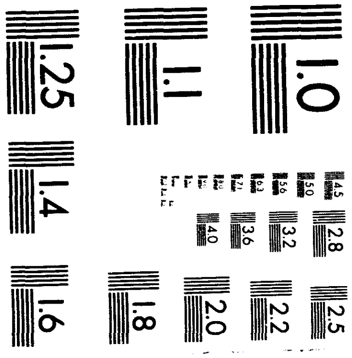
1.0
1.1
1.25
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Quarter report #9, 10/1/93-12/30/93
Advanced NMR-Based Techniques for Pore Structure Analysis of Coal

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Background

One of the main problems in coal utilization is the inability to properly characterize its complex pore structure. Coals typically have micro/ultra-micro pores but they also exhibit meso and macroporosity. Conventional pore size techniques (adsorption/condensation, mercury porosimetry) are limited because of this broad pore size range, microporosity, reactive nature of coal, samples must be completely dried, and network/percolation effects. Small angle scattering is limited because it probes both open and closed pores. Although one would not expect any single technique to provide a satisfactory description of a coal's structure, it is apparent that better techniques are necessary. Small angle scattering could be improved by combining scattering and adsorption measurements. Also, the measurement of NMR parameters of various gas phase and adsorbed phase NMR active probes can provide pore structure information. We will investigate the dependence of the common NMR parameters such as chemical shifts and relaxation times of several different nuclei and compounds on the pore structure of model microporous solids, carbons, and coals. In particular, we will study the interaction between several small molecules (^{129}Xe, ^{3}He, $^{14}N_2$, $^{14}NH_3$, $^{15}N_2$, $^{13}CH_4$, $^{13}CO_2$) and pore surface.

