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Project-Title: Separation and Desulfurization of Pure Macerals: Part A - Desulfurization of Pure Maceral Fractions

ICCI Project Number: 86-87/2.2A-4

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ABSTRACT

Coal is a difficult material to characterize in terms of chemical, physical, or process properties. Until recently the heterogeneous nature of coal has presented several intractable characterization problems. However, workers at Southern Illinois University at Carbondale have recently demonstrated the ability to obtain pure single maceral fractions using a density gradient separation (DGC) method developed with support from ICDB. The objectives of this project were to modify the (DGC) method to obtain lab scale samples (10-20 gm) of four target maceral fractions from three Illinois coals and to characterize the macerals under various desulfurization conditions with pyrolysis and supercritical ethanol and methanol extraction.

Of the three desulfurization processes investigated, pyrolysis was least effective. Supercritical ethanol extraction was slightly more effective than pyrolysis. Supercritical methanol extraction was significantly more effective than pyrolysis or supercritical ethanol extraction. In general, increased temperature, longer reaction times, and the presence of KOH increases desulfurization for all three processes. The type of sample preparation affects sulfur removal. In general, particle size reduction, demineralization, and floatation all increase sulfur removal. The sporinite and vitrinite concentrates are more reactive in desulfurization processes than any of the other materials that were studied. They also gave the highest levels of desulfurization. Because they are more reactive than whole coals or floated samples, the other constituents in the coal matrix must reduce sulfur removals. This phenomenon has not been reported previously. It implies that the inertinite macerals may behave in a manner similar to activated charcoal and chemically absorb copious amounts of sulfur during the desulfurization processes. The practical result of this is that selection of coals on the basis of maceral composition could be needed to optimize thermal-chemical desulfurization.

EXECUTIVE SUMMARY

Coal is an extremely complex, difficult to characterize, heterogeneous material. To date, the steel industry, using petrographic methods in which individual coal macerals are not separated, has performed many of the most successful characterizations of coal. An expansion of the use of coal characterization in areas such as coal combustion, gasification, liquefaction and desulfurization requires a better understanding of the properties of the individual macerals and the separation of pure maceral concentrates analyzed by modern coal analysis techniques.

The use of the medical technique of density gradient centrifugation has recently been reported as being successful in the separation of maceral groups in coal and, in some cases, there has been a claim of the successful separation of individual macerals.

This project centers on the separation of target macerals from three Illinois coals. Following separation, whole coals and maceral concentrates were desulfurized by various methods.

The objectives of this study were to modify the present maceral separation techniques to obtain 10-20 grams of target maceral concentrates; characterize the chemical properties of the target maceral concentrates; and especially to test the maceral concentrates under various desulfurization conditions.

Because no standard or proven methods of identifying and quantifying the types of organic sulfur exist and because research on developing them are beyond the scope of current work, the most needed work was to determine the reactivity or ease of removing the organic sulfur from the various macerals. Although the chemistry needed for this objective is not difficult, the accumulation of 10 to 20 gram quantities of "pure" petrographically verified single maceral concentrates has not been possible until now. The results of previous projects at SIUC have demonstrated that the macerals can be separated and petrographically verified. The accumulation of much larger quantities than were previously being separated is a problem that was overcome in the present project by preconcentrating target macerals at their density cut points.

Supercritical fluid extraction of coals was previously reported as a method in the production of liquid fuel products from coal under mild conditions and as a medium for selective desulfurization of coal. Alcohols are expected to exhibit greater solubility for polar organic molecules due to hydrogen bonding and dipole attractive forces; they also provide the opportunity for chemical reactions during the

extraction due to the nucleophilicity of the alcohol oxygen and the tendency to act as a hydrogen donor. In addition, enol rearrangements may play a role in desulfurization.

As previously reported, different supercritical reaction conditions produced different extents of desulfurization of coals (33.9 - 65.7%). The variable desulfurizations are probably a result of differences in extents of conversion of the pyritic sulfur (to various alteration products, such as pyrrhotite), as well as organic sulfur functionalities (thiophenol, sulfide, and thiophenes) to light gases such as dimethylsulfide, hydrogen sulfide, and methylmercaptans.

Initial development of the supercritical desulfurization process utilized a batch reactor system. A new microreactor system was recently developed which features several advantages over the batch reactor system, more closely approximating the operating conditions of the continuous reactor. Using the microreactor system, the heating and cooling times are reduced as compared with those required for the batch reactor. This reduction of heating and cooling time, from 60-120 minutes in the batch reactors to 2-3 minutes in the microreactors, provides a better understanding of the reaction kinetics under supercritical conditions. Previous optical characterization of the batch reactor residues suggests that mass and/or heat transfer resistance might be present in the batch system. The microreactor minimizes these mass and heat transfer gradients.

The modified DGC method employing a preconcentration of macerals at a specific cut point allows for accumulation of a sufficient quantity of pure maceral concentrates for testing the desulfurization properties of individual macerals. The concentration of 10gm aliquots of pure maceral concentrates represents a new advance in separation technology. This is the first time that such large quantities of pure macerals have been segregated by any technique.

Of the three desulfurization processes investigated, pyrolysis was least effective. Supercritical ethanol extraction was slightly more effective than pyrolysis. Supercritical methanol extraction was significantly more effective than pyrolysis or supercritical ethanol extraction. Under optimum conditions, 55-65% of the organic sulfur can be removed from whole coals, and up to 80% can be removed from single macerals.

The conditions under which samples are tested are extremely critical to the extent of sulfur removal. In general, increased temperature increases desulfurization for all three processes investigated. Also, sulfur removal tends to increase with longer reaction times. The presence of KOH enhances the rate of sulfur removal. Sulfur can be

reincorporated from sulfur-containing gaseous products, and KOH enhances the sulfur reincorporation. Some of the sulfur removal may be retarded by incorporation of products during diffusion of product gases through the pore system of the residual coal. Thus, very fine particle sizes are desirable for chemical desulfurization.

Increased solvent to coal ratio increases desulfurization up to a 2:1 ratio. For all three processes studied, the three coals varied in rate of sulfur removal, the maximum observed sulfur removal, and tendency to incorporate sulfur-containing product gases.

The type of sample preparation affects sulfur removal. In general, particle size reduction increases sulfur removal. Demineralization results in increased sulfur removal in subsequent processing. Variations in sulfur removal due to variations in coal properties are observed for the micronized and demineralized coals.

The demineralized coals contain pyrite. Pyrite is removed by floatation at a 1.6gm/ml solution. Floatation produces a very clean coal that is more reactive than the demineralized coal. For float samples, approximately the same maximum desulfurization level is obtained independent of desulfurization process and coal properties.

The float samples demonstrate that organic sulfur is more amenable to desulfurization than was previously thought. Since high levels of sulfur removal are obtained during pyrolysis, the sulfur removals reported are not an artifact of sample dilution. Furthermore, either pyrite is less reactive than the organic sulfur or the pyrite (or derived products of pyrite) aid in sulfur incorporation reactions. The results suggest the thermal-chemical desulfurization should be preceded by a thorough physical cleaning that removes both pyrite and other coal minerals.

Finally, the main objective of this study was to investigate the desulfurization behavior of individual coal macerals. The sporinite and vitrinite concentrates are more reactive towards desulfurization processes than any of the other materials that were studied. They also gave the highest desulfurization levels. Since they are more reactive than whole coals or floated samples, the other constituents in the coal matrix must reduce sulfur removals. This phenomenon has not been reported previously. It implies that the inertinite macerals may behave in a manner similar to activated charcoal and chemically absorbs copious amounts of sulfur during the desulfurization processes. The practical result of this is that selection of coals on the basis of maceral composition could be necessary to optimize thermal-chemical desulfurization.

INTRODUCTION AND BACKGROUND

Coal is an extremely complex, difficult to characterize, heterogeneous material. To date, the steel industry, using petrographic methods in which individual coal macerals are not separated, has performed many of the most successful characterizations of coal. An expansion of the use of coal characterization in areas such as coal combustion, gasification, liquefaction and desulfurization requires a better understanding of the properties of the individual macerals and the separation of pure maceral concentrates analyzed by modern coal analysis techniques.

The use of the medical technique of density gradient centrifugation has recently been reported as being successful in the separation of maceral groups in coal and, in some cases, there has been a claim of the successful separation of individual macerals (Dyrkacz and Horwitz [1]; Dyrkacz et al. [2-5]; and Karas et al. [6]).

This project centers on the separation of target macerals from three Illinois coals. Following separation, whole coals and maceral concentrates were desulfurized by various methods.

Supercritical fluid extraction of coals was previously reported as a method in the production of liquid fuel products from coal under mild conditions and as a medium for selective desulfurization of coal [7-10]. Alcohols are expected to exhibit greater solubility for polar organic molecules due to hydrogen bonding and dipole attractive forces; they also provide the opportunity for chemical reactions during the extraction due to the nucleophilicity of the alcohol oxygen and the tendency to act as a hydrogen donor. In addition, enol rearrangements [10] may play a role in desulfurization.

As previously reported [9], different supercritical reaction conditions produced different extents of desulfurization of coals (33.9 - 65.7%). The variable desulfurizations are probably a result of differences in extents of conversion of the pyritic sulfur (to various alteration products, such as pyrrhotite), as well as organic sulfur functionalities (thiophenol, sulfide, and thiophenes) to light gases such as dimethylsulfide, hydrogen sulfide, and methylmercaptans.

Initial development of the supercritical desulfurization process utilized a batch reactor system [8]. A new microreactor system was recently developed which features several advantages over the batch reactor system, more closely approximating the operating conditions of the continuous reactor [10]. Using the microreactor system, the heating and cooling times are reduced as compared with those required for the batch reactor. This reduction of heating

and cooling time, from 60-120 minutes in the batch reactors to 2-3 minutes in the microreactors, provides a better understanding of the reaction kinetics under supercritical conditions. Previous optical characterization of the batch reactor residues suggests that mass and/or heat transfer resistance might be present in the batch system [8]. The microreactor minimizes these mass and heat transfer gradients.

The objectives of this study were to modify the present maceral separation techniques to obtain 10-20 grams of target maceral concentrates; characterize the chemical properties of the target maceral concentrates; and especially to test the maceral concentrates under various desulfurization conditions.

Because no standard or proven methods of identifying and quantifying the types of organic sulfur exist and because research on developing them are beyond the scope of current work, the most needed work was to determine the reactivity or ease of removing the organic sulfur from the various macerals. Although the chemistry needed for this objective is not difficult, the accumulation of 10 to 20 gram quantities of "pure" petrographically verified single maceral concentrates has not been possible until now. The results of previous projects at SIU-C have demonstrated that the macerals can be separated and petrographically verified. The accumulation of much larger quantities than were previously being separated is a problem that was overcome in the present project by preconcentrating target macerals at their density cut points.

Since this was the first time that substantial quantities of pure maceral concentrates were studied under any process response conditions, this program is unique. In addition, this was the first time that sufficient quantities of sample were generated to obtain detailed chemical data. Thus, this program afforded a unique chance to test the hypothesis that the chemistry of individual macerals is less complex than the chemistry of whole coals.

EXPERIMENTAL PROCEDURES

Maceral Separation

The approach being used to separate the macerals was the density gradient centrifugation (DGC) technique, which provides a better separation of macerals than can be obtained by traditional float-sink techniques. The samples were broken up in a planetary ball mill and then fed to a fluid energy mill (FEM). Pregrinding in a ball mill was necessary because the FEM requires a feed of particles less than 200 microns. In the FEM micronization is accomplished in the presence of, and powered by, dry nitrogen gas. Demineralization of the ground samples was done by standard

techniques using HCl and HF. Once demineralized, the sample is suspended in water by means of an ultrasonicator. The sample solution is then layered on the top of a density gradient formed by using a commercial gradient maker. The gradient is then centrifuged in a Beckman J2-21M centrifuge using a JCF-Z zonal rotor. Run time is one hour at 10,000 rpm (16,000 x G). The gradient is then pumped into a fraction collector using a dense chase solution (Fluorinert FC-43). The weight of each fraction is measured after it is dried and collected. The density of each fraction is determined with a refractometer and/or a density meter. These results are then plotted as a density profile as shown in Figure 1.

