. (°C)	WEIGHT PERCENT												
				RECOVERY	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S			
3W5	[2]	5	150	94	13.08	67.29	4.65	1.28	10.83	2.87	0.19	1.05	1.62	11890	4.83	3
2W1	[3]	30	150	95	12.68	66.48	4.51	1.34	12.15	2.84	0.08	0.78	1.98	11760	4.83	5
1W35	[3]	60	150	93	12.08	65.63	4.32	1.26	14.39	2.32	0.10	0.22	1.99	11350	4.09	10
3W13	[2]	5	180	94	13.60	65.24	4.53	1.25	12.06	3.27	0.14	1.76	1.37	11650	5.61	4
2W37	[2]	30	180	97	12.09	64.92	4.07	1.24	15.60	2.08	0.08	0.31	1.69	11080	3.75	8
5W51	[4]	60	180	96	11.86	64.80	4.19	1.21	15.65	2.29	0.12	0.21	1.95	11070	4.14	8

1. Indiana Minshall (HvCb) seam coal, 200 x 0. 26 W/W slurry, 800 psig initial air charge at room temperature, stirring rate~1000 RPM.
2. Refer to 2W29S in Appendix 4.
3. Refer to W1C74 in Appendix 14.
4. Refer to 5W49S in Appendix 4.

Appendix 10. Effect of Residence Time on Several Coals Treated in the Modified Mode.

COAL SEAM (STATE)	EXPERIMENT NO.	TREATMENT[1] TIME (MIN)	TEMP. (°C)	AIR FLOW (SCFH)	MOISTURE FREE WEIGHT PERCENT RECOVERY (%)	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S	BTU/LB.	LBS. SO_2/MM BTU	BTU LOSS (%)
Lower Freeport (PA)	5W5S	NO TREATMENT				15.1	72.5	4.5	1.3	3.7	2.83	0.15	2.03	0.65	12775	4.43	--
	6W19	1	180	None	97	13.6	74.6	4.6	1.1	4.3	1.84	0.13	0.93	0.78	13100	2.81	0.5
	6W5	15	180	6.9	99	13.5	72.4	4.3	1.3	7.4	1.14	0.04	0.08	1.02	12617	1.81	2.2
	6W9	30	180	7.2	99	13.4	71.3	4.2	1.3	8.7	1.00	0.03	0.07	0.90	12341	1.62	4.4
	6W13	60	180	7.6	100	13.3	70.2	3.9	1.3	10.6	0.75	0.05	0.02	0.68	11944	1.26	6.5
	6W21	60	200	6.7	104	14.9	66.1	3.4	1.2	13.7	0.85	0.24	0.04	0.57	10782	1.58	12.2
Upper Freeport (PA)	6W7S	NO TREATMENT				22.4	65.0	3.6	1.1	5.9	2.14	0.28	1.37	0.49	11256	3.80	--
	6W7	15	180	8.0	96	21.4	66.4	3.6	1.2	6.5	0.93	0.06	0.02	0.85	11314	1.64	3.5
	6W11	30	180	7.7	97	21.3	65.6	3.5	1.1	7.6	0.84	0.02	0.05	0.77	11140	1.51	4.0
	6W15	60	180	7.6	97	21.1	64.7	3.4	1.0	8.9	0.75	0.06	0.04	0.65	10846	1.38	6.5
	6W23	60	200	7.0	95	21.4	62.0	3.0	1.2	11.8	0.63	0.09	0.04	0.50	10213	1.23	13.8
Minshall (IN)	5W49S	NO TREATMENT				14.85	64.35	4.53	1.17	8.59	6.51	1.19	3.78	1.53	11540	11.28	--
	5W55[2]	60	150	2.1	96	12.11	66.21	4.42	1.21	13.69	2.36	0.05	0.20	2.10	11510	4.10	4.2
	5W29[2]	120	150	1.8	83	9.96	63.97	3.27	1.04	20.26	1.50	0.01	0.07	1.41	10320	2.91	25.8
Pittsburgh (WV)	5W53S	NO TREATMENT				7.78	73.45	5.11	1.26	8.51	3.89	0.32	1.38	2.18	13390	5.81	--
	5W31[2]	120	180	8.0	100	9.12	66.14	3.68	1.13	18.07	1.86	0.01	0.05	1.80	10920	3.41	18.4
Lower Freeport (PA)	6W45S	NO TREATMENT				16.1	71.2	4.4	1.3	3.9	3.12	0.04	2.42	0.66	12782	4.88	--
	6W45[3]	60	180	5.8	100	15.1	68.7	4.1	1.3	9.8	1.05	0.02	0.30	0.73	11905	1.76	6.9
	6W47[3]	180	180	7.1	107	13.5	61.2	3.2	1.0	14.1	0.90	0.22	0.11	0.57	10098	1.78	15.5
	6W53[3]	180	150	4.4	100	14.5	71.1	4.4	1.2	8.1	0.82	0.01	0.18	0.63	12393	1.32	3.0

