PROGRESS IN RESEARCH

MINERAL INDUSTRIES EXPERIMENT STATION

College of Mineral Industries
THE PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania

Circular 69 1961-1965

CONTENTS

FOREWORD

Next to teaching, research is the most important activity of the faculty of a university. It provides thesis topics, an opportunity to learn by doing, and financial support for students who are candidates for the M.S., Ph.D., and various advanced professional degrees. It enables the teaching faculty not only to make contributions to new knowledge, but to whet interest in their subjects and to keep up with the most recent advances made by others in their field. Among the important side benefits are a more aggressive, more up-to-date staff of teachers; a steady outflow of valuable research results to industry and to the state and nation; and an atmosphere of competence which makes undergraduate programs more attractive to students.

Contrary to widespread belief, research in modern state universities is supported largely by the federal government, industry, and public and private foundations. For example, during the period 1961-1965 covered by this report, only 28 per cent of the $9,064,541 supporting research in the College of Mineral Industries came from the Commonwealth or the University. Another 55 per cent was provided by the federal government and 17 per cent was contributed by industry and foundations.

During the period of this report, the research program has steadily grown. In August, 1963, a large segment of the research in the College of Mineral Industries, the Materials Research Laboratory (with expenditures of about $700,000 per year), was transferred to the University's Institute for Science and Engineering because of its interdisciplinary nature. This transfer of funds is evident in Table 1 in the decline of research funds received by the College from $2,779,120 in 1962-1963 to $2,136,162 the following year. The amount climbed some 15 per cent by 1964-1965, however, which is roughly three times the normal per annum increase in research.

TABLE 1

FUNDS RECEIVED FOR RESEARCH*

July 1-June 30	University, Special State Appropriations, State Contracts	Federal Grants, Contracts	Industrial, Foundation Contracts, Grants, Fellowships	Total
1961-1962	$514,920	$ 698,360	$476,627	$1,689,907
1962-1963	664,242	1,711,444	403,434	2,779,120
1963-1964	666,712	1,117,387	352,063	2,136,162
1964-1965	733,242	1,391,600	334,510	2,459,352

* Including overhead

Table 1 also shows the gradual decline in support of research by industry and private foundations, a trend which was first noticed in 1959. This may be due in large part to increased support of basic research in the nation's universities and colleges by the federal government.

Most of the research is part of the training of graduate students, although occasionally a research project is undertaken to solve some specific problem of industry or government. Many research projects have been initiated by faculty members to provide thesis topics for their students, or to help provide their financial support. Of 368 graduate students in the College during 1964-1965, only 43 or 12 per cent did not have appointments as instructors, research assistants, fellows, or graduate assistants (see Table 2). Most of the 43 without College appointments were supported by National Science Foundation Fellowships, or by other U.S. Government fellowships or traineeships, or by foreign governments sending their nationals to this institution.

TABLE 2

DEPARTMENTAL STATISTICS 1964-1965

Department	Faculty	Funds Received for Research*	Graduate Students Supported	Graduate Students Unsupported
Ceramic Science	6	$ 98,029	22	3
Fuel Science	15	254,270	30	—
Geochemistry & Mineralogy	28	276,207	82	3
Geography	10	37,289	22	11
Geology & Geophysics	20	215,209	55	5
Metallurgy	12	163,977	28	1
Meteorology	7	261,411	23	15
Mineral Economics	4	30,000	10	2
Mineral Preparation	5	316,823	18	—
Mining	8	104,841	21	—
Petroleum & Natural Gas	6	77,190	14	3
	121	$1,835,246	325	43
			43	
			368	

* Excluding overhead and funds received by the Mineral Industries Experiment Station, some of which are allocated to departments.

There are 11 departments in the College of Mineral Industries: Ceramic Science, Fuel Science, Geochemistry and Mineralogy, Geography, Geology and Geophysics, Metallurgy, Meteorology, Mineral Economics, Mineral Preparation, Mining, and Petroleum and Natural Gas. Each department has its own research program, developed along the lines of interest of its faculty. Some departments are more research-minded than others, but all departments do conduct research and have graduate training programs.

Mineral Industries Experiment Station
M. E. Bell, Director

July 12, 1965

INTRODUCTION

This report is intended to provide information on the research activities of faculty members and graduate students in the College of Mineral Industries at The Pennsylvania State University. It is part of a series entitled "Progress in Research," the latest one of which was issued for the Biennium 1959-1961, Circular 59, of the Mineral Industries Experiment Station. The present report covers the four-year period July 1, 1961, through June 30, 1965.

The report consists of a section for each of the 11 departments in the College of Mineral Industries, arranged alphabetically, and a section on the Mineral Industries Experiment Station, which is responsible for providing administrative facilities, specialized laboratories, shops, and technical services. Each departmental section includes an introduction which gives some idea of the departmental emphasis and objectives in research.

A large sample of individual and group research projects is included under each department, with emphasis on those which are more easily understandable or applicable. Some of the projects described herewith closed during the four-year period of the report, while others have just been established. A third group of projects is long-term in character and may have been supported from several sources during their history, and probably contributed to the education and support of a number of graduate students.

The choice of individual topics for research is usually dictated by the interests of the professors and the availability of support. The University influences direction only through the professors it hires and the facilities it provides.

It should be pointed out that this report covers only one phase — research — and that a well-rounded professor in a university may be engaged in many other activities of an importance equal to, or perhaps greater than, research. Teaching, committee work, administration, continuing education, professional society leadership, public service, lecturing, and consulting are some of the other preoccupations of the average university professor today.

The Deike Building, constructed in 1965, provides modern facilities for research and instruction primarily in the earth sciences.

CERAMIC SCIENCE

Ceramics are materials made from earth or clay, such as glass, porcelain, brick, tile, china, and crystal. The Department of Ceramic Science conducts research both in the newer segments of the discipline, including nuclear, electronic, aerospace, and special ceramics, and in the older, more conventional areas. The department has excellent facilities for research on composition, structure, texture, and chemical and physical properties of nonmetallic, inorganic materials. High temperature preparative facilities are available and much equipment is on hand for examination of the structure and texture of both crystalline and X-ray amorphous materials (glass, gels, and colloidal bodies). Apparatus for mechanical, electrical, optical, and thermal property measurements on glasses and crystalline materials is actively used.

The major fields of interest in the department are:

(1) Phase equilibria, luminescence, mechanical and thermal properties;

(2) Electroceramics, especially ferroelectrics and ferromagnetics, magnetics, mechanical and electromechanical behavior, thermal and shock resistance, processing;

(3) Rheology and fluid properties, surface chemistry, microstructure, processing, high-temperature reactions;

(4) Glass composition, structure, and properties, especially anelasticity, nucleation, and radiation effects;

(5) Phase studies in oxide intermetallic systems, thermodynamics, thermal properties; and

(6) X-ray diffraction studies of polymorphic transitions, thermal expansion, and strain in crystals.

Fluorescent Materials

Research in this area is aimed at the discovery and understanding of luminescent materials used in fluoresent lamps, radar screens, black-and-white and color television, high-pressure mercury vapor lamps, and many other electronic devices. Investigations involve mineral synthesis, the application of phase equilibria data, measurements of the response of the phosphors to 2537Å and 3650Å ultraviolet light and cathode rays, and the correlation of emission data with composition, structure, and physical texture. Research on specific phosphors has included zinc borates, cadmium borates, calcium silicates, zinc phosphates, germania, cordierite, strontium orthophosphate, magnesium silicates, germanates and titanates, spinels, and cadmium phosphates. Current research is concentrated on the activation of the apatite structure with rare-earth ions.

Phase Equilibria in the Quaternary System Lithia-Soda-Alumina-Silica

The objective of this work was to study phase relationships and the thermal expansion properties of phases in the system Li_2O-Na_2O-Al_2O_3-SiO_2. The important compounds which appear in this system are cristobalite, tridymite, quartz, eucryptite, spodumene, albite, and nepheline. All of them are important in ceramic products, but the low expansion β-spodumene is especially important since it has been the basis for the development of commercial products known as Lithafrax (Carborundum Co.), Nucerite (Pfaudler-Permutit Co.), Pyroceram (Corning Glass Works), and CerVit (Owens-Illinois Glass Co.). It has also been used for the development of glass-ceramics for undersea vehicles, important to oceanography and the navy.

Oxide Systems

The crystal chemistry and phase relationships in systems involving ZnO and the physical and chemical properties of compounds and solid solutions which might have some application to ceramic processes or products are being examined. The binary and ternary equilibrium reactions of ZnO with the oxides of silicon, germanium, phosphorus, vanadium, niobium, and tantalum were studied by quench, DTA, strip-furnace, and high-temperature X-ray methods in an effort to discover new and possibly useful ZnO-containing compounds and solid solution series. In the second part of this study, dilatometric and, in some cases, axial thermal expansion data are presented for the phases contained in these systems.

Phase Equilibria and Physical Property Measurement in Systems Involving PbO

As a preliminary to experiments on high-frequency, low-loss ceramics made by crystallization from glass, compatability relationships were determined for the systems BaO-MgO-SiO_2, PbO-BaO-SiO_2, and PbO-MgO-SiO_2. Regions of glass formation were explored and observations were made on liquid-phase separations. The thermal behavior of five compounds in the system BaO-MgO-SiO_2 was investigated and liquidus relationships were determined for three joins in the system PbO-BaO-SiO_2 and for five joins in the system PbO-MgO-SiO_2. X-ray diffraction data were obtained for eight ternary compounds.

Effect of Pressure on Properties of Glass

Densification of a series of sodium borate glasses was carried out on —140 mesh glass powders on an opposed-anvil device at pressures up to 40 kilobars and temperatures up to 250°C. For samples at constant pressure and temperature, the per cent densification decreases with increasing Na_2O content. Heats of solution in 2N (HNO_3) of the unpressed and pressed glasses were measured in a simple vacuum-bottle calorimeter. Heats of solution of the pressed glasses were more negative than those of the unpressed glasses and were dependent on the pressures at which the samples were pressed. The maximum difference between the heats of solution of the glasses densified at 40 kilobars and the unpressed glasses occurred at the 20 mole per cent-composition.

Fundamental Studies of Glass Properties

The internal firiction of glass, as measured by the torsion pendulum, is being studied as a function of the melting history of the glass. Alkali silicate glasses containing one or two alkali oxides are subjected to either low or high melting temperatures for varying periods of time up to several hundred hours. Small fibers 50 microns in diameter and thin rods ½-mm in diameter are drawn and internal friction measurements are made. The melting history appears to be important in determining the low temperature anelastic properties, the rate of hydration, and the existence of immiscible phases in the glass.

Nucleation and Crystallization Studies of Glass

A study was made of the effect of inorganic surface treatments on the orientation of lithium disilicate crystals formed in fibers of a lithium silicate glass subjected to heat treatment. It was found that surface treatments can cause a change in the crystallization characteristics of a glass if ions can diffuse into the glass to alter the alkali concentration or subsequently form crystal nuclei. Metal salt treatments thus cause a decrease in the degree of orientation of the lithium disilicate crystals formed in the surface of the glass fiber. Among the salts studied, silver nitrate was among the most effective.

Relaxation Processes in Glass

Relaxation processes play an important part in determining the properties of glass, yet the mechanisms of many of these processes are not well understood. In seeking glasses of superior properties, it becomes important to understand the nature of these relaxations and their interrelationships in determining mechanical, electrical, and optical properties.

Experiments are underway in which mechanical processes are being studied as a function of glass composition and heat treatment. Strength measurements of pristine glass rods in air at room temperature are being made. These will be extended to measurements under liquid nitrogen to eliminate the effect of atmospheric hydration. Optical studies have been concerned with the luminescence of rare-earth ions in calcium lanthanum borate glasses. The viscosity of glasses in the viscoelastic region are under study as a function of the coordination of aluminum in soda-aluminosilicate glasses. There is evidence that the viscosity is at a maximum at the composition where the aluminum coordination starts to change from four-fold to six-fold.

Internal Friction and Dielectric Properties of Glass

An attempt is being made to correlate the internal friction of certain glasses with the dielectric losses of the same glasses measured at the same frequency. This necessitates that electrical measurements be made using an electrodeless method which elimates the problem of electrode polarization. Dielectric loss measurements at frequencies as low as 0.1 cycles per second, up to the kilocycle range, are being made. Current studies involve barium silicate glasses which have low losses, both electrically and mechanically, as a function of the addition of sodium ions which increase the losses.

Previously, the research had been concerned with measurements of the relative acidities of soda-aluminosilicate glasses using an electrochemical method. From the galvanic potentials, thermodynamic properties could be calculated which could be correlated with structural changes occurring as the glass composition was varied. It was found, for example, that a maximum entropy change for the cell reaction occurred when the ratio of $A10_4$ groups to non-bridging oxygen ions equaled one. The significance of this relationship was brought out by a correlation with other properties of these glasses containing the same ratio.

Refractories

The first study of basic refractories involves an analysis of the mechanism and kinetics of reactions which occur at ceramic-metal interfaces in systems such as $ZrB_2 + Zr$, $TiB_2 + Ti$. The purpose of the research is the determination of structure steps in these reactions, the correlation of the structure steps and the phase diagrams, and the study of kinetics and the rates of diffusion of atoms which are involved in the formation of the refractory coatings.

Another project on the basic refractories is the study, with the simple polycrystalline or single crystal systems, of the physical-chemical processes occurring in the basic refractories. The most important reactions occurring during the firing or in the use of these refractories are studied. The emphasis is not on the equilibrium situation or the phase diagrams but rather on the kinetics and diffusion.

Research on the diffusion in refractory systems involves an electron microprobe study of the reactions in polyphasic refractories. The objective is to obtain a better understanding of the reaction mechanism which leads to the formation of the bond in such refractories. For the first study, magnesia-chrome refractories were chosen. New information was obtained concerning the exsolution of spinels in the chrome to grains, the extent of diffusion of Fe^{3+}, Cr^{3+}, Al^{3+} from the chromite grains into the periclase grains, and the spatial distribution of the monticellite and forsterite in the silicate bond. A further objective is to refine the semi-quantitative results obtained and to extend application of the electron probe technique to a study of the processes in other polyphasic refractories.

Research on stability of refractive compounds involves the study of the mechanism of decomposition of the solid solutions in oxide systems. For the first study, the ZrO_2-MgO system was chosen and, as a first step, the phase diagram was established. The kinetics of decomposition were investigated, and it was found that decomposition comprised: (1) formation of the nuclei of the tetragonal phase on the grain surface; (2) growth of nuclei leading to the formation of an interface; (3) growth of the interface into the interior grain. The decomposition rate increased with the degree of ordering of defects and impurities and with the number of the anion defects. In the course of decomposition, magnesium oxide was precipitated at the grain boundaries. The grain boundary precipitation was studied in several oxide systems by using an electron microprobe, and it was found that the spatial distribution of the precipitate may be changed if the decomposition proceeds via a metastable phase. Study of the effect of the grain boundary precipitation on some mechanical properties of ceramic oxide bodies is in progress.

Clays

Maximum modulus of rupture and minimum porosity for semi-dry pressed Lower Kittanning clay, examined in the fired state, were correlated with critical water content for a given pressure, or critical pressure for a given water content. These critical quantities did not necessarily maximize or minimize the properties cited for unfired test pieces or those fired at very low temperatures. Other critical quantities were required. The irreversible thermal expansion of test pieces, with consequent increases of porosity at 600-800°C, was responsible for the lack of correlation.

Optical methods were used to determine the response of clay platelets to the stresses involved in plastic deformation or in decomposition. Analogies with "hard rock" fabrics were noted. In particular, it was found that the presence of slip bands retarded imbibitional swelling in the presence of water. These slip bands resulted from deformation. Test pieces made by filtration swelled more readily because slip bands, with their consequent restrictive effect, were absent.

Strain Energy and Reactivity of Solids

Mechanically-strained magnesium oxide showed enhanced chemical activity not ascribable to increases in specific surface. This activity manifested itself by increased rates of hydration by water vapor at room temperature and by enhanced rates of formation of magnesium silicates at elevated temperatures. The mechanically-strained oxide was less effective in forming magnesium ferrite than the normal oxide because recrystallization of the oxide at the reaction temperature used up energy that would otherwise have contributed to increased chemical activity. The Warren-Averbach X-ray technique gave data indicating stored energies of 3-5 Kcal/mole MgO.

Gases in Clay-Water Systems

Air bubbles are negatively charged over a wide range of pH. Kaolinite and dickite show edge-to-face flocculation at low pH and adhere to bubbles by their positively-charged edge faces. In slightly acid systems, adlineated floccules may link bubbles. Ca- and Pb-clays show card-pack flocculation and adhere to bubbles by their basal planes. Bubbles generally increase the viscosity of clay-water systems, although a decrease may occur in dispersed systems. Bubbles associated with, rather than separate from, clay flocs are especially effective in increasing viscosity. The wettability of kaolinite is more marked if the crystals show stacking faults. Adsorbed ammonia, methylamine, or ethylamine, and their corresponding cations, diminish the wettability. Both cations on exchange sites, and the areas between the sites, influence wettability. Partial or complete coverage of these areas by ammonia or amines reduces

wettability still further when the sites are already occupied by ammonium or alkylammonium cations.

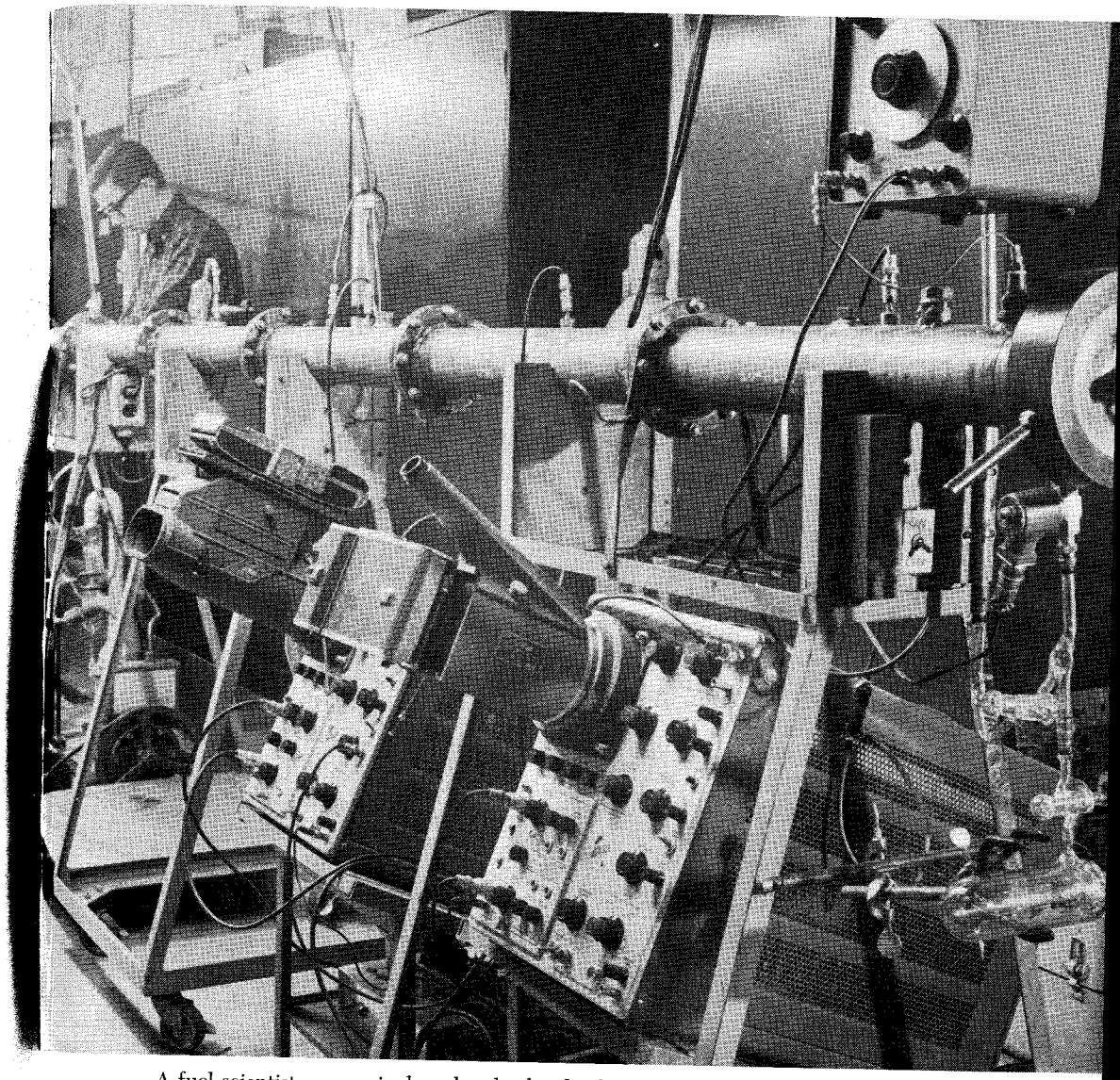
Extrusion of Clay-Graphite Mixtures

Graphite aggravates the differential drying-shrinkage of kaolinite-illite clay, while quartz diminishes it. These effects are consequent upon the relative intensities of clay platelet orientation. The extrusion of the clay or of clay-graphite mixtures gave yield values related to water-contents by the equation of Stull and Johnson. Graphite flakes and clay platelets tended to be parallel to the curved surfaces of the extruded cylinders except where the platelets were involved in slip bands that crossed the general fabric. Graphite flakes were fragmented during extrusion and the relatively low dry strength may be associated with this phenomenon.

FUEL SCIENCE

Research in fuel science can be divided into two general categories: (1) combustion processes and energy conversion and (2) physical and chemical properties of fuels and fuel-derived materials. The aims of the research program in the Department of Fuel Science are to add to the body of knowledge in both of these categories and, while doing so, to provide valuable research experience for graduate students. Current research areas may be grouped under seven headings:

1. **Carbons:** Formation; carbon blacks; gasification; active carbons; catalytic effects; graphitization.
2. **Coals:** Chemistry of macerals; pyrolysis; physical structure; gasification; graphitization; reactions in plasmas; mineral matter removal; desulphurization.
3. **Combustion:** Pulverized coal flames; hybrid rocket fuels; dust explosions; ignition of refuse piles; oil sprays; air pollution.
4. **Comminution:** Coal breakage mechanisms; fracture of brittle materials; ultrafine materials; shape factors.
5. **Fast Reactions:** High temperature gaseous reactions; shock tube techniques; flow system pyrolyses; plasma reactions; chemiluminescence; free radical reactions; atom recombination.



A fuel scientist uses a single-pulse shock tube for studying the decomposition of gaseous hydrazine.

6. **Graphites:** Gasification kinetics; catalytic effects; chemisorption; thermoelectric power; magnetic susceptibility; electrical resistivity; fission product release; graphitization; single crystal kinetics.
7. **Reactions of Fuel Molecules:** Diacetylene polymerization; polymerization in plasmas; thermal decomposition of hydrocarbons; cyclic organic sulfides; polarography of organics.

Comminution of Brittle Materials

The object of this research is to develop a unit operations theory of the performance of grinding equipment. Essentially, the grinding process is split into two factors: (1) the selection function, which concerns the fraction of a given size selected for grinding in a standard increment of grinding, and (2) the distribution function, which describes the size-weight distribution of a given size after primary breakage. Appropriate integro-differential equations of size-mass balance have been set up for the equations of batch and continuous grinding. Selection and distribution parameters have been measured experimentally and the values used in the solution of the equations. Studies of the grinding of martite, anthracite, and limestone in a small ball mill have shown that the theoretical treatment is correct and that the proposed unit operations approach is valid. It has been demonstrated that previous "laws" of grinding are empirical and of limited application.

Theoretical and Experimental Analysis of Basic Fuel Cell Data

A better basis needs to be developed for the design of fuel cells for space and military power systems. A theory has been developed for the combined effects of electrokinetics and mass transport in flooded porous diffusion electrodes. Experimental results have shown the theory to be correct. Porous flow-through electrodes were also treated and the combined equations of electrokinetics, mass transport, and ohmic resistance were solved on a digital computer. The general theory has been confirmed experimentally for redox systems. A number of reactions (methanol, hydrazine, ammonia) show a further rate-restricting factor at high current densities. Two models, the "Simple-Pore" model and the "Thin-Film" model, have been proposed to describe how gas diffusion electrodes work. The "Simple-Pore" model might be applicable to non-wetted electrodes, and experiments are underway to test its validity.

The Formation of Oxides of Nitrogen in Combustion Processes

Oxides of nitrogen formed in combustion processes are known to react photochemically and form smog when discharged into the atmosphere. The objective of this research is to apply existing knowledge of the kinetics and equilibria of NO and NO_2 formation to combustion in turbulent jet diffusion flames, with the aim of suppressing their concentration in the exhaust gases.

The most important parameters which can be expected to influence the production of oxides of nitrogen in flames are the concentrations of the reactants and the flame temperatures. The distribution of these properties in flames is a function of both the place and the time. The present investigation is concerned primarily with the spatial distributions of the time-mean average concentrations and temperatures. A systematic study is planned, using gas and pulverized coal in double-concentric jet turbulent flames in an experimental furnace. The heat input will be maintained constant — while varying the excess oxygen in the burner, varying the flame temperature by heat absorption in the furnace, changing the volumetric heat release rate by the variation of the jet momentum, and observing the effects of the premixing of the burner fluid with cold recirculated combustion products. The spatial distributions of concentrations and of gas temperatures will be determined in each flame.

The experimental furnace and sampling and temperature probes have been designed and are being constructed at present. The phenoldisulfonic acid method for analysis of the oxides of nitrogen has been set up, and preliminary experiments are in progress with the analysis of gas samples taken from Bunsen-type gas flames.

Analysis and Investigation of Model Furnace Behavior

Efficiency of industrial furnaces is known to change with load or output, generally rising to a peak at some optimum output. For steam boilers this is well known; but it is not known for furnaces in general. The value of knowing the optimum is economic, since it is then possible to determine whether a furnace is over- or under-rated.

The theory governing much of the relevant behavior is known as External Furnace Analysis, and it exists, at present, somewhat embryonically. In the work in progress, the existing furnace analysis is being extended to a wider range of conditions. It shows that the existence of a peak efficiency is dependent upon heat transfer limitations inside the furnace, with a resulting rise in gas-exit temperature and gas-exit enthalpy.

To test the modified analysis, a small gas-fired model furnace has been built with a water-cooled tube bank to simulate the load.

On tests run so far, expectation has been generally substantiated by the operational behavior.

Performance of the H.P. Inspirator Gas Burner with Furnace Pressure

The inspirator gas burner, operating on high-pressure gas, is one of the burners most widely used in industry, so its proper performance is a matter of some concern and economic importance. In operation, it inspirates atmospheric air; if correctly designed, it should inspirate a preselected fraction of stoichiometric air at any turn-down. If it fulfills this condition, it is a proportioning burner. In such circumstances, the correct proportioning is generally assumed to be independent of furnace pressure, but information has been recently obtained on the performance of sealed burners indicating that this is not so. It was reported that furnaces on draft were pulling in too much excess air, and the correct furnace temperature was only attained with a high expenditure of gas. As the draft was reduced, the excess air was reduced, but there was incomplete combustion with the formation of unburnt CO and H_2.

In conjunction with the operation of the model furnace, experiments were undertaken to determine the influence of furnace pressure on the excess air inspired and the degree of combustion. The results show very clearly that the completeness of combustion drops, and so does the excess of air, as the furnace pressure goes from negative to positive. At the balanced pressure point, the proportion of CO rises with firing rate. This demonstrates conclusively that the proportioning behavior of the burner is strongly influenced by furnace pressure.

Ignition Energy of Dust Clouds

Dust clouds of finely-ground materials that burn in air can explode with great violence if a suitable ignition source is present. In connection with determining and eliminating the explosion hazard, a prime quantity to be determined is the energy required for ignition.

The equipment consists of a vertical glass ignition tube, a dust chamber, and a heating coil. The dust is dispersed into a cloud by a blast of air. The coil is heated by direct current and the energy input to the coil is measured.

Experiments have been conducted with different sizes of cork dust, different numbers of turns on the coil, different coil diameters, and different wire diameters. Chromel A wire is being used for the coil at present; investigation will continue on Chromel P and Alumel wires to determine the effect of coil emissivity. The effect

of the number of turns per unit length of coil will be investigated. The correlation $i^2 = i_o^2 + k/n$ (where i is the ignition current, n the number of turns on the coil, and i_o and k constants) seems to hold very well. Variation of the average size of dust particles does not seem to affect ignition at large coil diameters and/or small numbers of turns on the coil.

Spontaneous Ignition of Mine Refuse Piles

The health hazard and safety problem caused by burning refuse piles have prompted a large search for a way to extinguish the fires and to control the formation of new ones. Current stringent regulations and recommendations are based on less than certain knowledge. To supplement this empirical knowledge by a more fundamental examination, a theoretical study was suggested of the conditions required for spontaneous ignition, for continued combustion, and for complete extinction and prevention of ignition.

A one-year preliminary examination of the problem has been carried out to determine whether a more complete theoretical study would be feasible and of practical value. The conclusions of this study were: (1) that a theoretical analysis is feasible; (2) that performance of an analysis would provide information of practical value in understanding the combustion behavior in such piles; (3) that practical recommendations in specific instances could probably be provided by detailed calculations (computer solution of the differential equations involved); and (4) that a full understanding would require supplementary information to be obtained by direct measurement on the refuse piles.

High-Moisture Coal Flames

The prospective use of water pipelines for the transport of coal — as slurry — to power stations is partially dependent, economically, upon either the ability to dewater the coal cheaply or the ability to use the slurry by direct injection, with the water, into the combustion chamber. Since direct injection saves the cost of dewatering, it is preferred. But this technique depends upon the ability to stabilize a flame when the fuel has a high moisture content. The problem is primarily one of determining combustion or inflammability limits in the presence of high moisture. The aim of work in progress is to complete the instrumentation, to modify the fuel feed, and to commission an existing furnace for research.

To the existing furnace, a probe positioning gear has been added and partially tested. The fuel supply equipment is being reorganized, and reconstruction for a test firing will shortly be com-

pleted. Other instruments include a gas analysis train and equipment for continuous gas sampling and analysis.

As a supplement to this, equipment to determine the time-to-ignition is also under construction. A controllable furnace and airflow system is almost complete and ready for testing.

