

EFFECTS OF EXCHANGEABLE CATIONS ON THE CONVERSION OF LOW RANK COALS TO GASES AND LIQUIDS

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INTRODUCTION

It has become evident that for low rank coals (generally of subbituminous C and lower) the inorganic constituents play major roles in their utilization. These coals are partly characterized by the presence of significant quantities of carboxyl and phenolic groups which are, to varying degrees, associated with alkali and alkaline-earth metal cations (1,2,3,4). As an example, in an earlier study (2) we reported that these exchangeable metal cations can account for approximately 3 wt% (dmmf) of a Montana Lignite. The dominant exchangeable metal cation in US low rank coals is calcium. However, appreciable concentrations of sodium and magnesium are found (2,3). Generally, approximately between 30 to 60% of the carboxyl groups are associated with metal cations (2,3).

It is important to differentiate between these exchangeable inorganic species and the mineralogical components when considering the behavior of low rank coals under processing conditions. The most significant differentiation is, of course, their dispersion throughout the coal matrix. In the case of the exchangeable cations, they are dispersed on an atomic basis; that is, each metal cation is associated with one or two carboxylic acid groups. There have been many electron microprobe studies (5), for example, which have shown that the inorganic elements under investigation are extremely uniformly distributed through a lignite. In essence, in that type of study, it is impossible to resolve precisely the distribution because the cations are of an atomic size, much lower than the resolution of the instrument. When considering the mineralogical species, it is well established that the great majority of the minerals exist in size ranges greater than 1 μm . Thus, they are several orders of magnitude greater in size than the cations. This size differentiation has, of course, ramifications on the chemical behavior of the species as well as physical considerations. It is extremely likely that the exchangeable metal cations are of much different chemical reactivity than a like atom in the lattice of some mineralogical species. Finally, it must be realized that on pyrolysis (which accompanies combustion, gasification and liquefaction processes) that the carboxylic acid salts will decompose to liberate a metal cation as some chemically reactive entity. Even after some degree of sintering, or agglomeration, the cation derived species will be finely dispersed, i.e., still much smaller than the vast majority of mineralogical particles.

It is the goal of this presentation to review several recent studies which have shown the importance of understanding the nature of the exchangeable cations in the utilization of low rank coals.

DIRECT LIQUEFACTION

It is well known that during direct liquefaction there is always some amount of material which appears as insoluble, residual solids (6,7). These solids are composed of a wide range of carbonaceous and inorganic materials. However, in this case we are only interested in those generated during the liquefaction of low rank coals. The most important feature of reactor deposits obtained from these coals is the formation of calcium carbonate as calcite and/or metastable vaterite (6,7,8,9). Detailed optical and SEM studies on these solids indicates that carbonate is precipitated and is not related to calcite grains which may occur in the feed low

rank coal (6,7). The source of the calcium is the exchangeable calcium present in these coals. A semi-quantitative relationship can be found between the amount of deposited solids and the ion-exchangeable calcium content of the feed coal (6). Liquefaction experiments made on an acid washed coal resulted in no production of calcium carbonate. A series of experiments were made on a Wyodak subbituminous coal which was first demineralized and then back exchanged with calcium acetate solution. The calcium loaded (5 wt%), dried coal was then reacted at 400°C in tetralin (N₂, CO₂ and H₂S atmospheres) for periods varying from 10 to 60 min. The quantity of calcium carbonate was determined quantitatively by measuring the volume of CO₂ evolved on treating the reaction products with 1N HCl. The results of this series of experiments are shown in Figure 1. The data are expressed as a first-order plot in terms of the conversion of carboxylates to the theoretical amount of CaCO₃ that could be produced. It is obvious that these data fit the first order plot rather well. Under these conditions 50% of the exchangeable calcium is converted to carbonate after about 23 mins. The calculated rate constant is $5 \times 10^{-4} \text{ sec}^{-1}$. In all cases, the crystallographic form of calcium carbonate produced was found to be a mixture of calcite and vaterite. From the data plotted in Figure 1, it can be seen that the rate of conversion of calcium cations to carbonate, under these conditions, is not affected by the presence of the three gaseous atmospheres utilized (H₂O, N₂ and CO₂).

COAL PYROLYSIS

In any investigation dealing with the role of exchangeable metal cations in coal pyrolysis one has to be concerned with several gauges of pyrolysis behavior. As examples, it is important to gain understanding of the effects of the cations on total weight loss, tar evolution, product gas composition, decarboxylation and kinetics. Several investigations have been made into this general area. Tyler and Schafer (10), Franklin et al. (11), and Otake (12) studied the effects of exchangeable cations on total weight loss and tar yield over a wide range of reaction conditions. They found, in general, that replacement of the metal cations by protons leads to an increase in weight loss. Murray (14) and Schafer (15,16) studied the decarboxylation of low-rank coals in fixed-bed reactors at slow heating rates. They found that removing the metal cations does result in an increase in the amount of decarboxylation at any given temperature.

In recent studies in these laboratories (17,18,19), Morgan found profound effects of the metal cations on rapid pyrolysis of a Montana lignite in an entrained flow apparatus. Total weight loss, at 1173 K in N₂/He, was found to be a function of the presence of metal exchangeable cations for a residence time of about 250 ms (Table 1).

TABLE 1
EFFECT OF CATIONS ON MAXIMUM WEIGHT LOSS IN ENTRAINED
FLOW REACTOR, 1173 K, DICF* BASIS (17,18)

<u>Sample</u>	<u>mmoles cation/g DICF Coal</u>	<u>wt Loss</u>
Raw	0.94	31
Ca A	1.11	30
Ca B	0.84	29
Ca C	0.75	35
Ca D	0.49	39
Acid Washed	--	49

* DICF: Dry Inorganic Constituent Free

As can be seen from Table 1, as the loading of calcium increases there is a drop in the total yield. The most significant reductions takes place after the initial

loadings. After a certain level of calcium cations the effects become essentially constant. Morgan's studies also suggested that presence of exchangeable cations caused a reduction in the amount of tars evolved when compared to the acid-washed sample. FTIR spectra of the tars evolved in these cases indicated that tars from the raw coal contain three times the amount of aliphatic hydrogen as do the tars from the acid-washed sample. Finally, it was found that the presence of the metal cations retarded the decomposition of the carboxylic acid groups. In this study, the carboxylic acid concentrations were determined directly on the pyrolyzed lignite samples.

GASIFICATION REACTIVITY

It has been well recognized that the measured gasification reactivities of coal chars, prepared under similar conditions, are a function of the rank of the parent coal (20,21). The chars of highest reactivities are those derived from lignites. Correlation have been made between the reactivities and the amount of exchangeable calcium cations in the coals or calcium in the chars (20,21,22). However, it was not until the work of Radovic et al. (23,24,25,26,27) that it was shown, in the case of calcium loaded onto a North Dakota Lignite, the catalytic species was calcium oxide. In addition, it was established that the observation that reactivity was a function of the severity of pyrolysis conditions was due to catalyst crystallite growth (sintering). As pyrolysis severity increased then the measured reactivities were reduced. A correlation was drawn between the observed gasification reactivities and the dispersion (as measured by crystallite size) of the catalytically active calcium oxide. Thus, the gasification reactivity of lignite chars was shown to be dominated by the concentration of their inherent catalyst sites.

It is important to recognize that the aforementioned reactivity measurements have been made on chars and not the corresponding raw or pretreated lignites. It is becoming evident that the exchangeable cations can have significant effects on combustion and gasification of the coals themselves. Some data reported by Morgan and Jenkins (19) and Morgan and Scaroni (28) have indicated relationships between the presence/absence of exchangeable metal cation and the rates of gasification/combustion of lignites. It is apparent from their data that the effects of the cations on rapid pyrolysis rates can ultimately result in enhancements in oxidation reactivity.

