DOE/PC/94216-T2

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

**Quarterly
TECHNICAL PROGRESS REPORT**

October 1995 - December 1995

by

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

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

Prepared for the U. S. Department of Energy

Grant No. DE-FG22-94PC94216

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.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

RECEIVED
USDOE/PETC
95 JAN 25 AM 9:43
ACQUISITION & ASSISTANCE DIV.

MASTER

6x

TABLE OF CONTENTS

	Page
Objectives.....	3
Summary.....	3
Technical Progress.....	4
Future Plans.....	13
References.....	15
Appendix: Figures 1-10.....	16

OBJECTIVES

The primary objective of this work is to use ^{129}Xe NMR to characterize the microporous structure of coals. As an aide in this characterization, which is by no means straightforward (Ripmeester and Ratcliffe, 1990, 1993; Moudrakovski et al., 1995), another objective is to combine this technique with volumetric adsorption techniques and track the effect of controlled opening of the micropores in a microporous carbon by oxygen chemisorption/desorption. The primary goal of the NMR work is to measure the micropore sizes in coal; more broadly, it is to better tailor the ^{129}Xe NMR method for use with coal, and to investigate other ways it may be used to describe pore structure in coal, with emphasis on determining whether micropores in coal are connected or isolated.

SUMMARY

In terms of the primary objectives of the project, the ^{129}Xe NMR spectra with pressure variation have been obtained for two more coals, completing this task for the sample set of six coals. In terms of the broad objectives of the project, examination of the influence on the xenon signal of packing the powdered coal has been undertaken. These data are of potential value for the determination of whether the porosity is open or closed (Ripmeester and Ratcliffe, 1993). Results of powder density and related experiments will be used in the final interpretation of our current data, including the determination of whether, in the NMR of loose powdered, the chemical shift is indicative of the "true" gas-solid interaction.

TECHNICAL PROGRESS

^{129}Xe NMR spectra of coals

Introduction. ^{129}Xe NMR has been demonstrated to be effective in measuring the pore sizes in zeolites, using a method developed empirically by Demarquay and Fraissard (1987). The inverse of the chemical shift in zeolites of known pore dimensions was found to be a linear function of the mean free path of the gas under conditions of low gas pressure (< 1 atm), and pore sizes sufficiently small to give a mean free path for xenon of 1-6 Å. The spectra were taken at a series of xenon pressures. The chemical shift is plotted vs. the pressure, and the mean free path of the entrapped xenon can be calculated from the intercept (see p. 7 for the details of this calculation).

The technique has been applied to a carbonaceous material of reasonably well defined pore structure by Wernett et al. (1990), and the calculated pore diameter was within the expected range. Thus, the technique may be applicable to coal, though it must be borne in mind that coal is much more heterogeneous than either zeolites or microporous carbons, and that paramagnetic species and/or impurities in coal can affect the NMR data. In a study by Tsiao and Botto (1991), analysis of the ^{129}Xe NMR spectra of three Argonne Premium coals gave micropore diameters in the 6-9 Å range. For their Illinois #6 coal sample, two distinct resonances were observed, suggesting that pore regions of different physical or chemical makeup may be distinguishable by ^{129}Xe NMR.

There were also unresolved issues in Tsiao and Botto's study; chief among them is the appearance of broad, sometimes asymmetrical resonance peaks of xenon adsorbed in coal. These were treated as overlapped peaks and all spectra were deconvoluted to decide on the chemical shift assignments; however, overlapping of peaks was clear for only one of the samples. There were also indications in this study that Demarquay and Fraissard's method may not be directly applicable to coals. The chemical shift vs. pressure relationship

was not linear at the pressures used; whether the chemical shift vs. pressure intercepts from the nonlinear fits give valid information on pore sizes is not clear. In our current study, the chemical shift vs. pressure relationships are more or less linear. The spectra obtained so far do not appear to be overlapped. Currently, the chemical shift values are assigned by taking the highest point on the peaks. The pore diameters were calculated following Demarquay and Fraissard (1987).

Given these uncertainties, our approach has been to take the spectra for our sample set, and apply Demarquay and Fraissard's method as a starting point only. We shall then investigate other ways to derive meaningful information from the NMR data through modification of the current methods or possibly development of a different method. We are currently investigating the ^{129}Xe NMR of pressed pellets of coal versus the loose powder as a way to determine whether the pore system is open or closed.

Coal samples examined to date have been loose powders. Spectra of pressed pellets of coal (and/or powders having different particle sizes) will be acquired. If the chemical shift increases with respect to the loose powder, at a given equilibrium pressure of xenon, this would be an indication that intra- and inter-particle gas is exchanging on the NMR timescale.