Devolatilization Kinetics of Coal Particles in Flames

To maintain the competitive position of coal as the principal fuel in thermal power stations (60 per cent of all power produced), there must be continued improvement in design of coal-fired boilers, based on increased fundamental knowledge of combustion behavior. One serious problem is the understanding of ignition because of the increasing incidence of flame-out (and therefore of increased explosion hazard).

Since ignition is believed to start in the coal volatiles, the conditions for their release and rate of release in a flame have been under investigation, using a modified "one-dimensional"-type furnace. A flame is stabilized in a vertical brick-lined duct, 6½ inches square (horizontal) and about 8 feet high (overall). The flame is stabilized just below a horizontal water-cooled tube bank, and solid samples and temperatures are measured at a number of points below the tube bank. The results show that the flame starts a little before the point of principal devolatilization. Most significantly, however, the temperature at ignition (flame front) is as high as 1000°C (600 degrees higher than the normal coal decomposition temperature); principal devolatilization sets in at 1300 to 1400°C. Since the rate of heating is 10^4 degrees/second, the inference is that there is an "induction" period or lag before pyrolysis sets in. Devolatilization takes about 0.1 seconds (with a burning time of up to one second), but is incomplete. Even at flame temperatures of 1300 to 1500°C, there is a "volatile residue" of 5 or 6 per cent remaining in the coal particles during final burnout.

Research on Carbon

The efficient use of carbon in industry requires knowledge of the reaction behavior of the different carbons to oxygen, carbon dioxide, and other gases. Empirical knowledge on the appropriate reactivity behavior is now very extensive, but the fundamentals of such behavior require further study. Interpretation of experimental data is frequently ambiguous.

The purpose of the present work is to set up an experimental system that will eliminate any ambiguity of interpretation. The method is to burn carbon spheres while they are continuously weighed and photographed.

The value of simultaneous weight and size measurements is that they enable the detection and measurement of any density changes during reaction. The preliminary results show that several stages of development and stable burning occur. Initially, the particles burn at constant radius, developing internal surface to a determinable "combustion depth." This depth then remains constant whilst the external surface regresses in a second stage. In the third stage, the particle either reverts to internal reaction at constant radius or to increased internal reaction at reduced radius. The combustion depths were from one to two millimeters and decreased with rising temperature. It is clear that a temperature can be reached quite easily at which the determinable combustion depth tends to zero, and the complications of internal reaction are eliminated.

Pyrolysis and Combustion of Hybrid Rocket Fuels

The hybrid rocket uses a solid fuel and a fluid oxidant. It has the advantage over the liquid fuel rocket of higher avaliability and over the solid fuel rocket of higher specific impulse. One of the main problems encountered in its application, however, has been the loss of unburned fuel by ablation from the solid fuel and ejection from the combustion chamber without reaction.

The key to correcting this situation is an understanding of the pyrolysis-ablation reaction mechanism of the solid fuel in an oxidizing atmosphere. This is being studied at fairly low thermal intensities and fairly long reaction times. The experimental methods include study of pyrolysis and combustion of ¼- to ½-inch spheres in a furnace or between heating coils, with continuous time measurements of the variations in size and weight.

The preliminary results show that materials high in carbon will coke if pyrolysis occurs during combustion. In materials exceeding a certain thickness, a pyrolysis wave can be defined moving from the surface into the solid, leaving the coke residue. The surface of this residue also regresses, either by combustion or by ablation. At high thermal intensities, the surface regression rate exceeds that of the pyrolysis wave, and combustion can occur without coking. This is the desirable condition for propulsion units.

Non-Aqueous Polarography and Electrolysis of Aromatic Substances

The broad objectives of this research project are to discover the mechanisms of electrode processes and to use electrochemical data in understanding the structure and behavior of aromatic substances. A versatile assembly of electrochemical instruments has

been built. The reduction of several aromatic hydrocarbons and carbonyl compounds has been studied by polarography and chronopotentiometry in dimethyl-formamide. It is confirmed that the second reduction step is usually irreversible, except in the case of anthraquinone (the latter result is in disagreement with published data). A series of derivatives of 4-thiopyrone has been studied, and its behavior suggests that the carbonyl group can be reduced to methylene through a carbonium or sulfonium ion intermediate. The structure of thiopyrone derivatives has been studied theoretically by quantum mechanical methods (molecular orbital). The calculated energy levels are in satisfactory agreement with the observed polarographic halfwave potentials and ultra-violet adsorption spectra.

Surface Oxygen Groups in Carbon Black

The nature of the oxygen-containing groups on the surface of carbon blacks has been investigated. In particular, the hydroxyl content has been studied by acetylation with C^{14}-labelled acetic anhydride and by thermometric titration, and it has been found that in many blacks this group accounts for 25-40 per cent of the oxygen present. Several carbons have been found to catalyze the polymerization of isobutene, the product being mostly a dimer (a-trimethylpentene), and also to catalyze the isomerization of methylpentenes. Thermodynamic equilibrium between isomers is attained rapidly, and the kinetics of the isomerization correspond to a reversible first-order reaction. The mechanism of these reactions appears to involve carbonium ion intermediates, which implies that the carbons can protonate the olefins.

Polymerization of Diacetylene

It had been concluded from earlier research that diacetylene may well be the last stable compound in the high temperature pyrolysis of organic compounds before carbon formation. It was also shown that even at room temperature diacetylene polymerizes slowly to a solid material, which yields a carbon on pyrolysis at only 400 degrees. The polymerization of diacteylene has now been studied, using a variety of catalysts to speed up the reaction. Free radical polymerization at 60-80°C, anionic polymerization with alkali metals at room temperature, and reactions initiated by coordinated catalysts of the Ziegler-Natta type all proceed rapidly to give brown or black solid polymers. These polymers are essentially aromatic in structure, but contain unsaturated non-aromatic side chains. When the extent of reaction is small, the kinetics of radical polymerization show the usual first order dependence on monomer

concentration and half-order dependence on initiator. At higher conversion, the kinetics appear to be complicated by the separation of solid polymer, with chains both terminating and initiating on the polymer surface.

Reduction of Sulfur in Pennsylvania Bituminous Coal

A bituminous coal was carbonized at 600°C in the presence of various additives. It was found that if 10 per cent (by weight) of ammonium chloride, sodium borohydride, pyromellitic dianhydride, or p-terphenyl is added to the coal before carbonization, the char contains a materially reduced amount of sulfur. It is thought that sulfur released by the pyrite is trapped by the additive.

Little information is available on heterocyclic aromatic compounds containing sulfur in 6-membered rings (thiopyrones and thiopyrans). A series of such compounds was made, and their spectra, chemical reactions, and pyrolysis were studied. It was concluded that such structures could account for some of the organic sulfur in coals, but not in high temperature chars.

Petrological Components of Bituminous Coal

An extensive organic and physical-chemical investigation of a series of pure macerals separated from bituminous coals was proposed. The object was to reveal the main features of their chemical structure and the characteristic differences between them. A detailed comparison was made between two pairs of pure vitrinites; one pair represented samples taken from different levels in a pillar section of one seam, and the members of the other pair were of quite different geological age, but of apparently the same rank (according to optical properties). Significant chemical differences were found between the members of each pair. Chemical techniques for studying vitrinites have been improved and used for studying a range of vitrinites at different levels of rank.

The use of electron spin resonance has been developed for investigating the thermal history of coal components and coals subjected to igneous intrusion. It was concluded that the fusinites have been subjected to relatively high temperatures (400-500°C perhaps) before incorporation into the organic sediment.

Hydrocarbon Decomposition Studies Related to Carbon Formation

The thermal decomposition of hydrocarbons to produce carbon, either in the form of carbon black or as carbonaceous deposits, is of great interest. In this research, hydrocarbons are pyrolyzed in a flow system in order to determine the kinetics of decomposition,

to observe the formation of intermediates and products, including carbon, and to hypothesize reaction mechanics that are consistent with observations and that will permit behavior predictions under conditions other than those of the experiments. The subjects of recent study have been acetylene, benzene, diacetylene, and methane. In all cases, useful additions to knowledge of the thermal behavior of these species have resulted from the work. The kinetics of homogeneous decomposition of methane and acetylene are now quite well understood over a range of 2000°C, while benzene and diacetylene have been examined over a limited range. The work is being extended to higher aromatics.

Reactions of Radicals Generated by the Sodium Flame Method

The vapor-phase reactions between alkali metals and various halides are capable of producing a variety of gaseous free radicals. The radicals then undergo further reactions among themselves or with other species in the gas phase. Most of these reactions are very rapid, and they may release large amounts of energy. In this research, interest centers upon the observation of those species in which large amounts of energy are found and upon determining the energy distribution in the excited species. Spectrographic techniques are employed.

Among the results of the work was the discovery of several spectra of flames that had been previously unreported. A study was also made of the reactions of carbon atoms with the radicals CH, CCl, CBr, and CI, all of which were found to produce diatomic carbon (C_2) in an electronic excited state, with the C_2 radicals exhibiting a strongly non-thermal distribution of vibrational energies. In all four cases, essentially all of the reaction energy appeared initially as vibrational energy of the C_2 radicals, and it appeared likely that these reactions represented examples of population inversions produced by chemical reactions.

Chemical Dissociation and Recombination in Shock Waves

Shock waves are being used in the laboratory as fast-acting thermostats for the study of the kinetics and mechanisms of gaseous reactions at high temperatures — like those encountered in flames, rocket exhausts, and high-speed flight. Two shock tubes are currently in use in the research. The first is a single-pulse shock tube in which reactants are subjected to a high-temperature pulse and then are quenched. In the second, studies are made of the progress of reactions behind the shock front or of the equilibrium conditions that may be achieved at some more-or-less extended time after the front has passed. The single-pulse tube has recently been used to

determine the kinetics of the thermal decomposition of gaseous hydrazine, a well-known rocket propellant. In other studies the kinetics of the radiative recombination of chlorine atoms have been determined.

Preparation of Highly Porous Carbons from Pennsylvania Bituminous Coal

Carbons have been prepared from bituminous coal in activated form. Such carbons may be useful as purifying agents for gases and liquids. Some suggested uses include the purification of water, (as in stream pollution), of gases (as in atmospheric contamination), and of other industrial gases and chemicals. The activated carbons were produced from the coal by stepwise conversion. The coal was oxidized to humic acids by nitric acid processes, the humic acids were pyrolyzed to chars at about 250°C, and the chars were converted to activated carbons by steam at 750° to 900°C. These carbons are quite similar to commercial activated carbons in their surface area, iodine adsorption, pore volume, and ash content and are less similar with respect to density. A micropore structure appears to be predominantly inherent in these carbons, as based upon characteristics of surface area, methylene blue adsorption, and mercury pore distibution values.

Basic Constitutents of Pennsylvania Bituminous Coal

One of the problems in studying the composition and structure of materials such as coal is that the original material must be transformed to a state which is suitable for instrumental analysis. One of the techniques for studying complex organic structures has been pyrolysis (thermal breakdown of the structure). Some idea of the original structure can be obtained by studying the pyrolysis products or fragments. However, attendant upon the pyrolysis of large amounts of material, many secondary reactions take place which make extrapolation back to the original structure difficult.

This investigation has concerned itself with the pyrolysis of micro-quantities of material in the vacuum chamber of a mass spectrometer. The results of this investigation are now being used in a project designed to study the pyrolysis of these microquantities *in situ*. This latter technique permits the study of heterogeneities in coal too small to remove by conventional techniques.

Reaction of Pennsylvania Bituminous Coals with Atomic Species

In solid-gas reactions the first step requiring high activation energy is the dissociation of the reacting gas molecule. In the usual reaction system, the energy is supplied by thermal excitation; however, it is possible to dissociate the gaseous species by an electrical

discharge (plasma). An example of the difference between these reactions is that of carbonaceous solids, such as coal, which have to be heated to 800°C to react with molecular oxygen at the same rate as they would react at room temperature with atomic oxygen. An interesting outgrowth of this work has been the development of a technique of "plasma synthesis". It is now possible to produce solids of widely varying compositions by choice of the composition of plasma feed materials.

Anthracites Affected by Heat Treatment, Oxidation, and Grinding

Pennsylvania anthracites are used in many high-temperature applications. Yet the changes in physical structure and properties which anthracites undergo due to high temperatures have not been thoroughly studied. Changes in the ultrafine structure of three 200 x 325 mesh anthracites of VM ranging from 4.5 to 9.0 per cent — upon heat treatment in an oxygen-free atmosphere — have been followed. After going through slight maxima at lower heat-treatment temperature, the total surface areas decreased sharply at 900°C. Helium and mercury densities increased monotonically with increasing heat-treatment temperature. Unsteady-state diffusion of gases from the anthracites has been measured. The diffusion rate decreased sharply and continuously upon heat-treatment temperatures between 600 and 1700°C, due primarily to a steady increase in activation energy for diffusion. The increase in activation energy is attributed to a continuous decrease in the size of the ultrafine pores with increasing heat-treatment temperature.

Ash in Anthracite

Several studies have shown that anthracite can have adsorption capacities comparable to commercial activated carbons. However, one drawback to the use of anthracite as a source of activated carbon is its high mineral matter content — not less than 12 per cent ash in the activated product. For many applications, this is too high an ash content. Results to date indicate that by activating a prechlorinated anthracite a lower ash content of activated carbon can be produced.

The CO_2-activated carbon at 950°C has a surface area of 1900 m^2/g at 50 per cent burn-off and 4 per cent chlorine. The chlorine content in the activated carbon was reduced to a negligible value by steam activation. This result is considered promising because it may well open up a potential market for Pennsylvania anthracite as a source of activated carbon.

Adsorption on Carbon Surfaces

Carbons chemisorb exposed oxygen at temperatures of about 300°C to 800°C. Below 300°C, the rate of chemisorption is low; above 800°C the chemisorbed oxygen is unstable and comes off the carbon surface primarily as carbon monoxide. It has been shown that at 300°C, oxygen chemisorption can be used to measure the active site area of carbon, which is reactive to oxygen during gasification at higher temperatures. Following exposure of the carbon to oxygen at 300°C for 24 hours, the sample is degassed at 950°C to recover the oxygen as carbon monoxide and carbon dioxide. By assuming that the oxygen chemisorbs on the prismatic faces, the active surface area can be calculated. Recently, it has been found that additional chemisorption of oxygen occurs if the adsorption is conducted between 450-500°C. It is thought that this chemisorption occurs on imperfections in the basal plane, which apparently is not active in the gasification reaction.

Natural Graphite

Natural graphite bodies have an apparent potential as solid lubricants. It has been found that natural graphite can be molded at room temperature and at pressures between 25,000 - 125,000 psi into strong bodies in the absence of a binder phase. Three graphites were studied: Ceylon, Madagascar, and Mexican. Structurally, the graphite of largest crystallite size and best crystallite alignment is the Ceylon, closely followed by the Madagascar. It was found that the strength of the bodies decreased in this order: Ceylon, Madagascar, and Mexican. The implication is that pellet strength is primarily determined by the extent of basal plane interaction between particles — the more perfect the particles, the greater the area of interaction between them upon molding.

Carbon Molecular Sieve Materials

Extensive use is being made of molecular sieve zeolites to separate gases and liquids of different molecular sizes. In this program, carbon molecular sieves are being produced both by the carbonization of thermosetting polymer systems and by the fabrication of bodies from activated carbons held together by a carbonized thermosetting polymer. Several molecular probes have been used to evaluate the pore structure of the carbons: carbon dioxide (3.3Å), butane (4.3Å), isobutane (5Å), neopentane (6.2Å), benzene (3.7, 7.0Å), and cyclohexane (4.8, 6.8Å). Carbons have been produced which show molecular sieve effects similar to the Type 4A zeolite; that is, they have a high capacity for CO_2 at —79°C and a low

capacity for N_2 at −196°C. Carbons have also been produced which have a sharp separation for isobutane and neopentane. In all cases examined, the carbon sieves appear to possess slit-shaped pores. For example, they show more rapid uptake of benzene and cyclohexane than of neopentane.

Anthracite: New and Improved Uses for Pennsylvania Coals

Research in this area has been concerned with (1) the low temperature chlorination of anthracite, (2) the activation of anthracite by carbon dioxide as affected by chlorine, and (3) the methane diffusion in anthracite. In the first program, it was found that chlorine at sea-level pressure removed hydrogen from anthracite much more effectively than did simple thermal treatment in an inert gas. Chlorine removed hydrogen by substitution, forming hydrogen chloride. At comparable maximum-heat treatment temperatures up to 1000°C, room temperature electrical resistivities of the particulate anthracites, heated in a Cl_2 atmosphere, were markedly less than when heated in an inert gas. In the second program, activation of anthracite in CO_2 was found to be greatly improved (both in surface area development per unit carbon burn-off and in enhanced activation rate) when activation was performed either after chlorine pre-treatment or in the presence of chlorine. Treatment in chlorine also sharply decreased the ash content of the activated anthracite. In the third program, CH_4 diffusion in anthracites was being measured, when the CH_4 was at elevated pressures, to better understand CH_4 diffusion from anthracite while still *in situ* underground.

Fission Gas Diffusion in Graphite

During the operation of nuclear reactors, gaseous fission products are produced. These fission products are radioactive and, therefore, can be hazardous if not properly disposed. In the gas-cooled nuclear reactor, graphite is frequently mixed intimately with the fissionable fuel. A significant number of the fission fragments produced during a fission event escape the fuel and, travelling at high speeds, imbed themselves in the graphite lattice. The research is concerned with the mechanism by which these fission fragments ultimately diffuse out of the graphite following this initial imbedding. Particular attention is paid to measurements of the kinetics of release of Xenon-133 from graphite and to how this rate of release is affected by temperature, graphite structure, prior graphite radiation damage, and oxidation.

Interaction of Oxidizing Gases With Carbon Surfaces

Although the oxidation of carbon is one of the most familiar and important reactions, it is one of the most complicated. This program is concerned with the manner in which oxygen reacts with carbon and the factors which determine the speed of the reaction. Experimentally, the investigation is involved with the oxidation of pure carbon (graphite) at low pressures. A mass spectrometer is used to follow the course of the reaction. The high sensitivity of the mass spectrometer permits direct measurement to be made, for the first time, on the extent of the "active surface" (the fraction of available surface on which the reaction can take place). The effect of the covering of the active surface by surface complex (chemisorbed O_2) can also be directly measured. This approach has permitted quantitative measurements to be made on reaction steps which hitherto have only been postulated.

Carbon-Oxygen Complexes

This is an investigation of the carbon-oxygen reaction at low pressures, using the O^{18} isotope as a tracer. Because O^{18} is non-radioactive, mass spectrometric techniques are used to differentiate it from the more abundant O^{16} isotope. The use of O^{18} as a tracer, coupled with the results of other work on the carbon-oxygen reaction, has produced information which has made it necessary to re-evaluate many of the existing theories of the carbon-oxygen reaction mechanism. Some of the findings have been: (1) oxygen molecules can dissociate and recombine at rapid rates on the carbon surface; (2) both of the oxygen atoms of the product CO_2 do not necessarily come from the same molecule; (3) carbon dioxide dissociates and recombines at a measurable rate on the carbon surface.

Sorption of Trace Amounts of Xenon-133 on Carbonaceous Materials

All solids have a certain dislocation and vacancy density. This density can be related to the activity of the solid in the presence of liquids and gases. It is, therefore, of interest to measure the density of dislocations and vacancies in solids. It is known that the degree of isothermal adsorption in the very low coverage region reflects the extent of surface homogeneity. Henry's law is obeyed for a homogeneous surface.

In this research, the adsorption of Xe-133, at a very low relative pressure (and coverage), is being measured on highly-graphitized carbon-black surfaces at various temperatures. From the slopes of the isotherms and the variation in heats of adsorption with coverage, information on defect density is being obtained.

GEOCHEMISTRY AND MINERALOGY

Geochemical research, as carried on in this department, includes phase equilibrium studies covering a range of temperature from 0-2000° centigrade and pressures up to 150,000 atmospheres (approximately equivalent to that of 600-km depth below the earth's surface.) This research is applied to studies of rocks — including the range from altramafic to granitic — ore deposits, and ore solutions, as well as to industrially-important cement rocks and minerals, slags, refractories, and saline waters. Variation in the isotopic composition of carbonate rocks and fossils is used to determine environments of deposition. Distributions of trace elements in stream sediments of Pennsylvania are being studied as possible guides to ore deposits.

Mineralogical research includes (1) X-ray crystal structure analysis, coupled with crystal chemistry, and (2) analysis of very fine-grained clay minerals and X-ray amorphous materials in soils, and their role in the weathering process.

Petrography of petroleum reservoir rocks and applications of statistics, computers, and operations research to exploration for, and to the production and development of, natural resources, including ores and petroleum, is a relatively new and exciting area of research.

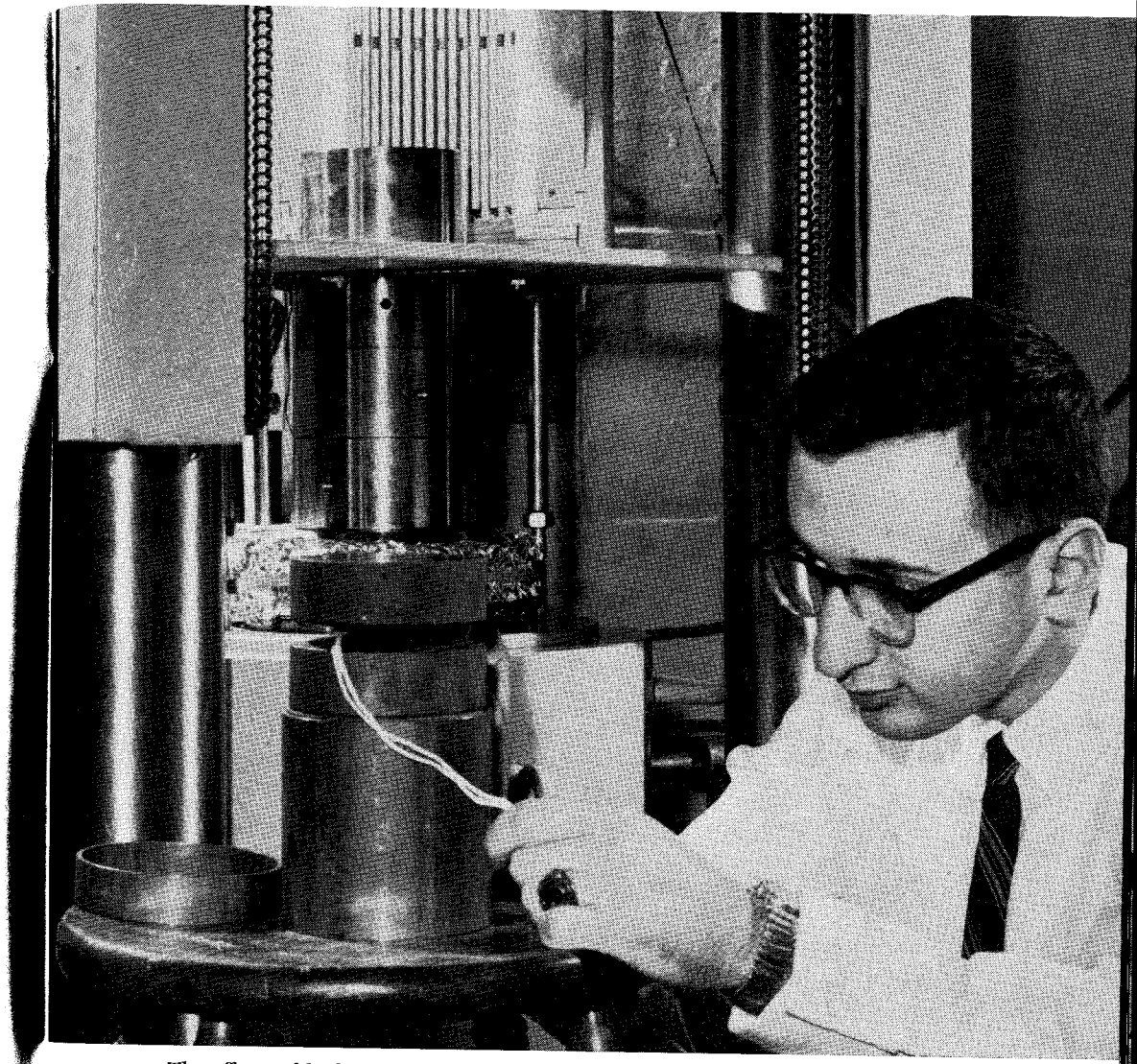
The following is a description of research which has been carried on during the past four years by the faculty of the Department of Geochemistry and Mineralogy.

Growth of ZnS Crystals From Hydrothermal Solutions

Sphalerite and isometric and many of the polytypes of wurtzite, a hexagonal zinc sulfide, have been grown successfully from solutions of sodium bisulfide and sodium hydroxide using temperature gradients of 10-50°C near 500°C at 5,000-10,000 psi. Higher alkalinites favor the hexagonal forms; high partial pressures of H_2S appreciably darken the crystals giving colors ranging from absolutely colorless to very dark brown. Now that a reproducible technique for crystal growth has been developed, it is proposed to study the extent of chloride ion substitution in ZnS crystals as functions of concentration, temperature, and pressure, and particularly the influence of various cations on the extent of solid solution.

Solubilities of Ore Minerals in Hydrothermal Sulfide Solution

In a general geochemical study of the mechanisms of transport and deposition of metallic sulfides forming ore deposits, perhaps



The effects of high pressure on various materials are analyzed by University geochemists and mineralogists.

the most critical information is the solubility of ore minerals in potential ore solutions. As part of a continuing program, an instrument has been designed for measuring these solubilities at elevated pressures and temperatures in precisely-controlled chemical environments. The solubility of sphalerite has been measured in solutions containing various aqueous species. Only the bisulfide complex, $Zn(HS)_3^-$, is sufficiently stable under appropriate chemical conditions to account for the transport of sphalerite into ore deposits. Similar stable bisulfide complexes have been found for covellite. Pyrite apparently requires complexing by either NH_4^+ or Cl^- instead of HS^- for ore transport. Work is now in progress on cinnabar and chalcocite.

It has been demonstrated that weakly alkaline bisulfide solutions are capable of transport of the base metals, Cu and Zn, to form ore deposits. Previously published thermodynamic arguments strongly suggest that similar complexes are formed by the other base metals. From these results the chemical causes of ore deposition, and the geologic habitat of ore bodies can be predicted, greatly facilitating the ore-finding process in prospecting.

Replacement Reactions in Ore Deposits

The process of ore emplacement in nature leads to diffusion of the base metals into common carbonate host rocks. As the first stage of the research, these diffusion gradients are being measured in Mississippi Valley-type deposits. The gradients will then be reproduced synthetically at the same temperatures and pressures, with the same host rock material and similar solutions. By application of diffusion theory and dynamic similarity theory, the time required and the concentrations of solutions involved for formation of this type of deposit can be approximated.

Ionic Equilibria in Supercritical Aqueous Fluids in Relation to Petrologic Reactions

The acidity of hydrothermal fluids in equilibrium with several alteration minerals has been calculated from experimental measurements for high pressures and temperatures. The results of these calculations indicate that coexisting muscovite, orthoclase, and albite, a very common granitic assemblage, are at equilibrium only with neutral-to-weakly acidic fluids.

X-ray Amorphous Mineral Materials and Their Role in Weathering

This study is being conducted in three parts: (1) laboratory studies of the chemical conditions which control the formation of amorphous versus crystalline forms of aluminum hydroxides; (2) field and laboratory investigations of mineralogical and chemical transitions in assorted kaolin and bauxite deposits in Georgia; (3) field and laboratory studies of the alteration by the weathering process of volcanic glass under various climatic situations in Hawaii. Research shows that amorphous aluminum hydroxides are, in fact, basic salts formed by the association of anions with positively-charged aluminum hydroxide polymers. The transformation of these amorphous forms to crystalline $Al(OH)_3$ is related to the nature and amount of the anions present — including clay particles that may be considered as anions in the solid state.

The Role of Water and Other Volatiles in Magmatic Processes

Investigations at high pressures and temperatures are being conducted (1) of the effects of water on the melting relationships of felsic igneous rocks; (2) of the solubility of water in silicate melts of both simple and complex composition; (3) of the effects of water on the viscosity of granitic melts; (4) of the aqueous phase transport of mineral and rock material along thermal gradients in a closed system; (5) of the solubility of rock-forming minerals in water and aqueous chloride solutions; and (6) of the composition of the aqueous phase in equilibrium with minerals as well as with granitic rocks and melts. The experimental results in each of the above categories may be summarized as follows: (1) water greatly depresses the melting temperatures of felsic rocks so that partial melting of deep-crustal rocks should be a widespread phenomenon in organic regions; (2) the solubility of water in silicate melts continues to increase with pressure, at least through 10,000 bars, which is contrary to previous beliefs that it reaches an extreme of about 10 per cent; (3) water greatly reduces the viscosity of granitic melts, the effects decreasing with increasing water content; (4) the direction and extent of mineral transport in an aqueous phase under a thermal gradient are consistent with the mineral solubilities; (5) rock-forming silicates are sparingly soluble in water at high temperatures and pressures, the total solute content reaching only about 10 per cent in water coexisting with granitic melts at 10,000 bars; (6) rocks and rock melts of granitic composition dissolve almost stoichiometrically in pure water, whereas alkalies and alkaline earths are selectively extracted by chlorine-bearing solutions.

Properties of Aqueous Solutions at High Pressures and Temperatures

The overall objective of this research is to obtain the necessary data for deriving equations of state, fugacities, and ionization constants of water and inorganic solutes at temperatures up to 1000°C

and pressures to 10,000 bars. These data are obtained largely through two different experimental approaches; one is through measurement of the pressure-volume-temperature relations of water and aqueous solutions, and the other is through measurement of their electrical conductivities. The P-V-T data obtained so far partially cover the pressure-temperature region to 7000 bars and 750°C, and are in good agreement where they overlap previous work at low pressures (up to 1400 bars). At pressures above about 3000 bars, considerable difficulty has been encountered in changing the specific volume of water either by compression or heating; the cause of this unexpected behavior currently is being investigated.