SUMMARY

As research proceeds in the area of low rank coal utilization, it is becoming obvious that the inherent inorganic constituents of these coals have profound influences on their behavior. The reason for this influence is related to the fact that a significant proportion of the inorganic components are in the form of atomically dispersed exchangeable metal cations. It is evident that variations in the metal cation content can bring about significant differences in the performance and behavior of these coals. With that in mind, it may well be that we should be looking in more depth at the "beneficiation" of low rank coals by effecting alterations in the chemical distributions of the cations associated with their carboxylic acid functionalities.

ACKNOWLEDGEMENTS

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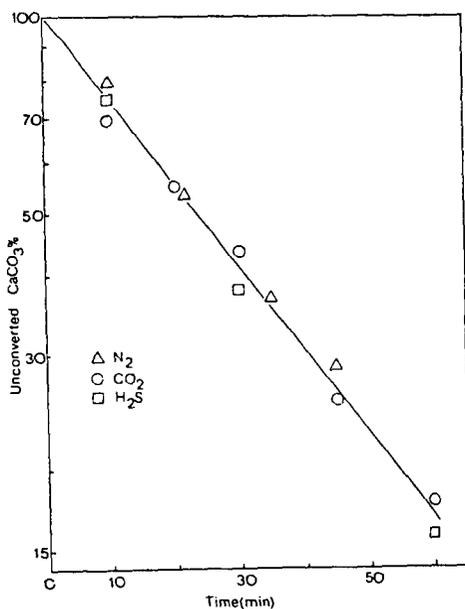


Figure 1. First Order Plot for Calcium Carbonate Formation at 400°C Under Pseudo-Liquefaction Conditions

Iron Sulfide Catalysis in Coal Liquefaction

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I. Introduction

The direct liquefaction of coal is a process that involves the interaction between coal, hydrogen, solvent, and catalysts. Mineral matter has been known to enhance the conversion of coal to liquid products.^(1,2,3) Addition of pyrite, pyrrhotite, and liquefaction residues to coal has been shown to affect the coal conversion yields and the viscosity of the products.⁽⁴⁾ Of all the minerals present in coal, pyrite (and marcasite) are the most important for coal utilization, especially in direct coal liquefaction.^(1,5) However, one has to remember that under coal liquefaction conditions pyrite rapidly transforms to a non stoichiometric iron sulfide $Fe_{1-x}S$ ($0 < x < 0.125$). It is noted that the sulfur formed as a result of the decomposition of pyrite is able to extract hydrogen from poor donor solvents. The stoichiometry of the pyrrhotite formed from FeS_2 depends strongly on the partial pressure of H_2S .⁽⁶⁾

A correlation between the conversion of coal to benzene soluble, and the stoichiometry of the iron sulfides was observed by Montano and Granoff.⁽⁷⁾ Higher conversion is accomplished by a more iron-deficient pyrrhotite.⁽⁸⁾ Stephens et al studied the effect of additives to an IL#6 conversion to liquid products. Their work strongly suggests that $Fe_{1-x}S$ and H_2S play a catalytic role in the conversion of coal to oils. These results, in good agreement with the ones obtained from in situ Mössbauer measurements,^(9,10) where there was clear evidence of interaction between the iron sulfides and some coal components. Many questions remain unanswered concerning the catalytic roles of H_2S and $Fe_{1-x}S$. Lambert⁽¹¹⁾ suggested that the catalytic activity observed for pyrite is solely due to H_2S acting as a hydrogen-transfer catalyst. In a recent study by Anderson and Bockrath⁽¹²⁾ on direct coal liquefaction more conversion was obtained when the ratio of sulfur added to an iron solution (the catalyst) was equal to the one needed to obtain pyrrhotite ($Fe_{1-x}S$). A very recent work by Ogawa, Stenberg, and Montano⁽¹³⁾ reporting the hydrogenation of diphenylmethane in the presence of pyrrhotite clearly shows that maximum activity is obtained when the partial pressure of H_2S is enough to maintain an iron deficient surface. Too high a partial pressure of H_2S in the reactor moves the composition of the surface towards FeS_2 and the conversion of diphenylmethane is reduced. Too low a partial pressure of H_2S leads to the formation of troilite (FeS) and lower conversion. These results indicate that optimum conditions are obtained when the surface of the sulfide is rich in metal vacancies, where dissociation of H_2S can take place forming highly reactive species.⁽¹³⁾ It is obvious that the understanding of the catalytic role of the iron sulfides lies in the investigation of their surface properties. We report in the present paper such a study, where surface techniques were used to observe the reaction of gases found under liquefaction conditions with the sulfides surfaces. A special reactor was developed to study the surface composition of the iron sulfides after reaction with oxygen containing compounds using conversion electron Mössbauer spectroscopy (CEMS). Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES) were used for determining the environment of iron species in the residues obtained from the study of the interaction of iron sulfides (FeS_2, Fe_7S_8) with pyrene.⁽¹⁴⁾

II. Experimental

Auger and electron energy loss spectroscopy measurements were performed using an UHV system with a base pressure of 10^{-10} torr. The system was attached to a reactor cell where the samples were exposed to high temperatures and gases. The reactions of FeS_2 , Fe_7S_8 , and FeS with CO , H_2 , O_2 , NH_3 , CH_4 , C_2H_4 , and higher hydrocarbons were studied between room temperature and 450°C . Figure 1 shows a schematic diagram of the system used in these measurements.

The CEMS measurements were carried out in a specially designed reactor to be described elsewhere. In this reactor the samples of ^{57}Fe foil were studied and treated with $\text{H}_2/\text{H}_2\text{S}$ to obtain the iron sulfides. The detector employed for the detection of the electrons was a $\text{He}/10\% \text{CH}_4$ flow counter connected in line with the reactor. The reaction of pure iron and iron sulfide with naphthoquinone were studied with this cell. The EXAFS and XANES measurements of the residues of the reactions of FeS_2 and Fe_7S_8 with model compounds were made at the Cornell High Energy Synchrotron Source.

Experimental Results

1. Auger and Electron Energy Loss Measurements on FeS_2 , Fe_7S_8 , FeS

Natural crystals of FeS_2 (pyrite) and Fe_7S_8 (monoclinic pyrrhotite) were used for the measurements. The (100) face of pyrite and the (0001) face of pyrrhotite were studied in the reactor, using a polycrystalline sample of FeS . All the samples show a characteristic $M_{2,3}$ VV Auger doublet with a separation of 5.0 eV (Figure 2). Two additional peaks (3 and 4 in Figure 2) are also observed for FeS . Peak 1 may correspond to transitions involving the s-3p ($2\sigma_v$) valence band while peak 2 may correspond to transitions involving the d-band. A typical set of Electron Loss spectra for FeS_2 is shown in Figure 3. Peak a is assigned to interband transitions from the $\text{Fe-}3d$ band to an empty state above the Fermi level. Peaks b and c may be assigned to transitions for one s-3p-like valence band (peak b to $1\pi_g \rightarrow 2\sigma_v$ and c to $2\sigma_g, 1\pi_u \rightarrow 1\sigma_g$ transitions.) Peaks d and e are attributed to collective oscillations of the conduction or valence electrons. Peaks f and g are assigned to surface and volume plasmons respectively. Peaks j and k are transitions involving the Fe-3p electrons ($M_{2,3}$ level). Peak l is due to transition from the M_1 level. The EEL spectra for the other sulfides are similar but the position and intensities of the peaks vary. In our measurements we observed EEL peaks with strong iron or sulfur character. Damaged iron sulfide surfaces show evidence of reconstruction through migration of sulfur after heating to 450°C . For undamaged sulfides, heating results in changes in the chemical composition of the surface; migration of sulfur also occurs. There is clear evidence of the presence of elemental sulfur on the pyrite and pyrrhotite surface but not on troilite (FeS). Since the maximum temperature attained was 450°C we do not expect that reduction of the FeS surface will take place. Essentially if the partial pressure of H_2S is low in the reactor the formation of FeS will occur by removal of sulfur from the Fe_{1-x}S surface. Once this state is reached no further loss of sulfur occurs and a fairly stable surface is obtained.

