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

TECHNICAL PROGRESS REPORT

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by

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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 completed for four coals, and N_2 and CO_2 adsorption isotherms with surface area measurement have been completed for three coals. A microporous carbon has been subjected to one oxygen chemisorption/desorption cycle and examined by ^{129}Xe NMR.

In terms of the broad objectives of the project, areas of potential value for further experiments have been identified and initiated. These areas include chemical shift anisotropy of xenon in whole coal, relaxation time (T_1) of xenon in porous adsorbates vs. nonporous solvents (as a way to differentiate signals arising from xenon in empty space vs. solid matrix), and examination of the influence on the xenon signal of packing the

powdered coal, which could give information on whether the porosity is open or closed. (Ripmeester and Ratcliffe, 1993). Results of these experiments will be used in the final interpretation of our current data.

TECHNICAL PROGRESS

Task 1. ^{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 certain conditions. Those conditions were low gas pressure (< 1 atm), and pore sizes sufficiently small to give a mean free path for xenon of 1-6 Å. This technique requires the spectra to be 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), 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.

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; 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. In our current study, the pressures used are somewhat lower than those of Tsiao and Botto, and the chemical shift vs. pressure relationships are linear. The spectra obtained so far do not appear to be overlapped, with the possible exception of Adaville hvCb coal (**Fig. 3**); currently chemical shift values are assigned by taking the highest point on the peaks, and for Adaville coal the midpoint of the most intense region is used. The pore diameters were calculated following Demarquay and Fraissard (1987).

The peak shape appears to change in a regular way with rank. If this trend holds for the remainder of the sample set, its implications will be investigated further. The shape and location of the resonance for one sample was followed over an eight-hour period and found to be stable, ruling out a strong dependence of the NMR data on achievement of adsorption equilibrium. The data on the slope of the chemical shift vs. pressure plots were compared to the intercepts, to coal rank and to coal surface area, to get a preliminary indication of whether they may contain information on coal physical structure.

Experimental

Preliminary setup. This work has been completed and included the following steps: (1) design and assembly of a glass vacuum/gas manifold with appropriate pressure and vacuum gauges and gas-tight resealable NMR tubes; (2) selection and acquisition of a microporous carbon and six coals ranging in rank from lignite to anthracite; and (3) preparation of the spectrometer to acquire xenon spectra, which included testing 5- and 10-mm probes, chemical shift calibration with xenon gas, and determination of the operating parameters using a microporous carbon.

Experimental procedure. 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.

Samples were outgassed at 100 °C under vacuum for a minimum of 20 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. (The effect of equilibration time on the xenon signal was investigated and will be discussed.) 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. Four coals from the Penn State/DOE coal sample bank, ranging in rank from lignite to low volatile bituminous have been examined. The spectra are shown in Figs. 1 - 4 as a function of xenon pressure. Plots of the chemical shift vs. pressure are shown in Figs. 5 - 8. 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-11 (Beulah)	lig A	74	140	0.99	5.9
DECS-26 (Wyodak)	subB	76	100	0.96	7.3
DECS-7 (Adaville)	hvCb	77	103	0.99	7.2
DECS-19 (Pocahontas)	lvb	90	143	0.96	5.8

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) is shown in **Fig. 9**. The apparent trend 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.

Shape and symmetry of signal. There is a qualitative relationship between ^{129}Xe signal symmetry and rank. Unlike the chemical shift, the trend in peak shape seems to progress smoothly with rank. For the four coals already examined, the shape is broad and asymmetrical for the 74 and 76 % C samples (**Figs. 1 and 2**). For these samples the width is ca. 100 ppm at 1/2 height, and there is marked downfield tailing. A change in the shape, becoming narrower (~70 ppm) and more symmetrical, is noticeable for the 77.4 % C sample (**Fig. 3**), and this trend becomes more pronounced at 90% C (width ~50 ppm, **Fig. 4**).

