Research on

CHARACTERIZATION OF POWDERS AND POROUS MATERIALS

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MANY RESEARCH opportunities for chemical engineers in high technology materials center around the relationships between the voids and the solids that are an inevitable part of powders and granular materials. Ceramics with a wide range of applications are formed by sintering a mixture of powders or porous particles. Creation of pores at the surface of a single crystal of silicon and subsequent oxidation can be used to provide vertical isolation for VLSI devices. In heterogeneous catalysts, reactant molecules must diffuse through the intricate pore structure of an oxide material to reach the active sites. The isolation of radioactive or chemical wastes depends on the permeability of the geologic formation and any near-field, man-made barriers. What is important to each of these applications are properties such as pore shape, pore size distribution, particle size, and structure of individual particles in the porous matrix. It is interesting to note that these application areas extend from traditional chemical engineering areas to high-tech ceramics and microelectronics. The Powders and Granular Materials Laboratory at the University of New Mexico was created as an interdisciplinary activity to support research efforts in a wide range of areas for which powder and porous material characterization is of interest. In addition to serving as a central facility for characterization work, the laboratory is expected to spur the development of new characterization technologies.

A number of faculty at the University of New Mexico have research interests in areas associated with the application of porous materials technology. In the Department of Mechanical Engineering, Mohsen Shahinpoor has an interest in characterizing the contacts made by particles in a bed. This is important to a number of engineering problems such as powder storage, packing and flow. In the Department of Chemical and Nuclear Engineering, A. Datye, R. Mead, E. Nuttall, D. Smith, and F. Williams have an ongoing interest in areas such as catalysis, transport phenomena, energy research and materials science. A common requirement in each of these programs is to characterize porous materials. Although no one research effort is large enough to support the equipment and manpower necessary to provide a complete characterization facility, by pooling resources we have been able to establish a state-of-the-art laboratory. This provides a sufficient user base to fully utilize the various characterization technologies and enables the laboratory to have trained personnel for each instrument. By training undergraduate students in their junior year to operate the laboratory's equipment, we can provide at least two-year continuity, help them to fund their education, provide an exposure to research, and motivate them to go on to graduate school. On the other hand, this approach frees up the time of graduate students which can then be devoted to their individual research projects.

Although research has been conducted on porous materials (primarily coal, oil shale, catalyst supports) for a number of years by Professors Mead, Nuttall and Williams, it was in 1984 that three new faculty (Datye, Shahinpoor, Smith) joined the UNM faculty. With the research projects and equipment that was brought from their former schools, a critical mass was in place with the resources (*i.e.*, funding, equipment, students) to operate a large central research laboratory.

After a short period of time, the need for this type of facility became apparent to other people within the university, local industry and the National Laboratories in New Mexico (Sandia and Los Alamos). This has led to a number of funded, collaborative research projects. It also furnishes an opportunity for our undergraduate and graduate stu-

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dents to benefit from exposure to a broader scientific community. The broad experience that students are exposed to provides more information that will aid in future employment/career decisions. Students graduating from our program have, in some cases, continued their research by gaining employment with the sponsoring agencies.

FACILITIES

During the first two years of the laboratory's formal operation, equipment/instrumentation for fairly complete state-of-the-art characterization was obtained. Sources of this equipment include previous research projects, funding from DOE and NSF, State bond issues, and donated equipment from Sandia and Los Alamos National Laboratories. Properties of powders and porous materials which we can study by a variety of techniques include

- **Mean pore size and pore size distribution**
- **Particle size, size distribution and shape analysis**
- **Pore shape, tortuosity, formation factor, pore connectivity**
- **Specific (chemisorption) and total surface area**
- **True and apparent density**
- **Diffusivity (Knudsen, surface, etc.), permeability**
- **Adsorption parameters**
- **Coordination number, distribution of coordination number**

A general listing of laboratory equipment is presented in Table 1. Also included is instrumentation located in other departments on campus which we can readily access. A complete range of sample pretreatment and preparation equipment is available. In addition to characterization instrumentation, we have facilities for powder synthesis (both vapor phase and wet-chemistry), surface modification, and sintering.

