EFFECTS OF SURFACE CHEMISTRY
ON THE POROUS STRUCTURE OF COAL

Quarterly

TECHNICAL PROGRESS REPORT

January 1996 - March 1996

by

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Prepared for the U. S. Department of Energy

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OBJECTIVES

The primary objective of this work is to use ^{129}Xe NMR to characterize the microporous structure of coals. Another objective is to use this technique to describe 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

During this quarter, we have: (i) investigated particle size effect on the chemical shift of xenon adsorbed in a set of size-graded vitrinites; (ii) tracked the progress of xenon adsorption via xenon NMR, including particle size effect on the adsorption process; (iii) completed a preliminary test for chemical shift anisotropy in coal; and (iv) examined a microporous carbon by ^{129}Xe NMR after two cycles of oxygen chemisorption/desorption.

TECHNICAL PROGRESS

^{129}Xe NMR spectra of coals: particle size effect on chemical shift

Introduction. To determine the effect of particle size on the ^{129}Xe NMR of coal, four particle size fractions of an Upper Freeport medium volatile bituminous vitrinite were examined. The pure vitrinite was selected for two reasons. First, since the powdered coal was to be size graded, the use of a single maceral avoids the problem of maceral segregation when the coal is size graded, which could result in size fractions of different chemical composition. Second, use of the vitrinite provided us with the opportunity to see whether vitrinite spectra are comparable to those of whole coals.

Experimental. Four size-graded samples of an Upper Freeport vitrinite were obtained, +60, 60-100, 100-200, and -400 U. S. mesh. Samples were dried for 12 hours at 100 °C and 24 hours at room temperature in 10 mm NMR tubes fitted with Rototite valves (Wilmad), which attach directly to the vacuum line. Samples were charged with xenon gas and allowed to equilibrate 40 minutes at 630-650 torr xenon. The tubes were then sealed and removed from the manifold. NMR spectra were acquired on a Bruker AMX 360 NMR spectrometer operating at 99.61 MHz. A 90° pulse width was employed with 1.5 s delay. Between 3,000 and 5,000 scans were acquired. Xenon gas at 700 torr was used as an external chemical shift reference.

Results and Discussion. The ^{129}Xe spectra of four particle size fractions of microporous Upper Freeport mvb vitrinite are shown in **Fig. 1**. There are no significant differences in the spectra for the 60, 60-100, or 100-200 mesh size fractions. The sorbed xenon signal is at 180 ppm, and the external-surface adsorbed gas signal is at 0 ppm. In the 400-mesh size sample, the external gas signal is at 5 ppm, an increase with respect to that

of the larger particle sizes. The sorbed gas signal is at ~170 ppm, a decrease with respect to that of the the larger sizes.

The displacement of the sorbed and external gas signals toward eachother in the 400 mesh sample is preliminary evidence that intra/extra particle exchange is occurring in this sample on the time scale of the experiment. The aquisition time was 130 ms. Additional experiments are needed to quantify the intraparticle diffusion rate.

The intra- and extra- particle xenon populations have distinct chemical shifts. Exchange between these populations would be caused by diffusion of a significant portion of the adsorbed xenon population through a particle and to the free gas population. The particle size could affect the degree to which intraparticle diffusion results in exchange on the time scale of the NMR experiment. If the diffusion path length is on the order of the particle size or greater within the time period of interest, the NMR signals will show evidence of exchange, which is a shift in the location of the two signals towards their weighted average value, with broadening of the peaks. In the case of fast exchange, a single, averaged signal would be seen (see, for example, Kaplan and Fraenkel 1980).

This experiment suggests that exchange on the time scale of ~130 ms is detectable in the 400-mesh Upper Freeport vitrinite, and not in the larger particles. The shift in the location of the sorbed gas resonance was 10 ppm. The signals were not dramatically affected by changes in particle size, and it may be concluded that for this vitrinite, the intraparticle diffusion rate is sufficiently slow that particle size itself will not, in most cases, significantly alter the chemical shift. The effect on ^{129}Xe chemical shift for solids with a higher intraparticle diffusion rate could be more marked than in this sample. This is potentially a significant consideration in the application of pore size measurement techniques (For e.g., that of Demarquay and Fraissard, 1987) that rely on proper definition of all contributors to the chemical shift.