Crystal Structure of Low, Intermediate-State and High Cordierites

The structural conversion of cordierite has been assumed by previous investigators to be related to order-disorder of one aluminum and five silicon cations in a six-membered ring of tetrahedra. The mineral can exist in all structurally-intermediate states ranging from high cordierite (a hexagonal modification with a distortion index of 0°) to low cordierite (a rhombic modification with a distortion index greater than 0.20°). In high and low cordierite, it is believed that the cations are disordered and ordered, respectively, whereas in intermediate states, the order is assumed to be intermediate. However, this interpretation of the structural conversion has been found to be untenable as it fails to account for three additional aluminum cations that have been arbitrarily assigned to the tetrahedra among the rings. A more reasonable interpretation is to treat the structural conversion as resulting from order-disorder of 4Al + 5Si in a tetrahedral framework of $(Al_4Si_5O_{18})^{-4}$ composition. The present study was undertaken to establish precise atomic coordinates for high, intermediate-state, and low cordierite which would permit an elucidation of the true nature of the order-disorder mechanism.

A set of 3D intensity data, collected from a crystal of low cordierite, has been submitted to a final refinement by least squares and Fourier methods. The refinement converged after a total of seven cycles and yielded a set of atomic coordinates that confirm the ideal arrangement. The relative contents of each tetrahedron in the structure, estimated by using the average tetrahedral bond lengths, reveal a completely ordered arrangement of the four Al and five Si cations in a framework of tetrahedra. This evidence clearly supports the conclusion that the polymorphism of corderite is related to order-disorder. However, to prove this conclusively, similar analyses are in progress on crystals of intermediate-state and

high corderite. The space group symmetries of these minerals have been determined and precise cell edges have been obtained from a least squares refinement of precision back-reflection Wissenberg data. Intensity data are currently being gathered from the crystal of intermediate state.

Petrographic Studies of Pennsylvania Oil and Gas Sands

In cooperation with the Appalachian Appraisal Project of the U. S. Bureau of Mines at Morgantown, West Virginia, the petrographic evaluation of oil reservoirs in the Appalachians has been continued. Reservoir behavior in selected oil reservoirs has been shown to depend on the petrography. There are two different kinds of reservoirs: (1) those in which grain size variation acts as the controlling factor and (2) those in which the cements, silica, and carbonates act as the controlling factors. These findings are useful in defining target reservoirs for exploration and are of more direct value in recommending palliatives to improve reservoir performance.

Granites, Pegmatites and Aplites

Coordinated field, experimental, and theoretical studies have been aimed at better understanding of three closely-related rock types — granites, pegmatites, and aplites. Work on the "granite system" has been extended experimentally to pressures of about 10 kb, and these results have been correlated with new data on the composition of the granitic rocks. The compositional data also have been used further to test the model of pegmatite genesis suggested earlier. It now seems more likely than before that pegmatites differ from granites mainly in having been derived from magmas saturated with water and/or other volatile components. Most igneous aplites evidently represent pegmatitic magmas that suddenly lost much of their contained volatile substances through major decreases in confining pressure; such losses prompted "quenches" in the subsolidus regions of the systems. Studies of trace-element distribution within granites, pegmatites, and aplites are now being made to supplement the data available for the major constituents.

Geochemistry of Stream Sediments in Eastern Pennsylvania

Stream sediments collected over a 7,600 square mile area of Southeastern Pennsylvania have been analyzed for trace metal content, using a new direct-reading spectrograph. Results will be used as a guide to prospecting for metalliferous ore bodies. Stream muds, ultimately derived from the rocks and soils of a drainage basin, absorb dissolved traces of metals which get into the stream

water from the weathering of rocks and ore bodies. As a consequence, the metal content of stream muds will generally be above average in drainage basins where ore bodies occur at the surface.

Isotopic Composition of Fossils and Limestones

A systematic survey is being made of carbon and oxygen isotopes in sedimentary carbonates. Following a preliminary study of sea shells, in comparison with the shells of fresh-water mollusks, the investigation included more than 500 samples of limestones and fossils of different ages and geographic locations. It was found that the carbon-13:carbon-12 ratio serves to differentiate marine limestones from continental (fresh-water) limestones in sedimentary beds formed as far back as the Devonian Period (400 million years). Current investigations deal mainly with the isotopic composition of carbonates formed in modern and ancient coral reefs. Regional studies may help to supplement other geologic methods used to plot ancient shorelines and to guide the search for mineral resources such as oil and gas which accumulate mainly in near-shore marine deposits.

Phase Equilibrium Studies of Refractory and Slag Systems

Phase equilibrium studies of oxide systems have been a major research interest at Penn State for more than a decade. Results of this work have been applicable especially to steelplant refractory and slag problems. A current effort is concentrating on "spinel" systems of special significance in steelplant refractories technology. Intensive studies have been made of the system having as end members the spinels: $MgAl_2O_4$, $MgCr_2O_4$, $MgFe_2O_4$, $FeAl_2O_4$, $FeCr_2O_4$, and $FeFe_2O_4$. Studies are made largely in an air atmosphere with determinations made of solidus temperatures and per cent liquid in a mixture as a function of temperature and composition of the mixture. This has led to a significant advance in the understanding of the effect of composition on refractoriness and, therefore, on the suitability for refractory use of various chromite ores.

Basaltic Magmas

Investigations directed toward a better understanding of basaltic magmas are an outgrowth of previous research at Penn State on high temperature reactions in oxide systems applicable especially to steel industry technology. The principal objective of the current investigations is to understand the chemical reactions occurring on a large scale within and below the earth's crust. Magmas are generated which erupt as volcanic lava or solidify below the surface as coarse-grained rocks, such as granite, or as various types of ore deposits. In this laboratory project, oxygen-partial-pressure is used as one of the variables. Studies are made of changes in composition and amount of the liquid and crystalline phases in samples of natural lava over the temperature range at which liquid and crystals coexist. The water content of the rock samples is also being varied in high pressure studies at these high temperatures. Solubility of water in the magma, as a function of temperature and composition of the rock, is being determined. From these studies, the nature of the effect of oxygen-partial-pressure and water content on the manner of crystallization of magmas is being determined. This is leading to an important clarification of the ideas on the manner of origin of different types of igneous rocks, illustrated in the Appalachians by such extremes as, for example, the high magnesium dunites and serpentinites on the one hand and the high silica rhyolites and granites on the other.

Origin of the Leucocratic Rocks and the Evolution of the Earth's Crust

Granite rocks make up by far the largest portion of the igneous rocks of the earth's crust. The stability relations among the various mineral phases of granites are being studied at high pressures and high temperatures. The effect of water and other volatiles on melting relations in these systems is being studied and the results are compared with natural analyzed samples collected throughout the United States and Canada.

Meteorite Impact Craters

Collection of material and field mapping is now complete for the following craters: New Quebec, Lac Couture, Brent, and Holleford. The sampling of Ries Kessel and Koffels (both in Germany) is also complete. Laboratory investigations include: (1) determination of the attitudes of microfractures and planes of fluid inclusions (Brent and sundry granite quarries); (2) shock deformation and the structural state of the feldspars; (3) the deformation lamellae and cleavage in Quartz (Lac Couture); (4) nature of the breccias and associated glass (Lac Couture); (5) general petrology (New Quebec, Lac Couture, and Holleford); (6) search for and concentration of coesite and stishovite from rocks associated with the craters and other geologic environments involving high stress concentrations. Planes of fluid inclusions in the rocks surrounding the Brent crater have been found to coincide with radial and concentric directions about the crater. Coesite has been found only in the Ries Kessel

breccias. Feldspars with anomalously low optic angles have been observed in the rim rocks of the Brent crater.

Distribution and Solubilities of Trace Elements in Sulfide Minerals

Although many analyses have been made, little is yet known as to whether the trace elements determined are present in solid solution — and to what extent — or are due simply to foreign mineral and fluid contaminants. Measurements are being made of (1) the solubilities of selected elements commonly occurring in certain sulfides and (2) the partition coefficients of appropriate elements between coexisting pairs of sulfides. Such data can be used to determine (1) temperatures-of-formation of ore deposits and (2) the composition of the solutions from which they crystallized. In the experimental procedure, the sulfide mineral is crystallized hydrothermally in the presence of a radioisotope of the element concerned at temperatures between 300° and 600°C under controlled pressure. The amount of the substituent is determined radiometrically, and its distribution, in favorable cases, is studied by autoradiography. The solubility of antimony, arsenic, silver, and tin in sphalerite, and of arsenic in galena, has been found to be less than 1 ppm up to 500°C. Indium is soluble in both sphalerite and galena in amounts somewhat less than 200 ppm at 500°C, the solubility decreasing with decreasing temperature. Partition of indium and selenium between galena and sphalerite is now under study, in addition to further crystalline solubility measurements.

Iron Ore and Diabase

The purpose of this investigation was to examine possible genetic links between the diabase-granophyre sills of Southeastern Pennsylvania and the associated magnetite ore deposits of the Cornwall type. A study of the magnetites in iron ore deposits has been followed by a study of the opaque minerals in the igneous rocks. The results obtained confirmed that the ore deposits could have been deposited from solutions derived from the igneous rocks at the intermediate stage of differentiation, but complexities in the later igneous rocks suggested that the solutions had a complicated history before forming the ore deposits.

GEOGRAPHY

There has been a notable increase in departmental activities during the past two years. Although the Department of Geography has always had a strong commitment to research — as evidenced in its output of papers, monographs, and books, and in the recognition by the geographic profession of its contributions — recent faculty additions have been a material stimulus to this program. Members of the department have received over $100,000 in grants from the National Science Foundation to support their research and the research of many graduate students. The recent award of six National Defense Education Act Fellowships is additional evidence of this growth. Members of the faculty also have received such grants as a Fulbright Award, a Guggenheim Fellowship, Social Science Research Council and Inter-University Committee Travel Grants, and the Ford Foundation Fellowships.

Departmental research has been concentrated primarily in the fields of economic and cultural geography, the geography of population, and electoral behavior. Future plans call for the development of an additional strong concentration in physical geography, particularly in the fields of landform analysis and climatology.

Geographical Variations in Mining in Eastern United States

The objective of this investigation is to compare and contrast geographical variations in the bituminous coal mining industries of the various coal fields in the Eastern United States. This involves the preparation and analysis of a series of maps covering such topics as employment and unemployment, labor productivity, number and types of mines, mining methods, accidents, coal production, shipment, and so forth. It is hoped that such an analysis will provide a better understanding of the relative strengths and weaknesses of Pennsylvania's bituminous coal industry as compared with that of other states.

Another phase of this project involves a continuing program of collecting available data concerning the mineral deposits and mining activities of Pennsylvania, the presentation of the data in map form, and the interpretation of the maps. Types of data utilized include the following: (1) distribution of mineral deposits, (2) historical evolution of mining activities, (3) distribution of types of mining operations, (4) distribution of mining employment and unemployment, (5) distribution of mineral output, (6) movement of mineral products, (7) utilization of mineral products and waste materials, (8) economic and social significance of mining activities,

(9) decline in mining operations and resulting unemployment, and (10) distribution of future potential mining activities. It is believed that maps prepared from such data, as well as the analyses of such maps, will be of interest and use to mining companies, research and planning organizations, area developers, educators, conservationists, unions, and mineral users, and to federal, state, county, and local governmental agencies.

Negro Voting in Flint, Michigan, 1932-1962.

A long-term research project in the field of micro-electoral geography has just been completed. The study analyzed the geographic patterns of Negro migration to the city of Flint, Mich., and the way in which the growing Negro population produced a revolution in the city's political complexion. Seventeen detailed electoral maps of each biennial election between 1932 and 1962 showed changes in the location of party strongholds, and these maps were compared with other maps of changing Negro population. This comparison revealed major changes in Negro political allegiance during this thirty-year period, and also the existence of radical differences within Flint's Negro community. Finally, it was shown that detailed electoral maps may be used in lieu of population maps under certain carefully defined conditions, and that such electoral maps are useful in revealing demographic anomalies in apparently homogenous populations.

Architectural Manifestations in Trans-Appalachian Migration

This investigation should determine the feasibility of using architectural styles as criteria in locating a major cultural boundary in the Northeastern Appalachian region. Migration from the Eastern Seaboard to the Midwest chiefly followed two major river routes: the Hudson-Mohawk and the Susquehanna's western tributaries. These same routes were used by migrants to western New York and Pennsylvania, who spilled northward and southward from the river valleys. Those from the Mohawk brought cultural traits derived from New York City and New England, while those from the Susquehanna brought traits from Philadelphia and vicinity. These traits included characteristic architecture for houses and farm buildings, with designs differing significantly between New England and Southeastern Pennsylvania. Distribution of architectural styles, therefore, should serve as a reliable indicator for establishing the southward limit of Mohawk influence versus the northward limit of Susquehanna influence. Preliminary surveys suggest that the boundary is surprisingly sharp and distinctive, and this study is to determine its precise location.

Demographic studies take University scientists to many parts of the world, including this rural area of the Philippines.

Geographical Analysis of the Economy of Pennsylvania

The trends of the economy of Pennsylvania are being analyzed with emphasis on changes in economic patterns. The studies seek to isolate factors which encourage or retard growth of the economy and to interpret the significance of these factors. They are carried out at local, state, and regional levels and the methodology includes both library and field investigations.

Migration into Kazakhstan, Russia, 1896-1913

Pre-revolutionary migration into Kazakhstan in Tsarist, Russia, was investigated. Through the use of government records, colonial administration reports, and census materials, a successful analysis of the numbers and characteristics of the migrants, their source regions, and the areas to which they moved was possible. Emphasis was placed on the impact of the migration in newly colonized areas. It is judged that this study is a pathbreaker, not only in the field of Russian historical geography, but also in the general field of migration analysis.

Southern Italy: Government Subsidization of Industrial Development

The impact of the Italian government's investment program on the industrial geography of southern Italy is being studied. During the past 14 years, vast sums have been spent in an attempt to narrow the economic and social gap between the Italian South (Mezzogiorno) and the more prosperous North. The loan and subsidy programs have not had the desired results, although income levels have risen in the region and there have been significant changes in the amount, composition, and locational pattern of industry. The focus of the study has been on the locational aspects of the development policy, emphasizing the contrasts between locational policy and practice.

Population Geography of Middle America

One aspect of the population geography of Central America and the West Indies has proved to be most crucial for an understanding of the nature and problems of the region: the description, explanation, and search for the implications of recent population change — its velocity, distribution, and other spatial aspects. A particular study is helping to understand (1) such matters as difference between city and countryside, between different cultural and economic areas, and between sex and age groups and (2) the vital trends and migrational currents that are producing these differences. This is, incidentally, probably the first such investigation of the spatial dynamics of population for any of the so-called

"underdeveloped" regions. The results of this study will help fill one of the larger areal gaps among the currently-available regional studies of population. It should also contribute to the understanding of the general geography of the Middle American region; and it should suggest some major, but previously unsuspected, problems in demography and human geography. More important, perhaps, from the scholarly point of view, is the possibility that this study may provide some significant material for a general theory of population geography for the "underdeveloped" regions, if not for the entire inhabited world.

A great deal of effort has gone into the procurement and reading of statistical materials, maps, and other necessary documents and into the preparation of a series of detailed maps and tables. Analysis has not yet reached the point where more than the most preliminary results can be reported. It is hoped that by the end of 1966 a substantial monograph and at least three shorter papers for periodical publication will have been completed.

GEOLOGY AND GEOPHYSICS

Research in the Department of Geology and Geophysics can be broadly categorized as follows:

I. Geology:

a. Studies of sedimentary processes, as evidenced in recent and ancient strata, both inorganic and organic, and as observed in laboratory experimentation.

b. Field and petrographic investigations concerned with the origin of certain deformational features of the earth's crust (i.e. low-angle faults of the North American Cordillera and the Appalachian Mountains, zones of high-angle faults in the Basin and Range Province, fracture traces in the Applachian Mountains and southern California).

c. Experimental, theoretical, and field investigations of the processes whereby useful minerals become concentrated in deposits of commercial value.

d. Studies of the geology of the human environment, especially as related to the conservation of water resources, to safety in building formulations and in other types of construction, and to the procurement of mineral raw materials necessary to urban development.

e. Paleontological research with emphasis on paleobotany, paleoecology, and evolutionary theory.

II. Geophysics:

a. Seismological investigations of various types, including the interpretation of earthquake data received at the University's seismic observatory, the simulation of earthquakes through the use of models, the use of man-made seismic signals in determining the thickness of the earth's crust, and the use of data analysis techniques in improving the interpretation of seismograms.

b. Investigations aimed at the improvement of geophysical methods for the exploration for iron deposits.

c. Studies of stable and unstable isotopes in the approach to problems of geochronology, human metabolism, and petrogenesis.

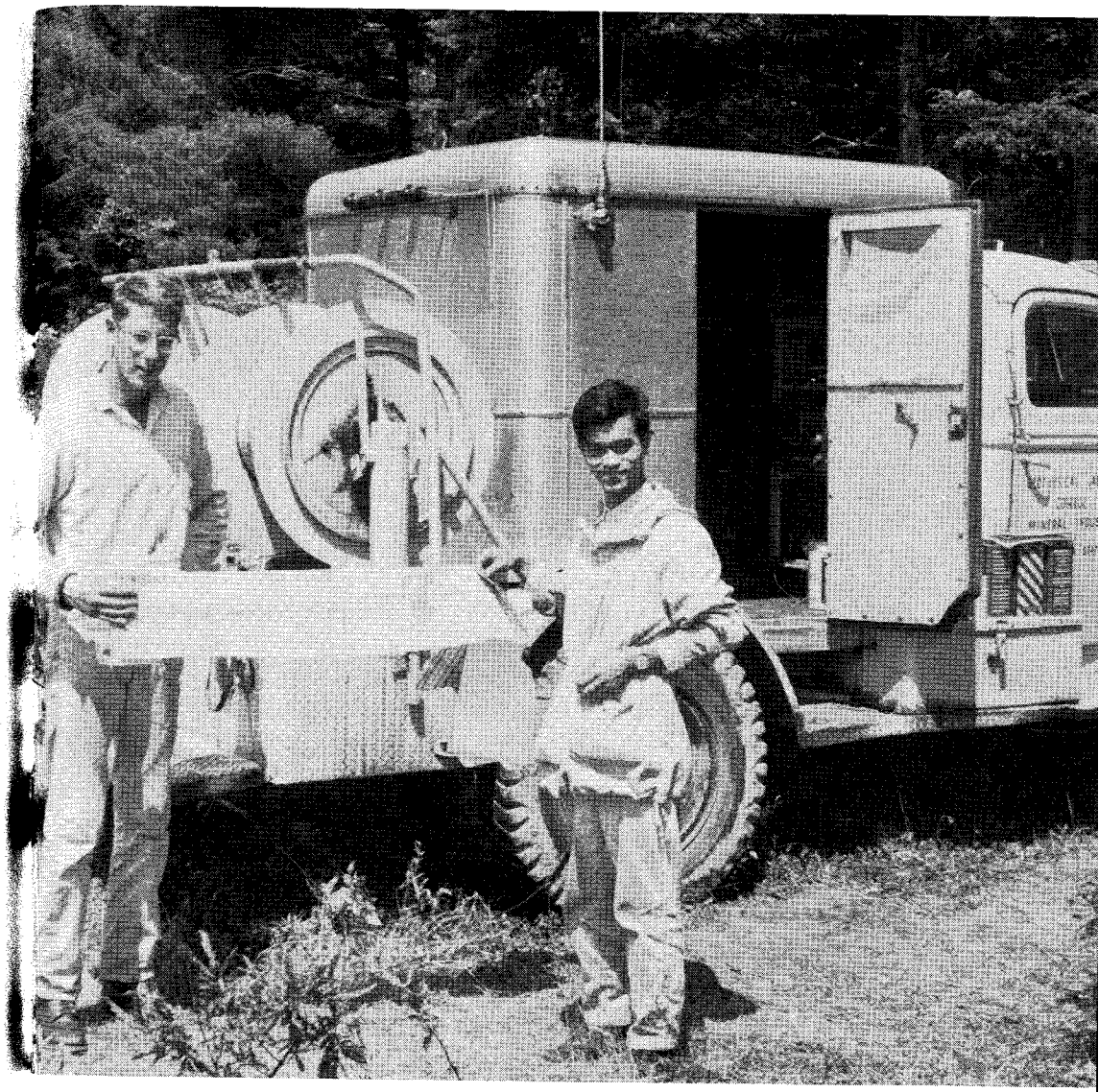
Future research in the department probably will follow the general pattern outlined above, but with increased emphasis upon theoretical geophysics, the chemistry of sediments, marine geochemistry, experimental structural geology, and the theoretical aspects of hydrology. With the completion of the Earth Sciences building at the University Park Campus, the department will have expanded facilities for nearly every phase of its research program.

Behavior of Anthracite Particles Under Thermal Stress

Petrographic studies combined with experimental decrepitation tests of anthracite lithotypes have shown that clarainic coal types exhibit a much lower resistance to decrepitation than do durainic particles. The data indicate that rate of heating influences both the frequency and intensity of decrepitation. When particles are shock heated, 70 per cent of the clarainic grains decrepitate, whereas less than one per cent of the durainic materials show signs of rupture.

Boron and Other Impurities in Silicon: Mass Spectrometry

Various parameters influencing the capability of mass spectrography for the analysis of impurities in solids have been investigated, with emphasis on the problem of determining microtrace impurities in semiconductors (e.g., B and Al in Si). Special emphasis was placed on considerations influencing the performance of rf, gas, and sputtering ion sources, electrical and electron multiplier detectors, vacuum system design, ratio measurement circuitry, and



Geophysicists use a mobile unit to gather seismic data in the field.

tandem analyzers. Several new components have been designed, constructed, and tested in this project. The knowledge gained has been used in the design and construction of a complete mass spectrograph which is now in the laboratory.

Human Cholesterol Metabolism Using Stable Isotopes

A cooperative venture with the Evanston (Illinois) Hospital was undertaken. Doctors at the hospital fed a selected group of seminary students stable carbon-13 labeled cholesterol, in an attempt to learn the extent to which the body can compensate for ingesting cholesterol by synthesizing less in the liver and other organs. At Penn State isotope ratio analyses of carbon from samples of blood collected by the hospital were performed. The results support the belief that, in contrast to the situation already elucidated for the dog, man has only a slight ability to moderate his synthesis rate to compensate for variations in the amount of cholesterol ingested. Additionally, analysis of "unlabelled" blood indicated that there was probably a rather large range of carbon isotope ratios in the human and a large variation between individuals as well. A "natural" variations study described below was therefore suggested.

The purpose of the "natural" variations study is to investigate the range of isotope ratios in humans, for the elements C, O, N, S, and H, as a function of dietary variations and other factors. Natural variations in these isotope abundances will be studied in breath, urine, blood, and other metabolites. Such variations constitute a limitation on the applicability of the stable isotope tracer technique to studies of human metabolism. This program is in an early stage.

Dating with Beryllium-10

Cosmic ray interactions with atmospheric nitrogen produce the nuclide, beryllium-10, which has been detected in recent deep-sea deposits. This nuclide is also produced by cosmic-ray spallation reactions in meteorites. Be-10 has a most interesting half-life, approximately 2.7 x 10^6 years, and should therefore be useful for such purposes as the determination of sedimentation rate and cosmic-ray exposure ages. A mass spectrograph is being constructed with the capability of measuring Be-10 in concentrations as low as 10^{-13} gm/gm in the presence of 10^{-6} to 10^{-7} gm/gm of "normal" Be-9 and appreciable contaminant boron-10. A design has been made, except for the ion source. The first stage, a spectrograph, has been constructed. Work on the ion-source and sample preparation problems is in progress.

Natural Seismic Motion of the Ground at State College

A seismic observatory is operated in State College, Pa., consisting of two sets of 3-component recorders — one for short-period signals and one for long-period signals — plus a low-gain visible recording seismograph for teaching and monitoring. The times of arrival of approximately 1,500 earthquakes per year are reported in an annual bulletin, together with the directions of first motions of each shock. Weekly reports are sent to the U.S. Coast and Geodetic Survey, Washington, D.C., and monthly reports to the World Data Center in Edinburgh, Scotland. Seismograms also are sent to Washington weekly to be photographed and these are made available to other cooperating observatories. In return for the above, similar data are made available to Penn State from more than 100 observatories in the world-wide network. These data are used in graduate and faculty research, in classroom teaching, and in educational exhibits.

Two Penn State crews participated in cooperative field experiments on the thickness of the earth's crust in Maine (1961) and in North Carolina (1962). In addition, a limited number of measurements have been made in Pennsylvania throughout the period of the project. Interpretation of the Maine records is complete. The crust seems to have a thickness typical of continental masses (about 30 km). There is some variation along the length of the profile studied. The records were studied for evidence of a transition zone from crustal to mantle rocks. Examination of the frequency spectra of the seismic pulses indicates that if there is a transition zone, it is no more than about one-half kilometer thick.

A third set of experiments was undertaken to observe the seismic signals produced by a series of one-ton blasts detonated in Lake Superior. Two mobile seismic laboratories from Penn State made 78 recordings each. Information on seismic-wave arrival times was exchanged with more than 40 other participants. Fourier integral frequency analyses of the first-arriving pulses have been made in a limited number of cases and are being studied to learn how seismic energy is absorbed in the different layers of the earth.

Effect of Depth of Focus on the First Seismic Pulse

The objective of this research is to improve means of determining the depths of focus of seismic disturbances in order to differentiate between blasts (which are shallow) and natural earthquakes (which generally originate at least 10 km from the earth's surface). A method is being tested which measures the time difference between the two most prominent families of pulses constituting the

record, on the assumption that one is a delayed, inverted image of the other. Each seismogram is passed through a series of ideal inverse filters, and the resultant filtered seismograms are tested, using a simplicity criterion to find which filtered seismogram is the "simplest".

Geology and Mineral Deposits of the Barre Region, Vermont

This work consisted of geologic mapping and study of 260 square miles of igneous and metamorphic rocks in central Vermont, including highly-detailed work on the granites of the Barre district and the verd antiques of the Roxbury district. An extremely thick section of layered rocks, representing the east flank of the Green Mountain arch, appears as a homocline comprised of schists, slates, quartzites, and marbles of low to moderately high metamorphic rank and of Cambrian to Devonian age. The detailed structure of these rocks is highly complex and reflects at least three distinct episodes of deformation. Scattered bodies of granitic rocks, including the large and irregular stock of the Barre district, were emplaced in part by dilation and in larger part by magmatic stoping. Smaller and older bodies of serpentinite are the alteration products of dike-like masses of ultramafic rocks. The episodes of deformation, metamorphism, and igneous activity have been dated with respect to one another. Of potential economic value are (1) conclusions concerning additional reserves of granite, slate, verd antique, and talc, and (2) recommendations of techniques of granite quarrying.

Marine Terraces of the Palos Verdes Hills, California

Well-defined terraces of composite origin form a very prominent series on all sides of the Palos Verdes peninsula. Each terrace comprises a wave-cut bench developed upon bedrock of Tertiary age, a thin and continuous-to-patchy veneer of marine beach and other near-shore deposits of late Pleistocene age, and an overlying cover of nonmarine deposits derived from landward sources. The nonmarine cover is very thick on the lowest and youngest terraces, but becomes progressively thinner on the progressively older terraces. Some of the terraces have been deformed by faulting and broad warping. The terrace deposits have been helpful in elucidating the highly complex history of Pleistocene uplift, deformation, erosion, and sedimentation in this part of coastal southern California. Both these geomorphic features and the deposits associated with them have a profound influence upon ground stability in this area and, hence, upon recommendation for safe development of the area for homesites and various works of man.

Debris Flows

Natural debris flows, characterized by chaotic internal structure and commonly by numerous large rock fragments, are abundant in the geologic section and are being formed in many areas today. When in motion they consist of unsorted rock debris and subordinate fluids, chiefly water, and their mechanism of flow is quite different from most transporting processes encountered in nature. Study of this mechanism has included theoretical analysis, scale-model experimentation, and detailed mapping and interpretation of natural occurrences in the desert region of southeastern California. Special attention has been directed toward determining the bulk density, viscosity, and shear characteristics of the materials, and toward deciphering the complex histories of several natural accumulations of these materials. A model has been generated to explain the nature of the various movements in different parts of a single flow and has been successfully tested against all known characteristics of the flows and their solid products.

Surficial Geology of the Greenfield-Holyoke Area, Massachusetts

This is a coordinated stratigraphic-geomorphic study of glacial and post-glacial deposits in an area whose Pleistocene history was complicated by the presence of a large, now extinct lake. Many kinds of deposits, some of considerable economic interest, were variously laid down by ice, by water, and by wind, and their space-time relationships are very intricate over a wide range of scales. Some have been particularly useful in deciphering the history of the large Connecticut Valley lake. They also provide an independent means for checking the ages of important events that have been dated by radiocarbon methods.

Fracture Traces in the Mohave Desert, California

Mapping and detailed studies of individual fracture zones in the Box Spring Mountains of California were carried out during this investigation. Several conclusions were reached, the most important being that all zones studied were of "extension" (tensional) origin. No shear zones showing crushing or mylonitization were found. The trends of the zones were not affected by movement along nearby major strike slip fault zones. In general the directions of extension show radial and tangential patterns around uplifts. Zones in the crystalline rocks could be traced into overlying unconsolidated sediments.

Geomorphology of Central Puerto Rico

A study concentrated on a segment of the coastal plain of northern Puerto Rico was conducted. A complex history of Pleistocene sea-level changes and of their impact on alluviation of major north flowing streams building the coastal plain was delineated.

Morphological units of the coastal plain were mapped in detail, including alluvial terraces merging into marine terraces, eolianites, beachrock, abandoned bars now integrated with the coastal plain, and swamp deposits. In addition to the history of the coastal plain, methods of distinguishing and mapping morphological units and the sequences of their deposition were developed.

Geophysical Investigation of Iron Ore Deposits

Anomalies in the earth's magnetic field indicated by aeromagnetic surveys in the Triassic basin of Southeastern Pennsylvania are being investigated by surface geophysical methods. The research in progress is aimed at finding a combination of geophysical methods which will distinguish between anomalies caused by bodies of massive magnetite (of possible commercial value) and anomalies caused by bodies of dibase containing disseminated magnetite. Resistivity and electromagnetic surveys have given inconclusive results because the bodies lie at considerable depth. Data from gravity, magnetic, and self-potential surveys are being analyzed.

Groundwater Geology near State College

Geologic controls affecting the occurrence, movement, availability, and quality of groundwater in sandy dolomite strata of the Gatesburg Formation were investigated. This was done to provide a regional hydrogeologic framework in which community sewage effluent could be disposed of by spray irrigation. It was found that up to eight million gallons of water daily could be pumped for municipal use and that sanitary landfills could be operated without contaminating the local groundwater reservoir. Detailed surficial geologic and water table maps were prepared for the entire study area. Previously unmapped members of the Gatesburg Formation — faults, folds, zones-of-fracture concentration — were mapped. Well-yields obtained from pumping tests were related to geologic variables when possible.