The interaction of the pyrrhotite with simple gases is more complex, damaged surfaces of FeS_2 and Fe_7S_8 react with CO at 450°C . We understand that as the result of the interaction of CO with Fe on the sulfide surface. This interaction is not detected with undamaged surfaces (pure single crystals) and with FeS . The formation of oxides on the surface is easily detected for FeS_2 and Fe_7S_8 after reaction with CO . It has been observed that CO undergoes a disproportionation reaction on Fe, $2\text{CO} \rightarrow \text{C} + \text{CO}_2$, with the formation of surface oxide due to the

dissociation of CO. (16) The surface oxide is rapidly removed by H_2 . The surfaces of the sulfides do not show any evidence in the Auger and EEL spectra of reactions with NH_3 , CH_4 , and C_2H_4 . However, they interact strongly with molecular oxygen forming a surface oxide. Figure 4 shows the surface oxide formed on pyrite after interaction with oxygen, for comparison purposes the EEL spectrum for $\alpha-Fe_2O_3$ is also shown. The present measurements indicate a high reactivity of the sulfide surfaces towards oxygen containing compound and very little towards light hydrocarbons and ammonia.

2. CEMS Measurements of the Surface Interaction of Naphthoquinone with Iron and Iron Sulfide Surfaces

A high purity ^{57}Fe foil was used for these measurements, such a foil was necessary in order to record rapidly a Mössbauer spectrum (less than one-half hour). The sample was placed in the holder inside of the reactor and H_2 was flown for 2 hours at $350^\circ C$ to reduce the surface and clean off any residual contamination. Figure 5a shows the Mössbauer spectrum at room temperature inside the reactor after cleaning. We studied the hydrogenation of naphthoquinone by introducing about 20 mg of the compound and flowing hydrogen at about 0.5 cc/sec. The temperature of the reaction was $305^\circ C$ and $405^\circ C$ and the time of reaction was one-half hour. After reaction the CEM spectrum was taken inside the reactor. No evidence of the formation of any known oxide was detected (Figure 5b). The same experiment was repeated using a sulfided sample (produced from the ^{57}Fe foil by flowing H_2/H_2S (10%) at $400^\circ C$). The spectrum for such a sample is shown in Figure 6a before reaction. After reaction with naphthoquinone we see clear evidence of the formation of Fe_3O_4 on the surface (Figure 6b). Magnetite is formed at the expense of the iron sulfide. This observation is in very good agreement with our earlier *in situ* Mossbauer work, (17) where a less surface sensitive technique was used for the measurements. We interpret these results as evidence of a greater reactivity of the iron sulfides surfaces towards oxygen containing organic molecules than the pure metal. It is noted that magnetite can be easily removed by further flow of H_2/H_2S . The magnetite layer is formed in the first few surface layers of the iron sulfide (see Figure 6).

3. EXAFS and XANES Measurements

Measurements were performed on the residues of the reaction of FeS_2 and Fe_7S_8 with pyrene. Pyrite and monoclinic pyrrhotite were used as chemical standards for the measurements. In Figure 7 the XANES spectra are shown for the residues of the reactions of pyrene with Fe_7S_8 and FeS_2 . The reactions were performed (14) at $440^\circ C$ in the presence of H_2 . One notices that the near edge structure is different for both residues, we attributed the difference to the presence of FeS in the reaction residues of Fe_7S_8 and pyrene. A compound that is not present in the residues of the pyrite run. The total EXAFS spectrum were analyzed and the Fourier transform for the residues of the FeS_2 run is shown in Figure 8a. (The peak positions are not corrected for phase shifts.) For comparison purposes the Fourier transform for pure pyrite and monoclinic pyrrhotite are also shown. The first prominent peak in all the spectra is due to Fe-S distances (2.262 Å for pure FeS_2). The second peak in pyrite (Figure 8b) is due to the other iron neighbors. For Fe_7S_8 the spectrum is complicated since there are many iron distances present (Figure 8c). For the residues of the reaction of FeS_2 with pyrene practically no Fe-Fe can be identified. This means that the iron atoms and vacancies in the $Fe_{1-x}S$ structure (14) (atomic % iron is 47.8) are extremely disordered and randomly distributed and that the only well defined coordination of the iron ions are the sulfur atoms. This (14) striking result since we should have expected as a result of the Mössbauer study (14) a better defined pyrrhotite structure.

III. Conclusions

We have observed that the behavior of iron sulfide surfaces depends strongly on the stoichiometry. Iron deficient surfaces show a higher reactivity than the troilite surface. At high temperatures (450 °C) there is elemental sulfur present on the iron sulfide surfaces. The metal vacancies can serve as centers for the dissociation of H₂S thus facilitating the transfer of hydrogen to organic entities. The pyrrhotite surface shows a great reactivity towards oxygen containing compounds. The surface oxide formed on the pyrrhotite surface are easily reduced when H₂ and H₂S are present in the reactor. The interaction between the pyrrhotites surfaces and light hydrocarbons is minimal.

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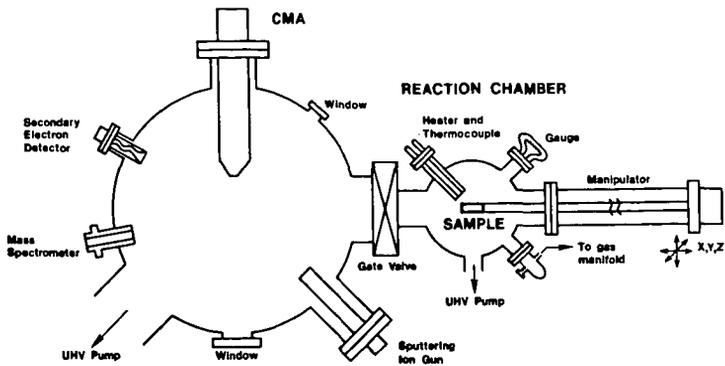


Figure 1. Schematic diagram of the UHV system used for the surface measurements

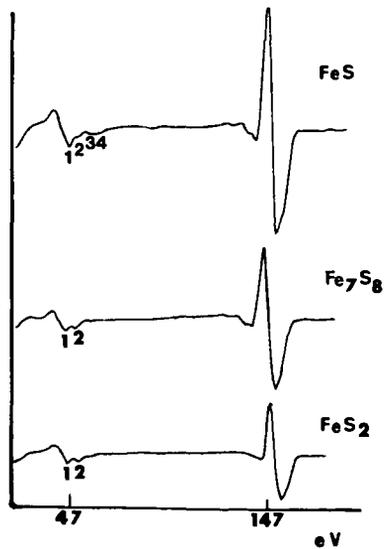


Figure 2. Low energy Auger spectra for the iron sulfides

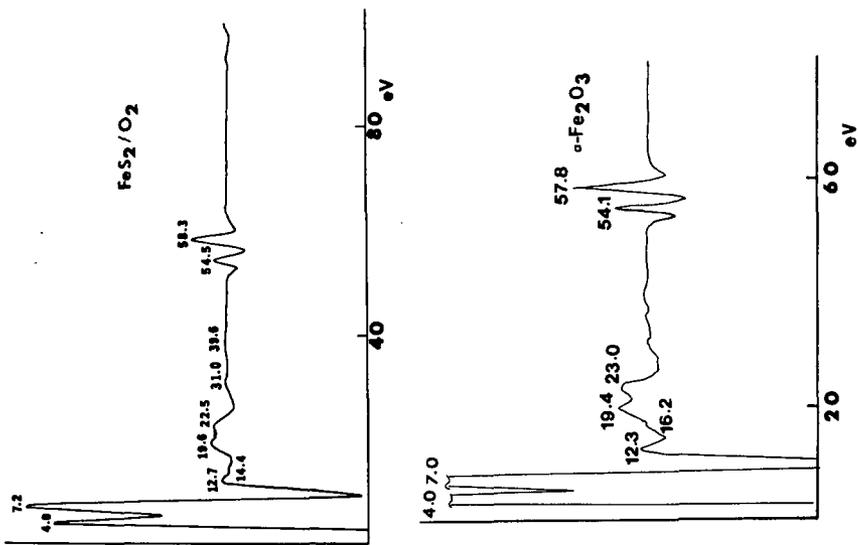


Figure 4. EEL spectra of FeS₂ after reaction with oxygen (a) and of α-Fe₂O₃ (b)