1. 1000 psig total system pressure indicated. 200 x 0 mesh coal. 35 gms in 100 ml H_2O 900 to 1000 RPM stirring speed, glass liner, heatup under 1 atm. N_2.
2. 200 ml H_2O.
3. 14 x 0 mesh coal.

Appendix 11. Effect of Air Pressure on Indiana Minshall (HvCb)
Seam Coal Treated in the Batch Mode

EXPERIMENT NO.	TREATMENT[1]				REFERENCE ANALYSIS	MOISTURE FREE												
						WEIGHT PERCENT										BTU/LB.	LBS. SO_2/MM BTU	BTU LOSS (%)
	TIME (MIN)	TEMP. (°C)	INITIAL AIR PRESSURE (PSIG)	PO_2 (PSI)		RECOVERY	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S			
1W35	60	150	800	163	[2]	93	12.08	55.63	4.32	1.26	14.39	2.32	0.10	0.22	1.99	11350	4.09	10
1W41	60	150	1500	303	[2]	94	11.83	54.08	4.13	1.21	16.89	1.86	0.01	0.31	1.54	10970	3.39	12
2W29	30	160	800	248	[3]	95	12.47	55.40	4.27	1.26	14.36	2.24	0.10	0.29	1.85	11300	3.96	8
3W39	30	160	1320	407	[5]	89	12.10	65.00	4.11	1.29	15.39	2.11	0.06	0.36	1.68	10960	3.85	13
2W13[4]	40	150	100	23	[3]	94	12.57	66.88	4.59	1.34	11.04	3.59	0.14	1.67	1.77	11900	6.03	5
3W45	60	150	1000	309	[5]	89	12.48	64.25	4.02	1.33	15.95	1.97	0.07	0.21	1.68	10870	3.62	14
(4W29S[6] / 4W43S)	NO TREATMENT					--	16.05	62.98	4.56	1.24	9.63	5.54	1.20	2.76	1.58	11275	9.83	--
4W29	5	160	200	43	--	93	13.29	66.47	4.77	1.31	10.36	3.80	0.18	1.91	1.71	11990	6.34	1
4W31	5	160	400	83	--	93	12.85	66.32	4.64	1.23	11.63	3.33	0.18	1.20	1.95	11890	5.60	2
4W33	5	160	600	123	--	93	12.71	66.61	4.67	1.30	11.71	3.00	0.15	0.86	1.98	11830	5.07	2
4W35	5	160	800	163	--	93	12.45	66.54	4.70	1.32	12.26	2.73	0.10	0.53	2.10	11730	4.65	3
4W37	5	160	1000	203	--	93	12.30	66.88	4.53	1.32	12.43	2.54	0.12	0.35	2.07	11660	4.36	4
4W39	5	160	1200	243	--	92	12.01	65.60	4.32	1.31	13.38	2.38	0.10	0.21	2.06	11590	4.11	5
4W41	5	160	1400	283	--	93	12.05	65.75	4.31	1.30	14.37	2.22	0.16	0.15	1.93	11390	3.90	6
4W43	5	160	1600	323	--	93	11.99	66.05	4.23	1.31	14.06	2.36	0.10	0.23	2.03	11470	4.12	5

1. Indiana, Minshall seam coal, 200 x 0. Stirring rate 900 to 1000 RPM, Initial air pressure is at room temperature.
2. W1074, Appendix 14.
3. 2W29S, Appendix 4.
4. Eight batch repressurizations, 5 minute residence time at 150°C. Reactor cooled and purged between repressurizations with 100 psig air. Total time at 150°C is 40 minutes.
5. Average of 4W29S and 4W43S in this appendix.
6. Average of 4W29S and 4W43S.

Appendix 12. Comparison of Batch and Modified Modes of Treatment.