The apparently slow intraparticle diffusion rate in the vitrinite along with the low overall uptake of xenon compared to other coal samples, implies that this material has highly constricted microporosity. The finding that exchange can occur suggests that the pores are open. This initial analysis of the particle size effect on the ^{129}Xe chemical shift is consistent with the existence of an open (or partly open), constricted micropore network in this vitrinite.

^{129}Xe NMR as a technique to follow the adsorption process

Introduction. One goal of this project is the investigation of new applications of ^{129}Xe NMR to the study of coals and carbons. In this study we are considering the possible utility of using ^{129}Xe NMR to track the xenon adsorption process. We are interested in what may be revealed about the rate of approach to equilibrium and the determination of achievement of equilibrium, particularly if there are changes detectable by NMR (e.g., gas location within the porous network) which are not apparent from gas uptake vs. time data. An anthracite was used as the adsorbent, and was prepared in two particle size fractions, so that we could also examine particle size effect on the adsorption rate.

Experimental. Two particle size fractions, 40-60 and -100 Tyler mesh, of Lykens Valley anthracite were dried 6 hours at 100°C and 24 hours at room temperature in 10 mm NMR tubes fitted with Rototite valves (Wilmad), which attach directly to the vacuum line. Samples were charged with xenon gas to a pressure of ~ 650 torr and not allowed to equilibrate; the tubes were sealed and removed from the manifold within one minute. NMR spectra were acquired on a Bruker AMX 360 NMR spectrometer operating at 99.61 MHz. Spectra were acquired at progressively increasing time intervals ranging from approximately 7 minutes to 16 hours were acquired on individual samples over a 24 hour period. A 90° pulse width was employed with 1.5 s delay. In order for each spectrum to represent a short window of time, minimum number of scans necessary to obtain adequate

signal-to-noise was employed; this was 88 scans for the -100 mesh, and 160 for the 40-60 mesh particles. Xenon gas at 700 torr was used as an external chemical shift reference.

Results and Discussion. The chemical shift and the signal width at half height were plotted as functions of time for both particle sizes of the anthracite (Figs. 2-5). Xenon uptake by the 40-60 mesh sample was measured separately on the vacuum line, plotted as pressure vs. time, Fig. 6, and used for comparison (the -100 mesh uptake measurements are in progress). For both particle sizes, the ^{129}Xe chemical shift, signal width, and xenon pressure drop (in 40-60 mesh) all decrease exponentially with time. Table 1 lists the time constants for the exponential decays, and summarizes the times at which the plots show transition from fast to slow change (bend), and when they have flattened out.

Table 1. Characteristic times for time-dependent chemical shift (CS), linewidth (LW) and xenon uptake plots for -100 and 40-60 mesh Lykens Valley anthracite.

Sample mesh	CS time constant	CS bend	CS flattens	LW time constant	LW bend	LW flattens	uptake bend	uptake flattens
40-60	-16.7 ppm	4-6 hrs	>15 hrs	-1370 Hz	2-3 hrs	>10 hrs	3-5 hrs	>20 hrs
-100	-11.9 ppm	0.5-1 hrs	3-4 hrs	-634 Hz	0.5-1 hr	3-4 hr		

These experiments both test this method as a way to track the xenon adsorption process, and use it to compare two particle sizes. We compared linewidths to chemical shifts to see if they are following the same pattern. In the -100 mesh sample the bends in both were in good agreement. In the 40-60 mesh sample, the linewidth approached a steady state somewhat faster than the chemical shift. The uptake vs. time data for the 40-60 mesh sample (Fig. 6) has a bend about midway between and overlapping that for linewidth and chemical shift. These three features for 40-60 mesh appear basically equivalent.

The achievement of a steady state in the uptake measurements occurs about 10 hours later than that for the linewidth, and about five hours later than for the chemical shift. This indicates that there is a point in the process beyond which, while diffusion/adsorption is still occurring, the adsorbed xenon nevertheless experiences an unchanging environment or experiences *equivalent* environments. (The term "environment" as applied to the ^{129}Xe signal means collision frequency with other gas atoms and with pore wall atoms.) We are continuing our work on interpreting these data.