In this research, the DGC technique was modified and improved to obtain larger size samples. This is being done in two ways. First, the coal is divided into its natural divisions, lithotypes, which are the easily identifiable natural associations of macerals that make up the coal seam. This can be done (and routinely is being done in the SIUC Maceral Separation Laboratory) by careful hand-picking, or by centrifugation at a particle size (-100 to -200 mesh) that liberates the lithotypes from each other. Pseudovitrinite and normal vitrinite have been successfully separated from each other in this manner. Second, low frequency maceral phases (those occurring at less than 5% of the whole coal) can be preconcentrated by centrifugation of bulk quantities (10 grams or more) at cut-off points for the target macerals. This procedure results in fractions which are enriched in the target maceral relative to the whole coal and allows relatively larger amounts of pure macerals to be obtained much more easily than starting with the raw coal. These feedstocks are then subjected to the DGC technique. The low density arm in Figure 1 (< 1.22 gm/ml) represents liptinite macerals. When the fraction < 1.22 is concentrated, the profile shown in Figure 2 is seen in which the various peaks represent specific liptinite macerals.

Target macerals for this study include sporinite, vitrinite, semifusinite and fusinite. These are the major maceral components which contain significant organic sulfur. Resinite and cutinite were not studied because the abundance of these macerals is low in Illinois coals and they contain relatively low concentrations of organic sulfur. Vitrinite contains most of the organic sulfur in the coal and was of primary interest. Semifusinite also contains significant amounts of sulfur but may be less amenable to desulfurization treatments.

Desulfurization

The desulfurization of the coal by pyrolysis and with supercritical ethanol and methanol extraction was carried out using the microautoclave system, shown schematically in Figure 3. The apparatus consists of a 10cc stainless steel

DENSITY PROFILE SIU 647J

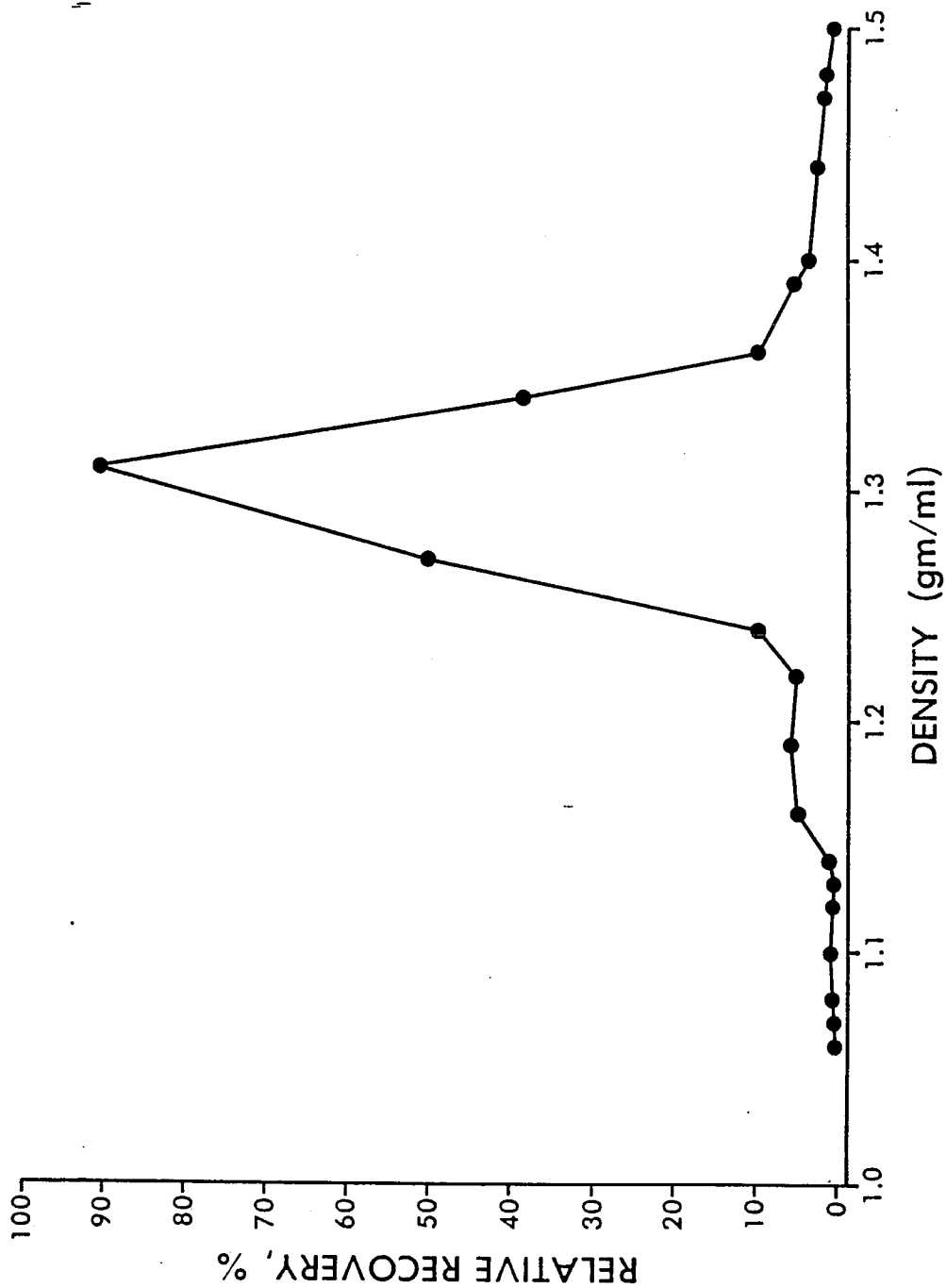


Figure 1. Density profile of a whole coal (SIU 647J). The peak represents the vitrinite macerals that make up the bulk of the coal. The arm on the low density side represents the liptinite macerals.

DENSITY PROFILE SIU 647J LIPTINITE

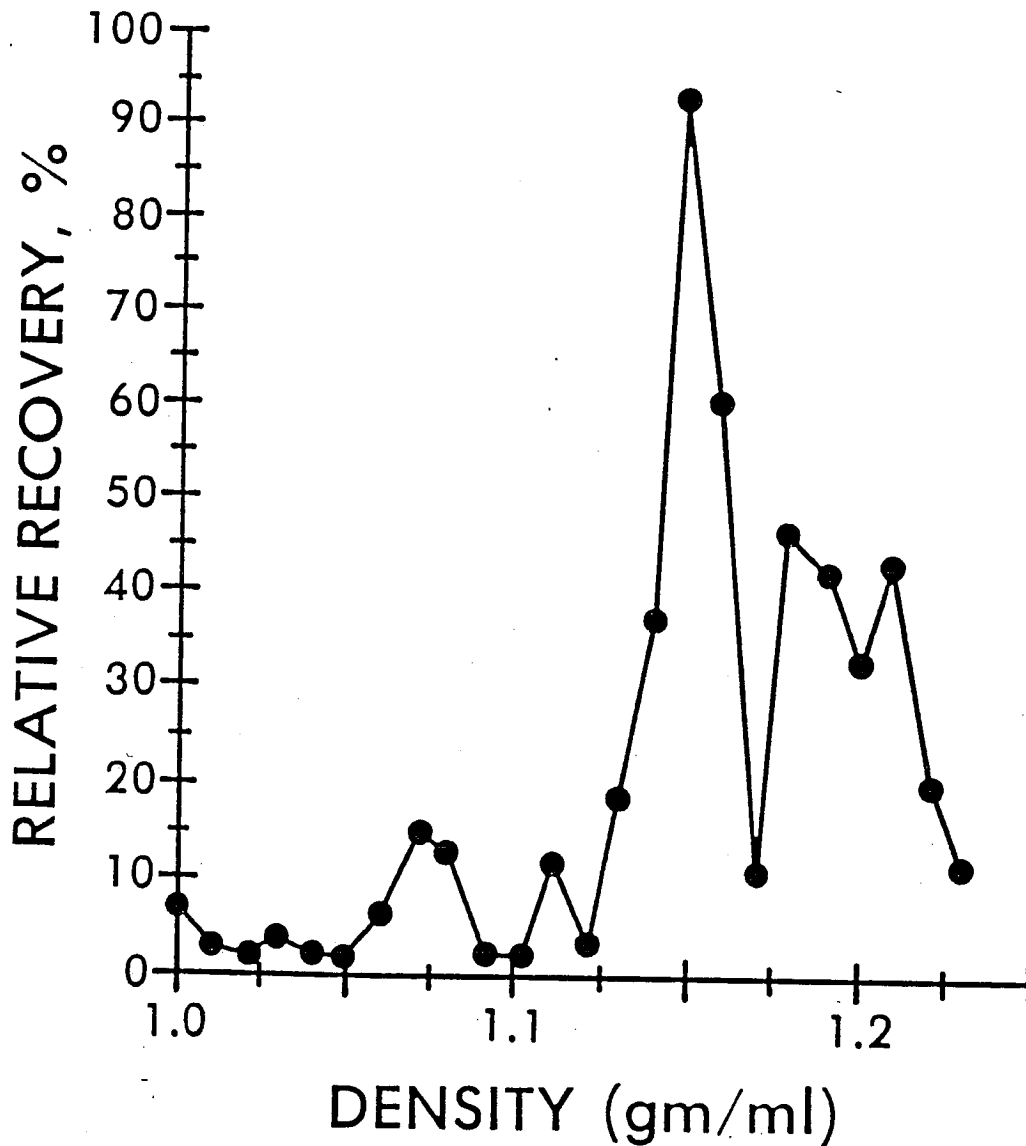
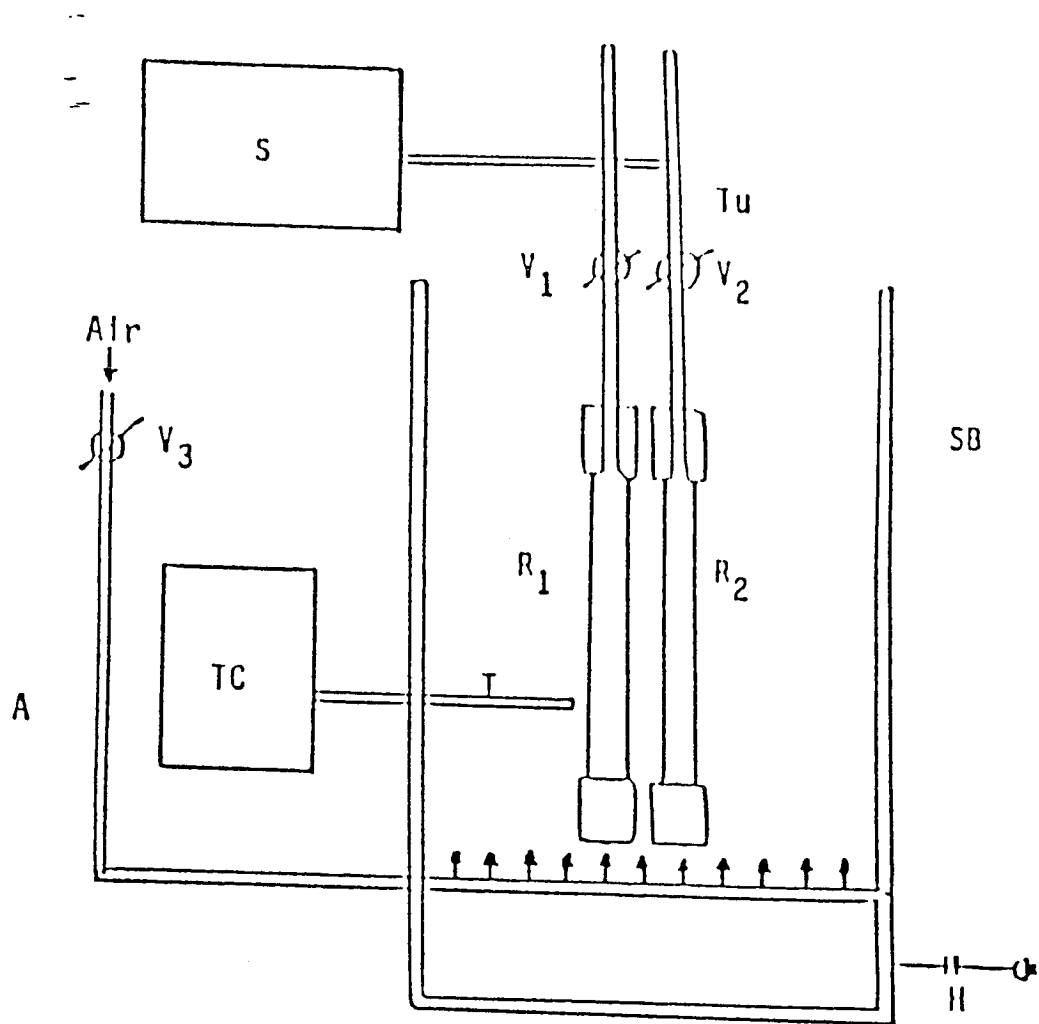


Figure 2. Density profile of the liptinite arm of the whole coal profile. This profile is from material preconcentrated from the coal at < 1.22 gm/ml. Much more detail is evident, and the strong peak at 1.15 gm/ml represents sporinite while the smaller peaks at 1.11 and 1.08 gm/ml represent resinite and cutinite respectively.



