ABSTRACT

The broad goals of this project are to determine by nondestructive magnetic resonance methods chemical and physical structural characteristics of organic parts of native and treated coals. In this project period, we have begun to explore a technique which promises to enable us to follow the course of coal cleaning processes with microscopic spatial resolution. For the past five years, our laboratory has worked on extensions of the EPR technique as applied to coal to address these analytical problems. In this report we (1) describe the world's first nuclear magnetic resonance imaging results from an Illinois #6 coal and (2) transmit a manuscript describing how organic sulfur affect the very-high-frequency EPR spectra of coals.

Magnetic resonance imaging (MRI) is a non-destructive technique that has found wide medical application as a means of visualizing the interior of human bodies. In collaboration with Prof. Paul Lauterbur and the staff of the Biomedical Magnetic Resonance Laboratory, we have used MRI techniques to study the diffusion of an organic solvent (DMSO) into the pores of Illinois #6 coal. Proton MRI images reveal that this solvent at room temperature does not penetrate approximately 30% of the coal volume. Regions of the coal that exclude solvent could be related to inertinite and mineral components. A multi-technique imaging program is contemplated.

PART I: Research Goals and Initiation of MRI in Coal

GENERAL SUMMARY

Detailed information on the chemical and physical structure of coal is needed by workers in many areas of fuel technology. High sulfur coals present special problems for which this information is especially important. Chemical characterization is needed to design sulfur removal processes, optimize their efficiency, and assess their effectiveness. Its goal is the identification and quantification of sulfur-containing molecular structures that exist in whole coal. Physical characterization helps to shed light on the distribution of sulfur compounds in different macerals, as well as their possible segregation around structural features such as pores. It also aims at measuring physical properties like average interatomic distances in macerals with differing sulfur content. This information is needed to engineer better coal cleaning methods, as well as to assess the effects of various cleaning approaches.

Almost all the work of the past fifty years dealing with the chemical and physical characterization of coal has been destructive to the native coal mineral structure. The opaque, relatively non-volatile, and heterogeneous nature of coal renders it difficult to study by optical, chromatographic, and mass spectral methods without first performing chemical or thermal procedures to break apart the mineral matrix and liberate organic compounds for study. The very serious drawbacks of such procedures have been appreciated for many years -- they are used by necessity, not always by choice. The shortcomings of destructive analytical methods have become more evident in the current period, when the need to remove organic and inorganic sulfur from midwest basin coals has raised important technological questions requiring information on the molecular forms and distribution of sulfur in whole coal. Clearly, new nondestructive analytical methods are needed to complement older, destructive techniques that analyze for the molecular forms and distribution of sulfur compounds in coal.

MASTER

Magnetic resonance imaging (MRI) has been developed over the last ten years as a very powerful tool for visualizing the internal structure of opaque samples, including large objects like dogs and human beings. It is nondestructive, and provides superb resolution. In collaboration with the world famous innovator of MRI, Prof. Paul Lauterbur (Chemistry and Medicine, UIUC), our laboratory has begun a program to apply MRI to the study of coal macromolecular structure. In the last several months, we have been able to obtain three-dimensional images of coal that has been infused with solvent. The images are maps of the distribution of solvent in the pore structure of the coal. Figure 1 illustrates one two-dimensional slice through the coal; the bright areas represent regions of solvent penetration, while the dark zones are regions of solvent exclusion.
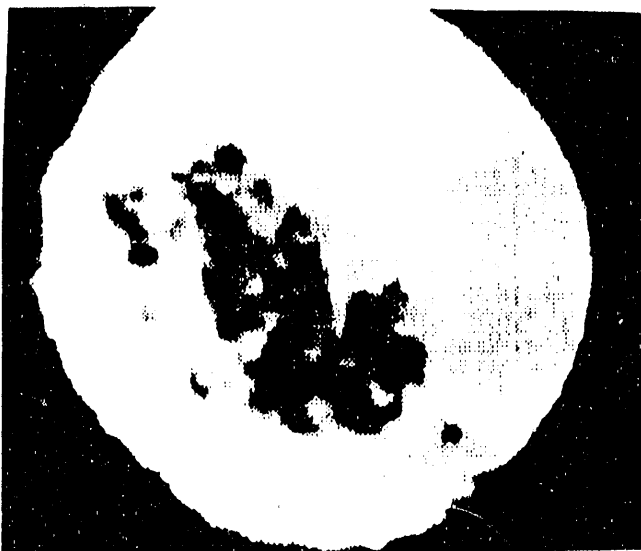

Figure 1. Proton MRI image of Illinois #6 infused with DMSO.