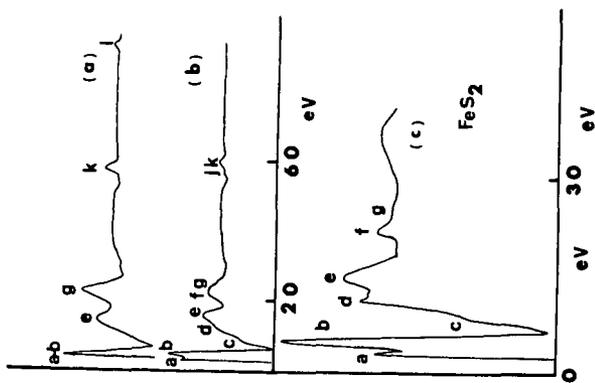


Figure 3. EEL spectra for FeS₂
 a) E_{primary} = 300 eV b) E_{primary} = 150 eV c) E_{primary} = 50 eV

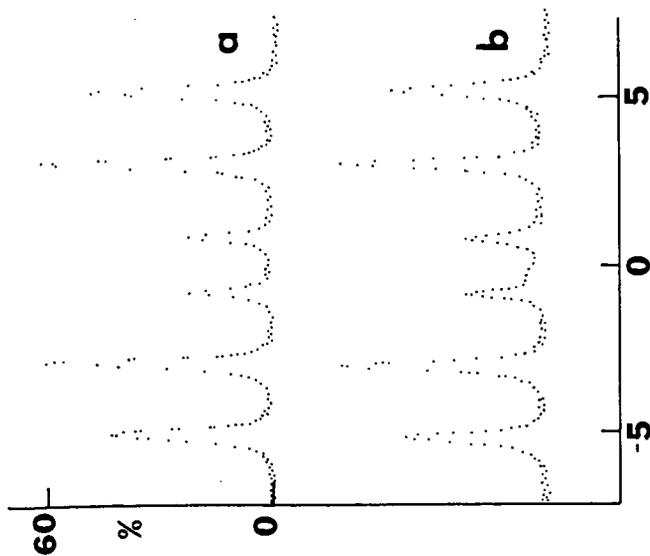


Figure 5. CEM spectra of ^{57}Fe foil (a) and after reaction with naphthoquinone (b). X-axis is in mm/sec.

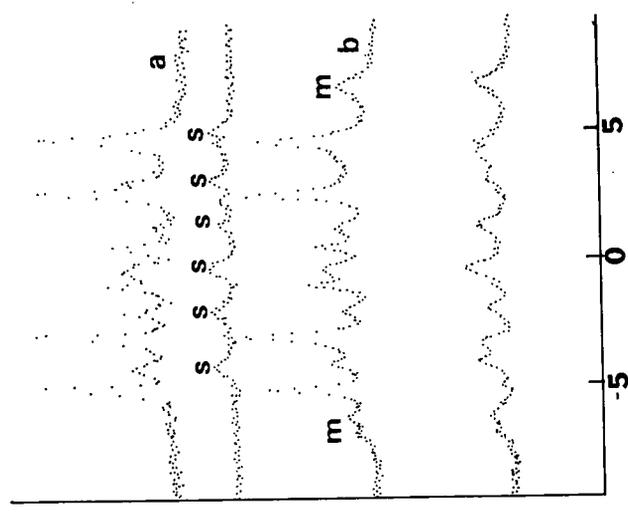
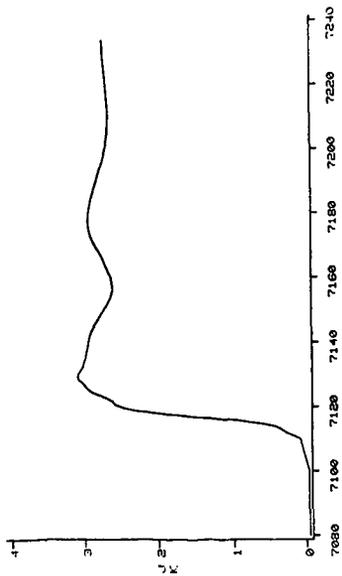


Figure 6. CEM spectra of a) sulfided ^{57}Fe foil, s; indicates the sulfide surface b) After reaction with naphthoquinone m; magnetic, bottom spectrum is the surface layers after reaction. X-axis is mm/sec.

FeS₂+H₂+PYRENE
AFTER BACKGROUND SUBSTRUCTION



Fe₇S₈+H₂+PYRENE
AFTER BACKGROUND SUBSTRUCTION

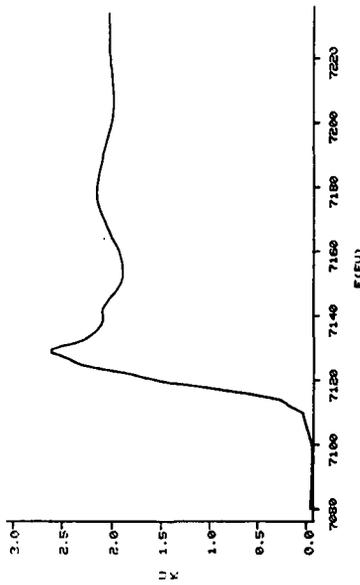


Figure 7. XANES spectra of the residues of the reactions of pyrene with a) FeS₂ and b) Fe₇S₈

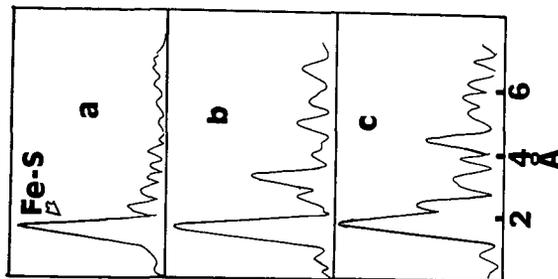


Figure 8. Fourier transforms of $\chi \cdot k$ (x EXAFS structure) for a) FeS₂ after reaction b) pure FeS₂ and c) Fe₇S₈. X-axis is in Å and without corrections for phase shifts.

NEW IRON OXIDE CATALYST REDUCTION ACTIVITIES
WITH HYDROGEN SULFIDE AND HYDROGEN

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INTRODUCTION

Various types of catalysts have been used for coal liquefaction. Among these catalysts, molybdenum and iron catalysts are most frequently used and they are usually combined with other metal oxides. Molybdenum catalysts, in the form of Co/Mo/Al₂O₃ wherein this notation represents some form of the metal oxides and the last species is the support, have been used in the H-Coal process. In others, iron catalysts have been used in the form of red mud which is mixed with elemental sulfur. The activity of iron catalysts has generally been regarded as low when compared with that of molybdenum catalysts. However, iron oxide catalysts became highly active for the conversion of coal-related model compounds when used in the presence of H₂S and H₂. For coal liquefaction in the absence of a heterogeneous catalysts, the use of a mixture of H₂S and H₂ instead of H₂ resulted in an increase in conversion.¹ Because of the interaction of H₂S with Fe₂O₃² and the fact that iron is presently the lowest cost transition metal, iron was selected as the basis metal for a new set of heterogeneous catalysts specifically designed for coal liquefaction using the H₂S-H₂ reducing gas medium.

EXPERIMENTAL

A series of 26 iron oxide catalysts were designed and synthesized. The supported iron catalysts prepared are listed in Table 1. The selection of the supports were based on the following objectives.

1. To clarify the effect of SiO₂ surface area, SiO₂ supports for catalysts 1, 2, and 3 were prepared at different pH's from a Na-free SiO₂ source.
2. To examine the effect caused by use of a different starting material to prepare SiO₂, catalysts 4, 5, and 6 were prepared from sodium metasilicate at different pH's and can be compared to catalysts 1-3.