- SB = Sand bath
- R₁, R₂ = Microreactor with inside volume of 10 cc.
- V₁, V₂ = Venting Valve
- V₃ = Air flow control valve
- S = Automatic shaker
- T = Thermocouple
- TC = On-Off Temperature Controller
- A = Air flow pipe
- H = Heating source wire
- W = Cooling water sink
- Tu = Connecting tubing

Figure 3. Schematic diagram of the microreactor used in the supercritical desulfurization system.

microautoclave linked to a metering valve and a quick disconnect fitting with high pressure tubing. The reactor system is attached to an automatic shaker, which is supported above a fluidized sand bath. The shaker allows the autoclave to be agitated during reaction to ensure uniformity of reaction. The fluidized sand bath is controlled using an Omega temperature controller to ensure temperature stability.

The microautoclave is first flushed with nitrogen to remove any oxygen present. The reactor is then charged with coal (1gm) and solvent (2gm). Further pressurized flushing with nitrogen is carried out to ensure the removal of oxygen following the sealing of the microautoclave. The valve is opened following successive flushes to release the pressurized nitrogen. The charged microreactors are then attached to an automatic shaker held above a sand bath. The fluidized sand bath is then raised so as to fully immerse the reactor in the fluidized sand which is preheated to the desired temperature. The shaker is then switched on for the desired reaction time. Pyrolysis tests are conducted in the same manner with the exception that no solvent is used.

Following reaction, the sand bath is lowered and the reactors are removed from the shaker. The reactors were vented by slowly opening the metering valve. Following approximately one minute with full valve opening, the reactors are quenched in a water bath.

The solid residues are removed from the reactors; the solid is ground and then dried in a vacuum oven at 95 degrees Celsius for approximately 90 minutes, with total sulfur being determined for all solid residues.

The three principal coals being studied are from the Illinois Basin. These coals include: 1) SIU 1386, from the Herrin No. 6 seam; 2) SIU 647J, from the Brazil Block seam; and 3) SIU 1749, a wash plant mixture of Illinois No. 5 and No. 6.

The maceral compositions of these coals show that SIU 1386 and 1749 are typical midwestern coals and that SIU 647J contains a higher than average content of liptinite macerals (Table 1). The experimental program for desulfurization is shown in Table 2.

TABLE 1. RESULTS OF PETROGRAPHIC AND CHEMICAL ANALYSES

Sample	#1	#2	#3
SIU No.	1386	647	1749
ISGS No.	22440	----	22443
Seam	Herrin #6	Brazil Block	Blend #5 & #6
PETROLOGY			
Vitrinite	62.5	51.6	67.1
Pseudovitrinite	20.2	14.1	18.4
Total	82.7	65.7	85.4
Sporinite	2.8	6.3	4.3
Resinite	0.4	0.5	0.3
Cutinite	1.3	4.1	1.0
Fluorinite	0.4	0.0	0.4
Bituminite	0.0	0.3	0.0
Liptodetrinite	1.3	0.4	0.7
Total	6.2	11.6	6.7
Fusinite	1.4	3.1	0.3
Semifusinite	8.1	16.0	6.6
Macrinite	0.0	0.1	0.0
Semimacrinite	0.6	0.5	0.5
Micrinite	1.0	3.0	0.4
Total	11.0	22.7	7.8
Reflectance, (%)	0.42	0.49	0.73
CHEMISTRY			
Total Sulfur			
Raw	4.30	1.43	2.11
Micronized	4.13	1.35	2.12
" & Demineralized	3.68	1.26	1.96
" & " Float	2.04	0.79	1.28
Sulfur Forms			
Micronized			
Sulfate	0.28	0.33	0.32
Pyritic	0.80	0.44	0.44
Organic	3.05	0.58	1.35
Total	4.13	1.35	2.11

TABLE 2 EXPERIMENTAL PROGRAM

Desulfurization Process -----	Sample Preparation -----
Pyrolysis	Raw (-60) mesh Micronized Micronized, Demineralized Micronized, Demineralized, 1.6 Float
Supercritical Extraction with Ethanol	Raw (-60) mesh Micronized Micronized, Demineralized Micronized, Demineralized, 1.6 Float
Supercritical Extraction with Methanol and KOH	Raw (-60) mesh without KOH Raw (-60) mesh Micronized Micronized, Demineralized Micronized, Demineralized, 1.6 Float Pure Separated Macerals

RESULTS AND DISCUSSION

Pyrolysis

The results of sulfur removal during pyrolysis are given in Table 3. The test conditions listed were chosen to simulate conditions being examined by the Illinois Geological Survey in ongoing related work. In general sulfur removal increased with increased temperature and time up to a maximum level for all three coals studied. Under mild pyrolysis conditions the raw (-60) mesh sample of coal #1 appears to have a faster rate of desulfurization than coal #2. However, as pyrolysis severity increases sulfur removal for coal #2 becomes equal to and then greater than that for coal #1. At maximum severity sulfur removal in coal #2 is greater than in coal #1. Under mild pyrolysis coal #3 is even less reactive than coal #2. Pyrolysis experiments under severe conditions for coal #3 show a similar pattern. However, from the results listed in Table 3 it can be concluded that the three coals have different properties that affect the sulfur removal. Both kinetic and ultimate yields appear to be a function of coal type. A larger suite of samples would need to be tested to establish the cause and effect relationships between coal properties and sulfur removal.

To determine the effect of particle size on the removal of sulfur during pyrolysis, tests were run on micronized samples of the three coals. In general, the micronized coals were found to be less temperature and time sensitive than the -60 mesh size fractions of the same coals. Maximum sulfur removal for coals #1 and #3 increased, but maximum sulfur removal for coal #2 decreased over the -60 mesh size fraction. Except for the high severity test of coal #2, sulfur removal in the micronized coals was greater than the -60 mesh size fraction of the same coal. Therefore, sulfur removal in pyrolysis seems to be related to particle size.

The decrease in sulfur removal at high severity noted for coal #2 may be due to a higher oxidation sensitivity for that coal. The data also indicate that mass transport is more limited in coals #1 and #3 than in coal #2. To confirm this observation, porosity in a series of raw and pyrolyzed samples would need to be determined. In general, sulfur removal of coal #1 is greater than coal #3, which is greater than in coal #2. Thus, the properties of the three coals markedly affect sulfur removal, and changes in order between -60 mesh and micronized fractions indicate that relationships between coal properties and sulfur removal are complex.

Pyrolysis tests on demineralized samples of the three coals indicate a higher temperature and time dependency in the demineralized samples than either size fraction of the raw coals. Under almost every process condition demineralized samples expel more sulfur than untreated coals. In general, sulfur removal increases with increased time and temperature.

TABLE 3. RESULTS OF PYROLYSIS DESULFURIZATION
(% SULFUR REDUCTION)

Sample	400		450		500		550	
	30	60	30	60	30	60	30	60
Raw #1	11	16	7	25	26	25	28	27
Raw #2	5	9	20	18	21	29	32	
Raw #3	2		10	17		27	23	31
Micronized #1		15		23	28	32	29	33
Micronized #2			22	22	22	23	23	22
Micronized #3			29	18		25	25	38
Demineralized #1	13		22	20	29	28	35	41
Demineralized #2	23	30	31	27	39	41	49	32
Demineralized #3	13		35	18	25	37	35	40
Float #1	25	15	63	31	5	22	51	
Float #2	24	25	48	21	33	41	48	
Float #3			44	32	32	32	42	

Murdie [11] has previously reported that these decreases are the result of sulfur capture by coal constituents. The observed decreases are repeatable and, therefore, are not the result of experimental inconsistencies. Sulfur removal under both mild and severe conditions are higher in a demineralized coal than in a micronized coal. Thus, both the kinetics and maximum removal are affected by the demineralization process.

The relative order of the reactivity of the coals are changed by demineralization. For demineralized samples, coal #2 desulfurized faster than coal #3, which is faster than coal #1. Maximum removals are greater for coal #2 than for coal #1, which is about equal to maximum removals for coal #3. The tendency to incorporate sulfur back into the coal during processing appears to be greater for coal #3 than coal #2, which in turn has a greater tendency to incorporate sulfur than coal #1.

The data for the demineralized coal demonstrate that demineralization affects sulfur removal during pyrolysis. At this point, the reasons for the effects are unclear and are opposite of those to be discussed for supercritical extraction experiments. The increased maximum removals, rate of removal, and reincorporation sensitivity could be attributed to one or more of the following explanations: 1) chloride and fluoride left on the surface may cleave sulfur bonds at elevated temperature or swell coals; 2) increase in porosity due to mineral removal; 3) sulfur groups may be activated by the acid treatments or secondary air oxidation during demineralization; 4) removal of sulfate sulfur from pyrite particles; 5) removal of minerals which inhibit desulfurization or catalyze sulfur incorporation reactions; and 6) demineralization may remove sulfur which is difficult to supercritically extract. Additional tests are required to evaluate these possibilities.

Data for sulfur removal during pyrolysis of the floated samples are limited. Tests of the float fraction of coals #2 and #3 have been completed, but analytical analysis of the pyrolyzed samples is unavailable at this time. Data from the float fraction of coal #1 is highly variable. Tests at selected conditions will be repeated to verify the reported data. The data do indicate that extremely high sulfur removal can be obtained by pyrolysis of the float fraction. Coals also become more susceptible to sulfur incorporation after floatation to remove pyrite and other residual minerals has been completed.

The extremely high sulfur removals observed after pyrite removal by floatation is an important observation. Either of two possible explanations of the experimental results may have important commercial implications. The first is that trace amounts of cesium cations are left after floatation and washing. Since the float samples have been washed and are known to contain small concentrations (less than 1000 ppm) of

cesium cations, the noted effect would suggest that cesium chloride could be used commercially to catalyze chemical desulfurization. An alternative explanation is that subsequent organic sulfur removal is enhanced by pyrite removal. This phenomenon could be the result of reducing sulfur incorporation that may occur in the presence of the iron pyrite or an altered pyrite material. A third explanation is that organic sulfur removal might decrease the overall molecular weight at the residual organic fraction. This may lead to the lowering of the coal's glass transitional temperature resulting in an increased solubility of sulfur compounds which would otherwise be found in the vaporous phase. Removal of pyrite may enhance sulfur liberation by allowing molecular structures within the organic phase to recondense at a faster rate and, therefore, minimize the melt phase. This explanation is supported by the observation that residues from tests conducted on float material is less consolidated than residues obtained from other samples.

Figure 4 shows a typical comparison between sulfur removal during pyrolysis and sulfur removal during supercritical methanol extraction (SME). Except for cases of sulfur incorporation, SME tests yield higher sulfur removals than corresponding pyrolysis tests. Both the rate and maximum sulfur removals are greater for the SME process. Because higher sulfur removals occur at mild conditions for the SME process, combustion properties are less likely to be deleteriously affected by SME. However, the float fractions liberated nearly the same amount of sulfur in the pyrolysis and SME tests, and this suggests that maximum sulfur removal is independent of process type.

Supercritical Ethanol Extraction

Sulfur removal during supercritical ethanol extraction (SEE) is listed in Table 4. The test conditions were chosen to include but expand conditions explored in previous CRSC projects. As in the case of pyrolysis, sulfur removal during SEE runs tend to increase with increased time and temperature. The rates of desulfurization in ethanol are higher than desulfurization during pyrolysis of equivalent samples. Again, sulfur incorporation is observed under certain conditions. For the -60 mesh size fraction sulfur removal for coal #2 is higher than for coal #1. Again, micronization increases the sulfur removal rate. Sulfur removal for the micronized sample of coal #1 is greater than sulfur removal in the micronized sample of coals #2 and #3 which have similar sulfur removal rates under SEE conditions. Demineralization appears to have a negative effect on sulfur removal. Since SEE has been reported to be extremely sensitive to oxidation, these results may indicate that the coal was oxidized during demineralization. The float samples desulfurized to a greater extent than the micronized or demineralized samples; they show more variability in

TABLE 4. RESULTS OF DESULFURIZATION WITH SUPERCRITICAL ETHANOL EXTRACTION (% SULFUR REDUCTION)

Sample	350		400		450		500	
	30	60	30	60	30	60	30	60
Raw #1	11		24		26	31	16	24
Raw #2	12		23		17	8		22
Raw #3			12		16	1	5	29
Micronized #1	24		26	24	24	31	38	45
Micronized #2	22		21	26	29	23	28	
Micronized #3	15		24	25			26	17
Demineralized #1	14		13	13		13		44
Demineralized #2	37			39			46	59
Demineralized #3	14		21					33
Float #1				19			48	66
Float #2	34		- 34					
Float #3	16							

Pyrolysis vs. methanol extn.

