DOE/PC/94216-T5

**EFFECTS OF SURFACE CHEMISTRY
ON THE POROUS STRUCTURE OF COAL**

**Quarterly
TECHNICAL PROGRESS REPORT
July 1996 - September 1996**

by
**Stasia A. Anderson
Patrick G. Hatcher
Ljubisa R. Radovic**

Issued October 1996

**Prepared for the U. S. Department of Energy
Grant No. DE-FG22-94PC94216**

**Fuel Science Program
Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802**

RECEIVED
USDOE/PETC
96 NOV -4 AM 11:11
ACQUISITION & ASSISTANCE DIV.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

in

MASTER

PENNSTATE

**College of Earth and
Mineral Sciences**

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**EFFECTS OF SURFACE CHEMISTRY
ON THE POROUS STRUCTURE OF COAL**

**Quarterly
TECHNICAL PROGRESS REPORT
July 1996 - September 1996**

**by
Stasia A. Anderson
Patrick G. Hatcher
Ljubisa R. Radovic**

Issued October 1996

**Prepared for the U. S. Department of Energy
Grant No. DE-FG22-94PC94216**

**Fuel Science Program
Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

TABLE OF CONTENTS

Objectives.....	3
Summary.....	3
Technical Progress.....	3
Future Plans.....	18
References.....	19

OBJECTIVES

The primary objective of this project is to use ^{129}Xe NMR to characterize the microporous structure of coals. We will use direct information on pore size, as well as indirect information from adsorption rates and evidence for intra/extraparticle diffusion, to characterize the connectivity of the micropore network. A second objective is to use ^{129}Xe NMR to describe the effect of controlled opening of the micropores in a microporous carbon by oxygen chemisorption/desorption.

SUMMARY

Our experimental focus in this quarter has been the low power presaturation of the NMR signal of ^{129}Xe adsorbed in coal. Preliminary work on this experiment was reported in the last quarter. Low power presaturation of ^{129}Xe adsorbed in two coals produces a hole-burning effect in the adsorbed xenon NMR signals, indicating that these signals are broad due to overlap of a series of chemical shifts. Saturation transfer to the entire adsorbed xenon signal and to the extraparticle gas is observed with increasing presaturation time. Differences in timing of saturation transfer to the external gas have implications for the nature of the connectivity of the pore structures in coal.

TECHNICAL PROGRESS

INTRODUCTION. Typical ^{129}Xe NMR spectra of coal consist of a broad signal due to xenon adsorbed in the internal porosity of the coal, and a sharper signal at about zero ppm from xenon on the external surface or in the interparticle space. The adsorbed and external gas signals are well separated. This study will explore adsorption site distribution and pore network connectivity using ^{129}Xe saturation and saturation transfer. These techniques have widely varied utility in NMR spectroscopy, as reviewed in Freeman (1988). Selective

inversion has been used in ^{129}Xe NMR studies to study intercage exchange in a zeolite (Larsen et al., 1993; Jameson et al., 1994), to demonstrate that two xenon populations are coupled (Ripmeester and Ratcliffe, 1993), and to measure diffusion coefficients in polystyrene (Simpson et al., 1995).

In the presaturation experiment we irradiated only a portion of the frequency range covered by the adsorbed xenon signal, through the use of a low power presaturation pulse followed by a high power 90° pulse. Saturation of the NMR signal from xenon in some but not all adsorption sites will cause the loss of a portion of the signal, or a hole burning effect on the signal. Saturation of the entire signal without the hole burning effect indicates that the signal arises from xenon adsorbed in one environment. In this case, if the signal is broad, other possible causes of signal broadening are likely. These include short T_2 of xenon in coal or chemical shift anisotropy.

We have examined the effect of presaturating the adsorbed xenon signal for progressively longer times. The effect of presaturation on the spectrum depends on the extent of diffusion of adsorbed xenon during the time the pulse is applied. The possibility that xenon atoms are to some degree mobile means that a xenon atom that is saturated while in one environment can move to another in a given time frame, carrying the saturation with it. Spin-lattice relaxation is a competitive process. Once the diffusing, saturated xenon atom leaves the environment in which the saturating pulse included its resonant frequency, the resonant frequency of the atom will change due to the change in environment. Thus, even with the presaturation pulse still applied, the pulse will no longer be affecting that particular atom. From this point on, this atom will carry its saturation for a period of time no longer than its T_1 , which is also dependent on the environment. In general, ^{129}Xe will have longer T_1 in the less restricted space.