A second study, still underway, concerns the measurement and evaluation of precipitation, surface runoff, groundwater discharge, changes in groundwater and soil moisture storage, and evapotranspiration for the basin during years of normal, below normal, and above normal precipitation. Field pumping tests will be run under varying geologic conditions to determine spatial variations in porosity and permeability. In addition to providing information on changes in groundwater storage, these data will be related to low flow of Spring Creek. Rock type, structure, topography soil-type, and variation in precipitation are being evaluated to determine their relationships to the spatial distribution and geologic controls of permeability, porosity, groundwater recharge and discharge, and stream flow. A hydrologic budget will be determined for the drainage basin which can be used in water resource development and management studies. Ultimately, hydrogeologic factors to be considered in land-use planning, urban development, and waste disposal will be evaluated.

The results of the above studies will be used in the Waste Water Renovation and Conservation Research Project, the objectives of which are (1) to determine the feasibility of a non-aqueous means of disposal of sewage effluent, (2) to renovate sewage effluent by means of biological and mechanical processes in soils, (3) to conserve water by returning it to the groundwater supply, and (4) to determine the effects of effluent on crops, forest trees, and wildlife. The recent problems associated with pollution of lakes and streams require basic studies of the entire complex of geological, biological, and engineering systems. The aim is to develop methods for disposal, renovation, and conservation by distribution of effluent on land, thereby reducing pollution of streams, using the nutrients to grow food crops, timber, and game, and reclaiming water for recharge of the groundwater reservoir.

In the waste water project, chlorinated effluent is delivered by a six-inch buried pipe line to two sites (one is two miles and the other four miles from the sewage plant) and is distributed through a system of portable aluminum pipes and rotating sprinklers. Levels of application range from one to six inches per week. At present 20 per cent of the effluent from the University treatment plant is used. Sod, small grains, hardwoods, conifers, and idle fields are the vegetation extractors and users of constituents in the effluent. An extensive monitoring program follows the passage of water and nutrients in the soil. Changes in crops, trees and birds, mammals, and mosquitoes are being measured.

Fracture Traces and Movement of Groundwater

This study is intended to test further the concept that fracture traces of carbonate rocks, shales, and sandstones reflect underlying zones of fracture concentration and localized zones of increased weathering, solutioning, and permeability. Effects of varying rock

type, geologic structure, topography, and erosional history will be isolated as each influences well yields. The width, depth, length, and nature of fracture traces will be studied further on air photographs, in drill holes and water wells, and at rock exposures. Field pumping tests will be run under controlled conditions to isolate the variables of well diameter, well depth, depth-of-water table, pumping period and rate, well losses, and barometric effects for wells located under varying field conditions. Statistical studies will be used to isolate sources of variation in well yields.

Analog Computer Models as They Apply to Groundwater Problems

The application of electrical analog models to the analysis of of groundwater problems is being investigated. It is intended that techniques will be worked out to account for such hydrologic variables as rainfall, evaporation, variable stream flow, and variable well discharge. Existing excitation-response apparatus will be simplified to reduce costs of equipment and to improve read-out devices. Ultimately, an electrical-analog model will be built to simulate the complex hydrogeologic environment near State College. An array of electrical resistors and capacitors has been assembled to simulate three hypothetical field models: (1) an infinite-strip aquifer bounded by impermeable strata, (2) the same aquifer bounded by a river, and (3) a leaky artesian aquifer bounded on three sides by impermeable strata. The model will be probed under varying recharge and discharge schedules. Electrical analog solutions will be compared to mathematical solutions.

Transportation and Deposition of Ore Minerals

An attempt is being made to relate the compositions of minerals found in ore deposits with the chemical characters of solutions that formed them. There are probably two general processes by which deposition of ore minerals took place: (1) through the neutralization of anions by cations and (2) the removal of screening anions from metal-sulfur ion complexes. The products of neutralization of anion by cation are known as oxy-salts (if the anion of the complex is oxygen) and as sulfo-salts (if the anion of the complex is sulfur). If the mineral is precipitated through the removal of screening anions, the product is either a simple sulfide or a simple oxide. On occasion, the removal of screening anions is carried so far that the native metal is produced. Such a reaction requires both the reduction and oxidation of the gold ion. The problems of the oxidation and reduction of elements that exhibit more than one valence in ore minerals, like copper, and of the reduction and oxidation reactions that must pair with these, are being considered.

Addition and Subtraction of Material in Hydrothermal Replacement

This project is concerned with the determination of the exact amounts of materials added and subtracted in the replacement reactions vital to the development of large-scale mineral deposits. In the generality of replacement reactions, there is no loss or gain of volume, and such reactions, therefore, cannot be described by the usual chemical equation in which no account is taken of the volumes of reactants and products. A scheme by which such volume-based equations could be written was proposed in 1949, and further work has shown that this method has wider application than was previously thought possible. Enough is now known of the character and behavior of hydrothermal solutions to make it possible to write a series of equations to explain a series of replacement reactions. If the volumes of the solid reactants and products are kept constant from one equation to the next, simple addition and subtraction permits (1) determination of the actual amounts of materials added and subtracted during the replacement processes and (2) determination of the changes that these additions and subtractions cause in the ore-forming fluid.

Physical Chemistry of Carbonate Mineral Assemblages

Laboratory and library studies of a variety of problems associated with carbonate phase equilibria are being conducted.

FUNAFUTI: Core samples from the Royal Society boring at Funafuti Atoll were examined by X-ray diffraction to confirm the original mineralogical identification. The results were in nearly complete accord with earlier results, but admit of physical-chemical interpretations previously impossible.

ARAGONITE-CALCITE: Surface energy studies have led to the hypothesis that aragonite is thermodynamically stable when precipitating from solution.

KINETICS: Two studies of carbonate reaction kinetics are presently underway: (1) to reexamine the rate of dissolution and ionization of CO_2 in aqueous solutions, and (2) to determine the rates of nucleation and crystal growth for calcite and aragonite from distilled water and seawater solutions. The study is intended to cast further light upon the problem of carbonate polymorph equilibria in geologically-significant environments.

ALGAL CARBONATES: Electron microprobe studies of *Goniolithon* demonstrate that this high-magnesium calcite (30 mol per cent) is, in fact, two phases: high magnesium calcite, plus brucite. Studies of other algal species are underway to determine which algae secrete brucite and to establish the limits of Mg-solid

solution in organically-deposited calcites. Further studies will attempt to define the process of secretion and the mechanism and rate at which metastable high-Mg calcites recrystallize in nature.

Deposition of Early Evaporite Salts From Seawater in an Open System

Most deposits of marine evaporite salts in the geologic column are believed to have been formed in shallow water, and may have thicknesses in excess of 100 feet. Because of the small amount of salt in seawater (3.5 per cent by weight), it is clear that these deposits could not have been formed by evaporation of a closed basin to dryness. Rather, some continuing influx of seawater is required to account for the thickness observed. The majority of evaporite deposits must therefore be considered as thermodynamically "open" systems. The chemical conditions in such an open basin are substantially different from those in a closed basin, and different mineral assemblages might be anticipated. Only closed systems have been investigated previously. This study is intended to fill this gap.

A reservoir filled with filtered Sargasso seawater supplied an open evaporating pan in such a fashion as to maintain a constant volume of brine in the pan. The pan was enclosed in a controlled temperature and humidity environment. For 50 days pH measurements, density determinations and sediment samples were taken every 24 to 48 hours. Calcite (plus aragonite), gypsum, and halite precipitated, in that order. Calcite precipitated under conditions of pH in excess of 8.0; with the first appearance of gypsum, the pH began to fall, and earlier precipitated carbonate began to redissolve. A two-phase region of changing pH then gave way to a single-phase (gypsum) interval (pH = 7.5+) followed by a two-phase (gypsum + halite) interval, again marked by falling pH.

The results suggest a significant difference between mineral assemblages in an open and closed evaporating system and also cast light upon the problem posed by carbonate-deficient evaporite sequences. Further study is necessary, and investigations employing carbonate-buffered open systems and more refined measuring methods are underway.

Surface Energy of Carbonate Minerals

"Equilibrium" pH measurements of aqueous solutions in contact with standard carbonate minerals permit the determination of molar-free energies as a function of particle size and, therefore, allow the determination of specific surface energies for the minerals studied. The magnitude of the energies involved (Ca 200-400 ergs/cm^2) suggests that surface energies may play a decisive role in controlling phase equilibria, solubility, and reaction kinetics in natural environments where small particles are abundant. Such environments would include areas of inorganic precipitation (Bahama Bank), high-energy beaches, and the like, where anomalous molar energies occasioned by surface effects might lead to apparent supersaturation and reversed equilibrium relationships between dimorphic pairs.

Measurements were made of the molar free energy for calcite, as a function of particle size in the range 1 cm to 0.05μ; replicate determinations gave a specific surface energy for calcite of approximately 280 $\pm$ 50 ergs/cm^2. This value is in close agreement with results reported by other investigators employing different measurement techniques. Similar measurements for aragonite are now underway. Consideration of the preliminary results leads to the conclusions (1) that aragonite is stable relative to calcite at one atmosphere and 25°C by as much as 1 kilocalorie when particle sizes approach 0.01μ and (2) that, accordingly, aragonite will form as the thermodynamically-stable precipitate in natural systems and may persist metastably at larger grain sizes.

Investigations in the field were directed toward furthering understanding of the role of surface energy (and energy stored as lattice distortions) in controlling the supersaturation of tropical surface marine waters. Saturometer measurements in over 100 localities showed that sediments (25 ppm with respect to calcite) are in equilibrium with actively stirred sediment in suspension.

Ridge Province in Pennsylvania

The structural framework of the Blue Ridge Province of the Appalachian Mountains in Pennsylvania is being studied in relation to the carbonate belt to the northwest. The study is of particular academic interest because of the recently proposed hypothesis of gravity tectonics as a key to Appalachian structure. Results obtained to date are locally suggestive of this hypothesis, but much more work needs to be done. A practical by-product of this work will be more accurate and detailed geologic maps and cross-sections, which could provide a more adequate basis for any future mineral exploration in the region.

Thrust Belt North of the Snake River Plain

The objective of this project is to test a new hypothesis of the tectonic evolution of the northern Rocky Mountains. According to this hypothesis, the present structural framework is the result of

vertical crustal movement due to warping and upthrusting, followed by widespread gravity gliding of numerous individual masses in directions determined by locally available structural slopes and land surfaces. A large part of the area occupied by the Tendoy, Beaverhead, and Lemhi Ranges has been or is being mapped under this project, and the data obtained so far seem to confirm most predictions based on this hypothesis. The proposed hypothesis and the data gathered appear to have practical applications in petroleum exploration and atomic waste disposal in the Snake River Basin south of the mountains studied. This basin is one of the great unexplored petroleum provinces in the United States. The geologic maps resulting from this research will aid any future mineral exploration in the mountain area (thorium, copper, lead, gypsum, and others). Before this work began, geologic maps were virtually nonexistent.

Other stratigraphy research concerning Central Idaho and southwestern Montana supports structural studies of this region and seeks to understand the mechanisms of tectonic transport. This research cannot be successful, however, without a more adequate knowledge of the Upper Paleozoic rocks. Preliminary results indicate that well-known stratigraphic units of Montana can be carried westward into Idaho, although facies changes and additional units are recognized. This should be of great importance to the petroleum industry when exploration extends into Snake River Basin of Idaho. Wells are also being planned for atomic waste disposal by the National Reactor Testing Station at ARCO, Idaho, on the Snake River Plain; therefore, knowledge of the Paleozoic rocks to be encountered is of vital importance.

Spores and Pollen of the Potomac Group of Maryland

The spores and pollen from the Potomac Group of Maryland have been subjected to a detailed investigation. The stratigraphic range of various sporomorphae has been used to zone the Potomac Group. It is believed that the zones will prove more useful in subdividing the Lower Cretaceous section than the formational units. The microflora of the Patuxent and Arundel are so similar that the supposed disconformity between them may represent a change in the drainage system rather than a significant hiatus. The change in the microflora from Zone 1 in the Arundel clay to Subzone A in the Patapsco suggests a disconformable contact. The low frequencies of the newly-introduced forms in most of the lower part of Subzone A do not indicate any great lapse of time. The macroflora suggest a significant stratigraphic break between the Patapsco

and the overlying Raritan Formation. The palynological nature of this boundary would make an interesting problem.

Spores and Pollen in Lower Kittanning Coal

One hundred and forty species, in 59 genera, were recognized as being present in the Lower Kittanning coal of Western Pennsylvania. Thirty-four species and two genera are described as new. The vertical distribution of spore and pollen zones in the Lower Kittanning holds closely to a definite sequential arrangement, markedly different from either the Brookville or Lower Clarion seam. The geographic segregation of spore and pollen assemblage zones compares closely with the variation in the facies of the overlying juxtaposed rocks. The affinity of *Lycospora* to 'fresh-water' rocks and densospores and *Punctatisporites obliquus-Laevigatosporites globosus* to 'marine' rocks is noted. At the 'fresh-water' localities, *Lycospora* predominates in the seam from the base to the top; whereas, at the 'marine' localities, *Lycospora* predominates at the base, but is replaced towards the top by *Densosporites* and *Punctatisporites obliquus-Laevigatosporites globosus.*

Maceral and Mineral Concentration in Chance Cone Products

Two methods of microscopic analysis provided data from which the following conclusions were drawn: (1) the Chance Cone process effectively produced specific maceral concentrations in the resultant products of the Chance Cone, (2) the pattern of maceral and mineral concentration in each resultant product remained relatively constant for two sampling sessions, (3) the petrographic composition of the subject feed coals was approximately the same from sampling period to sampling period, (4) the maceral and mineral concentrations which characterize each separatory product were different, in all instances, from those maceral and mineral concentrations of the respective subject feed coals, (5) the subject feed coals and Chance Cone separates each are characterized by distinctive reflectivity values which are directly related to the specific vitrinoid macerals concentrated within these coal products, (6) the rank factors of the subject feed coals and resultant Chance Cone products indicate that each of the coal products remained relatively constant, in terms of relative abundance of vitrinoid materials, for both sampling periods, (7) large percentages of saleable coal entities are discarded with the total refuse products, and (8) further crushing of the middling products would possibly liberate a large percentage of the inherent mineral materials.

Recent Vegetation of North Central Appalachia

The pollen profiles of six bogs or swamps at high elevation in the Appalachian Highlands were studied. The profiles of these six stations were compared to existing profiles throughout the region and a synthesis of the combined results was prepared. A spruce-fir forest was prominent on the Appalachian Plateau within 100 miles of the Cary border in Pennsylvania during Cary-time, while at the lower elevations in the folded Appalachians a forest cover of pine with subordinate elements of spruce, fir, and birch existed within 120 miles of the Cary drift. No palynological evidence for tundra conditions was found south of the glacial border. The long sought tundra zone is suggested to have never existed south of the ice in temperate regions. Paleozoic spores encountered in the basal silts of the two true peat bogs studied are believed to be wind-blown in origin. This suggests, in addition, that the basal silty clays so characteristic of Appalachian peat bogs may, in part, represent isolated remnants of aeolian loess deposits in the northeastern United States that were elsewhere removed by such processes as congeliturbation.

Interest in modern sediments has increased in recent years, but little of this work concerns the plant-derived sediments that represent the progenitors of coal seams. Investigations of modern organic sediments have been initiated with three basic objectives: (1) to determine the petrographic and palynological characteristics of the more common phytogenic sediments of the Atlantic and Gulf Coastal Plains, (2) to describe the relationship of each sediment type to the botanical and geological setting in which it is accumulating, and (3) to establish the equivalence of certain modern peat types with the lithotypes encountered in the Tertiary lignites of the Coastal Plain.

The Everglades of Florida were chosen for this study because of their simple plant communities associated with 6 to 15 feet of peat. Samples from the banks of the Shark River were collected, representing a range of environments from the coastal mangrove swamp to the intermediate mixed hardwoods and to the fresh water saw grass marsh. Chemical analyses of these samples have shown distinct distributional patterns for uranium and manganese, but not sulfur. Pollen analyses reflect the ecological amplitude of *Rhizophora* and *Avicennia,* and the assemblage contains more open marsh elements as fresh water environments are approached. Cores were obtained of the carbonaceous sediment both on the coast and offshore. They have shown that autochthonous peat, which is continuous with the peat of the mainland, extends out beneath the Gulf. Chemical and pollen analyses of the cores also provide convincing evidence of a recession of the coastline and a relative rise in sea level throughout the last 4,000 or 5,000 years. The net effect of erosional and sedimentary processes seems to be a gradual dissection of the previously-developed blanket of organic sediment.

Fossil Woods of the Tertiary Brandon Lignite

Fossil specimens obtained from Tertiary lignitic sediments located in west-central Vermont included flower, fruit, seed, pollen, stem, and root material. Evidence indicates that the Brandon flora is related, as an evolutionary stage, to certain of the swamp associations now living on the Coastal Plain of the southeastern United States, although intermingled with a number of genera restricted to southeastern Asia. The low interfluvial areas in southern Georgia and northern Florida are commonly occupied by a "bay swamp", a "Titi swamp", or a "gumwood swamp", or by a complex mixture of of these plant associations. Specific plants are abundantly represented in the Brandon deposit by more than one plant part. This is evidence that the Vermont area possessed a much warmer and more humid climate in Brandon time than today. A warm temperature and perhaps a sub-tropical climate existed. Under these climatic conditions, swamp forests formed on the flood plain of a north-south trending valley in Central Vermont.

Minerals in Anthracite Related to the Chemistry of Ash

This was the initial study of the mode of occurrence of mineral matter in anthracite. The mineral content of 156 strata from 12 coal columns was determined. Ash yield data for 11 of the columns were also analyzed. One column was studied for relative concentration of maceral material in one-inch intervals. Each four-inch interval of this column was analyzed for sulfur concentration. Geologic age and geographic location appeared to be correlated, to some extent, with the types of minerals in the seams. The Allegheny coals yielded the highest ash residue and the greatest variety of minerals. Seam samples collected in the Southern Anthracite field contained the greatest concentrations of metamorphic minerals.

A petrographic procedure permitting the differentiation of anthracite seams into compositionally-different zones has been provided through creation of a provisional classification of vitrinitic macerals common in anthracite coal. Quantification of the reflectance of various anthrinoid macerals has made it evident that anthracite coal seams are stratified rock bodies consisting of layers or lenses that are distinctive mixtures of maceral and mineral ma-

terials. The compositional heterogeneity encountered appears to be far greater than that previously ascribed.

Petrography of Southern Appalachian Coking Coals

Detailed petrographic investigation of medium and low volatile coals from the Southern Appalachia has uncovered relationships between basic coal composition and the development of excessive pressures on oven walls during carbonization. Studies of the lateral variability of coal seams indicate that important compositional parameters can be contoured geographically in a manner which has both geologic and industrial significance.

Metallurgical Coke from Blends of Anthracite and Bituminous Coal

The petrographic composition of anthracite was investigated. The anthracites were observed to have the same banded structure as bituminous coal, except that little durainic material was encountered. Anthracite, therefore, appears to consist of the anthracitic equivalents of vitrain, clarian, fusain, and durain. Phyteralically, the clarain differs from that present in bituminous coal by virtue of the general absence of microspores. Studies of size fractions of three anthracites have shown heterogeneity in composition which causes definite compositional differences between the fractionated products, which appear important in the quality of coke produced when anthracite is blended with bituminous coal.

Taxonomy of Fossil Spores and Pollen

Taxonomic research concerned with genera and species of fossil spores and pollen has been continued in association with the compilation and publication of the *Catalog of Fossil Spores and Pollen*. Twenty-two volumes have been published and distributed. Cumulative indexes have been published. Two volumes of translations have been published, containing English translations of original species descriptions that were originally presented in the Russian language.

Mineralogy, Petrography, and Paleobotany of Uranium-Bearing Lignites

This ten-year program was completed during the current report period. It has involved the study of some 2,657 samples that have been analyzed for as many as 36 chemical elements, autoradiographed, evaluated for spore and pollen content, and subjected to petrographic and mineralogic evaluation. Some 40 graduate students have been involved in the work. Seven have completed advanced degrees. Forty-five undergraduate students have been

assisted by the support provided. The research has resulted in the delivery of 18 papers at national meetings and 52 technical reports.

The results include new understanding of: (1) the nature of the uranium complex in uraniferous lignites; (2) the manner in which the uranium complex is held in the rock mass and the ease with which it can be removed; (3) the parameters that control the precipitation, distribution, and retention of uranium; (4) the specific role played by carbonaceous matter and the relationship of organic matter to uranium distribution; (5) the conditions that promote the concentration of uranium in these rocks; and (6) the geological, mineralogical, petrographic, and paleobontanical criteria which may be of assistance in locating other sources of uranium.

Reduction of Sulfur in Metallurgical Coals

Studies of the mode of occurrence of sulfur-bearing minerals in metallurgical coals have suggested the possibility of using preferential maceral-mineral associations in reducing sulfur in prepared coal products. The investigation to date has served to define some of the more common pyrite-maceral associations and to describe the physical forms in which the pyritic minerals usually occur. The distribution of pyritic materials in coal seams appears to be strongly influenced by the swamp environment in which they accumulated. This also determines the type of coal that forms. Thus, knowledge of the various coal types should be useful in developing new beneficiation procedures.

Properties of the Macerals of Pennsylvania Bituminous Coal

Eight vitrinoid types have been described in terms of optical properties and chemical compositions. As expected, the carbon content of the vitrinoid materials decreases in proportion to the rate at which their reflectivity increases. The hydrogen, nitrogen, oxygen, and sulfur contents are not similarly correlated, suggesting that more than a single linear series is involved in connection with the metamorphosis of vitrinic materials. Studies of a similar suite of vitrinic samples, including xylinoids, vitrinoids, and anthrinoids, have suggested the same conclusion on the basis of investigations of microhardness, textural morphology, and various optical properties.

Petrology and Geochemistry of the Vanport Limestone

The physical and chemical conditions under which the Vanport limestone was deposited have been determined. The Vanport, the principal marine limestone in western Pennsylvania, is an important

source of lime for steelmaking. Detailed isopachous and lithofacies maps of the Vanport were constructed. Approximately 500 samples were analyzed for total insoluble residue, bulk chemical compositions (Si, Al, Co, Mg, Fe, K), carbon isotope content, and gross petrography. The analysis enabled detailed reconstructions of the ancient Vanport environments. These results make possible the accurate prediction of the chemical composition of the Vanport in any part of the basins.

Distinguishing Sedimentary Environments by Settling Velocity

The purpose of this study was to determine the hydrodynamic character of beach and dune sands to develop criteria to aid in their recognition in ancient environments. New methods were developed to accurately measure the settling velocity of quartz and heavy minerals. Hydraulic ratios determined on the IBM 7074 were found to characterize adequately the various sand deposits. The criteria have value in discriminating between environments of ancient rocks.

Stratigraphy and Paleogeography in Pennsylvania

The factors which control local and regional variation in the composition of the economically-important coals, clays, and limestones in the Carboniferous of western Pennsylvania are being studied. The first objective of the study, now reached, was to describe accurately, to classify, and to correlate the lower part of the coal measures. The second objective, still being pursued, has been to sample and analyze the economically-important beds and to relate, subsequently, the observed variations to the stratigraphic variables. Principal conclusions are as follows:

1. The composition of coal beds is directly related to the slopes upon which they were deposited and to the character of the overlying sediment.
2. The compositions of Carboniferous limestones are a complex function of depositional slope and distance from shore.
3. The composition of clays are a direct function of ancient topography.

Part of the study was aimed at developing criteria to distinguish between transported and residual clays in the Carboniferous of western Pennsylvania. The clays cannot be accurately mapped until such distinctions are made. Two clays — the origins of which were known on the basis of field evidence — were sampled and analyzed by spectrochemical, X-ray, and petrographic methods. A

distinct chemical and mineral profile was obtained in the residual clay, whereas the transported clay exhibited no systematic variation. This will result in an increased ability to predict the regional variability in the compositions of Pennsylvanian underclays.

Seismogram Interpretation

The purpose of this research is to improve the interpretation of seismograms, with particular application to oil finding. The objective is to parameterize the internal layering of the earth into a tractable, yet still useful, number of unknowns. These unknowns are related to the reflection coefficient strata and their depth of occurrence. An attempt is being made to learn how to construct an artificial seismogram which will closely match a given field seismogram. The values of the parameters which bring about the best match are assumed to be correct. There is assumed to exist an approximate solution to the problem, and its usefulness is being tested.

Evolution of Death Valley

The stratigraphy and the structural evolution of the Death Valley region of California and Nevada are being studied.

The first phase is a reconstruction of the history of sedimentation in (1) the earliest stages of the development of the Cordilleran geosyncline and (2) in the trough of Precambrian sedimentation that preceded the Cordilleran geosyncline. The succession of marine sedimentary rocks and diabase which occupies the earlier trough contains numerous talc deposits. These have been shown to lie at the same stratigraphic position. Conclusions reached include the following:

1. The earlier trough was oriented mainly east-west and, thus, differently from the north to north-northwest trending geosyncline.
2. The detritus that accumulated in the earlier trough was derived first from the south and later from the north, indicating ancient areas of uplift.
3. The earliest detritus in the geosyncline proper was carried from a westerly source, in contrast with the easterly derived material higher in the section.
4. Isopachs and facies changes within the Eocambrian and Paleozoic strata reflect the present structural framework of the region and suggest that it is an ancient feature.

The second phase of the study has resulted in field investigations of a 5,000-square-mile region. The region contains a very

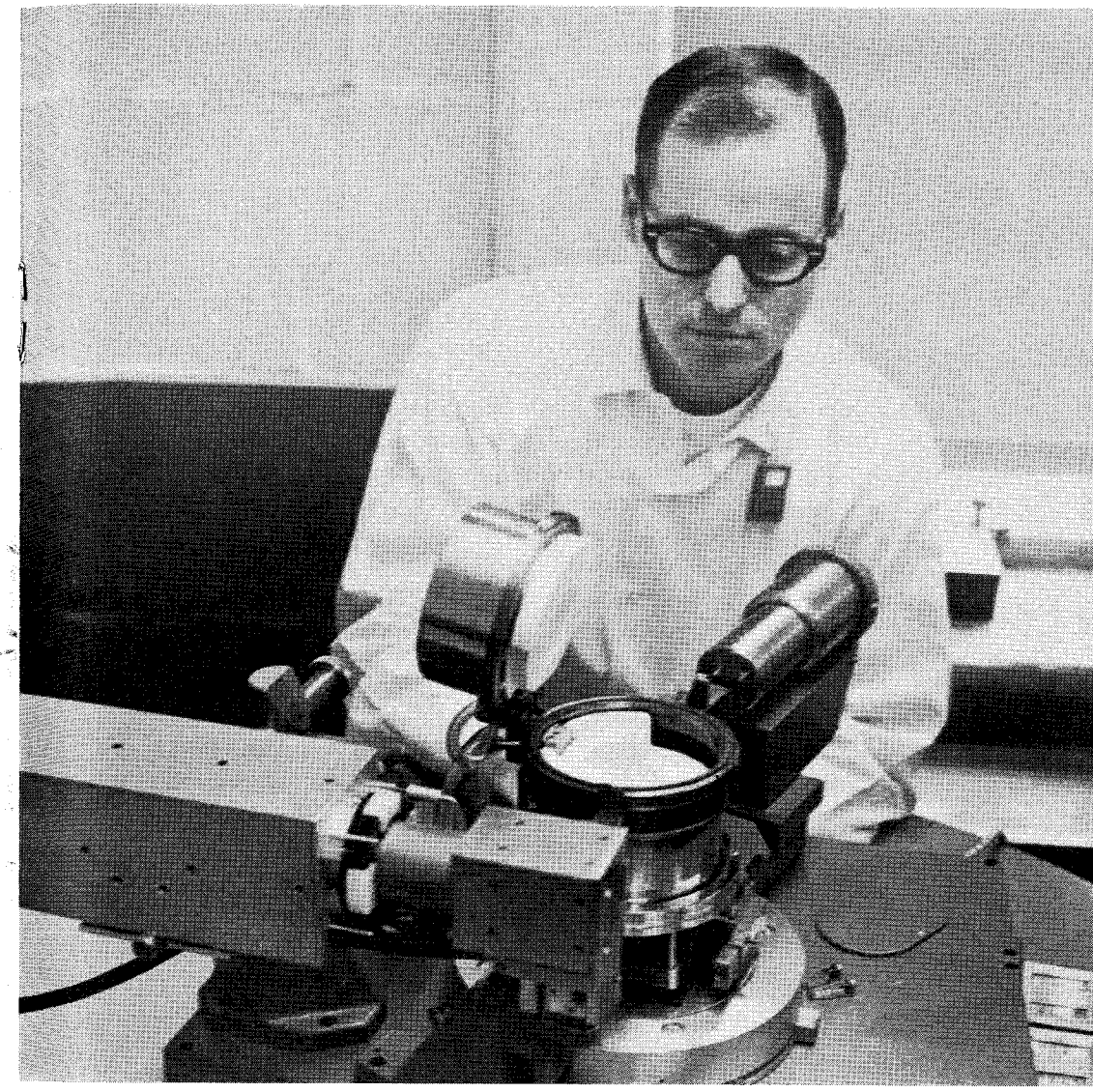
complex structural framework which includes faults of three major types: (1) high-angle, through-going faults — Garlock and Death Valley fault zones — with horizontal displacements possibly totalling a few tens of miles each; (2) low-angle faults, originally believed to be parts of one or more thrust faults of regional extent, and (3) normal faults, typical of the Basin and Range Province, commonly with vertical components of movement measurable in tens of thousands of feet. The studies are directed mainly at an understanding of the real nature and origin of each of the three types, their historic development, and the relationship that each bears to the others. Also involved is an investigation of the mid-Mesozoic to the recent igneous rocks of the region and the role played by plutonism and volcanism in the structural history. Detailed mapping of the igneous in critical areas is planned to provide the geological background for radiometric dating.

It has been tentatively concluded that (1) the high-angle faults have predominently vertical components and that the low-angle faults are confined to uplifted blocks bounded by the high-angle faults and (2) the orientation of the through-going faults reflects an ancient tectonic framework that dates from Cambrian or earlier time.