Ref.1 coal (-60 mesh)

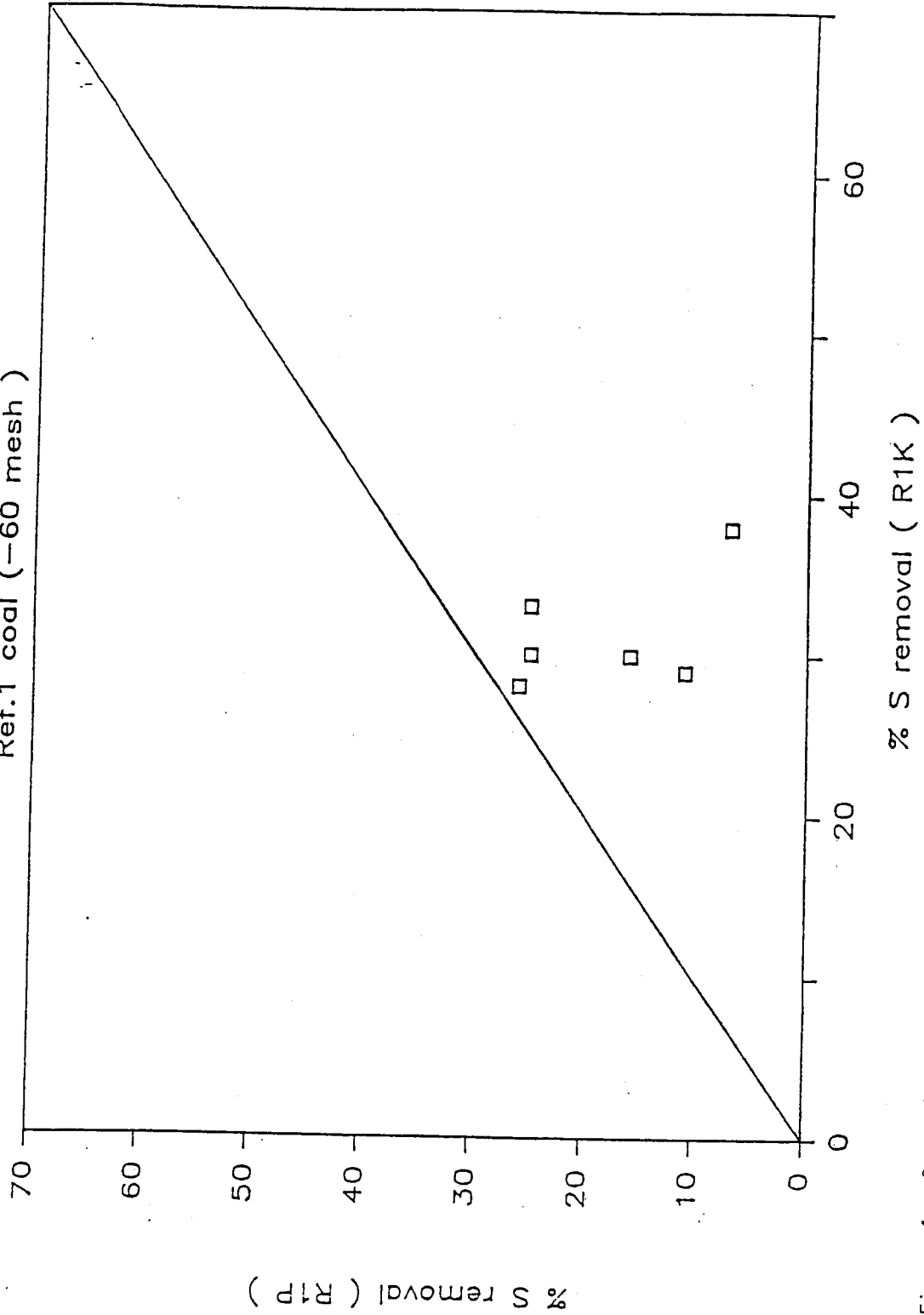


Figure 4. Comparison of the results of sulfur removal with pyrolysis and supercritical methanol extraction (SME) techniques. The location of all points below the parity line indicates that the sulfur removal is greater under all conditions with the SME process.

sulfur removal and a maximum desulfurization similar to pyrolysis and SME processes.

From the above data we conclude that: 1) coal properties affect desulfurization under SEE conditions; 2) SEE is mass transport limited; 3) demineralization has a negative effect on SEE under mild severity conditions; and 4) floatation results in higher sulfur removal.

Figure 5 is a typical parity plot comparing SEE and SME results on coal #1. Each data point represents sulfur removals at a specified time and temperature employing ethanol and methanol as solvents. The plot indicates that SME removes more sulfur than does SEE. In general, SEE and SME sulfur removals asymptotically approach a maximum as desulfurization severity is increased. Approach to the maximum is faster for SEE than for SME. Thus, although a larger amount of sulfur is removed by methanol, supercritical ethanol extraction has faster kinetics.

Supercritical Methanol Extraction

Data for sulfur percent removal during supercritical methanol extraction (SME) are listed in Table 5. The conditions tested include but expand the range of conditions employed in other CRSC projects. Major emphasis of the work has been placed on the SME process because SME gives the widest range of sulfur removals and, thus, is more likely to yield more information pertaining to sulfur removals in macerals than other processes. The data in Table 5 are for a standard test employing 2gm of methanol, 1gm of coal, and 0.05gm of KOH.

Prior to standardization the effect of 5% KOH loading on sulfur removal was tested against no KOH addition. Figure 6 gives typical results for SME tests conducted with and without KOH. At low-severity (350 degrees Celsius, 60 minutes) the presence of KOH shows a slight positive effect on sulfur removal. Under slightly more severe conditions (450-500 degrees Celsius, 30 minutes) the difference between sulfur removal in tests with and without KOH addition increases. The sulfur removals under high-severity conditions (500 degrees Celsius, 60 minutes) show no effect or a negative effect of KOH addition. In many tests at higher temperatures sulfur removals decrease as reaction times are increased from 30 to 60 minutes (see Table 5). These patterns are independent for the three coals studied and the preparation the coal receives. However, the extent of the reduction is coal dependent. Coal #1 and #2 show a slight reduction in sulfur removal, whereas coal #3 gives large amounts of sulfur incorporation. This phenomenon has been observed previously by Murdie [11]. The incorporation is short-lived at moderate-severity and conditions at which maximum sulfur incorporation occurs are difficult to pinpoint with batch reactors. At higher severity sulfur incorporation

Methanol vs. Ethanol extn.

Ref.1 coal (-60 mesh)

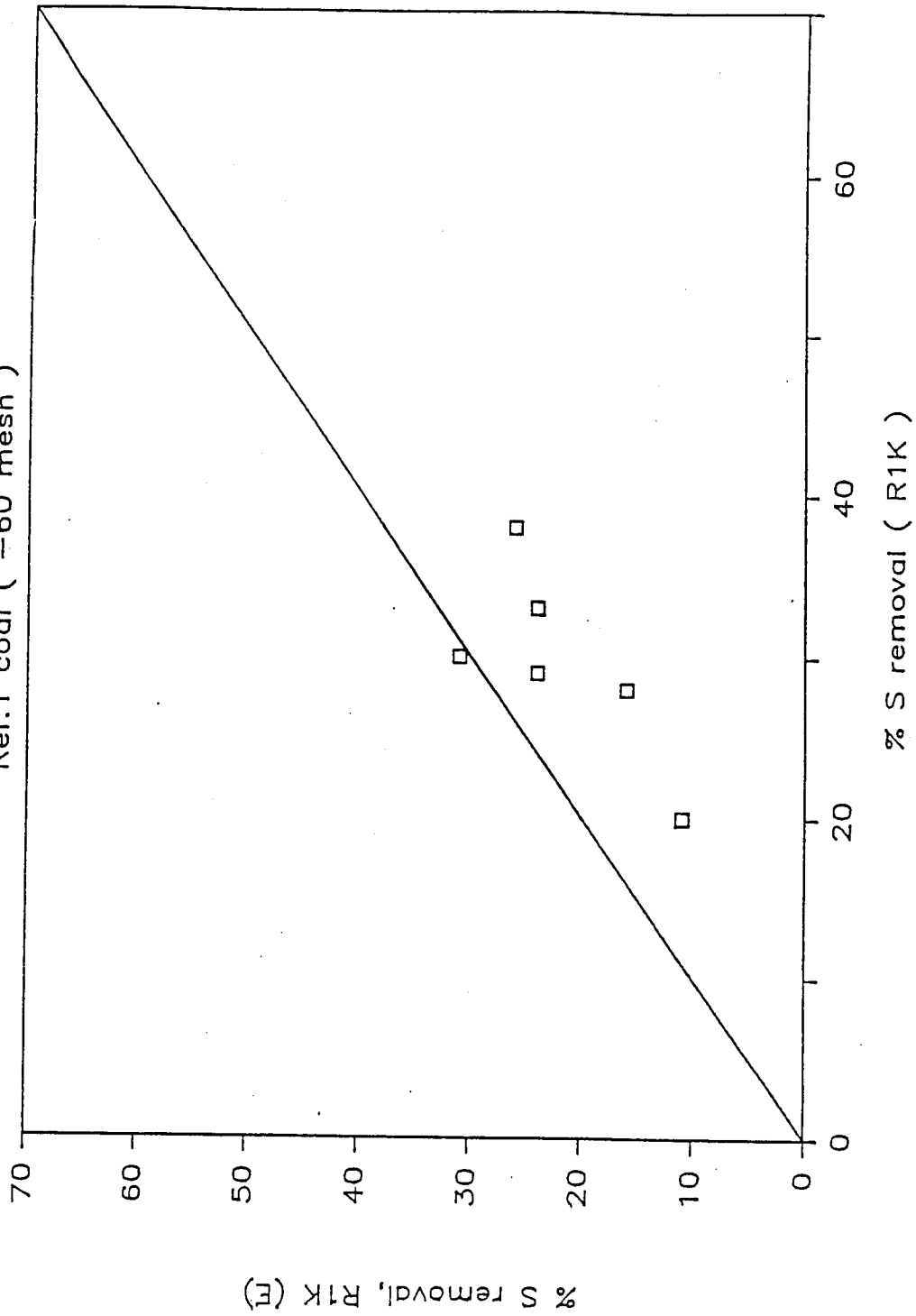


Figure 5. Comparison of the results of sulfur removal with supercritical methanol and ethanol extraction techniques. The location of all points on or below the parity line shows that the SME process removes a greater amount of sulfur for any given condition.