				TREATMENT[1]			MOISTURE FREE												
							WEIGHT PERCENT												
COAL SEAM (STATE)	ASTM RANK	EXPERIMENT NO.	REFERENCE ANALYSIS	TEMP. (°C)	AIR FLOW (SCFH)	FINAL[2] PO_2 AT 25°C (psi)	RECOVERY	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S	BTU/LB	LBS. SO_2 / MM BTU	BTU LOSS (%)
Minshall (IN)	HvBb	1W35	3	150	4	5	93	12.08	65.63	4.32	1.26	14.39	2.32	0.18	0.22	1.99	11350	4.09	10
		5W55[6]	7	150	2.1	19	96	12.11	66.21	4.42	1.21	13.69	2.36	0.05	0.20	2.10	11510	4.10	4
		5W51	7	180	4	33	96	11.86	64.80	4.19	1.21	15.65	2.29	0.12	0.21	1.95	11080	4.13	8
		4W95	8	180	2.2	19	93	13.37	62.14	3.69	1.16	17.82	1.82	0.0	0.29	1.49	10400	3.50	17
		5W5	3	180	5.5	16	85	8.98	65.57	3.76	1.25	18.72	1.72	0.0	0.23	1.48	10740	3.20	22
		7W9	3	180	7.0	99	82	9.6	64.6	3.5	1.3	19.2	1.78	0.0	0.20	1.51	10647	3.34	21
Pittsburgh (WVA)	HvAb	W1174	--	NO TREATMENT		--	--	8.19	74.77	5.14	1.31	6.70	3.89	0.11	1.86	1.94	13550	5.74	--
		2W21	10	150	4	133[11]	99	6.79	72.69	4.96	1.22	11.86	2.48	0.08	0.05	2.35	12910	3.84	6
		5W57[6]	12	150	2.4	134	100	7.64	72.19	4.74	1.15	11.99	2.29	0.09	0.03	2.24	12650	3.62	6
		5W53	12	180	4	38	99	6.77	71.03	4.46	1.22	14.43	2.09	0.04	0.02	2.03	12190	3.43	10
		4W99	13	180	2.2	35	99	7.02	69.18	4.03	1.17	16.64	1.95	0.06	0.15	1.77	11510	3.41	16

1. Unless noted; 35 gm 200 x 0 mesh coal in 100 ml H_2O, heatup under 1 ATM n_2, 1000 psig total pressure at reaction temperature, one hour residence time, stirring rate 900 to 1000 RPM, glass liner.
2. Based on analysis of residual gas vented while depressurizing reactor at room temperature.
3. Refer to W1074 in Appendix 14, stainless steel liner.
4. Batch mode, 800 psig initial air charge at room temperature.
5. No gas analysis.
6. 35 gm coal in 200 ml H_2O.
7. Refer to 5W49S in Appendix 4.
8. Refer to 4W91S in Appendix 13.
9. Refer to Appendix 3, Footnote 2.
10. W1174, this Appendix.
11. Initial air charge contained 30.6 percent O_2.
12. Refer to 5W53S in Appendix 10.
13. Refer to 4W85S in Appendix 3.

Appendix 13. Effect of Air Pressure on Several Coals Treated in the Modified Mode

COAL SEAM (STATE)	EXPERIMENT NO.	TREATMENT[1]				MOISTURE FREE												
		TIME (HR.)	TEMP. (°C)	PRESSURE (PSIG)	FLOW RATE (SCFH)	WEIGHT PERCENT										BTU/LB.	LBS. SO_2/MM BTU	BTU LOSS (%)
						RECOVERY	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S			
Indiana Minshall (IN)	4W91S	NO TREATMENT				--	14.86	63.40	4.59	1.19	9.25	6.71	0.54	4.22	1.55	11630	11.54	--
	5W3	1	180	200	2.3	92	11.50	67.59	4.80	1.23	10.03	4.85	0.12	2.94	1.78	12290	3.95	3
	5W15	2	180	200	2.6	94	11.34	64.87	3.58	1.28	15.66	3.27	0.01	1.60	1.65	10820	6.04	12
	5W13	1	180	500	2.0	91	9.94	66.42	4.13	1.27	16.22	2.02	0.01	0.29	1.69	11250	3.59	12
	5W9	2	180	500	2.0	85	9.41	64.24	3.58	1.23	20.02	1.52	0.01	0.23	1.28	10480	2.90	23
	4W95	1	180	1000	2.2	93	13.37	62.14	3.69	1.16	17.82	1.82	0.04	0.29	1.49	10400	3.50	17
	5W7	2	180	1000	1.5	79	9.15	63.47	3.32	1.24	21.29	1.53	0.01	0.24	1.28	10210	3.00	31
	5W25[2]	1	200	300	8.9	93	12.31	66.18	4.45	1.30	10.61	5.15	0.25	3.11	1.79	11840	8.70	5
Pittsburgh (WV)	5W11S	NO TREATMENT				--	7.99	73.23	5.15	1.27	8.53	3.83	0.02	1.34	2.52	13370	5.73	--
	5W27[3]	1	200	300	9.4	76[4]	7.34	73.57	4.96	1.31	9.40	3.42	0.04	1.16	2.21	13160	5.20	25[4]
	4W99	1	180	1000	2.2	98	7.02	69.18	4.03	1.17	16.64	1.96	0.04	0.15	1.77	11510	3.40	16

