PROGRESS IN RESEARCH

MINERAL INDUSTRIES EXPERIMENT STATION

College of Mineral Industries

THE PENNSYLVANIA STATE UNIVERSITY

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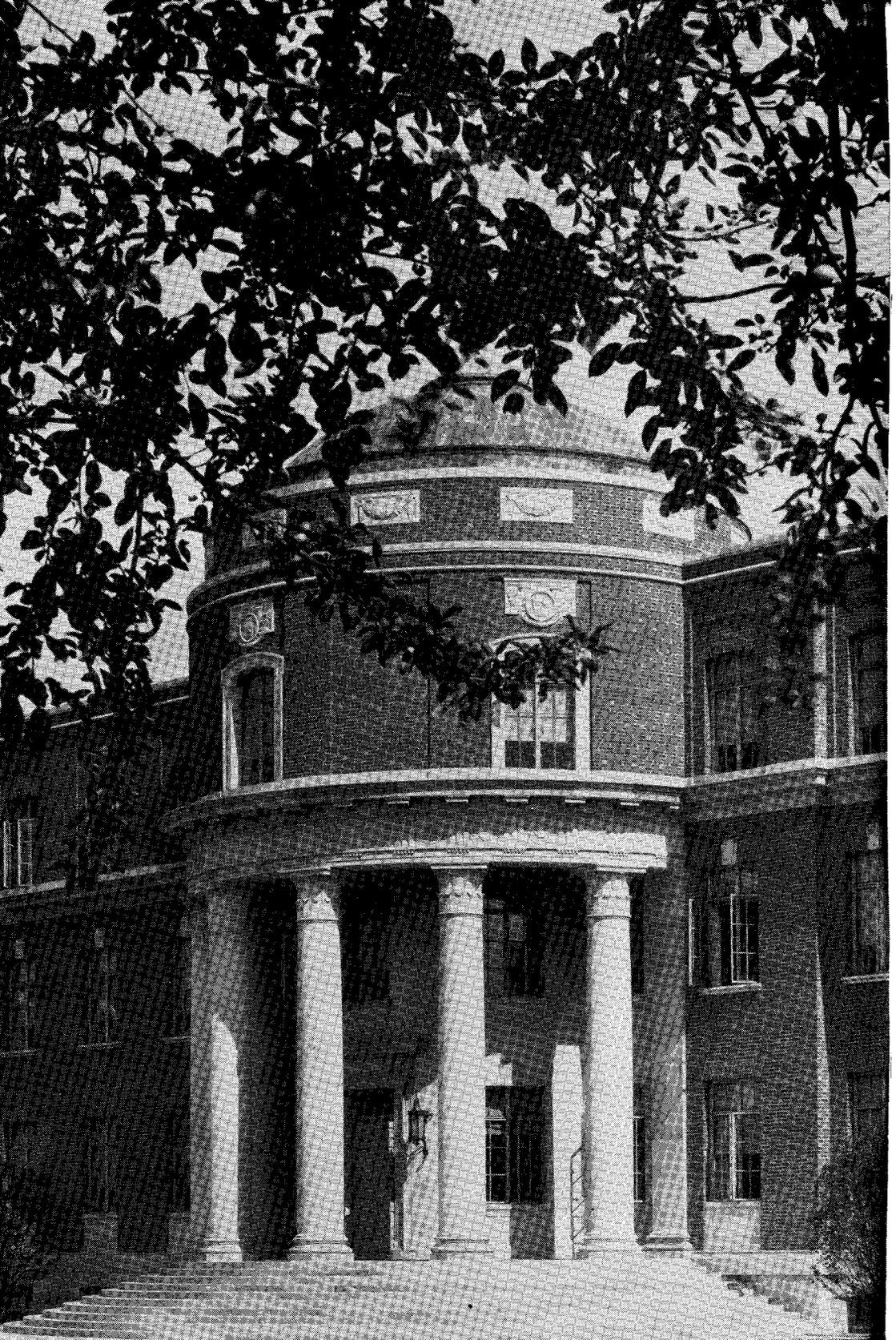

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PREFACE

The research described in this report has, for many years, been organized and grouped around the mineral raw materials used by industry. It is one of the largest university research programs of its kind and includes disciplines of both science and engineering. The close association of these different disciplines with common research objectives has proved valuable to each of them. The College of Mineral Industries has thus for many years had an interdisciplinary approach to research in raw materials.

With the increasing emphasis on high-temperature, high-strength materials for use in aviation and extraterrestrial research, we now have an opportunity to apply many of the scientific observations and techniques gained through research on natural rocks and minerals to the development of new synthetic materials analogous to synthetic minerals, and to learn how to incorporate in synthetic materials the physical and electrical properties which would be regarded as desirable from the application standpoint.

One trend of this research is toward a study of the conditions surrounding the preparation of new synthetic mineral phases, research on their purification and production in single-crystal or polycrystalline form as required by the use envisaged, and analysis of the physical and electrical properties of these synthetic materials and correlation with their atomic and molecular structure.

Because of the increasing scarcity of high-grade deposits of ores and fuels, another trend in research is developing. This is evidenced by a search for developing better methods of prospecting; by research on mining methods and secondary recovery of petroleum; and by research on mineral beneficiation and coal preparation. The latter techniques, when developed, will enable lower-grade ores to be utilized economically and thus will increase in importance as concentrated ores are depleted.

This report describes, mostly in layman's language, the research under way or completed in the College of Mineral Industries of The Pennsylvania State University during the two-year period from July 1, 1959 to June 30, 1961. It is in one sense a report of results to the people of Pennsylvania, for about 33 per cent of the cost of the research came either from the general University budget or from direct appropriation of public funds. The remaining financial support was derived almost equally from U. S. government and from industrial sources. For example, during the 1959-60 fiscal year, $1,229,841, exclusive of overhead, was spent on the research program described herewith, of which $406,673 was derived from the University or from

direct legislative appropriations; $411,644 from the federal government; and $411,524 from industry, including $73,875 for research on anthracite and bituminous coal under contracts with the Coal Research Board of the Commonwealth of Pennsylvania.

The research described in this report is carried on with three aims in view. The first and most important of these—since the primary purpose of the University is to train students—is to provide a research program within the framework of which students may be trained to carry on or to administer research, or to go out into the world as engineers. The research program must provide vital and important topics for thesis researches and for the inspiration of faculty supervisors who are workng at the boundaries of knowledge. In addition, the research program should provide financial assistance for students of limited means during the long period of their post-graduate study.

The second important purpose of this program is to provide an opportunity for professors to carry on scholarly activities in their chosen fields. It is through the adequacy of such opportunity that the quality of the faculty is determined.

Third, as the State university and the land-grant institution of Pennsylvania, the University has a definite responsibility toward the citizens of the State in carrying on research and giving advice which will assist in the solution of important industrial and social problems.

It is with these purposes, and by balancing emphasis between objectives, that the present program has been developed over the past 20 or 30 years. With these same three objectives in mind, the program and those who are carrying it on are facing the future with expectations of even greater productivity.

M. E. BELL, *Director*
MINERAL INDUSTRIES
EXPERIMENT STATION

Dec. 15, 1960

EARTH SCIENCES

The responsibility of the earth scientist is to provide the fundamental information on which all branches of the mineral industries build. The earth and the space around it provide the environment in which all of us live and work. From the solid earth, the oceans, and the atmosphere we draw our mineral raw materials, e.g., coal and petroleum from the ground, bromine from the sea, nitrogen from the atmosphere. We travel over and through the earth by train, ship, and aeroplane. On it and in it we build our skyscrapers and bridges, factories, homes, and even bomb shelters.

Research in geology tells what rocks we should find if we dig beneath the surface for a foundation. Research in mineralogy and petrology tells us how the rocks are put together by nature so that we can understand why different minerals occur where they do and hence predict where it is reasonable to look for them. Research in geophysics gives us a means of finding the deposits of raw materials not exposed at the surface needed to keep our industries growing. Research in geochemistry tells about the physical and chemical properties of minerals used by these industries, and how minerals can be modified more efficiently to manufacture the good things which enrich our lives. Research in geography tells where the markets for our raw materials are and how to develop them most economically to provide jobs for Pennsylvanians. Research in meteorology tells us how to predict the weather faster and more accurately so that we can better plan ahead in our business and private lives.

And most important of all, research in earth sciences tells us why our world is the way it is. It helps to satisfy man's deep yearning to understand himself and his relation to the universe. It reveals to him something of the creation and evolution of our globe and the organisms which have lived and died in its many ages. It tells why mountains rise and are destroyed, why the atmosphere is rich in oxygen, and how the oceans have developed.

Below are short descriptions of some of the important discoveries of earth science research during the past two years.

GEOLOGY

Research in the Department of Geology contributes to knowledge and likewise serves a major role in training graduate students to become professional geologists for coming decades. The research studies are diversified. They include field and laboratory investigations of sedimentary rock bodies and geologic structures in parts of

the Appalachian and Rocky Mountain regions; consideration of factors that affect use of animal and plant fossils in interpretation of geologic phenomena; enquiries into coal characteristics as well as into relations between coal components and processes such as those observed in modern swamps; studies of stream and glacial sedimentation in relation to land features, soils, and occurrence of deposits of gravels useful for construction; work on the chemistry of accumulation of marine carbonate sediments that are modern counterparts of the limestones and dolomites which form important rock bodies in many parts of the world. The following research programs are now in progress:

CAMBRIAN AND ORDOVICIAN LIMESTONES AND DOLOMITES

Field investigations in parts of Blair and southeastern Centre Counties, Pennsylvania, of the Cambrian Pleasant Hill limestone, Ore Hill limestone and Stacy dolomite, as well as of the Ordovician Lark dolomite and Stonehenge limestone, have provided systematically collected samples that have been analyzed for percentage of non-ignited, acid insoluble residue, and, in composite samples, for calcium, magnesium, silica, iron and alumina. The data have been used for preparation of reports that furnish preliminary assessments of the commercial possibilites of each of the rock bodies. Part of the analytical work has been accomplished by employing X-ray fluorescence techniques. (A report will be published concerning some of the problems and values offered by this mode of analysis.) Work also is in progress on chemical characteristics of the Ordovician Nittany and Bellefonte dolomites at several localities in northern Blair County, and on features of their residues which may be of value for the identification of geologic horizons in these formations. Siliceous sponge spicules have been recovered in residues from the lower part of the Bellefonte dolomite.

UPPER SILURIAN CYCLIC SEDIMENTS

The Upper Silurian Wills Creek shale and Tonoloway limestone of the Middle Appalachians are characterized by cyclic sedimentary strata, believed, in each instance, to reflect gentle subsidence of the floor of the shallow seas in which deposition took place, followed by sedimentary upbuilding and outbuilding. In the Wills Creek shale in central Pennsylvania, thin limestones that in part are oolitic tend to be overlaid by laminated limestones, and then by calcareous shale and calcareous mudrock. The shale and mudrock represent clays that spread westward from the more easterly region of the Bloomsburg delta. Cyclic sediments in parts of the Tonoloway limestone have, at the base, sediments deposited in waters in which waves and currents

were active, and overlying mudrocked layers that appear to have been deposited on widespread tidal flats. Southwards from Pennsylvania, the basal sediments are more fossiliferous, indicating an approach toward the oceanic connections of the Tonoloway seas.

STRATIGRAPHY OF CARBONIFEROUS ROCKS

Maps have been completed showing the lithologic and faunal variation of the Kittanning formation in western Pennsylvania. These maps have led to the establishment of new concepts of Carboniferous paleogeography which are useful in predicting the thickness and composition of coal beds and the characteristics of the rocks which overlie them. Similar studies are being made for other formations in the Allegheny Series.

Detailed stratigraphic and petrographic studies of Pottsville and Lower Allegheny rocks have shown that ancient topographic highs were important factors in controlling the composition and thickness of commercially valuable limestones and refractory clays. Further research has been undertaken in order to refine understanding of these relationships so that more accurate predictions can be made of the occurrence and characteristics of clay and limestone deposits.

EVOLUTIONARY AND ENVIRONMENTAL RELATIONSHIPS IN MIDDLE PALEOZOIC FOSSIL FAUNAS

Many of the Middle Paleozoic sedimentary rocks that are extensively exposed in Pennsylvania and elsewhere along the folded Appalachians contain fossil shells of animals that lived in the marine or brackish waters in which the sediments were deposited. The fossil faunas differ markedly in differing geologic horizons. In part, the changes involve successive appearances of related species and reflect the progress of their evolution. In other instances, the faunas undergo marked modification in general biologic constitution, and evidently were responsive to changes in water salinity, depth, temperature, and degree of turbulence, as well as to characteristics of the bottom sediments. Recognition of the controlling causes of faunal differences contributes to interpretation of environmental relations of the fossil faunas and associated strata, and also affects concepts concerning the use of fossils in age correlations.

ORGANIC SEDIMENTS OF MODERN SWAMPS IN RELATION TO COAL ORIGIN AND CHARACTERISTICS

Variations among and within coal seams in types and proportions of botanically-derived macerals, as well as of mineral matter, affect

coal characteristics, benefication and utilization, and in large part are the result of the environmental conditions of the bogs in which the coal material originally accumulated in the form of peat. To aid understanding of the types, manner of occurrence, and interrelationships of coal components, research has been undertaken in swampy regions of the earth which seeks to distinguish the kinds of organic sediments that accumulate in the many differing environments of modern swamps and to follow progressive modifications that affect various component substances as organic sediments are transformed into lignite and subbituminous coal. It also is hoped that clues may be found concerning the fundamental nature of components of coals of higher ranks.

Investigations of swamp environments in southeastern Florida show that mangrove forests occupy the relatively more marine sites and appear to be migrating inland, invading the extensive everglade environments that are associated with brackish and fresh waters. Both the mangrove and everglade environments include distinctive complexes of botanically and geologically recognizable sites in which organic sediments are accumulating. Inland migration of the environments is being induced by the marine transgression occurring along the West Florida coast, and is evidenced by pollen profiles of the Recent sediments, by the historical destruction of small islands, and by submarine extensions of peat horizons, as well as by several other types of geological and botanical data.

At certain levels in the organic sediments, analyses of several cores show unexpectedly high concentrations of uranium. The uranium concentration is inversely correlated with the ash content, and positively correlated with the carbon content. Thirty samples of surface sediment taken in a transect through marine, brackish, and fresh water environments show a general decrease in uranium content with increasing distance from the open sea. Sulfur concentration also appears related to sediment type, reaching magnitudes quite comparable to those encountered in many Paleozoic bituminous coals. Although sulfur concentrations exceed five per cent in some samples of dry peat, no megascopically detectable pyrite has been observed. The sulfur content is positively correlated with carbon content. In the sediments studied, sufficient sulfur is present to account for the sulfide content of the average coal seam. The concentration of iron tends to vary with the sulfur content, but the increase or decrease is not always proportional.

URANIUM-BEARING COALS

Under sponsorship of the United States Atomic Energy Commission, a program of research which seeks to describe the manner in

which uranium occurs in carbonaceous sediments is in its final phase. The lignite deposits of North and South Dakota have been studied extensively and have been shown to consist of a series of seams, each different from the others by virtue of the geologic history that has been associated with its development. The individual seams generally consist of inter-tonguing strata, each stratum being formed of a particular coal lithotype. The permeability and porosity exhibited by respective coal lithotypes appear to have played a role in the concentration of uranium. The separate coal seams are identifiable on the basis of their distinctive and characteristic pollen profiles. The sequence of pollen assemblages encountered in each seam reflects changes in vegetation that occurred during the course of the accumulation of the peat that later was altered to the lignitic deposit now encountered.

SOUTHERN APPALACHIAN COALS

Continuation of petrographic studies of low and medium volatile coals from the Southern Appalachian fields, coupled with coking tests, has resulted in the establishment of a relationship between coal composition and the expansion exhibited by the coal during carbonization. Studies of particular coal types have yielded information about the preparation characteristics of these lithotypes, and microscopic "hot stage" studies have demonstrated that thermal reactions exhibited by some of the coal constituents are important in controlling the manner in which such coals behave in coke ovens.

MODE OF OCCURRENCE OF SULFUR IN BITUMINOUS COALS OF PENNSYLVANIA

Nine column-samples of coal seams were collected from three general areas in the bituminous coal fields of Pennsylvania. The Lower Clarion, Lower Kittanning, and Upper Freeport seams were sampled in each of the three areas, whereas the Thick Freeport and Pittsburgh seams were sampled in the western portion of the Commonwealth only. Four hundred and sixty-three analyses were made for total sulfur and pyritic plus sulfate sulfur content, with organic sulfur determined by difference. Each sample represented a particular one-inch level of the coal seam in question. Petrographic examination of these samples revealed the major modes of sulfur occurrence, both as pyrite and as sulfate sulfur. From these data, the following conclusions appear to be justified: (1) The average total sulfur content for each seam increases in a westward direction across Pennsylvania. (2) The Lower Clarion seam, from sediments deposited in a marine environment, has the highest average sulfur content in each sampling

area, whereas the Upper Freeport seam, from sediments of brackish or fresh water origin, contains the least amount. (3) Organic sulfur shows the least variation within a column sample, and generally is between 0.5 and 1.5 in percentage. (4) The sulfur which is within the seams is neither top nor bottom preferential, but is concentrated in certain strata, suggesting that there may be relationships between petrographic characteristics of the strata and degree of concentration of sulfur.

IMPORTANCE OF COAL TYPE IN BLENDING ANTHRACITE AND BITUMINOUS COAL FOR METALLURGICAL COKE PRODUCTION

Studies of the occurrence of mineral matter in several anthracite seams have shown that there has been differential concentration of inorganic substances during the course of each seam's development.

Kaolin, quartz, and mica minerals were found in every seam, but not in all strata within the seam. In strata in which carbonate minerals are present, muscovite and similar micas are absent. Carbonate minerals were encountered in only three of the twelve seams examined. Pyrophyllite was found at only one locality, but was present in both of the seams sampled at this site. Various minerals appear to be preferentially associated with one another and with certain of the organic entities composing the seam. Aggregates of the organic and mineral entities form strata within the seam that probably possess considerable lateral extent as well as distinctive physical differences. It may be possible to exploit the physical differences between these strata in any given seam, in the interest of controlling the ash content of a prepared product, as well as in controlling the quality of the product with respect to its organic composition.

THERMAL BEHAVIOR OF COAL CONSTITUENTS

Because vitrinoid substances form the greater part of most bituminous coal seams, research has been continued on the thermal reactions exhibited by these particular materials. A narrated motion picture film, in color, depicting some of the important reactions and discussing the significance of coal petrology in predicting coke quality, has been prepared in cooperation with the Applied Research Laboratory of the United State Steel Corporation. The thermal studies have been extended to include other groups of coal constituents, including the resinoids and exinoids, in an effort to define the properties characteristic of the major components of bituminous coal that become fluid upon carbonization.

Research has been continued on the thermal reactions exhibited

by petrographically distinct anthracite particles in an effort to understand the relationship, if any, between composition and tendency for decrepitation. Preliminary results suggest that certain lithotypes are decrepitation prone, whereas others exhibit little tendency toward decrepitation.

PALYNOLOGY OF PENNSYLVANIA COAL SEAMS

Studies of the spore and pollen content of Lower Allegheny coal seam in western Pennsylvania have yielded data which should provide a favorable basis for identification. Each seam appears to be divisible into zones on the basis of the relative concentration of particular pollen or spore types, and, by virtue of the sequence of zones that is typical of a particular seam, the seams are readily distinguished, one from the other. The ability to make seam identification in this manner should facilitate correlation of coal beds from one area to another and improve our understanding of the extent of the coal reserves of the Commonwealth.

EASTERN KENTUCKY COALS

A new project has been initiated that is designed to determine relationships between various concentrations of natural aggregates of coal entities, and such characteristics as grindability, specific gravity, fluidity upon heating, and expansion and contraction during carbonization. At present, the detailed petrographic composition of the Elkhorn No. 3 Seam is being determined in an effort to delimit the coal types present. Descriptions of the chemical and thermal properties of these coal types will be prepared.

SIMULATED COALIFICATION

An investigation has been initiated in an attempt to induce the coalification of woody plant tissues as a means of understanding the process of vitrinization. Four different woods (*Araucaria cunninghami* Sweet, *Picea glauca* [Moench.] Voss., *Guiaicum officinale* L. and *Taxodium distichum* [L.] Rich) have been subjected to various temperatures and pressures in a cold seal pressure vessel. Temperatures ranging between 60°C and 472°C were employed with pressures ranging from atmospheric to 15,000 psi, and times ranging from two hours to several days.