Experiment control, data acquisition and data reduction in the laboratory is accomplished with a number of computers including a IBM CS-9000, a DEC PDP-11/03, and several HP-85's. Extensive calculations may be conducted on the department's Ridge-32 computer or the university's VAX-8650 super mini-computer. For very large scale calculations, access to the CRAY supercomputers at Sandia and Los Alamos National Laboratories is possible. A complete range of microcomputers, graphics terminals and plotters is available for use by graduate students.

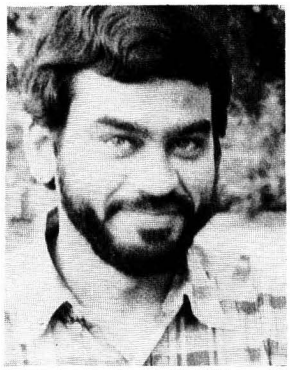
TABLE 1
Laboratory Facilities and Equipment

- **Autoscan-33 mercury porosimeter (0-33,000 psia)**
- **Quantasorb flow-type surface area analyzer**
- **Quantector multiple station outgassing instrument**
- **Spin-lock 20 MHz pulse NMR**
- **Quantimet 720 image analyzer**
- **Volumetric chemisorption apparatus**
- **Dupont 990 thermal analyzer (TGA/DTA)**
- **Micropycnometer for helium density determination**
- **Flow permeation apparatus**
- **Hydrodynamic chromatograph**
- **Wicke-Kallenbach diffusion cell**
- **Chromatographic determination of diffusion/adsorption parameters**
- **Cahn microbalance for sorption measurements**
- **JEOL 100-B TEM[1]**
- **Hitachi S-450 SEM[1]**
- **JEOL 2000-FX TEM[2]**
- **X-ray diffraction[2]**
- **General Electric GN-300 300 MHz NMR[3]**

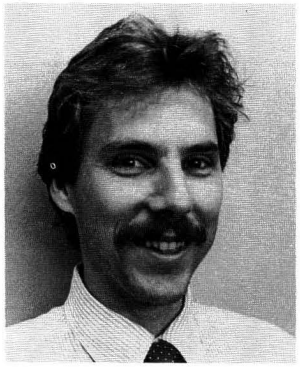
[1]College of Engineering:
[2]Department of Geology:
[3]UNM Center for Non-Invasive Diagnosis:

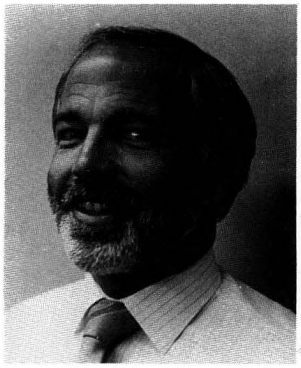
CURRENT RESEARCH TOPICS

In the area of catalysis, the ability to determine BET surface area, pore volumes and pore size distri-



Abhaya Datye received his BTech degree from the Indian Institute of Technology, Bombay, and spent three years in industry working in the areas of process design and development. He received his MS and PhD degrees from the University of Cincinnati and the University of Michigan, respectively. His research interests include heterogeneous catalysis, materials characterization and electron microscopy of VLSI devices. **(L)**





Douglas Smith is associate professor of chemical engineering and co-director of the UNM Powders and Granular Materials Laboratory at the University of New Mexico. He received his BS and MS degrees from Clarkson College of Technology and his PhD from the University of New Mexico. Current active research programs include porous materials characterization, microparticle synthesis, NMR imaging of porous materials and transport phenomena in porous materials. **(C)**

Frank Williams is professor and chairman of chemical engineering at the University of New Mexico. He received his BS degree from Northwestern University and his MS and PhD degrees from Stanford University. His research interests are in the areas of shock wave induced synthesis and enhanced catalytic activity of materials and the characterization of the physical structure and diffusion in coal. **(R)**

bution is very useful. One project under way in the laboratory is in the area of metal-support interactions. Professor Datye is using submicron-sized oxide particles as model supports for heterogeneous catalysts. The surface structure and chemistry of these particles is much easier to understand than that of conventional supports used for heterogeneous catalysts [1]. An additional advantage is that the metal crystallites can be imaged "edge-on" so that the three-dimensional structure of these metal particles can be seen in unprecedented detail. Figure 1 shows an electron micrograph of ruthenium metal crystallites supported on model MgO support. The support in this case is formed simply by burning Mg ribbon in air, and it consists of almost perfect cubes with exposed {100} surfaces. Another project that Professor Datye is working on involves a study of pore size and structure in porous silicon. This is important for device applications where one is interested in forming an island of perfect Si on SiO_2.