1. Pressure is total pressure at reaction, stirring rate, unless noted, ±1000 RPM, glass liner, heatup under 1 ATM. N_2.
2. 200 ml H_2O, stirring rate ~700 RPM
3. 135 ml H_2O, stirring rate ~700 RPM
4. Some sample lost through handling

Appendix 14. Experiments Investigating Slurry Concentration and Water Recycle

COAL SEAM (STATE)	EXPERIMENT NO.	SLURRY COMPOSITION	TREATMENT [1] TEMP. (°C)	TREATMENT [1] AIR FLOW (SCFH)	MOISTURE FREE WEIGHT PERCENT RECOVERY	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S	BTU/LB	LBS SO_2 / MM BTU	BTU LOSS (%)
Minshall (IN)	W1074	--	NO TREATMENT		--	16.50	64.76	4.54	1.30	7.14	5.76	0.29	4.16	1.31	11770	9.79	--
	1W35	35 gm coal: 100 ml H_2	150	[2]	93	12.08	65.63	4.32	1.26	14.39	2.32	0.10	0.22	1.99	11350	4.09	10.3
	2W29S	--	NO TREATMENT		--	16.49	64.63	4.51	1.22	7.34	5.81	0.56	3.85	1.40	11650	9.97	--
	2W25	50 gm coal: 100 ml H_2O	150	[3]	93	11.99	66.46	4.39	1.30	13.38	2.48	0.12	0.40	1.96	11570	4.29	7.6
	2W5	70 gm coal: 100 ml H_2O	150	[2]	96	15.12	65.82	4.68	1.23	7.84	5.31	0.01	3.85	1.44	11990	8.86	1.2
	2W31	35 gm coal, NO H_2O	150	[2]	88	14.92	64.16	3.06	1.22	11.85	4.78	0.10	3.28	1.41	10525	9.08	20.5
	7W85S	--	NO TREATMENT [4]		--	14.7	61.0	4.5	1.1	12.4	6.30	2.59	1.71	2.00	10744	11.73	--
	7W85	70.27 gm coal: 200 ml H_2O	150	7.2	91	13.1	64.0	4.2	1.2	14.9	2.48	0.03	0.15	2.30	11036	4.49	6.5
	7W87	29.88 gm coal: 200 ml H_2O	150	7.2	89	12.0	64.7	4.3	1.2	15.4	2.35	0.03	0.11	2.21	11082	4.24	8.2
	7W89	13.90 gm coal: 200 ml H_2O	150	7.2	89	12.7	64.3	4.2	1.2	15.4	2.07	0.02	0.07	1.98	10952	3.78	9.3
	7W91	6.72 gm coal: 200 ml H_2O	150	7.3	89	13.3	64.4	4.3	1.3	14.9	1.76	0.01	0.12	1.63	10598	3.32	12.2
	7W93	6.59 gm coal: 400 ml H_2O	150	7.3	88	12.4	64.7	4.2	1.3	15.6	1.77	0.14	0.14	1.49	10943	3.23	10.4
	7W95	3.27 gm coal: 400 ml H_2O	150	7.1	89	13.5	64.8	4.1	1.2	14.5	1.94	0.11	0.21	1.62	[5]	--	--
	7W99	27.81 gm coal: 400 ml H_2O	150	7.1	90	13.0	64.4	4.2	1.0	15.0	2.36	0.02	0.24	2.10	11215	4.21	6.1
Upper Freeport (PA)	6W69S	--	NO TREATMENT		--	22.4	64.9	3.7	1.2	5.6	2.23	0.28	1.24	0.71	11148	4.00	--
	6W69	35 gm coal: 100 ml H_2O	180	7.7	96	21.6	65.0	3.5	1.1	8.1	0.69	0.02	0.07	0.60	11096	1.24	4.4
Pittsburgh (WVA)	[6]	--	NO TREATMENT		--	8.10	75.17	5.21	1.32	6.11	4.09	0.04	1.60	2.45	13410	6.10	--
	4W3	35 gm coal: 100 ml H_2O	150	[2]	98	6.70	72.65	4.54	1.31	12.40	2.40	0.02	0.35	2.02	12780	3.76	6.6
	4W5	79 ml from 4W3 [7]	150	[2]	96	6.19	72.58	4.62	1.30	12.78	2.52	0.04	0.13	2.36	12540	4.02	10.2
	4W7	83 ml from 4W5 [7]	150	[2]	96	5.94	72.91	4.61	1.30	12.74	2.50	0.02	0.16	2.32	12400	4.03	11.2
	4W9	87 ml from 4W7 [7]	150	[2]	99	6.40	71.94	4.90	1.28	12.97	2.50	0.04	0.35	2.11	12728	3.93	6.0
	4W11	83 ml from 4W9 [7]	150	[2]	100	6.46	71.55	4.60	1.32	12.44	2.64	0.04	0.10	2.50	12580	4.20	6.2