Comparison of the timing of change in chemical shift and linewidth between two particle sizes indicates that the location of the bend is 2-3 hours earlier for the -100 mesh than for the 40-60 mesh sample, that the flattening of chemical shift is reached about 10 hours earlier for -100 mesh, and the flattening in linewidth is reached about 6 hours earlier. The smaller particles approached and reached equilibrium xenon adsorption faster than the larger particles. The results of this experiment are a clear indication that particle size does affect the rate of approach to equilibrium adsorption, at least for xenon in anthracite.

This is a significant finding with important implications for the structure of the micropore network. It is consistent with the earlier work of Radovic and coworkers (Menon et al. 1993; Radovic et al. 1996). In agreement with the interpretation offered there, and elsewhere (Mahajan, 1991; Walker and Mahajan, 1993), it is taken to represent support for the open-but-constricted microporous structure of coal. If diffusion of xenon occurred by dissolution into the solid matrix, such severe particle size effects would not be observed. The trends observed here suggest that the surface density of pore constrictions decreases as the particle size decreases. Further verification of this conclusion is needed and is in progress.

Chemical shift anisotropy of xenon in coal

Introduction. We have previously noted that the shape of the signal for xenon adsorbed in coals becomes narrower and more symmetrical as rank increases (Fig.7) An interesting possibility is that this could be an indication of the existence of chemical shift anisotropy in coal, and if so, it would also indicate rank-dependent changes in the asymmetry of the geometry of micropores in coal. A low and a high rank coal were chosen for this series of experiments and single pieces were cut from blocks in which the bedding plane was visible. Pieces cut parallel and perpendicular to the bedding plane were examined by ^{129}Xe NMR.

An asymmetrical signal very similar to that of a 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 chemical shift anisotropy exist in coals, it would be pertinent to this project.

Experimental. Blocks of Wyodak subbituminous B coal and Lykens Valley anthracite were obtained and the bedding plane located by inspection. Pieces were removed from the blocks using a chisel and files. One piece cut parallel to the bedding plane and one perpendicular to it were obtained for each coal, and were inserted into 10-mm NMR tubes. Perpendicular cuts broke easily, and were made shorter than parallel cuts in order to keep them intact. Perpendicular cuts were placed over small glass pieces in the NMR tube to elevate the sample into the receiver coil detection region of the NMR instrument. The tubes were then constricted, so that they could be flame sealed after preparing the sample.

Samples were dried for 24 hours at 80 °C and three days at room temperature. They were then charged with xenon to a pressure of about 800 torr and equilibrated four hours on the vacuum line. (More xenon was added to the Wyodak sample as adsorption progressed in order to keep the xenon concentration high and produce strong NMR signals.

Additional xenon was not needed for the anthracite, which adsorbed less xenon than the subbituminous coal.) The samples were then flame-sealed.

NMR spectra were acquired on a Bruker AMX 360 NMR spectrometer operating at 99.61 MHz. A 90° pulse width was employed with 1.5-3 s delay. Between 1,000 and 5,000 scans were acquired. Xenon gas at 700 torr was used as the external chemical shift reference.

Results and Discussion. The ^{129}Xe NMR spectra at about 700 torr for the Wyodak coal parallel and perpendicular cuts are shown in **Figs. 8-9**. The data for Lykens Valley anthracites are shown in **Figs. 10-11**. A comparison of the signal locations and linewidth for the anthracites is shown in **Table 2**. Due to the possibility that the Wyodak spectrum had two overlapped peaks, we did not compare peak widths.

Table 2. Chemical shift (in ppm) and linewidth (in Hz) of ^{129}Xe NMR signals in whole pieces of coal cut parallel and perpendicular to the bedding plane.

Coal	adsorbed gas, major signal	adsorbed gas, additional signal	external gas	width, major signal
Wyodak, parallel	170	132	0	n/a
Wyodak, perpendicular	166	133	0	n/a
Lykens Valley, parallel	116	none	none	2212
Lykens Valley, perpendicular	134	none	-2.0	3427

The Wyodak parallel and perpendicular spectra are very similar. The major signal is broad with maximum height at 166-170 ppm. Given the signal shape, the 4 ppm difference between them is probably not significant. There is a distinct shoulder at 132-133 ppm, which is better resolved in the parallel-to-the-bedding-plane spectrum. Interestingly, the shoulder is not seen in the spectrum of Wyodak powder, **Fig. 12**, which has a signal at 160 ppm at 565 torr. (This is consistent with the 166-170 ppm maximum of the signal from solid Wyodak at ~700 torr.) There is also an external surface gas peak at 0 ppm for both samples. Overall, the Wyodak spectra do not indicate a bedding plane orientation dependence of the chemical shift.