The solvent in this study was dimethyl sulfoxide (DMSO). It was chosen because it is a moderately good swelling solvent, and because it contains only one magnetically unique proton, thus giving it a low-resolution NMR spectrum consisting of a single peak. The sample was a chip of Illinois #6 coal approximately 1mm by 3mm by 0.5mm. The very small size of the sample was made necessary because of the dimensions of the microprobe used, and it caused severe problems in sample handling and preparation. Work now is under way to make images using a new probe that will accommodate centimeter-sized pieces of coal, and this should greatly improve our ability to control the shape of the sample.

Figure 1 clearly shows light and dark regions, representing areas of solvent penetration and exclusion. Because of the very small size of the coal samples used in this study, it is clearly premature to draw any general conclusions about the extent of solvent penetration based on the images. What can be said is that solvent does not penetrate uniformly throughout the coal, and is clearly excluded from regions on the order of 20 to 100 microns in size. This dimension is similar to typical maceral and mineral dimensions in this coal, leading one to speculate that a correlation may exist between exclusion zones and particular macerals and minerals. When it is possible to make images of larger pieces of coal (with the new imaging probe), we plan to correlate MRI images with optical and SEM images in an effort to make correlations between zones of solvent penetration and exclusion and individual components of the coal.

OBJECTIVES

Our broad aims in coal research include determination by nondestructive means the chemical and physical structures of the organic parts of native and treated coals, and following the course of coal cleaning processes with microscopic spatial resolution. Some goals which we have identified are as follows:

1. The nondestructive determination of atomic and molecular structure of sulfur-containing organic species in coal, particularly high-sulfur coal, both in its natural state and at various stages during desulfurization;

2. Determination of interatomic distances, numbers, and orientations in individual macerals with differing sulfur content by pulsed EPR (ESE) microscopy;

3. Development of nondestructive high-resolution microscopic images of internal structure in coal, including chemical information on the location and distribution of sulfur-containing compounds;

4. Determination of sulfur compound chemical structure from highly localized regions in a whole coal sample;

5. By means of the techniques used to accomplish the above goals, to measure the effects of various coal cleaning methods on the molecular forms and spatial distribution of organic sulfur, and on internal structural characteristics like pore size and maceral density;

6. Following by these microscopic methods the rate and extent of solvent intrusion into the pores and matrix of whole coals and separated macerals.

This year, we are addressing all of these, utilizing W-band (96 Ghz) EPR, X-and Q-band ENDOR, and S-band ESE, as well as magnetic resonance imaging (MRI). The MRI studies reported this Quarter are directed at items 3 and 6 in the above list. Work performed on projects directed at other Task areas has been, and will be, described in other Quarterly Reports, as well as in Part II.

INTRODUCTION AND BACKGROUND

A major objective in coal science continues to be the nondestructive determination of atomic and molecular structure in the individual components that comprise this heterogeneous mineral. Work on questions seemingly as different as the geologic origin of different macerals and the effects of various coal cleaning technologies would benefit greatly from detailed atomic information about coal structure. Because of its heterogeneous and complex nature, the microscopic structure of coal will not be entirely understood through the use of a single physical method, and it is not productive to view research in this area as a contest between various techniques. Rather, several different approaches should be used in a complementary way, each contributing part of the information that is needed to develop a more comprehensive and useful map of coal atomic and molecular structure.

Since nondestructive techniques are all relatively new, most of what we know about the composition of coal comes from destructive methods. Attempts to deduce the native structure of coal from mass spectral, NMR, separation science, and infrared data on components derived from chemically or thermally treated samples have led to the development of two main approaches for the modeling of maceral structure -- parameters and average molecular construction. Parameters include such average structural information as aliphatic/aromatic carbon ratios and number of aromatic rings per molecule. Average molecular construction approaches attempt to devise a solid maceral structure that

will account for the molecular structures found in products. Several examples of this second method are given in the following references [1, 2, 3, 4, 5]. Figure 2 illustrates one of these structures, that developed by Shinn for an average bituminous coal maceral [3].