We have also performed inversion-recovery experiments on several coals, and particularly for the lower rank coals, the recovery of the adsorbed and external gas signals are nonexponential. We are currently analysing the relaxation data. There are four possible scenarios for the effect of presaturation centered on the adsorbed gas signal. For simplicity, we will assume that the T_1 is longer than the pulse length.

(1). The xenon atoms are in distinct internal adsorption sites and are effectively immobile during the time the pulse is applied. In this case we would expect to see a well defined break or a dip in the outline of the adsorbed gas signal in the area where the low power pulse was applied.

(2). The xenon atoms do have distinct internal adsorption sites, but diffuse among them during the presaturation time. Here we would expect to see saturation of the adsorbed gas signal, or overall loss of signal intensity, which may be accompanied by a change in the signal shape.

Note that outcomes (1). and (2). are related in that they are only distinguished by the time frame of site to site diffusion. For example, if the xenon atoms sample all the sites in 100 ms, then in a 10 ms period they are effectively immobile in their adsorption sites. A 10 ms presaturation pulse, assuming it is sufficiently narrow and delivers enough power to cause saturation, would be able to selectively saturate a portion of the overall adsorbed gas signal. A 100 ms pulse, however, should saturate the entire signal. Variation of the time frame of the experiment can identify the transition from one effect of presaturation to another.

(3). Xenon atoms are diffusing both into and out of the particle during the time the sample is presaturated. In this case, we would expect the intensity of both adsorbed and external-surface signals to decrease or completely saturate.

(4). The linewidth is not due to a distribution of sites, but to a short T_2 and/or magnetic field inhomogeneity. The signal intensity could be decreased by presaturating the

peak maximum, but the shape should remain the same, and presaturating the signal off center should have much less or no effect.

EXPERIMENTAL. Powdered samples of Wyodak subbituminous (subB; 76.3% C) and Sewell medium volatile bituminous (mvb; 88.9% C) coals were obtained from the Penn State/DOE coal sample bank and sieved to 60-100 Tyler mesh particle size. They were dried overnight in 10 mm NMR tubes with rototite valves (Wilmad), heated to 90° C for 2 to 4 hours, then kept under vacuum at room temperature for 24 hours or more. Once dry, the samples were charged with xenon to ~ 1 atm pressure (730-760 torr). Equilibration time was 6-12 hours.

NMR spectra were acquired on a Bruker AMX 360 NMR spectrometer operating at 99.61 MHz. A low power presaturation pulse was applied with the carrier frequency centered on the signal of interest followed by a 90° high power pulse and 3 s delay. The low power pulse length was varied as described in the next section. Spectra were run 300 to 1000 scans depending on the individual sample. All sets of spectra for a particular sample were run the same number of scans. Xenon gas at 700 torr was used as an external chemical shift reference.

RESULTS. *Presaturation of the ^{129}Xe NMR spectrum of coal.* The ^{129}Xe NMR spectrum of xenon gas adsorbed on Wyodak coal, with the presaturation pulse well separated from the xenon signals for reference, is shown in **Figure 1**. The signal centered at 160 ppm is from xenon adsorbed on the internal surfaces of the coal, and that at 0 ppm is the interparticle or external gas signal.

FIGURE 1. ^{129}Xe NMR spectrum of Wyodak coal with 40 dB presaturation pulse centered at -1000 Hz (approx. -60 ppm).

The Wyodak coal powder was presaturated at four different regions of the adsorbed gas signal, and the results are shown in **Figure 2**.

FIGURE 2. ^{129}Xe NMR spectra of Wyodak coal. 40 dB presaturation pulse is centered at (a) 22,594 Hz (~176 ppm), (b) 21,234 Hz (~163 ppm), (c) 20,618 Hz (~156 ppm) (d) 17,654 Hz (~126 ppm).

The four spectra have a 2 ms presaturation pulse centered at four different sections of the broad adsorbed gas signal. The spectra clearly show a trough, or hole burned, located at the center of the presaturation pulse. A change in the location of the pulse changes the location of the hole. The greatest effect is at 156 and 162 ppm, near the center of the signal.

Presaturation at the outer edges leaves more residual signal, particularly in the spectrum presaturated at 126 ppm. Comparison with the reference spectrum shows that there is overall signal intensity loss accompanying the change in signal shape.

Variation of power level. The effect of presaturation pulse power level on the appearance of the "hole" was tested for the Sewell coal from 33 to 43 dB, **Figure 3**.