A Bridgeman type uniaxial pressure apparatus was used to subject samples of *Taxodium* to uniaxial pressures of up to 100,000 psi for periods up to several days, and the temperatures employed ranged

between room temperature and 450°C. Materials have been produced which, in thin section, are optically indistinguishable from naturally occurring coal macerals. The bulk of the residue is translucent and presumed to be of vitrinitic character, being derived almost exclusively from the cell walls of the subject materials. It was observed that: (1) Temperatures over 400°C generally produce opaque residues. (2) The outer rims of the pit borders are accentuated by a lower degree of translucency. (3) Material filling the cell lumens and that between walls of adjoining cells becomes darker than the cell wall matter under identical conditions. (4) Two processes are acting and these tentatively are referred to by use of the terms vitrinization and micrinization.

ELECTRON MICROSCOPIC OBSERVATION OF VITRINITIC MATERIALS

Samples of vitrinitic materials selected from coals ranging in rank from subbituminous C to anthracite have been examined, utilizing the electron microscope. Two-step carbon replicas were prepared of the surface samples, and microchemical analyses have been obtained for all the samples. The micrographs show that there is an increase in the uniformity of the microfracture pattern with increasing carbon content. This may be noted in three ways: first, there is an increase in the degree of parallelism of the fracture edges; second, there is an increase in the unidirectionalism of the fracture traces; and third, to a limited extent, there is an increase in the conchoidal type of fracture. The compactness of the texture of the samples increases with the increasing carbon content up to and through the high-volatile A rank category. The trend is reversed in the anthracites. Micrographs of two of the lower rank materials have revealed the presence of mold spores and bacilli, as well as of crystalline material which is tentatively thought to be inorganic.

SPECIES OF FOSSIL SPORES AND POLLEN

Bibliographic research into the validity of described species of fossil spores and pollen has been continued and has led to the compilation and publication of portions of a *Catalog of Fossil Spores and Pollen*. During the last biennium, a total of eight volumes has been produced and distributed to subscribers throughout the world, bringing the total number of volumes to twelve. The Catalog will be an invaluable aid to palynologists in their attempts to keep pace with developments in this rapidly growing field.

TECTONIC DEVELOPMENT OF GEOSYNCLINES

Most major mountain chains have grown out of "geosynclines," which are large and elongate depressions of the earth's crust filled mostly by marine sediments during the millions of years preceding the stage of active mountain growth. Field studies, including mapping together with stratigraphic, paleontologic, and petrographic analyses in the Tendoy, Beaverhead, and Lemhi ranges of Montana and Idaho in the marginal region of the Rocky Mountain geosyncline, have been in progress since 1954 and are continuing. In addition to yielding such immediate benefits as the production of geologic maps and elucidation of the regional stratigraphy and structure, the integrated data reveal the paleotectonic and paleographic history of the geosynclinal margin, which was a hinge zone that appears to have been a persistent belt of weakness, marked by crustal mobility during parts of Paleozoic, Mesozoic, and Tertiary Time.

Similar studies also are in progress in north-central Nova Scotia in the northern part of the Appalachian geosynclinal belt, and have revealed a long history of tectonic instability with successive cycles of mountainous uplift, erosion, and renewed subsidence and sedimentation.

FAULT RELATIONS IN THE THRUST BELT OF SOUTHWESTERN MONTANA

A major fault belt follows the eastern margin of the Paleozoic Rocky Mountain geosyncline. The portion of this belt passing through southwestern Montana was the subject of an intensive study during the summer of 1960 involving detailed mapping in selected localities. Among major aspects of the structural style revealed by this study are (1) consistent detachment of the Upper Paleozoic carbonate sequence from underlying quartzites and basement rocks, facilitated by intervening shales; (2) a strong tendency of the carbonates to collapse into major recumbent folds and small nappes; (3) gliding of the Upper Paleozoic carbonates off wedgelike basement uplifts formed by earlier high-angle upthrusts and, perhaps, normal faults; (4) emergence of the upthrusts at the surface during the orogeny to form cliffs, followed by overriding of the thrust blocks across the conglomeratic debris eroded from these cliffs.

These results involve modifications of earlier interpretations of the tectonic pattern of the region. They moreover provide new insight into behavior of different types of rocks under tectonic stress together with the force of gravity, as well as into the role played by the geosynclinal hinge zone during mountain building.

EMPLACEMENT OF PLUTONIC MASSES IN PART OF THE NORTHERN ROCKY MOUNTAINS

Igneous masses, ranging in composition from diorites and syenites to granite, occur near the Continental Divide in the Rocky Mountains north of the Snake River Plain. They appear to follow a northeast-trending zone of extremely intense fracturing and faulting and of metalliferous mineralization. One of these plutons is the subject of a detailed field and laboratory investigation in the hope that data may throw light upon the problem of origin and emplacement of acidic igneous rocks. The genetic process appears to have involved intrusive activity of a syenitic magma, accompanied by hydrothermal action which produced granitoid rocks from surrounding quartzites.

FLOOD PLAIN SEDIMENTATION

Study during the past year of the distribution of sediment in a stream valley revealed that gravel is concentrated at the sides and bottom of the valley fill. This information is of value to engineers and contractors, since gravel is an important construction material.

A further study has been begun on the distribution of chromite in river sediments in southeastern Pennsylvania. Chromite was mined here in the last century, and the present study aims to determine whether there is sufficient chromite left to permit commercially profitable recovery by modern methods.

PLEISTOCENE GEOLOGY AND SOIL GEOLOGY

The Pleistocene geology of Tioga County, Pennsylvania, was mapped during the past year. This area, which previously has not been mapped in detail, is vital to our understanding of the Pleistocene history and soil geology of northern Pennsylvania. The study revealed that the glaciers were very thin in this area and that the consequent glacial deposits are local in occurrence. Some are important sources of sand and gravel.

FRACTURE TRACE MAPPING

Continuing studies in mapping and analysis of fracture traces during the last year have shown that folds and faults may be delineated clearly by fracture analysis, even though they are not obvious on the surface. Studies of fracture traces were made in Centre County, Pennsylvania, and in the Aleutian Islands, Alaska.

MARINE SEDIMENTATION

Large volumes of the rocks of present-day land surfaces accumulated in oceanic waters under the changing geographic conditions of the geologic past. The mechanical and chemical processes of marine sedimentation accordingly are of geologic interest, both because of their present work and their relations to the origin and characteristics of rock bodies with which the geologist must deal.

Research studies being undertaken in marine chemical sedimentation are concerned especially with solution and precipitation of calcium carbonate, the principal constituent of limestone rocks, at temperatures comparable to those found in the sea, and with laboratory control of various chemical substances, including gases, that occur in solution in sea waters.

GEOGRAPHY

GEOGRAPHIC ANALYSIS OF THE BITUMINOUS COAL MINING INDUSTRY OF PENNSYLVANIA

The continuing program of geographical analysis of the Pennsylvania bituminous coal mining industry has resulted in publication of additional studies during the biennium just completed. Foremost among these is the *Atlas of Pennsylvania Coal and Coal Mining, Part I, Bituminous Coal,* issued as Mineral Industries Experiment Station Bulletin No. 73. Representative of other studies published are the following: *Maps of Currently Producing Bituminous Coal Seams in Pennsylvania; Distribution of High-Efficiency Bituminous Coal Mines in Pennsylvania;* and *Coal Strip Pits in the Northern Appalachian Landscape.*

Currently, emphasis is being placed upon means for restoring lands affected by coal stripping, and upon methods whereby stripped areas may be employed productively for other economic pursuits. The need for such studies is evidenced by the presence of some 90,000 acres of stripped land in the western and central parts of the Commonwealth (Figure 1), and by the prospects for continued accretions to such lands. Several interesting possibilities for employing and restoring strip pits presently are under investigation.

GEOGRAPHIC ANALYSIS OF THE ANTHRACITE MINING INDUSTRY OF PENNSYLVANIA

Progress is being made on Part II of the *Atlas of Pennsylvania Coal and Coal Mining,* which deals with anthracite. Studies of an-

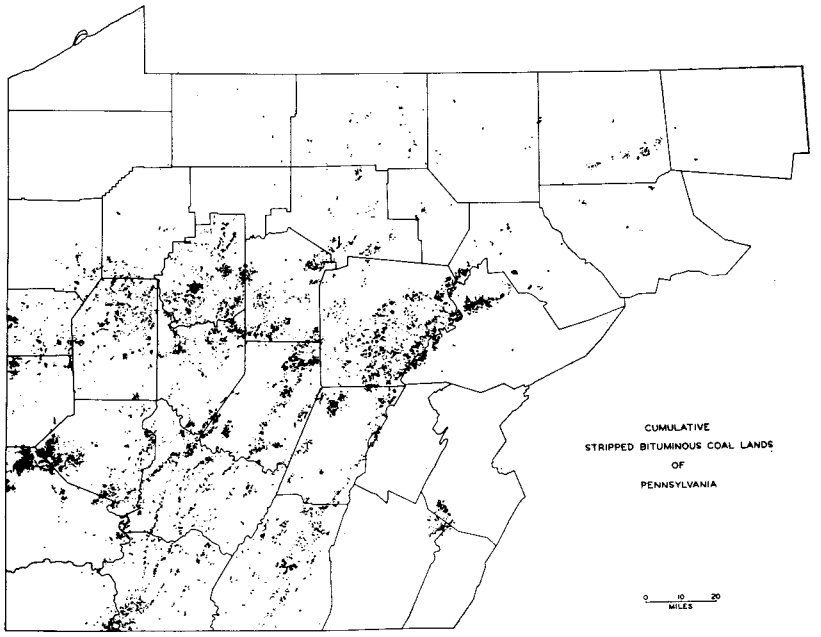
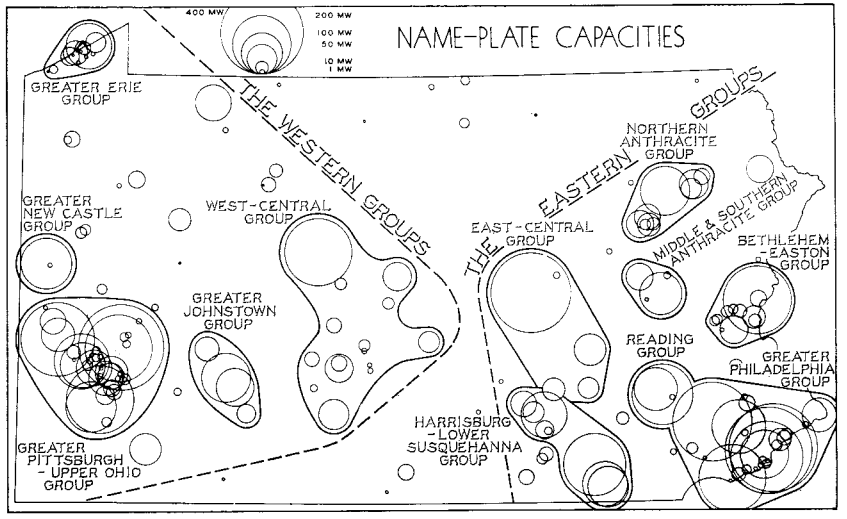
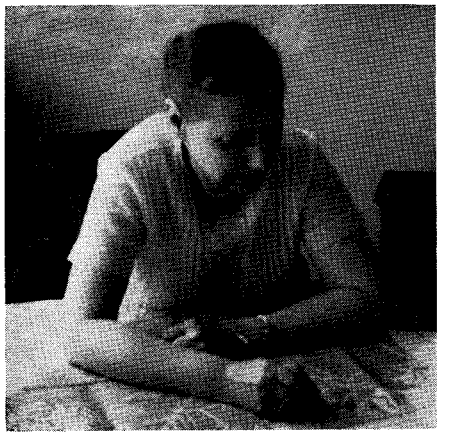


Fig. 1—Map of the counties of western and central Pennsylvania showing areas that have been stripped to obtain bituminous coal.

Fig. 2—Map of the major electric-generating plants in Pennsylvania. Each circle represents one plant, with areas of circles proportional to plant generating capacity. The plants are classified regionally into groups.





Dr. Phyllis R. Griess checking a map of the bituminous coal fields of Pennsylvania in her office, prior to field inspection of a strip mine.

thracite strip mining, based upon field work and analysis of aerial photographs, are being carried on. Materials for Part II of the atlas, as well as for other publications, will result from this research.

ELECTRIC-GENERATING INDUSTRY OF PENNSYLVANIA

Research continues on Pennsylvania's electric-generating industry with emphasis upon types and sources of fuel supply, competition between Commonwealth and out-of-state fuels for the electric generating market, and upon factors influencing the location of the almost 200 generating plants in the State (Figure 2). The latter research includes analysis of the effects upon plant locations of fuel supply sources, market areas, and distribution of suitable water resources.

Among recent publications resulting from such study are the following: *Regional Differences in Primary Energy Sources for the Generation of Electricity in Pennsylvania; Competitive Capabilities of Pennsylvania's Electric Generating Plants in the Coming Atomic Era; Preliminary Statement on Fuels for Electricity in Pennsylvania;* and *Factors Influencing Distribution of Steam-Electric Generating Plants.*

PHYSICAL GEOGRAPHIC FEATURES OF NORTH AMERICA

A comprehensive survey is in progress that will bring together key information about each significant physical geographic feature of the United States and Canada. These materials will update and expand earlier studies of a similar nature, and will provide a basic and authoritative reference source. Over 100 major articles, and more

than 200 minor items, have been prepared to date. Included are studies of individual rivers, mountains, plateaus, hill-lands, plains, peaks, valleys, physiographic regions, lakes, seas, bays, gulfs, straits, swamps, falls, islands, peninsulas, etc.; as well as comprehensive surveys of the physical geography of each state and province in the United States and Canada.

RECENT MIGRATION TO ARIZONA

Since World War II, Arizona has gained rapidly in population, surpassing all but a few of the fifty states in terms of relative growth. A study of the contribution of net migration to Arizona's recent growth has been completed. Results of this study indicate that nearly two-thirds of the population gain has been contributed by net migration from other states, of which California is the leading contributor. Recent migration into Arizona has not been shared equally by all parts of the state; nearly four-fifths of the total movement has been directed to the urban areas of Phoenix and Tucson.

Questionnaires received from over 1,000 newly arrived families in Arizona indicate that climate, especially its benefits to health, draws the largest number of migrants. Summaries of this study have been published by the Arizona Development Board.

POPULATION GROWTH AND REDISTRIBUTION IN CENTRAL AMERICA

Rates of population growth in Central American republics are among the most rapid for the nations of the world. Despite implications inherent in this rapid growth, few studies of population phenomena in Central America have been undertaken. Principal hindrance to such studies has been the paucity of comparable data for the republics. This handicap has now been partially overcome. In 1950, and again in 1960, the nations of Central America cooperated in the timing and nature of their enumerations. The results of this cooperation permit an analysis of the changes in the Central American population over the 1950-1960 decade.

Plans are under way for a study of these changes. Mapping of the 1950 population distribution of Central America by minor civil divisions has been completed, as well as an analysis of certain of the population characteristics, i.e., age structure and sex ratios. As findings of the 1960 censuses become available, these results will be compared to the base data obtaining for 1950. In this manner, identification of major changes and trends will be possible. Field work in Central America is anticipated to obtain information on causes and consequences of population trends observed during the 1950-1960 decade.

CHANGING PATTERNS OF THE MINERAL ECONOMY IN THE UNITED STATES 1939-1954

Between 1939 and 1954 the value of mineral shipments in the United States increased from $6,826,000,000 to $15,147,000,000 (1939 values are converted to the 1954 purchasing power of the dollar). During the same period the number of production workers declined from 774,130 to 666,621. The change in value and in production workers is primarily due to a change in the structure of the coal and petroleum industries. In the coal mining industry, although value of shipments rose from $1,864,000,000 to $2,476,000,000, the number of production workers declined from 454,056 to 232,681. In contrast the value of crude petroleum and natural gas shipments rose from $3,318,000,000 to $9,341,000,000 and the number of production workers increased from 148,996 to 235,483.

The purpose of this study is to define and analyze the trends in the localization of mining in the United States from 1939 to 1955 with particular emphasis on changes in regional patterns. Such aspects as the significance of changing patterns of exploitation, factors in the migration of the mineral economy, and the importance of minerals in the economy of regions are investigated in this study.

The data for the study are presented by means of maps which measure differences in mineral distribution, based on county units, in terms of employment and value of shipments. These criteria were selected for two reasons: (a) regional changes are readily reflected on the maps, and (b) employment and value data are directly related to other geographic elements of a mining region.

A GEOGRAPHICAL ANALYSIS OF THE INFLUENCE OF THE EUROPEAN COMMON MARKET ON THE LOCALIZATION OF INDUSTRY

The European Common Market has as its goal the removal of customs, tariffs and quotas within a six country area. It is hoped that from this step, economic union and ultimately political union will evolve. A study of the coordination of six separate economies into a single unit may reveal steps toward greater international cooperation.

This project has three procedural steps. The first involves the collecting of data in the United States. The second entails field work in the European Common Market area, and the third involves the analysis of data and preparation of the final report. This investigation will include the study of such considerations as the raw material base of the area, transportation patterns, effects of the removal of country tariff and quota barriers, movements of labor force from country to country, and stages of technological advances from country to country.

ORIGIN OF ALIGNED TOPOGRAPHY IN LOESS

In most regions which are underlain by loess, surface features are the result of erosion by running water, and in such regions the stream pattern is commonly dendritic. In the Palouse Hills of southeastern Washington and northeastern Oregon, however, an extensive area is characterized by aligned ridges and valleys, and recently completed research suggests that this alignment resulted from Eolian accretion and not by fluvial erosion. Grain-size analyses of loessial samples from the Palouse, combined with data from nearby weather stations, further suggest that such lineation is associated with relatively coarse loess, whose mode of deposition is controlled by winds of highly preferential direction.

LONGITUDINAL DUNES

Aligned topography is a common phenomenon in areas of sand dunes. The term "longitudinal dune" has been used to denote any linear dune whose long axis lies parallel to effective wind direction. Similarities, however, are often superficial because there are many kinds of longitudinal dunes, each with a different mode of origin. Factors which determine these differences include wind regime, depth of sand, presence and form of fixed obstacles to the wind, and the nature of vegetation if any. Work now in progress is aimed at providing meaningful distinctions between various kinds of longitudinal dunes. A variety of type studies will be drawn together to illustrate these distinctions.

THE PHILIPPINE MINERALS INDUSTRY

Although minerals and their recovery comprise an important segment of the Philippine economy, they serve primarily an overseas market. The Philippines has not progressed industrially to the stage when minerals can be processed and consumed within the country. Nevertheless their contribution should not be minimized. The total value of mineral production exceeds $110,000,000 and mineral exports rank third in value following coconut products and sugar. Some 150,000 - 200,000 persons are supported by the 35,000 workers employed directly in mining operations.

Unfortunately the Philippines mineral base is rather imperfectly known. Only five per cent of the area has been systematically surveyed for minerals. This study aims at an understanding of the mineral resources in the Philippines and an assessment of their potentialities.

PHILIPPINE FISHERIES

Fish and fish products supply the bulk of the protein consumed in the Filipino diet. Whereas the East Indian realm is the greatest center of fish life in the world, this wealth in variety is not accompanied by a corresponding wealth in usable species. The Philippine fishing industry does not provide fish sufficient to meet the present inadequate national consumption.

A geographical analysis of the Philippine fishing industry points toward the understanding of Philippine fish resources, the location, extent, and relative productivity of more important fishing grounds, fishing techniques, and the preservation and marketing of fish products. One aspect which warrants careful study is the possible expansion of *bangas* or fishponds, thereby enabling fish to be harvested as a crop.

METEOROLOGY

BIOMETEOROLOGY

Electrostatic charges in the air, called air ions, have been known to affect physiological processes for some time. There is also good reason to suspect that mental processes are also affected by the ionization of the air we breathe. A study is contemplated of the effects of air ions on learning. However, the equipment necessary for measuring ions is very complicated and expensive. For this reason a preliminary investigation was made in the possibility of using a very much simpler method for determining the amount of space charges. This method involves the measurement of the vertical change of the electric potential gradient, which is a function of the space charge. Conventional measurements of space charge involve the counting of the electric charges per unit volume of air. Promising results have been obtained outdoors with the new method, and some indoor measurements have shown that the method is also applicable in closed rooms in which the major study will be carried out. Further work is under way to improve the equipment that has been developed and to increase its sensitivity.

STRATOSPHERIC OBJECTIVE ANALYSIS

A weather map is made up of thousands of pieces of information gathered by an elaborate communications network from all over the world. Electronic data handling machines ("computers") can take electrical impulses from this network and convert them directly into a weather portrait. An attempt will be made to apply these modern techniques to the stratosphere where the chaotic nature of the air

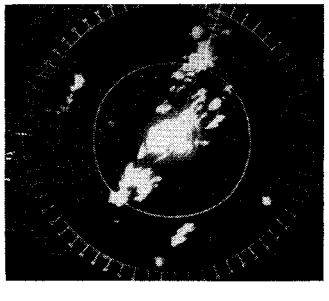
motion at certain seasons and the scarcity and unreliability of the data have so far precluded their usage.