METALLURGY

Research in the Department of Metallurgy is supervised by eight faculty members with the following areas of interest: (1) physical and mechanical metallurgy of ferrous (iron-base) alloys, including irons, steels, and cast irons — unalloyed and alloyed; (2) chemical metallurgy, including applications of physical chemistry to complex systems, the importance of defect structures, and studies of process simulation; (3) electrodeposition of metals and alloys, including the study of variables and their influences upon the structures and properties of electrodeposits; (4) crystal structure studies, including the structure and theory of intermetallic compounds; and (5) electronic structure studies of solids and liquids, the kinetics of phase transformation, and dislocation interactions in relation to magnetic properties.

No attempt is made to emphasize any one facet of the research program at the expense of others. It might be pointed out, however, that during the past two or three years the chemical metallurgy



A high-temperature furnace mounted on an X-ray diffractometer is used in a metallurgy laboratory.

and electrodeposition aspects of the program have been strengthened to the point where extreme competence can be claimed. Four faculty members are actively engaged in these fields and are noted for their contributions.

Research activities in the department have been aided by many industrial firms in Pennsylvania and nearby states through the Cooperative Program in Metallurgy established in 1936. The program has brought thousands of dollars to the department to help sponsor research projects, to launch new faculty members in their chosen research efforts, to furnish stipends for graduate students, to provide undergraduate scholarships, and to purchase supplies for instruction and research.

Solid-Solid Phase Transformation Nucleation Kinetics

Both the mechanical and magnetic properties of a large number of commercial alloy systems are dependent on the size, dispersion, and composition of a precipitated second phase. A correct theory of nucleation kinetics for such systems would have practical and fundamental implications. At present it is not possible, for lack of adequate data, to discriminate between the various proposed theories of nucleation kinetics of solid-solid reactions. This investigation is aimed at securing such data by a quantitative study of the nucleation kinetics in Alnico V_2, using electron transmission microscopy. To date, a new technique for thin film preparation has been developed which works successfully on the alloys under study. Current study involves a careful examination of the alloy in the solution-treated condition. The purpose is to determine size, number, and type of defects present in the solution-treated condition. The relevance of this determination is that these defects may prove to be the sites at which the second phase is nucleated.

Sulfur Capacity of Solid Lime

The immediate objective of this research is to determine the solid solubility of sulfur in lime at elevated temperatures, such as those encountered in iron- and steelmaking. Ultimately the results of the investigation will be applied to develop improved desulfurization techniques for iron and steel.

This could affect utilization of natural resources of the Commonwealth of Pennsylvania in two ways. (1) It would enhance the value of the low-impurity limestone deposits of Pennsylvania, and (2) it would permit the utilization of coal and coke of higher sulfur levels without penalty to steel quality.

Composition and Stress: High-Strength Steels

Most brittle failure work has been directed toward evaluation of failure susceptibility and external or environmental variables, rather than toward a detailed study of the effects of internal or metallurgical variables. Such internal variables can be classified broadly into two groups — composition (including purity) and structure. Current departmental research emphasizes the compositional variables.

Work to date has extended knowledge about the correlation between stress-hydrogen cracking tendencies and cracking susceptibility — as determined by mechanical test methods, such as notched-bar impact. However, certain differences have also been noted due to the increased importance of the crack-growth step in the fracture process. Compositional variations are presently being investigated through a series of vacuum-melted high purity alloys.

Stress Corrosion and Hydrogen Embrittlement

In addition to major variables known to influence susceptibility to stress-corrosion-type failure in high-strength steels, evidence indicates that elusive compositional (impurity) and structural variables also exist.

Two areas are being investigated. The first involves commercial materials of essentially the same composition (Type 410 stainless steel), but with different cracking tendencies. Heat treating variables have been shown to influence cracking tendencies, but attempts to correlate such behavior with compositional variations (trace elements) have been unsuccessful. The second approach involves the study of high-purity alloys and the effects of intentionally added contaminants.

Element Partitioning in Complex Alloys

Complex microstructures develop in superalloys for high-temperature service. If element partitioning among the microconstituents present were known, important information about the phase relations in such materials would be available, as well as useful information pertinent to future alloy development. The intent of this investigation was to determine the applicability of the electron beam microprobe to such studies. If successful, future phase-diagram investigations would be greatly simplified. Vacuum-arc-melted, modified iron-chromium alloys of complex microstructure were successfully examined by the microprobe, thus demonstrating the applicability of this tool to metallurgical phase-diagram studies.

Precipitation Hardening of Aluminum Alloys

Although age-hardening of aluminum alloys has long been known and utilized commercially, certain aspects of the precipitation process still are not clear. Recently it has been shown that conditioning prior to aging produces some unanticipated trends with possibilities of improved properties. A thorough investigation is being made on solution-treated 2024 alloy to determine what effects conditioning at various temperatures and at various times — prior to aging — has on strength-properties after aging.

Recrystallization of Low-Carbon Steels

The predominant reason for annealing cold-worked steel is to restore the ductility which will be necessary for subsequent fabricating operations. The metallurgical phenomena which occur during this heat-treatment are recovery, recrystallization, and grain-growth; of these, recrystallization is the most important in restoring ductility. Therefore, an understanding of the recrystallization process and the relationship of factors influencing it are of utmost academic and commercial importance.

The purpose of this investigation was to compare, quantitatively, the recrystallization characteristics of rimmed, low-carbon steels produced by two steel-making processes — the basic oxygen converter (BOC) and the basic open-hearth (BOH). The basic oxygen converter is a recent addition to American steelmaking technology and, if the trend continues, will soon be the predominant refining technique. Hence, it is important to ascertain if the steels produced by this process recrystallize in a manner analogous to the steels produced by the familiar open-hearth process.

The following conclusions were drawn: (1) BOC steels have recrystallization characteristics equivalent to BOH steels, but at recrystallization temperatures 25 to 30 degrees F lower. The difference is attributed to the higher residual contents of molybdenum and chromium in BOH steel. (2) The grain coarsening behavior of BOC and BOH steels is very similar, excepting that BOC steels exhibit a slightly larger grain size under any given condition of time and temperature. Heating rate has little effect on grain size; grain size is more a function of temperature than of time at temperature. (3) The oxide inclusion contents of BOC and BOH steels are not sufficiently different to show any influence on recrystallization or grain growth.

Mechanism of the Conditioning of Retained Austenite

High-speed tool steels — when quench-hardened in the usual commercial heat treatment practice — contain 15 to 25 per cent retained austenite. During tempering of the hardened steel, this retained austenite is "conditioned" for transformation upon cooling, into the hard constituent martensite. It has been postulated that this conditioning may be dependent upon the amount of martensite already coexisting with the retained austenite during the tempering treatment. The purpose of this investigation was to establish the role of martensite in the conditioning of retained austenite and, if possible, to confirm or refute some of the previous theories concerning this phenomenon.

It was found that the rate of conditioning of retained austenite in 18-4-1 high-speed steel is greatly accelerated by the presence of martensite coexisting with retained austenite during tempering. It is thought that conditioning occurs because of the diffusion of carbon from retained austenite into the martensite and of the subsequent precipitation of this carbon as an alloy carbide in the tempered martensite. The mechanism seems to provide a possible and plausible explanation of the experimental results. (1) No conditioning occurs in the absence of martensite. (2) The rate of conditioning increases as the percentage of martensite coexisting with the retained austenite increases. (3) The lattice parameter of austenite decreases during tempering. (4) The mechanism is consistent with the fact that a driving force is known to exist within alloyed martensites, during the overlapping third and fourth stages of tempering, to obtain carbon for the precipitation of alloy carbides.

Vacuum Melting and Pouring, Influence on Ni Hard Cast Iron

Liquid-cast iron might dissolve gases from a particular atmosphere with which it is in contact. For example, melting in contact with air, cast iron could dissolve oxygen, nitrogen, and hydrogen. If melting is done under reduced air pressure, pickup of such gases would be less likely.

The purpose of this investigation is to compare the behavior of a special cast iron, Ni Hard, after melting and casting (1) in contact with air and (2) in contact with reduced air pressure (vacuum). The behavior will be compared by microscopic examination and by certain hardness and bend property tests. The results will be related to extensive chemical analyses, for oxygen, nitrogen, and hydrogen. The findings could assist in deciding whether sufficient improvement might be gained in castings poured from vacuum degassed Ni Hard cast iron to warrant the higher costs of its production.

Magnetic Properties of Manganese-Zinc Ferrite

This study was aimed at the quantitative determination of the compositional, structural, and textural parameters of an important ferrite (manganese-zinc) and at the application of these parameters to the theoretical interpretation of the ferrite's magnetic properties. This is the same type of ferrite (a magnetic ceramic) which is finding wide application in telecommunications today.

The study was limited to a single Mn-Zn ferrite composition containing excess iron. All samples were obtained from the same batch of starting material and were prepared under processing conditions which would maintain the spinel structure. The sintering temperatures and the atmospheres used in the investigation were: (1) 1270°C and 1400°C, and (2) CO_2, air, and oxygen.

The relationship of the important magnetic properties to the parameters derived from structural, compositional, and textural features permit a limited quantitative treatment of the ferrite. Important textural parameters to be controlled for the optimization of the properties are grain size, porosity, and homogeneity. Parameters derived from compositional and structural features include magnetocrystalline and induced anisotropy. Conclusions are also drawn concerning the temperature at which the effects of internal stress and line imperfections appear to be the controlling features. Also, certain stress formulae of coercive force are reasonably applicable at the temperature of the secondary peak in permeability.

Other work deals with the second delineation of phase relations among oxide phases present in steelplant refractories. Specifically, a thorough study has been made of the system CaO-MgO-Iron oxides under experimental conditions similar to those encountered in steelmaking furnaces. The data obtained have shed much light on problems associated with tar-bonded dolomite brick which is finding widespread use as linings in modern oxygen steelmaking vessels.

Thermodynamic Properties of Solid Solutions

Present research is aimed at deriving thermodynamic properties of inorganic materials at high temperatures. Alloy phases, as well as oxide phases, of common structure types are being investigated.

Activity-composition curves have been obtained for Pt-Co, Pt-Ni, Pt-Mn, Pd-Fe, Pd-Co, and Pd-Ni alloys which are high temperature materials with interesting magnetic properties. Activity-composition relations have also been delineated for oxide solid solutions of periclase-, spinel-, olivine-, and pyroxene-type structures.

These results will permit the calculation of O+ equilibria among refractory oxide phases in which previously expensive experimental work would be required to predict reactions taking place at high temperatures.

Electrosynthesis of Metals and Alloys

The relationship between electrodeposition processes and the structural and mechanical properties of the resulting deposits was investigated. Such information is needed in commercial electroforming, a method of precise fabrication.

Two specific lines of investigation have yielded interesting information. In a study of the electrodeposition of brass, it became apparent that even for a constant composition of deposits, the mode of nucleation and growth was markedly affected both by the solution employed and by the nature of the substrate to which the deposit was applied. This means that, in the fabrication of electroformed alloys, both the mandrel and the deposition process must be selected with care in order to obtain the desired results.

In another area, it has long been known that hydrogen affects the mechanical properties of many metals. In electroforming nickel, a metal widely used in electrofabrication, some hydrogen generation is inevitable. The effect of this hydrogen on mechanical properties has been scarcely investigated in the past. In the present work, the effect of hydrogen has been found to be extremely variable, depending not only on the solutions involved, but also on the character of the electrical current used in the operation. In particular, a change from ordinary direct current to periodically reversed current may change significant stress at fracture from 230,000 to 109,000 psi., with, oddly enough, no change in ductility.

Structure of Electrodeposits

Aluminum-manganese alloys have been deposited from a fused-salt bath by the National Steel Corporation and show much promise as a substitute for tin in the plating of steel for can production. This project involved a study of the structural characteristics of a series of such electrodeposited alloys containing 0-25 per cent manganese. Those containing about 16 or more per cent of manganese were bright in the as-plated condition. Transmission electron microscopy and X-ray diffraction showed that the dull alloys consist entirely of supersaturated solid solutions of manganese in aluminum. Electrical conductivity work confirmed this finding. The bright, high-manganese alloys comprise two phases: (1) a supersaturated solid solution, and (2) an intermetallic compound,

$MnAl_6$. Although the appearance of the second phase is coincident with the beginning of brightening in the as-plated alloys, no definite cause and effect relationship has been established. Grain size of the deposits is small, and particles of the intermetallic compound are very small. The as-planted deposits containing $MnAl_6$ possess electrical properties characteristic of semiconductance, but heat treatment restores them to normal metallic behavior.

Crystal Structures of Yttrium Intermetallic Compounds

The objectives of this investigation are (1) to determine the crystal structures of yttrium intermetallic compounds and (2) to determine the nature of the bonding between atoms in these compounds. The element yttrium is a prolific compound-former, and it is often observed that in combination with one other metal as many as nine compounds may be formed. By determining and comparing the crystal structures of the intermetallic compounds which occur in the same binary metal system, it should be possible to state how fiexible yttrium atoms are in forming various coordinations for the different compounds. This sort of study is now nearly complete for the system yttrium-zinc. The structures of the compounds YZn, YZn_2, YZn_3, Y_3Zn_{11}, and Y_2Zn_{17} have been determined, and only the compounds YZn_5 and YZn_{11} remain unknown. For the known compounds, a regular progression of increasing B-atom coordination around A atoms, with both in the same layer, has been observed; it seems obvious that yttrium-zinc intermetallic compounds form on the basis of spatial considerations alone. The only compounds formed are those in which close packing of A and B atoms can be accomplished. Directional effects and the shape of the coordination shell seem to have no bearing on formation.

AB_4 Stoichiometry in Rare Earth Intermetallic Compounds

The purpose of this study is to resolve a disagreement between various investigators on the stoichiometry and the crystal structures of the intermetallic compounds which occur in the AB_4-AB_6 composition range (where A=rare earth and B=copper). $RECu_4$ compounds have been reported by some investigators, and $RECu_5$ by others, and the structures are claimed to be isostructural with $CaCu_5$. If the correct composition of the compounds is AB_4 with the $CaCu_5$ structure, there must exist a defect structure to account for the difference in stoichiometry. By making careful measurements of the intensities of X-ray reflections for a particular compound with favorable scattering characteristics, it should be possible to determine the nature of the defect structure.

Intermetallic Compounds of Yttrium

The phase boundaries in the yttrium-cadmium binary metal system and the crystal structures of the compounds which occur in this system are being analyzed. It is hoped (1) that information can be obtained on how yttrium atoms in solid compounds accommodate different numbers of cadmium atoms around them, and (2) that the bonding between atoms can be characterized. In this program, the phase diagram for the yttrium-cadmium system has been almost completely determined, and work on the crystal structures of the intermetallic compounds which have been discovered (YCd, YCd_2, YCd_3, YCd_4, and YCd_6) is in progress.

Transformations in AB_2 Intermetallic Compounds

While most AB_2 intermetallic compounds have a crystal structure which corresponds to the Laves-phase structure, a group of AB_2 intermetallic compounds (between Group II A or III B metals and copper or zinc) has been discovered which exhibits structures quite different from the Laves-phase structure. In addition, there is evidence that at least some of the compounds exhibiting this structure undergo a martensitic phase transformation upon cooling from high temperatures, producing a highly-twinned grain structure.

The objectives of this investigation are to study the crystal structures of many of these compounds and to characterize the transformation, if any, which occurs in each. In this program almost all possible $REZn_2$ compounds, as well as YCu_2, $ThZn_2$, and YZn_2, have been prepared. The occurrence of the unusual crystal structure for some of them has been confirmed, and the structures of $YbZn_2$, $DyZn_2$ and $ThZn_2$ are now being studied in detail. These compounds are also being examined by high-temperature X-ray diffraction and thermal analysis techniques in an attempt to characterize the transformation. The crystal chemistry of this structure-type is being examined in relation to a related structure, the AB_2-type, and the Laves-phase structure.

METEOROLOGY

The Department of Meteorology conducts a broad program of research with heaviest emphasis in three areas: (1) atmospheric turbulence (physical and statistical properties); (2) cloud microphysics

and dynamics; and (3) synoptic and dynamic meteorology. A great deal of original work has been done at Penn State in these areas.

In recent years the radar and cloud facility has grown rapidly and, together with the instrumented aircraft, now provides one of the finest research laboratories for cloud studies in the world.

Heat and Momentum Flux

A theoretical model of the wind flow in the atmosphere's lowest mile has been proposed and tested. This model accounts for the horizontal pressure and temperature gradients, the roughness of the ground, the rotation of the earth, and the rate of heating of the atmosphere by the underlying surface. It is now possible, for the first time, to make quantitative estimates of winds near the ground from the pressure analysis on weather maps. This model is potentially useful in providing low-level wind forecasts from numerical forecasts of surface pressure patterns, which are now being computed operationally up to 48 hours in advance from the dynamical equations of the atmosphere.

Time Variability of Atmospheric Parameters

High-resolution radiosonde observations were made at trihourly intervals for a period of five days at a network of U.S. Weather Bureau stations in the spring of 1964. The observational methods, the network locations, and the time of the observations were worked out by project personnel in collaboration with NASA. Simultaneous observations with conventional radiosonde equipment (GMD-1) and high-precision radar were analyzed to determine the limit of accuracy of these special observations. From the comparison studies and the network data, the time variability of atmospheric parameters will be determined to the smallest feasible time and space scales. The conclusions of this work will be applied to wind profile predictions for Saturn rockets launched from Cape Kennedy, Florida.

Cloud and Moisture Analysis

Analyses of five cases of extratropical cyclones over the United States will be made to determine the motion, cloud, moisture, and radiation characteristics. All available conventional observations and meteorological satellite and U-2 aircraft photographic and radiometric data will be used. Cross sections and isentropic analyses will be made and trajectories will be computed from the isentropic analyses to reveal the Lagrangian vertical motions.

An objective analysis scheme will be formulated to interpolate and modify the observed wind and height fields for use as initial

data in a primitive equation forecast model. The analyses of the case studies will be evaluated (1) to determine the type and scale of moisture and cloud features which maintain spatial and temporal continuity for at least 24 hours, (2) to determine the relationships of the cloud, moisture, and radiation features to dynamically important parameters, such as vertical motion and potential vorticity, and (3) to evaluate the usefulness of such relationships in making inferences from the satellite data in regions of sparse conventional information.

Mixing Processes and Radioactivity Transport

The purpose of this project is to study (1) the removal of radioactivity from the atmosphere by turbulent mixing caused by surface heating, producing dry fallout, and (2) the removal by mixing and entrainment in developing showers and thunderstorms, where it can be incorporated into the precipitation. Data collected in Project Springfield are being used. These include air filter sample analyses and weather data from aircraft flights, precipitation samples at Illinois and at The Pennsylvania State University, radiosonde data from U.S. Weather Bureau stations, and radar measurements at precipitation sites. Periods selected for study were April 17-19 and April 21-24, 1963. Cooperative studies with the Colorado State University will be made.

Stratospheric Objective Analysis

Synoptic analysis of conventional meteorological observations entails interpolation and synthesis. The accuracy with which meteorological data can be specified and the scale of the analysis are the bases for determining appropriate analytical procedures. Both factors were considered in this research concerning objective methods of analysis with particular reference to stratospheric data.

The first part of the project entailed the derivation of two relatively simple methods of estimating data accurately and the corresponding weight that should be assigned to the data in an analysis. Results obtained by applying these methods to a sample of aerological data yielded estimates of errors in the geopotential height reports which were considerably smaller than previously published values. The difference was attributed primarily to variations in the procedure used to calibrate radiosondes immediately prior to launching.

In the second part of the project, a theoretical study of the scale problem was carried out. From consideration of adjustment mechanisms in the atmosphere, it was shown that different observed parameters should define the different components of the analysis

according to scale. A method of accomplishing this objective through use of the calculus of variations (Sasaki's method) was devised, and a sample analysis was performed.

One of the most important problems involving the stratosphere is the manner in which mass, momentum, potential vorticity, and radioactivity are injected into the lower atmosphere. The process can be examined best by means of vertical cross-section analysis. The last part of this project dealt with an objective method of cross-section analysis. Again Sasaki's method was used to obtain an appropriate compromise between interpolated fields of different types of data. The results indicated that significant layer structure in the atmosphere can be outlined by this procedure. In most instances, this structure would be undetected by a simple combination of horizontal analyses of standard isobaric surfaces.

Ultraviolet-Integration by Plastics

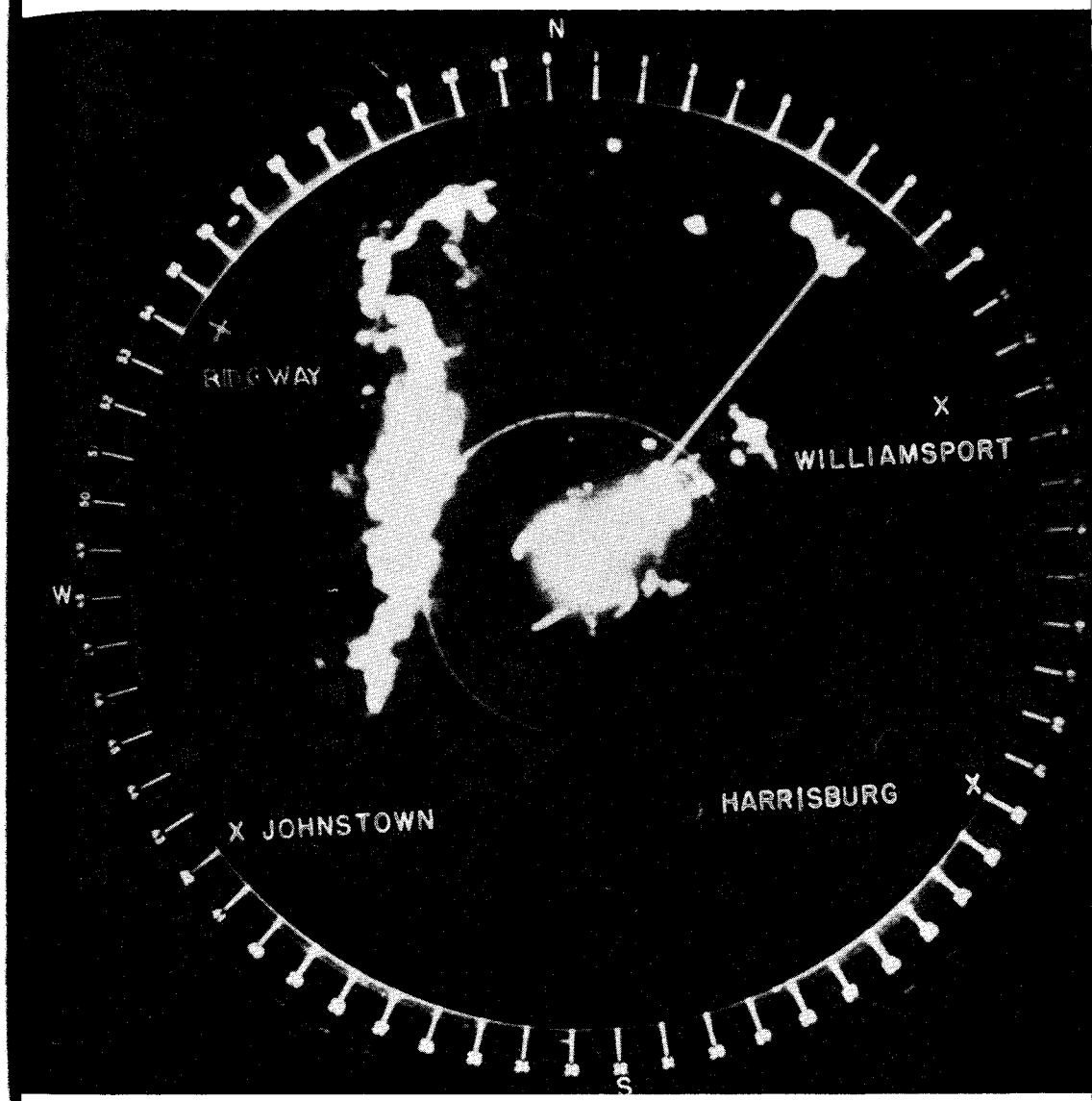
In preparation for studies of air pollution, in which the measurement of ultraviolet radiation from sun and sky is of significance, various plastics were tested for their suitability in integrating the long-wave ultraviolet radiation over one or more days. Three types of plastics were found to show considerable promise as inexpensive means for UV-radiation surveys. Under the influence of radiation in the wave-length range between 3000 and 4000Å, these plastics show diminished transmittance after exposure; this is due to depolymerization of the plastics.

Terminal Forecasting From a Small-Scale Network

In order to determine the concentration and nature of condensation nuclei, an automated fog chamber was designed in which artificial fogs were produced by expansion of air samples in a saturated environment. Attempts were made to correlate the density and sedimentation rates of the artifically created fog droplets with several meteorological parameters, as recorded prior to the formation and dissipation of natural fogs. This research is being continued with a fog tube based on a different principle, which may improve fog forecasting for aviation.

Analysis of Tower Data

Hour mean temperatures and wind speed were obtained from the instruments at Tyson's Corner, Va., for 69 periods. From these, Richardson numbers were estimated. The wind profiles were grouped by Richardson numbers and plotted for various wind directions. The variation with Richardson numbers is systematic in



Radar is used by University meteorologists in their study of air-flow patterns in mountainous areas as exemplified in the Appalachians of Central Pennsylvania.

the usual way. The plots also show the effect of terrain roughness; in some directions, roughness increases with distance, while in others it decreases. It is anticipated that the ratio of wind at 300-foot altitude to that at 100-foot altitude can be estimated well from mean wind direction and Richardson numbers near the surface.

Infrared Satellite Data and Meteorological Variables

One of the purposes of the weather satellite program is to supplement normal meteorological data for the purpose of improving weather prediction by means of the equations of meteorology. At present, meteorology data are particularly sparse in oceanic regions.

Unfortunately, satellites mainly transmit information on cloud formations, whereas information is needed for pressure, temperature, and wind velocity. This project compares infrared "window" radiation from the satellite with distributions of various meteorological variables, particularly over the ocean, so that upper air analysis can be improved with the aid of satellite information.

Clear-Air Turbulence

Clear-air tubulence between 25,000 and 35,000 feet is a serious problem in operation of jet aircraft, particularly since it is encountered without warning. There is now a theory which postulates the distribution of temperature and wind in regions where clear-air turbulence occurs. However, to check this theory, wind and temperature data of extremely good vertical resolution must be available. For some other purposes, special observations of wind and temperature were made during various periods. In this research, it has been determined — by using aircraft pilot reports — that clear-air turbulence occurred in the areas suggested by the theory. It is believed that some of the worst clear-air turbulence now can be avoided by circumnavigation.

Meteorological Analysis of Pennsylvania Air Quality Data

Air pollution is an increasing problem everywhere. The Pennsylvania State Department of Health is making simultaneous observations of meteorological variables and air quality at several sites in Johnstown, Pa., using two 150-foot towers. The Penn State group is analyzing the results in order to establish what combination of meteorological conditions leads to dangerous or uncomfortable levels of air pollution. Such information could be used by industry to change fuel or reduce operations on certain days. Similar studies are planned for Erie and Bethlehem-Allentown.

MINERAL ECONOMICS

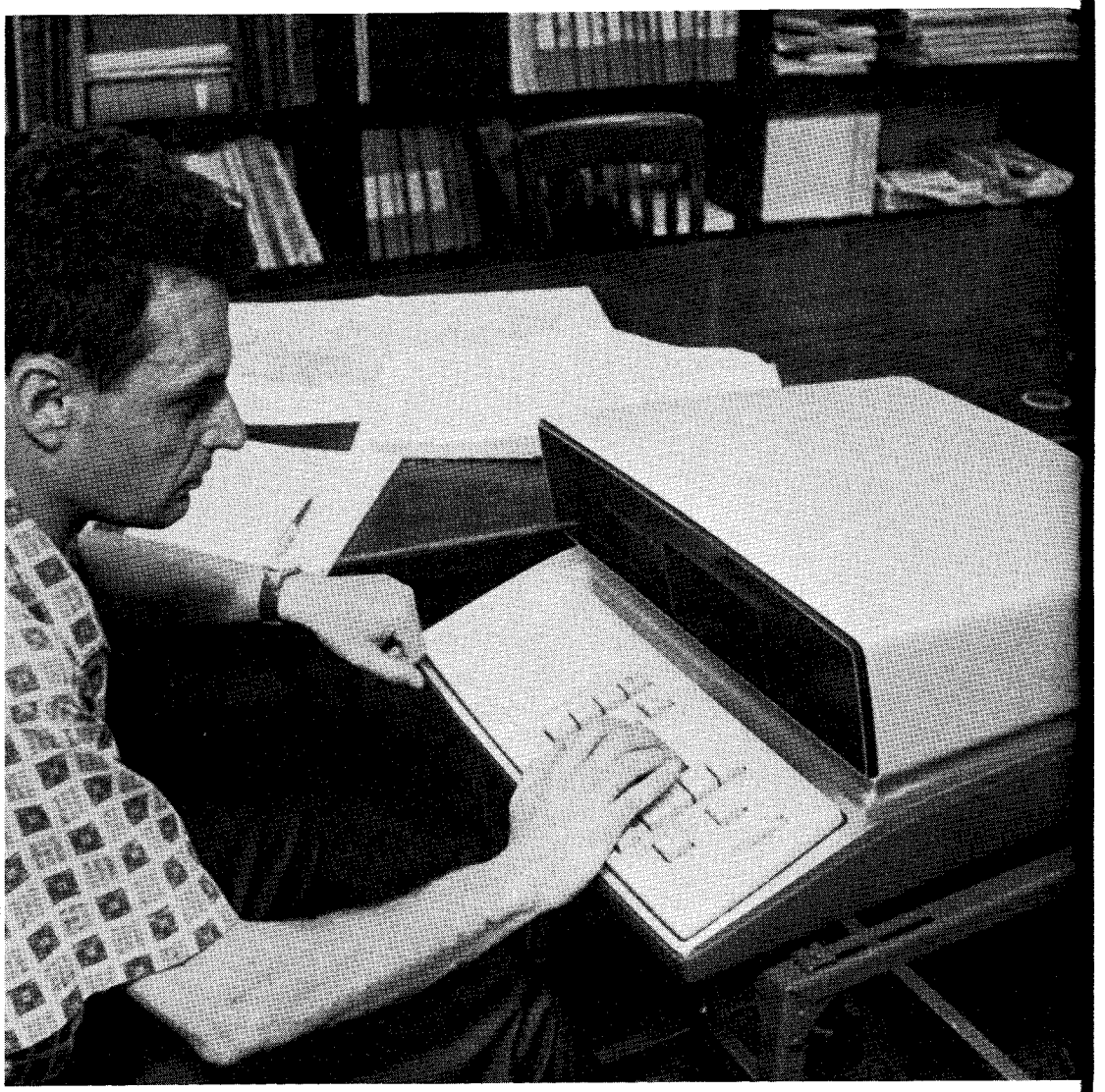
Within recent years research conducted by the Department of Mineral Economics has been increasingly concerned with quantitative methods of studying economic problems of the mineral industries. Although no mathematical approach can replace soundly collected, well-organized data, the use of mathematical techniques in the collection and analysis of such data makes possible a far greater depth and breadth of study than would have been possible by less exact methods. The use of computers for routine mathematical calculations required in such mineral-economic studies makes possible further gains in the scope and validity of the results and in the speed with which they are obtained.