3. To examine the effect of the precipitating reagent, catalysts 7 and 8 were prepared from $\text{Si}(\text{OC}_2\text{H}_5)_4$ with H_2SO_4 or NaOH , respectively. Catalysts 7 and 8 results are to be compared with those of catalysts 1 and 3.
4. To examine the effect of basic supports, metal oxides with basic properties were used for the supports of catalysts 9, 10, 11, 12, 13 and 14.
5. To examine the effect of the sulfate ion on the TiO_2 support, it was prepared in the presence of sulfate ions and the resulting catalyst 15 is to be compared with catalyst 14.
6. To examine the effect of additives to Fe/SiO_2 , small amounts of Mo, W, Co, and Ni oxides were added (catalysts 16, 17, 18, and 19) to the Fe_2O_3 on the surface of the catalyst.
7. To examine the effect of the sulfate and nitrate anions on the deposition of the iron layer, catalysts 20 and 21 were prepared.
8. To examine the effect of acidic sites on the Fe/SiO_2 catalyst, sodium- and potassium-poisoned catalysts were prepared (catalysts 22 and 23).
9. To examine the effects of the commercial TiO_2 and SiO_2 supports, catalysts 20 and 24 were prepared to be compared to catalysts 1 and 14, respectively.
10. To examine the effect of activated carbon which possesses an extremely high surface area as the Fe_2O_3 supports, catalyst 26 was prepared to be compared to catalyst 20 (SiO_2) and 24 (TiO_2).
11. To examine the effect of a simple admixture of Fe_2O_3 and SiO_2 , catalyst 28 was prepared to be compared with catalyst 20.
12. To enable comparison to a known commercial hydrogenation catalyst, $\text{Co}/\text{Mo}/\text{Al}_2\text{O}_3$ (catalyst 29) was included as a part of the series.

The catalysts were subjected to two reactions: hydrocracking of diphenylmethane to toluene and benzene, a model compound for the Ar-C bond cleavage of the coal structure, and hydrocracking of diphenyl ether to phenol and benzene, a model compound for the Ar-O bond cleavage of the coal structure. The reaction conditions for these reactions are summarized in Table 2.

RESULTS AND DISCUSSION

The design of the iron oxide catalysts was based on the following experimental findings.

1. For the hydrocracking of diphenylmethane, the effect of H_2S addition was augmented with iron oxide catalysts.³

2. The promotional effect of the H_2S addition on the catalytic activity varied with the preparative method for iron catalyst.³ Among Fe catalysts supported on SiO_2 , ZrO_2 , and TiO_2 , the Fe/SiO_2 showed the highest activity for the hydrocracking of diphenylmethane.
3. The Fe/TiO_2 catalyst was active not only for hydrocracking of diphenylmethane but also for hydrocracking of diphenyl ether.³

Besides these findings, it has been generally observed that the catalytic behavior of active components vary with the types of supports.

The time dependence of the diphenylmethane conversion is depicted in Figure 1. The value of 20 minutes reaction time was selected for the tubing bomb tests in order to differentiate catalyst effects.

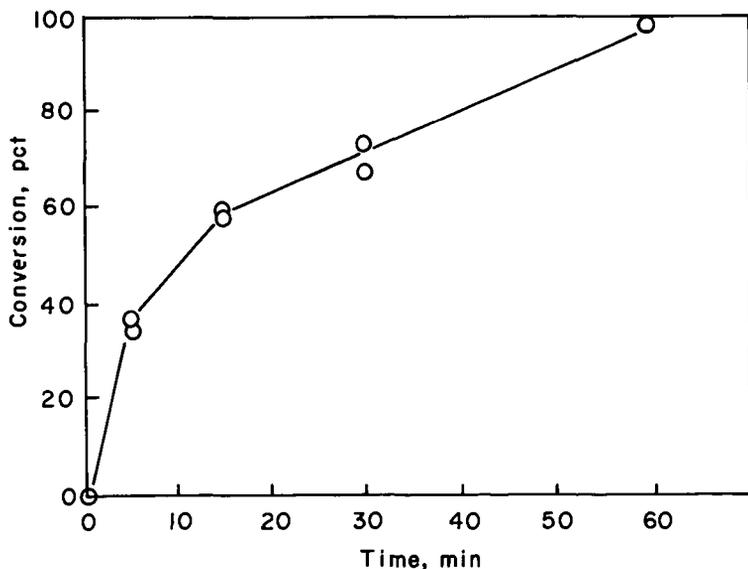


Fig. 1. Time dependence of conversion for hydrocracking of diphenylmethane. Catalyst, $\text{Fe}_2\text{O}_3/\text{SiO}_2$ (catalyst 20); catalyst/reactant, 50 mg/500 mg; reaction temperature, 425°C ; pressure at room temperature, H_2 700 psi, H_2S 100 psi; and reactor, 12-ml capacity.

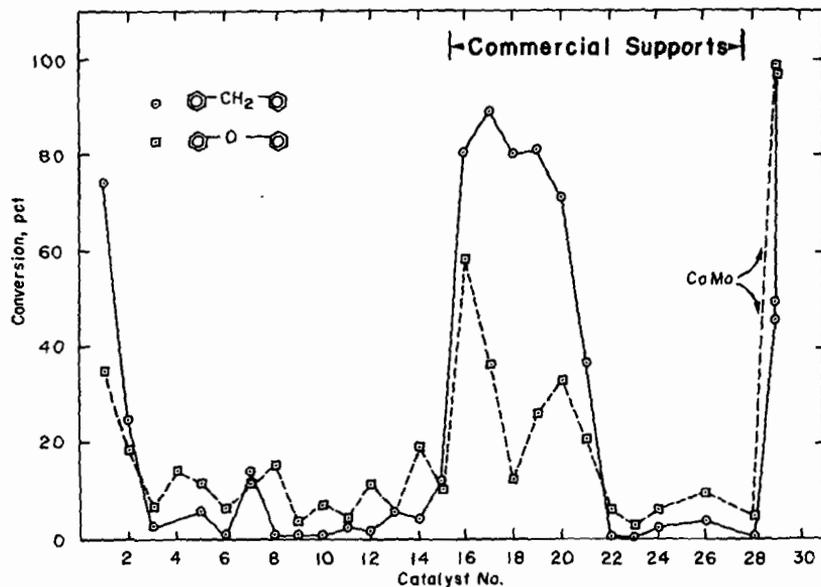


Fig. 2. Conversion of diphenylmethane (—) and diphenylether (---) with various catalysts.

The results of the catalytic reactions are given in Figure 2. For hydrocracking of diphenylmethane, the activities vary with different supports. This indicates that an interaction of Fe_2O_3 with the support occurred. The activity increased with an increase in surface area of support (catalysts 1, 2, and 3). Enhanced catalytic activity was observed by addition of Mo (no. 16), W (no. 17), Co (no. 18), and Ni (no. 19) oxides to the surface Fe_2O_3 as compared to Fe/SiO_2 (no. 20). The introduction of sodium or potassium to Fe/SiO_2 eliminated the catalytic activity (nos. 22 and 23 vs. no. 20). Similar phenomena were observed for catalysts 5, 6, and 8, which possibly contain sodium on the support. The sulfate ion had a negative influence on catalytic activity, cf. catalyst 5 with 2.

For the hydrocracking of diphenyl ether, the catalyst containing Mo and Fe (catalyst 16) was twice as active as the iron oxide catalyst. However, hydrogenated products such as methylcyclopentane and cyclohexane were produced in larger quantities with catalyst 16 than with 20. The Fe/SiO₂ catalyst activity increased with increased surface area of the support (catalysts 1-3), and was poisoned by sodium and potassium ions, cf. catalysts 22 and 23 with 20. The presence of the sulfate ion again retarded the Fe/SiO₂ activity, cf. nos. 15 to 14 and 20 to 21, as it did with diphenylmethane.

