DOE/PC/94216--T6

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

**Quarterly
TECHNICAL PROGRESS REPORT
October 1996 - December 1996**

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Issued January 1997

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

MASTER

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ABSTRACT

Selective presaturation and saturation transfer ^{129}Xe NMR experiments were performed on a high volatile C bituminous coal and an anthracite. The experiments detect the movement of xenon atoms among different regions of the internal surface, and to the external surface of the coal particles. The results indicate that adsorbed xenon atoms can move to the external surface of the bituminous coal significantly faster than in the anthracite. The results are interpreted in terms of the porous structure of the coals.

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SUMMARY

During this quarter, the experimental work on this project has been concluded and the final report has been in preparation. The experiments performed in this quarter have been an extension of NMR experiments using low power presaturation and saturation transfer that were reported in detail for two coals in the last quarter (July-September 1996). We have applied this technique to two additional coals in order to better correlate the results to coal rank.

Low power presaturation of ^{129}Xe adsorbed in all four 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 for all four coals with increasing presaturation time. The timing of saturation transfer to the external gas has implications for the nature of the connectivity of the pore structures in coal, and has a strong relationship to coal rank. The results for the two additional coals will be reported here, with a detailed analysis to be included in the final report.

INTRODUCTION

There is wide acceptance of the following general model for the porous structure of coal; that "coals contain an interconnected pore network of high surface area, the slit-shaped pores having constricted openings of molecular dimensions...[and] coals contain both open and closed porosity." (Mahajan, 1991). The question of open or closed porosity

is an area of continuing controversy, the major source of which is the large differences in coal surface area (Larsen et al., 1995) determined by adsorption of gasses of similar molecular dimensions, or the molecular sieving effect. There are several critical reviews on the subject (Marsh, 1987; Mahajan, 1991, Walker and Mahajan, 1993).

This study will explore adsorption site distribution and pore network connectivity in coal using ^{129}Xe NMR with the techniques of presaturation and saturation transfer. These methods give information about xenon dynamics and are used to detect the movement of xenon atoms to different regions of the coal sample. Presaturation and saturation transfer have widely varied utility in NMR spectroscopy, as reviewed in Freeman (1988). ^{129}Xe NMR studies that, while not the same as the one to be described here, use some similar basic concepts, have been performed. 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). 2D-EXSY has been used by Moudrakovski et al (1995) to monitor xenon intra/extra particle diffusion in zeolites.

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. 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. We are interested in whether and to what extent presaturation produces saturation of the signal it is focused on, and how the other signal(s) in the spectrum are affected. The key ideas used in conceptualizing this experiment are as follows: NMR signals from ^{129}Xe adsorbed inside the coal particles are distinguishable from those outside; xenon atoms are to some degree mobile in their

adsorbed state; and if a xenon atom is saturated in one environment, it can carry the saturation with it if it moves to a new environment in less than its spin-lattice (T_1) relaxation time. The possible outcomes of the presaturation experiment were included in the last quarterly report and will be repeated here for clarity.

(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 Adaville high volatile C bituminous coal (hvCb; 77.4%C) and Lykens Valley anthracite (91.9 %C) 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 8-12 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 AND DISCUSSION

Sets of spectra are acquired using increasingly longer low power presaturation pulses focused on a narrow frequency band in the center of the primary adsorbed xenon signal. As it is increased, the pulse length becomes long enough for intra-, and subsequently extraparticle diffusion of xenon in the coals to occur during the experiment time. The experiment can map out the time frames of loss of a portion of the original

xenon signal, (hole burning, if any), saturation of the adsorbed signal, and saturation of the extraparticle gas signal.

Reference spectra are acquired with presaturation 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 are phased relative to the reference.

The Lykens Valley anthracite was presaturated at 40 dB on the 157 ppm signal for increasing times from 1 to 300 ms. The results are shown in **figure 1**. There is a 'hole' at 1, 2, and 5 ms that persists through 10 ms as the signal loses intensity. The external gas signal is reduced in intensity at 100 ms, and is almost saturated at 300 ms.

Figure 1. Effect of increasing presaturation pulse length on ^{129}Xe NMR spectra of the Lykens Valley anthracite. (a) Reference; 0.1 ms, 80 dB. (All subsequent spectra are at 40 dB power, 20,296 Hz) (b) 1 ms; (c) 2 ms; (d) 5 ms; (e) 10 ms; (f) 50 ms; (g) 100 ms; (h) 300 ms.

The Adaville coal reference spectrum shows that there are two overlapped adsorbed xenon signals. The lower frequency signal (130 ppm) was presaturated for increasing times from 0.4 to 40 ms, **figure 2**. The effect at 0.4 ms appears to be the removal of the 130

ppm signal, with the 176 ppm signal surviving with slight intensity loss. From 1 to 5 ms, the 176 ppm signal continues to lose intensity, saturating at 10 ms. The external gas signal begins to lose intensity at about 5 ms, saturating at 40 ms.