RADAR METEOROLOGY AND CLOUD PHYSICS

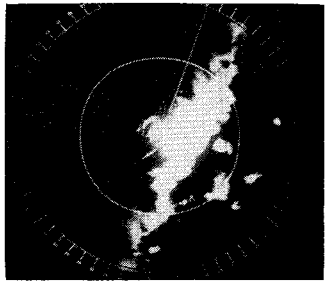
Using a one million watt search radar and funds provided by the National Science Foundation, the detailed distribution of showers and thunderstorms over Central Pennsylvania is being studied. In addition, a 250 kilowatt radar is being used to track balloons and obtain upper wind data coinciding with the data on shower distribution. These data, together with teletype and facsimile data, are being used to study the relationship between the topography of Central Pennsylvania and the places in which showers form, how they move, and where and when they dissipate. The study will provide a measure of the magnitude of the influence of topography of this type on weather and also serve to aid forecasters in adjusting forecasts to account for local influence of topography on weather.

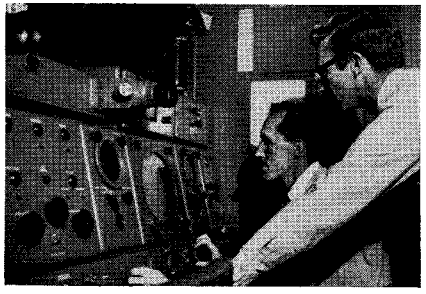
The growth of small aggregates of ice crystals has been observed between —6°C and —25°C by mounting an ice sphere in a moving cloud of ice crystals. The density of the aggregate formed increased with increasing temperature, and observations of the aggregate growth showed that the bonds between ice crystals permit folding of crystal towers, i.e., of linear crystal aggregates. The higher the temperature, the more folding was noted. The proportion of the ice crystals in the path of the aggregate that became attached to it was temperature-dependent showing a maximum collection efficiency at —11°C. Plates formed aggregates at a greater rate than did columnar crystals; hence, when the cloud composition changed from plates to columns as the temperature increased above —11°C, the amount of aggregation diminished. These data and other evidence are interpreted as indicating that the aggregation of the ice crystals depends upon the existence of a liquid film on the ice surface. The film thickness is greater at higher temperatures.

Squall line approaching State College, Pa., from the northwest as it appeared on radar scope on May 17, 1960, at 1:50 p.m.



Same squall line at 3:00 p.m. after passing State College, Pa.





Portion of radar equipment in radar van.

LOW-LEVEL WIND STRUCTURE

The detailed vertical distribution of wind in the lowest 30 feet of the atmosphere plays a fundamental role in many theoretical and practical problems. In designing buildings, towers, or elevated highways, engineers must take into consideration the entire vertical distribution of wind, even though observations are usually available at only a single level. Also the force of the wind on the surface of lakes and oceans is responsible for wave generation and the piling up of water on coasts facing the wind.

Building on theoretical and observational studies that began in Germany 30 years ago, scientists at Penn State have developed a theory that accurately predicts the wind at different heights and the drag at the surface when the wind at one height and the temperature distribution are given. The next problem being studied in this project is to predict these quantities from data which can be measured on weather maps or on prognostic charts turned out by an electronic computer.

DYNAMIC WEATHER PREDICTION

One of the most revolutionary trends in modern meteorology has been the application of high-speed electronic digital computers to the solution of the dynamical equations of the atmosphere. Methods are being studied at Penn State for reducing the staggering volume of computation through application of graphical methods. Using such techniques it has been found possible to investigate rather complicated models of atmospheric circulation, including the relatively unknown effects of friction. The goal of the research now being undertaken is to develop simplified prediction models which can later be programmed for high-speed automatic computation and to show how these models can best be applied to predict cloudiness and precipitation up to 30 hours in advance.

MINERALOGY AND PETROLOGY

Fundamental research into the petrology and petrography of rocks leads to applications of use in exploration and exploitation of raw materials in the earth's crust. The program presently under way encompasses studies of interest to the development of the petroleum, uranium, and refractories industries, including clays and clay products and quartzites.

SEDIMENTARY PETROLOGY

Sedimentary rocks can be studied in detail with the microscope or as larger units in the field. The first is prerequisite to the second.

After adequate solution at Penn State of the most basic aspects of microscopic rock study several years ago, considerable effort has recently been devoted to field relations. As a result one of the most basic problems of sedimentary geology, which had been bedeviling geologists for a hundred years namely the problem of FACIES, has been successfully solved. Through the application of principles, analogous to those of physical chemistry, insofar as model construction goes, it was shown that changes in facies, i.e., changes in the apparent aspects of the same or of equivalent sedimentary rock bodies in time and space, are due to a series of interactions, carried out at three levels of organization within and between three basic components, namely sedimentary phases, systems, and complexes. The mechanism of these interactions is ultimately controlled by structural movements of the earth's crust.

As the next step, another problem, particularly interesting in the study of limestones and coal-bearing rocks, was also solved. This is the problem of rhythmically repeated or *cyclic* sedimentation. As with facies, this study led, first, to the discovery of the actual building blocks that make cyclicity in a physical sense—there are two of these: the influx and the fill-in cycle; and, second to the clarification of the basic principles and actual operative mechanism which produce cyclicity. Both in a scientific and in a practical sense, these discoveries should be of value for any kind of future work involving sedimentary rocks.

FACIES

A rigorously operational, physico-chemical phase-system type approach, free of stratigraphic semantics, shows that lateral changes within sediments, or "facies" in order of decreasing extent, are

(1) First-order changes, subcontinental to geosynclinal:

(a) Static, synchronous coexistence of diverse sedimentary systems.

(b) Dynamic, isochronous movement of a "rolling complex" of coupled sedimentary systems during major tectonic episodes.

(2) Second-order changes, either cross-basinal or limited to tectonic sub-blocks (15-40 miles):

(a) Changes within a system, as one phase encroaches upon another through ratio fluctuations in factor 3 (a).

(b) Changes within one phase along a gradient, utilizing factor 3 (b).

(3) Third-order changes, more or less local:

(a) Inherent to a system, i.e., ordered juxtaposition of inevitable phases, and their migration as a fixed systemic property.

(b) Inherent to a phase, namely its character either as an influx locus (essentially a systematically varying singleton) or a fill-in locus (essentially an expansion-susceptible doublet). Satellitic rock types, secular tendencies, and accidental chance occurrences characteristic of a given locus add minor complications.

At any space-time point the general character or "facies" of a sediment represents the interaction of factors 1, 2, and 3, as shown by examples from the Appalachian and Rocky Mountains geosynclines. Methods are being devised to unscramble these interactions.

Incidentally, most of the interesting and tantalizing phenomena of sedimentary cyclicity, periodicity, and rhythm can be theoretically derived, operationally defined, and empirically checked from the system-phase model.

SEDIMENTARY CYCLES

Two basic discrete polar elements build all sedimentary cycles, i.e., series that repeat themselves: (1) influx cycles, where effective utilization of energy decreases asymptotically toward the end of a sedimentary episode, and (2) fill-in cycles where the opposite is true. In clastic rocks the simplest examples respectively are upright vs. inverted graded stratification. A chemical crystallodepositional fill-in cycle is the limestone-evaporite sequence. Cyclicity develops laterally as well as vertically, from wave layerlets to regressive complexes.

Basic combinations are simple influx; simple fill-in; carbonates; fill-in followed by influx; cyclothems; and influx followed by fill-in (playas).

A cycle shows a basic sovereign lithologic sequence and several satellitic rock types potentially present at determined positions.

Cyclicity is caused first by primary or immediate sedimentary factors, rarely accidental but generally systematic, produced by interplay of phases within systems of sedimentation for short distances.

Second come the ultimate factors, either tectonic sub-blocks, 15-35 miles across, with oscillatory facial changes, or subregional tectonic blocks controlling major regressive-transgressive complexes. Climatic and eustatic factors are less potent. Fill-in cycles depend entirely on basinal tectonics; influx cycles are complicated.

Factor interaction produces certain polar-model mass resultants, namely the classical cyclicity types; coal cyclothems; primary-secondary dolomite coupled pairs; banded carbonates; sandstone-shale complexes; red beds.

Finally cyclicity is treated first empirically, then analytically, and last theoretically through the four basic tectonic types, the five sedimentary rock series, and the six major environments of deposition groups.

SEDIMENTARY PETROGRAPHY

Definition of a Rock

One of the most fundamental problems in geology concerns the definition of the basic units such as minerals and rocks. A definition commonly used is: (1) A rock is an aggregate of minerals, which may be generalized to: (2) A population is an aggregate of elements.

It then becomes necessary to delimit the population and state criteria for recognition of the *elements;* the problem is now the usual statistical one of deciding how to characterize a population by sampling its elements.

A sample is a set of elements where the size of the set may vary from 1 to "m"; the characteristics of the population are parameters and the analytical procedure is performed on samples; the samples yield *statistics* which estimate the population parameters. It would be desirable to use *best estimators* where feasible because they fulfill the requirements of being unbiased, consistent, efficient and sufficient. In practice the first two criteria are fulfilled, but efficiency and sufficiency are often difficult to achieve.

It is now necessary to select parameters which the procedures are required to estimate and if we express the objective as: Each rock-specimen (≡ population) should be characterized by a unique index P, we may then write P as a function of the parameters: (3) P = f (M, S, Sh, O, Pk) where M represents the proportions of different kinds of elements (constituents, minerals, etc.) which enter the specimen; S represents the grain size of these elements; Sh, their shape; O, their orientation and Pk, their packing.

Now analysis leads to statistical estimators of these five parameters and they should fulfill the basic criteria for best estimators. In practice each parameter represents a concept and these concepts must be reduced to operations before analysis may be performed; the defining equation then becomes: (4) P = f (m, s, sh, o, p). Where m estimates M; s estimates S, etc., and some suitable combination of these estimators yields a sample estimate p of P.

It may be argued that if P is to be unique then the parameters represent the fundamental properties and the five listed in (3) fulfill the necessary and sufficient conditions to result in a unique index P. Variation in P from rock specimen to rock specimen will then lead to definition of rock bodies of various kinds and by integration to the stratigraphic column and ultimately the crust of the earth. The advantage of this defining equation is that it may be universally applied to any set of elements which may be looked upon as a population from an atom to the universe. Apparently the defining equation has the desirable property of invariance across scales of magnitude.

Procedures and techniques for measuring (estimating) the properties (parameters) have been evolved and their frequency functions are known; one of the advantages of knowing the frequency function is that a random sample (set of elements) may be precisely defined; the frequency function acts as a model and, by collecting a set of observations according to the prescription for randomness, a test of observed against expected may be performed. Departures from the model arise because the exact conditions implied in random sampling are not fulfilled and this reflects heterogeneity in the population. Thus a replica of the structure or arrangement within the population may be specified by repeated sampling using different designs.

Modal analysis of thin sections by point counting indicates whether the rock-specimen possesses a layered or massive structure; sampling gravels and measuring the size and shape of contained "quartzite" pebbles again indicates whether the arrangement is layered or not, illustrating that these procedures are applicable quite generally to populations of interest in the earth sciences.

The observation that when any parameter characterizing a rock-specimen is estimated by sampling statistics the structure is reflected by varying the sampling arrangement, illustrates that *all* of the measures so far proposed for petrographic analysis are interdependent. In other words, when a measurement technique is applied to an aggregate (≡ rock-specimen ≡ population) it supplies statistical estimators of the parameters and the parameters are characteristics of the population. Each measure obtained in practice contains confounded information on all five parameters, and to separate the effects of one from the other requires multivariate analysis. Assumptions of independence and theo-

retical models which contain this assumption ignore this interdependence and its accompanying interactions; insofar as the interdependence is characteristic and the interactions are important contributors to variation in the statistical estimators, predictions based on models using independence assumptions will fail to be realized in varying degrees. The proposed program arising from the defining equations (3, 4) appears to avoid this dilemma.

MINERALOGY AND CHEMISTRY OF URANIUM-BEARING LIGNITES

Lignites from South and North Dakota and California and peats from Florida have been extensively investigated in a program sponsored by the U. S. Atomic Energy Commission. Approximately 600 samples from appropriate locations have been studied chemically, by X-ray diffraction and fluorescence analysis, with the microscope, and by autoradiographic techniques in order to define the nature and degree of association of uranium with mineral and organic portions of the material. Complementary studies of the coal macerals, spores, and pollens have been made in the Anthracological Laboratories of the Geology Department. This study supplements the extensive work reported hitherto on the mineralogy, petrography, and chemistry of uraniferous black shales. The two A.E.C.-sponsored programs constitute an extremely thorough investigation of the interrelationships of organic and inorganic constituents in these rocks.

The research has shown that the Florida peats resemble the black shales in that the occurrence of uranium can be explained on the basis of reducing conditions favoring direct association of the element with carbon-, hydrogen-, and sulphur-bearing components. The California and Dakota lignites, however, reflect a geological situation complicated by greater variation in redox potential, availability of uranium, structural and textural control of uranium-bearing solutions, and other factors more difficult to interpret in terms of the chemical, mineralogical and paleobotanical data.

Statistical analysis of many thousands of items of data is being made with the IBM 650 digital computer to determine the nature and degree of interrelationship among some 25 quantitatively measured variables. Evaluation of selected groups of samples reveals important regional and local differences as reflected by the degree of association between certain variables and uranium.

These differences are commonly explicable in terms of geological and mineralogical relationships observed in the field and the laboratory, and serve as the basis for successful explanation of: (1) the occurrence and distribution of uranium both in these specific regions and in general in rocks of the type studied; (2) the nature and cause of the intimate relationship of carbonaceous and mineral matter; (3)

the geochemistry of the solutions that have been involved in the emplacement of the mineral and organic components; and (4) the trace and major element assemblages found in sediments of the type studied.

MINERALOGY OF KAOLIN CLAY DEPOSITS OF THE SOUTHEASTERN UNITED STATES

Seventeen complete drill cores supplied by several clay companies, together with 200 samples collected on trips to the area, have been used in a study of the mineralogy and origin of America's largest kaolin clay deposits.

A total of 406 individual samples have been examined and a measure has been made of each for one or several of the following variables: degree of crystallinity, montmorillonite content, major chemical components, major detrital grains, number of kaolinite books, proportion of sample greater than 200 mesh, depth of sample, texture, and bulk density.

Methods have been devised or adapted to permit quantitative estimates to be made of all of the variables but texture. Methods of handling and processing data have been developed which utilize IBM cards and thus the data are amenable to analysis by programs designed for computers and other data processing machines.

A study of the data provided by these methods on the 172 samples analyzed initially shows the existence of several interesting conditions and relationships. Crystallinity measurements of Piedmont material show that the kaolin derived from feldspar ranges from very poorly crystallized to moderately well crystallized, and that this variation takes place over a distance measured in inches. Similarly, variations in the Coastal Plain occur within short vertical distances within the deposits, but in contrast to the Piedmont situation the greatest variation occurs with greater distance, i.e., between deposits.

Variations in montmorillonite content, major chemical components, detrital grains, and kaolinite books also indicate that the Coastal Plain deposits are inhomogeneous and may be stratified. Good correlations between certain variables have been found and these indicate that distinct and measurable differences exist between the hard and soft type clays which are used for different commercial purposes.

Analyses performed on subsequent samples, taken according to a different experimental design, have provided data which substantiate the earlier results and emphasize the strong negative correlation between iron and the degree of crystallinity, and the strong positive correlation between the presence of kaolinite books and the degree of crystallinity. In the soft clay a strong negative correlation exists between mica and kaolinite books whereas in the hard clay this

relationship is reversed. An analysis of variance indicates significant differences exist between the hard and soft clay types with respect to iron and degree of crystallinity. Examination of thin sections shows remarkable differences in the appearance of birefringent areas which may relate to conditions of flocculation, which in turn may relate directly to the iron variation and indirectly to the degree of crystallinity.

The data are in the process of being summarized for presentation discussion in publications and a Ph.D. thesis.

ROCK WEATHERING AND CLAY FORMATION IN HAWAII

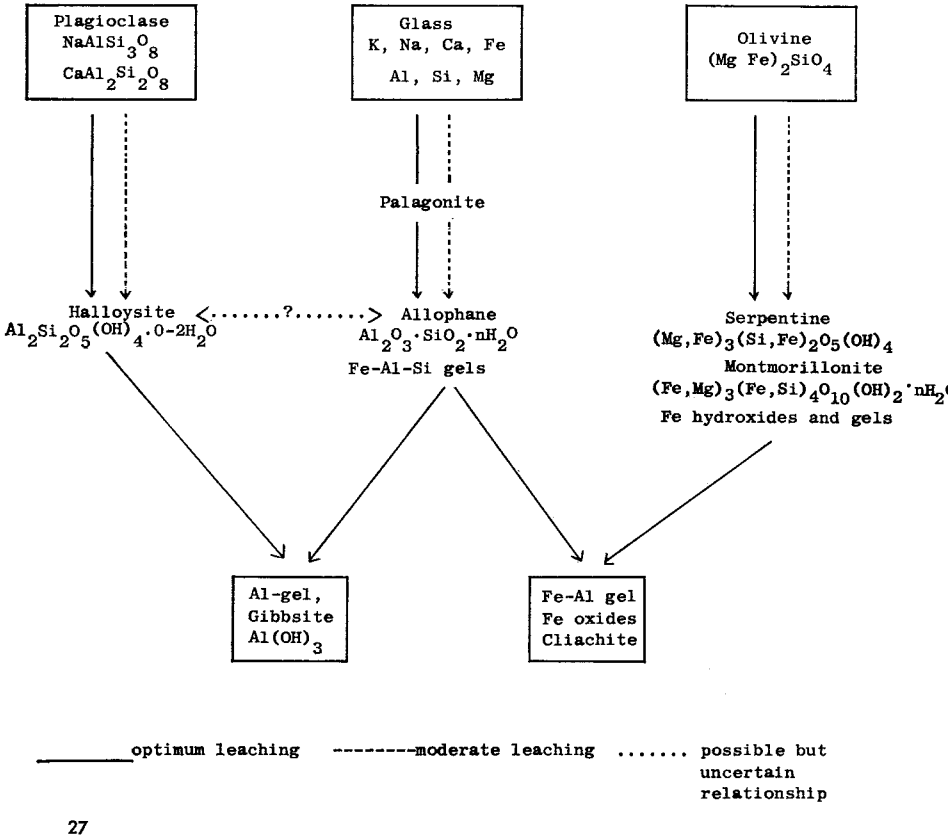
The changes produced when minerals and rocks are subjected to various climatic conditions are of concern to the geologist, mineralogist, petrographer, geochemist, soil scientist, and engineer; and knowledge of the weathering process is important to both the scientist and to the many industries concerned with the exploitation and use of numerous types of weathering products.

Hawaii offers unusual opportunity for research on rock weathering because of: (1) the very large variation of annual rainfall within short distances; (2) the extreme differences in slope and therefore leaching action of solutions (Fig. 3); (3) sharp changes in rock composition and texture; and (4) easy accessibility to a large variety of sample localities. Consequently, during a one-year sabbatical leave supported by a National Science Foundation Senior Post-doctoral Fellowship, plus a National Science Foundation Research Grant, Dr. Bates conducted field and preliminary laboratory research in the Islands. His studies showed that weathering in Hawaii is largely a process of desilication. As silica, together with bases, is taken into solution and removed to the sea, the primary silicates change to clay minerals (largely halloysite, allophane and nontronite) and ultimately to oxides and hydroxides of Fe, Al, and Ti. Gels produced largely by the hydration of volcanic glass are common in wet areas and, in places, dry out to form similar oxide and hydroxide end products. Locally the process of desilication is interrupted and even reversed where dry conditions, impounding of Si-rich solutions, or variations in rock composition and texture impede the attack of rainwater and leaching solutions.

Fig. 3—Waikolu Valley, East Molokai. 60-80 inches of annual rainfall supports luxuriant forest growth in this valley with 3000-foot relief.

Fig. 4—Completely altered basalt with halloysite-clay and gibbsite filling former vesicles. Haiku area, East Maui. (Millimeter scale at top of photograph.)

The accompanying diagram summarizes the mineral changes observed in the weathering of feldspar, glass, and olivine of the parent rocks. Optimum leach conditions (solid arrows) for a sufficient time produce the Al and Fe end products shown at the bottom of the chart. As part of the process, development of intermediate products is the usual step, though perhaps not a necessary one.