In general the catalysts required the presence of hydrogen sulfide⁴ and the commercially supplied sample of silica with its high surface area worked very well. The pH of the silica preparation method proved to be crucial to generating high surface area silica. The catalysts in which the iron oxides were deposited on silica exceeded or equaled the activity of a simple admixture of iron oxide and silica (catalyst 28). The iron oxide catalysts were the better than the commercial hydrogenation-hydrocracking catalyst Co/Mo/Al₂O₃ for the hydrocracking of diphenylmethane (e.g., catalyst 20 vs. 29) but the latter exhibited both hydrocracking and hydrogenation ability. However, the Co/Mo/Al₂O₃ was more active in the conversion of diphenyl ether.

ACKNOWLEDGEMENT

We are grateful for the financial support of the Department of Energy.

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Table 2. Reaction conditions

Reaction	Temperature (°/C)	Ratio of reactant/catalyst by wt.	Pressure (psi cold charge)		Reaction time (1 min)
			H ₂ S	H ₂	
Hydrocracking of diphenylmethane	425	10/1	100	700	20
Hydrocracking of diphenyl ether	425	10/1	100	1400	60

Table 1. List of catalysts prepared

No.	Catalyst		Source of Fe ₂ O ₃	Surface area (M ² /g)	Starting Material	Support	
	Composition (wt. ratio)					Precipitation Reagent	pH
1	Fe/SiO ₂ (1/9)		Fe(NO ₃) ₃	579	Si(OC ₂ H ₅) ₄	HNO ₃	1
2	Fe/SiO ₂ (1/9)		Fe(NO ₃) ₃	382	Si(OC ₂ H ₅) ₄	HNO ₃	5
3	Fe/SiO ₂ (1/9)		Fe(NO ₃) ₃	28	Si(OC ₂ H ₅) ₄	NH ₄ OH	11
4	Fe/SiO ₂ (1/9)		Fe(NO ₃) ₃	578	Na ₂ SiO ₃	H ₂ SO ₄	1
5	Fe/SiO ₂ (1/9)		Fe(NO ₃) ₃	349	Na ₂ SiO ₃	H ₂ SO ₄	5
6	Fe/SiO ₂ (1/9)		Fe(NO ₃) ₃	318	Na ₂ SiO ₃	H ₂ SO ₄	11
7	Fe/SiO ₂ (1/9)		Fe(NO ₃) ₃	568	Si(OC ₂ H ₅) ₄	H ₂ SO ₄	1
8	Fe/SiO ₂ (1/9)		Fe(NO ₃) ₃	39	Si(OC ₂ H ₅) ₄	NaOH	11
9	Fe/CaO (1/9)		Fe(NO ₃) ₃	1	Ca(OH) ₂	-(calined at 500°C)-	
10	Fe/La ₂ O ₃ (1/9)		Fe(NO ₃) ₃	11	La(NO ₃) ₃	NH ₄ OH	9
11	Fe/ZrO ₂ (1/9)		Fe(NO ₃) ₃	74	ZrOCl ₂	NH ₄ OH	9
12	Fe/ZnO (1/9)		Fe(NO ₃) ₃	5	Zn(NO ₃) ₂	NH ₄ OH	9
13	Fe/SnO ₂ (1/9)		Fe(NO ₃) ₃	28	SnCl ₂	NH ₄ OH	9
14	Fe/TiO ₂ (1/9)		Fe(NO ₃) ₃	41	TiCl ₄	NH ₄ OH	9
15	Fe/TiO ₂ (1/9)		Fe(NO ₃) ₃	56	TiCl ₄ + (NH ₄) ₂ SO ₄	NH ₄ OH	9

Table 1. (continued)

No.	Catalyst Composition (wt. ratio)	Source of Fe_2O_3	Surface area (M^2/g)	Support	
				Starting Material	Precipitation Reagent
16	Mo/Fe/SiO ₂ (1/9/90)	Fe(NO ₃) ₃ + (NH ₄) ₆ Mo ₇ O ₂₄	477	Commercial, Fisher Sci. Co.	
17	W/Fe/SiO ₂ (1/9/90)	Fe(NO ₃) ₃ + (NH ₄) ₁₂ Mo ₁₂ O ₄₂	496	Catalog No. S-156. 14-20 mesh Lot No. 744571	
18	CoFe/SiO ₂ (1/9/90)	Fe(NO ₃) ₂ + Co(NO ₃) ₃	550		
19	Ni/Fe/SiO ₂ (1/9/90)	Fe(NO ₃) ₃ + Ni(NO ₃) ₂	502		
20	Fe/SiO ₂ (1/9)	Fe(NO ₃) ₃	521		
21	Fe/SiO ₂ (1/9)	Fe ₂ (SO ₄) ₃	344		
22	Na/Fe/SiO ₂ (2/10/90)	Fe(NO ₃) ₃	200		
23	K/Fe/SiO ₂ (2/10/90)	Fe(NO ₃) ₃	205		
24	Fe/TiO ₂ (1/9)	Fe(NO ₃) ₃	11	Commercial, MCB, TX068501, Anatase	
26	Fe/Activated C (1/9)	Fe(NO ₃) ₃	946	Commercial, Union Carbide, LCK, Columbia ^R	
28	Fe ₂ O ₃ + SiO ₂			Commercial JMC, Puratronic + Fisher SiO ₂	
29	Co/Mo/Al ₂ O ₃	(Co, 3%; Mo, 9%)		Harshaw Co-Mo-0401	

The Influence of Mineral Matter on
The Rate of Coal Char Combustion
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Introduction

The rate of coal combustion can, in some instances, influence the design of boilers. The intrinsic rate of char combustion is, however, poorly known. Figure 1 shows that estimated intrinsic rate of char combustion can vary by a factor of 10^4 (1). The largest uncertainties are (2):

Property	Factor of Uncertainty
Surface Area	100
Effectiveness Factor	50
Catalysis	100
Crystal Structure	30

Other uncertainties account for less than a factor of four in the estimated intrinsic rate of coal char combustion.

Changes in the apparent rate of char combustion by a factor of 10 can influence the predicted performance of boilers. An example of these changes for a 660 MWe boiler is shown in Table 1. These figures were calculated using a well tested model of boiler performance (3). Increasing the accepted apparent rate constant by a factor of 10 predicts slightly improved performance, but decreasing the accepted rate constant by a factor 10 predicts severely degraded and unacceptable boiler performance.

This paper assesses one of the major uncertainty in estimating intrinsic rate constants, the influence of catalysis of the combustion rate of coal char.

Mineral Matter

Mineral matter contained in the coal could influence the rate of char combustion by blocking part of the coal surface or by catalytically increasing the rate of combustion. Figure 2 shows that the measured rate of combustion of purified nonporous graphics is uncertain by less than a factor of 3. This is a small difference compared to the spread in the overall rate data and suggests that some of the scatter in the measured rates of coal combustion are caused by the mineral matter in the coal.

Blocking of the surface area of coal by ash is unlikely to significantly change the rate of char reaction. Calculations for a coal with 25 percent ash indicate that, except at high levels of burnout, much less than 1 percent of the surface area of char will be blocked with ash particles.

Experiments have shown that small amounts of certain metals can accelerate the rate of char combustion (4,5,6,7,8,9). A number of anions and cations have been shown to accelerate the combustion of carbons at concentrations of 10 to 1000 ppm. Table 2 shows the relative influence on the combustion rate of various salts added as solutions to purified graphite. Relatively small amounts of metals can accelerate the rate of combustion by many orders of magnitude. Metals which appear in coal in significant concentrations which will accelerate the combustion of coal are 1) sodium and 2) calcium. Sodium can be present in coal in concentrations of 100-6000 ppm and calcium at concentrations of 50-12,000 ppm. The in-

fluence of relatively minor levels of sodium on the combustion rate of graphite is shown in Figure 3. Addition of sodium to a concentration of 15 ppm accelerates the reaction by one to two orders of magnitude; higher levels of sodium accelerate the reaction at a lower rate. Calculations show that the sodium must be distributed on nearly the molecular level to be effective. In addition, the influence of catalysis will be less pronounced at the higher temperatures of combustion where noncatalytic combustion proceeds much faster. No data exists at these higher temperatures. The available data indicates that combustion of carbon is accelerated by up to two orders of magnitude by levels of sodium normally present in coals at temperatures only slightly lower than combustion temperatures.