Figure 2. Effect of increasing presaturation pulse length on ^{129}Xe NMR spectra of the Adaville coal. (a) Reference; 0.1 ms, 80 dB. (All subsequent spectra are at 40 dB power, 17,629 Hz.) (b) 0.4 ms; (c) 1 ms; (d) 5 ms; (e) 10 ms; (f) 20 ms; (g) 40 ms.

Next, for the Adaville coal, the presaturation pulse was centered on the higher frequency (176 ppm) signal for 1 and 5 ms, **figure 3**. At 1 ms, the 176 ppm signal is nearly saturated. There is significant intensity loss to the signal at 130 ppm, whereas when the pulse is on the 130 ppm signal (**figure 2**), the signal that was not presaturated had lost little intensity. For the pulse on the 176 ppm signal for 5 ms, both signals are saturated. By contrast, with the pulse on the 130 ppm signal, complete saturation occurs at 10 ms presaturation time. The extension of saturation from the 130 to the 176 ppm region is slower than that from 176 to 130ppm. The reasons for this could be in part related to the relative speed of diffusion of xenon through the two pore regions that are indicated by the two signals, but is likely to also be an effect of the experimental conditions.

The relative lengths of time the two Adaville coal signals survive are not necessarily direct indications of the rate of motion of xenon atoms through the corresponding porous regions if the way the pulse is applied also affects relative intensity of the signals. An example is if the pulse was applied off center for one of the signals. The location of the presaturation pulse can affect how long a signal survives it, and if the pulse is off center, there is more residual intensity.

Figure 3. Effect of presaturation on the higher frequency ^{129}Xe signal in the Adaville coal. Pulse is centered on signal at ~ 176 ppm. (a) Reference; 0.1 ms, 80 dB; 19,057 Hz. (subsequent spectra are at 40 dB power; 21,968 Hz.) (b) 1 ms; (c) 5 ms.

An important consideration related to the location of the presaturation pulse is whether the overlap region between the signals is more affected in one experiment than in the other. This could occur in a situation where the peak center for one signal overlaps a portion of the other signal, which does appear to be the case for the Adaville signals. The 130 ppm signal is more asymmetrical, tailing to the high frequency end. This means some of the 130 ppm signal area is under the maximum of the 176 ppm signal, meaning

presaturating that spot affects the 130 ppm signal directly, due to the pulse, as well as indirectly, through diffusion of saturated xenon atoms into the second pore region.

Caution must be exercised in using this technique as a definite measure of diffusion time, because the times can be affected by the presaturation pulse power level and carrier frequency. We have applied the technique in a standardized way to each coal sample before making time comparisons. Each was run at similar power level, and it was established that this power was sufficient to use to produce saturation in a time shorter than the T_1 or the inter-extraparticle diffusion rate - that is, each run was run under conditions where a spectral hole could be produced. The saturation transfer times are thus expected to provide reliable information for the comparison of the coals to each other.

CONCLUSION

We have been able to produce a spectral hole in the ^{129}Xe spectra of a total of four coals. Two have been examined in this quarter, but all will be included in the interpretation of the results. These conclusions will also be discussed in the final report. The fact that a spectral hole can be produced in the adsorbed xenon signal indicates that the signal source is the overlap of multiple chemical shifts. Wernett (1991) has speculated that the ^{129}Xe NMR signal profile describes the pore size distribution. This interesting hypothesis is supported by these results and has not been verified previously.

The different times required for saturation transfer of the extraparticle gas to occur come from differences in diffusion rate of xenon through the void spaces in coals. The short times (30 - 40 ms) to produce saturation of the external surface gas signal in the low rank coals examined here, Wyodak and Adaville coals at 76.3 and 77.4 %C, are interpreted as due to relatively easy motion of xenon atoms that were saturated while in the internal surface, to the external surface. They indicate that the low rank coals have larger porous

connectivity of the pore network to the outside. This is consistent with the presence of larger, feeder pores acting as routes from the external surface to the microporosity in the coal.

The significantly longer times (300 - 800 ms) to produce saturation of the external surface gas signal in the higher rank coals examined indicate hindered motion of xenon atoms from the internal to the external coal surface, compared to low-rank coal. The slow rate of intra/extra particle exchange in the Sewell coal (88.9 %C) and the Lykens Valley anthracite (91.9 %C) point to fewer openings to the external surface compared to low-rank coals; an equivalent effect on diffusion rate would come from constricted, microporous connections to the outside. Either is consistent with the notion of a highly interconnected microporous system lacking a significant amount of larger porosity.

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