The importance of coal models (and detailed information on microscopic structure) is growing as work on more complex processing methods seeks to relate coal properties with coal molecular and atomic structure. Because of the many uncertainties in
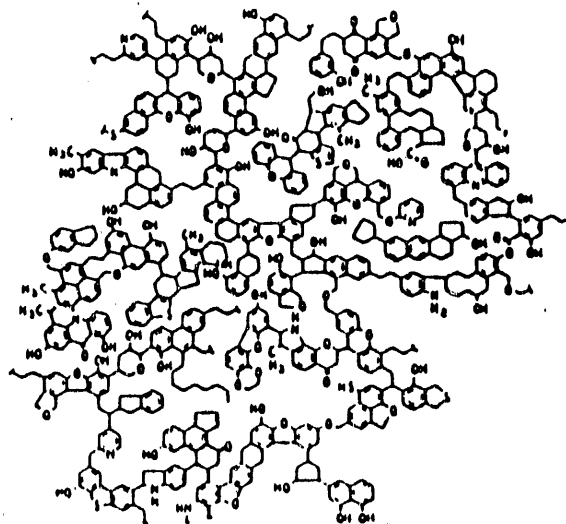

Figure 2. Shinn's model of bituminous coal structure [3].

relating composition data obtained from destructive analytical methods to the native structures in coal, there is a need both for nondestructive approaches to the determination of atomic and molecular structure and for information about specific coal samples rather than statistical information on average properties. Among the relatively few nondestructive methods capable of observing coal structure on this microscopic scale, magnetic resonance methods (EPR, NMR, ENDOR, ESE) are showing great promise. This is because these methods have, in many cases, developed theoretical and experimental ways to achieve the 1) sensitivity, and, 2) resolution needed to determine microscopic structure in non-crystalline, opaque, and relatively non-volatile solids like coal.

Among magnetic resonance spectroscopies, none is more sensitive than Electron Paramagnetic Resonance (EPR). It was natural that two of the first studies ever undertaken with the then-new technique (ca. 1953) were investigations of the unpaired electrons naturally occurring in coal [6, 7]. From the very beginning of EPR work on coal, it was apparent that the technique had enormous sensitivity, but that by itself it lacked sufficient resolution to observe the very small hyperfine splittings that contain information on the atomic and molecular structure "observed" by the electron. Although NMR usually has the ability to resolve much smaller splittings, it also was unable to achieve the necessary resolution to determine coal molecular structure directly, and was hampered by sensitivity problems as well. One potential solution to these difficulties emerged with the advent of Electron-Nuclear Double Resonance (ENDOR) spectroscopy, a hybrid technique that can be characterized as NMR with detection by EPR (e.g. NMR resolution with EPR sensitivity), and which is specifically designed to resolve hyperfine interactions.

In 1981, Retcofsky and co-workers reported the first successful resolution of electron-nuclear hyperfine interactions (other than matrix effects) in several Pennsylvania whole coals using ENDOR [8]. They saw hyperfine couplings characteristic of those expected in aromatic hydrocarbons, as well as one

coupling possibly from an aliphatic moiety. The similarity of couplings from several coals generally supported the view that macerals may be composed of a limited number of functional groups, linked together in varying combinations and concentrations. Such information is exactly the sort needed to develop specific information on the molecular structure of coal, and demonstrated the potential of the technique. The overall approach of using unpaired electrons in coal to observe atomic and molecular structure was termed **HYPERFINE FINGERPRINT SPECTROSCOPY**.