The adsorbed, intra-particle xenon has a significantly higher frequency resonance signal than the inter-particle gas. The interparticle gas is free gas in intermittent contact with the external surface of the particles, with chemical shift of 0-4 ppm. Both intra- and inter-particle gas signals are distinguishable for all coals examined with the exception of the Lykens Valley anthracite. They occur about 100-200 ppm apart.

In an open, interconnected pore system, the gas may exchange in and out of the pores. If this occurs fast on the NMR timescale, the result is one signal which is a weighted average of the two environments sampled by the gas. The relevant timescale is defined as

the time equivalent of the frequency difference between the two signals (for further discussion, see Kaplan and Fraenkel, 1980). As an example, for xenon signals at 0 and 160 ppm in an 8.4 T magnetic field, the frequency difference is 16,000 Hz. Diffusion into or out of a coal particle in about 6×10^{-5} s or less would affect the NMR signal. In general, at exchange rates that are slow on the relevant timescale, the signals are distinct and representative of the two environments, but at intermediate rates, the signals are displaced from these positions towards the average of their chemical shifts. Particle size is clearly a significant factor, since for a given rate of intraparticle diffusion, whether the distance the intraparticle gas has diffused takes it out of the particle in the relevant time period depends on the size of the particle.

One way to test whether exchange is affecting the NMR signals is to increase the powder density. The NMR signal should not be affected if exchange is slow or is not occurring (all other things being equal). The NMR signal should be displaced to greater chemical shift values for a given xenon pressure if exchange is intermediate. This is because there will necessarily be less exchanging gas in interparticle space if the amount of this space has been decreased, and the gas will experience more solid contact, increasing the chemical shift. The implication of increased chemical shift with increased powder density is that the pores are connected and open to the external surface, since this would allow exchange to occur. It should be noted that with the possible exception of Lykens Valley anthracite, exchange is not fast for the coals we have examined, because the interparticle gas peak at 0-4 ppm is visible; in the case of fast exchange, only one, averaged signal would be seen.

A possible drawback of pressing the powder is that it is unclear whether the micropores may be deformed in the process. Fairly low pressure was thus used (3000 psi); nevertheless, experiments that do not require compression of the sample will also be done. These include variation of particle size, and a saturation exchange experiment which can

indicate whether the intra- and inter-particle xenon populations are coupled (Jeener et al., 1979).

Experimental

Samples are prepared on a two-arm vacuum/gas manifold. A 10-mm NMR tube fitted with a Rototite J. Young-type valve (Wilmad) was filled to a height of approximately 4 cm with size-graded coal (-60 mesh). The NMR tube attaches directly to the vacuum line, and may be opened to vacuum or gas without removal of the tube. Loose powder samples were loaded directly into the NMR tubes. Pressed pellets were prepared using a die press at 3000 psi for approximately one minute. Pellets were broken into pieces about 4 mm in diameter and loaded into the tube. Smaller pieces and dust were discarded.

Samples were outgassed at 100 °C under vacuum for a minimum of 18 hours to a pressure of 5 μ m Hg. Each sample is cooled to room temperature under vacuum and natural abundance xenon gas (99.97% purity) is then introduced by closing the vacuum side and opening the gas side valves. The pressure in the xenon side of the manifold is monitored with a Barocel dual capacitance manometer and Televac MM200 digital gauge controller. No drop in xenon pressure in two minutes was taken as a reasonable equilibrium criterion. Samples were equilibrated for an average period of 40 minutes.

The ^{129}Xe NMR spectra were taken at a series of at least four xenon pressures between 250 and 700 torr. Xenon pressure was changed for samples already exposed to xenon by returning the NMR tube to the manifold and applying vacuum to 10 μ m Hg or less, then opening the tube to xenon. For pressures over 500 torr, two or more aliquots (fillings of the gas arm of the manifold) were required.

The spectra were acquired on a Bruker AMX 360 NMR instrument operating at 99.61 MHz for xenon. A 90 degree pulse width was employed with 1.5 or 2 second delay. Between 1,500 and 5,000 scans were required for good signal-to-noise ratio for most coals. Spectra were referenced to the chemical shift of 1 atm xenon gas, set as 0 ppm.