Gibbsite, the chief ore of aluminum, forms in at least three ways in Hawaii: (1) by removal of silicia from halloysite (Fig. 4); (2) by dehydration of Al and Fe-Al gels; and (3) by precipitation from Al-rich solutions. All three are common and often evident in a single thin section of a weathered rock. However, in contrast to types 1 and 3, type 2 is to be expected only where desiccation has been possible either through surface exposure or the advent of dry climatic conditions.

Gel material plays an important part in the weathering picture and is most easly accounted for as a product of glass alteration. The possibility exists that gel may also result if disorded intermediates involved in mineral transformations (such as feldspar $\longrightarrow$ halloysite $\longrightarrow$ gibbsite) are removed by weathering solutions before the transition is complete. The presence of, or necessity for, such disordered intermediate states has not been definitely established.

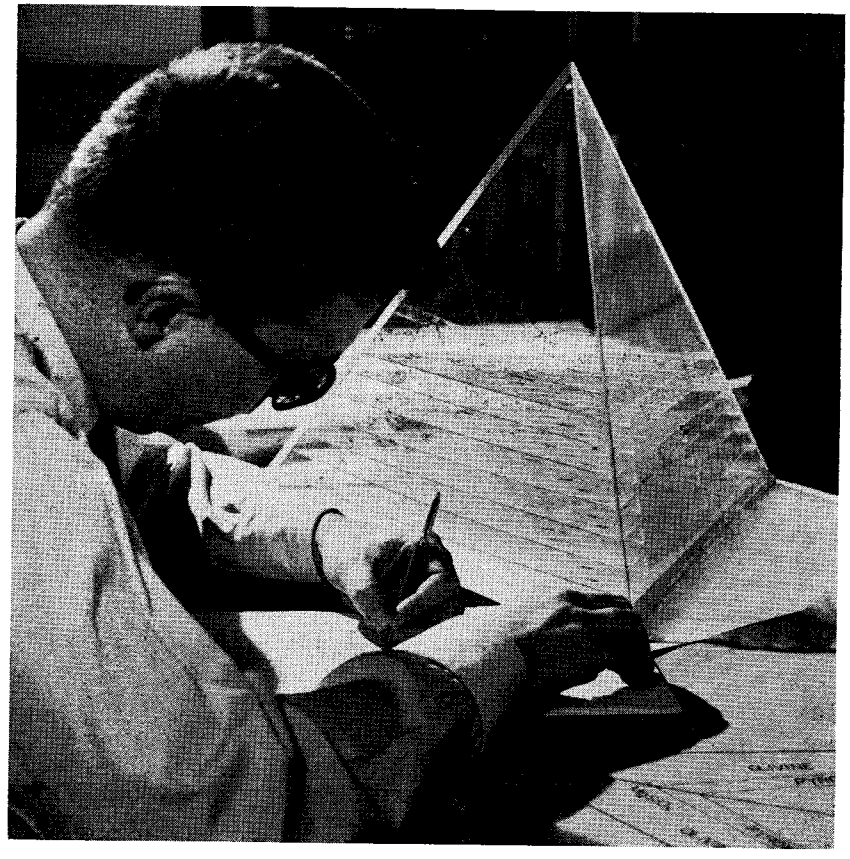
Detailed laboratory studies of collected samples are in progress in order to provide more precise information on the mineral transformations, and thus to add to our knowledge of the solid state not only further information on well-crystallized mineral substances but also essential data on the character and role of poorly-crystalline to non-crystalline material.

GEOPHYSICS AND GEOCHEMISTRY

Geophysics and Geochemistry are the branches of earth science in which the principles and practices of physics and chemistry are used to study the earth and the materials of which it is composed. The characteristic feature of the various research efforts described below is that in each one some specialized physical or chemical technique is used to gather data with which the frontiers of earth science can be expanded.

ISOTOPIC COMPOSITION OF MOLLUSK SHELLS AND LIMESTONES

Investigation shows consistent differences between the carbon and oxygen isotopic composition of marine mollusk shells and fresh-water mollusk shells. The calcium carbonate of fresh-water shells contains carbon and oxygen which are isotopically lighter than those of marine carbonates, as shown by mass-spectrometer measurements of carbon dioxide extracted by acid treatment of shell samples. The observed differences are large in relation to the reproducibility of measurement and provide the data necessary for evaluating relationships between the shell composition and the environment in which the mollusks grew.



Use of a three-dimensional model to picture phase relations in a complex quaternary silicate system.

The second stage of the investigation, involving comparison of fossil shells and limestones, is under way. Preliminary data indicate that the oxygen isotope ratio (O^{18}:O^{16}) is not permanently retained in ancient carbonates, but is altered by post-depositional changes and therefore cannot be used as a reliable indicator of the conditions of formation of sedimentary carbonate rocks. However, the carbon isotope ratio (C^{13}:C^{12}) appears to be more permanently fixed and to be related to the original environment of deposition in a consistent manner. Therefore, measurements of the carbon isotope ratio of ancient carbonates, both of fossils and of limestones, offers promise of providing an additional tool for studying the origin of sedimentary

rocks and specifically for differentiating marine formations from continental formations and thus facilitating paleogeographic studies of the extent of the oceans and continental areas of the geologic past.

PHASE EQUILIBRIA OF CERTAIN MINERAL SYSTEMS

By holding mixtures of oxides under controlled conditions of temperature and pressure until equilibrium is established among the various compounds which form, then quickly freezing the mixture and noting what mineral phases are present, the stability fields of mineral systems can be established. Among the mineral reactions on which work has recently been completed are:

(1) calcite + diopside + forsterite $\leftrightharpoons$ monticellite + CO_2
(2) calcite + diopside $\rightleftharpoons$ akermanite + CO_2
(3) calcite + forsterite + akermanite $\leftrightharpoons$ monticellite + CO_2
(4) diopside + monticellite $\leftrightharpoons$ forsterite + akermanite
(5) calcite + forsterite $\leftrightharpoons$ monticellite + periclase + CO_2
(6) spurrite + monticellite $\rightleftharpoons$ merwinite + calcite

In addition, several reactions in the hydrothermal systems MgO—H_2O—CO_2 were investigated, and selected parts of the system nepheline-kalsilite-silica-water were studied. Data on the pressure-temperature stability of $MgCO_3$ and $Mg(OH)_2$ in the presence of CO_2—H_2O vapor were obtained. It was shown that $MgCO_3$ does not melt even in the presence of water up to 1400°C and 1000 bars pressure. The extent of leucite and analcite solid solutions under various conditions was delineated. Information of this type is fundamental to an understanding of the genesis of igneous rocks.

CARBONATITE INVESTIGATIONS

The carbonatites are intrusive bodies of carbonate rock that occur widely in a volcanic setting generally associated with alkaline rocks. Carbonatite studies are of particular importance both for the light they cast on an unsolved petrological problem and for their economic significance, inasmuch as many carbonatites contain large tonnages of rare earth minerals. The chief problems presented by carbonatite complexes are the source of so much lime and carbon dioxide, and the difficulty of holding a large body of carbonate in a liquid state at petrologically reasonable temperatures and pressures. Experimental work has been directed toward possible solutions of the latter problem.

In view of the alkaline nature of most carbonatite complexes, various combinations of the alkali and calcium carbonates and calcium hydroxide have been investigated by hydrothermal quenching techniques in sealed tubes at 1000 bars total pressure. These systems all

represent planes in the quaternary systems CaO—Na_2O—CO_2—H_2O and CaO—K_2O—CO_2—H_2O. Those studied so far are

Na_2CO_3 — $Ca(OH)_2$
Na_2CO_3 — $CaCO_3$
K_2CO_3 — $Ca(OH)_2$
Na_2CO_3 — $CaCO_3$ — $Ca(OH)_2$

In addition to this the effect of fluorine has been studied by working out the systems

CaF_2 — $CaCO_3$
CaF_2 — $Ca(OH)_2$
CaF_2 — $CaCO_3$ — $Ca(OH)_2$

again at 1000 bars. These systems are thought to bear also on the problems of calcite-fluorite mineral veins.

In those parts of the systems that represent possible carbonatite compositions it is found that complete melting occurs in the range 500-700°C in the dry state. Since it is also possible that a body of carbonate may behave in a highly if not completely fluid state when less than 50 per cent liquid, it is likely that this temperature range may be a reasonable one for the naturally occurring carbonatites in it.

HYDROTHERMAL STUDIES USING LARGE SAMPLES

Phase equilibrium studies at high pressures (10,000 atmospheres) and temperatures (1500°C) using very small samples have delineated the stability fields of many minerals. In natural systems, the range of minerals present tends to be large, and the formation of mineral species involves progressive steps which cannot easily be traced using very small samples. For this reason, experiments using larger samples (several cubic centimeters) are needed. Five units for such work are now operational and in use studying the composition of water-rich vapors in coexistence with various silicate mixtures. The data being gathered are giving increased understanding of the formation of pegmatites and mineral deposits of hydrothermal and metasomatic origin.

PHASE EQUILIBRIA AT HIGH TEMPERATURES IN DRY OXIDE SYSTEMS

Systematic studies are being made of phase relations in three, four and five component systems of the common oxides: SiO_2, Al_2O_3, FeO, Cr_2O_3, Fe_2O_3, CaO, MgO, TiO_2 and MnO. Investigations are being carried out largely in the temperature range of 1000° to 2000°C and at oxygen partial pressures of 10^2 to 10^{-12} atm. The results are applicable especially in the two areas of: (1) steel plant refractories and slag technology, and (2) igneous petrology. Current emphasis is being

placed on systems containing transition elements, where the valence change of an element is a function of oxygen pressure and temperature and where total composition is an important factor in determining the nature of the phase assemblage present. The spinel phase containing various combinations of Fe^{2+}, Fe^{3+}, Ti^{4+}, Mn^{2+}, Mn^{3+}, Mg^{2+}, Cr^{3+} and Al^{3+} is of critical importance in this research, with much attention being devoted to its changing composition, structure, and thermal stability as the principal variables are changed.

CRYSTALLIZATION PHENOMENA IN SIMPLIFIED BASALT MAGMAS

Impressive progress has been made in our understanding of crystallization phenomena in basaltic and related magmas through the laboratory study of systems much simpler than the natural magmas, but sufficiently similar to demonstrate and illustrate fundamental principles. An example is the system MgO—FeO—SiO_2. Extending the laboratory investigations to more complex but still simplified basalt systems is being done as an important step in the further elucidation of crystallization and differentiation processes in natural magmas. Investigations under conditions of controlled oxygen partial pressure, as well as temperature, are being made of the three systems:

(1) MgO — FeO — Fe_2O_3 — SiO_2 — $CaAl_2Si_2O_8$
(2) Mg_2SiO_4 — Fe_3O_4 — $CaMgSi_2O_6$
(3) Mg_2SiO_4 — Fe_3O_4 — $CaMgSiO_6$ — $CaAl_2Si_2O_8$

ROLE OF OXYGEN PRESSURE IN THE CRYSTALLIZATION AND DIFFERENTIATION OF BASALTIC MAGMA

Studies of phase equilibria in simplified basaltic magma have led to the development of an hypothesis that the rate and direction of change of oxygen partial pressure during fractional crystallization of a primary olivine-basalt magma is critically significant in determining the major differentiation trend, i.e., whether in the direction of the calc-alkali series or in the direction as exemplified by the Skaergaard series. Actual lava specimens are now being studied under conditions of controlled oxygen partial pressure as well as temperature to find the effect of oxygen pressure on liquidus temperatures on FeO/Fe_2O_3 ratios in liquids and on phase assemblages. Rock specimens being used are from the Hawaiian Islands and from the Cascade Province of Northwestern United States.

EXTREMELY-HIGH-PRESSURE STUDIES

During the last two or three years, The Pennsylvania State University has moved into the forefront of the laboratories doing chemical

research above 20 kilobars (about 300,000 psi). It appears likely that significant results have been obtained here at higher pressures than at any other laboratories. Operations can be carried out conveniently at 100 kb and the maximum is near 200 kb pressure. Moreover, due to the absence of any reliable piezometer in this range, direct chemical evidence obtained in this research is the best that has been obtained to date to prove that pressures of such magnitudes were actually reached and maintained.

In the equipment-design field another substantial contribution is the development of apparatus in which "displacive shearing" stresses can be set up in the sample at pressures of up to 100 kb. The value of this device is shown in its acceleration of certain solid-solid reactions by two or three orders of magnitude.

A possible major contribution to high-pressure science was the development of a continuous-function piezometer for use to nearly 200 kb and at least 500°C based on the densification of SiO_2 glass.

The main direction of the high-pressure research is to investigate systematically the influence of pressure in crystal chemical relations and to study the influence of high pressures on the kinetics of solid-solid transformations. It has proved possible to synthesize a large number of new phases and to preserve them metastably at atmospheric pressure, among these being BPO_4, which represents the phase requiring the maximum pressure for its formation at equilibrium—more than twice that required for diamond at the same temperature. Also studied thoroughly has been the olivine-spinel transition for compositions near Mg_2SiO_4, which is said to be the most important phase transition in understanding the internal structure of the earth.

SOLID-STATE-CHEMISTRY STUDIES

The work in the chemistry of the solid state has both continued along previous lines and broken new ground. Systematic work on phase transitions has continued with attention being concentrated on the variation of transition temperature with compositional disorder. The compositional disorder encompasses both substitutional randomization of similar ions (e.g., Al, Si in nepheline and carnegieite) or the disorder of atomic displacements by intense neutron bombardment. The most important result among those dealing with order-disorder is the discovery of extensive order-disorder of different types in most spinel phases. Not only has normal-inverse disorder been shown to be common in spinels reacted in the usual range (600-1600°C), but ordering on the octahedral site is found for other cases. The fact that, at least in a few cases, the order-disorder is shown to be an equilibrium phenomenon (with a particular distribution character-

istic at a particular temperature) demonstrates a weakness of present crystal field theory in omitting a temperature-dependent term. The influence of large concentrations of well-defined types of defects on the diffusion coefficient, the critical parameter in solid-state reactions, is being studied for one or two simple structures.

MINERALOGICAL AND GEOCHEMICAL STUDIES OF LAYER AND NETWORK SILICATES

This work is directed toward understanding the physico-chemical behavior of these minerals. This laboratory's most important contribution in this field is the new approach taken to the understanding of the infrared absorption spectra of complex crystalline phases. We have been able, by hydrothermal techniques, to prepare series of synthetic phases, controlling the replacement of any ion in any particular site. For example, Mg has been replaced by Ni; Al, by Ga; Si, by Ge; H, by D. By examining series of spectra, it has been possible to correlate certain bands with the presence of certain ions unequivocally. Even though the vibration mode is unspecified, this method has avoided many earlier mistakes in assignments. It has become clear that, except for stretching moments of very highly charged cations (Si^{4+}, P^{5-}), it is quite meaningless to assign frequencies to particular modes of certain ions because the environment changes the frequency so radically.

A second area of work concerns the mechanism of the processes by which a "rock" is weathered in nature. Again using synthetic models, the control exercised by the structure of the phase (s) (whether glassy, crystalline or a gel) and the environment (temperature pressure, salinity, CO_2-saturation) has been delineated. Further, the fate of trace elements (Ni, Ga, B, Rb, Sr) has been followed quantitatively through the same processes and the concentration or dilution in the clay, zeolite and solution phases.

Over a decade ago, when experimental work on synthetic clays was first started here, the general features of the calcification of clays were fairly well understood; but the situation with respect to the details and the relationships among and within groups was confused. The situation in the clay mineral family is now essentially resolved. The analogous situation, with even greater confusion, exists in the zeolite family. The long-range problem now being tackled is understanding the crystal chemistry of the zeolites. Here, the experimental difficulties are much greater, since not only are three dimensional network rearrangements involved, but the temperatures of reaction are much lower. So far, perhaps the most important finding is the fact that many of the zeolites undergo several structural changes, some

due to water loss and some pure phase transitions in the temperature range of their "zeolitic behavior." Hence the crystal structure of a zeolite determined at room temperature is relatively unimportant, since a "different zeolite" may be involved at the temperature of reaction.

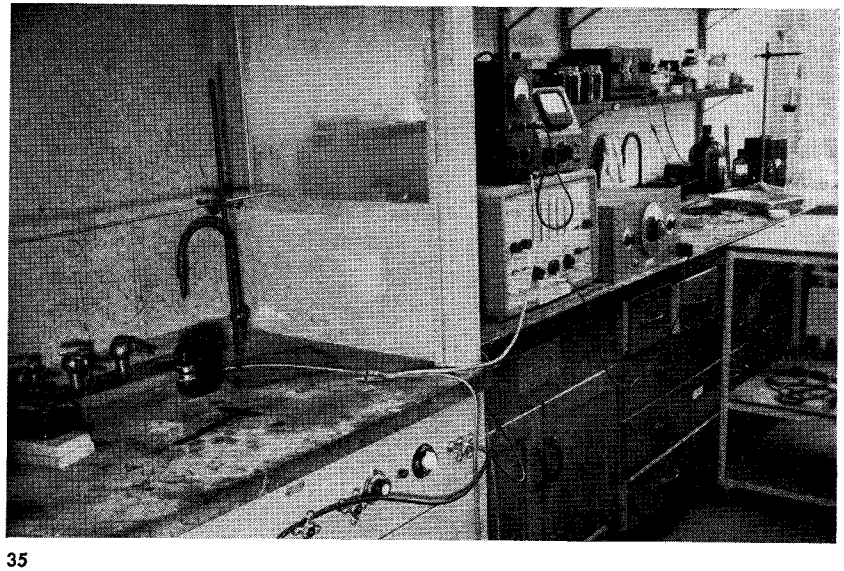
IRON ORE DEPOSITS OF SOUTHEASTERN PENNSYLVANIA

The Pennsylvania Geologic Survey has recently issued a series of areomagnetic maps of parts of Pennsylvania. On these, a number of moderate local anomalies appear. Detailed field magnetic and gravity surveys have been carried out on one group of these in State Game Land No. 43, with the objective of determining more exactly the size and extent of the anomalies, their relations to the geologic structure, and the possibilities of their representing mineable iron-ore deposits. Several different magnetic instruments were used to compare their convenience and effectiveness in field use. The field work is complete and interpretation is in progress.

GEOPHYSICAL PROSPECTING FOR CLAY DEPOSITS

A commercial deposit of white kaolinite clay contained in the sandy overburden of the Gatesburg formations of central Pennsylvania was successfully mapped by combined self-potential and resistivity methods. The self-potential anomaly is believed to be the result of diffusion and membrane potentials produced by interactions of clay

Laboratory set-up for measuring the absorption of elastic vibrations in rock.



lenses and the surrounding rocks. The characteristic SP-high in the center or flank of a resistivity minimum provides a new, useful prospecting technique.

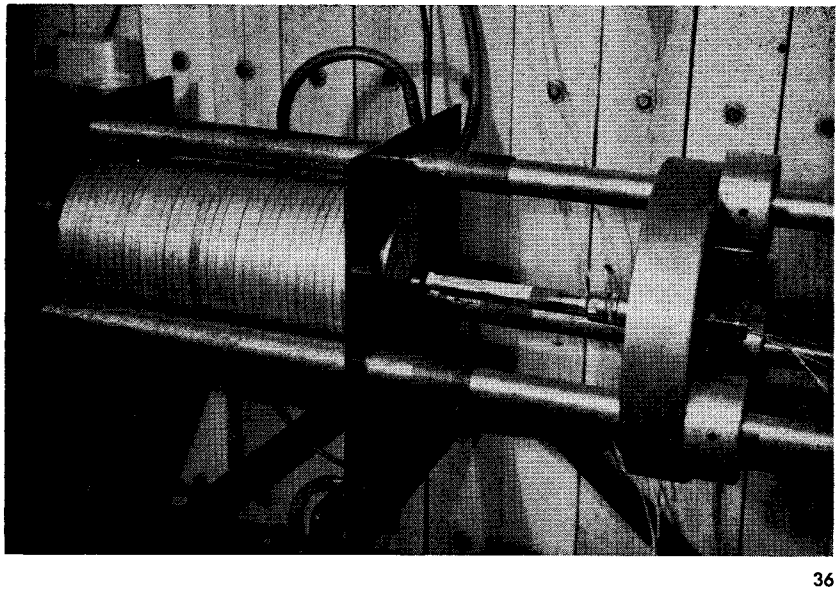
DIELECTRIC CONSTANTS OF ROCKS AND MINERALS

A reconnaissance study of the dielectric constants of twenty-three common minerals and seventy-one rock samples was completed. Dispersion was observed for all the rocks and some of the minerals in the range 50 cps to 30 megacycles. It was shown that this dispersion is primarily due to the moisture content of the samples tested. The dispersion was similar to a type predicted theoretically by Maxwell and Wagner, but was much greater in amount. The most likely explanation is some form of membrane or electrode polarization involving water-coated surfaces in the rock. Traces of water are enough to produce the effect. Water content is the primary factor controlling the dielectric constant of porous sedimentary rocks.