At present, the department emphasizes studies on the impact of coal on the Pennsylvania economy; on the effect of electricity rates on the location of industry within the Commonwealth; on the relationship of the general cyclic behavior of business to the supply and use of mineral raw materials, particularly in the steel industry; and on the use of operations research techniques in mineral exploration, in investment analysis, and in decision making under uncertain conditions. More specific problems have also been studied, many of which are of immediate value to the state. These include studies of the aggregate industry in Pennsylvania, of the sources and uses of petroleum and coke, and of potential markets for fly ash. Thus, the department attempts to balance long-range, more theoretical studies with those that have direct and immediate application to the problems of various phases of the Commonwealth's mineral industries.

The department proposes to maintain this balance between the theoretical and practical aspects of its investigations and to emphasize those facets of its results that particularly benefit the mineral industries of Pennsylvania.

Economics of Mineral Industries in Pennsylvania

This project has been underway for several years. It has shown that the economics of the mineral industries in Pennsylvania cannot be compartmentalized for study within the boundaries of this single state. The problems of the mineral industries, therefore, have been considered on a national and international level since processing plants of the Commonwealth import many mineral raw materials from the other 49 states and from abroad. Studies have been carried out which considered: (1) the price of gold and its effects on the economy at large and on the mineral industries, (2) the ex-



Both small and large computers are used by mineral economists to analyze problems of the mineral industries.

ploitation of copper resources in a sample state (Arizona), (3) the rules that govern trade in mineral raw materials, (4) the mineral requirements and supplies for the United States and the world, (5) the problems of mineral exploration, and (6) the national mineral policy. Other studies of this character are being carried out or are planned, such as the impact of the exploitation of iron ore reserves on the economy of Brazil and the problems of producing and trading in energy-producing materials in Argentina.

Mineral Supply and Business Cycle

An attempt is being made to demonstrate and explain the relationship between fluctuations in general business conditions and the production and sale of and the international trade in mineral raw materials. Considerable data have already been obtained about the raw materials used in steel in both the United States and Western Europe. The American data have been seasonally adjusted and charted.

Aggregates

The natural aggregate industry of Pennsylvania (sand, gravel, and crushed stone) have been analyzed. In this analysis, the nature of the industry, economic factors, and the relation between aggregate availability and market use were considered. Present research is concerned with industrial and mining mineral wastes as potential sources of aggregate in Pennsylvania. Information is currently being gathered on materials such as iron and steel slag, cinders, fly ash, waste slate, and coal mine waste. Some of these materials have already received wide acceptance as aggregate materials, while others are still in the early stages of development. It is hoped that a better understanding of the economic problems of these raw materials will point the way toward use of these materials. Not only would this solve a disposal problem, but it would lead to better utilization of the mineral resources of Pennsylvania and remove some of the pressure on reserves of other aggregates.

Classification of Ore Deposits

A new method of classifying ore deposits — on the basis of the genetic processes that produced them — is being tested. It should give their ages or the time at which such depositions occurred. Deposits from all parts of the world have been examined. When all of the data have been assembled, they will be analyzed on the IBM 1620 computer. If the result shows that the distribution of deposits is probably not due to chance, a definite step forward will

have been achieved in the search for new ore deposits hidden under various types and thicknesses of rock cover. It will be possible to predict with greater confidence the spatial and temporal associations of ore bodies.

Coal Economics

The effect of electricity rates on industrial location is being investigated. Pennsylvania was chosen as the most convenient and suitable area for study. A field study has been made of electrical rates through the years in Pennsylvania, utility system by utility system. Government data on employment, number of individual industrial enterprises, and value of manufacturing have been collected for these same years and correlated with changes in the rate structure.

Petroleum Economics

Two major studies in petroleum economics have been undertaken. The first was a complete investigation of sources and utilization of petroleum coke. The study was the first in a series on non-fuel uses of petroleum, an aspect of the end-markets of petroleum which has received little attention in research on the economics of the industry. In addition, a better understanding of the qualities of petroleum coke and the reason for its commercial acceptance was needed as part of a parallel research project on the non-fuel uses of carbon.

The second was a study of the role of host governments in the future development of world oil production. Many of the nations which possess the bulk of the world's known petroleum reserves will be eager in the future to play a more active role in the development of their petroleum resources, as well as to receive a larger share of the profits. The investigation covered the historical development of relationships between host governments and the major international oil companies. Recommendations were also made concerning the best policies and practices for the host governments to follow.

Economic Importance of the Coal Industry to Pennsylvania

A detailed analysis of the economic impact of the various bituminous and anthracite coal mining enterprises in the state is underway. The contribution of primary coal producers, their suppliers, and customers (in providing employment, attracting new industry, and adding to community and state income) is being assessed. A pilot survey was conducted in Indiana County prior to circulation of a state-wide questionnaire. The survey showed that

a majority of the revenues received from the sale of coal is spent in the area where the coal is mined. Of the $25 million value of Indiana County coal production, over $11 million was paid directly as wages and salaries and another $5 million was spent with local distributors of parts and supplies. These funds were spent for goods imported for consumption and use by coal company employees or by the companies themselves. Over $2 million was spent to purchase future social benefits for coal mine employees through such programs as the Miner's Welfare Fund and Social Security.

Despite the restricted nature of the present analysis, the study has already yielded supplemental results that may be valuable to the future of coal mining and utilization in Pennsylvania. For example, a continuing education program for coal industry managers is under active consideration. In addition, the electronic data processing of Pennsylcania coal production records for 1963 may prove to be of future value in preparation of Department of Mines and Mineral Industries reports.

Carbon Markets

The first of three studies of the carbon markets was a complete analysis of activated carbon, primarily through direct interviews with producers and through letters or questionnaires to consumers. It was determined that the market is highly segregated among existing producers, that entrance into the market might be difficult for new producers, that the market for activated carbons to be used in processing is the most attractive portion, and that the outlook for activated anthracite could be favorable if certain technical information were available and if an existing producer chose to start using anthracite.

A second study was directed toward the use of carbons for electrodes. In this, all of the carbon materials used for electrode fabrication were studied to determine cost and/or physical factors that control their acceptance by various electrode producers. Also, users of electrodes were consulted for their views on the acceptability of electrodes in current use. Although coal has been accepted as a raw material in certain parts of the electrode industry, it was not expected that this market could be enlarged until coal could match the attractive features of petroleum coke.

The third study, now nearing completion, is similar to the electrodes investigation, but covers crucibles and related products. A final investigation of the remaining markets, most of which are either small or offer little known attractiveness as potential new markets for coal, has just begun.

Potential Markets for Fly Ash

Research was conducted to determine whether fly ash passesses any physical or chemical characteristics that would make it either technically adaptable, or commercially feasible, for new uses in Pennsylvania. The investigation started with a survey of known uses of fly ash, both in the United States and in other parts of the world. This was followed by visits to power plants producing fly ash in Pennsylvania to determine quantities, physical form, and current disposal practice. The final phase of the work was to identify those markets which offered some promise of being both large enough and sufficiently practical from a technical standpoint to warrant further study. Methods for further market investigation were suggested.

Operations Research in Mineral Resource Development

The application of operations research techniques to problems in mineral exploration and mineral investment analysis is being investigated. The ultimate objective in the first of these areas is to optimize the search for new mineral deposits. Research has thus far been devoted to determining a methodology in which the concepts of mineral wealth, geology, and probability can be related. It has been found that geologic information at the reconaissance level can be quantified by constructing measurement variables. With these variables, the multiple-discriminant model and the classification model — based upon the multivariant normal probability distribution — constitute two-phase probability models of geology and mineral wealth.

Research in the second of the general areas has been directed toward optimizing the allocation of a fixed budget (under conditions of uncertainty) to various investment alternatives that might be available to a petroleum producer. It was found that dynamic programming and simulation on the electronic digital computer provide a means of solving this complex decision problem.

Mineral Industries in Pre-Modern and Modern China

The development of certain mineral industries in China from the 18th to the 20th Century, with emphasis on iron, coal, and copper, has been traced. The organization, technology, management, and government policy with regard to these industries during the traditional period are presented through material gathered from Ch'ing dynasty sources. In the late 19th Century, a number of changes began to take place that were to affect later development; the deviations from old practices and policies, as well as attempted adjustments to new conditions in the economy, are described. The place of the mineral industries in the traditional economy will be compared with their role in the modern period.

Chinese source materials necessary to the completion of the project were consulted at Harvard University. As a result, certain specific points in the inquiry were clarified, including governmental regulations concerning copper transportation, the composition of mining labor during the Ch'ing period, and the type of personnel appointed to staff the first provincial mining companies.

MINERAL PREPARATION

The objectives of research in the Department of Mineral Preparation are:

1. To discover and use fundamental principles and relationships which will allow economical but adequate mineral processing;
2. To characterize available mineral resources and understand the specifications for products which will assist in mineral preparation procedures and processes;
3. To design machines and plants for mineral preparation and to construct and test working models and pilot plants; and
4. To evaluate the economics of mineral preparation processes.

The specific categories in mineral preparation now being investigated include:

1. COAL. The largest program in the department covers most phases of coal preparation. Fine coal cleaning, sulfur reduction, preparation of coal for special uses, comminution and grinding procedures, and fundamental flotation studies are carried on.
2. COAL BY-PRODUCTS. The preparation of coal refuse to prevent air and water pollution, to create useful products (lightweight aggregates and fillers, investigation of the properties of fly ash basic to its preparation for special uses), and to aid in dust collection are objectives of present research.

3. METAL ORES. Beneficiation studies of iron, aluminum, chromium, molybdenum, rare earths, and the less common materials (thorium, tantalum and niobium) are conducted.

4. NON-METALLICS. Beneficiation of silicates, clays, and silicon carbide is investigated.

5. WATER PURIFICATION. Application of mineral preparation processes: flotation, interfacial phenomena, solid-fluid separation, purification of sewage effluents, minimizing stream pollution from mine drainage, improving inplant water supplies, and preventing stream pollution from industrial sources.

6. FLOTATION THEORY. Measurements of streaming potentials and zeta potentials of various minerals and coal macerals, synthesis of flotation collectors with chelation characteristics, flocculation studies.

7. BENEFICIATION THEORY. Electromagnetophoresis, cyclone mechanisms, following film processes, system engineering.

8. COMMINUTION. Study of the Hardgrove grindability method, attritional scrubbing, development of comminution theory.

Elimination of Air Pollution From Burning Refuse Piles

Coal refuse piles that have been ignited either by spontaneous combustion or by external causes are a serious atmospheric pollution problem. A method of eliminating this problem is the removal of combustible material present in the refuse piles. A detailed study has been made of the distribution of combustibles in refuse piles by size and specific gravity, as a design basis for a process to beneficiate these piles. Tests are being performed to better define the combustion characteristics of such beneficiated refuse. These data were utilized in establishing a flow sheet for processing bank material into a clean, non-burning refuse and a low-grade fuel. Heyl and Patterson, Inc., Pittsburgh, has been selected to build a 50-ton per hour pilot preparation plant. The first test location selected is Spangler. Operation of the pilot plant began in February, 1965. Evaluations will be made of the degree of technical and economic success of the operation as a feasible approach to the elimination of air pollution from burning refuse piles.

Reduction of Ash and Sulfur in Bituminous Coals

Several approaches have been considered to reduce ash and sulfur in the preparation of the finer sizes of Pennsylvania bituminous coals. A detailed study of the "classification-design" cyclone has indicated its favorable attributes in regard to solids concentration, slime removal, ash reduction, and size separation, and its basic incapabilities in separating a coal product low in pyrite content. On the other hand, tests with small angle cyclones show encouraging results. Preliminary tests for separation by electromagnetophoresis are most interesting. Using a sodium chloride electrolyte, a magnetic field of 10,000 gauss, and a current density of 0.7 ampre per cm^2, successive float products varied between 4 per cent and 7 per cent ash and reject products contained 68 per cent ash.

Removal of Impurities from Drainage Streams

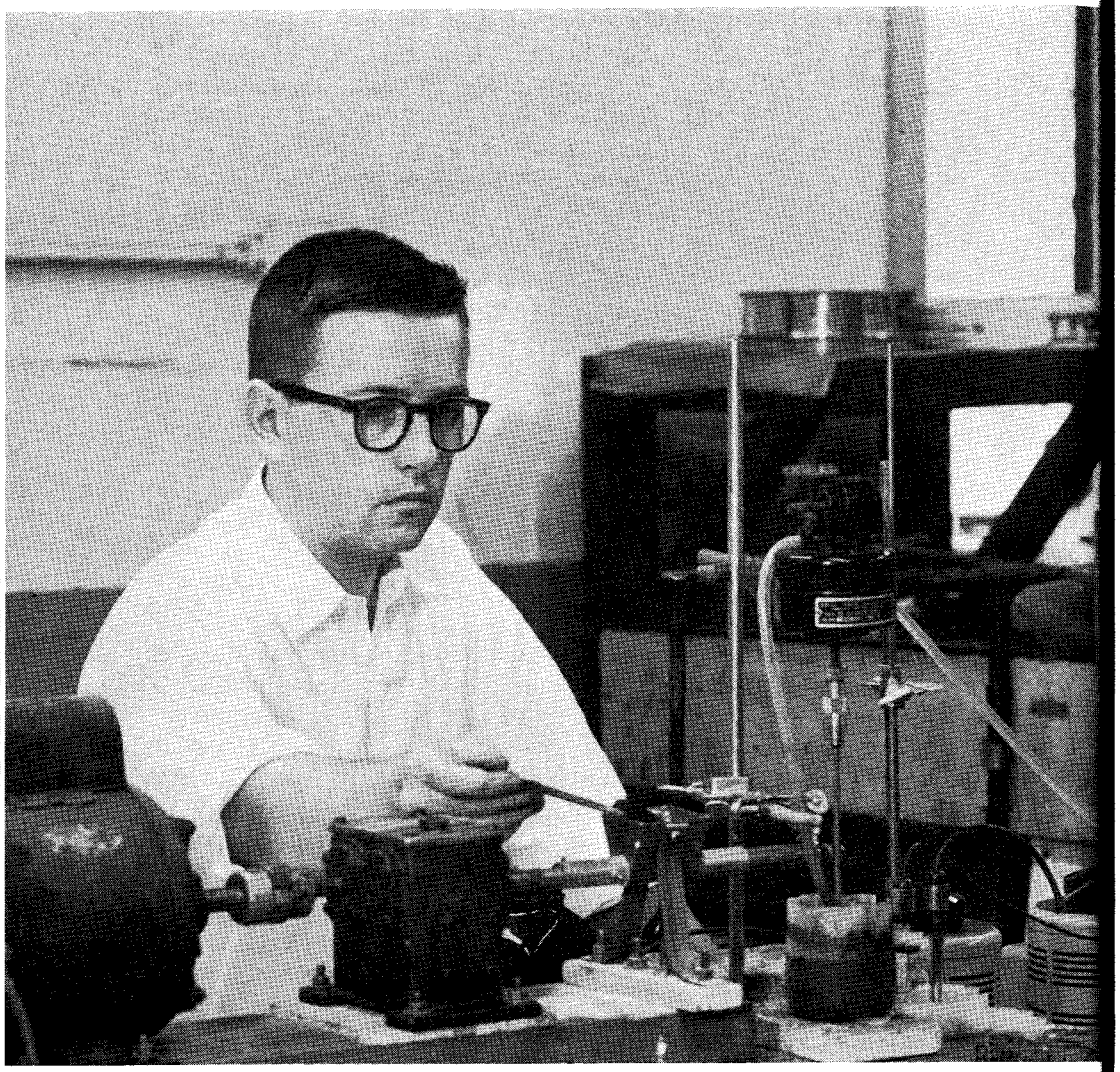
The basic goal of this project is to prevent contamination of the major Commonwealth waters by removal of mine drainage pollutants in their more concentrated form from the smaller streams prior to dilution. Especially of interest is the possibility of using finely-divided coal for this purpose. Such treatment will improve the quality of acid-iron polluted water, resulting in a decrease in acidity and iron. The nature and feasibility of the treatment is being considered.

Sewage Effluent Purification

This investigation is being carried out on a reversed system wherein a sewage effluent, which is a dilute aqueous solution carrying pollutants, is treated with an added solid phase, an avaliable, inexpensive material such as coal or fly ash, in order to transfer the pollutants to a froth flotation product, producing a purified water effluent. Pursuant to information obtained from various bench scale and small pilot plant studies (at flow rates up to 30 gallons per minute), a process is being evolved which is capable of removing in excess of 90 per cent of ABS substances, 60 per cent of materials contributing to COD, and 90 per cent of total phosphates from municipal sewage effluents. The unit operations will include conditioning, flotation, and solid-fluid separation. It appears that the final effluent will contain less than 20 ppm suspended solids, while the collapsed froth volume will be less than one per cent. The solid materials added and recovered have potential uses and will be small in quantity. The proposed process appears technically feasible for substantially reducing sewage effluent pollutants at a high capacity and low cost operation.

Properties of Fly Ash

The physical and chemical properties of fly ash which affect its beneficiation and utilization have been analyzed. Among the prop-



The use of coal to treat mine drainage is analyzed by a mineral preparation engineer.

erties which have been considered are size, absorptive capacities, and surface and magnetic characteristics. A series of tests were made with a new device which sizes the larger fly ashes which result from most of the larger stoker operations.

Rare Earths

A variety of topics has been considered under the title of this project over a number of years. Among these are rare earth mineral flotation, rare earth thermite reactions, preparation of niobium, tantalum, and other high-melting metals, preparation of special rare earth salts, and complex analytical chemical problems.

Currently, efforts are being directed to the recovery of molybdenum from waste products. This is timely because of the shortage of molybdenum and because of the stage of development of the flotation theory for materials with oxidized surfaces. Grades and recoveries which appear feasible have been determined. Other phases which are being studied include preparation of a complex columbium ore which is especially interesting due to its thorium content.

Anthracite Refuse

The removal of old and current anthracite refuse piles through the utilization channel is the objective of this study. Active and stored refuse is being sampled and tested in order to determine if a low-grade fuel of about 9000 BTU/lb can be produced at a marketable price. The rewash rejects may be useful to industry. There are many facets of this overall project. They include economic transportation studies of the low-grade fuel from the preparation plant to the consumer. A pipeline study has been completed, but rail, truck, and conveyor studies remain to be done. Studies to ascertain the suitability and feasibility of rewashed products for highway materials, lightweight aggregrate, and cement are in progress. A report has been completed on the mechanics of refuse disposal by underground stowing.

Anthracite Preparation

The improvement of the combustion characteristics of Pennsylvania anthracite, in an effort to make it more competitive at home and abroad, is the subject of investigation. Raw coals are given various degrees of beneficiation. The resultant products are then assayed and compared to foreign coals. An attempt is made to correlate the coal and ash properties with actual combustion performance.

Disapore Clay

This project is aimed at establishing an effective method or combination of methods, such as flotation and gravity concentration, for upgrading Pennsylvania disapore clays. The resulting high-grade disapore clays, being free from iron and silicate impurities, will find their market not only in the ceramics industry, but also in the aluminum and abrasive industries.

Concentration work shows that the silicate impurities of a Pennsylvania disapore clay could be lowered considerably by means of amine flotation. Tests will be carried out on the removal of iron impurities, which are objectionable in the sulfuric-acid extraction of alumina from disapore clays. Extraction work shows that silica up to 10 per cent is not a deterrent for the extraction of alumina from a disapore clay, Chinese bauxite, by means of ammonium sulfate.

Benefication of Abrasive Materials

A suitable method or a suitable combination of methods for the removal of impurities from industrial silicon carbide is being sought. Mineralogical studies show that the main impurities are graphite and various forms of silica. Concentration tests reveal that the coarse-size fraction can be upgraded by means of gravity methods in conjunction with a high-tension electrical process, while the fine particles can be beneficiated by froth flotation. Samples used in this investigation consist of several kinds of furnace products.

In the process of investigation, the electrostatic behavior of both silicon carbide and silica has been studied with the aid of a newly-constructed distribution analyzer. The electrokinetic behavior of silicon carbide has also been studied in a streaming potential apparatus.

Fine Coal Cleaning, Sulfur Removal, and Evaluation of Grindability

The phase of these studies active at this time is concerned with coal lithotype flotation mechanisms. The anthracite and bituminous coal lithology theory, electrokinetic characteristics, flotation mechanisms, and separation techniques are being considered. Many different properties of coal lithotypes have been measured. Electrokinetic results of completed work indicate that the surface adsorption characteristics of anthracite lithotypes are different. The isoelectric points occur between pH values of 3.5 and 5.5 for vitrain and 2.0 and 4.5 for durains and fusains. It is concluded that hydrophobicity of anthracite lithotypes vary for different seams and is pH-controlled; thus, the flotation rates vary.

Present emphasis is being placed on bituminous coals. Included is the associated response of collectors, frothers, inorganic electrolytes, and organic depressants.

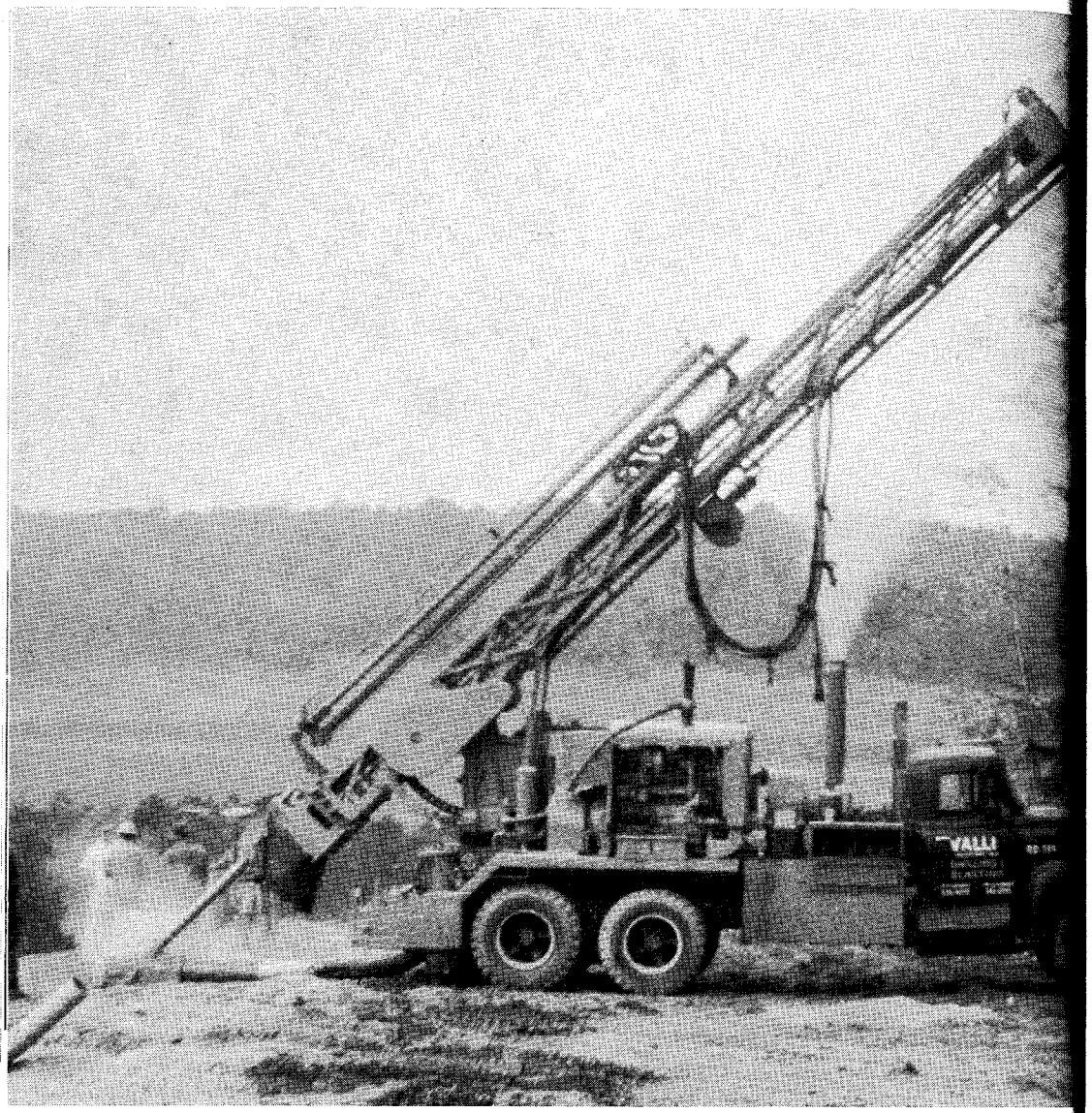
Another phase of the project is concerned with the theoretical and practical aspects of the pulverization of coal based on the Hardgrove grindability. It includes experimental, theoretical, and mathematical work dealing with factors affecting the pulverization of coal and the Hardgrove Grindability Index. Four Pennsylvania coals, from anthracite through high volatile (A) bituminous, were used. This study indicates that inaccurate H.G. Indices may result from a variation in the size-consist of the 50 gram (1190 x 595 micron) feed sample, segregation of the sample as indicated by ash content, and inaccuracy of the 200 mesh screen aperature. Methods of compensating for these inaccuracies have been suggested. The resulting analysis of the fundamental energy-size relationship in the comminution of solid materials led to the derivation of a new equation.

MINING

The Department of Mining has developed strong instructional and research programs in the following areas in which the future of mining engineering is thought to lie: rock mechanics, operations research, and mine environment control. A few years ago, practically all research in the department was in some phase of rock mechanics: drilling, blasting, strata control, and fundamental behavior of rock under loads.

Rock mechanics research has continued to increase with the greatest rate of growth in strata control: underground support, stress distribution, and subsidence. Operations research techniques are being applied increasingly to a wide variety of mining problems. Specific projects include: haulage simulation, unit train applications, and optimization of mine production systems. Within the past year, research in mine environmental control has been accelerated and two specific projects are underway: acid mine drainage and gas and dust control.

The pioneering efforts of the department in these areas are widely recognized and the department expects to remain in the forefront. The Rock Mechanics Laboratory is especially well-equipped for the work undertaken in the rock mechanics area. The excellent facilities which the University's Computation Center and



Slanted drilling methods are studied by mining engineers.

the College of Mineral Industries' IBM 1620 satellite computer offer have stimulated the application of operations research to mining.

Rock Drillability and Crater Formation

PART I. Study of fractures produced by a drill bit: Preliminary drilling experiments with a drop-tester apparatus for dynamic loading and hydraulic press for static loading have shown that there is a significant difference in crater volume per unit energy input under the two loading conditions. There is also a significant difference in crater volumes for each loading method if rock type is varied. Penetration rates ranged between 0.002 and 0.015 inches per second for static loading; for dynamic loading the range was from 4 to 35 inches per second. The ratio of dynamic to static test energy consumed per unit crater volume ranged from 5.7 to 7.2 for Vermont marble and from 1.9 to 5.5 for Bedford limestone.

The present objective is (1) to explain the larger amount of energy consumed, per unit crater volume, by dynamic tests than by static tests and (2) to explain different energy consumptions per unit volume for different rock types. Preliminary manipulations suggest that a rheological model, such as a Burgers visco-elastic model, might describe the difference between static and dynamic tests. A model centered on the significance of the ubiquitous central extension fractures might be operationalized to explain differences among different rock types.

PART II. Effect of rock properties on drillability: During the last six months of 1964, most of the work was devoted to the preparation of triaxial testing equipment; however, a few preliminary tests were performed. This apparatus permits triaxial compression to be made of rock specimens, with the application of pore pressure through the bottom of the specimen. The working capacity of the chamber is 10,000 psi for both confining and pore pressures.

Preliminary triaxial compression tests were performed, with and without pore pressure, for both dry and water-saturated Bedford limestone cores, one by two inches. Results indicated the following:

(1) The compressive strength of the dry specimens is higher than the strength of wet specimens at all confining pressures.

(2) The total deformation at the yield strength of dry specimens is higher than that of water-saturated specimens for a given confining pressure.

(3) The compressive strength increases with the confining pressure at a given pore pressure, both for dry and wet specimens.

After further modification and instrumentation of the apparatus, experiments will be conducted to study mechanical properties and elastic constants of rocks which may contribute to the knowledge of the drillability of rocks.

The Effect of Stress Waves in Rock Impact

A three-dimensional photoelastic stress investigation is underway to experimentally determine the stress concentration at the bottom of a borehole. The analysis is being conducted by the "frozen stress technique", using araldite. To simulate the bit load, a weight is applied through a chisel bit which rests on the bottom of a cylindrical hole drilled in the model. Point-by-point values of stress are obtained by the method of shear difference. In addition to the experimental investigation, the possibility of obtaining a numerical solution to the problem is being studied. The method under consideration is capable of analyzing the elastic stresses as well as the plastic flow which may occur in the region beneath a chisel-shaped bit.

The investigation also entails the impact of a wedge-shaped tool on a photoelastic plate and the recording of data by means of ultra-high-speed photography. The camera, which is capable of taking up to half-a-million frames per second, was designed and constructed in the laboratory. The tool shape, blow energy, impact velocity, specimen material, and boundary conditions are the parameters under study, and it is intended to determine their influence on fringe information, critical shear, stress at crack initiation, crack propagation velocity, and surface markings. Measurement of crack propagation velocity has been the primary aim so far. It is believed that the crack begins at low velocities of 500 feet per second and accelerates to a constant velocity of about 1400 feet per second for Columbia Resin CR-39. A theoretical analysis is planned in which the displacements and stresses within the plate will be determined.