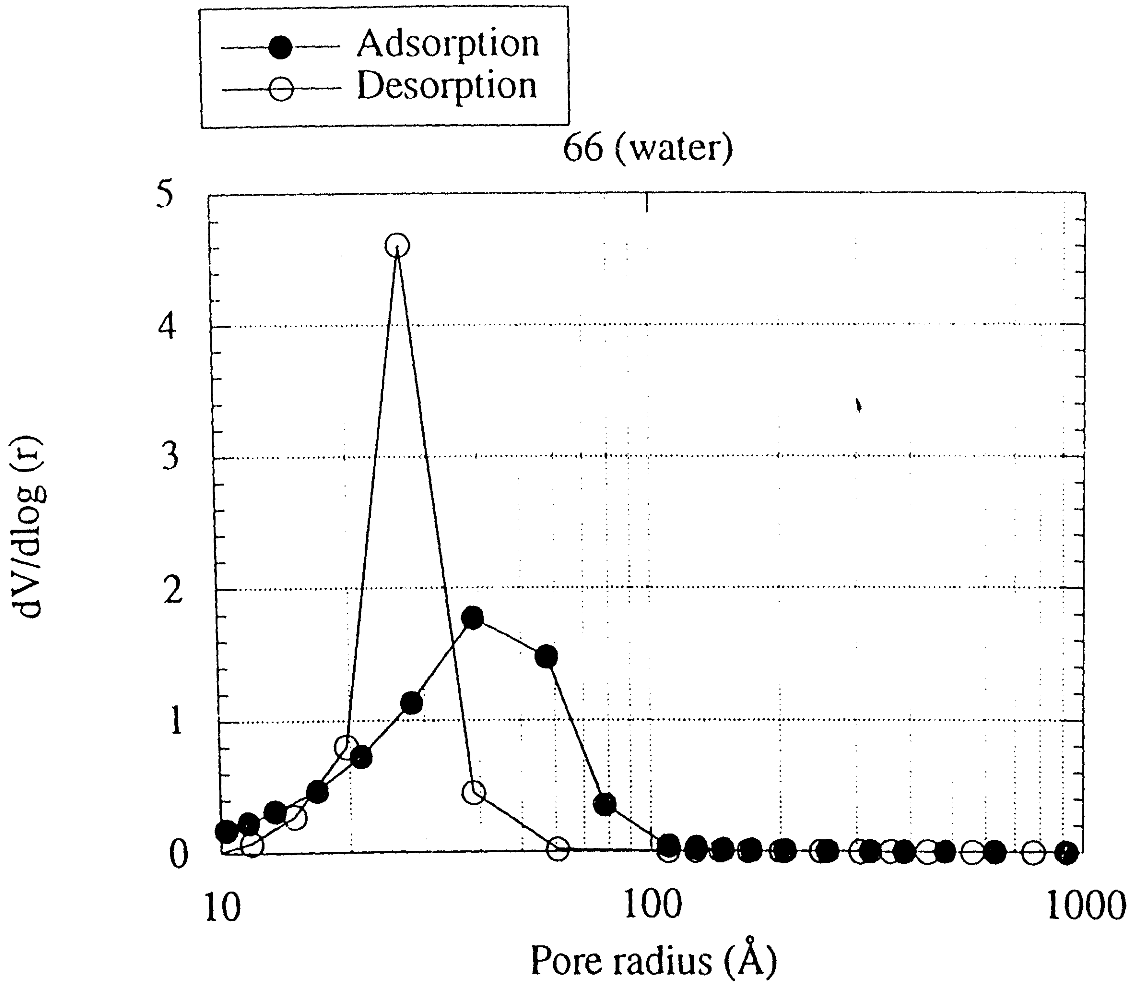
Work completed during the last quarter

Our current work may be divided into three areas: small-angle X-ray scattering (SAXS), adsorption, and NMR.

1. SAXS.

In the last report, we said that the three objectives of the SAXS-contrast matching portion of this project were; a) distinguish between pores and particles, b) determine the change in surface roughness and c) to determine the average pore size. This quarter, we conducted experiments on a silica xerogel synthesized in our laboratory from 4 nm Nalco particles. The dry xerogel should show two characteristic sizes on the SAXS curve. In principle, one should correspond to 4 nm and the other should correspond to the pores present in the xerogel. The nitrogen adsorption data shows the pores are present in the range of 30 Å to 80 Å radius with a large percentage of them lying in the 30 - 50 Å radius. The adsorption-derived pore size distribution is shown in Figure 1. We than performed dibromomethane adsorption on the xerogel at different relative pressures (P/P_0) and measured SAXS. The results were very interesting. We observe two sizes or humps from the blank (unloaded) sample. One was 5.1 nm and the other was 2.9 nm. The former (lower q) value should correspond to the pores and the latter should be the particles. The curves for the samples at different dibromomethane loading are shown in Figure 2. The samples at higher loadings show a distinct change in the peak position. Taking a normal Guinier analysis, we find that the size increases. But since it is a peak we can not say so for certain. The results that we get for the samples at different P/P_0's are shown in Table 1. However, the hump at lower q when seen on a Guinier plot is manifested as a peak and therefore, normal Guinier analysis is not applicable. We must perform additional experiments to determine the quantitative changes in the peak position.

In order to address the question of why a 4 nm size was not observed in the gel, SAXS was performed on the precursor sol which contains monodisperse particles of nominal 4 nm diameter. During processing, we expect this structure to be maintained. We measured scattering from both the sol and certain specific dilutions of the sol. From the curves in Figure 3 we find that the humps are still present in the dilution as humps but they are not peaks any longer. In Figure 2, we do not observe any change in the peak position with vapor loading. Therefore, we conclude that these humps arise from the d-spacings between particles which should be the distance between the centers of the particles. This distance should not change even as we load the sample with different amounts of the adsorbate however it will change with dilution (as the particles are separated). This is a preliminary interpretation and more detailed investigations will be conducted during the upcoming quarter.


Adsorption
Desorption
66 (water)
dV/dlog (r)
0
1
2
3
4
5
10
100
1000
Pore radius (Å)