The signal shape could be a significant clue to the coal physical structure. One possibility is that it is due to chemical shift anisotropy (CSA) of xenon in asymmetrical spaces such as lamellae. An asymmetrical signal very similar to **Figs. 1 and 2** 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 (vs. powdered samples) is being undertaken to clarify this issue.

Stability and fine detail of peaks. The time dependence of the peak size, shape and location was checked for the Adaville coal to detect any changes that may be attributed to longer gas exposure, particularly any related to slow achievement of equilibrium. Spectra were acquired over one-hour periods after 0.5, 4, and 7 hours of exposure of coal to xenon (Fig. 10). No significant change was seen, indicating that the signal is stable, and the amount of xenon adsorbed in about 30 minutes is not distinguishable, under these conditions, from that obtained at longer adsorption times.

Long acquisition (20,000 to 40,000 scans vs. 1,500 to 5,000 typically employed) with longer delay (3 vs. 1.5 second delay in normal operation) was done for Adaville and Beulah coals. This served to better define the peak shapes and distinguish possibly weak signals from noise. An increase in delay would also allow other possible signals with longer T_1 to be detected, although none were found. An illustration of the effect of increased number of acquisitions and delay time is shown in Fig. 11.

Slope of chemical shift vs. pressure plots. The location of the chemical shift is influenced by both the chemical makeup of the pore region 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 four coals were plotted vs. rank (% C). A comparison to the intercept (δ_0 , ppm) vs. rank data is shown in Fig. 12. Their relationships to rank are clearly not similar; thus the determinants of δ_0 and slope may be different properties of the adsorbent. This is interesting and warrants further investigation. In addition, for three of the four coals the slope has been found to increase with the Dubinin-Radushkevich surface area (Fig. 13). The intercept decreases with surface area in an apparently linear fashion (Fig. 14). When surface area data on the remaining samples are completed, these relationships may be clarified.

Task 2. Oxidation and ^{129}Xe NMR spectra of a microporous carbon

Introduction. One aspect of this study is to use ^{129}Xe NMR to determine the effect on pore structure of controlled removal of carbon through oxygen chemisorption/desorption. A microporous carbon was chosen as the study material because it is homogeneous and has a fairly well defined pore structure. This removes some of the uncertainties associated with the NMR spectra of coal samples. The samples are slowly oxidized at low temperature (ca. 150 - 350 °C), so that oxidation is expected to be occurring within the pores rather than primarily at the external surface. At low temperatures the rate of oxidation is not greater than the rate of diffusion of oxygen into the pores.

One of the three oxidation cycles to be done is complete. The changes observed in the spectra after CO and CO₂ desorption, compared to the unoxidized sample, are a lower intercept on the chemical shift vs. pressure plot, and a greater linewidth. The change in intercept indicates widening of the pores, and this change was large compared to the weight

loss after desorption. The degree of widening and the increased linewidth may be due to faster intra- and/or interparticle exchange for the oxidized sample.

Experimental. A microporous carbon (Sphero carb, 60-80 mesh, Analabs) was selected to examine the effect of increasing the micropore diameter in a controlled manner through oxygen chemisorption/desorption. One of a projected three oxidation cycles have been completed. Oxidation was carried out in air, using a Thermolyne 21100 tube furnace, for 14 hours at 150 °C and 1 hour at 250 °C, followed by heating in N₂ at 900 °C. The sample was weighed before and after the desorption step. Weight loss for this cycle was ~3%.

The sample preparation procedure for NMR spectroscopy was the same as used for coals. The spectra were taken on a Bruker AMX 360 instrument operating at 99.61 MHz. A 90 degree pulse width was used with 1.5 second delay, and 100 to 300 scans were required to obtain good signal-to-noise ratio.

Results and Discussion. The spectra were obtained for the oxidized and unoxidized samples at a series of Xe pressures (Figs. 15 and 16). The chemical shift was plotted vs. pressure (Figs. 17 and 18), and the pore diameter was calculated assuming cylindrical pores. The results are shown in Table 2.

Table 2. ^{129}Xe NMR data for Sphero carb.