1. One hour residence time, stirring rate -- 900 to 1000 RPM, 1000 psig total system pressure in modified mode.
2. Batch mode, no air flow, 800 psig initial air charge at room temperature.
3. Batch mode, no air flow, 1000 psig initial air charge at room temperature.
4. All samples in this series rifled to assure homogeniety.
5. Insufficient sample for analysis
6. Average of two separate determinations.
7. 35 gm coal, distilled water added to increase slurry liquid volume to 100 ml.

Appendix 15. Size Consist of Lower Freeport (HvAb) Coal Used in Fractional Factorial Experiment

ON	THRU	PERCENT
+60 MESH	--	1.0
80	60	3.1
100	80	2.4
170	100	16.2
200	170	7.6
270	200	24.0
325	270	21.5
--	325	24.2
		100.0

69.7% THRU 200 MESH

Appendix 16. Fractional Factorial Data

EXPERIMENT NO.	TREATMENT[1]			MOISTURE (WT. %)	MOISTURE FREE										BTU/LB.	BTU LOSS (%)	LBS. SO_2/MM BTU
					WEIGHT PERCENT												
	PRESSURE (PSI O_2)	TEMP. (°C)	TIME (MIN.)		RECOVERY	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S			
7W25S	—— NO TREATMENT ——			1.0	--	17.9	69.7	4.4	1.1	4.6	2.34	0.01	1.68	0.65	12419	--	3.77
7W41S	—— NO TREATMENT ——			0.8	--	17.9	69.5	4.4	1.2	4.5	2.46	0.09	1.63	0.74	12377	--	3.98
7W67S	—— NO TREATMENT ——			0.9	--	17.9	69.9	4.4	1.2	4.2	2.37	0.07	1.71	0.59	12397	--	3.82
				0.9	--	17.9	69.7	4.4	1.2	4.4	2.39	0.06	1.67	0.66	12398	--	3.86
7W25	200	170	32	0.1	100.1	17.1	67.9	4.1	1.2	8.7	0.94	0.07	0.13	0.74	11847	4.35	1.59
7W27	164	188	49	0.1	101.0	16.7	65.6	3.6	1.2	12.0	0.81	0.08	0.10	0.63	11031	10.14	1.47
7W29	164	188	15	0.5	99.9	17.3	68.0	4.1	1.1	8.3	1.16	0.08	0.39	0.69	11906	4.06	1.95
7W31	164	152	49	0.3	99.1	17.2	68.8	4.2	1.2	7.5	1.10	0.04	0.08	0.98	12107	3.23	1.82
7W33	164	152	15	0.2	98.8	17.2	69.3	4.3	1.2	6.4	1.54	0.06	0.72	0.76	12314	1.87	2.50
7W35	110	200	32	0.1	100.5	16.7	66.3	3.8	1.1	11.1	0.98	0.08	0.19	0.71	11383	7.73	1.72
7W37	110	170	60	0.4	100.3	16.9	67.6	4.1	1.2	9.3	0.95	0.07	0.10	0.78	11808	4.47	1.61
7W39	110	170	4	0.2	99.1	17.6	69.7	4.4	1.3	5.0	1.97	0.03	1.31	0.63	12360	1.20	3.19
					REPLICATE EXPERIMENTS												
7W41	110	170	32	0.9	99.4	16.9	68.5	4.1	1.2	8.1	1.15	0.04	0.28	0.86	12071	3.22	1.96
7W43	110	170	32	0.4	99.6	17.0	68.5	4.2	1.2	7.9	1.20	0.06	0.32	0.82	12054	3.16	1.99
7W45	110	170	32	0.4	99.2	17.1	68.6	4.2	1.2	7.6	1.23	0.03	0.32	0.88	12047	3.61	2.04