The anthracite parallel and perpendicular spectra are different in chemical shift, linewidth and external-surface gas signal. The perpendicular cut has a chemical shift of 134, about 18 ppm greater than in the parallel cut; it also has a strong gas signal at -2 ppm, while none is evident for the parallel cut. While these spectra could indicate the existence of chemical shift anisotropy, all other things being equal, we are not making such a claim at this time since the spectra also suggest differences in sample preparation. For example, one possibility suggested by the difference in gas signal is that there is more unadsorbed gas in the perpendicular sample tube; the higher chemical shift is also to be expected if the gas pressure is higher in this tube than in the parallel sample tube.

The difference in linewidth, which is approximately 1000 Hz wider for the perpendicular cut, is not expected as a result of higher pressure for samples at equilibrium. The samples were equilibrated over a period of weeks before the spectra in **Figs.8-11** were acquired. Possible explanations of the chemical shift and external gas signal differences in the spectra include different pressures in the tubes due to a pinhole leak in one seal and/or a difference in the composition of these two samples. Although taken from the same block, the smaller size of the perpendicular cut could mean it has more of one band than would be representative of the whole block. If, for example, the perpendicular

cut was primarily a vitrinite band and the parallel cut composition was different, the result could be both higher chemical shift and less adsorption in the perpendicular cut. We have previously noted that the xenon uptake in a pure mvb vitrinite was low and the chemical shift was higher compared to whole coals. In addition, low xenon uptake in vitrinite bands compared to the rest of the block in a whole Kentucky coal has been observed by Davis et al. (1983).

It should be noted that the preparation of two cuts did not present a problem in the Wyodak sample (in which one cut was also smaller), indicating that it is not necessarily the source of the spectral differences in the anthracite. These preliminary anthracite spectra warrant further analysis, and we are currently preparing new anthracite samples in order to improve the sample consistency. A method to eliminate uncertainties inherent in the preparation of two samples is to prepare one and examine it in a solids NMR probe where its orientation can be changed. (We have access to a solids NMR instrument which can be tuned to ^{129}Xe and will follow up on this option.)

Pore structure changes in a microporous carbon following oxygen chemisorption and desorption

Introduction. The changes in the ^{129}Xe NMR signal for xenon adsorbed on a microporous carbon after successive oxidation and oxygen desorption steps were observed in an effort to describe the effect of these treatments on the pore size and/or structure. The sample was chosen because it is chemically homogeneous and already well characterized. ^{129}Xe NMR was used to examine each successive step so both oxidized and desorbed samples were observed. This study was designed used to confirm (or disprove) the intuitively obvious decrease in micropore diameter when oxygen functional groups

'decorate' the pore walls following oxidation, and increase, with possible removal of pore constrictions, when these groups are decomposed as CO and CO₂.

Experimental. Sphero carb 60-80 mesh (Phase Separations, Norwalk CT) was obtained and ¹²⁹Xe NMR spectra were acquired after each successive treatment as follows: As-is, oxidized (cycle 1), desorbed (cycle 1), oxidized (cycle 2), desorbed (cycle 2). Oxidation and desorption were carried out in a Thermolyne 21100 tube furnace. The sample was oxidized by heating in a shallow tray at 250 °C for 4-5 hours. Air flow was 170 mL/min. The sample was cooled under air, weighed, and examined by NMR. The sample was desorbed by heating to 850 °C under 200 mL/min N₂. The sample was then cooled under nitrogen, removed, weighed, and examined by NMR. Subsequent oxidation/desorption was carried out on the same sample, so that the changes produced in the sample are cumulative.