Strip Mining and Land Restoration

An economic feasibility is being conducted which will lead to the development of a model to permit simultaneous continuous strip mining and land restoration. The main goal is to achieve maximum land restoration in Pennsylvania's strip mining areas at minimum costs. Results include: (1) Blast tests designed to slope the highwall at an angle of 45° have shown that the cost of explosives in 45° holes, and hence the drilling performance of this model, was not satisfactory. Further tests with a suitable drill are required.

(2) Several blasts where the overburden is thrown out to the spoil bank by explosives have been surveyed and studied. (3) About 80 mines located in Pennsylvania, Ohio, Indiana, Kentucky, Missouri, and Illinois were visited. In each mine, time studies on drill, shovel, and draglines were carried out, and more than 400 protographs were taken. Information on cost data has been gathered. The problem of land restoration and various approaches to its solution under different conditions has been studied.

Optimization of Mine Production Systems for Low Cost Mining

Decision problems in the following areas of mine organizational design are being considered:

(1) A model to predict the optimum design of belt conveyor systems.

(2) A model to predict the optimum design of rail haulage systems.

(3) A model to derive a set of decision rules for mine production scheduling.

The above models have been written and are currently being tested against a real situation. Models 1 and 2 are stochastic and standard simulators, respectively, and are being tested at a Central Pennsylvania coal mine. Model 3 is a linear programming model written in the context of a coal mine operating in the Pittsburgh seam. The objectives involve constraints on producing and stockpiling abilities, available resources, and systematic development plans.

Mine Operations Research

Research was proposed for the development of a non-automated integral train system to be located at a centralized transshipment point where the overall transportation charges as an economic factor would be minimum. This centralized location would contain the expensive storage and loading facilities necessary for integral train operation, thereby eliminating individual requirements for this costly auxiliary function.

These objectives have been incorporated into a mathematical model formulated under the "systematic" and "genesis of linear programming" methods. This model was written for the analysis of rail traffic problems as they exist in the shipment of coals from multiple mine sites located in the open-pit region of Central Pennsylvania. Coincident with model formulation, questionnaires concerning the necessary operational data for model input were sent

to the various coal mining enterprises located in the area. Currently the data are being coded for a simplex solution. An activity analysis code, designated as P.S.U. Library Program S.G. 1001 Loader, is being explored.

Microseismic Activity in Rock

Rock under stress generates subaudible seismic disturbances. Little is known, however, concerning this phenomenon. The objective of this program is to correlate microseismic activity in rock with factors of deformation, so that the process of rock deformation may be correlated with stress level, time, repeated loading and unloading, and time of rest periods between repeated loading. Other factors which may be investigated are anisotropy and elastic and inelastic strain.

Several rock varieties are under investigation. The intensity and nature of microseismic activity generated by rock when subjected to external stress seems to furnish a powerful tool which can be used to obtain a better understanding of the behavior within the interior of a rock specimen. Such information would, of course, be of immense value in detecting incipient failure and predicting the life of rock structures.

Subsidence

More than 100 letters have been dispatched to coal mining companies in the Commonwealth of Pennsylvania to determine the extent of subsidence studies conducted by industry and the nature of data obtained. Thus far, the response has been very poor, with only eight companies replying. It appears that little work has been done in connection with the problem, except by the U.S. Bureau of Mines. One of the mining companies in Central Pennsylvania has agreed to allow an investigation on its property, and several stations have been laid out in a grid pattern over a butt entry. These have been surveyed by triangulation to an accuracy of $\pm$ 30 seconds leveled correct at 0.01 feet. Other stations are planned whenever weather permits.

Underground Stress

The influence of rock creep on anchorage characteristics of rock bolts has been studied. Testing has revealed that the major cause of tension loss is due to the migration of the leaves into the rock at the periphery of the hole, permitting displacement of the plug with a resultant load release. The tendency of rock creep to reduce the coefficient of friction along the leaf-rock interface, permitting a displacement of the anchorage assembly as a unit, has been found to be significant. In addition to the physical factors of the shell and rock, installation load and procedure, moisture, and retightening effects were evaluated. Cementation or grouting techniques employing epoxy resins and polyesters have been found to improve the bleed-off characteristics of a bolted installation. Field investigations are now underway to obtain absolute and relative convergence measurements which would be employed to determine the effects of seam characteristics, strata, and physical mining factors.

Roof Bolts

Since excessive bleed-off occurs with two-point anchorage, other methods or techniques of anchorage are desirable to improve bolt performance. Research to date reveals that the configuration of the commercial anchorage shell results in high stresses being induced at the shell-rock interface. Since the deformation of rock is time-dependent, as well as stress-dependent, creep in the rock results in a displacement of the entire bolt assembly. With the resultant loss of tension on the bolt, the friction along the rock-bedding planes is reduced, and bed separation ultimately occurs. Thus the object of this research is to improve the long-term capability of the anchor. Two methods of accomplishing this are being investigated: (1) distributing anchorage along the entire borehole using resins, and (2) belling out of the hole at the anchorage site to increase the area of shell contact, thus reducing the rock stress to a low value and minimizing creep.

Control and Disposal of Mine Water

Research to date has been concerned with abatement and disposal of acid mine water to help minimize stream pollution. From field data concerned with abatement, the following conclusions can be made:

(1) All coal seams sampled produce acid drainage.

(2) Water entering underground mines is generally neutral or slightly alkaline.

(3) Acidity increases with the time the water is in the mine.

(4) Gob run-off, in all but one of the cases studied, was very acid.

(5) Slate dumps produce much acid during periods of precipitation.

From the information gathered to date on disposal wells, the following conclusions can be made:

(1) Wastes similar to acid mine water are presently being successfully disposed of by injection wells.

(2) Injection pressures for these wells are very variable.

(3) Possible chemical reaction between the acid mine water and the formation rock is of primary concern.

(4) Plugging of the formation pore spaces by autotrophic bacteria is a potential problem.

(5) Reactions observed in the laboratory may differ in the formation environment.

(6) A depleted gas horizon would be a good disposal zone, since much information is generally available on the reservoir properties.

(7) Any disposal would have to be physically isolated from zones of fresh water and producing petroleum zones.

(8) A general injection well and surface plant could be designed at the present time.

Slate Mining and Processing

The purpose of this project is to provide service and conduct research which will benefit the non-metallic mining industry of Pennsylvania, with emphasis on slate. Areas investigated include: utilization of waste slate, rotary drilling and slate planing, and applications of management science.

(1) Use of waste slate: Technical and economic factors have been explored in the manufacture of composition slate from powdered slate and a resin binder. Two inventors have independently developed such processes. One slate quarrying firm has commenced a small pilot plant study. The market for the product appears to be good. Its potential uses include electrical insulating panels, chalkboard, billiard table tops, and structural panels.

(2) Rotary drilling and slate planing: Laboratory experiments were conducted to investigate the effect in rock cutting of bit clearance angle, flushing medium and flow rate, and temperature using a form of drag-bit rotary drilling. The principal parameters measured were penetration rate and bit wear. In addition, a new clamped-on type slate planer blade was designed, fabricated, and field tested. The new blade performed very well, practically eliminating the breakage encountered during planing operations

with the presently utilized equipment. An operational problem developed in that there are no adequate facilities at the slate quarry mill to resharpen the blades satisfactorily, but this problem should not be insurmountable.

(3) Applications of management science: Studies and investigations have resulted in a report on capital investment planning. A computer program was developed for the calculations. The new field of management accounting has been studied and a preliminary paper has just been written.

Effective Measures to Combat Mine Disasters

Mine disatser research has been conducted in the areas of strata control, ventilation, and gas monitoring. One underground stress installation has been completed. This installation included differential sag measurements and load loss on roof bolts over a period of time. Results include:

(1) In a normal bolting procedure, a wide variation in installed bolt loads was detected.

(2) Bed separation was detected at two different horizons. The magnitude of each bed separation was cosiderable.

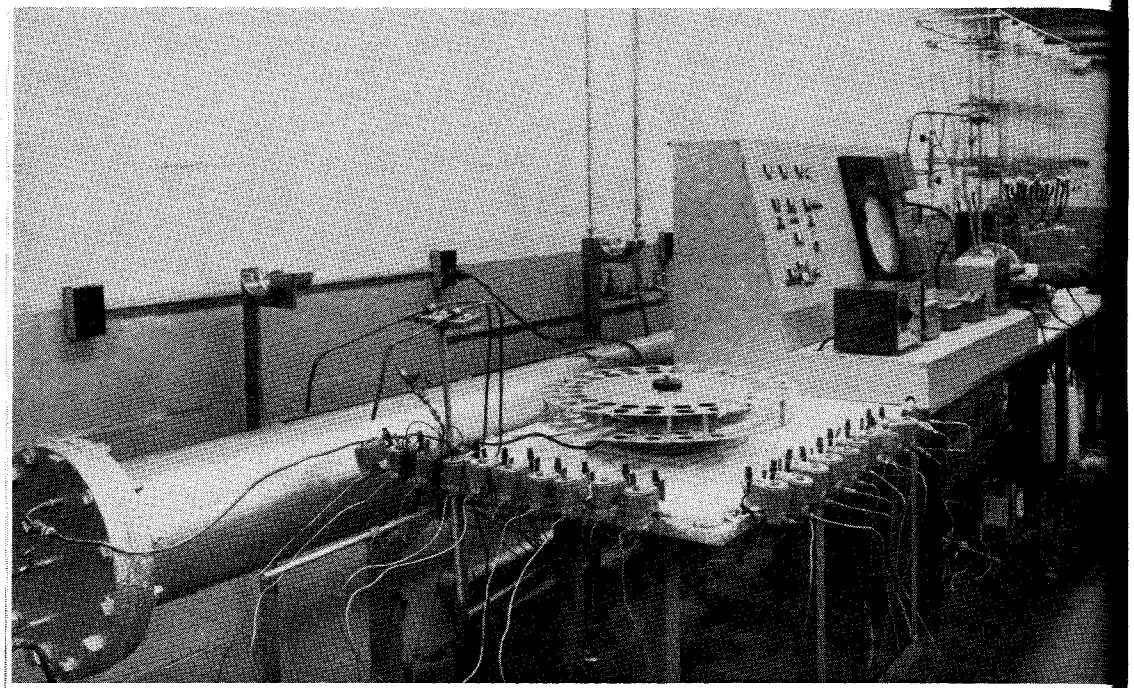
(3) Blasting had a very adverse effect on bolt loads. A perceptible drop occurred each time blasting took place, and actual bed separations occurred during blasting operations.

A new type of ring cell bolt load dynamometer has been developed, tested, and produced in quantity. Future underground installations will be made with the new equipment.

PETROLEUM AND NATURAL GAS

Research in petroleum and natural gas is designed primarily to provide fundamental knowledge in the areas of petrophysics and fluid flow in porous media. Emphasis is given to research in the miscible and immiscible displacement of crude oil and other fluids from porous media.

The physical displacement of fluids from porous media is of particular interest to the petroleum industry. Pennsylvania fields long have been produced by techniques of secondary recovery — these processes, although economic, leave relatively large amounts



One of the largest sandstone cores of its type in the country is used in experimental studies by a petroleum engineer.

of petroleum unrecovered. It is this unrecovered petroleum which constitutes a potentially great source of Pennsylvania-grade crude oil for the future. The research effort of this department is aimed at the development and evaluation of reservoir recovery processes which can make the recovery of this reserve economic. Such processes are called "tertiary recovery" techniques and they take many forms. Emphasis to date has been given to the miscible-phase processes — techniques involving the injection of fluids miscible with both the in-place crude oil and the natural and injected waters and brines.

For the purpose of research on fluid flow or displacement in porous media, columns of consolidated and unconsolidated materials are used. These flow columns — or cores — are assembled and integrated with other equipment in order that tests can be run under controlled conditions.

The department laboratories are equipped to handle research in most aspects of secondary and tertiary recovery. Some emphasis is placed, for instance, upon the determination of the phase relationships governing the miscibility characteristics of various fluids. Equipment has been developed to measure volumetric saturations of in-place fluids and to determine volumetric fractions of produced material.

Other recovery methods and techniques are being investigated — for example, the foam-drive process. This process involves the generation and transport of a foam band within the porous core specimen. A promising area of research lies in the area of thermal recovery methods. These techniques use either steam injection or underground combustion as the displacing agent.

Presence of Foam in Consolidated Porous Media

This investigation was conducted to determine the effect of several parameters upon the displacement of brine from a consolidated porous medium by the foam-drive process. The conclusions drawn were:

(1) The breakthrough recovery of an air-drive displacement can be improved as much as 50 per cent from a brine saturated sandstone if a surface-active agent is present.

(2) The only direct evidence of the existence of a foam occurred when the sandstone was saturated with the surfactant solution. Otherwise, the presence of foam was assumed because of the great reduction in flow rate at a constant pressure as the displacement progressed.

(3) Recovery increases with increasing surfactant slug size for a given concentration.

(4) Recovery increases with increasing surfactant concentration for a given slug size.

(5) Loss of the surfactant concentration through dilution and adsorption is responsible for the early breakdown of any foam bank which is formed.

(6) Ultimate gas storage space in an aquifer can be increased by the use of a surfactant prior to the injection of the gas.

(7) Reduction of relative permeability to gas during the displacement may be detrimental to the use of this process for the dewatering of an aquifer to be used for gas storage.

(8) The ability of the surfactant solution to form foam is the primary property which dominates the recovery. Secondary properties are stability of foam and static surface tension.

Mechanistic Studies of Problems of Interest to the Gas Industry

The behavior of a brine-saturated long core during gas injection was investigated. A study of the relationships between gas injection and throughput versus brine saturation and of the effects of various gas injection pressures upon saturation distributions was included. A brine-saturated consolidated Berea sandstone core was desaturated by air, and the saturation distribution profile of the core was measured electrically at chosen intervals of brine displacement and air throughput.

Conclusions and results follow:

(1) The desaturation of brine in any segment was relative to the degree of desaturation of the other segments of the core after air breakthrough. At ten pore-volumes of air throughput, the termination point of all experiments, the desaturation mechanism resulted in a decreasing difference between the relative amounts of brine saturation in each segment.

(2) At irreducible brine saturation, the saturation patterns noted after air breakthrough and during air injection to ten pore-volumes air throughput were no longer evident.

(3) The brine desaturation pattern of any core segment was primarily a function of the distance of the core segment from the air injection end. This is in accord with displacement theory. The air injection pressure applied has a secondary influence upon the brine desaturation pattern.

(4) The change in brine saturation in any core segment as compared to the brine saturation change of the entire core was independent of applied pressure for the pressure range of this study.

Foam Drive Process for Removal of Brine From a Consolidated Sandstone Core

The storage of natural gas in watered-out oil and gas reservoirs or in aquifiers involves the problem of an effective displacement of water from the sand by gas. The very unfavorable viscosity ratio of the fluids hinders this displacement. Using unconsolidated sands, some investigators have improved such displacements by injecting a foam into the sand ahead of the gas. The purpose of this study is to determine the effect of a gas-driven foam upon brine displacements from a naturally-consolidated sandstone core:

(1) It is possible to generate a foam in a consolidated porous medium.

(2) It appears that more efficient foam generation can be accomplished if a gas space exists between the injected surface-active solution and the brine being displaced.

(3) For in-situ generation, the ability of a surfactant solution to foam is more important than the stability of its foam.

(4) The presence of a foam bank between the driving gas and the brine being displaced improves not only the breakthrough displacement but also the ultimate displacement of the brine.

(5) That externally-generated foam can be injected as foam into a consolidated sandstone appears dubious.

Use of Gas Chromatography in Miscible Phase Displacement

This study of gas/gas displacements used linear, horizontal, and unconsolidated porous media of different lengths (0.5 inches diameter) packed with glass beads or crushed sandstone. The fluid systems consisted of air and nitrogen flowing at rates from 0.02 to 0.14 cm^3 per second. The effluent analyses were done by gas chromatography. It was found that the concentration profile of the transition zone as a function of time conformed to an error-function distribution, except at the highest velocities. Mixing was predominately governed by molecular diffusion rather than by mechanical dispersion. Calculated mixing coefficients showed an

increase with increase in core length. The volume of the mixed zone was an increasing function of the time of contact between the two gases, and a decreasing function of the flow rate. The volume of the mixed zone grew approximately as the 0.75 power of the distance traveled, as predicted by theory and observed in many liquid-liquid displacements.

Increased pore size-range caused additional mixing. This was observed by replacing a 40-60 mesh glass bead pack with a 20-200 mesh crushed Berea sandstone pack.

Studies of gas/gas displacements in a consolidated sand were made at low velocities. The purpose was to determine whether the relation between tortuosity, as determined by electrical conductivity, and dispersion coefficient was valid for highly consolidated sands in the manner found for unconsolidated sands.

The flow rates used were approximately 0.21 to 0.80 cm^3/sec., or in terms of average linear velocities, about 0.01 to 0.04 cm/sec. The effluent gas composition was determined continuously by a recording thermal conductivity cell. The gas systems used were: air displacing nitrogen, nitrogen displacing hydrogen, hydrogen displacing nitrogen, and methane displacing nitrogen.

The K/D ratios for these fluid systems at these low velocities closely approximated the value of the reciprocal of the tortuosity of the porous medium. This is the theoretical value when longitudinal molecular diffusion is the sole mechanism in determining transition zone lengths. Displacement mixing was found to be impeded by the tortuosity of the consolidated porous medium. Molecular diffusion was the chief mechanism in determining transition zone lengths. No serious fingering was detected with adverse viscosity ratios, such as had been observed in liquid systems.

Phase Equilibria in the System Hydrocarbon-Carbon Dioxide-Water

The purpose of this investigation was (1) to study the mutual solubility of Bradford crude oil, liquid carbon dioxide, and several pure hydrocarbons of relatively low molecular weight and (2) to determine which is the most effective co-solvent for the crude oil-liquid carbon dioxide system. The light hydrocarbons investigated were propone, pentane, iso-octane, and normal decane; of these, the iso-octane was found to be the most effective co-solvent at 1,250 psig and 72°F.

Recovery of Oil by Steam Hot Water Injection

Preliminary investigations, currently in progress, are being performed to describe the physical properties of crude oils at elevated temperatures. In addition, a series of experiments are planned wherein hot water and/or steam will be used to displace crude oil from porous media. Special emphasis will be given to Pennsylvania crude oils.

The Alcohol Slug Process

Alcohol in consolidated cores is being studied both experimentally and theoretically. Some of the experimental work has been devoted to a study of the effect of rotation of the porous medium in which the displacement is being conducted. A number of experiments in a 20-foot long, 9-inch diameter consolidated core showed that increased length seems to have a beneficial effect on the mechanism of alcohol displacement (recovery of oil and water from a porous medium by injecting an alcohol or other solvent). This was reflected in increased oil recovery and later alcohol breakthough, compared to the results obtained for 6-foot cores.

The theoretical study consisted of the simulation of the alcohol displacement process in a consolidated porous medium, using several digital computer models. The models successfully reproduced the dominant features of alcohol displacement, such as bank formation, phase behavior effects, and relative mobility effects.

The present research in alcohol displacement consists of (1) a continuation of experiments in consolidated cores, employing special alcohol-oil-brine systems, (2) experimental studies of sweep efficiency, using laminar sandstone models, (3) theoretical studies of alcohol slug breakdown behavior, using a digital computer, and (4) computer studies of sweep efficiency in alcohol flooding, for well geometries commonly employed in field practice.

Fluids used were naphtha, iso-propyl alcohol, and methyl alcohol. Porous medium included an 18-foot length of one-inch nominal I.D. galvanized steel pipe packed with unconsolidated Ottawa banding sand.

A significant gravity effect due to the density differences of the fluids is present in the horizontal system and seriously affects the displacement mechanism. A channeling or packing effect due to packing defects or settling of the sand grains also has a significant effect on the displacement process. Continuous rotation of the core at a speed of 1 rpm eliminates gravity effects due to the density difference of the fluids and eliminates any channeling effects. Rotation speed is important, but a speed of 1 rpm was found sufficient to eliminate the above-mentioned effects of injection rates lower than 128 ft/day. Transition zones are shorter at low flow-rates approaching field conditions than at high flow-rates commonly used in the laboratory. Breakthrough recovery is higher at flow

rates approximating field conditions than at common laboratory flow rates.

A study of the displacement of oil and water by combination solvent slugs was made using an unconsolidated core having a length of one hundred feet. The slug combinations used were ethyl alcohol-naphtha-ethyl alcohol, isopropyl alcohol-naphtha-isopropyl alcohol, and normal amyl alcohol-methyl alcohol.

Isopropyl alcohol was found to displace water very efficiently, even when small slugs were used, and was not bypassed by naphtha. It was found that a sharp break existed in the curve of slug size versus recovery — this break occurred at 4 per cent IPA, 4 per cent naphtha, and 5 per cent IPA. Greater slug sizes gave high recovery with little improvement for increased slug sizes, whereas smaller slug sizes gave sharply-decreased oil recoveries.

Comparison of these recoveries with those from two-step slugs showed that three-step slugs gave better results. The order of injection was found to be a parameter: greater recoveries were obtained when the leading edge was an alcohol rather than a mixture of hydrocarbons.

Fluids used included distilled water, Soltrol C, methyl alcohol, ethyl alcohol, isopropyl alcohol, normal butyl alcohol, secondary butyl alcohol, and normal amyl alcohol. The porous medium was unconsolidated Ottawa banding sand having the following screen analysis:

Screen size	50	70	100	140	200
Cum.% retained	2	32	73	92	89

The core consisted of 100 feet of 10-foot lengths of 1-inch nominal inside diameter galvanized steel pipe.

Complete oil recovery from the system can be obtained by normal amyl alcohol-methanol, normal butanol-methanol, and secondary butanol-methanol combination slugs at volumes only slightly larger than that required by IPA. Little difference exists in the displacement performance of the three combinations, although normal butanol-methanol required a smaller volume of oil-soluble alcohol to obtain essentially total recovery. This reduction in slug size may be a partial answer to the problem of reducing alcohol costs. Solubility relationships cannot be used to develop a consistent theory of displacement mechanism and performance.

Some Ternary Systems: Alcohol-Brine

(A) The phase behavior characteristics of certain alcohol-oil-brine systems were studied. Several ternary systems consisting of

an alcohol, 2 per cent calcium chloride brine, and iso-octane or toluene were analyzed, with regard to the phase behavior characteristics. These have been shown to be of considerable importance in the recovery of oil from a waterflooded reservoir by means of alcohols. It was found that the location of the plait point is governed by the types of alcohol, of brine, and of hydrocarbon, and not by the alcohol alone, as assumed by some earlier research.

Other ternary system studies concerned phase behavior when concentrated brines are used. It was found that, in the ternary system involving concentrated calcium chloride brine, the position of the plait point shifted from one side to the other as soon as the concentration of brine exceeded a value of 21 per cent by weight. The shift was in plait point location and was accompanied by a change in the phase behavior characteristics of the system used. This fact was used in alcohol displacements. Displacements conducted with a short concentrated brine slug ahead of the isopropyl alcohol slug yielded much higher oil recoveries compared to those in which no brine slug was used. Finally, four ternary systems consisting of Bradford crude, an alcohol, and brine were studied in detail. Such multicomponent systems are difficult to analyze by conventional techniques. Therefore, new methods were devised. It was found that the Bradford crude behaves roughly as if it were composed of two different hydrocarbons. The behavior was rather adverse in the presence of isopropyl alcohol, precluding the use of isoproply alcohol by itself as a displacing fluid.

(B) For some time now, liquid carbon dioxide has been gaining increasing importance in the tertiary recovery of oil. It is used in conjunction with light hydrocarbons. The chief advantages of carbon dioxide are lower cost and an overall behavior which is intermediate to liquid ethane and liquid propane. The present project is concerned with an investigation of the applicability of liquid carbon dioxide in recovering Bradford crude from sandstone cores. The first phase of the project employs the experimentally-obtained phase behavior data for carbon dioxide — light hydrocarbon — and crude systems, obtained previously in this department. The second phase of the project will be more theoretical in that computer techniques for the prediction of oil recovery will be developed, and theoretical methods for determining the phase behavior data will be devised.

Recovery of Oil with Carbon Dioxide at High Pressures

The aim of this study was to determine if crude oil could be produced successfully by a process of crude oil vaporization using

carbon dioxide repressuring. The process appears to have application to highly-fractured formations where the major oil content of the reservoir is contained in the nonfractured porosity with little associated permeability.

Crude oil was introduced into the windowed cell, and carbon dioxide was charged to the cell at the desired pressure. A vapor space was formed above the oil, and the crude oil-carbon dioxide mixture was allowed to come to equilibrium. The vapor phase was removed and the vaporized oil collected as condensate. Samples of all produced and unproduced fluids were analyzed. Tests were also performed to evaluate the amount of vaporized oil that could be produced by rocking from a high to a lower pressure. The carbon dioxide repressuring process was applied to a sand-filled cell to investigate the performance in a porous medium. A test was performed to evaluate how the condensate recovery changes as the size of the gas gap in contact with the oil changes.

Boundary Problem in Water Flooding

Often a secondary recovery project is initiated in a field that comes short of a full-field development, so that there is a boundary between the developed and undeveloped portions. This investigation consisted of a study of the production and sweep characteristics as well as fluid migration across such a boundary when the development pattern was a five-spot and the boundary consists of alternating intake and producing wells.

Two rectangular glass plates separated by a U-shaped gasket were used as the basic model, forming a Hele-Shaw type of fluid mapper.

Curves were plotted showing the variation of total areas swept by water, as well as areas swept by water outside the unit area. Other curves were drawn to indicate the total cumulative production, the cumulative oil production, and the oil left inside and outside of the unit.

Induction Method of Measuring Brine Saturation in Porous Media

A need exists for a method of determining fluid composition *in situ* during flow in porous media. Withdrawal of samples for analysis has the disadvantage that only efflux compositions are measured, which may be different from the average compositions at the point of withdrawal. Also, if fluid samples are taken at other points than the efflux end of the system, the flow lines may be disturbed. A method was developed for measuring compositions at any point along a cylindrical or other system of small

cross-section, without withdrawing samples. The method depends on the change in dielectric constant with composition. The method has since been used successfully in these laboratories for studying various problems in connection with new methods of oil recovery.

Interphase Material Transfer in Porous Media

When one liquid is displaced by another in a porous medium in the presence of a second phase (moving or stationary) there is a transition zone in which the composition changes from essentially that of the displaced phase to that of the displacing phase. This change in the transition zone may be governed by a mixing process in the direction of flow and the extent to which the second phase is present. The effects of an interphase material transfer on the rate of growth of the transition zone must also be considered.

This investigation was primarily designed to gain knowledge of the effect of a second moving or stationary phase and of interphase material transfer on the growth of the transition zone. Miscible displacements in the aqueous phase and in the oil phase were carried out in a six-foot pyrex tube packed with crushed Berea sandstone. Runs were made with only one phase present, with one phase stationary, and with both phases moving. The transition zone lengths were determined in the moving phases. The effect of interphase transfer of tertiary butyl alcohol on the transition zone length was also determined for the case in which both phases were flowing. Continuous methods of phase separation were devised.

Theoretical Plate Concept in Miscible Phase Displacement

A mathematical model has been developed which stimulates miscible phase displacements in porous media. The model is based on the "theoretical plate" concept which assumes that the pore space of a medium is equivalent to a certain number of plates or cells and that in each cell only a fraction of the fluid volume is movable. During displacement simulation, the movable volume from each cell moves on to each succeeding cell, establishing equilibria with the respective stationary volumes. The validity of the model has been demonstrated by comparison of computer simulations with experimental results for both single phase and various water-hydrocarbon-alcohol liquid displacements in linear flow systems. The results of this work, and, in particular, the mathematical model should be of considerable help to future experimental work as well as in the development of a unified theory of lower alcohol miscible displacements.

Statistical Analysis of Oil Reservoirs

Statistical methods are gaining increasing importance as an engineering tool. This is particularly true in the field of petroleum engineering which deals with inexact data. The present project, nearing completion, concerns methods of obtaining useful information from core data, using statistical techniques. Core data from several thousand wells are being analyzed by a digital computer to illustrate the correlation techniques. The ultimate goal is to test the hypothesis that, given the core data, uniform layers having different properties may be assumed to extend throughout the oil field. It is expected that this is not always the case. Methods will be suggested for making waterflood calculations on oil reservoirs.

Recovery of Oil by Light Solvents in the Presence of Movable Water

There has been some question as to the efficiency of oil recovery by solvents, such as gasoline, in the presence of high water saturations, comparable to those in a watered-out sand. It was found that oil could be recovered by a solvent, such as naphtha, from a watered-out Berea sandstone core. Fingering could be reduced by the simultaneous injection of water and naphtha. A larger bank of pure oil was formed when water was injected with the naphtha than was formed by naphtha alone. "Pure" crude oil recovery was comparable to that in similar experiments with alcohol slugs.

The process, of course, requires that a miscible driving medium, such as high-pressure gas, be used to drive the solvent; otherwise, the volume of solvent required would be equal to the volume of oil recovered.

Since fluid movements from and toward wells are radial rather than linear, it was considered pertinent to study transition zone widths during plane radial miscible displacements. Experimental work has been confined to "favorable" viscosity ratios to avoid viscous fingers. To insure sufficient growth of transition zones for measurement, a natural, rather than an artifically-consolidated, sandstone was used — a pie-shaped slab of Berea sandstone, one inch thick.

Gravity Drainage with Counterflow

It has been customary, in predicting saturation changes, to use the Leverett "fractional flow formula", obtained by eliminating the unknown pressure gradient from the generalization Darcy equations for the separate phases. The formula presents difficulties in the case of counterflow, since the "fractional', flow may be negative,

greater than unity, or, in the case of a closed system, infinite. Recently it has been shown by several authors that the corresponding equations (with capillary pressure and gravity terms) for actual flow of the phases may be used just as well.

The present study was undertaken because of an apparent lack of experimental data on gravity counterflow with which to test the theory.

It was shown that the Darcy equations, as modified for the separate phases, are generally valid for counterflow due to density differences. The usual method of predicting saturation changes, which involves a continuity equation and the elimination of the unknown pressure gradient from the flow equations, was therefore found to be applicable.

Areal Sweepout in Pilot Floods

A new analytical method was developed for calculating areal sweep efficiency, before and after breakthrough, in bounded and unbounded reservoir systems. The five-spot, line drive, and staggered line drive patterns were studied.