TABLE 5. RESULTS OF DESULFURIZATION WITH SUPERCRITICAL METHANOL EXTRACTION (% SULFUR REDUCTION)

Sample	350			375			400			425			450			500			550	
	30	60	120	30	60	120	15	30	45	60	120	15	30	60	15	30	60	15	30	60
Temperature (°C)	20	38	41	33	43	53	14	29	39	30	34	43	38	50	28	53	51	41		
Time (minutes)	28	58		22	36	48	22	18	40	33	44	16	41	29	39	28	48	28	48	
Raw #1	9	21		18	35		21	15	18	30		18	32	43	37	28				
Raw #2																				
Raw #3																				
Micronized #1	34	10	13	36	55	25	31	57		44	34	20	44	57	29	51				
Micronized #2	10	10	15				25		40	41		14	26	18	36	51				
Micronized #3																				
Demineralized #1	18											18	48	43	41	52				
Demineralized #2	4	19	32	23	27		25	30	16	24		35	54	31	28					
Demineralized #3	15	39		33	7		31		26	49		55	48	45	45					
Float #1	54	42	29	29	42			53	31	27		53	53	53	44	64				
Float #2	27	20		28			21	11	11	34			28	37	47					
Float #3	11	27		41			26	44	34	34			57	46	47	35	6			
Vitrite #2																				
Sporinite #2																				

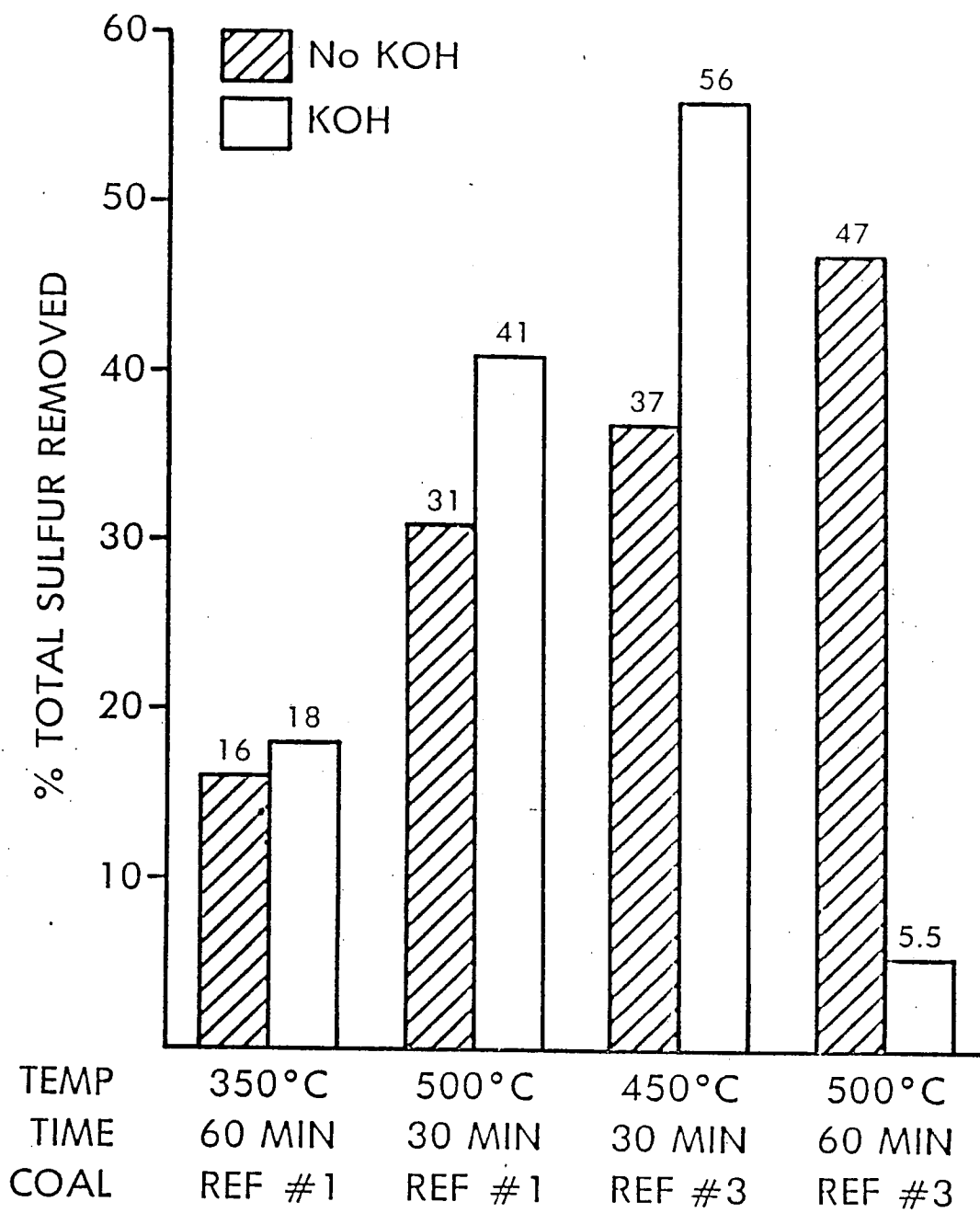


Figure 6. Typical desulfurization results with supercritical methanol extraction and KOH as a catalyst. Desulfurization is increased with the KOH in all but the most severe conditions.

may be permanent. The severe incorporation noted with coal #3 may be an experimental coincidence in obtaining the maximum incorporation at the specified temperatures. However, coal #3 did show a consistent linear decrease in sulfur removal as a function of reaction time at 500 degrees Celsius. At 15 minutes reaction time 65% sulfur removal was obtained. At 60 minutes reaction time 6% sulfur removal was obtained. Although incorporation reactions complicate data interpretation, the increased sulfur removals in the presence of KOH were significant enough to standardize use as an operational procedure. Thus, most of the data reported are for 5% KOH loadings.

Figure 7 demonstrates some typical sulfur removals for the -60 mesh size fractions of the three coals being investigated. The data in Figure 6 indicate that coal #1 is generally more reactive than coal #2 under mild-severity conditions. At moderate-severity sulfur removals for coal #2 are equal to sulfur removals for coal #1. At high-severity, coal #2 shows less sulfur incorporation than coals #1 or #3. Sulfur removals for coal #3 are always equal to or less than sulfur removals for coals #1 and #2. Maximum sulfur removals are greater for coal #2 than for coals #1 or #3 which are approximately equal. Sulfur removals for coal #3 appear to be temperature independent and time dependent.

Also shown in Figure 7 is a comparison of the effect of solvent to coal ratio on sulfur removal for coal #1. As expected, 2gm of solvent and 1gm of coal yield higher sulfur removals than 2gm of solvent and 2gm of coal (see dotted and cross-hatched bars at 350 degrees Celsius, 120 minutes reaction time). Figure 8 shows comparison of sulfur removal for coals #2 and #3 in supercritical methanol. The data show that except for temporary sulfur incorporation coal #2 is always more reactive than coal #3.

Figure 9 shows typical particle size effects on sulfur removal. Under mild-severity, micronized coal is less reactive than -60 mesh coal. At moderate-severity the micronized coal tends to be slightly more reactive than the -60 mesh size fraction of the same coal; and at high-severity the micronized coal is substantially more reactive than the -60 mesh size fraction of the same coal.

The data imply that slight oxidation retards desulfurization under mild conditions, but mass transport effects are more significant at high-severity. Retardation of sulfur removal under mild desulfurization conditions may be the result of surface oxidation of pyrite particles or oxidation of freshly exposed coal surfaces. The surface oxide on pyrite particles would be expected to be less susceptible to desulfurization at low temperatures. However, at higher temperatures the sulfates would be expected to decompose to SO_x.

RELATIVE SUPERCRITICAL DESULFURIZATION OF COALS IN METHANOL

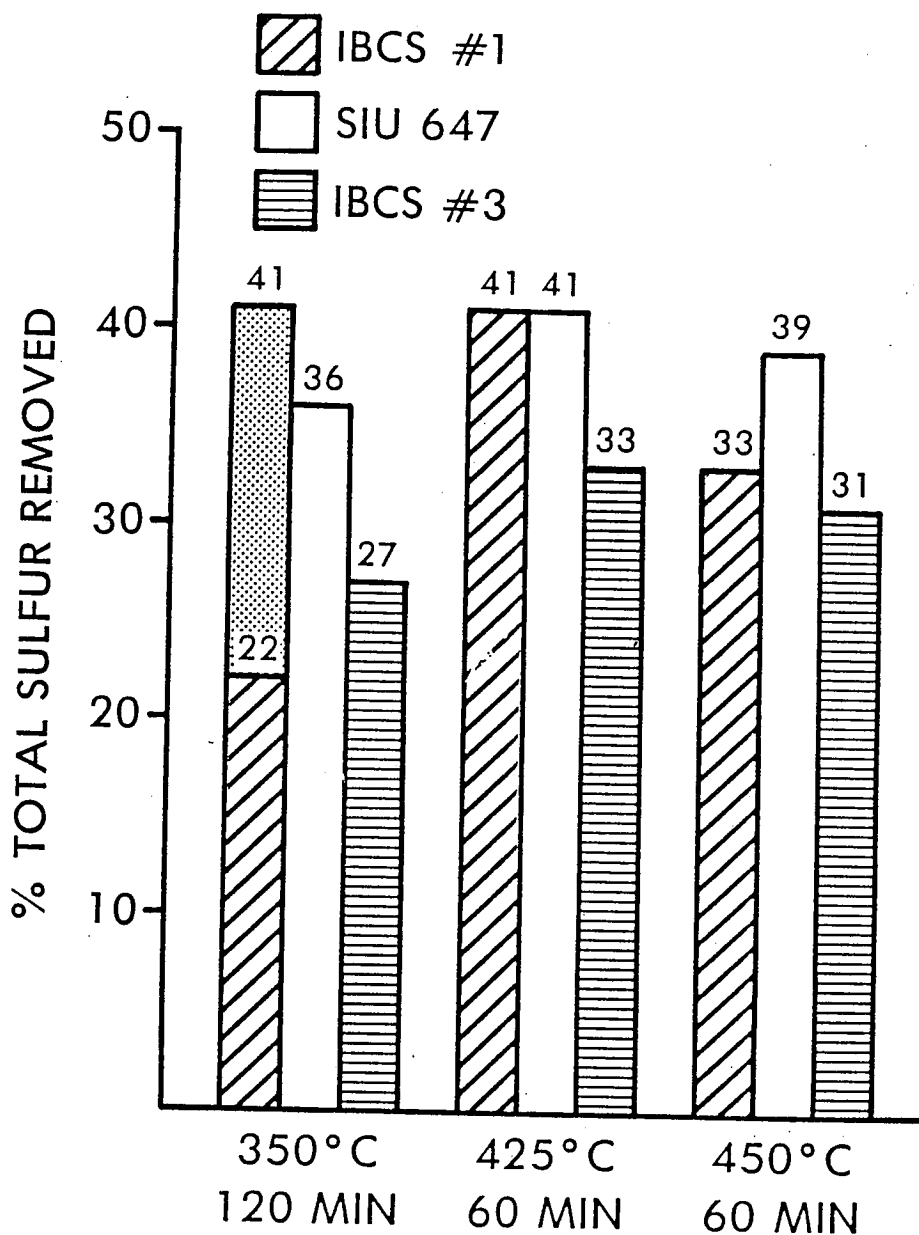


Figure 7. Typical desulfurization of the three coals under investigation with supercritical methanol extraction. The results for coal #1 at 350° also show the effects of solvent to coal ratios. At 1:1 (cross-hatched) 22% of the sulfur was removed, while at 2:1 (dotted) 41% of the sulfur was removed.

MeOH extn. of -60 mesh coals

R2K vs.R3K

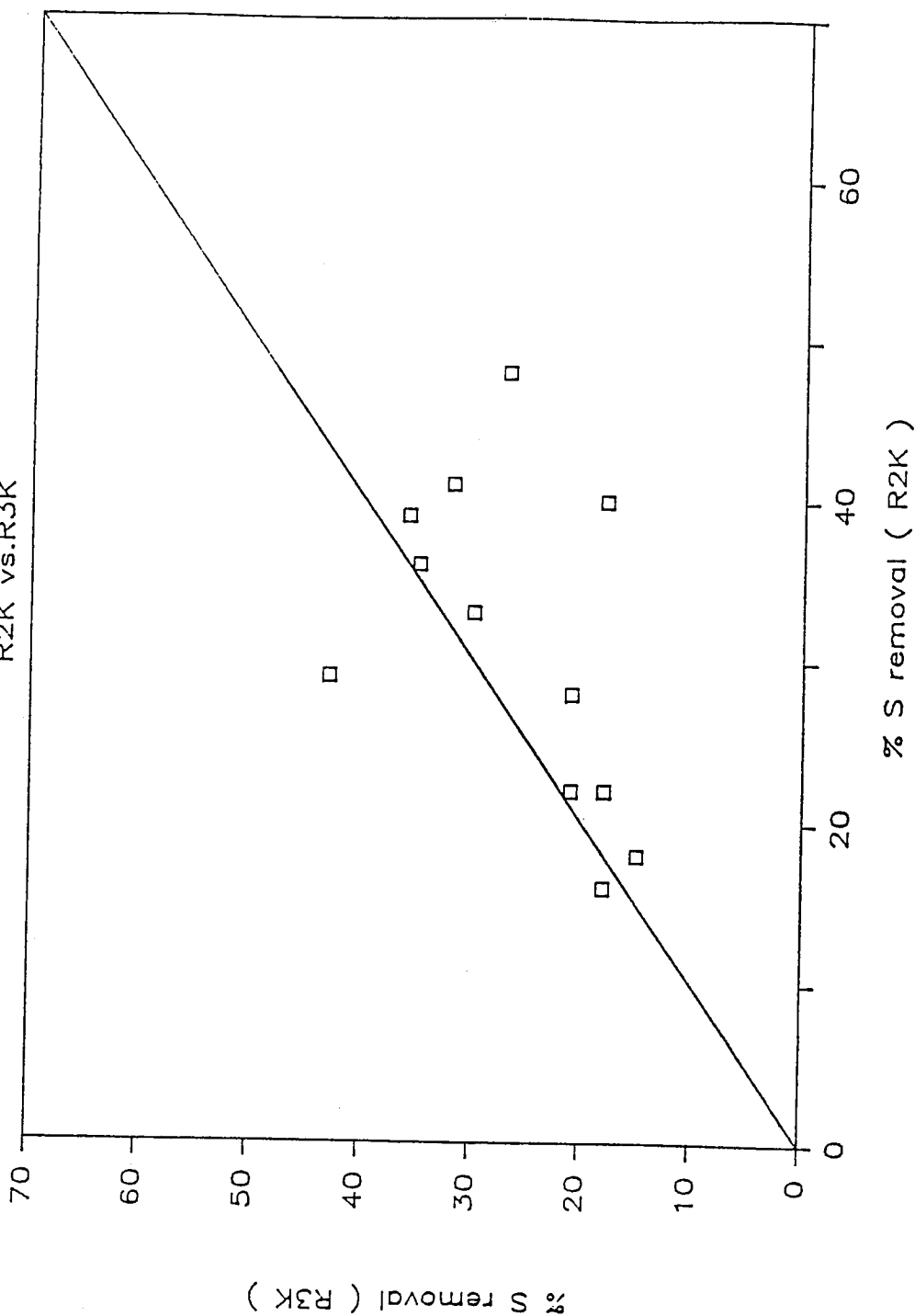


Figure 8. Comparison of the results of sulfur removal with supercritical methanol extraction on two different coals - #2 and #3. The presence of most of the test points below the parity line indicates that coal #2 is more reactive.