7W61	110	170	32	0.5	99.6	17.2	68.6	4.1	1.2	7.9	1.10	0.04	0.25	0.81	11984	3.72	1.84
7W63	110	170	32	0.3	99.3	17.1	69.1	4.3	1.1	7.2	1.25	0.04	0.33	0.88	12051	3.48	2.07
7W65	110	170	32	0.3	99.4	17.2	68.4	4.2	1.2	7.9	1.16	0.06	0.23	0.87	11970	4.03	1.94
7W47	110	140	32	0.3	98.7	17.3	69.3	4.4	1.2	6.2	1.70	0.01	0.76	0.93	12324	1.89	2.76
7W49	56	188	15	0.5	99.0	17.3	69.6	4.3	1.2	5.7	1.86	0.00	1.13	0.73	12243	2.24	3.04
7W51	56	188	49	0.1	99.9	16.7	68.5	4.1	1.2	8.2	1.17	0.01	0.26	0.90	11831	4.67	1.98
7W53	56	152	49	0.7	98.6	17.2	69.0	4.2	1.3	6.9	1.44	0.01	0.53	0.90	12225	2.78	2.36
7W55	56	152	15	0.6	98.7	17.7	68.7	4.3	1.3	6.0	1.98	0.01	1.21	0.76	12344	1.73	3.21
7W67	20	170	32	0.2	99.2	17.6	69.5	4.5	1.2	5.3	1.87	0.04	1.12	0.71	12356	1.14	3.03

1. Glass liner, stirring rate ~950 RPM, heatup under 1 atm inert gas, gas flow ~ 2.1 SCFH, 26 wt% slurry. Lower Freeport (HvAb) seam coal.

Appendix 17. Thermal Ballistic Experimentation Data

EXPERIMENT NO.	AIR[1] ADDITION TEMP. (°C)	HIGHEST TEMP. ATTAINED (°C)	MOISTURE FREE										BTU/LB.	LBS. SO_2/MM BTU	BTU LOSS (%)
			WEIGHT PERCENT												
			RECOVERY	ASH	C	H	N	O	S	SULFATE S	PYRITIC S	ORGANIC S			
[2]	NO TREATMENT		--	15.08	63.47	4.50	1.16	9.24	6.55	1.21	3.68	1.66	11444	11.44	--
5W77	140	160	92.4	11.48	67.69	4.58	1.19	11.94	3.11	0.08	0.75	2.28	11921	5.22	3.7
5W79	150	174	92.3	11.31	66.94	4.52	1.12	13.25	2.86	0.14	0.61	2.11	11701	4.89	5.6
5W81	160	187	92.0	11.54	66.73	4.33	1.21	13.18	3.01	0.09	0.98	1.94	11684	5.15	6.1
5W83	170	205	93.1	12.14	66.56	4.06	1.07	13.07	3.09	0.06	1.12	1.91	11434	5.40	7.0
5W85	180	210	93.2	12.32	66.07	4.10	1.09	12.89	3.54	0.10	1.64	1.81	11500	6.16	6.3
5W87	190	226	93.8	12.44	64.23	3.62	1.20	14.97	3.54	0.29	1.76	1.49	10809	6.55	11.4
5W89	200	233	92.1	12.56	65.08	3.67	1.21	12.56	3.67	0.05	2.09	1.52	11180	6.56	10.0
5W95[3]	140	146	97.1	12.11	63.42	4.02	1.22	13.70	5.53	0.64	3.24	1.66	11066	9.99	6.1
5W97[3]	170	176	95.3	12.18	64.32	4.17	1.07	12.81	5.44	0.46	3.48	1.49	11356	9.58	5.4
5W93[3]	200	217	92.7	12.64	67.09	4.57	1.21	8.80	5.70	0.04	3.98	1.68	12155	9.38	1.5

1. Indiana Minshall seam coal, 200 x 0 mesh. Treatment: 15 minutes, stirring rate~1000 RPM, heat-up under 1 atm N_2 1000 psig reaction pressure.
2. Average of analyses on three samples. All samples for this series are riffled.
3. Blank experiments with N_2 instead of air.