Results and Discussion

Chemical shift vs. pressure. One bituminous coal and one anthracite from the Penn State/DOE coal sample bank have been examined. The spectra are shown in **Figs. 1** and **2** as a function of xenon pressure. Plots of the chemical shift vs. pressure are shown in **Figs. 3** and **4**. Pore diameters were calculated from the intercept (δ_0) of the chemical shift vs. pressure plot, following the method of Demarquay and Fraissard (1987):

$$\text{mean free path } l \text{ of Xe in the pore (in } \text{\AA}\text{):} \quad l = \frac{(243)(2.054)}{\delta_0} - 2.054$$

$$\text{pore diameter } d, \text{ assuming a cylindrical pore (in } \text{\AA}\text{):} \quad d = l + 4.4$$

The results are summarized in Table 1.

Table 1. ^{129}Xe NMR data for coals.

Coal		Rank	% C (dmmf)	Intercept δ_0 (ppm)	Correlation coefficient	Pore diameter ($\text{\AA}$)
DECS-6	(Blind Canyon)	hvAb	82	139.6	0.96	5.9
DECS-21	(Lykens Valley)	Anth	92	98.8	0.92	7.4

The determining factor for obtaining the pore diameter by this technique is the value of the intercept δ_0 , which is inversely proportional to the pore diameter. The plot of intercept vs. rank (% C) for the entire sample set (six coals) is shown in Fig. 5. There is no apparent trend in intercept with coal rank when considering the entire sample set. The relationship for a subset of the group is bowl-shaped, with larger intercepts at low rank, first decreasing and then rising again with rank, a pattern reminiscent of coal surface area vs. % C (Gan et al., 1972). This gives pore diameters with the opposite tendency, small to larger to small again, as rank increases. A correlation between the NMR results and surface area measurements is just beginning to be noticeable from these data, and requires further scrutiny before reliable conclusions can be drawn.

NMR data from the Blind Canyon hvA bituminous coal sample proved to be difficult to obtain. The signal was far weaker than for the other coals, and acoustic ringing was pronounced in the spectra. The weak signal could originate from closed or inaccessible microporosity, either as a natural characteristic of this coal, or due to oxidation or other alteration of the sample during handling. This sample was the most deviant from the rank-dependent trends in intercept, slope, and peak shape. We will continue to work with this coal because it is possible that spectral quality prevented proper assessment of the shape and location of the resonance. In an effort to distinguish the signal from acoustic ringing, an echo sequence of the form $\pi/2 - \tau_1 - \pi - \tau_2 - AQ$ is now being tried on this sample. Using this pulse sequence, acquisition of the ^{129}Xe signal is delayed while the ^{129}Xe magnetization is refocused. This allows the xenon signal to be acquired (as an echo) after the acoustic ringing of the probe has decayed to some extent.

Intensity of the external surface adsorbed gas peak. This signal appears at about 0-4 ppm for five of the six coals. The absolute intensity of the peak may vary with the number of scans collected for the spectrum and with the pressure of the gas, more pressure and/or more scans corresponding to stronger signals. The gas peak intensity relative to the

adsorbed gas signal intensity (at 100-200 ppm) is usually consistent for a particular coal. It may increase at higher pressures - an indication that at the higher pressure, more gas is outside the particles, thus less of the added gas was actually adsorbed. Analysis of relative intensity of this peak with pressure changes may give useful information on the adsorption behavior of the coals. For example, once the gas peak begins to increase in relative intensity, the micropore filling stage may be completed.

Lack of a gas peak, which occurs for Lykens Valley anthracite and for the microporous carbon previously examined, may be an indication of exchange averaging of the signals due to fast intra/inter-particle exchange, which we are currently investigating. The low frequency of the anthracite signal (ca. 110 ppm) compared to the other coals (140-200 ppm) supports this possibility.

Shape and symmetry of signal. There is a qualitative relationship between ^{129}Xe signal symmetry and rank. ^{129}Xe spectra for six coals of increasing rank are shown in Fig. 6. The trend in peak shape is toward a narrower, more symmetrical signal as rank increases. The effect is most pronounced in the 90 and 92 %C samples. Possible sources of the change in peak shape are increasing chemical homogeneity within the pores, decreasing pore size distribution, and, if chemical shift anisotropy exists for xenon adsorbed in coal, increasingly ordered pore structure.

A particularly interesting possibility is that the trend observed in Fig. 6 is due to chemical shift anisotropy in asymmetrical spaces such as lamellae. An asymmetrical signal very similar to low rank coal was observed for xenon in randomly oriented montmorillonite platelets by Ripmeester and Ratcliffe (1993); the shape became more symmetrical for ordered platelets and the chemical shift changed as the orientation of the ordered sample changed with respect to the magnetic field. Should this effect exist in coals, it would be pertinent to this project. A study of the orientation dependence of the chemical shift for xenon in a whole piece of coal is being undertaken to clarify this issue.