Summary

Minerals present in coal can accelerate the rate of char combustion by as much as a factor of 100. Molecularly attached Sodium and Calcium Compounds are likely to increase the char combustion substantially at low temperatures. However, information is not available and work should be undertaken to assess the acceleration of char combustion by minerals at the temperatures of combustion.

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TABLE I INFLUENCE OF COMBUSTION RATE ON POWER PLANT PERFORMANCE FOR A 660 MW_e COAL-FIRED BOILER

Kinetic Constant, g/cm ² s Atmosphere	Furnace Efficiencies (%)	Mean Furnace Exit Temp (°F)	Mean Heat Flux (Btu/ft ² ·hr)	Maximum Heat Flux (Btu/ft ² ·hr)	Position of Maximum Heat Flux (ft)	Maximum Flame Temp (°F)	Percent Unburned Fixed Carbon	Percent Combustibles In Ash (%)
43.1	2190	39,000	61,500	116	2650	0.66	5.97	
44.2	2160	40,300	62,800	102	2670	0.04	0.38	
33.6	2200	26,000	64,700	224 ^b	2350	32.17	69.03	

^aNormal Value

^bBoiler Exit Plane

TABLE 2 INFLUENCE OF METALS ON THE RATE OF GRAPHITE COMBUSTION (9)

Meta1	ppm	Relative Reactivity
Be	120	1
B	80	1
Al	70	3
Ca	120	4
mg	120	6
Sr	120	8
Ni	150	32
Cd	120	90
Ba	120	100
Na	120	230
Au	120	240
V	120	340
Cu	120	500
Ag	120	1,340
Cs	120	64,000
Mn	80	86,000
Pb	130	470,000

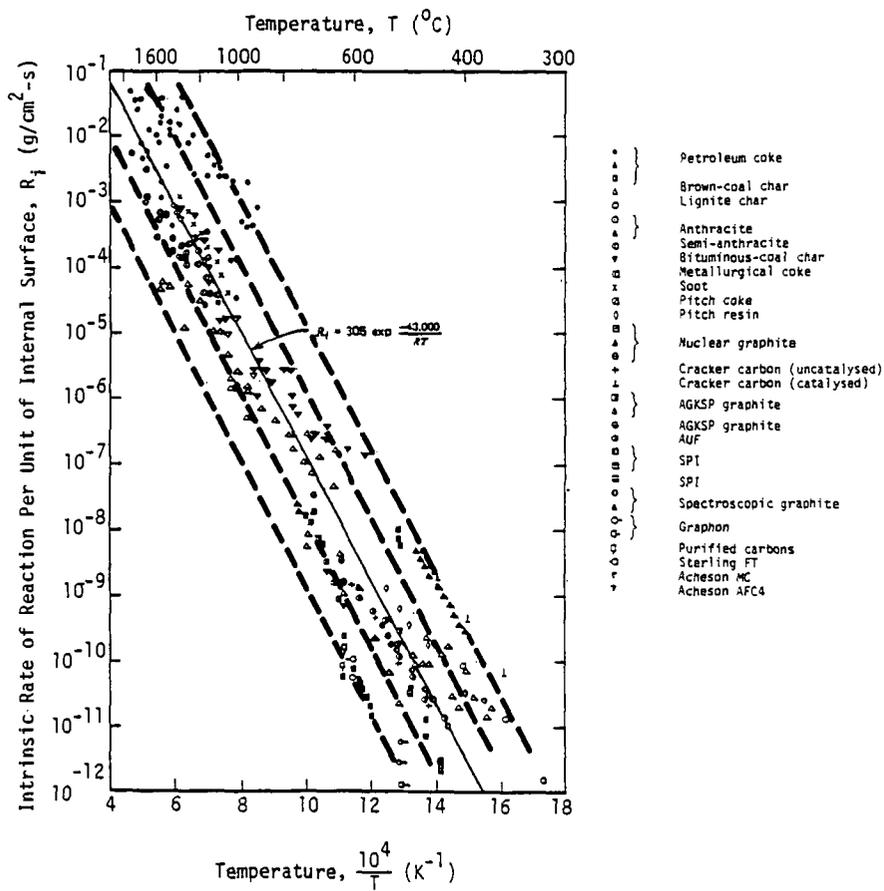


Figure 1. Intrinsic Rate of Reaction of Chars (1)

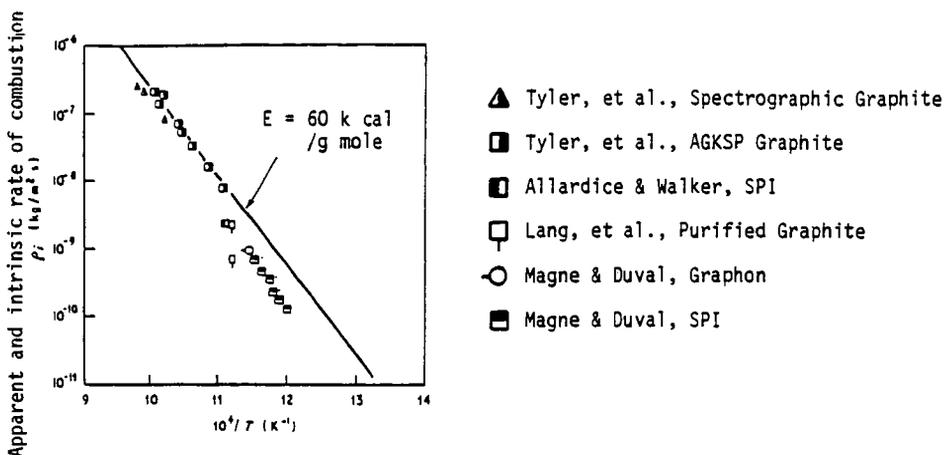


Figure 2. Combustion Rates of Highly Purified Graphite (4)

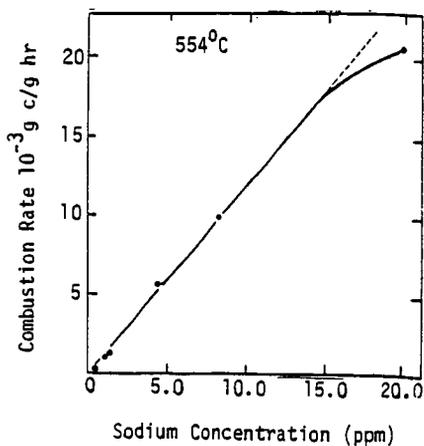


Figure 3: Catalysis of Graphite Combustion by Sodium (9)

BEHAVIOR OF MINERAL MATTER DURING COAL BENEFICIATION

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Each coal beneficiation unit operation responds to the physical and chemical properties of its feed. The response is as a "collage" of the individual particles but specifically as the frequency distribution of the component particle properties. These particle responses are not totally independent with particle property-process parameter interactions, but are also significantly controlled by the overall distribution of particle properties. Diligence is appropriately applied to establish the "collage" distribution by certain particle properties of the plant feed. This distribution provides the design bases for each unit operation in the flow sheet - including its capacity, flow rate, and unit loading: thus ultimately defining the separational performance, efficiency, and unit costs. Each unit operation should be sized and operated such that its optimum performance is well within the sensitivity range of its feed property distribution. The concern that the feed distributions may, at times, exceed the sensitivity range for some unit operation within in the system, is normally related to in situ coal variability, which can be extreme. The concern may extend to coal feeds from different seams and/or paleo-geological origin, mining system, or handling-storage system. Unfortunately, seldom are the concerns extensive and rarely are the feed characterizations detailed to each down stream operation.