ABSORPTION OF SEISMIC WAVES IN ROCK

Several series of experimental studies have been carried out in an attempt to determine the manner in which seismic vibrations are absorbed in rock. For many years there has been a controversy as to whether the absorption of vibrational energy increased as the first or the second power of the frequency of vibration. A first-power absorption would mean that solid friction was the principal mechanism

Large high-pressure bomb-assembly used for hydrothermal studies of pegmatite genesis.



involved, whereas a second-power rate implies viscous friction. For sound waves and for shear waves, much experimental evidence has accumulated favoring solid friction. Observed attenuation of both impulsive and continuous surface waves is consistent with the same explanation.

In the case of partially fluid-saturated rocks, a third mechanism appears to be the most important one. In rock samples tested in the laboratory, the attenuation of bar waves correlated most clearly with surface tension and energy of adhesion. This suggests that the energy is used up in pulling liquid surfaces free from the pore walls in the rock (or in pushing them against these walls) as well as in sliding fluid or rock surfaces along one another.

EARTHQUAKE OBSERVATORY

The program of recording natural earthquakes was continued along the same lines as in previous years except that bulletins reporting observations were issued quarterly instead of annually for the International Geophysical Year. Over five hundred and thirty earthquakes were recorded, the largest number in any two-year period of the observatory's history, including the great Chilean earthquakes of May 1960, one of which was the largest earthquake to occur anywhere in the world in at least a decade.

TERRESTRIAL HEAT FLOW

The energy for many tectonic processes such as mountain building and ore formation is believed to come from the heat energy of the earth's interior. Relatively few studies have been made in Pennsylvania (or in nearby states) of this important physical quantity. Probes for the measurement of thermal conductivity and diffusivity of crustal rocks *in situ* and for the determination of the geothermal gradient are being constructed. Heat flow is the product of the conductivity and the gradient.

MINERAL ENGINEERING

The Division of Mineral Engineering during this biennium has continued its active research program of developing new and improved methods for the recovery and beneficiation of minerals and the study of economic factors relating to their use and conservation. Many of the mineral problems studied are particularly critical to the economy of Pennsylvania.

PETROLEUM AND NATURAL GAS

During the past biennium the Department of Petroleum and Natural Gas has concentrated its research effort on methods of increasing the oil recovery from established petroleum reservoirs. This research has been oriented toward the investigation of the factors controlling the recovery characteristics of field techniques which should be applicable to semi-depleted reservoirs, such as those commonly found in the Commonwealth of Pennsylvania. These techniques include the miscible-phase group in general, the alcohol-slug process in particular, and also the "combustion drive" procedure. The research program has also been concerned with factors involved in the production of natural gas. Gas-viscosity values applicable to pressure conditions in the reservoir have been determined. Other work in this general area has to do with the effects of clay-minerals upon the deliverability properties of gas reservoirs.

The research in waterflooding has progressed in the general field of pattern sweep efficiencies and pilot floods. Important data have been gathered to show the sweep-out behavior of field input-well patterns. The results of this work will be summarized later.

MISCIBLE PHASE DISPLACEMENT — ALCOHOL SLUG PROCESS

Miscible phase methods for recovery of oil involve the injection of a relatively small amount of material miscible with the crude oil. This injected material in effect is used as a solvent to recover the oil which is held in the reservoir rock by the action of interfacial forces. The commercial success of the process is contingent upon the use of an injected agent which will remove the oil efficiently even though the agent is used in relatively small amounts. The amount of injected phase is of critical concern because, as would be expected, the "solvent," generally an alcohol, must mix rapidly with the crude oil and the other interstitial fluids. Because of this mechanical mixing a blended zone of varying composition is set up. The blended zone increases in volume with flow-path length, thus the concentration of the alcohol in the zone is decreased. The process breaks down at a critical "solvent" concentration—that at which miscibility is lost. This critical concentration, together with the increase of size of the blended zone, dictates the required amount or "slug" size required for successful operation of the technique. A great deal of work has been done in this laboratory to increase the state of knowledge in this general area of interest.

The immediate problem encountered was scaling the laboratory experiments in order to make the results meaningful. The general

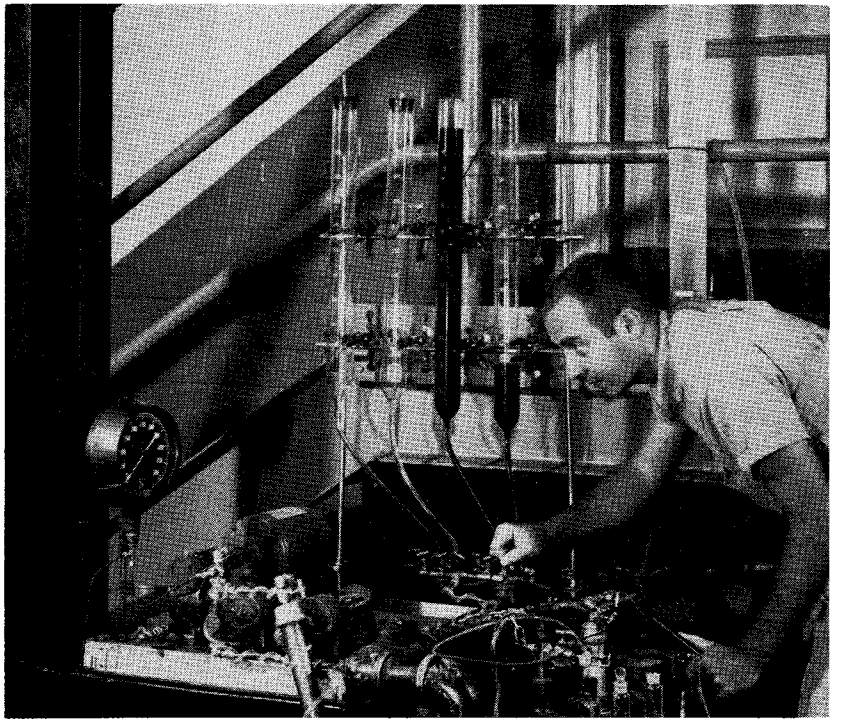


Fig. 5—Wellhead assembly used in long-core tests of miscible-phase flooding.

technique employed synthetic unconsolidated linear porous systems through which various fluids were displaced. The produced concentrations were determined by separate means to evaluate the extent of the blending zone. The laboratory results were found to be sensitive to the grain sizes of the porous body and to the dimensions of the flow system. It was found that the test sections should have a one-inch diameter as a minimum value. Further, it was learned that the process is path-length sensitive. Much of the work has been done in one hundred-foot columns in order to get representative results. These columns are suspended in a shallow well. Figure 5 shows some of the equipment used in these tests.

Considerable progress has been made in the development of knowledge of the alcohol slug process. The mechanism of the process is now more clearly understood and laboratory evidence has been obtained to show that the alcohol, if the amount added is above a certain critical value, completely displaces all of the contacted oil and water in the test columns. A value of the critical alcohol concentration has been obtained for the laboratory systems studied. This value is equal to approximately 70 per cent by volume in the flowing stream.

Moreover, several modifications of the basic process have been

studied in the laboratory with a view toward reducing the amount of the required chemicals. Isopropyl alcohol was first proposed for the basic process because of that chemical's favorable solubility characteristics. This material, however, is perhaps excessively expensive for use in the waterflood fields of Pennsylvania. An alternative to the use of pure isopropyl alcohol is the injection of the less expensive methyl alcohol as a buffer zone before and after a decreased slug of the isopropyl alcohol. In this way the cheaper methyl alcohol would provide the material for the blended zone and the solubility characteristics of the isopropyl alcohol would be enjoyed. This procedure has been successful in laboratory tests, with the possible oil recovery values approaching 100 per cent.

In another modification of the process, butyl alcohol followed by methyl alcohol also proved to be successful and the most effective slug combination used. This combination, although highly effective, probably cannot be made commercial because of the attendant high cost of the butyl alcohol.

With the object of developing a process which might be of commercial interest, another modification of the basic technique has been evaluated in the laboratory. In the studies, a light oil, such as propane, is injected prior to the introduction of an alcohol. This combination was adopted because of the more favorable solubility relations for the propane-alcohol system, as compared to the crude oil-alcohol system. The laboratory work to date indicates that the use of propane reduces the total cost of solvents needed for recovery of the oil.

It is apparent that the main part of the research dealing with the recovery of crude oil by miscible-phase techniques has dealt with the acquisition of sufficient data and experience to warrant a field test of the technique. An industrial group in the State has already obtained the funds necessary for initiating a field test in the very near future. The actual process used in the field will be based on the laboratory results mentioned above. The field test will consist of the injection of a large slug of liquefied-petroleum gas (largely propane), followed by a relatively large volume of isopropyl alcohol. Additional laboratory work will be helpful in determining the optimum conditions for field application of this process.

MECHANISM OF OIL DISPLACEMENT

Direct observation of the displacement of oil by water, gas, and miscible fluids has been continued as a portion of the study on the mechanism of oil recovery. Special observation cells have been constructed of transparent material packed with glass beads to form a porous medium in which displacement operations can be observed

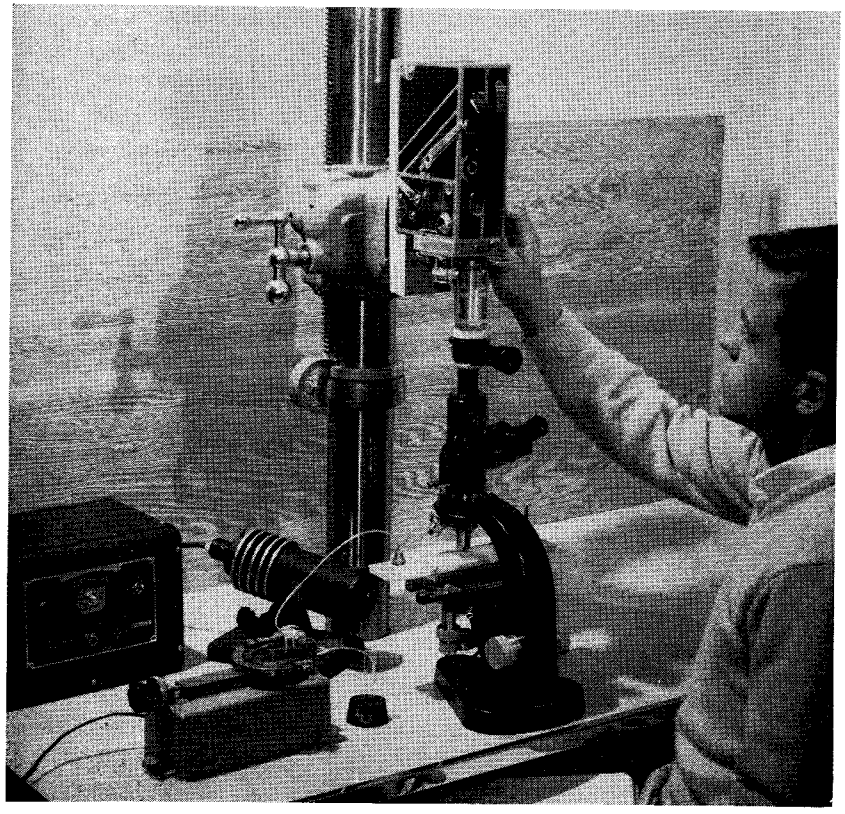


Fig. 6—Experimental apparatus used to make photomicrographs of two-phase miscible displacement phenomena in porous systems.

directly under the microscope. A photograph of the experimental set-up is shown in Figure 6. Basic studies on the location of the oil, water, and gas in a porous medium were first carried out with this equipment. Color photographs and black and white pictures have been obtained to record these findings. Motion pictures showing the pertinent action in a displacement operation have also been obtained. Studies have been made on the location of the phases in a porous medium, the mobility of connate water, and the compatability of what have been considered incompatible waters. Considerable time has been devoted to direct observations on the mechanism of the alcohol slug process. Photographs have been obtained which show how this miscible phase displacement occurs, how residual globules of oil or water are left when miscibility is lost, and how the continued injection of additional alcohol picks up these droplets to effect the complete displacement of oil. These studies also show how the water originally in the system is picked up and displaced ahead of the alcohol and how the

presence of this water complicates the ultimate displacement of the oil. In general, the direct observations have confirmed the mechanism as postulated from the long core runs in which field conditions were simulated by using flow-path lengths of several feet to 100 feet.

STUDIES OF UNSTEADY-STATE FLOW PHENOMENA IN MISCIBLE-PHASE DISPLACEMENT

This laboratory has been concerned with a study of the causes, effects, and mitigation of the unsteady-state advance, in porous media, of a fluid injected to displace the original fluid, the two fluids being miscible. The advance is often characterized by the formation of rapidly-advancing local zones of the displacing fluid giving rise to an irregular or "wavy" boundary between displaced and displacing fluids. This condition is undesirable in field operation because a decreased recovery could result from this type of flow behavior.

The rapidly advancing zones, called "fingers," are caused by small heterogeneities in the pore structure of the rock matrix, and are most evident when the viscosity of the displacing fluids is less than that of the displaced fluid. Laboratory work has been completed to develop criteria for the quantitative measurement of the "fingering" effect. Data have been gathered to show the degree of the effect as a function of flow model width, model length, and fluid flow rate. It has been definitely established that the degree of "fingering" depends on the mobility ratio between the displaced and displacing phases.

A method of reducing "fingering" has been conceived and tested. In brief, the method consists of the introduction of a viscosity buffer between the displaced and displacing fluids. The initial tests showed good results. The work has been extended to include the use of a blended zone between the two fluids. This zone is graded in viscosity so that at each cross-sectional area in the system there exists only a very small viscosity gradient. Thus the large mobility ratio of the overall system is replaced by a graded series of small, stepwise ratios. This technique has yielded extremely successful results—in fact the "fingering" effect was eliminated in many cases. This work is being continued using the extreme mobility ratios which might be encountered in the field.

INTERPHASE MATERIAL TRANSFER DURING FLOW IN POROUS MEDIA

The transfer of a component from one phase to another during flow in a porous medium has been under study for a number of years. This might, for instance, involve the transfer of carbon dioxide from

the gaseous phase to the oil phase, while both gas and oil are flowing, in contact with each other, through a sandstone formation. Because of the current interest in the alcohol slug process, the more recent experimental studies have involved the transfer of an alcohol (such as isopropyl alcohol) from water to oil or from oil to water. As a result of such experiments, certain basic behavior patterns have been found from which the behavior in systems of field dimensions might be predicted. These behavior patterns have been corroborated by other experiments not specifically designed for study of the interphase transfers. The present experimental work consists of obtaining certain numerical values needed to solve the general equations. A by-product of these studies is a correlation of the various existing theories on material transfer within a single phase during flow through a porous system. Studies on both inter-phase and intra-phase material transfer are necessary for an understanding of any solvent recovery process applied to oil fields.

PRODUCTION AND MIGRATION OF OIL AND WATER AT THE BOUNDARY OF A SECONDARY RECOVERY PROJECT

When an oil field in which a depletion-type recovery has earlier been carried to economic limits is drilled for water flooding, the flooding may be started over a certain area before adjacent areas are drilled. Sometimes this flood may involve only a few wells, as in a "pilot flood." Because of the primary oil production, low-pressure gas partially fills the sand pores. Therefore water, and any oil banked up ahead of the injected water, moves easily into the undrilled area. In fact, as water and oil move into the producing wells, these wells offer more resistance to flow than the undrilled area, at least for a time. To study the movement of oil and water at such a boundary of a water flood project, laboratory scale models have been constructed and flooded under various conditions to simulate what might happen in the field. Models have been made for the special cases of producing wells only, input wells only, and alternate producing and input wells along the boundary, taking a five-spot as the pattern for the drilled area. The object is to find the amounts of water injected, amounts of oil and water produced, and the migration of oil and water, for various oil viscosities and various amounts of movable oil. The results should serve as a guide in deciding field operating conditions.

As a corollary to this study, a research project concerned with the recovery efficiency of the immiscible displacement of oil by water has been initiated. This study is being made upon a synthetic porous medium designed so that radial flow will be obtained. The area of the study is to obtain numerical data to check the validity of extending

linear-displacement theory to radial-flow systems. The equipment has been assembled and preliminary testing is now under way.

STUDIES OF INPUT-WELL PATTERNS AND SWEEP EFFICIENCIES

An important consideration in the prediction of oil recovery by the injection of any displacing material is the sweep efficiency of the input-well pattern. This factor is also important in the evaluation of pilot-flood data. This laboratory is engaged in a program set up to determine the sweep characteristics of various well patterns. The program is concerned with the practical testing of various pattern models, and also with the formulation of basic mathematical theory governing behavior of multiphase flow in porous media.

Laboratory work to date has resulted in the accumulation of sweep-factor data for the seven-spot and staggered-line-drive patterns. In this work the mobility ratio and well spacing have been taken as variables. The data have been obtained on synthetic models of the various patterns. The X-ray shadowgraph technique has been used to evaluate the sweep-efficiency values.

A further study has been undertaken to determine whether the Schwarz-Christoffel mathematical transformation can be used in the determination of areal-sweep data in model studies. Experimental work is being done as an integral part of, and a check on, the mathematical study. This laboratory work is being conducted at a mobility-ratio value of unity, and the fluid-flow rate is being held constant.

Both closed-edge and open-edge models have been constructed. The open-edge models are used to simulate the effect of the edge of a developed flood or an isolated flood pattern, i.e., a pilot-flood area. The closed models are used to simulate the usual field case of constrained flow in an intensely developed field. It is expected that the mathematical flood-front positions as a function of time, will require the use of high-speed computing equipment.

COMBUSTION DRIVE

"Combustion drive" is the process by which oil is produced by the oxidation of part of the in-place crude oil in the reservoir. The heat front created by the oxidation moves through the reservoir pushing the unburned portion of the crude oil toward the producing wells. The recovery efficiency of this technique approaches one hundred per cent in that part of the reservoir contacted by the heat front. The exact mechanism of the recovery of oil is extremely complex and has not yet been fully analyzed. It is apparent that the process is sensitive to the characteristics of the rock and fluids, the rate of oxygen

supply, the attendant heat losses, and the amount and types of initial in-place fluids. A major economic requirement is that the fuel requirement, derived from the oil content of the reservoir itself, be fairly small. This laboratory has, in part, investigated the question of the fuel supply representative of crude oils. The particular problem attacked is the study of the low-temperature oxidation rate as a function of temperature and other variables which affect the process.

The results obtained to date may be summarized as follows: The low-temperature rate of oxidation of crude oils varies over wide limits depending on the nature of the oil. Tenfold differences in the rate of oxidation have been observed and even wider limits are probable when a greater variety of samples have been investigated. With few exceptions, the rate of oxidation increased as the specific gravity and refractive index of the crude increased. The rates of oxidation of three typical crudes were investigated as a function of temperature and the rate was found to increase about threefold for each 20°C rise in temperature. Naphthenates of copper, iron, and cobalt when added to a crude oil in small amounts were found to have a very marked catalytic action on the rate of oxidation. This work is being continued in an effort to investigate more fully the variables which determine the rate of oxidation of crudes.

NATURAL GAS RESEARCH

A fundamental study of the flow of natural gas in reservoir rock has been made during the biennium. At the pressures commonly encountered in producing or storage reservoirs, the viscosity values in the literature show discrepancies attributable to the methods of determination. In order to provide more reliable data, a fundamental approach was taken. Flow experiments were conducted using natural consolidated porous media. The viscosity values were then determined by a method of back calculation. The study has been completed and it has been concluded that gas viscosity data, as determined by the capillary-tube technique, are applicable to the flow of gases through porous media in the pressure range up to 70 atmospheres.

Recently two new studies have been undertaken. The first study has to do with the water sensitivity of gas reservoir rocks. This is of direct applicability in underground storage of gas, an increasing factor in the gas industry of the Commonwealth. It is known that the introduction of foreign waters into gas reservoir rocks frequently decreases the deliverability of the wells in the reservoir. The study is aimed at the determination of the cause of harmful effect as well as its mitigation and prevention. The second new study deals with the displacement of a gas by a second gas in porous media. Considerable research effort is under way to establish the roles of various parameters in the

displacement behavior of liquid-liquid systems; this new effort, however, will be concerned with miscible gas displacement. The results obtained should have a wide range of applicability, particularly in such activities as the dry-gas cycling of condensate reservoirs.