Sample	Intercept δ_0 (ppm)	Slope (ppm/torr)	Correlation coefficient	Pore diameter (Å)	Linewidth (ppm)
As received	50	0.014	0.95	12.3	6.3
Oxidized (one cycle)	40	0.033	0.97	14.8	8.5

Of particular interest was the large (20%) decrease in the intercept δ_0 given the relatively small weight loss for the sample (3%). The physical meaning of a decrease in δ_0 , as it is currently understood, is an increase in the pore diameter, which was indeed expected after removal of carbon from the pore walls. The observed degree of decrease in δ_0 could be attributed to greater freedom of movement and thus faster diffusion of xenon through enlarged pores, leading to more intra- and/or interparticle exchange. Such exchange on the NMR timescale could produce a signal that is a weighted average of the internal and external particle environments (Ripmeester and Ratcliffe, 1993).

Xenon adsorbed on the external surface and exchanging with the free gas has a resonance at 1-5 ppm in coal samples in which it is observed (**Figs. 1-4**). The averaging effect of exchange of intraparticle xenon with the external surface is to decrease the observed chemical shift. The signal would also be broadened, and this was observed for the oxidized Sphero carb. It may be significant that a 'surface' xenon signal near 0 ppm has not been observed in any Sphero carb spectra; this could be an indication that it is averaged into the primary signal.

Further work will be done to complete the set of oxidation cycles and to determine whether xenon exchange is affecting the NMR data. The amount of extraparticle xenon

could be decreased by increasing the powder density or possibly by coating the particles after xenon adsorption (Ryoo et al., 1994).

Task 3. Adsorption isotherms of coals

Introduction. Surface area measurements of the coal samples by standard techniques are used as a basis for comparison with the less well established NMR data on the pore structure. Nitrogen adsorption isotherms are analyzed with the BET equation, and carbon dioxide with the Dubinin-Radushkevich equation (Gregg and Sing, 1982). The three coals examined to date have surface areas and pore volumes in the expected range.

Experimental. Surface areas were measured by N₂ and CO₂ adsorption using an Autosorb-1 sorption system (Quantachrome). Approximately 0.3-0.4 g of each sample was outgassed 12 to 24 hours at 110 °C. The N₂ adsorption isotherms were taken at 77 K. Seventeen adsorption points and nine desorption points were recorded, and standard BET plots were prepared. The CO₂ isotherms were obtained at 273 K. Fifteen adsorption and nine desorption points were recorded, and standard Dubinin-Radushkevich plots were prepared.

Results and Discussion. The surface area measurements of three of the coals have been completed. The N₂ isotherms are shown in Figs. 19 - 21 and BET plots in Figs. 22 - 24. The CO₂ isotherms are shown in Figs. 25 - 27, and D-R plots in Figs. 28 - 30. The results are summarized in Table 3. The unusually high surface area for the Wyodak sample, and the hysteresis in its N₂ isotherm, indicate significant mesoporosity in this sample. Currently, the surface area data are used for comparison with the NMR data.

Table 3. Coal surface areas.

Sample	N ₂ BET surface area (m ² /g)	CO ₂ D-R surface area (m ² /g)
Beulah ligA	0.87	221
Wyodak subB	22.7	491
Pocahontas lvb	0.62	177

FUTURE PLANS

In addition to completing the sample sets for the experiments discussed in this report, 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). The third experiment, on the existence of chemical shift anisotropy in coal, is necessary to confirm or discard a possible source of the variations in peak shape seen in coals. If CSA is found to exist, it would also provide new information on the macroscopic structure of coal.

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.

NMR of pressed pellets of coal. 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 that of loose powder, at a given equilibrium pressure of xenon, it would be a strong indication that intra- and/or interparticle exchange is occurring on the NMR timescale. Following the argument outlined in Ripmeester and Ratcliffe (1993), the implication is that the pores are connected. This is a new way to address the question of whether pores in coal are open or closed.