FIGURE 3. ^{129}Xe NMR spectra of Sewell coal presaturated on the principal signal (~ 170 ppm) using four different power levels; from highest to lowest: (a) 33 dB, 0.2 ms; (b) 37 dB, 0.3 ms; (c) 40 dB, 0.4 ms; (d) 43 dB, 0.6 ms.

For the higher power levels used (40, 37, and 33 dB), a hole with signal remaining on either side could be produced in 0.3 to 0.5 ms; the best defined hole, with the most

remaining signal, was the 0.4 ms/40 dB combination. There was least residual signal at 0.2 ms/33 dB which had only one shoulder. At the lowest power levels examined, 43 and 46 dB (not shown), pulse lengths in the range 0.3 to 100 ms at 46 dB, and 0.6 to 1 ms at 43 dB, did not produce a hole. There was overall intensity loss and signal shape change in the form of a small shoulder, and saturation of the adsorbed xenon signal was complete in 100 ms at 46 dB, compared to 5 ms at 40 dB.

Saturation transfer to the interparticle gas . The low power pulse length was increased to observe the effect of presaturating the adsorbed xenon long enough for intra-, and subsequently extraparticle diffusion to occur. Two coals were presaturated on the principal adsorbed xenon signal for increasing lengths of time. The low power pulse length was varied in order to map out the time frames of hole burning, if any, saturation of the adsorbed signal, and saturation of the extraparticle gas signal.

The reference spectra for both coal samples are presaturated on the center of the adsorbed gas signal at very low power (80 dB power for 0.1 ms). All subsequent spectra for a given sample were phased relative to the reference. The Wyodak coal was presaturated at 40 dB power on the 150 ppm adsorbed xenon signal for increasing times from 1 ms to 40 ms. The results are shown in **Figure 4**.

FIGURE 4. Effect of increasing presaturation pulse length on ^{129}Xe spectra of Wyodak coal. (a) Reference; 0.1 ms, 80 dB. (All subsequent spectra are at 40 dB power.) (b) 1 ms; (c) 2 ms; (d) 5 ms; (e) 10 ms; (f) 15 ms; (g) 20 ms; (h) 30 ms; (i) 40 ms.

The spectra show a clear "hole" at 1 and 2 ms which is almost saturated at 5 ms. From 1 to 5 ms, the interparticle gas signal at 0 ppm is unchanged. At 10 ms, the adsorbed signal is

completely saturated and the interparticle gas signal has some insensitivity loss. At 30 ms the gas signal is reduced to a little over the noise level, and at 40 ms it is saturated.

The Sewell coal was presaturated at 37 dB on the 177 ppm adsorbed xenon signal for increasing times from 0.1 ms to 800 ms. The results are shown in **Figure 5**.

FIGURE 5. Effect of increasing presaturation pulse length on ^{129}Xe NMR spectra of Sewell coal. (a) Reference; 0.1 ms, 80 dB. (All subsequent spectra are at 40 dB power.) (b) 0.3 ms; (c) 1 ms; (d) 200 ms; (e) 400 ms; (f) 800 ms.

There is a "hole" in the signal at 0.3 ms accompanied by overall intensity loss. At 1 ms the signal is almost saturated. There was no effect on the interparticle gas signal. At 200 ms the adsorbed signal was completely saturated while the interparticle gas signal was less intense. At 400 ms the gas signal intensity decreased noticeably, and at 800 ms it was nearly saturated.

DISCUSSION. *Hole-burning in the ^{129}Xe NMR spectrum of coal.* We have been able to produce a spectral hole in the ^{129}Xe spectra of both coals. A spectral hole, or the loss of a portion of the adsorbed xenon signal, is evidence that some of the xenon atoms contributing to a broad signal have a resonant frequency close to the applied pulse; some do not, however, hence the residual portions of the signal. The sensitivity of the ^{129}Xe chemical shift to the dimensions and chemical composition of the space in which it is adsorbed is well known; a signal that is broad due to an overlap of isotropic shifts indicates that there exist slightly different adsorption sites from which the different xenon chemical shifts arise.

[Wernett (1991) has speculated that the ^{129}Xe NMR signal profile describes the pore size distribution. This interesting hypothesis has not been verified previously. It is addressed for the first time in our presaturation experiment. Given, however, that coal not only has a distribution of pore sizes, but a distribution of chemically distinct areas due to its heterogeneity, we will note here that the ^{129}Xe chemical shift is sensitive to both dimension and chemistry of the space in which xenon is adsorbed. Thus the more accurate term to reflect the environment contributing to the ^{129}Xe chemical shift is adsorption site distribution, rather than pore size distribution. This study does not aim to define these sites as to their size or chemistry, but demonstrates only the movement of adsorbed xenon atoms between them.]