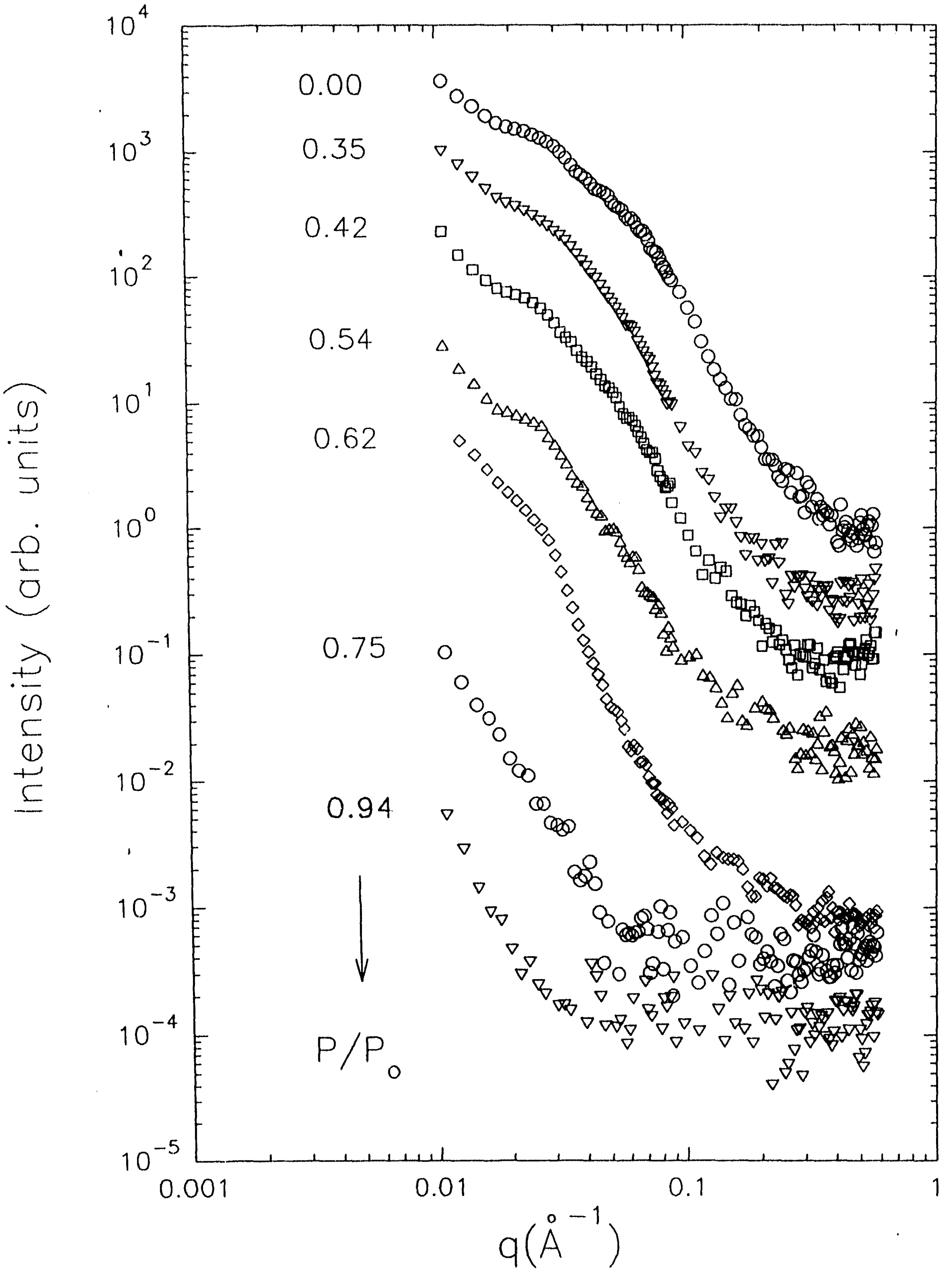


Fig. 2: Graph of the Nalco xerogel loaded with dibromomethane to different relative pressures.