APPENDIX 18. SUMMARY OF COALS TREATED BY AIR/WATER OXYDESULFURIZATION

COAL ORIGIN AND TREATMENT							MOISTURE FREE									
							WEIGHT PERCENT						BTU,LB.		LBS. SO_2/MM BTU	
							TOTAL S		PYRITIC S		ORGANIC S					
#	COAL SEAM	MINE	STATE	ASTM RANK	TEMP (°C)	RECOV-ERY	UNTR.[1]	TR.[2]	UNTR.	TR.	UNTR.	TR.	UNTR.	TR.	UNTR.	TR.
1	BLACK CREEK	NATURAL BRIDGE	AL	Mvb	180[3]	94	1.22	0.65	0.42	0.16	0.69	0.47	13595	11694	1.79	1.11
2	[4]	PEACOCK	CO	HvBb	200[3]	92	1.88	0.67	0.95	0.10	0.60	0.57	13123	11001	2.87	1.22
3	IMBODEN	PARAMOUNT ELKHORN NO. 1 STRIP	VA	HbAb	150[3]	100	1.19	0.95	0.26	0.04	0.78	0.79	14273	13977	1.67	1.36
4	LOWER FREEPORT	LUCIUSBORO STRIP	PA	HvAb	180[3]	99	2.83	0.75	2.03	0.02	0.65	0.68	12775	11944	4.43	1.26
5	LOWER KITTANNING	[5]	PA	Lvb	150	98	0.96	0.57	0.53	0.08	0.39	0.47	14590	13630	1.32	0.84
6	MIDDLE KITTANNING	CONGO STRIP	OH	HvCb	180[3]	89	1.08	0.60	0.26	0.04	0.78	0.55	11184	9648	1.93	1.24
7	MAMMOTH	STORM KING	MT	SbA	150	92	0.83	0.57	0.32	0.16	0.45	0.36	11770	10910	1.41	1.04
8	PITTSBURGH	BRUCETON	PA	HvAb	150	100	1.31	0.80	0.61	0.05	0.68	0.71	14170	13430	1.85	1.19
9	UPPER FREEPORT	BAKER	MD	Mvb	200[3]	99	1.58	0.54	0.32	0.02	0.56	0.50	12642	11117	2.50	0.97
10	UPPER FREEPORT	COAL JUNCTION STRIP	PA	Mvb	200[3]	95	2.14	0.63	1.37	0.04	0.49	0.50	11256	10213	3.80	1.23
11	BROOKVILLE	HUMPHREY	PA	HvAb	180	96	4.20	1.17	3.06	0.13	1.11	1.01	13250	11346	6.34	2.06
12	LOWER FREEPORT	WEST VALLEY STRIP	PA	HvAb	180	98	4.14	1.04	3.09	0.22	1.01	0.78	13112	11395	6.31	1.83
13	PITTSBURGH	PITKULSKI STRIP	PA	HvAb	160	100	1.67	0.89	0.71	0.03	0.82	0.83	11650	10890	2.87	1.63
14	PITTSBURGH	NO. 43 STRIP	OH	HvAb	180	98	3.88	1.05	2.36	0.19	1.48	0.84	12657	10780	6.13	1.95
15	PITTSBURGH	NO. 43 STRIP	OH	HvBb	180	98	3.01	0.98	1.93	0.16	1.05	0.80	12846	10787	4.69	1.82
16	WHITEBREAST	LOVILIA NO. 4	IA	HvCb	150[6]	81	5.85	1.07	3.95	0.13	0.90	0.76	10870	9140	10.76	2.34
17	WYOMING NO. 9	RELIANCE	WY	HvCb	150	101	1.75	0.90	0.36	0.03	1.14	0.82	12410	11480	2.82	1.57
18	BEVIER	NO. 22 STRIP	KS	HvAb	150	93	5.00	1.98	2.92	0.36	2.04	1.60	12203	12224	8.19	3.24
19	ILLINOIS NO. 5	[7]	IL	HvCb	150	90	3.34	2.03	0.92	0.12	2.06	1.82	12650	11600	5.28	3.50
20	ILLINOIS NO. 6	RIVER KING	IL	HvBb	150[8]	89	3.69	2.12	1.13	0.11	2.25	2.00	12190	10030	6.05	4.23
21	INDIANA NO 5	ENOS	IN	HvBb	250[8]	91	3.27	1.84	0.70	0.20	1.98	1.64	12340	10095	5.30	3.64
22	[9]	HOMESTEAD	KY	HvAb	160	93	4.80	2.34	1.08	0.12	2.33	2.14	11380	11250	8.44	4.16
23	MINSHALL	CHRISNEY NO. 1	IN	HvCb	200	85	5.65	1.43	3.01	0.10	1.53	1.22	11320	10230	9.98	2.80
24	PITTSBURGH	IRELAND	WV	HvAb	180	99	3.89	2.09	1.38	0.02	2.18	2.03	13390	12190	5.81	3.43