Results and Discussion. ¹²⁹Xe NMR spectra were acquired at a series of pressures for each sample treatment, **Figs. 13-17**. Chemical shift vs. pressure data were plotted for each treatment of the sample, **Figs. 18-22**. The slopes and intercepts of these plots are compared in **Figs. 23-24**. The pattern in change of intercept with sample treatment, which holds through the second oxidation, is that the oxidation increases the intercept with respect to that of the sample before oxidation. This does not hold from the untreated Sphero carb to the cycle 1 sample, however, where there is a slight decrease in the intercept. The desorption decreased the intercept compared to the previously oxidized sample in the first cycle, but increased it in the second. The slope exhibited the same pattern as the intercept, except in reverse, as can be seen from comparison of **Figs. 23-24**.

Interpretation of the meaning of the slope and the intercept is necessary to analyze these trends. We will first discuss the intercept. The chemical shift extrapolated to zero pressure from the chemical shift vs. pressure plot (the intercept) is used in the pore

diameter calculation of Demarquay and Fraissard (1987) as representative of that portion of the chemical shift that is due to the xenon-pore wall interaction. Larger values correspond to smaller pore sizes and vice versa. Thus a decreasing chemical shift at zero pressure indicates an increasing pore size. This is applicable in the pore size range in which the chemical shift vs. pressure plot is linear, up to about 20Å.

The intercept is inversely related to the mean free path of xenon adsorbed in the pore, and thus is related to pore size, in the range of size where the chemical shift/ xenon pressure dependence is linear (Demarquay and Fraissard, 1987). Pore diameters were calculated from the intercept (δ_0) of the chemical shift vs. pressure plot, following the method of Demarquay and Fraissard (1987):

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

pore diameter d , assuming a cylindrical pore (in Å): $d = l + 4.4$

The calculated pore sizes for each treatment of Spherocarb are listed in Table 3.

Table 3. Pore diameter calculations for oxygen chemisorption and desorption of Spherocarb.

	as received	oxidation 1	desorption 1	oxidation 2	desorption 2
Weight change, %	n/a	-3	-16.7	+7.9	-5.8
intercept, ppm	55.6	47.7	34.7	56.9	66.3
Diameter, Å	11.3	12.8	16.7	11.1	9.8

The pore size calculation shows a decrease in pore size from untreated sample to oxidation 1, which may indicate desorption of functional groups that are unstable at ~250 °C (e.g., carboxyl groups). Pretreatment of unoxidized Spherocharb by heating to 250 °C in N₂ will be carried out to verify this effect. From oxidation 1 to desorption 1, the calculated pore size increased; substantially, this is in agreement with the expected trends due to the removal of oxygen functional groups from pore walls. Oxidation 2 then decreased the pore diameter, as would be expected from addition of oxygen functional groups to the pore walls. Desorption 2 indicates further decrease in pore diameter, however, which is not in keeping with the prior pattern.

There are two ways to interpret this, bearing in mind that the first consideration in this situation is to determine whether these results are reproducible. One possibility is that the pore size calculation method is for some reason inapplicable for the last sample. If the micropores had become too large, we would expect the chemical shifts to appear at lower frequency and/or to lose their linear pressure dependence, and this did not occur. Another possibility is that physisorption of xenon may not be the only process occurring. Significant heating of the Spherocharb samples during adsorption has been observed; thus there is a possibility that Spherocharb can also chemisorb xenon, or that a possible leak in the vacuum line allowed the introduction of air. Chemisorption of water or O₂ from the air would, of course, change the environment probed by the coadsorbed xenon. The effect of coadsorbed water on the ¹²⁹Xe signal in Y zeolites, in which the chemical shift was higher in the presence of water, is discussed in Bansal and Dybowski, (1990).

Another way to interpret the pore size patterns is from the point of view that it is indeed correct. In this case, a decrease in pore diameter following second desorption of would only be logical if the removal of carbon opened previously inaccessible micropores. The manufacturing method for Spherocharb is proprietary; however many microporous carbons exhibit molecular sieve properties. If Spherocharb is this type material, we may

have removed just enough carbon to destroy these properties and probe a larger fraction of narrow micropores. As a test, we will run xenon spectra of crushed Sphero carb. If regions of sufficiently different pore sizes are exposed, they may be resolvable as more than one xenon signal.