In addition to Professor Datye's interest in producing metal oxide particles for model catalyst supports, Professor Smith's students have been fabricating uniform, sub-micron metal oxide spheres of very narrow size distributions via wet chemistry methods. The high degree of shape and size uniformity is illustrated in Figure 2 for silica spheres with a mean diameter of 130 nm. By pelleting these spheres, a model porous media is obtained with the same well-defined pore size and shape as observed in random packings of uniform spheres. This type of solid is of interest since many agglomerated materials such as catalyst supports and ceramic green-bodies have similar structure. Our model porous solids are used for assessing pore size measurement techniques, for the study of transport phenomena in porous media and for the study of sintering mechanisms.

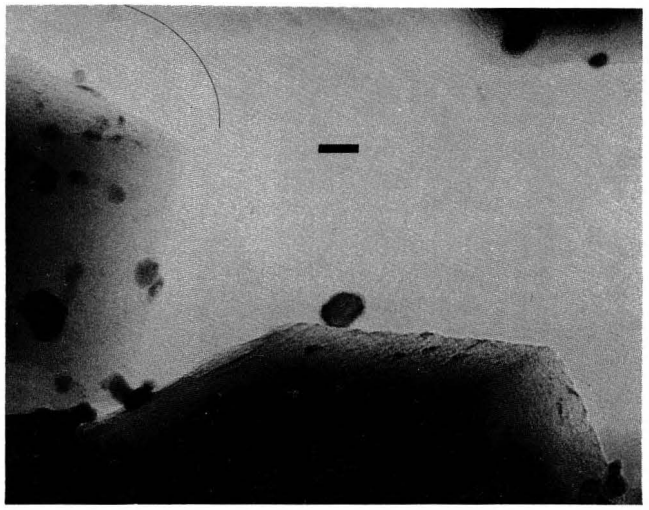


FIGURE 1. Burning magnesium wire in air produces magnesium oxide with almost perfect crystal faces. (Marker = 10nm)

Conventional analysis of mercury porosimetry data for agglomerated materials may indicate a bimodal pore size distribution even when the material is formed from uniform particles. By taking the actual structure of the solids into account, a correct description of mercury penetration into the pores and toroidal regions (*i.e.*, particle contacts) was developed [2]. A similar analysis has been extended to the analogous problem of gas adsorption and condensation in sphere packings [3]. Many times, the rate of fluid transport through porous media is what one is trying to predict from given pore structure information. Conversely, one may perform transport experiments to ascertain pore structure information which may not be available from conventional techniques. We have used Knudsen diffusion measurements as a tool to study random microsphere packings [4,5]. By studying surface transport of adsorbed gases in these solids, we hope to extract further information about particle-particle contacts. Some pore size measurement techniques are not successful for large pores ($>1\mu m$). Professor Smith and collegues at Sandia National Laboratory are exploring the use of colloid tracers as a sensitive tool for size analysis in large pores. The rate of colloid migration through these large pores is a strong function of the colloid to pore size ratio. By studing the change of the tortuosity factor with changing colloid size, information concerning pore shape may be extracted [6,7].

The conventional pore size measurement techniques of mercury porosimetry and nitrogen adsorption/condensation suffer from several disadvantages [8]. An assumption about the pore shape must be made, the size of the smallest pore constriction is often measured, sample size must be small, and the porous solid must be completely dry. To avoid these problems, Professor Smith and his students have explored the possibility of using NMR techniques for pore size analysis. In principle, protons of water contained in pores will undergo spin-lattice relaxation at rates related to the pore size. The smaller the pore size, the faster the relaxation. No assumption concerning pore shape is required as the actual pore volume to surface area ratio is obtained. By performing $180°$-τ-$90°$ relaxation measurements on a series of porous solids with well-defined pore geometry and size, the advantages, and some disadvantages, of NMR analysis have been demonstrated. This project was aided by close cooperation with scientists at Los Alamos National Laboratory who arranged for the in-