MINING

The research program of the Department of Mining has been greatly strengthened with the recent organization of a Rock Mechanics Laboratory. Here is conducted research of broad scope, both basic and applied, dealing with the behavior and failure of rock under static and dynamic loads, stress instrumentation, determination of physical properties, design of mine and other subsurface openings, and the improvement of processes such as drilling, blasting, stone cutting, hydraulic filling, and roof bolting.

In the belief, however, that diversification as well as specialization is necessary in academic research, the Department is also engaged in research projects in the areas of operations analysis, human engineering, and mine mechanization. Industrial as well as federal and State grants are currently active.

MECHANISM OF BRITTLE FRACTURE IN ROCK

A research project to investigate the rock failure process under impact loading is being sponsored by the National Science Foundation. Although the phenomenon of rock failure has been exploited by man since the inception of civilization, incredibly little is known regarding its mechanism, especially under dynamic loads. In the field of drilling, particularly, the importance of impact studies hardly needs emphasis. The striking of a chisel edge on rock forms the fundamental action involved in most common methods of drilling: percussion, vibration with rotary bit, cable tool, pneumatic hammer, and even roller-bit.

A synthetic stone has been developed to simulate natural rock in its mechanical properties. This enables electronic transducers to be embedded within it. Using these measurements, the stress distribution in a rock mass around the area of bit impact has been determined. This knowledge of the disposition of stresses, their attenuation with time, and an analysis of stress wave motion in solids, is making it possible to formulate a rather comprehensive hypothesis explaining the mechanics of rock failure.

An ultra high-speed camera of the spark-gap type taking up to 500,000 frames per second has been designed and built. This is being employed in the study of stress pulses in plastics, which are found to exhibit brittle behavior under impulsive loads. With the aid of photo-

elastic techniques, these experiments will lead to a better understanding of stress wave propagation and crack extension, and thereby serve to complement investigations with natural rock.

ROCK PENETRATION BY WEDGE-SHAPED BIT

Research jointly supported by the National Science Foundation and the American Petroleum Institute is being conducted on the stress pattern developed beneath a wedge-shaped drill bit and the mechanism of rock penetration by such a bit. The test procedure involves the use of models of gelatin and other transparent plastics loaded by a simple chisel in a polariscope. When such materials are deformed under polarized light, the stress pattern is revealed.

Investigations have been completed under static loading using two-dimensional analysis. With the aid of slices taken through the material and immediately placed under refrigeration, it is possible to measure the stresses created three-dimensionally by the so-called "frozen-stress" technique. Such tests are now being conducted. The final phase of the experimental work will be an investigation of the stresses created in a model under dynamic loading, closely simulating the action of rock drilling processes.

As a check of the laboratory work, theoretical stress analysis is also being conducted. The objective is the determination of the magnitude and direction of the principal stresses beneath a wedge-shaped bit under static loading, and the stress trajectories and fracture dynamics under dynamic loading.

MODEL STUDY OF ROCK FRAGMENTATION IN BENCH BLASTING

All mining and quarry operators are interested in obtaining the best fragmentation with the smallest amount of explosive. A study of this subject has been made in the laboratory using blocks of plexiglass and small charges of lead azide explosive in a project supported by industry.

Numerous tests were made with varied spacing (S) and burden (B) patterns, while the bench height, subdrilling depth, and loading factor were constant.

The number of fragments obtained in bench blasting tends to increase as the ratio of spacing to burden (S/B) increases, but at a sacrifice of the total volume broken. Blasting efficiency, computed by Bond's work index, shows a poor correlation with the degree of fragmentation.

When all criteria for evaluation of fragmentation are considered, there seems to exist an optimum S/B ratio for given conditions.

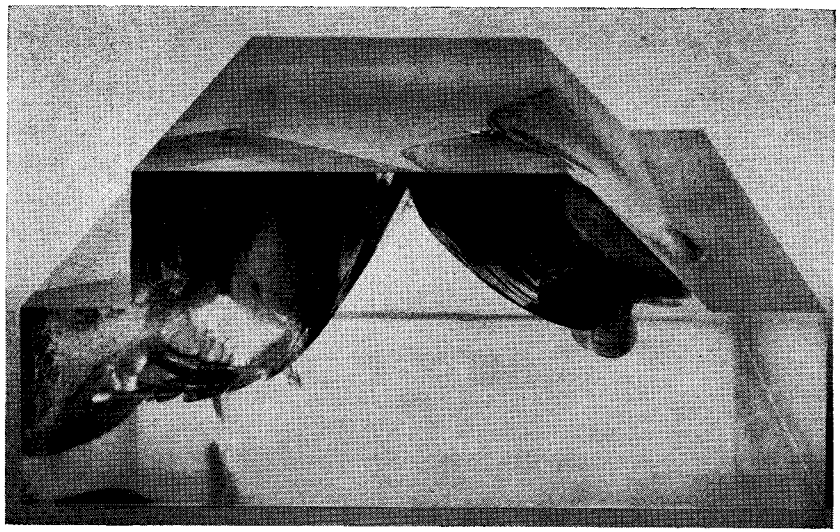
This ratio must be determined experimentally. On the basis of these laboratory scale tests, it appears that a much wider ratio of spacing to burden (S/B) can be used in practice than the one commonly accepted today.

INCLINED DRILLING IN SURFACE MINING

In the great majority of cases, a vertical borehole pattern is used in quarry and open-pit operations for bench blasting. A number of years ago, it was suggested to industry that vertical boreholes should be replaced by inclined ones drilled at an angle of 20 to 40° to the vertical and parallel to the bench face. This thesis is being investigated under a grant sponsored by industry.

By inclining the bench, the area of free face is increased. In so doing, the rock resistance to blasting, which is maximum at the bottom of the bench, is decreased because more explosive energy of the reflected shock wave per volume of rock is concentrated in this region. Less vibration due to blasting also occurs, and quarry operators using this method have virtually eliminated the toe problem and obtained better fragmentation.

Tests in plexiglass (see photograph) have shown that with a 40 per cent smaller loading factor, a much larger volume of plexiglass can be broken with a borehole inclined at 45° than with a vertical one.



Plexiglass block in which lead azide explosive charges have been detonated. Experiment simulates open-pit bench blasting. Breakage pattern shown at left was produced from vertical hole, while that at right was formed by inclined hole.

From the test, it can be seen that when using a vertical bench face, the explosive force is trapped at the bottom of the bench underneath the quarry level without producing any useful work; with inclined holes, on the contrary, it is utilized completely.

Further tests in plexiglass and other materials are planned to determine the loading factor, powder factor, and borehole footage that can be expected for different borehole inclinations.

ANCHORAGE STUDIES OF ROOF BOLTS

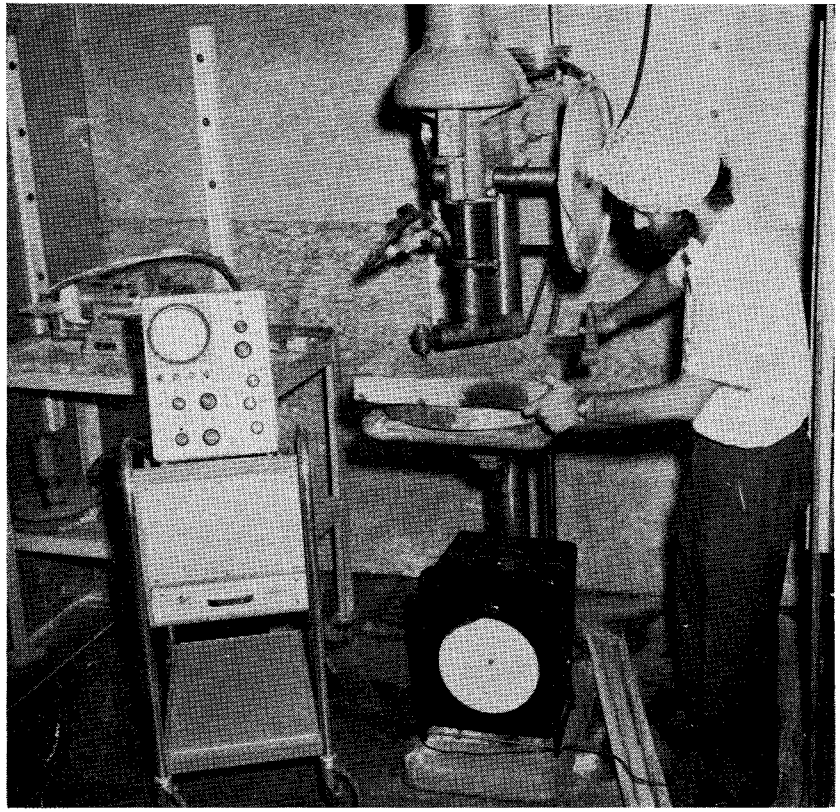
Research is continuing into the behavior of roof-bolt shells subjected to extremely complex loading while providing anchorage in the rock strata composing a mine roof. The tendency for bolt tension to change after placement is one of the most puzzling and unpredictable aspects of roof bolting. Some answers have been obtained, but the action is a complex one and needs further concentrated research.

HYDRAULIC FILLING

Mixtures of sand, mill tailings, and similar material with water can be flushed through pipelines to fill abandoned mine workings and prevent the caving of adjacent rock into the openings. This procedure, called hydraulic filling or flushing, is widely used where such caving would endanger active workings in the mine or in structures on the surface. It has been proposed as a means of combating the subsidence and the water flooding due to anthracite mining which is occurring in heavily populated areas of eastern Pennsylvania.

The fill material must, of course, be able to support the load of the overburden which is imposed upon it. It must also be sufficiently permeable to allow rapid drainage of water, so that a "quicksand" condition will not occur. Not all materials meet these requirements, and State funds are supporting research in the Rock Mechanics Laboratory to determine what materials are most suitable. Emphasis is placed upon those materials which are available in the anthracite area, but basic permeability studies are also being conducted which should be of benefit to all mines using hydraulic filling.

The permeabilities of various mixtures of glass spheres have been measured in a falling-head permeameter to determine which size distributions provide the required drainage rate. Similar tests are being conducted on samples of anthracite washing plant refuse, boiler ashes, sand, and flotation mill tailings. In addition, the load-bearing capacities of these materials are being determined by confined compression tests.



Drill press instrumented to record rate of penetration, rotation speed, torque, and thrust as slate samples are cut by experimental carbide and ceramic bits.

SLATE QUARRYING AND PROCESSING

Research to aid the slate industry of Pennsylvania through improvement of quarrying and processing practices is supported in the Department by State funds.

During the present biennium a new dimension has been introduced to the slate research project, that of ascertaining the machinability of slate. Machinability is a term that has long been used in the metal industry to rate the difficulty of working metal, but has never been applied to the processing of a dimension stone. However, since the end result of such a rating is primarily the optimization of the feeds and speeds used in milling, there is no real barrier to the employment of such procedures with reference to any raw material, natural or otherwise. Tests already completed or being conducted in the Rock Mechanics Laboratory of the Department of Mining will

permit the determination of such factors as optimum cutting feeds and speeds, related torque requirements, economic machine tool lives, machine tool geometry, and penetration rates that will facilitate the future design of new and improved slate-cutting and milling equipment that is greatly needed.

Slate for many decades remained essentially a one-product industry (roofing). It has only been during a recent period of diversification that a need has arisen for property standards that would assure slate consumers of the material's adequacy in any given installation. Working closely with three interested organizations (American Society for Testing Materials, United States Bureau of Mines, and the Pennsylvania Slate Producers Guild), a series of chemical, physical, and mineral-property standards are being evolved that will enable the industry's products to achieve wider acceptance while at the same time discouraging inferior substitutes and imported raw materials.

Modern standard-data time studies recently completed for all of the various operational phases of the slate industry are enabling the slate operator to exercise better control over his labor dollar, as well as to detect obvious shortcomings in his present system. A newly designed slate-planing blade has been made available to the industry as the slate research project continues toward its objective of machine development to supplement research.

PERFORMANCE AND POWER CONSUMPTION OF CONTINUOUS MINING MACHINES

The performance and power consumption of continuous mining machines is comparatively unexplored. The entire subject is interwoven with problems of industrial applications, improvements in machine design, and the mechanism of coal failure, and is a very complex one. Part of the research effort supported by the State to exploit its thin-coal resources has been directed toward measuring the performance and power requirements of continuous mining machines engaged in different operations, e.g., room driving and pillar extraction, or in different mining methods, to improve mining practices.

Investigations were carried out in the bituminous coal mines of central Pennsylvania and West Virginia, using a self-recording wattmeter and voltmeter. The power chart of a continuous miner was analyzed during sumping, shearing, and retracting operations, and the power was computed for each of these operations separately. Statistical methods were employed to analyze the data. The principle employed for coal breakage, the mode of operation, and roof pressure were all important factors.

Test results indicate that the power consumption to cut coal and the rate of cutting is faster, if an additional free face is available. The effect of the presence of another free face is more prominent with a narrow width of cut; the greater the width of the cut, the less the time required to cut a ton of coal. Pillar extraction was also faster and more efficient than room driving.

With one type of continuous miner, sumping required more power and time than shearing. The power consumption for shearing decreased with increasing height of coal.

HAULAGE IN SURFACE MINING

A detailed study of the economics of various haulage methods in open pits, quarries, and strip mines has been completed. Operating factor and cost data have been gathered from all over the country to determine the optimum system to use under varying conditions. State and industrial funds have supported this research.

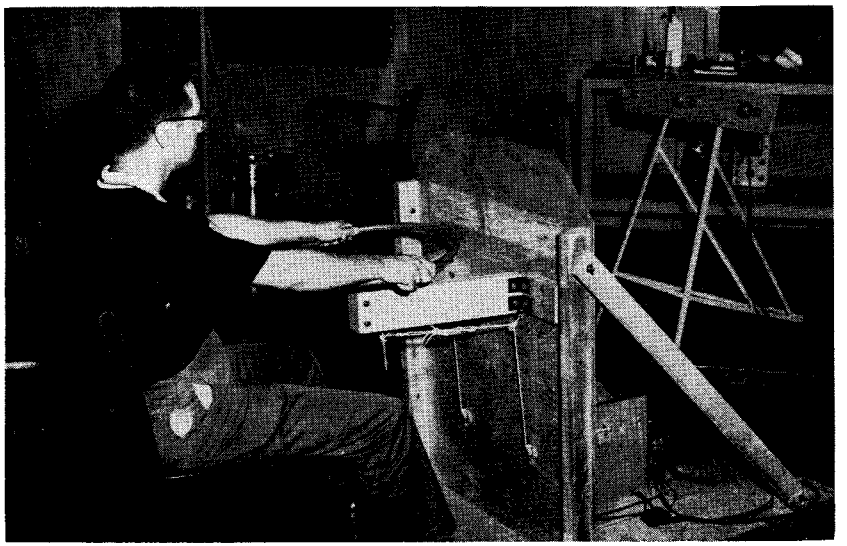
One novel transport combination that has been proposed as a result of the study is an excavator-portable crusher-belt conveyor system for handling ore or overburden. It would appear to have substantial economic advantages, particularly in stripping where large volumes of material must be spoiled a considerable distance beyond the excavator. A modified system permits the use of a cheaper, faster short-boom power shovel with separate conveyors to spoil coarse and fine overburden in place of the more expensive, slower long-range stripping shovel for casting usually employed.

HUMAN ENGINEERING IN COAL MINING EQUIPMENT

At the present time the United States mining industry is faced with a dual problem of increased operating costs for extraction of ore under more difficult mining conditions. The Pennsylvania coal industry has not been spared in this profit squeeze; thinner seams now being exploited require expensive specialized equipment which must be highly efficient to produce economically. State and industrial funds are supporting research to improve mining efficiency in these thin seams.

The coal mining equipment manufacturers are now producing equipment for use in seams as low as 30 inches. To assist the equipment designers, a study was made of the application of human engineering principles, many of which are widely used in other industries, to coal mining equipment. The study was divided into two parts: anatomical and psychological.

The anatomical study, based on several thousand pre-employment physical examinations given to men actually employed in coal mines,



Subject being tested for response to reversal in direction of steering mechanism of mock shuttle car.

statistically indicates that there is no significant difference between this group and the adult male population of the United States as a whole. This permits the utilization in the design of coal mining equipment of considerable data and recognized design principles now being used in other industries to facilitate comfortable and efficient operation. The solution to such problems as control placement dictated by limb size, control cab layouts based on preselected percentiles of bodily size distributions, etc., have already been successfully applied to other equipment. They may now be modified for use in thin-seam coal equipment.

The psychological study, utilizing a combined stimulus and recording device built in the Department, indicated that the present steering arrangement in use on underground coal haulage equipment, while on first inspection apparently contradictory to common practice, is entirely adequate due to the ability of the operators to adjust themselves. However, a learning period is undoubtedly necessary.

MINERAL ECONOMICS

ENERGY RESOURCE STUDIES

The study of energy sources and fuel markets in the Pennsylvania economy has continued to be one of the major areas of research con-

ducted by the Department. Fuel interchangeability and coal consumption trends have been investigated during the current biennium.

It has always been recognized that there is a high degree of competition for markets between fuels, but for the first time the fuel consumer's relative freedom in changing from one fuel to another has been measured. The Department's study of interchangeability, which was sponsored by the Mineral Conservation Section, was restricted to Pennsylvania for two reasons. First, by taking a single state, the sampling and other measurements were kept within the time and financial limits of the project. Second, in addition to the Department's natural interest in anything having to do with the Commonwealth, Pennsylvania has a higher degree of fuel intercompetition than most regions. See Figure 7.

The investigation disclosed that 17 per cent of the energy consumed in the State at the present time is subject to immediate (less than one year) convertibility from one fuel to another. Most of this utilization involves utility or industrial consumers with dual-firing facilities. Many other consumers may also change the fuel they are using, but such a change would involve replacing their existing combustion equipment with new units. Fuel users of this type

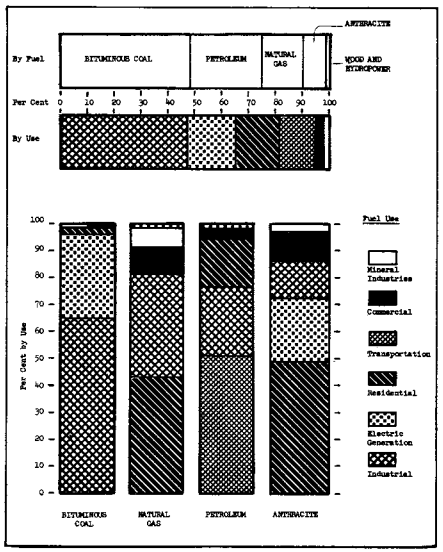


Fig. 7—Current fuel sources and fuel utilization in Pennsylvania.

consume 48 per cent of the total energy consumed in the State. Any shift in this market from one fuel to another would have to take place gradually over a period of several years. Finally, 35 per cent of the fuels consumed in Pennsylvania are used in a manner that could be changed only by the appearance of new technology or a drastic departure from traditional practice. Several decades would probably be necessary for the complete shift from one fuel to another to be completed.

In addition to the investigation of interchangeability, two related studies were also completed. A paper on estimating the long-term growth in United States bituminous coal consumption and its annual variations was presented at the February 1960 meeting of the A.I.M.E., and later published. The other paper was concerned with the outlook for bituminous coal production in Pennsylvania.

During the past year, the principal research effort of the Department concerning energy resources has been specifically directed toward coal economics. Work is in progress to investigate bituminous coal distribution costs and the manner in which the industry establishes its delivered prices.

INTERNATIONAL TRADE IN METAL RAW MATERIALS

Work on this project continued through the biennium, and a paper summarizing the conclusions for the years 1953 through 1957 was presented at the February 1960 meeting of the Mining Society of the A.I.M.E. in New York. Eighteen rules explaining the behavior of international trade in the metals were set forth, and summary tables for each of the 21 commodities studied were given. One of the more interesting items of data developed came from the iron ore import-export study which showed the United States rising from third to an undisputed first place as an importer, far ahead of West Germany which had been the leading importer in the past. The iron ore table is reproduced here as an example of the data assembled in the February 1960 paper. The complete tables, in which the tonnages traded are detailed for each importing and each exporting country, have been prepared and published. These tables have been of great value to private industry and the federal government. Work has now begun on developing comparable information on international trade in non-metallic materials and fuels.