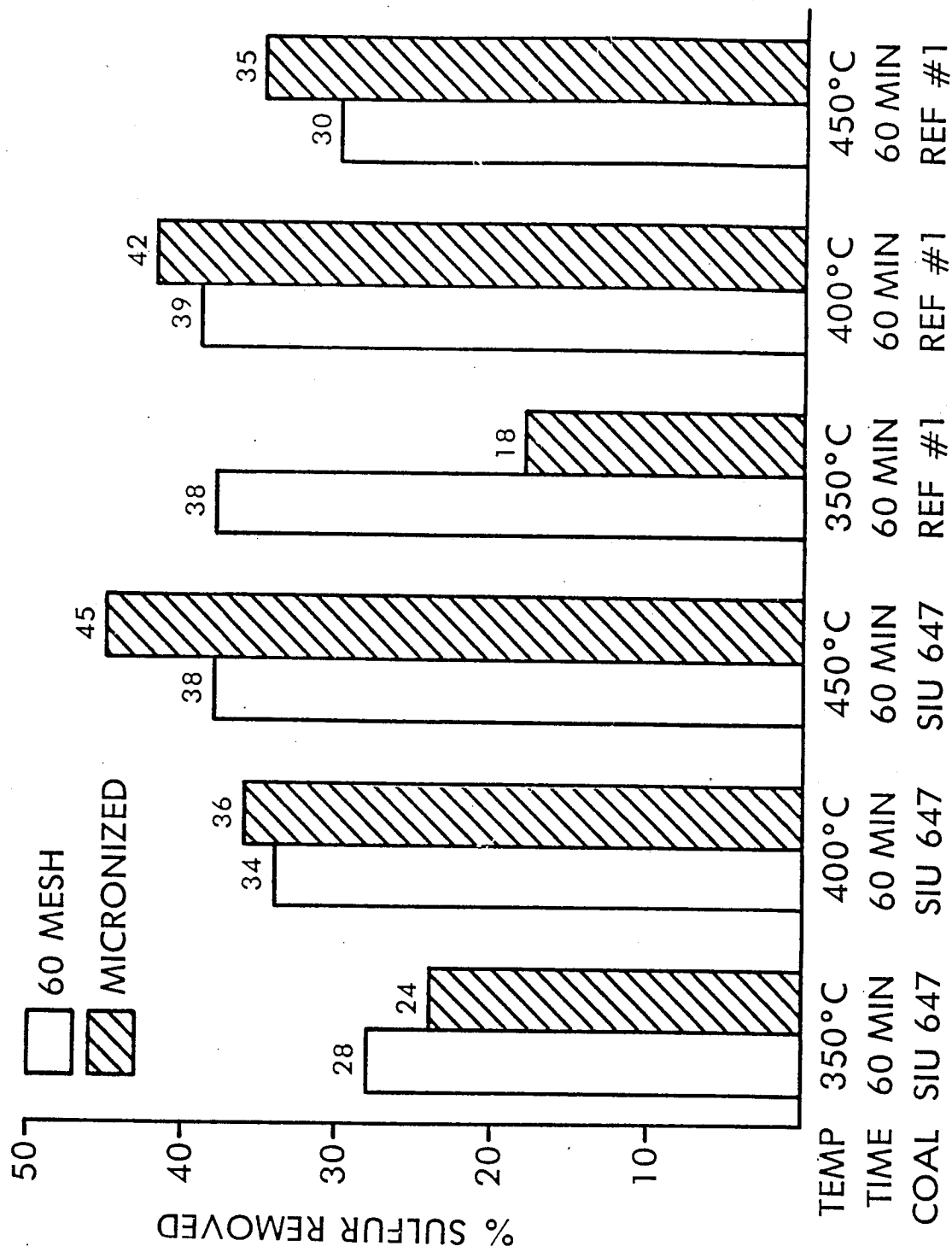


Figure 9. Typical desulfurization results showing the effects of particle size. At the mildest conditions the coarser samples (-60 mesh) show greater sulfur removal. However, at all more severe conditions more sulfur is removed from the micronized coal. This is true as shown for coals #1 and #2 (SIU 647) and for coal #3 (not plotted).

Sulfur incorporation is more likely to occur at elevated temperatures. The micronized particles allow the product less time to react with components on the pore walls than -60 mesh size particles. Thus, micronization reduces the chance of incorporation during the process of product diffusion to the bulk gas. Thus, higher sulfur removals can be observed in the micronized samples. On the other hand, when conditions in the bulk gas and/or phase transitions in the coal favor sulfur incorporation, the smaller particle size of the micronized coal will enhance sulfur incorporation.

The effect of demineralization and floatation on sulfur removal under SME conditions is demonstrated in Figure 10. The figure contains data for coal #1, but coals #2 and #3 show a similar pattern. Demineralization has a negative effect on sulfur removals under conditions that yield low desulfurization rates. These conditions correspond to the lowest temperatures being studied. However, as temperature is increased sulfur removal from the micronized/demineralized samples become greater than sulfur removals from the micronized coal. This is further demonstrated in the parity plot (Figure 11) of sulfur removals for micronized and micronized/demineralized samples of coal #1.

As discussed earlier, the relative order of sulfur removals of micronized coal samples are approximately the same as those for the -60 mesh size fractions. Demineralization tends to equalize the sulfur removals in the three coals. And maximum sulfur removals are slightly higher for coals #1 and #2 than for coal #3 after demineralization. In addition, demineralization seems to increase sulfur incorporation tendencies for coals #1 and #2.

Figure 10 also demonstrates that sample preparation by a 1.6gm/ml floatation process yields samples that are always more reactive than micronized or micronized/demineralized samples. The increase in sulfur removal between floated and other samples decreases with increase in reaction temperature or time. This is demonstrated in Figure 12 where sulfur removals from demineralized and floated samples are plotted. At low sulfur removal levels the difference in desulfurization is large. But at high sulfur removal levels desulfurization rates are nearly equal.

As with the case of the pyrolysis process the floated samples produce a higher fluctuation in sulfur removal. Again, these fluctuations are believed to be the result of temporary sulfur incorporation which is enhanced by removal of pyrite or the presence of cesium. This pattern is similar in all three floated samples.

Figure 13 demonstrates the effect of the trend in sulfur removal as a function of sample preparation. These results are typical of high-severity SME processing and reflect trends in maximum sulfur removal. The data are reported for

EFFECT OF TREATMENT ON SULFUR REMOVAL OF REF COAL #1

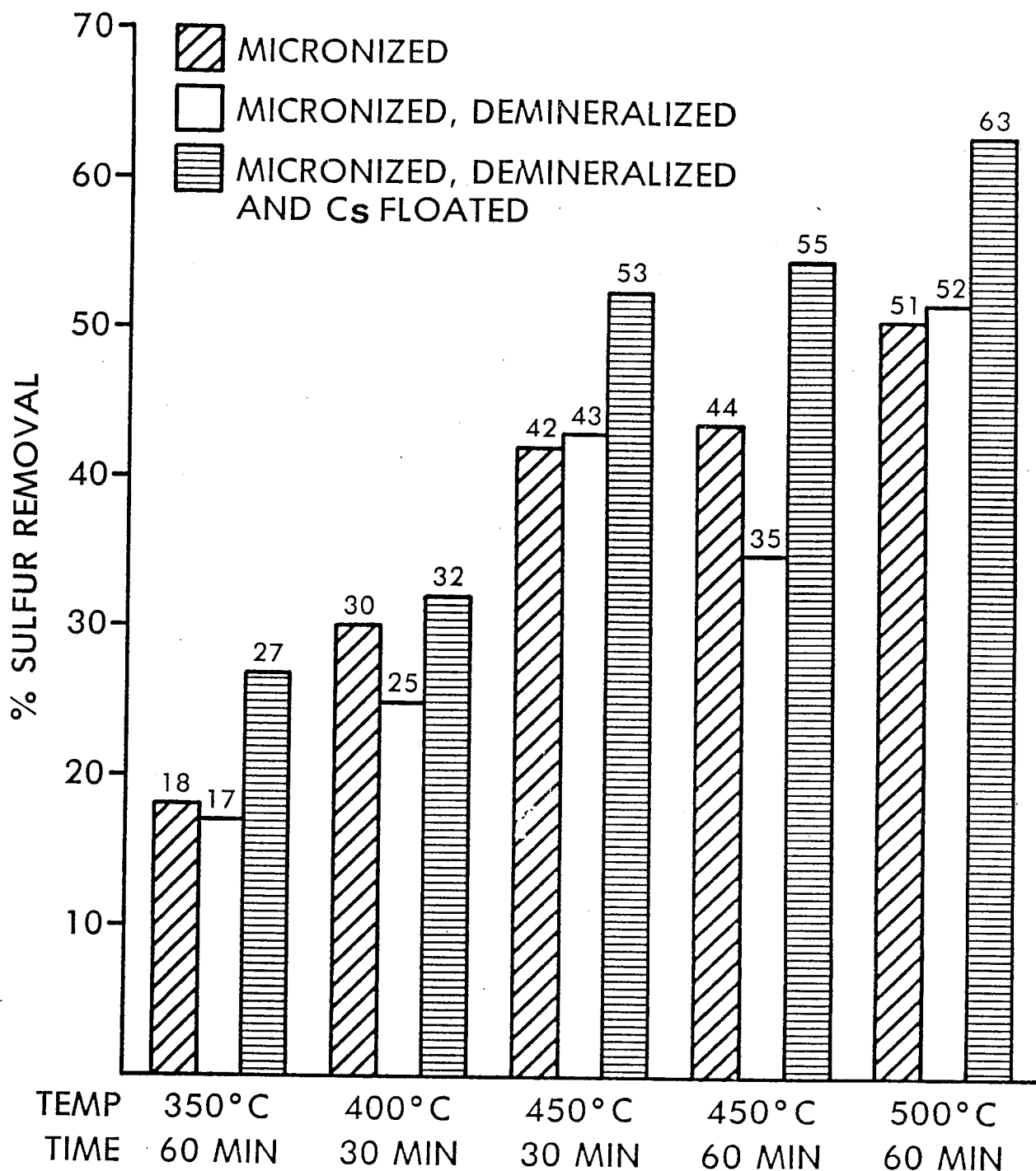


Figure 10. Typical results of desulfurization with supercritical methanol extraction on samples of the same coal after different preparation treatments. The results show that the highest sulfur removals are in the samples that have been micronized, demineralized, and floated at 1.6 gm/ml.