The theoretical method consisted of transforming the systems onto the infinite half-plane by use of the Schwarz-Christoffel transform. In the transformed system the pressure and streamline functions were obtained as closed analytical functions. Then, by differentiating the pressure function, it was possible to obtain the velocity function in both transformed and untransformed space. Thus, since the velocity function was known, it was possible to determine sweep efficiency. A number of points were selected about the injection well and their velocities determined. Next, selecting a suitable time step, these points were moved forward using a numerical technique. Thus a record of the movement of these points represented the movement of the displacing phase interface as a function of time and since the injection rate was known the sweep efficiency could be determined.

Mixing in Mechanism of Miscible Phase Displacement

A. Fluids: iodobutane, ASTM naphtha, mineral oil, and carbon tetrachloride. Porous Medium: Ottawa sand (150-200 mesh).

In the case of miscible displacement at adverse mobility ratios ranging from 1 to 16, the growth of fingers in the longitudinal direction is linear with the pore volume injected. The rate of change of finger length with respect to the mobility ratio decreases with increase in mobility ratio. The rate of change of efficiency of displacement, first increasing slightly and then stabilizing at a definite

level, decreases with increase in mobility ratio. The joining of fingers at highly adverse mobility ratios creates unswept islands behind the front.

In the case of miscible displacement using a graded viscosity zone inserted between displacing and displaced phases, the use of a graded viscosity zone reduces the amount of fingering to the point where breakthrough or displacing phase across the zone occurs. After breakthrough the extent of finger growth is the same as that without the graded zone. The graded zone stability is presumably in inverse relation to the overall mobility ratio. Use of graded viscosity zone consisting of in-porous-medium mixed blend, reduces fingering only if a sufficiently long transition zone is used.

B. Fluids: naphtha, isopropyl alcohol, methyl alcohol, carbon tetrachloride, toluene, and distilled water. Porous Medium: galvanized steel pipe 18 feet in length and 1 and 3 inches nominal diameter, packed with Ottawa banding sand.

Continuous rotation of the core at a speed of 1 to 5 rpm eliminates gravity effect due to a density difference of any reasonable magnitude and it does not appear to have any effect on the displacement mechanism. In the two component displacement, for flow rates exceeding 19 feet per day, the small diameter systems tend to make the displacement more efficient as evidenced by a shorter transition zone length and greater breakthrough recovery. The alcohol slug process is more efficient at the lower flow rates as compared to the higher flow rates. At 100 per cent recovery, comparatively smaller slugs of alcohol are required at lower flow rates than at higher flow rates. At low flow rates, more efficient displacement is observed in the larger diameter system than in the smaller diameter system.

Fluid Flow and Oil Displacement

Specific objectives of this work included determination of (1) the effects of methanol, isopropanol, tertiary butanol, and normal butanol on the water-Soltrol or brine-Soltrol interfacial tension, (2) the microscopic mechanisms of displacement involving two partially miscible fluids, and (3) the mechanisms of the various banks of fluids generated during the displacement of Soltrol and water by isopropanol.

It was found that plots of Soltrol-water inferfacial tension versus alcohol concentration are non-linear, and at low alcohol concentrations the addition of small amounts of alcohol causes large reductions in interfacial tension. The length of transition zones developed by displacements involving two partially miscible

fluids is directly proportional to the path length. It was shown that reduction of interfacial tension plays a large role in miscible-type displacements. Three-component displacements were found to be highly rate-sensitive and to require larger slug volumes than two-component displacements.

Areal Sweepout Studies of 7-Spot and 5-Spot Patterns

Synthetically consolidated sand models representing elemental volumes of seven-spot and five-spot flooding patterns were constructed and used in flow tests involving miscible displacement of the initial in-place fluid. The displacing fluid used was X-ray absorbent and the X-ray shadowgraph technique was used to determine sweepout patterns as functions of time, fluid throughput, injection rate, well geometry, and mobility ratio.

The breakthrough sweep efficiencies of normal and inverted seven-spot patterns are the same over the range of mobility ratios from 0.25 to 4.0. The area swept after breakthrough per unit injection is slightly greater for the inverted pattern than for the normal pattern. The ratio of model length to well-bore diameter has no effect upon areal sweepout in the case of the seven-spot pattern. The injection rate ratio required to give maximum sweepout was found to be approximately four to one. An unfavorable mobility ratio decreased the areal sweepout in both patterns at all injection rates studied.

Role of Mixing in Mechanisms of Miscible Phase Displacement

This work concerns the miscible displacement of crude oil from consolidated and unconsolidated core systems. The main objective of the study was and is to determine the effect upon the displacement process itself of gravity segregation of the fluids within the porous medium. Corollary objectives deal with the effect of core rotation to offset gravity segregation, the effects of front advance on displacement and the effects of phase behavior, core diameter and oil viscosity on oil recovery.

The method of procedure involved the construction of three unconsolidated cores, each 18 feet in length, having diameters of one, three, and six inches, respectively. A consolidated core of Berea sandstone was used as well. The fluids used included calcium chloride brine, isoproply alcohol, naphtha, Soltrol and Kendex. The cores were rotated at constant velocity during the displacement runs.

The data indicate that it is possible to eliminate gravity segregation by means of core rotation. The elimination of segregation

results in increased transverse mixing. It was found further that displacement efficiency is decreased with increased core diameter at unfavorable viscosity ratios — the opposite is true if the viscosity ratio is unfavorable. The efficiency of the alcohol slug process is increased at low-flow rates, and phase behavior effects are not significant in unconsolidated porous media.

Recovery of the System Crude Oil-Alcohol-Water in Long Consolidated Cores

(A) The first part of the project was devoted to an investigation of the effect of rate on the alcohol slug process. A consolidated sandstone core was employed for this purpose for the first time. Two oil-water-brine systems, characterized by basically different types of phase behavior, were used in the experimental studies.

It was found that an increase in the flow rate had a favorable effect on the total oil recovery for both types of systems. (Rates of frontal advance varying from 5 to 30 feet per day were employed.) The increase in oil recovery due to an increase in rate was more noticeable in the tertiary butyl alcohol-Soltrol-brine system than in the similar system employing isopropyl alcohol. It was also found that the oil recovery increased with the slug size as the rate was increased, though the increase in oil recovery was not significant in the case of large slugs. This was especially found to be true for the isopropyl alcohol system. Slug breakdown also occurred earlier in the same system.

The second part of the project was concerned with an investigation of the displacement of Bradford crude in a consolidated sandstone core by various alcohols, being the first study of its kind. The present research was designed to study the general displacement mechanism using different pure alcohols and pure hydrocarbons. It was found that, contrary to previous conjectures, isopropyl alcohol by itself is not very effective in displacing Bradford crude because of its adverse phase behavior in alcohol-brine systems. Slugs of amyl alcohol and of amyl alcohol followed by short slugs of isopropyl alcohol gave recoveries as high as 70 per cent of the oil in place. It was also found that increased length of the porous medium has a beneficial effect on oil recovery.

(B) The first part of this project was a continuation of a similiar previous study concerned with the effect of the rate of frontal advance on the efficiency of the alcohol slug process. A wider range of rates, extending from 1.5 to 70 feet per day, was investigated. The results of the previous study were confirmed that the oil recovery increased with an increase in rate. The relative increase in recovery was found to be greater in the range of 10 to

70 feet per day than at the lower rates. Several displacement runs with the core in the vertical position indicated the presence of appreciable gravity segregation.

The second part of this project was concerned with a study of the recovery of Bradford crude from consolidated cores, using solvent slugs, more from the point of view of the economics of the operation. A number of impure alcohols were obtained and used as buffer slugs, followed by isopropyl alcohol slugs. It was found again that, if the impure alcohol contained amyl alcohols the oil recovery showed an improvement. In addition, two hydrocarbons, naphtha and mineral oil at the extremes of the viscosity range were used as buffer slug materials. The observed "pure" oil recovery was higher in the case of mineral oil (60 cp), while the total oil recovery was higher in the case of naphtha (0.5 cp). An infrared spectrophotometer was used to analyze some of the multi-component mixture obtained in the experiments. An analytical technique was developed for this purpose.

(C) This research consists of (1) a study of some viscosity effects in miscible displacement, and (2) a study of the recovery of Bradford crude, using composite alcohol and propane slugs.

The first part of (1) was a study of the effect of anomalous mixture viscosity behavior (i.e., non-linear viscosity-concentration curves) on the mechanism of two-component miscible displacement. It was found that, depending upon the shape of the viscosity-concentration curves, the effective viscosity ratio may be "favorable" for part of the displacement and "unfavorable" for the rest, even though the overall viscosity ratio is apparently favorable (or unfavorable). It was also found that in miscible displacements conducted at a favorable viscosity ratio, the absolute viscosities of the individual liquids are of significance, in addition to the viscosity ratio. Several experimental studies were designed to investigate the behavior of viscous instabilities in miscible displacement at favorable and unfavorable viscosity ratios. A few experiments were conducted to evaluate gravity segregation effects in miscible displacement.

The second part (2) was a study of the recovery of Bradford crude from consolidated porous media by means of pure and impure alcohols and propane. In most of the runs the slug sizes were kept nearly unchanged, while various slug materials were tested. It was found that the recovery of Bradford crude when using a slug of propane, was nearly as high as that obtained when using a slug of Pentasol (mixture of amyl alcohols). Both slugs were followed by short slugs of isopropyl alcohol. This is interesting,

since the viscosities of the two fluids are widely different. Additional useful information was obtained on the effect of the rate of injection, viscosity of the flood water, etc.

Effect of Diameter in Miscible Phase Displacement Studies

(A) The fluids used in this study were: Kensol 50, Soltrol 170, and a mixture of Soltrol 170 and $CaCl_4$. Two types of unconsolidated Ottawa sand cores were used for the displacement: bonded wall and unbonded wall types.

Unless core-wall effects are minimized, the results from small diameter cores of limited path length in miscible displacement are not reliable. Even where core-wall effects are eliminated, the system must be sufficiently long to yield unequivocal miscible displacement results over a complete rate range. A bonded one-inch diameter core, 12 inches long, is invalid when subjected to slow displacement rates. One-inch diameter "bonded wall" core, 48 inches long, gives results consistent with those obtained in unconsolidated cores having lengths in excess of ten-feet. Rate studies have indicated that, at constant temperature, using fluids with matched viscosities and densities, miscible displacement in unconsolidated systems is truly rate insensitive over the range of moderate to high rates. At slow displacements of the order of a foot per day, improved displacement efficiency is reflected in a diminished transition-zone length.

(B) The fluids used were: ethyl alcohol, isopropyl alcohol, tertiary butyl alcohol, naphtha, Soltrol 170, and carbon tetrachloride. Ottawa banding sand was the porous media. Screen size varied from 50 to 200 mesh, with 2 per cent retained on a cumulative basis at 50 mesh, 32 per cent at 70 mesh, 72 per cent at 100 mesh, 92 per cent at 140 mesh, and 98 per cent at 200 mesh.

The effect of gravity segregation on the length and shape of the mixing zone curve is a function of viscosity ratio, density difference, and rate. When viscosity ratio and density difference both are favorable, the effect of rate is small and gravity segregation is negligible. When the viscosity ratio is favorable and the density difference unfavorable, the amount of gravity segregation is dependent on rate, becoming negligible at high displacement ratios. For an unfavorable viscosity ratio and a favorable density difference, the amount of gravity segregation decreases with increasing rate. When viscosity ratio and density difference are both unfavorable, the amount of segregation is large at slow rates, but decreases with increase in the displacement rate. By applying Darcy's law, it is seen that the viscous and gravitational forces dominate the displacement mechanism.

THE MINERAL INDUSTRIES EXPERIMENT STATION

Conduct of the large research program described in this report is coordinated by the Mineral Industries Experiment Station. The Experiment Station provides the auxiliary facilities and services necessary to permit investigators to devote their attention to research and teaching without worrying about separate accounting, administrative, or service problems.

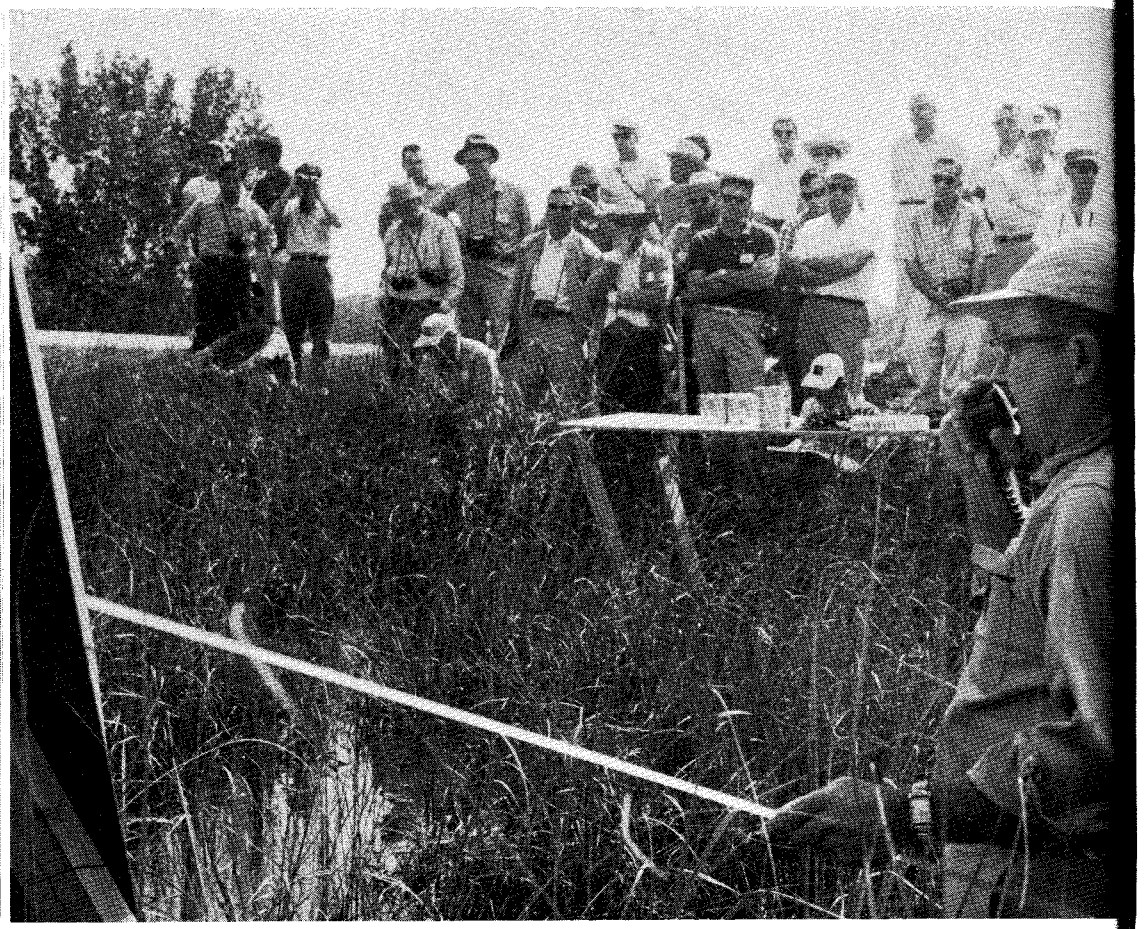
Particularly, the Experiment Station is responsible for proposal and contract supervision and for daily budget and accounting information to assist in project financial management, personnel administration, and purchasing. It is also responsible for improving major research equipment and for operating the shops and technical services within the College.

Major research activities operated through the Experiment Station are described in detail below.

MINERAL CONSTITUTION LABORATORIES

These Laboratories are a centralized facility with specialized personnel and equipment to provide chemical and instrumental analyses. Staff members of the Laboratories constantly investigate new analytical procedures; for example, a special program is being conducted to investigate and evaluate instrumental methods now commonly used in the earth sciences. Also because of an unusual combination of instruments, the Laboratories are frequently requested to provide special services to Pennsylvania industry. Another special service provided is the analysis of samples distributed by the U. S. Geological Survey and similar organizations. These samples are subjected to conventional chemical methods and then to special intensive studies using emission spectroscopy, X-ray florescence spectrometry, colorimetric photometry, mass spectrometry, electron probe analysis, and neutron activation analysis. The samples selected for these studies are available to analysts in other laboratories, where considerable interest exists in comparing results. A detailed description of the Laboratories' major sections and projects follows:

(1) **Analytical Laboratory:** The Analytical Laboratory provides references or control samples for emission spectrographs, X-ray instruments, and electron probes. There is a heavy demand for precise chemical analyses of rocks, minerals, and synthetic compounds. Such analyses for chemical variations within mineral



The early stages of coal formation as evidenced in the Florida Everglades are studied by a University paleobotanist.

groups and for crystallographic and phase equilibria characteristics commonly require the combining of conventional chemical and instrumental methods.

In addition, many research projects require the development of special analytical procedures. Phase equilibria experiments, for example, frequently call for special methods because of the limited size of the samples that can be handled in high-temperature and high-pressure apparatus. These samples may contain such unusual elements as boron, fluorine, the rare earths, and gold. Some of the materials which have been successfully analyzed include beryllium ore, apatite containing strontium and the rare earths, uranium in lignite ash, vanadium-bearing arkose, and metallic boron films used in nuclear research.

(2) **Spectroscopy and X-ray Laboratory:** A highly-versatile, direct-reading spectrometer, recently acquired for this Laboratory, supplements the original 3-meter spectrograph and greatly extends the services available in emission spectroscopy. The new spectrometer can determine as many as 20 elements on a sample and can analyze large numbers of samples in a fraction of the time that would be required with the standard instrument.

Several thousand samples of stream sediments have been analyzed. Methods have also been developed for quantitative spectrographic determination in rocks and minerals of such elements as barium, boron, chromium, nickel, strontium, and vanadium, with accuracy at least equal to wet-chemical methods and with an appreciable saving in time. The technique is now being applied to samples of granite which contain different trace elements which may give a clue to their different origins.

Absorption spectroscopy is being applied to an increasing number of problems. Qualitative and quantitative spectra in the ultraviolet, visible, and infrared regions of the electromagnetic spectrum all are used. X-ray equipment is also a commonplace tool in studies in geochemistry, mineralogy, metallurgy, ceramics, and related fields.

(3) **Electron Microprobe Laboratory:** The electron microprobe can provide an elemental analysis of sample volumes ranging down to less than one cubic micron, $\frac{1}{100}$ of the thickness of a human hair. All elements heavier than boron can be analyzed with the probe, as long as they exceed concentrations of about 0.02 weight per cent. For example, a particle of iron as small as one-millionth of one-trillionth of a gram can be detected. The instrument operates by detecting X-rays excited by bombardment of the

sample surface with a very finely-focused beam of electrons. Each element has its own characteristic X-ray spectrum in much the same manner that every element has a unique set of emission lines in the visual spectrum. A few of the specific problems which have been solved with the microprobe since its installation in March 1962 include:

(a) The fine needle-like inclusions which cause the "star" in sapphires and rubies, long thought to be inclusions of rutile (TiO_2), were shown to be composed largely of alumina with small amounts of TiO_2.

(b) It was demonstrated that the so-called silicon monoxide which is used to coat optical lenses is not silicon monoxide at all, but is a mixture of silicon metal and silicon dioxide.

(c) Small light-scattering centers in calcium tungstate laser crystals were found to be crystals of iridium that were dissolved in the melted tungstate and recrystallized when the calcium tungstate single crystal was grown.

(d) Flaws in glass used to make corrective lenses in eye glasses were shown to contain zirconium which indicated to the manufacturer the source of the trouble and led to the elimination of the flaws.

(e) Non-uniformity in the ratio of bismuth to antimony in single crystals of the alloy was found to be the cause of poor electrical properties of this particular alloy.

(f) Special techniques have been developed for obtaining the composition of clay-sized particles by dispersing the particles on the surface of polished beryllium.

(4) **Electron Microscopy Laboratory:** The electron microscope is used primarily to obtain extremely high resolution images of materials. The useful magnification, which may be greater than 100,000 diameters, is many times that of ordinary light microscopes. The microscope is also capable of producing high-quality electron diffraction images for identifying small particles and for studying their crystal structure.

The structures of sepiolite and palygorskite, for example, have been studied recently. These clay minerals are too fine-grained for investigations by the single-crystal X-ray diffraction techniques. In addition, the structure and orientation of electrodeposited metal coatings, such as tin on steels, the movement of dislocations in thin metal films subjected to stress, and the mode of strain-producing flaws in bottle glass were also other typical studies. The combined

techniques of electron microscope and electron microprobe have been used also to determine crystal structure and composition and to obtain pictures of single particles with a volume of one cubic micron or less.

Research in Silicate Analysis with Emphasis on Instrumental Methods: This special project is an evaluation of instrumental analytical methods now commonly used in the earth sciences. Comparative studies will be made of available or new reference samples by conventional chemical methods and by emission spectroscopy, X-ray fluorescence spectrometry, colorimetric photometry, and mass spectrometry. Some principal objectives are (1) to develop rapid and accurate methods of rock and mineral analysis, (2) to analyze reference samples which will be generally available to laboratories, (3) to refine and extend present instrumental analyses, and (4) to develop new methods and combinations of methods to facilitate and extend the usefulness of analytical procedures for investigations in the earth sciences.

COAL RESEARCH SECTION

This Section serves (1) to stimulate activity in new areas of coal research, (2) to implement negotiations with research sponsoring agencies, and (3) to expedite investigations once they are undertaken. During the last four years the Section expanded its scope to include research in coal preparation, mining, and marketing. Twenty-seven projects have been active; 13 have been completed. Nine new investigations were begun under the auspices of the Coal Research Board of the Commonwealth of Pennsylvania. Thirty comprehensive Special Research Reports have been submitted to the Board and made available for general distribution. To date, 2,174 copies of such reports have been sent by request to all parts of the world. Fifteen of these reports have also constituted either Master's or Doctroal theses. A portion of the research of 22 faculty members was supported by these programs, with 54 graduate students participating in the investigations. During the first two years of the report period, funds received in support of the Section's programs averaged $65,000 per year. Funds received during the last two years averaged $150,000 per year.

The following projects (with the department indicated in parenthesis) are currently supported, or have been supported, as part of the program sponsored by the Pennsylvania Coal Research Board:

Study of the Ignitability of Pennsylvania Bituminous Coal (Fuel Science)

The Reduction of Sulfur in Pennsylvania Bituminous Coal During Carbonization (Fuel Science)

Preparation of Highly-Porous Carbons from Pennsylvania Bituminous Coal (Fuel Science)

The Production of Metallurgical Coke from Blends of Anthracite and Bituminous Coal (Geology and Geophysics)

The Mineral Constituents of Anthracite and Their Relationship to the Chemical Characteristics of Ash (Geology and Geophysics)

Investigations of the Chemical Nature, Physical Structure, and Distribution of Ash in Anthracite (Fuel Science)

The Behavior of Petrographically Distinct Anthracite Particles Under Thermal Stress (Geology and Geophysics)

Identification of Basic Chemical Constitutents of Pennsylvania Bituminous Coals with the Mass Spectrometer (Fuel Science)

Reaction of Anthracite with Atomic Species (Fuel Science)

Physical Structure of Anthracites as Affected by Heat Treatment, Oxidation, and Grinding (Fuel Science)

Use of Anthracite as a Molecular Sieve Material (Fuel Science)

Factors Affecting Ignition and Burning Rate of Pulverized Fuels, Especially of Pennsylvania Anthracite (Fuel Science)

Reaction of Pennsylvania Bituminous Coal with Atomic Species (Fuel Science)

The Reduction of Ash and Sulfur in Bituminous Coals During Preparation (Mineral Preparation)

Chemical Structure and Physical Properties in the Macerals of Pennsylvania High, Medium, and Low Volatile (Bituminous) Coal in Relation to Coal Utilization (Geology and Geophysics and Fuel Science)

Streaming Potential Studies of Petrographically Distinct Anthracite Particles for Increasing the Technological Applications and Markets of Anthracite (Mineral Preparation)

Studies of Solid State Reactions of Anthracite Coals Subjected to Super-Pressures at Moderate Temperatures (Geochemistry and Mineralogy)

To Determine Characteristics of Extremely Fine Anthracite Particles Looking to Increase Markets for a Size that is now a Waste Product (Mineral Preparation)

The Characteristics and Preparation of Anthracite Breaker Refuse and the Suitability of Derived Products for Industrial Use (Mineral Preparation)

Investigation of the Technical Aspects in the Control and Disposal of Mine Water to Minimize Stream Pollution (Mining)

Strip Mining and Land Restoration (Mining)

Optimization of Mine Production Systems for Low-Cost Mining (Mining)

Control of Mine Stream Pollution by Removal of the Impurities from Drainage Streams (Mineral Preparation)

Study of High-Moisture Pulverized Coal Flames, with Supplementary Study of Time-to-Ignition Temperatures of Coal Dusts and Their Dependence on Moisture Content (Fuel Science)

The Economic Importance of the Coal Industry to Pennsylvania (Mineral Economics)

Investigation of Effective Measures to Combat Mine Disasters (Mining)

Dissipation and Removal of Fog from Airfields by the Application of Energy Derived from Coal (Meteorology)

MINERAL CONSERVATION SECTION

This Section continues to support research programs aimed at finding, developing, and utilizing mineral resources in Pennsylvania. Present emphasis is on ground water resources, prospecting methods, and regional variation in properties of the Commonwealth's extensive coal and clay beds.

The following projects (with the department indicated in parenthesis) are currently supported as part of the Mineral Conservation program:

Regional Stratigraphy and Correlation (Geology and Geophysics)

Geochemistry of Stream Sediments (Geochemistry and Mineralogy)

Ground Water Investigations (Geology and Geophysics)

Preparation of Mineral Atlas (Geography)

Geophysical Methods of Locating Iron Ore (Geology and Geophysics)

Beneficiation of Disapore Clay (Mineral Preparation)

Blasting Research (Mining)

Operations Research on Mine Haulage (Mining)

Underground Stress in Mines (Mining)

Limestone for Portland Cement (Geochemistry and Mineralogy)

Treatment and Pressing of Clay (Ceramic Science)

Carbon Markets (Mineral Economics)

Specifications for Mineral Aggregates (Mineral Economics)

Genetic Relationships Between Iron Ore and Diabase (Geochemistry and Mineralogy)

Regional Variation in Composition and Ceramic Properties of Kittanning Clay (Ceramic Science and Geology and Geophysics)

Mine Subsidence (Mining)

Coal Petrology and Geochemistry (Geology and Geophysics)

GLASS TECHNOLOGY RESEARCH GROUP

The gradual replacement of Na_2O by K_2O in a glass causes its electrical conductivity to go through a pronounced minimum for the molar ratio 1:1. This "mixed alkali" effect has been attributed to a "compaction" of the glass that lowers the mobility of the alkali ions. However, experimental work on silicate glasses has revealed that this explanation is not acceptable. In the systems Na_2O-K_2O-SiO_2-LiO_2-Na_2-SiO_2 and Li_2O-K_2O-SiO_2, the volume shows both positive and negative deviations from additivity. For glasses which show compaction, maximum deviation from additivity is not located at the 1:1 ratio.

A theoretical explanation of the "mixed alkali" effect was given on the basis of the different atomic weights of the alkalies, which cause their vibrations to be out-of-phase. This anharmonicity of thermal vibrations leads to a much stronger bonding of the alkali ions to the oxygen network of the glass. This concept could be utilized to prepare phosphate glasses in which Hg^{2+} ions are retained. Whereas, in melts in the system HgO-P_2O_5, the mercury is lost through valatilization; melts in the system Li_2O-HgO-P_2O_5 form glasses. Mercury glasses with more than 20 per cent HgO could be prepared.

STATE AND FEDERAL GOVERNMENT SPONSORS

Advanced Research Projects Agency (Department of Defense)

Commonwealth of Pennsylvania

Harry Diamond Laboratories

National Aeronautics and Space Administration
National Science Foundation

Pennsylvania Coal Research Board
Pennsylvania Geological Survey

U.S. Air Force Cambridge Research Center
U.S. Air Force Command and Control Development Division
U.S. Air Force Systems Command

U.S. Army Ordnance Corps
U.S. Army Research Office

U.S. Atomic Energy Commission

U.S. Coast and Geodetic Survey

U.S. Department of Health, Education, and Welfare

U.S. Public Health Service

U.S. Weather Bureau

PRIVATE SPONSORS

Alcoa Foundation
Allegheny Ludlum Steel Corporation
American Chemical Society
American Iron and Steel Institute

American Petroleum Institute
American Smelting and Refining Company
American Society for Testing Materials
American Zinc Institute
Armco Steel Foundation

Babcock and Wilcox Company
Basic, Incorporated
Bausch and Lomb Optical Company
Bethlehem Steel Company
Blaw-Knox Company

Carborundum Company
Carpenter Steel Company
Continental Oil Company
Corning Glass Works
Council of Corrosion Research
Crucible Steel Company of America

Engineering Foundation
E. I. duPont de Nemours Company

Ferro Foundation
Ford Motor Company

General Electric Company
Geological Society of America
Glass Container Industry Research Corporation
Glen Alden Foundation, Incorporated
Gulf Oil Corporation

Holcab Realty of New York, Incorporated

International Business Machines
International Nickel Company

J. M. Huber Corporation
Jones and Laughlin Steel Company
Joy Manufacturing Company

Lead Industries Association
Linde Company

Magnesita, Incorporated
Marathon Oil Company

Mobil Oil Company
Molybdenum Corporation of America

National Steel Corporation
Owens-Corning Fiberglass Corporation
Owens-Illinois Glass Company

Pan American Petroleum Foundation
Penn-Birmingham Bolt Company, Incorporated
Pennsylvania Electric Association
Pennsylvania Grade Crude Oil Association
Pennsylvania Natural Gas Men's Association
Pennsylvania Research Corporation
Pennzoil Company
Pfaudler-Permutit Company
Pittsburgh Plate Glass Company
Prismo Safety Corporation

Resources for the Future, Incorporated (Division of Ford Foundation)
Reynolds Metals Company
Rochester and Pittsburgh Coal Company
Roll Manufacturers Institute

Sharon Steel Foundation
Shell Companies Foundation, Incorporated
Shell Development Company
Speer Carbon Company
St. Joseph Lead Company
Stackpole Carbon Company
Standard Pressed Steel Company

Union Carbide Metals Company
U.S. Steel Foundation
U.S. Steel Corporation

Vesuvius Crucible Company

Youngstown Sheet and Tube Company