The slope of the chemical shift vs. pressure plot is less easily interpreted than the intercept. It is logical to consider larger pores, or those with less constrictions, as more accessible to xenon; thus more 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). Based on our previous work, there also remains the possibility that the slope is directly related to the surface area, as preliminary results on coal have indicated. The possible correlation of slope and surface area is compatible with the concept of steeper slope indicating a more open porosity as well. When the coal surface area measurements are completed, we will determine whether the new data support the preliminary indications.

In this study, increases in intercept correspond to decreases in slope, and vice versa. The slope and intercept of the xenon chemical shift vs. pressure plots are directly related, as shown in **Fig. 25**. Examination of the coal data previously acquired shows that between coals of different rank, no such correlation was found, **Fig. 26**. The slope/intercept correlation in this study could in itself provide more information on the significance of the slope to pore structure.

With the Sphero carb sample set we have presumably produced some change in pore wall dimensions with each treatment. In addition, we expect to have two subgroups of differing wall chemistry: one with pore walls lined with oxygen functional groups (the oxidized samples), and one lined with primarily carbon atoms (the desorbed samples). The correspondence of the intercept and slope across these samples indicates that the relationship of slope and intercept *to each other* is not dependent on wall chemistry, or pore

size, within the range of our samples. It has been established that the intercept has sensitivity to pore size and possibly also to wall chemistry, since xenon dissolved in liquids shows sensitivity to chemical makeup. For a review of applications of ^{129}Xe NMR using different types of materials, which gives a general idea of the different properties (i.e., physical, chemical) of materials that can influence chemical shift, see Dybowski et al., (1991).

FUTURE PLANS

We will continue with our previously described plans to acquire NMR spectra for Blind Canyon hvA bituminous coal using an echo sequence to improve spectral quality, and to complete the N_2 and CO_2 isotherms for three of the coals. The Sphero carb oxidation experiment described in this report will be repeated without change except that xenon adsorption isotherms will be collected at each step. In addition, we have plans for the following:

T_1 for dissolved xenon (no empty space) vs. T_1 in microporous solids. 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. We have begun this study, examining two coals and one microporous carbon. We intend to examine xenon dissolved in a liquid and in an amorphous polymer, and then to determine whether significant differences in T_1 can be ascribed to materials on the basis of having, or not having, microporosity. Relaxation time is an indicator of molecular (or atomic in the case of xenon) 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.

CSA of xenon in a whole piece of coal. In order to follow up on the differences in the xenon signal for parallel and perpendicular to the bedding plane solid pieces of anthracite, we intend to repeat the sample preparation, and/or prepare the solid piece of anthracite for examination in a solids probe which can orient the sample as necessary. If differences in the xenon signal persist, we will follow with Magic Angle Spinning of the powdered anthracite in a solids probe for verification of the existence of chemical shift anisotropy. If this is verified, 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.

Selective saturation transfer experiment. The particle size effect experiments performed during this quarter on Upper Freeport vitrinite indicated that the intraparticle xenon diffusion rate was sufficiently slow that the ^{129}Xe signal in the particle size range above 400 mesh was not affected by intra/extra particle exchange effects. Thus, it may not be essential for this project that we determine the intraparticle diffusion rate of xenon in our samples. However, in the event that we do determine that finding the intraparticle diffusion rate for xenon in selected coals is pertinent, we will perform selective saturation transfer experiments on the coals.

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. Variation of the mixing time can be used to find the rate of intraparticle diffusion by determining the time at which the magnetization transfer is first detectable.

REFERENCES

- Bansal, N. and Dybowski, C. *J. Magn. Reson.* **89**, 21 (1990)
- Demarquay, J. and Fraissard, J. *Chem. Phys. Lett.* **136**, 314 (1987)
- Davis, A., Kuehn, K. W., Maylotte, D. H., and Peters, R. L. *J. Microscopy* **132**, 297 (1983)
- Dybowski, C., Bansal, N., and Duncan, T. M. *Annu. Rev. Phys. Chem.* **42**, 433 (1991)
- Hirsch, P. B. *Proc. Royal Soc., (London)* **A226**, 143 (1954)
- 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 Fuels* **9**, 324 (1995)
- Mahajan, O. P., *Carbon* **29**, 742 (1991)
- Menon, V. C., Kyotani, T., Danner, R. P., and Radovic, L. R. *Proc. 7th International Conference on Coal Science*, (K. H. Michaelian, Ed.), Vol.I, Banff, Alberta, Canada, p. 398 (1993)
- Radovic, L. R., Menon, V. C., Leon y Leon, C. A., Kyotani, T., Danner, R. P., Anderson, S., and Hatcher, P. G. *Adsorption*, accepted 4/96.
- Ripmeester, J. A. and Ratcliffe, C. I. *Anal. Chim. Acta* **283**, 1103 (1993)
- Walker, P. L. Jr., and Mahajan, O. P. *Energy Fuels* **7**, 559 (1993)