Slope of chemical shift vs. pressure plots. The location of the chemical shift is influenced by both the chemical makeup of the pore surfaces and the frequency of collisions of Xe with the pore walls. In samples such as coal, in which neither the pore size nor the chemical composition can be controlled, the influence of each cannot be separated in order to treat chemical shift as a direct indication of pore diameter. Given these considerations, measurements of pore diameters in coals using the method of Demarquay and Fraissard (1987) cannot be assumed *a priori* to be reliable. This will be of major concern in our future work. Currently, the slope is being considered as an alternative to the chemical shift as a source of information on the pore structure. The slope varies considerably for the samples studied. The origin of this variation is unknown at the present time. While the slope of chemical shift vs. pressure has not been previously used in the measurement of pore sizes, it may be an indicator of some aspect of pore structure. For example, it is logical to consider larger pores as more accessible to xenon, and more xenon may enter a larger pore for a given pressure increase, resulting in a steeper variation of chemical shift with pressure (i.e., a greater slope).

The slopes (ppm/torr) for six coals were plotted vs. rank (%C) in Fig. 7. There is not a regular trend with rank (%C) for this group. Comparison with the rank dependence of the intercept (Fig. 5) shows that the relationships of slope and intercept to rank are clearly not similar. This does indicate that the determinants of δ_0 and slope may be different properties of the adsorbent. The possibility remains that the slope is directly related to the surface area, as preliminary results indicated. Surface area measurements on the remaining samples are in progress.

Spectra of pressed pellets vs. loose powder. Adaville hvCb coal pressed pellets were examined by NMR at a series of xenon pressures, shown in Fig. 8. The plot of chemical shift vs. pressure is shown in Fig. 9.

There was significant effect on both the chemical shift and peak shape as a result of increasing powder density. The peak shape was fairly symmetrical for the loose powder, but became less symmetrical and broader after pressing the powder (Fig. 10). In both cases an external-surface adsorbed gas peak is visible at about 0 ppm.

Table 2. Summary of NMR data for Adaville hvCb coal, pellet vs. powder.

	Pellet	Powder	Effect of increased density
Calculated pore diameter	6.34 Å	7.18 Å	decrease, 12%
Chemical shift vs. pressure intercept	124.9 ppm	103.1 ppm	increase, 21 %
chemical shift vs. pressure slope	0.0913 ppm/torr	0.0526 ppm/torr	increase, 73%

The chemical shift extrapolated to zero pressure (δ_0) increased from 103.1 to 124.9 ppm, decreasing the calculated pore diameter from 7.18 to 6.34 Å. The increase in chemical shift may be interpreted as due to greater gas-solid interaction and less exchange averaging with gas adsorbed on the external surface. This interpretation of the result is a positive indication that exchange is occurring. The difference in pore size calculated after pressing the pellet would be due to a more accurate δ_0 , and would not indicate an actual change in pore size. An alternative interpretation is that the change in chemical shift, and thus calculated pore size, is due to an actual physical change in the microporous structure of the coal caused by compression.

The results of this experiment do not allow us to differentiate between these interpretations at the present time. This experiment will be followed up with a particle size effect experiment and a saturation transfer experiment, which will determine whether exchange between the intra- and inter-particle gas populations is occurring on the timescale that affects the NMR signal.

FUTURE PLANS

In addition to obtaining the Blind Canyon spectra using an echo sequence, several new experiments will be performed, as discussed briefly below. The first two, determination of T_1 in porous vs. nonporous materials and analysis of changes in chemical shift with powder density, are new ways to address the issue of whether the micropores in coal are connected or isolated. This is an area of continuing controversy, most recently addressed by Larsen et al. (1995). Support for the powder density experiment would be provided by a particle size effect experiment and a saturation transfer experiment on powdered coal, to establish whether the intra- and inter-particle xenon populations are coupled. A fourth experiment, on the existence of chemical shift anisotropy for xenon adsorbed in coal, is necessary to confirm or discard a possible source of the variations in peak shape seen in coals.

T_1 for dissolved xenon (no empty space) vs. T_1 in microporous solids. Relaxation time is an indicator of molecular mobility and thus could be significantly different for xenon dissolved in a solid matrix as opposed to that adsorbed on a surface or in a pore. A method to differentiate xenon NMR signals arising from dissolved vs. adsorbed xenon would be very useful in validating (or invalidating!?) the assertion of Larsen et al. (1995) that most adsorbates must dissolve in and diffuse through 'solid' coal to reach most of the microporosity.