1. Untreated.
2. Treated.
3. Modified Mode, 7-8 SCFH, all others batch mode.
4. Uncorrelated coal seam.
5. From Cambria slope preparation plant.
6. Four repressurizations in batch mode.
7. Information not available.
8. 1500 psig initial air batch mode
9. Blend of Kentucky seams No. 9, No. 11, and No. 13.

APPENDIX 19. SUMMARY OF COALS TREATED BY AIR/WATER OXYDESULFURIZATION

COAL[1]	MOISTURE FREE - WEIGHT PERCENT									
	ASH		CARBON		HYDROGEN		NITROGEN		OXYGEN	
	UNTR.[2]	TR.[3]	UNTR.	TR.	UNTR.	TR.	UNTR.	TR.	UNTR.	TR.
1	3.7	2.6	76.9	71.6	5.2	3.8	1.6	1.6	11.4	19.8
2	6.5	5.2	73.7	68.0	5.3	3.6	1.6	1.9	10.9	20.5
3	3.7	3.4	80.2	79.6	5.1	4.9	1.6	1.4	8.4	9.9
4	15.1	13.3	72.5	70.2	4.5	3.9	1.3	1.3	3.7	10.6
5	7.1	7.0	83.5	79.8	4.4	4.1	1.4	1.4	2.6	7.2
6	16.9	15.3	64.6	59.6	4.4	3.4	1.2	1.1	11.8	20.0
7	9.5	7.5	68.4	66.4	4.5	4.0	1.2	1.2	15.6	20.4
8	5.5	4.6	79.4	76.5	5.3	4.8	1.5	1.5	7.0	11.7
9	16.2	14.6	72.3	67.7	4.3	3.3	1.3	1.2	4.3	12.7
10	22.4	21.4	65.0	62.0	3.6	3.0	1.1	1.2	5.9	11.8
11	9.3	6.6	73.3	68.2	5.2	3.9	1.7	1.4	6.3	18.7
12	11.7	8.8	73.5	68.2	4.9	3.7	1.3	1.2	4.5	17.0
13	21.4	20.1	65.4	63.0	4.4	3.9	1.3	1.3	5.9	10.7
14	12.7	10.4	70.7	66.1	4.8	3.8	1.6	1.4	6.4	17.2
15	11.2	9.3	72.1	66.1	4.8	3.6	1.8	1.3	7.0	18.7
16	17.4	16.4	63.0	56.3	4.2	3.3	1.2	1.1	8.3	21.9
17	3.2	2.1	72.4	69.2	4.7	4.2	1.6	1.5	16.4	22.0
18	14.8	12.0	68.6	69.3	4.8	4.7	1.1	1.2	5.7	10.8
19	8.7	6.6	70.8	68.2	5.0	4.3	1.4	1.4	10.7	17.6
20	11.6	11.0	68.4	61.0	4.6	3.4	1.2	1.1	10.6	21.2
21	9.1	11.5	69.4	63.4	4.9	3.1	1.6	1.5	11.8	18.7
22	14.1	11.4	63.8	65.4	4.6	4.2	1.3	1.4	11.3	15.3
23	15.9	11.1	62.8	63.2	4.6	3.3	1.2	1.3	9.8	19.7
24	7.8	6.8	73.4	71.0	5.1	4.5	1.3	1.2	8.5	14.4

1. See Appendix 18.
2. Untreated.
3. Treated.