Effect of demineralization

M1K vs. D1K

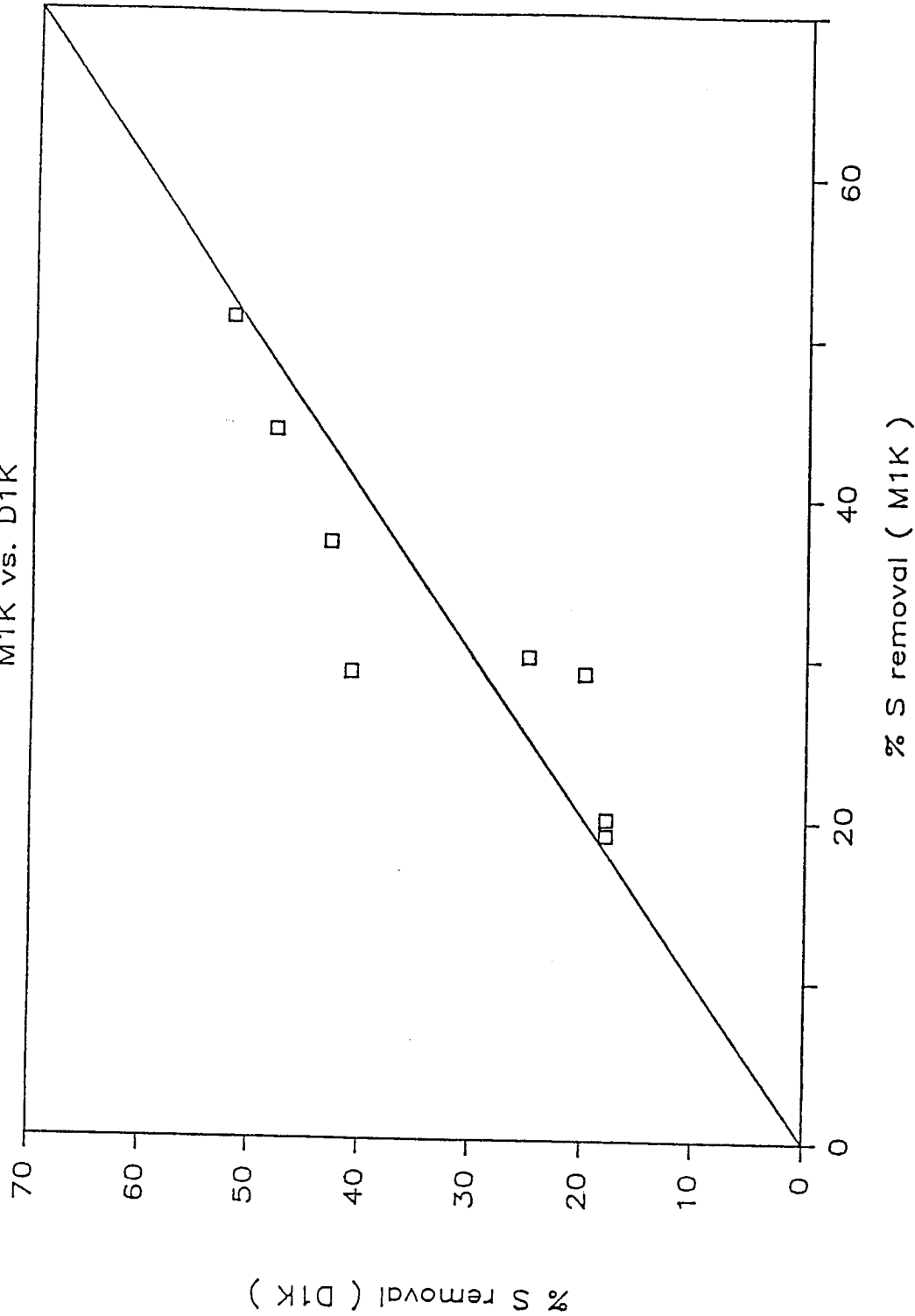


Figure 11. Comparison of results of sulfur removal with methanol supercritical extraction on micronized (M1K) and micronized and demineralized (D1K) samples from the same coal. The results show that at low sulfur removals (<30%) demineralization is not important. However, higher sulfur removals are attained with demineralization. The higher sulfur removals also correspond to more severe test conditions.

Effect of CsCl flotation

D1K vs. F1K

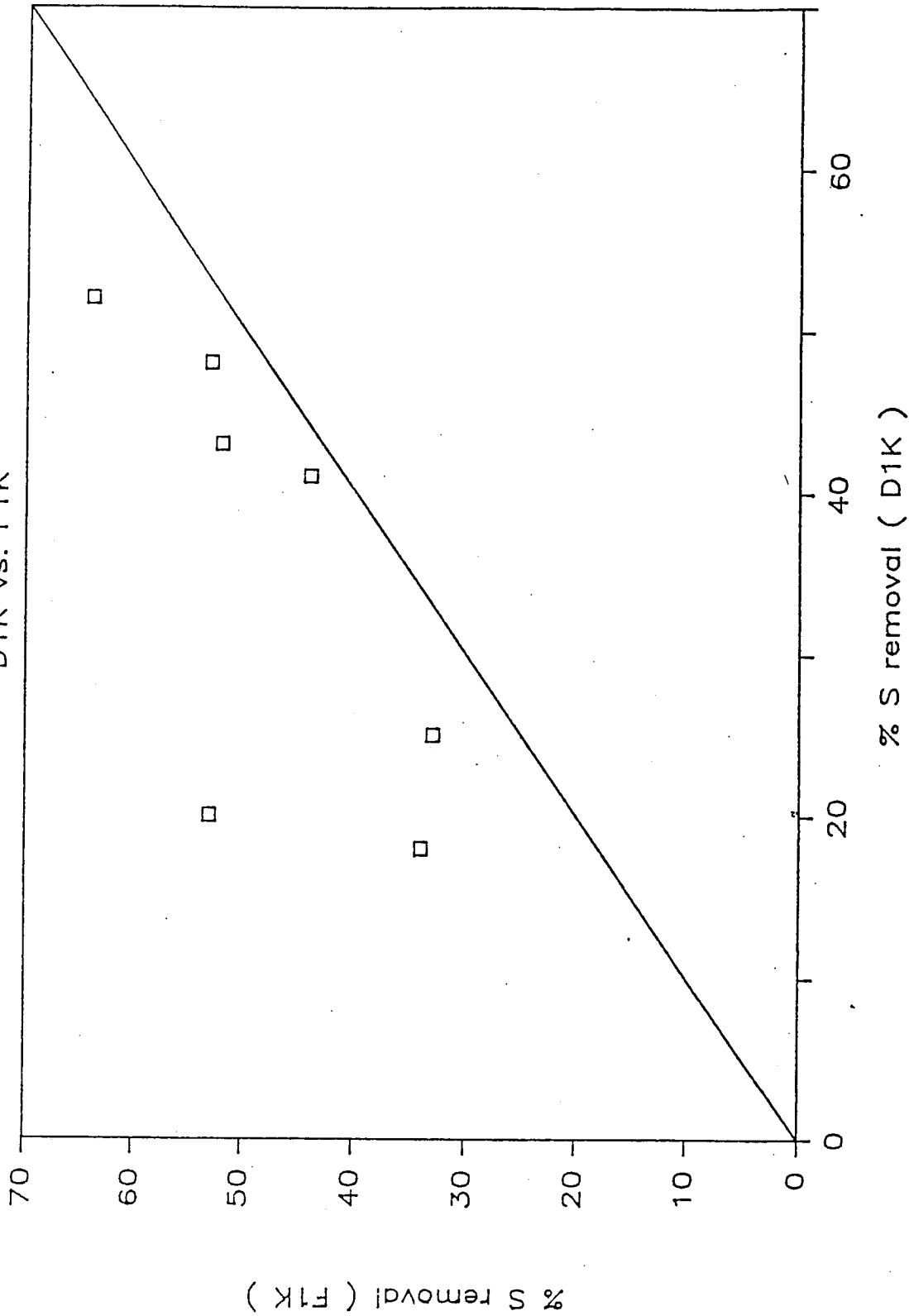


Figure 12. Comparison of results of sulfur removal with supercritical methanol extraction on deminealized (D1K) and deminealized and 1.6 gm/ml floated samples of the same coal. The presence of all the test points above the parity line indicates that the sulfur removal is better in the floated samples.

MeOH Extrn. (5 % KOH)

450°C, 30 min.

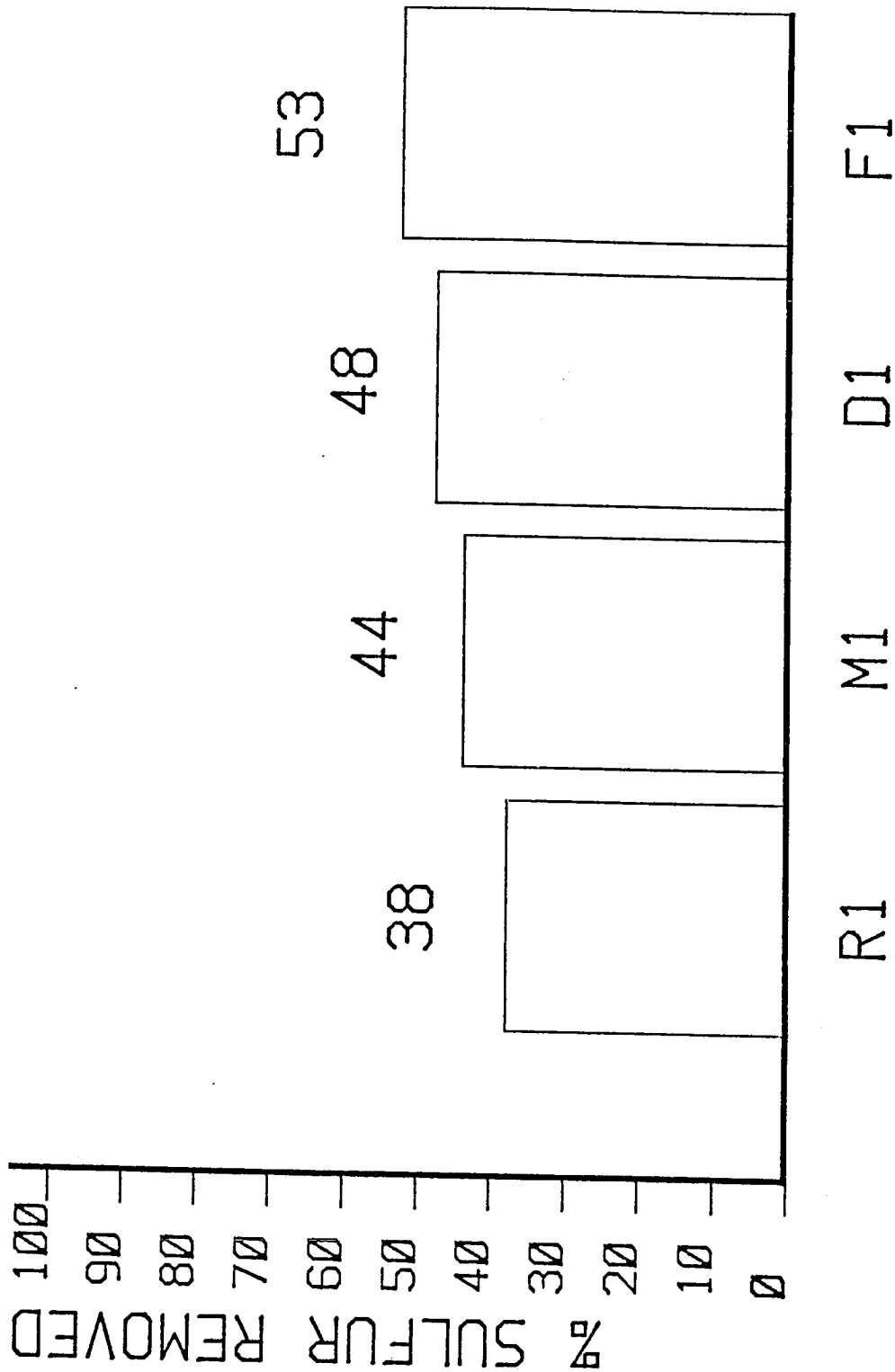


Figure 13. Typical results from a single coal sulfur removal with supercritical methanol extraction showing the effects of pretreatment of the sample. (R = raw, M = micronized, D = micronized and demineralized, F = micronized, demineralized, and floated at 1.6 gm/ml.) Sulfur removal increases with each treatment.

samples prepared from coal #1, but the trend is applicable for sulfur removals from coals #2 and #3. Less sulfur is removed from the -60 mesh size fraction than is removed from the micronized coal; less sulfur is removed from the micronized coal than is removed from the micronized and demineralized coal; and less sulfur is removed from the micronized/demineralized coal than is removed from the micronized/demineralized/ cesium-floated coal. The data reflect trends that are applicable for all process conditions studied at or above 450 degrees Celsius. The patterns are also independent of the sulfur incorporation phenomenon. In other words, if sulfur incorporation is observed for a condition, the percentage of incorporation appears to be about equal regardless of the sample preparation.

Figure 14 shows sulfur removal under 500 degrees Celsius and 60 minutes reaction time for vitrinite and sporinite maceral concentrates of coal #2. Sulfur removal in the vitrinite and sporinite concentrates are substantially higher than sulfur removal in the micronized coal (see Figure 13) or the sample prepared by a 1.6gm/ml floatation process (see Table 5). The vitrinite and sporinite concentrates contain 86% of the total organic sulfur in the coal. Assuming that none of the sulfur in the other macerals is removed, the results on the vitrinite and sporinite concentrates suggests that 65% of the organic sulfur should be removed in the micronized or floated samples. Since both the float and maceral concentrates contain about the same amount of cesium introduced during the preparation process, catalytic desulfurization effects can be eliminated as a cause for the high desulfurization rates in the maceral concentrates. Thus, the data suggest that there is a coal matrix effect in which the association of other macerals inhibits sulfur removal or traps products of the desulfurization process.