For the past five years, our laboratory has worked on extensions of the ENDOR technique as applied to the structural determination of coal. We have developed computer-controlled instrumentation capable of performing complex ENDOR experiments involving **two variables**, which we term 2-dimensional ENDOR, and which have shown tremendous promise in increasing still further the spectral resolution of the technique for coal work. We also have developed theoretical methods for analyzing the powder ENDOR spectra obtained from coal samples, and have performed many experiments on model systems as well. We are developing a library of ENDOR spectra from powders containing model compounds (eg, anthracene, naphthalene, pyrene, perylene, dibenzothiophene, etc), which we will use to begin the analysis of data from whole coals [9]. In addition, we have built a time-domain (pulsed) EPR spectrometer optimized for coal studies, and have begun to employ it to do Electron Spin Echo (ESE) spectroscopy with excellent results [10]. Also, the Illinois EPR Research Center has completed construction of a W-band (96 Ghz) EPR spectrometer. This instrument is providing spectra from coal which seem uniquely sensitive to organic sulfur and oxygen, and which can resolve spectral features not visible at lower field strengths [11]. The MRI studies reported in this Quarterly Report represent a new and very powerful technique which we have adapted for the study of coal structure.

EXPERIMENTAL PROCEDURES

MRI images of the solvent distribution in an Illinois #6 coal were made on a special 4.7T (200 Mhz) instrument in the Biomedical Magnetic Resonance Laboratory at UIUC. Professor Paul Lauterbur, director of the BMRL, was the key collaborator with our group on this work. The microscopic imaging probe was constructed by the BMRL, and could accommodate samples of approximately 1mm diameter.

The solvent chosen for this first set of experiments was dimethyl sulfoxide (DMSO), since it is a moderately strong swelling solvent and has a simple, one-line NMR spectrum. Very small pieces of the Illinois #6 were placed in quartz capillary tubes together with the solvent and allowed to soak for 24 hours or more at room temperature. Since the repetition rate of the NMR data acquisition sequence depends on nuclear T_1 values, it was deemed advisable to add a small amount of chromium acetyl acetonate {Cr(acac)} to the solvent to shorten proton T_1 and speed up the experiment. Ultimately, 10mM Cr(acac) solutions of DMSO were used, allowing a full three-dimensional image of the coal sample to be acquired in about 40 minutes. Undoped DMSO required about 5 hours for the acquisition of a full data set.