Particle size effect experiment. A series of particle size fractions of a pure vitrinite will be examined by NMR at roughly equal pressures of xenon. Change in chemical shift with particle size would indicate that exchange of xenon in and out of the particles on the timescale of the NMR experiment is occurring.

Selective saturation transfer experiment. For a sample of powdered coal, the external surface-adsorbed gas peak (interparticle gas), which typically occurs at 0-4 ppm, will be selectively inverted. Transfer of magnetization to the adsorbed (intraparticle) xenon indicates that exchange is occurring.

CSA of xenon in a whole piece of coal. Chemical shift anisotropy of xenon in coal has not been discussed in the literature. We will investigate the possibility that it exists, based on the similarity of ^{129}Xe spectra of lower rank coal spectra to that of randomly oriented montmorillonite platlets, which show chemical shift anisotropy (Ripmeester and Ratcliffe, 1993).

A whole piece of coal will be examined by ^{129}Xe NMR with orientation of bedding plane parallel and perpendicular to the magnetic field. (Because the shape and orientation of the micropores in coal are not known, the only directional reference point available is the bedding plane.) Existence of anisotropy would indicate nonrandom orientation, relative to the bedding plane, of asymmetric spaces in the coal. There is currently evidence for the development of ordered crystallites in coal, which are thought to be randomly ordered with respect to each other, but not for larger-scale order. If evidence for chemical shift anisotropy in coal is found, it would be worthwhile to follow with CSA studies over a range of rank. This approach has the potential to add new information to the well known x-ray diffraction work of Hirsch (1954), as well as other studies, which indicate a sudden and quite intriguing change in the physical structure of coal around 88% C.

REFERENCES

- Demarquay, J. and Fraissard, J. *Chem. Phys. Lett.* **136**, 314 (1987)
- Gan, H., Nandi, S. P., and Walker, P. L. Jr. *Fuel* **51**, 272 (1972)
- Hirsch, P. B. *Proc. Royal Soc., (London)* **A226**, 143 (1954)
- Jeener, J., Meier, B. H., Bachmann, P., and Ernst, R. R. *J. Chem. Phys.* **71**, 4546 (1979)
- Kaplan, J. I., and Fraenkel, G. NMR of chemically exchanging systems. Academic Press, New York (1980)
- Larsen, J. W., Hall, P., and Wernett, P. C. *Energy and Fuels* **9**, 324 (1995)
- Moudrakovski, I. L., Ratcliffe, C. I., and Ripmeester, J. A. *Appl. Magn. Reson.* **8**, 385 (1995)
- Ripmeester, J. A. and Ratcliffe, C. I. *J. Phys. Chem.* **94**, 7652 (1990)
- Ripmeester, J. A. and Ratcliffe, C. I. *Anal. Chim. Acta* **283**, 1103 (1993)
- Tsiao, C. and Botto, R. E. *Energy and Fuels* **5**, 87 (1991)
- Wernett, P. C., Larsen, J. W., Yamada, O., and Yue, H. J. *Energy and Fuels* **4**, 412 (1990)

APPENDIX

Figure 1. ^{129}Xe spectra of Blind Canyon hvA bituminous coal. (a) 657 torr; (b) 519 torr; (c) 432 torr; (d) 387 torr.

Figure 2. ^{129}Xe spectra of Lykens Valley anthracite. (a) 620 torr; (b) 517 torr; (c) 395 torr; (d) 350 torr.

Figure 3. Chemical shift vs. pressure for Blind Canyon hvA bituminous coal.

Figure 4. Chemical shift vs. pressure for Lykens Valley anthracite.

Figure 5. Intercepts (δ_0 , ppm) of chemical shift vs. pressure plots for six coals, plotted vs. rank (%C).

Figure 6. ^{129}Xe signals for six coals of increasing rank. (a) lignite; (b) sub bituminous; (c) hvC bituminous; (d) hvA bituminous; (f) anthracite.

Figure 7. Slopes (ppm/torr) of chemical shift vs. pressure plots for six coals, plotted vs. rank (%C).

Figure 8. ^{129}Xe NMR spectra of Adaville hvC bituminous coal pressed pellets. (a) 517 torr; (b) 455 torr; (c) 382 torr.

Figure 9. Chemical shift vs. pressure for Adaville hvC bituminous coal pressed pellets.

Figure 10. ^{129}Xe NMR spectra of Adaville hvC bituminous coal. (a) pressed pellet; (b) loose powder (-60) mesh.