OTHER RESEARCH PROJECTS AND GRANTS

Three other projects have been sponsored in the Department by the Mineral Conservation Section during 1960-1961. Statistics have

TABLE 1
Iron Ore 1953-1957
(metric tons)

Major Importing Countries	*Five-Year Import Totals*	*Five-Year Production Totals (long tons)*	*Major Suppliers (by rank)*
United States	116,239,096	503,152,000	Canada, Venezuela, Chile, Peru, Sweden, Brazil, Liberia, British West Africa, Mexico, Dominican Republic, Cuba
West Germany	70,074,669	77,346,000	Sweden, Spain, Canada, Norway, France, Algeria, Portuguese India, Brazil, Liberia, Venezuela, Spain, Morocco, Belgium-Luxemburg, Peru, Sierra Leone, Turkey, Chile, French Morocco, Greece, Tunisia, French West Africa
United Kingdom	66,746,418	80,697,000	Sweden, Canada, Algeria, Tunisia, Spain, Sierra Leone, France, French West Africa, Brazil, Venezuela, French Morocco, Liberia, Spanish Morocco, Norway, Portugal
Belgium-Luxemburg	63,104,084	35,698,000	France, Sweden, Portuguese India
Japan	31,795,354	8,704,000	Malaya, Philippines, India, Hong Kong, United States, Portuguese India, Canada, Korea, China, Brazil, Venezuela
Canada	19,367,786	66,867,000	United States, Brazil
Netherlands	6,066,119	----------	Sweden, Algeria, Spain, France, Liberia, Tunisia, Spanish Morocco, Sierra Leone, Brazil, Canada
Italy	5,237,562	6,546,000	Sweden, Portuguese India, Algeria, Venezuela, Tunisia, French West Africa, Greece
Austria	3,670,937	14,832,000	Sweden, Norway, Greece, Portuguese India, Spain, Algeria
France	3,548,151	243,140,000	Belgium-Luxemburg, Sweden, Algeria, Spanish Morocco, Spain, Tunisia, West Germany
Finland	551,264	945,000	Sweden
TOTAL	386,401,440	1,037,927,000	

Major Exporting Countries	*Five-Year Export Totals*	*Five-Year Production Totals (long tons)*
Sweden	76,833,050	87,191,000
France	63,078,406	243,140,000
Canada	59,792,909	66,867,000
Venezuela	42,661,241	41,885,000
United States	22,783,744	503,152,000
Algeria	15,019,097	15,046,000
Brazil	11,601,603	19,369,000
Spain	11,514,390	19,255,000
Peru	10,864,536	11,002,000
Chile	10,523,085	11,870,000
Malaya	9,111,134	9,159,000
Liberia	8,682,090	8,415,000
Portuguese India	8,358,084	8,924,000
India	7,474,255	22,712,000
Philippines	6,606,696	6,753,000
Sierra Leone	6,157,498	6,172,000
French Morocco	5,600,356	2,078,000
Norway	5,507,047	6,483,000
Tunisia	5,407,696	5,404,000
Spanish Morocco	4,015,874	5,637,000
French West Africa	3,474,268	3,528,000
Belgium-Luxemburg	2,011,154	35,698,000
West Germany	1,523,784	77,346,000
Turkey	1,377,124	4,061,000
Greece	1,202,007	946,000
Finland	1,095,870	945,000
TOTAL	402,276,998	1,223,038,000

been assembled on all aspects of Pennsylvania's mineral industries for the period 1956-1960. This has been done in preparation for the publication of a supplement to Mineral Industries Experiment Station Bulletin 69, *Historical Statistics of Pennsylvania's Mineral Industries, 1759-1955*. The historical statistics have not only been brought up-to-date, but the coverage has been expanded.

A systematic investigation of current industrial specifications for common mineral raw materials that occur in the Commonwealth has been started. This information is being assembled by both the mineral and consuming industries for ready reference. This information will prove extremely helpful in evaluating the commercial potential of undeveloped mineral deposits now known, or yet to be discovered, in Pennsylvania.

Finally, the Department has undertaken a market research project in support of laboratory research done in Fuel Technology. Information is being assembled about the present producers of activiated carbon, the quality and performance of their product, and the current market prices for activated carbon. This information has been utilized both to evaluate activated carbons produced in the Fuel Technology laboratories and to indicate where future research emphasis should be placed.

Also, the Department conducted an industrial research project on a study of markets for natural graphite during 1960-1961. In the fall of 1959, the Department received its second grant from the Muse Foundation of Pittsburgh for the distribution of research results in coal economics. Three papers have been published and given wide circulation with the aid of these grants.

MINOR RESEARCH STUDIES

In addition to the major research projects already discussed, shorter studies have been made of many phases of the mineral economy of the Commonwealth and the nation, and have been published on the *Mineral Economics* page of *Mineral Industries*. The following titles are representative of the scope and variety of the subjects studied in these short papers:

Soviet Mineral Trade—A Key to Soviet Mineral Supply
The Not-So-Rare Metals
Oil in the United Kingdom Fuel Economy
Inflation, Economic Growth, and the Price of Gold
The Cost of American Labor

MINERAL PREPARATION

During the past biennium many research activities were conducted by the Department of Mineral Preparation. Although the problems studied were very diverse, the research may be grouped as: (1) studies of coal, clay, other non-metallic minerals; (2) metallic minerals; and (3) theoretical flotation research.

COAL PREPARATION RESEARCH

Handling Anthracite Fines

Samples of anthracite slimes with up to 95 per cent minus 400 mesh material were examined. Size distribution studies by centrifuging and by microscopy were performed, as well as moisture and ash determinations. Flow characteristics with and without additives were investigated to reveal handling methods which could be used by utilities.

Flocculation of Coal

Flocculation studies on Pennsylvania bituminous coals using cationic flocculants derived from corn products were performed on both a laboratory and plant scale. These flocculants, however, were less effective than presently available commercial flocculants.

Circular Table Concentrator

Investigations are in progress on sulfur reduction with the Cannon circular concentrator table, a circular array of pinched-sluice launders. The effects of splitter position, feed rate, pulp density, launder deck surface, vibration, and other variables are being studied by utilizing sink float methods. Washability analyses and petrographic studies are being conducted to determine the occurrence and nature of sulfur in coal.

Crushing Anthracite

Detailed pilot plant experiments were conducted on the crushing characteristics of egg, stove, and nut anthracite sizes with an impact crusher. The samples were tested at high and low feed rates with rotor speeds of 620, 1090 and 1280 rpm. The power consumption on each test was recorded. Screen analyses of the crushed products showed that impact crushers could be used to reduce domestic sizes of anthracite to steam sizes with the minimum production of fines.

Petrographic Constitutents of Coal

The effects of various concentration methods on the distribution of macerals in the products of two Pennsylvania bituminous coal-cleaning plants have been determined. The sulfur and ash contents of the fractionized maceral concentrate were also determined. The correlation between petrographic constituents and the coking quality of coal is being studied.

Plant Survey

The bituminous coal preparation plants of Pennsylvania are being studied to determine the problems relative to their operation, with special emphasis on sulfur removal. Results of the survey will be correlated to determine specific problems related to the types of equipment being used in the plants as well as the characteristics of the coal being cleaned. Research projects will then be designed and carried out to help the coal industry with its preparation problems.

CLAY RESEARCH

Pennsylvania has abundant clay deposits of various kinds, but many are not usable without preparation.

White Clay

This investigation resulted in the establishment of the optimum flotation conditions for the beneficiation of three different Pennsylvania siliceous white clays. The concentrated clay products are of sufficient grade to be used as industrial fillers.

Siliceous Clay

Flotation tests are being made to remove a portion of the clay from the high-silica Pennsylvania fire clay from Alexandria, Pennsylvania, and also from the siliceous tailings of the Pennsylvania white clays. The resulting siliceous grit has many industrial applications.

High-Alumina Clay

Chemical high-temperature roasting tests are being made on high-alumina clay. The raw material used for this project is a high-alumina, high-iron clay from Central Pennsylvania, which is not suitable for industrial use under present conditions. It is proposed to extract the alumina from this clay by a chemical beneficiation method, in order to produce a material suitable for use in the Hall process for the production of metallic aluminum.

OTHER NON-METALLIC RESEARCH

Beneficiation of Pennsylvania Ganister

Attritional scrubbing, as a means of reducing the alumina in Pennsylvania ganister to less than 0.3 per cent to make it suitable for refractories, was investigated. Five samples, ranging from easy to most difficult, of the factors affecting the scrubbing, i.e., time of attrition, pulp density, weight of sample, and impeller speed were investigated. Good results were obtained in the laboratory and larger pilot-plant scale tests are scheduled.

Abrasives Recovery

The manufacture of silicon carbide by fusion of silica and graphite results in a product having approximately 1.5 per cent free carbon and 2 per cent iron as contaminants. At present the iron is removed by acid leaching and, during the process, free carbon is floated to the surface and removed as a scum. The manufacturers would like to replace this batch process with a continuous process which will eliminate leaching.

Preliminary tests indicate that free carbon can be reduced to less than 0.5 per cent in a single flotation stage without serious loss of silicon carbide. Iron removal will also be attempted by flotation and by dry and wet magnetic methods.

Phosphate

A fatty-acid flotation method was established for the effective reclamation of phosphate discarded with the slime from Florida phosphate ore wastes. The relative effectiveness of various components of tall oil as collectors for flotation is also being investigated.

Asbestos Minerals

A study was made for a leading producer of asbestos. The type and nature of the silicate minerals in asbestos ore and products was determined by analysis of their infrared spectra.

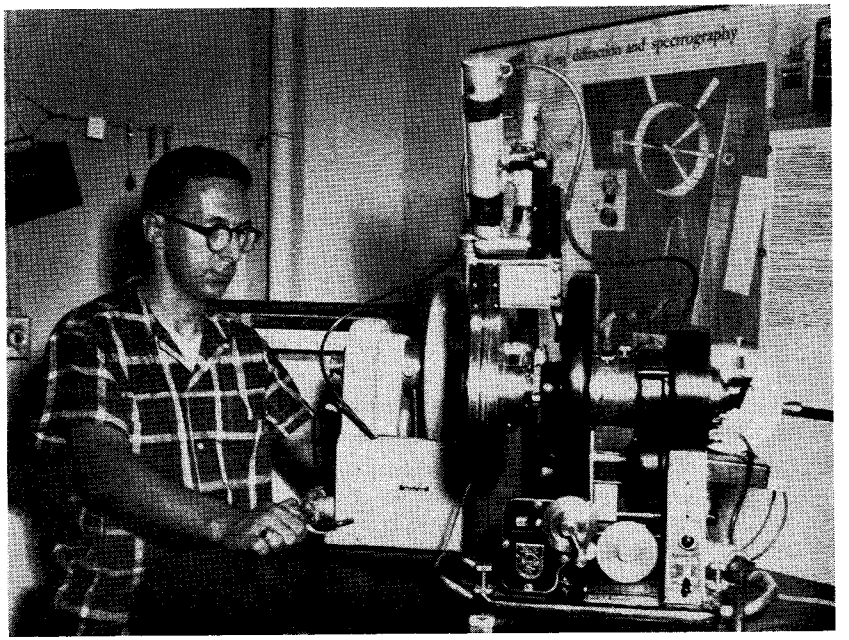
METALLIC MINERAL PREPARATION

The Utilization of Thermal Shock for the Liberation of Quartz Grains from Iron Oxide Ores

The current practice of beneficiating low-grade deposits consists of their size rduction followed by concentration. Comminution processes for their reduction consist of crushing and grinding. All these processes cause particle breakdown without regard to mineral boundaries and, consequently, over-grinding is generally required to attain satisfactory liberation before concentration. By exposing ore particles to high temperatures, followed by quenching, it was found that severance occurs along the boundaries between the different crystals. This results in better liberation with larger sizes.

The Relationship Between Some Factors and Their Influence on the Reduction of Iron Ore

Pellets of iron oxide were prepared in order to determine the influence of porosity, particle size, and time and temperature on reduction of the iron oxide. The influence of the above factors on the velocity of reduction can be helpful for economical determination of the particle size to be used for thermal shock treatment.



X-ray diffraction instrument being used to study crystal structure of rare earth salts prepared from bastnaesite ore.

Magnetic Susceptibility

The magnetic susceptibility of titanium and copper minerals in relation to their chemical composition was investigated. The data are not only of academic interest, but also have industrial applications for the beneficiation of titanium and copper minerals.

Characteristics of Rare Earth (Ethylenedinitrilo) Tetraacetic Complex

Several methods of preparation of the (ethylenedinitrilo) tetraacetic acid complex with lanthanum, cerium, neodymium, and praesodymium were studied. The composition of the various compounds was established by determination of acid hydrogen, (ethylenedinitrilo) tetraacetic acid content, and ultimate analysis. Various properties were studied including solubility, X-ray diffraction patterns-crystal characteristics, and water content. Studies were carried out to evaluate lanthanum recovery and lanthanum separation capabilities. Lanthanum analysis was determined by a spectrochemical procedure.

Bastnaesite Rare Earth Research

This program has been concerned with the utilization of the bastnaesite rare earth minerals deposit at Mountain Pass, California, and with the separation of the individual rare earth elements. Results

of the first phase of the program have indicated that complex rare earth salts may be prepared from this ore and that the salts may be used in the steel industry. Industrial research and development work have indicated that certain of these salts, prepared for the first time in the Mineral Preparation Department's laboratory, may be used in steel-making processes. One complex salt is now being made on a commercial scale and is being sold as a flux. To date, over a half million pounds of this flux have been used in the steel industry.

The liquid-solid extraction technique has been applied to the rare earth bastnaesite concentrate from Mountain Pass, California, in order to separate and isolate the individual rare earths. Definite tendencies have been obtained, particularly with alkyl phosphates, but specific elements have not been isolated.

An X-ray spectrographic technique has been worked out which makes possible the rapid and accurate analysis of cerium, lanthanum, praseodymium, and neodymium.

THEORETICAL FLOTATION RESEARCH

Streaming Potential Study on Rutile.

Very pure synthetic rutile is now commercially available and its crystalline form makes it suitable for use in a streaming potential cell.

Streaming potential studies involve the use of electrodes which should be reversible, and the ion in solution to which the electrodes are reversible must not interfere with the experimental work. When this problem is solved, an investigation will be made of the effect of the addition of very pure 18 carbon, unsaturated fatty acids, to the streaming solution and the results will be correlated with flotation tests in a modified Hallimond tube.

Gas Chromatography of Fatty Acid Flotation Reagents.

Correlation between the chemical composition and the collecting power of 43 commercial fatty acids has been established. The adsorption of individual fatty acids by single minerals will also be determined. This work involves gas chromatographic analysis and mineral flotation studies.

MINERAL TECHNOLOGY

Better utilization of our existing materials, and the search for new materials with improved properties, are the keynote of our research program. This applies equally to fuel technology, where efforts are being made to convert fuel directly into electricity; to metallurgy with its search for stronger, lighter, and tougher construction materials;

and to ceramic technology with its emphasis on the structure of matter and development of materials with superior thermal, electrical, and magnetic properties. In their research activities the three departments are closely related, since each is concerned with certain aspects of the physical chemistry of solids. In addition to problems of immediate interest to the industry of Pennsylvania and the nation, basic research of long-range interest is carried out in the Division.

METALLURGY

The interests of the faculty and the graduate-student body in the Department of Metallurgy in the period 1959-1961 have been in the following areas: physical metallurgy of iron-base alloys; powder metallurgy; production-function analysis; properties of electrodeposits; gas-metal systems; oxide systems involved in steelmaking; and ultra-purity metals and alloys. Research is also being conducted in certain phases of extractive metallurgy.

The investigations in several of these areas are of a continuing nature. Staff changes made in 1960 resulted in some change in the program and developed interest in the properties of metals and alloys at elevated temperatures, and in the structure and properties of intermetallic compounds.

PHYSICAL METALLURGY OF IRON-BASE ALLOYS

A study is in process of the influence of cerium on an austenitic alloy of nominal composition 25 per cent chromium; 25 per cent nickel; remainder, iron. There are two parts to the investigation. First, the limit of solid solubility of cerium in this basic composition is being established at typical hot-working temperatures. Second, the influence of cerium on the cast structure and hot deformability of the basic composition is under investigation.

The influences of melting conduct, finishing practice, and annealing atmosphere on secondary recrystallization of an alloy with 50 per cent iron and 50 per cent nickel are under investigation. It is the intention to study the effects of varying the partial pressure of air over the melt and the effects of various late additions such as silicon, manganese, and lanthanum on establishing inclusions of variable stability which might have a bearing on the recrystallization behavior of this alloy.

An investigation is being initiated on the inter-relations between the tempering of quench-hardened steel and the course of the stress-strain curve in tension. The aim is to clarify the influence of residual

stresses, the effect of retained austenite in the quenched structure, and the importance of the various stages of tempering on the yield strength.

An investigation has been completed of the influence of deformation by swaging before and/or after the austenite-martensite transformation on the properties of Types 410 and 420 martensitic stainless steel. Significant increases in tensile strength and yield strength were produced by deformation at any point in the thermal history of the steels; however, the increase in strength was accomplished at the expense of a decrease in the ductility properties as measured in the tension test. Nevertheless, these procedures may prove to be a means of general improvement of the mechanical properties of these types of stainless steel.

The effect of phosphorus on the temper embrittlement of vacuum-melted iron-carbon, and iron-carbon-chromium alloys has been investigated. It appears that temper embrittlement in these alloys is associated with carbide distribution; the carbide is distributed in random fashion in the unembrittled condition, and is located at grain boundaries in the embrittled samples. The susceptibility to temper embrittlement increased in both groups of alloys with increasing phosphorus content. It is suggested that chromium decreased the susceptibility to temper embrittlement.

POWDER METALLURGY

One phase has been completed of a study of composites containing silver and a fine dispersion of alumina. The principal aim was to establish the conditions under which silver could be made to infiltrate a compact of particles of alumina. The variables which were investigated were the source of alumina, the nature of the atmosphere under which infiltration was conducted, the nature of the silver infiltrant, and various additions to the alumina. It has been found that oxygen and copper oxide are necessary to permit infiltration of alumina with silver. The results of the investigation show that a theoretical model of infiltration proposed by previous investigators in the Department is reasonable. However, complex interactions between the alumina skeleton and the infiltrant make any predictions from theory difficult.

A study has been initiated concerning the properties of thermoelectrics produced by powder-metallurgical techniques. It has been proven possible, by sintering above the melting point of the lowest melting component (liquid-phase sintering), to prepare specimens of ZnSb, CdSb, PbTe, Bi_2Se_3, and Sb_2Te_3 which have thermoelectric powers of at least two-thirds of the reported value. In several cases (ZnSb, CdSb, and possibly PbTe) X-ray diffraction examination has indicated the presence of uncombined material. This seems to indicate

that large excesses of the elements may not appreciably affect the thermoelectric power of some compounds. It has also been proven possible to prepare specimens of ZnSb, CdSb, and Sb_2Te_3 by liquid-phase sintering of the elemental powders with thermoelectric powers greater than that of specimens prepared by co-melting the same powders.

PRODUCTION-FUNCTION ANALYSIS

A linear-program model has been developed for the iron blast furnace. A quantitative analysis of the process can be made from the model. An attempt was made to minimize the cost of materials with respect to the consumption of materials and energy. It has been found from the analysis of the model that a linear program for the iron blast furnace is possible, and that input materials can be evaluated and classified with respect to the restrictions imposed and to each other. This analysis also shows that slag requirements limit the model more than do the pig-iron requirements. Materials chosen for lowest-energy consumption by the model are not always the same as the materials chosen for lowest cost. It has been found that blending of input materials becomes more profitable as the price differential between these inputs increases, and that some high-grade materials should be chosen for blending regardless of their higher cost.

This is the final report on work in this area in the Department.

PROPERTIES OF ELECTRODEPOSITS

Although the metallurgical properties of thick electrodeposits have been quite thoroughly determined in connection with the production of electroformed articles such as phonograph record stampers and electrotypes, the mechanical and physical properties of the comparatively thin electrodeposits used for decorative and protective purposes are almost unknown. A program comprising both the devising of experimental techniques and the gathering of data on the mechanical properties of thin deposits has been under way for some time.

A thorough investigation of the X-ray diffraction technique for internal stress determination in electroplated nickel has revealed that this method can be applied to the examination of deposits *in situ* on fabricated work pieces such as automobile bumper bars or other large plated articles. Sources of probable error and the limits of accuracy have been extensively investigated.