CSA of xenon in a whole piece of coal. The spectrum of randomly oriented montmorillonite platelets, in which xenon is adsorbed in asymmetric lamellar spaces, was observed by Ripmeester and Ratcliffe (1993). This spectrum bears a striking resemblance to the spectra of coals, particularly low-rank coals. When the montmorillonite platelets were ordered, and examined parallel and perpendicular to the magnetic field of the NMR instrument, both the chemical shift and the peak shape were significantly changed. Interestingly, the shape became more like that of a higher-rank coal. Chemical shift anisotropy of xenon in coal has not been discussed in the literature. We will investigate the possibility that it exists.

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.

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APPENDIX

Figure 1. ^{129}Xe spectra of Beulah lignite: (a) 690 torr; (b) 510 torr; (c) 374 torr; (d) 289 torr.

Figure 2. ^{129}Xe spectra of Wyodak subB coal: (a) 619 torr; (b) 565 torr; (c) 393 torr; (d) 303 torr.

Figure 3. ^{129}Xe spectra of Adaville hvCb coal: (a) 656 torr; (b) 514 torr; (c) 347 torr; (d) 280 torr.

Figure 4. ^{129}Xe spectra of Pocahontas lvb coal: (a) 683 torr; (b) 538 torr; (c) 491 torr; (d) 366 torr; (e) 322 torr.

Figure 5. ^{129}Xe chemical shift vs. pressure for Beulah lignite.

Figure 6. ^{129}Xe chemical shift vs. pressure for Wyodak subB coal.

Figure 7. ^{129}Xe chemical shift vs. pressure for Adaville hvCb coal.

Figure 8. ^{129}Xe chemical shift vs. pressure for Pocahontas Irb coal.

Figure 9. Intercept δ_0 of chemical shift vs. pressure plots: variation with coal rank.

Figure 10. Effect of adsorption time on the ^{129}Xe spectrum of Adaville hvCb coal prepared 0.5 (a), 4 (b) and 7 (c) hours after adsorption at 650 torr.

Figure 11. Effect of longer acquisition and delay times on the spectrum of Adaville hvCb coal under 659 torr xenon: (a) 500 scans, 1.5 second delay; (b) 40,000 scans, 3 second delay.

Figure 12. Comparison of the rank dependence of slope (a) and intercept (b) of ^{129}Xe chemical shift vs. pressure plots.

Figure 13. Correlation between slope of ^{129}Xe chemical shift vs. pressure plots and D-R surface area of coals.

Figure 14. Correlation between intercept of ^{129}Xe chemical shift vs. pressure plots and D-R surface area of coals.

Figure 15. ^{129}Xe spectra of unoxidized Sphero carb: (a) 630 torr; (b) 514 torr; (c) 346 torr; (d) 195 torr.

Figure 16. ^{129}Xe spectra of oxidized Sphero carb (one oxidation cycle): (a) 650 torr; (b) 564 torr; (c) 450 torr; (d) 340 torr.

Figure 17. ^{129}Xe chemical shift vs. pressure for unoxidized Sphero carb.

Figure 18. ^{129}Xe chemical shift vs. pressure for oxidized Sphero carb (one oxidation cycle).

Figure 19. N₂ adsorption isotherm for Beulah lignite.

Figure 20. N₂ adsorption isotherm for Wyodak subB coal.

Figure 21. N₂ adsorption isotherm for Pocahontas lvb coal.

Figure 22. BET plot for Beulah lignite.

Figure 23. BET plot for Wyodak subB coal.

Figure 24. BET plot for Pocahontas lvb coal.

Figure 25. CO₂ adsorption isotherm for Beulah lignite.

Figure 26. CO₂ adsorption isotherm for Wyodak subB coal.

Figure 27. CO₂ adsorption isotherm for Pocahontas lvb coal.

Figure 28. Dubinin-Radushkevich plot for Beulah lignite.

Figure 29. Dubinin-Radushkevich plot for Wyodak subB coal.

Figure 30. Dubinin-Radushkevich plot for Pocahontas lvb coal.