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Quarter report #1, 9/1/91-11/31/91
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, image analysis) are limited because of this broad pore size range, the presence of micropores, the 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. We believe that measurement of the NMR parameters of various gas phase and adsorbed phase NMR active probes can provide the resolution to this problem. It has long been recognized that NMR relaxation times of adsorbed molecules are shortened when they come in contact with pore surfaces and these effects can be exploited to obtain information about pore structure. However, only recently have several groups gone back to the early NMR work and begun to exploit those principles to extract pore information. One of the principle investigators on this proposal (D.M.S.) has made several of the recent advances in low-field NMR relaxation measurement of pore structure. We now propose to 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, $^{2}H_2$, $^{14}N_2$, $^{14}NH_3$, $^{15}N_2$, $^{13}CH_4$, $^{13}CO_2$) and the pore surfaces in coals. These molecules have been selected for their chemical and physical properties. In particular, NH_3 is likely to be strongly interacting with surface sites, Xe and He should be weakly interacting, N_2 and CO_2 are the common gases used as adsorption probes in surface area measurements such as BET, and CH_4 is commonly found in coal and should provide interesting information about its interaction in pores. Additionally, He is a very tiny atom so it should penetrate the smallest pores and should have few problems associated with diffusion in small pores. A special NMR probe will be constructed which will allow the concurrent measurement of NMR properties and adsorption uptake at a variety of temperatures. All samples will be subjected to a suite of "conventional" pore structure analyses. These include nitrogen adsorption at 77 K with BET analysis,

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CO_2 and CH_4 adsorption at 273 K with D-R (Dubinin-Radushkevich) analysis, helium pycnometry, and small angle X-ray scattering as well as gas diffusion measurements. The project will combine expertise at the University of New Mexico (pore structure characterization, NMR), Los Alamos National Laboratory (NMR), and Air Products (porous materials).

Work completed during the last quarter

Our work during the last quarter (the first of the project) included the hiring of staff, experiment fabrication, literature review, and sample selection. In order to build the special low temperature NMR probe, we have hired a post-doctoral fellow (Dr. Kim) who has prior experience in very low temperature NMR. During the first quarter, he primarily worked on familiarizing himself with the operation of our advanced Varian Unity 1 400 MHz NMR on which we will perform the NMR experiments. This instrument is located at Los Alamos National Laboratory and is jointly owned by LANL and UNM. Two graduate students have also been hired. One will perform small angle x-ray scattering (SAXS) measurements on our porous samples and the second will perform both sub-ambient and high pressure (<1000 psia) adsorption measurements. Work in the experiment fabrication area primarily revolved around building new high pressure adsorption rigs and the construction and calibration of these is on-going. Up-dating the recent literature in the areas of pore structure characterization and coal science is currently in progress by the students and post-doc for each of their respective research areas. Sample selection for the three year program is to involve three tiers of samples. The first is a set of well-characterized microporous oxide materials including zeolites and silica gel. The second phase is a set of microporous carbons. The third phase will include a range of coal samples. The first two sets of samples will be selected in conjunction with our partners from Air Products. The coal samples will be selected in conjunction with DOE/PETC advice following the coming annual review meeting. Because of time constraints, we were unable to make a trip to Air Products in Allentown, PA before the end of the reporting quarter.

Work planned for next quarter

Our goals for the next quarter include:

1. Complete construction and calibration of our two new high pressure (0-50 and 0-1000 psia) volumetric adsorption rigs.

2. Visit Air Products in Allentown, PA and select our oxide and carbon test samples.

3. Start SAXS and adsorption measurements on test samples.

4. Start to perform ^{129}Xe NMR measurements.

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