The time frames of diffusion of saturated xenon through the solid and out into the interparticle space can be clearly illustrated by increasing the pulse length until the

saturation extends to the remainder of the signal it is focused on, and to the external gas signal. The relative changes in time or sequence of these events can be used to compare materials with different pore structures. Caution must be exercised, however, in using this technique as a definite measure of diffusion time, because the times are dependent on the presaturation pulse power level. Thus, details of the experimental conditions need to be discussed before describing the results of increased-pulse-length experiments.

Choice of experimental conditions. There are a range of possible low power levels that can be used in this experiment. In addition to a narrow excitation bandwidth, the power level should be able to induce saturation in the desired range of pulse lengths. The pulse length required has to be shorter than the intraparticle diffusion time in order to observe removal of part of the signal. Workable time/power combinations vary with the sample used and so should be tested for each.

The power level used significantly affects the appearance of the spectral hole as well as the length of time the signals survive presaturation. The different lengths of time required to saturate the entire signal at two different power levels can have two sources. On one hand, the higher power level has a wider excitation bandwidth, leaving less residual intensity which would appear to survive a shorter time as the pulse is lengthened. On the other hand, some lower power levels are insufficient to cause saturation at all. These signals have reduced intensity but survive long periods of presaturation. At the least, an optimum power level would have to be defined for this technique to be meaningful for *quantitative* measurement of the diffusion time of xenon through porous particles. As a means to compare different porous solids, however, relative changes in the saturation transfer results are clearly useful.

Implications for the pore structure of the coals. The different times required for saturation transfer to occur come from differences in diffusion rate of xenon through the void spaces in coals. Longer time for saturated xenon atoms to diffuse among the internal sites in

Wyodak coal is coupled with much shorter time to diffuse to the external surface compared to Sewell coal. We interpret this, first, as indicating that Wyodak has a wider distribution of internal sites, or less connectivity between the sites. (The wider distribution is more likely, as the connectivity between sites is at least good enough that signals from individual sites are not resolved, likely due to exchange between sites.) Second, the relatively easy access of adsorbed xenon to the external surface indicates greater connectivity of the pore network to the outside. The Wyodak coal, at 76.3%C, has meso- as well as microporosity as determined by N_2 and CO_2 adsorption, as is expected based on its rank (Gan et al. 1972). The NMR data in this study is in keeping with the presence of larger pores, in which diffusion of xenon would be faster, acting as feeder pores to the microporosity in this coal.

In the Sewell coal, the situation is reversed. First, an apparently shorter time to diffuse among the internal sites (i.e., for the saturation transfer from the "hole" effect to saturation of the entire signal) indicates a narrower distribution of adsorption sites than in the Wyodak coal. It should be noted that the signal itself, without presaturation, is narrower than in the Wyodak coal - this too is an indication of greater site homogeneity. Second, the longer time to diffuse to the external surface shows that the access of adsorbed xenon to the external surface in the Sewell coal is far more restricted than in Wyodak. This indicates a significantly different type of pore network in the two coals. The evidence points to a greater number of internal pore network connections than there are openings to the external surface in the Sewell coal. This is consistent with the notion of a highly interconnected microporous system lacking a significant amount of larger porosity. Gan et al. (1972) determined such pore size distribution variations with coal rank or carbon content; the presence of meso- and macroporosity decreases as coalification progresses. Sewell coal, at 88.9% C, is in the range where coal becomes predominantly microporous. Although micropores are typically too small to observe directly, such a network has been

suggested from TEM studies by Harris and Yust (1981) which showed a microporous region that was exclusively microporous and also highly interconnected.

The features of the pore structure emerging from the ^{129}Xe NMR results are in keeping with what can be derived from other studies on the relationship of pore structure to rank. Surface area and porosity as functions of rank (Gan et al., 1972) decrease through a minimum at about 81% carbon, then again increase, rising sharply after about 88% carbon. X-ray diffraction studies (Hirsch, 1954) indicate that low rank coals, up to 85% carbon, are amorphous; higher rank coals develop randomly oriented aromatic layers in the 85-90% carbon range, while the highest-rank coals develop ordered aromatic lamellar regions at >90% carbon.