The plant feed characterization usually is limited to particle size distribution and, if detailed, will include a particle gravity distribution for several size groupings greater than 28 or 16 mesh (washability). There is no generally accepted range for either the size or density groupings. The characterization of the individual particle fractions are usually limited to moisture, high temperature ash, and total sulfur content. In some unusual instances the low temperature ash and sulfide sulfur content may be determined. Pragmatism, procedures, and economics prevent the direct determination of minerals whose concentrations will be modified in the process. These levels are expressed in terms of ash content. If there is any characterization of the individual macerals or minerals, they are evaluated on the basis of the "total-composite" feed sample. Should flotation processes be anticipated, some "laboratory floatability" studies (1), may be carried out on some minus 16 or 28 mesh or other sized fraction. The origin of the particular fraction thus tested, seldom relates to that which will exist within the plant flow sheet. Feed hardness or friability tests (as Hardgrove Grindability Index, Drop-Shatter, etc.) may also be determined on the composite feed sample. If any comminution evaluations are made for the particular feed coal in the course of selecting a particular comminution device, they are usually made on a sample purported to be representative of the plant feed. Attempts to evaluate variations of particle strength or stability, maceral, mineral, or elemental composition, have been limited to research characterizations, as those reported by the author (2). We are almost totally devoid of pragmatic techniques to establish the particle sizes or volumes of individual components within a given individual coal particle (Richardson and Lovell (3)).

These observations can but lead to the conclusion that, in contrast, to typical unit operations in chemical engineering, the coal processing engineer assumes a feed to each unit operation within the plant system based upon the defined plant feed. Further, it is assumed that the collage of particles entering the plant as feed DOES NOT CHANGE in passing through the processing system and that the same number of particles 2 by 1-inch having densities between 1.40 and 1.45 gm/cc (or any other fraction) leaves the plant as enters! We know that this is not

correct even if we ignore the comminution operations within the plant designed to make such changes!

The composition of any individual coal beneficiation feed particle ranges from a nearly uniform metamorphized, phyto component through an almost infinite mixture series with macerals-minerals to an opposite end member as a nearly uniform mineral component. The behavior of a beneficiation feed during processing is determined by this almost limitless (and changing) distribution of individual particle compositions whose responses to process parameters are established by the particle properties as size, shape, density, hardness, porosity, and gas-liquid-solid interfaces. The particle responses establishes its direction and rate of movement toward one of the process product ports.

With coals as sedimentary rocks of paleophyto origin, their inorganic contents incorporate those components which were part of the original phyto system and associated substances, as well as those that have been introduced through all the subsequent geologic events. Accordingly, the mineral components found in coals reflect the nature of the originating plant systems, their environment, degree of water existing (whether of fresh or marine water character), oxidation-reduction conditions, temperatures, and pressures as well as those conditions to which the coal-forming strata have been subject during all the ensuing geologic epochs, including past and current circulating ground waters. Thus the observed complexity of the resulting physical characteristics is to be expected.

The minerals found in United States coals continue to be studied with the availability of improved instrumental procedures as X-ray diffraction, infrared absorption, and scanning electron microscopy beyond the traditional optical and chemical mineralogical techniques as applied to thin sections, polished pellets, and isolated particles. The minerals may be grouped into the silicates (kaolinite, illite, monmorillonite, and chlorite); the oxides (quartz, chalcedony, hematite); the sulfides (pyrite, marcasite, and sphalerite); the sulfates (jarosite, gypsum, barite, and numerous iron sulfate minerals); the carbonates (ankerite, calcite, dolomite, and siderite); and numerous accessory minerals as apatite, phosphorite, zircon, rutile, chlorides, nitrates, and trace minerals).

The greatest interest in mineral occurrences in coal particles for processing engineers relates to their potential liberation as an essential first step for their physical removal. Further the concern relates to the mineral behavior in each of the unit operations within the preparation plant and environmental implications within the preparation operations, for utilization of the clean coal product and the disposal of the refuse materials. The greatest attention has been given to the former interests, especially as applied to the liberation of pyrite in efforts to achieve the greatest possible sulfur reduction during processing.

Specific Responses of Coal Mineral Components During Processing

The "collage" of particles entering a coal processing plant are subject to a series of unit operations designed to achieve the desired level of quality improvement. The development of the initial set of particles is determined by the mining and preprocessing storage and handling systems. Undoubtedly these operations introduces stresses within the coal particles that lead to subsequent fracture failures. Any potential control of the nature of this particle set is usually extremely limited - being determined by production and economic factors. Situations which lead to oxidation, decrepitation, and absorption of excessive levels of moisture may be modified. The introduction of moisture prior to processing probably enhances clay swelling, tends to increase the amount of mineral fines (usually clays) into the plant stream, and may enhance localized heating, swelling, and oxidation. Initiation of dispersion of clays may begin here. Uncontrolled comminution during the handling and storage due to dropping from stackers, compaction by graders, etc. tend to create fines and probably selectively favors reduction of

the softer particles, especially certain clays. Other handling steps as particle movement through pumps, jigs, etc. tend to accent the production of fines. The oxidation of coal and temperature increases may favor the production of water soluble salts leading to acid plant waters and potential corrosion.

Primary crushing which usually involves breakers or single roll crushers may be preceded by a scalping operation to remove large particles of hard shales and sandstones. Such operations though not rejecting large amounts of refuse, do prevent wear, save energy, and prevent the introduction of additional refuse fines into the plant feed. The primary comminution devices usually are designed to control top size rather than achieve particle liberation, as such, they offer an opportunity to minimize fines production and show some selectivity toward the large, harder particles as shales and sandstones. Pre operational testing of comminution devices should consider the production of minimal amount of mineral fines. In coal processing systems where classifying rotating mills may be used, the selective build up of harder components within the mill can affect system performance.

In coarse coal sorting operations, as jigs and heavy media vessels, the softer minerals will tend to comminute due to attritional actions of particle movements and result in further dispersion into the plant circulating water system. In jigs, the production of mineral fines may be desirable to enhance hindered settling effects. In the Haldex heavy media system (4) and water only cyclones, the presence of mineral fines are essential to serve as an autogeneous heavy media system. Operational care must be taken to prevent the build up of unacceptable levels of fines leading to unacceptable fluid viscosity levels. Although quartz, clays, and other very fine mineral particles enhance these conditions, several type of clays, notably kaolinite and montmorillonite (especially sodium), are especially responsive. Suspended clay levels above five percent in such systems are most undesirable and may limit control of density in magnetite heavy media systems. The viscosity effect increases with decreasing particle size and with spherical shape which enhances settling rates. These concerns can also become critical in coal-water transport systems.

In fine coal sorting systems, heavy media cyclones, water only cyclones, tables and spirals the density and viscosity responses of suspensions are even more critical. In froth flotation the presence of clay fines is undesirable and usually require a desliming step ahead of flotation if their concentration becomes excessive.

It is in the water circuit that the build up of fines, especially clays must be controlled. The responses become evident in dewatering devices as centrifuges and filters. In the latter case, clays may enhance blinding resulting in unacceptable water contents of the filter cake, thin watery cakes, and unacceptable performance. Difficulties in the filtration of refuse fines has lead recently to the introduction of expensive processes as pressure and belt filters to meet environmental standards. In thickeners, excessive clay fines may reduce settling rates, minimize the formation of desirable underflow slurry densities, and lead to plant failure. It is in the dewatering stages and water circuit, as processes at the end of the flow sheet that these responses become acute. Although the use of one or more polymeric flocculants can usually control these situations, unexpected changes in plant feeds may require feed rate reductions or plant shut down.

Recent environmental regulations which essentially require closed water circuits make the problems of mineral fines buildup especially severe. Similar difficulties are associated with the disposal of refuse fines.

These examples describe some of the more prominent responses of mineral components in coal processing operations. Control of these problems can be achieved with better detection and analytical systems to identify the problems.

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