Figure 15 depicts sulfur removal of maceral concentrates at milder experimental conditions. Similar trends are observed. Namely, vitrinite and sporinite concentrates evolve more sulfur than whole or floated coals. Thus, sulfur removals in the vitrinite and sporinite occur at a faster rate as well as reaching a higher maximum. Not enough tests have been conducted on the maceral concentrates to judge sulfur incorporation tendencies.

Figure 15 also contains data for one test conducted on the vitrinite concentrate of coal #1 at a high-severity condition. The sulfur removal in the vitrinite concentrate was found to be higher than the sample prepared by sequential micronization, demineralization, and floatation. The difference in sulfur removal between the maceral concentrate and the floated sample is not as great as the equivalent tests on samples prepared from coal #2. The reasons for this difference are still being investigated.

PURE MACERAL DESULFURIZATION DATA

500°C, 60 Minutes

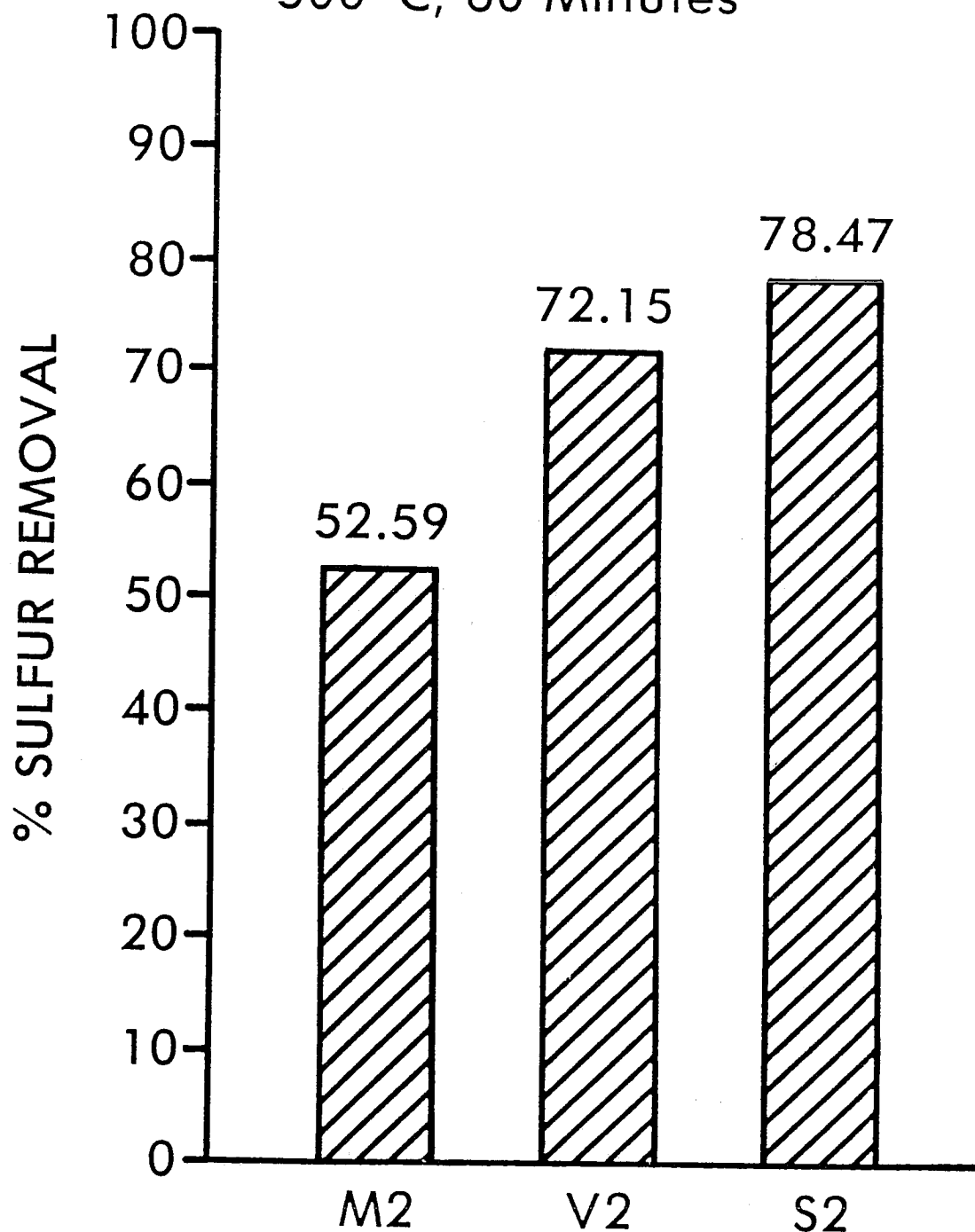


Figure 14. Results of sulfur removal with supercritical methanol extraction (SME) on pure maceral fractions from the same coal sample (M = micronized coal, V = vitrinite, S = sporinite). It should be noted that the high removal notes (72-78%) represent the removal of organic sulfur from these samples. Pyritic and sulfate sulfur have been removed in steps before the SME tests.

PURE MACERAL DESULFURIZATION

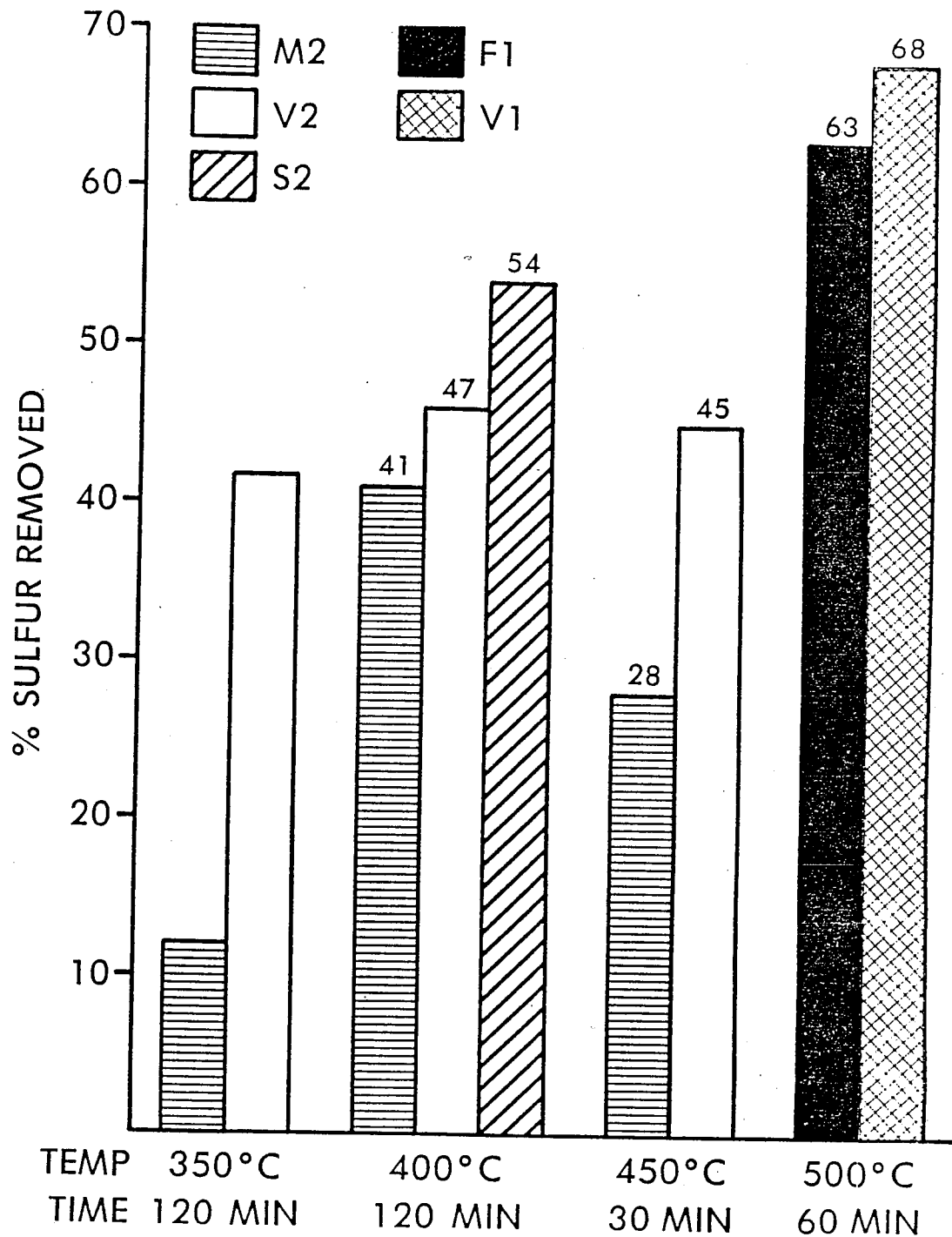


Figure 15. Results of sulfur removal with supercritical methanol extraction on pure maceral concentrates. In all cases more sulfur is removed from the macerals than the micronized and/or floated coal. (M2 = micronized coal #2, V2 = vitrinite from coal #2, S2 = sporinite from coal #2, F1 = floated coal #1, and V1 = vitrinite from coal #1.)

CONCLUSIONS

The modified DGC method employing a preconcentration of macerals at a specific cut point allows for accumulation of a sufficient quantity of pure maceral concentrates for testing the desulfurization properties of individual macerals. The concentration of 10gm aliquots of pure maceral concentrates represents a new advance in separation technology. This is the first time that such large quantities of pure macerals have been segregated by any technique.

Of the three desulfurization processes investigated, pyrolysis was least effective. Supercritical ethanol extraction was slightly more effective than pyrolysis. Supercritical methanol extraction was significantly more effective than pyrolysis or supercritical ethanol extraction. Under optimum conditions, 55-65% of the organic sulfur can be removed from whole coals, and up to 80% can be removed from single macerals.

The conditions under which samples are tested are extremely critical to the extent of sulfur removal. In general, increased temperature increases desulfurization for all three processes investigated. Also, sulfur removal increases with longer reaction times. The presence of KOH enhances the rate of sulfur removal. Sulfur can be reincorporated from sulfur-containing gaseous products, and KOH enhances the sulfur reincorporation. Some of the sulfur removal may be retarded by incorporation of products during diffusion of product gases through the pore system of the residual coal. Thus, very fine particle sizes are desirable for chemical desulfurization.

Increased solvent to coal ratio increases desulfurization up to a 2:1 ratio. For all three processes studied, the three coals varied in rate of sulfur removal, the maximum observed sulfur removal, and tendency to incorporate sulfur-containing product gases.

The type of sample preparation affects sulfur removal. In general, particle size reduction increases sulfur removal. Demineralization results in increased sulfur removal in subsequent processing. Variations in sulfur removal due to variations in coal properties are observed for the micronized and demineralized coals.

The demineralized coals contain pyrite. Pyrite is removed by floatation at a 1.6gm/ml solution. Floatation produces a very clean coal that is more reactive than the demineralized coal. For float samples, approximately the same maximum desulfurization level is obtained independent of the desulfurization process and coal properties.

The float samples demonstrate that organic sulfur is more amenable to desulfurization than was previously thought. Since high levels of sulfur removal are obtained during pyrolysis, the sulfur removals reported are not an artifact of sample dilution. Furthermore, either pyrite is less reactive than the organic sulfur or the pyrite (or derived products of pyrite) aid in sulfur incorporation reactions. The results suggest the thermal-chemical desulfurization should be preceded by a thorough physical cleaning that removes both pyrite and other coal minerals.

Finally, the main objective of this study was to investigate the desulfurization behavior of individual coal macerals. The sporinite and vitrinite concentrates are more reactive towards desulfurization processes than any of the other materials that were studied. They also gave the highest desulfurization levels. Since they are more reactive than whole coals or floated samples, the other constituents in the coal matrix must reduce sulfur removals. This phenomenon has not been reported previously. It implies that the inertinite macerals may behave in a manner similar to activated charcoal and chemically absorbs copious amounts of sulfur during the desulfurization processes. The practical result of this phenomenon is that selection of coals on the basis of maceral composition could be necessary to optimize thermal-chemical desulfurization. Work in this area is continuing at Southern Illinois University at Carbondale.

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