RESULTS AND DISCUSSION

Figure 1 illustrates one image of the coal obtained by this MRI technique. Since the full three-dimensional data set was obtained for each sample studied, it was possible to develop two-dimensional slices of any orientation through the sample in order to probe the solvent penetration pattern. Figure 3 shows several slices taken at 20 micron intervals. These images demonstrate that the zones of solvent exclusion have average dimensions between 20 and 100 microns. Some stratification of the exclusion zones may be seen. In all, approximately 30% of the volume of the coal samples studied was not penetrated by the DMSO solvent. The size and distribution of exclusion zones corresponds very closely to the size and distribution of certain maceral and mineral constituents in this coal. In particular,
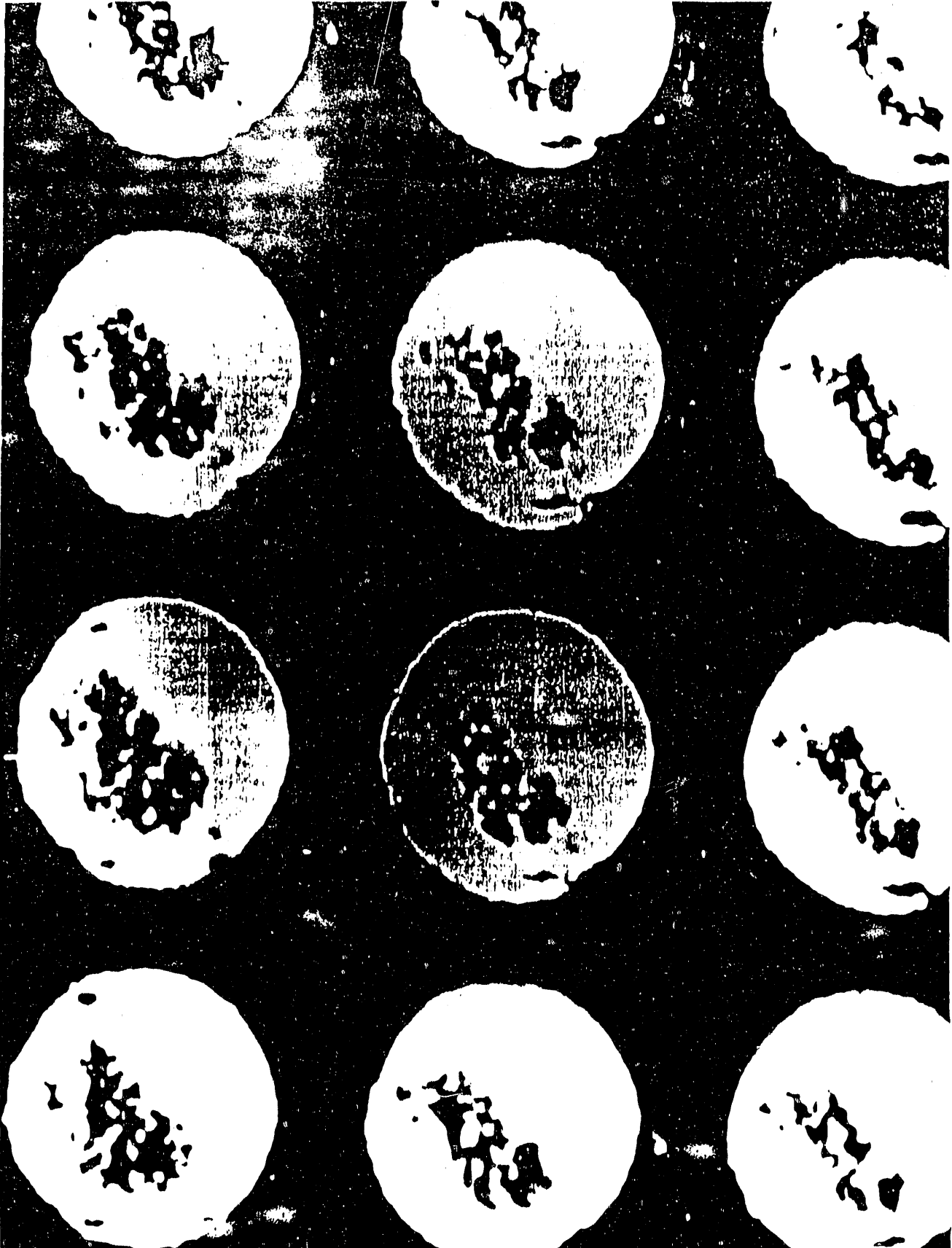
Figure 3. Two-dimensional slices showing the distribution of DMSO throughout a small sample of Illinois #6 coal. Slices are taken at 20 micron intervals.

inertinites show a size and distribution pattern very similar to that seen in the exclusion zones as measured by MRI. It is very tempting to attempt to make this correlation, but to do so at this stage in our experiments would be premature. Much more needs to be learned about the interpretation of these MRI data before any detailed model of solvent penetration involving macerals can be safely proposed.

CONCLUSIONS AND RECOMMENDATIONS

We have obtained the world's first MRI images of the distribution of a solvent in coal, and have begun to develop a protocol for such experiments that will be utilized in subsequent experiments. The images clearly resolve features smaller than 10 microns, and demonstrate the utility of this technique in studying patterns of solvent penetration in coal.

These experiments are exploratory, not having been contemplated when the original DOE grant proposal was submitted. However, the results are sufficiently promising that we expect soon to propose funding for a substantial program of such experiments. Future experiments would need to address the following issues:

1. An imaging probe that can accommodate larger samples needs to be employed. Such a device is now being tested at the BMRL with our assistance, and should greatly improve our ability to characterize samples, as well as suppress susceptibility artifacts.
2. When images are taken using the larger probe, this will permit the parallel characterization of the samples by optical and SEM microscopic methods. The results from several different imaging modalities will then be correlated using new software developed at the National Center for Supercomputer Applications here at UIUC. Such multi-image correlations will help us to identify the structure of regions in coals that are penetrated by solvents, as well as those that exclude solvents.
3. It will be important to do more rapid experiments involving two-dimensional images in order to follow the time course of diffusion of solvents into pieces of coal.

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(This work also has been reported to the Center for Research on Sulfur in Coal in the State of Illinois, which has provided additional assistance.)

PART II. Paper: INFLUENCE OF ORGANIC SULFUR IN VERY HIGH FREQUENCY EPR OF COAL. This manuscript was written to accompany a symposium presentation. It is a preprint, refereed and accepted for publication, to appear in 1990.

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