Taken with the X-ray data, the rise in surface area at high rank corresponds to developing microporosity that is due to the development of aromatic crystallites (probably the space between them). This porosity is of a very different nature from porosity present in low-rank coals, which are predominantly in the spaces between poorly packed macromolecular chains (Spiro 1981, 1982). Our NMR data seem to be providing important additional insights into the pore structure of coals. For a higher rank coal, these are the following: relative isolation of internal porosity, as shown by long saturation transfer time, and narrower adsorption site type distribution, as shown by the narrower xenon linewidth. We are currently examining more coals to better describe the changes in these features with coal rank.

Further information on pore network connectivity would be useful in resolving the continuing controversy on whether coal micropores are primarily open or closed (Larsen et al., 1995; Walker and Mahajan, 1993). In the Wyodak coal the complete saturation of the adsorbed xenon signal, with no portion resistant to saturation after allowing 1-5 ms diffusion time, demonstrates *interconnection* of larger to smaller porosity. There was no isolated adsorbed xenon signal for either coal, an indication that the xenon atoms are

diffusing through an open porous network. If a significant portion of the porosity existed as isolated pockets, diffusion through the coal would require passing through regions of both solid matrix and pores. If dissolved in the solid, an NMR signal would be expected either resolved from xenon in porosity, or overlapped but detectable by its longer lifetime in the saturation transfer experiment. It is very unlikely that xenon can diffuse through the solid matrix at a rate comparable to its passage through pores, and this experiment reveals no indication in either coal that a detectable proportion of the adsorbed xenon is dissolved in solid coal.

Conclusion. The technique of selective presaturation applied to xenon adsorbed in porous material can clearly demonstrate the existence of a distribution of similar environments for adsorbed xenon in solids where the signals from xenon in these sites are not resolved as individual xenon signals. Differences in inter/extra particle xenon diffusion in two coals, available from saturation transfer techniques, are significant. These techniques can be used to investigate connectivity and adsorption site type distribution in microporous materials of unknown pore structure.

FUTURE PLANS

Low power presaturation. We are currently examining two additional coals using low power presaturation, as described in this report, in order to better define the rank effect of the results. The first two coals examined showed a marked difference in saturation transfer; it is important to verify that this is a rank dependent effect.

T₁ of xenon dissolved in several coals. We have performed inversion recovery experiments on four coals. This information is to be used to determine how the time frames for the the saturation effects seen in the low power presaturation experiment compare to the

T_1 relaxation time. We have found the magnetization recovery is nonexponential, especially for two low-rank samples. These data cannot be interpreted in a straightforward way to determine the T_1 ; additional mathematics describing the exchange rates must be introduced. This analysis is currently in progress.

Chemical Shift Anisotropy. Determination of whether chemical shift anisotropy exists for xenon adsorbed in coal is an important area in terms of the overall goals of this project. We have done initial work on sample preparation for magic angle spinning experiments. Magic angle spinning spectra for three coals will be done in the next quarter.

REFERENCES

- Freeman, R. A Handbook of Nuclear Magnetic Resonance, J. Wiley, N.Y. pp. 198-202 (1988).
- Gan, H., Nandi, S. P., and Walker, P. L. Jr., *Fuel* **51**, 272 (1972).
- Harris, L. A. and Yust, C. S. in Coal Structure, A.C.S. Washington, D. C. pp. 321-336 (1981).
- Hirsch, P. B. *Proc. Royal Soc., (London)* **A226**, 143 (1954).
- Jameson, A. K., Jameson, C. J., and Gerald, R. E. *J. Chem. Phys.* **101**, 1775 (1994).
- Larsen, R. G., Shore, J., Schmidt-Rohr, K., Emsley, L., Long, H., Pines, A., Janicke, M. and Chmelka, B. F. *Chem. Phys. Lett.* **214**, 220 (1993).
- Larsen, J. W., Hall, P., and Wernett, P. C. *Energy Fuels* **9**, 324 (1995).
- Ripmeester, J. A. and Ratcliffe, C. I. *An. Chim. Acta* **283**, 1103 (1993).
- Simpson, J. H., Wen, W.-Y., Jones, A. A., Inglefield, P. T., and Bendler, J. T. *Appl. Magn. Reson.* 349 (1995).
- Spiro, C. L., *Fuel* **60**, 1121 (1981).
- Spiro, C. L. and Kosky, P. G. *Fuel* **61**, 1080 (1982).
- Walker, P. L. Jr., and Mahajan, O. P. *Energy Fuels* **7**, 559 (1993).
- Wernett, P. C. Ph. D. Thesis, Lehigh University (1991).