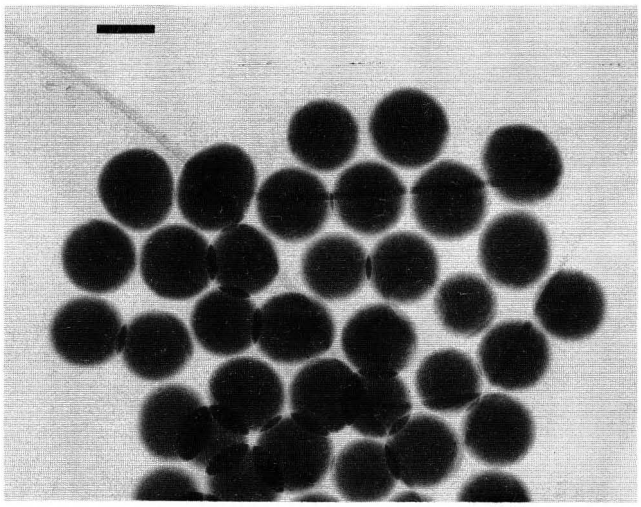


FIGURE 2. Electron Micrograph of 130 nm silica spheres that have been heat treated at 750°C for three hours. (Marker – 100 nm)

definite loan of a 20 MHz pulse NMR for the investigation. Work continues on this project as we address questions about the effects of pore shape, surface chemistry and the lower pore size limit for this technique.

In addition to characterization work and powder synthesis, research is also being conducted on powder modification techniques. Professor Williams has been investigating the dynamics of shock treating inorganic materials by exposing the powders to extremely large shock waves. Four characteristic behaviors as a function of peak shock pressure have been observed for shock induced changes in the specific surface area of inorganic powders. Abrupt phase change, comminution of particles and interparticle bonding appear to be the mechanisms producing the observed response. The nature of morphological changes in powders is of interest in understanding shock activated sintering, shock-enhanced catalytic activity, dynamic compaction, and shock-enhanced solid state reactivity. Recently, classical BET surface area measurements were reported for compacts of aluminum oxide, zinc oxide, aluminum nitride, titanium carbide, and titanium diboride after they were subjected to controlled shock loading to a mean peak pressure from 4 to 27 GPa [9]. Extension to specific surface area measurements of shock loaded hematite, magnetite, manganese dioxide, and well-annealed alumina powders has been accomplished [10]. Sampling from the edge, center and the bulk of shock loaded compacts of these powders reveals variation in the degree of modification consistent with the calculated variation of the pressure and temperature excursions.

Professor Mead is using chromatographic means to explore gas diffusion and adsorption in various coals. The pore structure of coal is difficult to probe since sample compression effects dominate mercury intrusion and nitrogen cannot access the coal micropores at liquid nitrogen temperatures. By using a number of inert and/or adsorbing tracers, a more complete picture of the pore structure of coal will be obtained. Professor Shahinpoor has been studying the structure of random packings of uniform spheres with the support of the National Science Foundation. By passing a reactive gas through a random sphere packing, for which the surface of the spheres has been coated, discoloration of the sphere surface will occur in the region of sphere contacts. From image analysis of the spheres, the coordination number, distribution of particle contacts, and the spatial variation of sphere contacts is determined. Professor Nuttall is interested in relating the reactivity of various coals to the reactivity and concentration of the different materials contained in the coal. In addition, he is involved with a collaborative research project with the Los Alamos National Laboratory on colloid transport mechanisms as applied to radionuclide release scenerios.

EDUCATIONAL OPPORTUNITIES

Graduate and advanced undergraduate students may take advanced courses related to powders/porous media characterization, including: transport phenomena in porous media, powder technology, catalysis and TEM/SEM techniques. In addition, a 3-day short course on porous media characterization is presented at UNM by members of the Powders and Granular Materials Laboartory and other national experts under the tutelage of the Materials Research Society. A monthly seminar series features visits from nationally recognized speakers with a wide range of backgrounds in powder and porous materials technology.

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