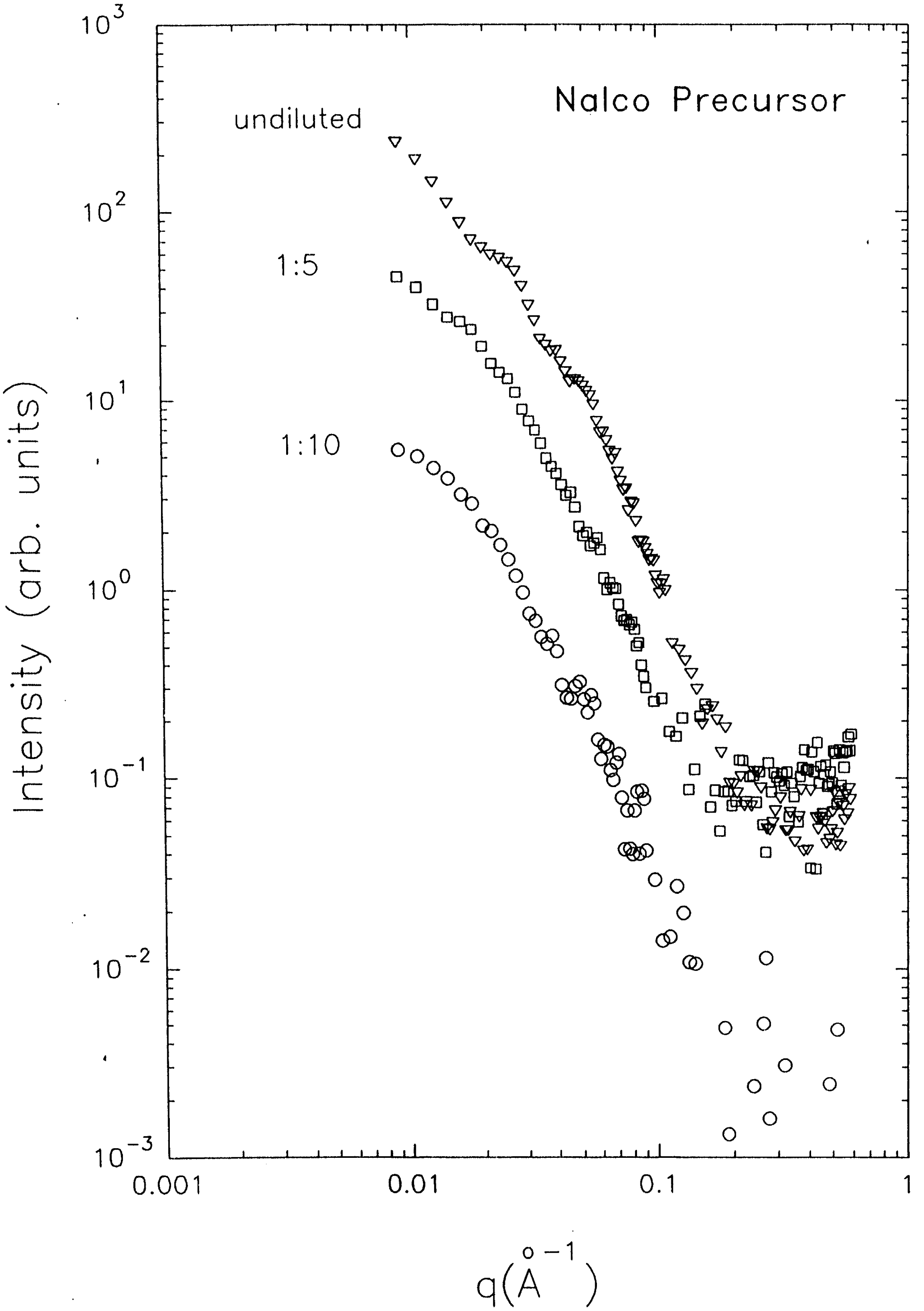


Fig. 3: Combined plot of various dilutions of the sol from which the gel is formed.

P/P_o	larger size (Å)	smaller size (Å)
0.0	51	29
0.35	52	34
0.42	62	36
0.54	68	35
0.62	85	>30

Table 1. Structure sizes for a silica xerogel as a function of dibromomethane loading.

During the quarter, a study was conducted on a second series of activated carbons, which are described in the adsorption section in more detail. Scattering plots for these samples are shown in Figure 4. The porod slopes and the sizes (R_g) obtained from SAXS are tabulated in Table 2. We see that the radius of gyration can not be reasonably estimated for some carbons. For the carbons AC2-32 and AC2-33, we find that the Guinier region is very indistinct. But for carbon AC2-17 the pore size distribution is very broad. Hence a reasonable estimate can not be made of R_g for some of the carbons at this time.

Sample ID	Porod Slope	Radius of gyration (Å)
AC2-09	-3.5	5.0 Å
AC2-17	-3.57	NA
AC2-23	-3.7	5.6 Å
AC2-31	-4.0	6.1 Å
AC2-32	-4.0	NA
AC2-33	-2.7	NA

Table 2. Porod slope and the radius of gyration obtained from SAXS for AC2 series of carbons.