APPENDIX

Figure 1. ^{129}Xe spectra of Upper Freeport mvb vitrinite, particle size graded, at 620-630 torr xenon. (a) +60 mesh, (b) 60-100 mesh, (c) 100-200 mesh, (d) -400 mesh.

Figure 2. ^{129}Xe chemical shift vs. time for Lykens Valley anthracite, 40-60 mesh

Figure 3. ^{129}Xe chemical shift vs. time for Lykens Valley anthracite, -100 mesh.

Figure 4. ^{129}Xe linewidth vs. time for Lykens Valley anthracite, 40-60 mesh

Figure 5. ^{129}Xe linewidth vs. time for Lykens Valley anthracite, -100 mesh.

Figure 6. Xenon pressure readings (torr) during gas uptake by Lykens Valley anthracite, 40-60 mesh.

Figure 7. ^{129}Xe signals for six coals of increasing rank. (a) lignite; (b) sub bituminous; (c) hvC bituminous; (d) hvA bituminous; (e) low volatile bituminous, (f) anthracite.

Figure 8. ^{129}Xe NMR spectrum of Wyodak sub bituminous coal, solid piece cut parallel the bedding plane.

Figure 9. ^{129}Xe NMR spectrum of Wyodak sub bituminous coal, solid piece cut perpendicular to the bedding plane.

Figure 10. ^{129}Xe NMR spectrum of Lykens Valley anthracite, solid piece cut parallel to the bedding plane.

Figure 11. ^{129}Xe NMR spectrum of Lykens Valley anthracite, solid piece cut perpendicular to the bedding plane.

Figure 12. ^{129}Xe NMR spectrum of Wyodak sub bituminous coal, powdered -60 mesh, 565 torr.

Figure 13. ^{129}Xe NMR spectra of untreated Sphero carb at various pressures. (a) 280 torr, (b) 405 torr, (c) 538 torr, (d) 619 torr.

Figure 14. ^{129}Xe NMR spectra of Sphero carb, oxidation 1, at various pressures. (a) 283 torr, (b) 364 torr, (c) 455 torr, (d) 530 torr, (e) 605 torr.

Figure 15. ^{129}Xe NMR spectra of Spherocarb, desorption 1, at various pressures. (a) 323 torr, (b) 395 torr, (c) 463 torr, (d) 510 torr, (e) 590 torr.

Figure 16. ^{129}Xe NMR spectra of Sphero carb, oxidation 2, at various pressures. (a) 271 torr, (b) 440 torr, (c) 537 torr, (d) 613 torr.

Figure 17. ^{129}Xe NMR spectra of Sphero carb, desorption 2, at various pressures. (a) 267 torr, (b) 400 torr, (c) 477 torr, (d) 522 torr.

Figure 18. ^{129}Xe chemical shift vs. pressure for untreated Sphero carb.

Figure 19. ^{129}Xe chemical shift vs. pressure for Sphero carb, oxidation 1.

Figure 20. ^{129}Xe chemical shift vs. pressure for Sphero carb, desorption 1.

Figure 21. ^{129}Xe chemical shift vs. pressure for Sphero carb, oxidation 2.

Figure 22. ^{129}Xe chemical shift vs. pressure for Sphero carb, desorption 2.

Figure 23. Intercept of ^{129}Xe chemical shift vs. pressure plot for each treatment of Sphero carb.

Figure 24. Slope of ^{129}Xe chemical shift vs. pressure plot for each treatment of Sphero carb.

Figure 25. Slope vs.intercept of ^{129}Xe chemical shift vs. pressure plot for each treatment of Spherocarb.

Figure 26. Slope vs. intercept of ^{129}Xe chemical shift vs. pressure plot for six coals of varying rank.