2. ADSORPTION.

In the previous quarter experiments were reported on the adsorption of CO_2 on activated carbon at a low temperature (193 K). However the experiments were inconclusive in proving the temperature-independence of adsorption in microporous materials. If the experiments had worked out as hoped, it could have been possible to obtain a CO_2 adsorption isotherm over the full range of relative

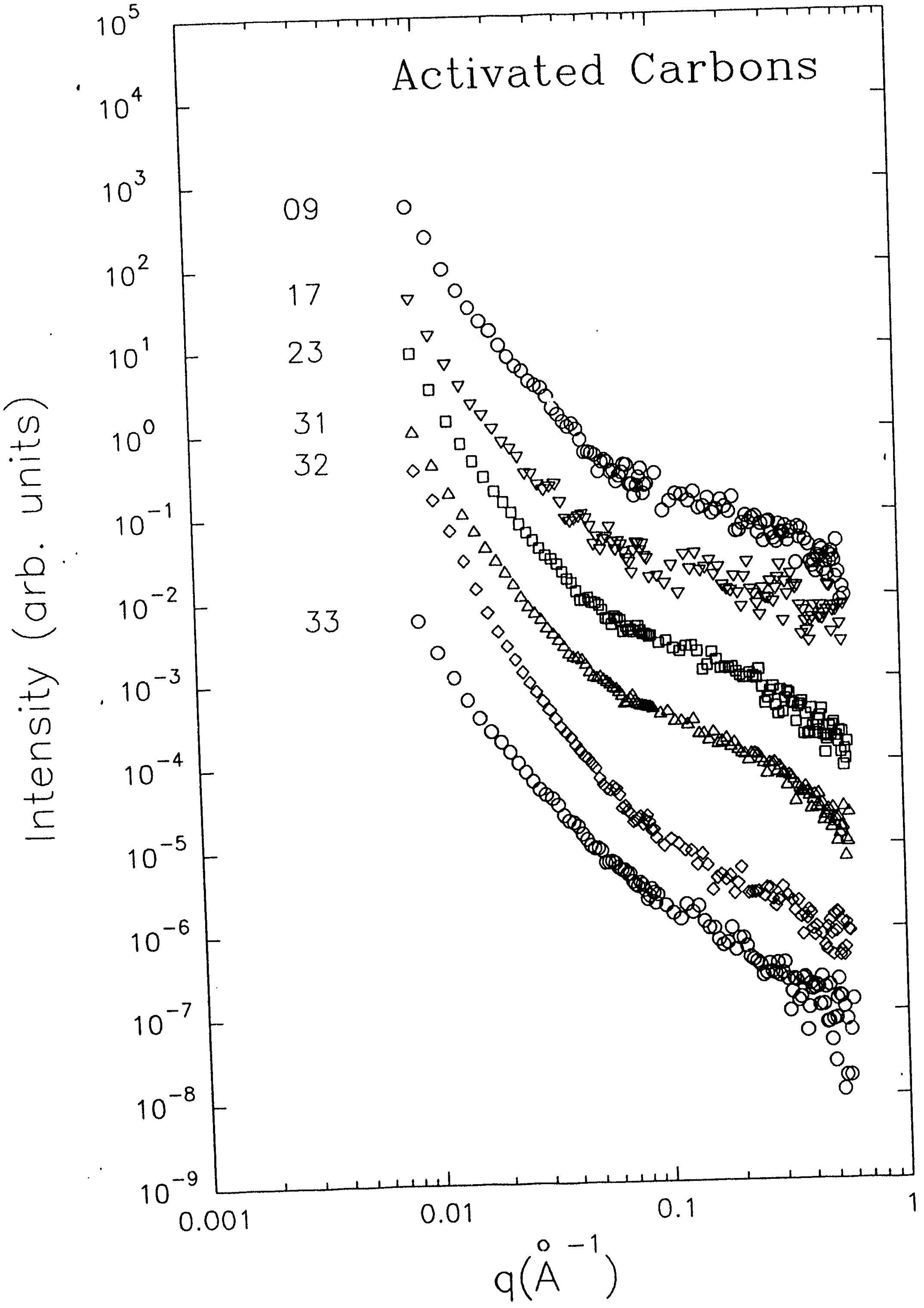


Fig. 4 Stack plot of the activated carbons from Air Products.

pressures without carrying out high pressure measurements to ~ 35 atm. The resulting data could have been used to obtain micropore distributions for a given material.

In the present quarter it was decided to further test the applicability of the Dubinin-Astakhov (DA) equation to activated carbons. A set of 6 carbons, numbered AC2-09 through AC2-33, was procured from our industrial partner, Air Products. This second set differs from the first in that while the first set consisted of a series of progressively activated coconut shell carbons, the second set contains materials of a variety of origins (See Table 3). Measurements on these carbons were carried out using CO_2 at 274 K, as with the previous set. The complete isotherms were combined from low-pressure measurements (to 1 atm.) carried out on a Micromeritics ASAP 2000M, and high pressure measurements (1 to 35 atm.) carried out on a VTI HPA 100 automated high pressure adsorption system. As before (please refer to previous quarterly reports), DA analysis was carried out on the CO_2 isotherms to a relative pressure of 0.4. The analysis allowed the determination of the micropore volume for each material and the DA exponent, which, as reported before, is a measure of the heterogeneity of the pores/surface. At this point it is not clear if the heterogeneity in the pore size can be separated from the heterogeneity in the surface itself. The net adsorption potential felt by an adsorbate molecule as it approaches the surface will be the sum of the contributions from enhancement in potential due to the small size of the pore, and from surface groups that cause electrostatic forces to come into effect which are different from the purely physical dispersion interactions characterizing the potential enhancement in the pore. Experiments on the more general set of carbons obtained during this quarter enables us to probe the generality of the methods used for characterizing the first set. It is clear that the DA exponent represents a distribution in the micropore energy of filling. The trends observed in DA exponent variation with degree of activation and pore volume, however, need not hold for an arbitrarily selected material. Table 4 contains preliminary results for this set of carbons.

It is apparent that the trends established earlier do not hold for an arbitrary set of materials. The final product of a set of processes depends not only on the processes themselves, but also, to a large extent, on the raw material on which the processes are carried out. This is clearly the reason why the trends observed for a series of progressively activated carbons, do not hold when the materials are randomly chosen from different sources and undergo different treatments. So while it is safe to say that the DA exponent is a measure of adsorbent heterogeneity, micropore volume and SAXS radius of gyration (R_g) need not follow a trend with respect to the exponent for a set of randomly selected materials.

Table 3. Origin of AC2 series of activated carbons.

Sample ID	Source	Micropore Vol., cm^3/g (from t-plot)
AC2-09	Peat	0.46
AC2-17	Coconut	0.21
AC2-23	Coke	>3.5
AC2-31	Coconut	0.71
AC2-32	Unknown	0.46
AC2-33	Wood	NA

Table 4. Preliminary adsorption results on AC-2 series

Sample ID	Total pore vol. via N_2, cm^3/g	Micropore vol. from CO_2 (274 K) DA analysis, cm^3/g	DA exponent from CO_2 (274 K) DA analysis
AC2-09	0.24	0.261	2.09
AC2-17	1.451	1.286	1.39
AC2-23	NA	0.607	1.39
AC2-31	NA	0.624	1.49
AC2-32	0.929	0.719	1.42
AC2-33	1.178	0.770	1.28

3. NMR Techniques.

Work during the quarter focused on two different applications of ^{129}Xe spectroscopy. The first was to assess how, and if, xenon may be used as a reliable probe of pore structure as it is with zeolites. This is being conducted using the first homologous series of carbons discussed in earlier reports (AC1-xx). The xenon results will be compared to our previous adsorption (CO_2 and N_2) and SAXS results. This work is in progress and will be reported next quarter. The second is a new approach which may give us spatial information about pore size distributions. We have performed some two-dimensional ^{129}Xe experiments which appear to give us information about the spatial separation between different pores. However, these are time-consuming experiments with detailed data analysis and hence, results will not be reported until next quarter.

Work planned for next quarter

1. It is planned to carry out further characterization of the AC2 series of carbons procured from Air Products. Low temperature CO_2 adsorption will be carried out using a different method and it will be investigated if the adsorption process in micropores is temperature invariant, at least over a limited range of higher temperatures.
2. Compare ^{129}Xe NMR for carbons to adsorption and SAXS results.
3. Develop a further understanding of two-dimensional xenon experiments.
4. Continue SAXS-contrast matching experiments concentrating on materials of different pore surface roughness/fractal dimension.

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