The modulus of elasticity of plated metals is required for making internal stress calculations. A completed investigation of a variety of copper deposits, in the form of very thin-walled tubes, showed that the modulus depends markedly on the type of solution employed and

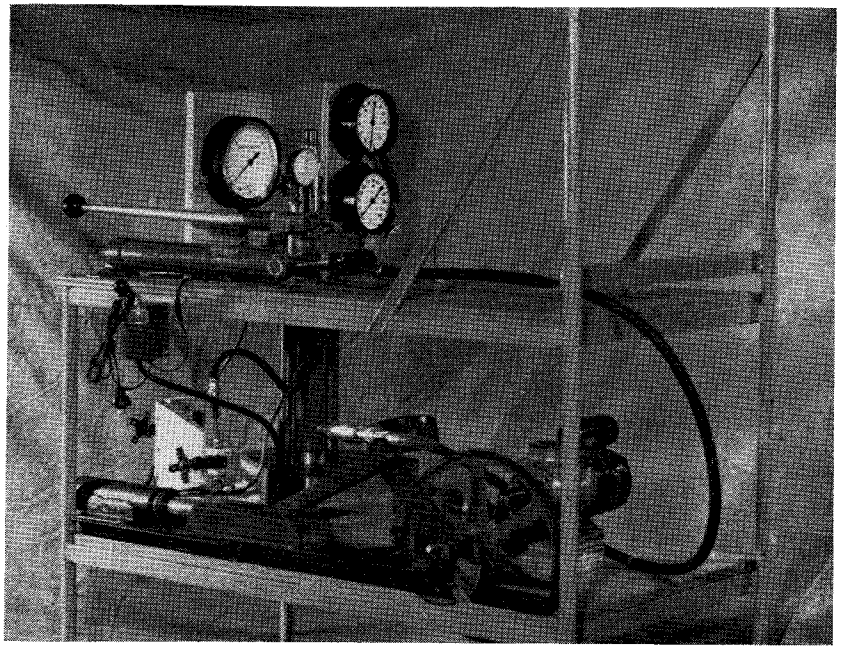
on the structure of the deposits. Deviations were observed of nearly 25 per cent from the commonly accepted modulus value for wrought copper.

Among current activities is a study of the tensile strength and ductility of electrodeposited brass. Nothing has been published on these properties for any thin, alloy electrodeposit. The rather extensive commercial use of electroplated brass makes it a useful and important example for an exploratory investigation.

Nickel is one of the few thin electrodeposited metals which has been intensively studied with regard to metallurgical properties. Nickel alone, however, is never used as a protective coating without a thin tarnish-resistant coating of chromium. The effect of the chromium on the strength and ductility of the nickel is completely unknown, but a current investigation is aimed at providing data for nickel deposits prepared under several sets of plating conditions and chromium plated by the usual method.

In both the work on brass and on chromium-plated nickel, mechanical property data will be secured by means of the hydraulic-bulge test, using the apparatus and methods developed in our Department in earlier investigations.

Hydraulic bulge tester developed for determination of strength and ductility of thin electrodeposits.



An investigation has been initiated to develop a theory for the extremely low elastic moduli of certain electrodeposits. It is felt that the behavior of the modulus might be related to internal stress, and to the presence in the microstructure of the electrodeposit of markings which resemble slip bands with cross-slip linkages. An attempt will be made to correlate change in the number of slip bands per unit area during a recovery anneal with changes in internal stress and elastic modulus.

GAS-METAL SYSTEMS

In extension of a study of the rates of reaction of steam-bearing atmospheres with ferrous metals of several compositions, the influence of surface structure upon the rate is being investigated by use of a number of standardized surfaces on one material.

Measurement of the occlusion of hydrogen by cold-deformed iron-carbon alloys has proven the simultaneous operation of an exothermic and an endothermic mechanism at 250-400°C, both of which are completely reversible. Enthalpy changes computed from the equilibrium data show that the heat of solution of hydrogen by a deformed iron lattice is greater than that for annealed iron. Enthalpy and entropy changes both suggest that the exothermic process is a chemisorption of hydrogen atoms on internal surfaces within the steel.

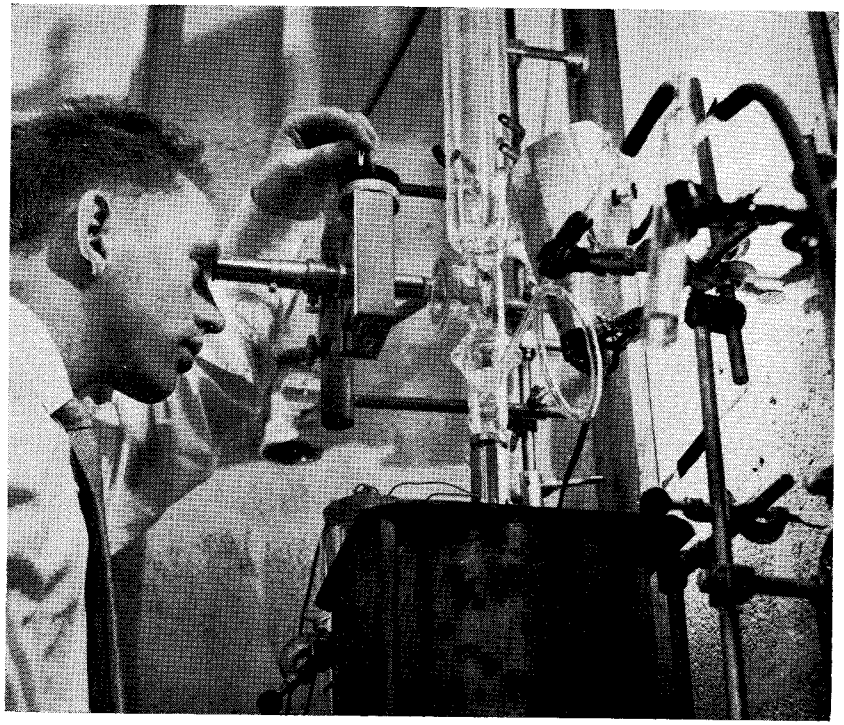
In related work, the prolonged investigation of the occlusion of hydrogen is being extended by an examination of the behavior of that light element toward defective crystals of an austenitic alloy. Measurement of the rate of permeation of iron-iron carbide systems by hydrogen is also being undertaken.

HETEROGENEOUS EQUILIBRIA IN OXIDES AND IN OXIDE-METAL SYSTEMS

Equilibrium relations at high temperatures are being studied in systems made up from among common oxides (CaO, MgO, MnO, NiO, Al_2O_3, Fe_2O_3, Cr_2O_3, TiO_2, SiO_2), and the metals Fe and Ni. Sponsored by the American Iron and Steel Institute, this broad research program has yielded results which are of importance to extractive metallurgical industries in general and to the iron and steel industries in particular.

The approach is to investigate systematically phase relations and thermodynamic behavior in chosen binary, ternary, and quaternary combinations of the above-mentioned compounds. The systems are conveniently divided into the following groups:

1. Systems with bearing on sintering and slag problems. Phase



Thermogravimetric study of equilibria in iron oxide-containing systems.

relations in the complicated system $2CaO.Fe_2O_3$-$FeO.Fe_2O_3$-Fe_2O_3 at liquidus temperatures have been delineated.

2. Systems related to basic brick problems. These studies include two types of systems, one with Cr_2O_3 as the dominant component, the other with MgO as the dominant component. In the case of the former, the system iron oxide-Cr_2O_3-SiO_2 has been studied in great detail. Work on the MgO-containing systems has been concentrated on MgO-iron oxide in air, and MgO-FeO-Fe_2O_3 over a large range of oxygen pressures.

3. Systems with titanium oxide as a main component. These studies shed light on the general problems of ore deposits, extraction of iron and titanium from these ores, and the role of titanium in slags and refractories. Combinations of oxides in this group under active study at the present time include iron oxide-TiO_2 under strongly reducing conditions, and Fe-Ti-O over a large range of oxygen pressures.

4. Systems continuing manganese oxide as a major component. These studies are aimed at explaining reactions taking place between

ferromanganese alloys and the oxide phases with which they come into contact in iron and steelmaking processes. Systems under investigation include MnO-Mn_2O_3-SiO_2, iron oxide-manganese oxide in air, and iron oxide-manganese oxide-SiO_2 in air.

5. Oxide solid solutions. Activity measurements are being carried out in order to gain more fundamental knowledge of the thermodynamic behavior of crystalline oxide phases. Combinations of oxides used in this investigation include MgO-NiO, MgO-FeO, CaO-FeO, MnO-MgO-NiO.

An outgrowth of these research activities has been the construction of a set of ten of the most important ternary oxide systems. Published by the American Ceramic Society, these large-scale diagrams in three colors are expected to be in great demand by metallurgists and ceramists concerned with equilibria where oxide phases are involved. The diagrams published are: CaO-Al_2O_3-SiO_2; CaO-MgO-SiO_2; MgO-Al_2O_3-SiO_2; Na_2O-Al_2O_3-SiO_2; K_2O-Al_2O_3-SiO_2; FeO-Fe_2O_3-SiO_2; CaO-FeO-SiO_2; MgO-FeO-SiO_2; FeO-Al_2O_3-SiO_2; and CaO-Fe_2O_3-SiO_2.

GENERAL EXTRACTIVE METALLURGY

In addition to the investigations described above on oxides and oxide-metal systems, work is being conducted in other areas of extractive metallurgy.

Low-grade Pennsylvania manganese ore is not suitable for use in traditional metallurgical procedures. A process for leaching these ores with sulphur dioxide was worked out at the University some years ago, but no treatment was devised for the recovery of manganese from the pregnant leach solution. Electrolytic recovery of manganese from the leach solution is now under investigation.

Thermodynamic analysis of available data indicates that the reduction of zine oxide by carbon monoxide might be expedited by incorporating an alkaline earth oxide into the solid to be reduced. This would come about through the formation of a stable carbonate from the reaction between the alkaline earth oxide and the carbon dioxide generated when zinc metal is formed. An investigation is under way to study the kinetics of zinc production from such systems.

Work is continuing on the investigation to determine the factors that influence the wetting of various ceramics by titanium just above its melting point. It is still the intention to use the sessile-drop technique in this study.

The thermodynamic studies on liquid iron alloys containing copper have been completed. The efficacy of calcium sulfide, calcium oxide, and manganese (II) sulfate slags was studied. The effect of copper on the activity coefficient of sulfur was studied, and found to be small; hence, sulfur removal from liquid iron alloys should

not be affected by the presence of copper. The activity coefficient of carbon was found to increase when copper was added to carbon-saturated liquid iron alloys. The presence of copper appeared to lower the heat of solution of carbon.

ULTRA-PURITY METALS AND ALLOYS

A study has been made of surface phenomena in high-purity iron and high-purity iron-boron alloys. Vacuum-melted iron was purified by vertical (crucibleless) zone melting in an atmosphere consisting first of wet hydrogen and then of pure hydrogen. The estimated minimum purity of the material so produced is 99.995 per cent of iron by weight. Iron-boron alloys (6 to 60 ppm boron by weight) were produced by zone-leveling elemental high-purity boron into bars of the purified iron. Determinations were made of the surface and grain-boundary tensions of pure iron and of the iron-boron alloys by measuring the rate of filling of V-shaped grooves, previously made in the surfaces, during prolonged heating at 1300°C, in an essentially inert atmosphere. Measurements were made on specimens of pure iron and on one of the iron-boron alloys. Grooves exhibited filling only if an associated grain boundary ended in the root of the groove. Grooves with no accompanying grain boundary were observed to deepen with time instead of filling, and these exhibited extensive crystal-face development. The results of calculations indicate that the surface and grain-boundary tensions of the iron-boron alloy were greater than those of pure iron. The results of this investigation may have important applications to the theory of sintering, and may have a bearing on the boron hardenability effect in steel.

Internal-friction studies have been conducted on vacuum-melted iron, zone-refined iron which had been previously vacuum-melted, and an iron-boron alloy made by zone-leveling high-purity boron into the zone-refined iron. The internal-friction spectrum was measured for each of these materials over the temperature range from —180° C to + 100°C. It is concluded that the addition of boron to essentially pure iron-carbon alloys has a definite measurable effect on the internal friction spectrum of the alloy. The predominant effect is an increase in the height of the carbon peak. The activation energy of the carbon peak in the presence of boron is not materially affected. The value of the activation energy, and the D_0 values obtained for boron with reference to those for carbon, indicate that boron forms an interstitial solid solution with alpha iron. Some side phenomena were observed in the investigation. These included an amplitude dependence found in the high-purity iron and the iron-boron alloy, as well as a relatively rapid aging effect at room temperature and below.

The vertical zone-melting apparatus has been used to investigate the possibilities of zone refining beryllium. The investigation served to point out the problems of further purification of beryllium by this approach. Principal difficulties arose from severe ionization of the hydrogen atmosphere at temperatures below the melting point of beryllium, and nonuniform swelling of the metal when heated near its melting point in a hydrogen atmosphere. The latter was attributed to an internal reaction between the hydrogen atmosphere and a constituent of the starting beryllium.

The design of an electron bombardment melting unit has been completed and its construction is well under way. This unit will extend the zone melting facilities of the Department, and make possible studies on metals and alloys with higher melting points than iron.

FUEL TECHNOLOGY

Research in the Department of Fuel Technology covers the following broad subject matter areas: bituminous coals, anthracite, carbons, gaseous combustion, fuel cells, and reactions of fuel chemicals. It is concerned with basic and applied questions ranging from the desorption of chemisorbed gases from graphite to the operation of fire-jet stokers; from vapor-phase pyrolysis of pure compounds to the effect of gamma irradiation upon the fluidity of coals; from the role of halogens in gaseous flame inhibition to nitric acid oxidation of the organic matter in shales.

The over-all aim of the research programs is to add to knowledge of the physical, chemical, and engineering aspects of fuels and their utilization, and in some instances to develop the principles upon which practical applications may be based.

BITUMINOUS COAL RESEARCH

Stoker Combustion of Bituminous Coal

Combustion problems of a cross-flow type, commercial-size stoker burning bituminous coals were investigated, as follows:

1. Relationship of fines in stoker feed to grate deposits.
2. Study of tail-end smoking.
   - (a) use of coal feed modulator
   - (b) use of hot-steam jets
   - (c) use of hot-blower jets
3. Design, development, and testing of a new standardized factory precut ignition arch.
4. Use of a chemical additive to reduce caking.

5. The use of low coke button coal as a fire-jet fuel.
6. The use of coke as a fire-jet fuel.

Briefly, the results of these studies were:

1. No relationship could be found between the amount of fines and grate deposits with Pennsylvania coals. Actually, grate deposits have not been a problem with the laboratory unit.
2. The coal feed modulator idea proved to be unsuccessful in reducing smoke.
3. The hot-steam jet will eliminate smoke during both the "on" and initial "off" period of stoker operation with high volatile coals.
4. The hot-blower jet will likewise eliminate smoke and appears to be more applicable to commercial size units where low-pressure steam prevails.
5. A new type of arch was developed which shows promise of simplifying field installations and reducing costs.
6. The limited study of the use of a chemical additive to reduce caking indicated that it was not effective. More work is needed, however, before definite conclusions can be reached.
7. Low coke button coal can be used satisfactorily on a standard anthracite fire-jet stoker.
8. Regular metallurgical coke breeze appears to be a poor fire-jet fuel.

Combustion of Pulverized Bituminous Coal

Exploration was made of the possible application of shock tube techniques to the study of the ignition process and burning rates of very finely divided bituminous coal and similar combustibles. Although ignition was obtainable, the method lacked precision and was set aside pending possible refinements.

Apparatus was constructed for producing a fully deagglomerated dispersion of micron-size pulverized coal in a supporting atmosphere. An injection nozzle and wall-free combustion chamber were built, with the intention of studying flame propagation rates in very finely divided fuel suspensions, as well as the role of flame radiation in the ignition and propagation processes. The interest in these subjects continues but the prime emphasis is shifting to anthracite as fuel.

Effect of Radiation on the Physical and Chemical Properties of Bituminous Coal and Coal By-Products

Work has been completed in three areas of research using the University nuclear reactor as a source of gamma irradiation: (1) effect of gamma irradiation at ambient temperatures on the subsequent carbonization of bituminous coal; (2) coal carbonization in the presence of gamma irradiation; and (3) effect of gamma irradiation on coal tar pitch.

In the first phase of the program, coals of varying fluidity (during carbonization), held in closed containers, were exposed to a total gamma dosage of 10^8 roentgens under vacuo, oxygen, air, and ammonia atmospheres. Following irradiation, these data were determined: (1) amount and analysis of gas in the coal container; (2) subsequent plastic properties of the coal during carbonization; (3) amount and analysis of gases released from coal during carbonization; and (4) properties of the coke produced, such as surface area, crystallite size, and reactivity to oxidizing gases. Whereas there were large differences in the amount and nature of the gases found in the coal container following irradiation for the different atmospheres used, the total amount of gas recovered was too small to be of any commercial interest. Prior irradiation in any of the atmospheres studied produced negligible differences in items 2, 3, and 4 above, over the results obtained without prior irradiation of the coal.

Eight bituminous coals were irradiated continuously at a power level of 100 kilowatts during carbonization up to 600°C for periods lasting either three or eight hours. No significant changes in the rate of gas evolution or gas composition were found which could be attributed to gamma irradiation. The cokes produced did not show any unusual properties.

The effect of irradiating a typical high temperature coal-tar pitch with gamma dosages ranging from 10^5 to 10^8 roentgens on the fluidity of the pitch was studied. For measurements over the temperature range 100-170°C, no detectable change in the viscosity of the pitch was observed.

All the above results emphasize the extreme resistance which coal and its pitch by-product have to gamma irradiation.

Grindability of Coal

The grindability of coals of different rank from high volatile bituminous to anthracite was studied. A pronounced maximum in the Hardgrove Grindability Index (as the Index increases, the coal becomes easier to grind) was found for the low volatile bituminous coals. This maximum in the Index is paralleled by a minimum in the surface area to volume shape factor of the ground material. Thus a reasonably good linear relation is found between the Grindability Index and shape factor, which suggests a quick way to estimate what the shape factor of a ground coal will be.

Purification of Bituminous Coals by Solution in Aromatic Oils and Their Utilization as a Source of Organic Chemicals

Studies have been conducted on a process of thermal solution of bituminous coals in aromatic oils and their filtration to remove mineral matter, fusain, and other insoluble components. The thermal solution

of coals in aromatic oils can be improved by the use of hydroaromatics, but this is not as effective as using an atmosphere of hydrogen. No way has been found to catalyze the transfer of hydrogen from the hydroaromatics to the coal as effectively as the direct addition of hydrogen at temperatures below the coking point. Filtration of the coal solutions is difficult at all temperatures, but the rate is higher at temperatures where the viscosity of the solution is less. There is an upper limit to the solution and filtration temperature, which is governed by the coking temperature of the coal. Coking can be avoided by using hydroaromatics or hydrogen, and filtration proceeds more freely. Filtration is improved greatly by using solids such as diatomaceous earth, powdered coke, or fusain. Cellulose filter aid is also very effective but cannot be used much above 200°C.

Reactions of Sulfuric Acid with Bituminous Coal

The study of the reactions of sulfuric acid with bituminous coals has been undertaken to discover what reactions occur, what is the structure of these coals, and whether the sulfonated coals have uses other than ion-exchange materials. Sulfuric acid eliminates most of the aliphatic hydrogen by a process of oxidation, leaving an essentially aromatic structure which has char-like properties. The sulfuric acid also oxidizes the carbon structure, forming carboxylic acid groups and carbon dioxide. Hydroxyl, ketonic, sulfonic, and acid sulfate groups are also introduced. While the sulfonated coal is not soluble in alkaline solutions to a very large extent, short oxidations with other oxidants produce soluble products.

Identification of the Basic Chemical Constituents of Bituminous Coal Using the Mass Spectrometer

One of the methods for investigating the structure and composition of coal has been vacuum pyrolysis. By thermally breaking the complex structure of coal into simpler components and identifying these components, it should be possible to work back to the original coal structure. To accomplish this end, a mass spectrometer is being constructed which will permit the direct pyrolysis of coal in the spectrometer vacuum system. It is planned to determine with this system the mass distribution pattern of the pyrolysis products of the various petrographic constituents of coal, and to compare these patterns with those of pure materials of known structure.

Porous Carbons from Humic Acids Derived from Nitric Acid Treatment of Bituminous Coal

Chars prepared from humic acids by pyrolysis at about 250°C were activated in a steam atmosphere from 750° to 900°C. The resulting carbons were evaluated for their adsorptive capacity and compared to several commercial carbons.

The carbons prepared at higher temperatures of activation compare favorably with the commercial samples in their characteristics such as surface area, iodine adsorption, pore volume, ash content, and less favorably with respect to density. Based on surface area, methylene blue adsorption, and mercury pore distribution values, the activated carbons from humic acids appear to contain essentially a micropore structure. Research is continuing on preparation and further evaluation of the carbons.

The Ignitibility of Bituminous Coals

An exhaustive survey was made of the literature on previous investigations of the ignitibility of combustible materials. An inflammability apparatus, originally used to study the explosibility of coal dusts, was selected to study the ignition of fine particle sizes of bituminous coals corresponding to pulverized coal firing. A crossing-point ignition apparatus was also employed for correlation purposes. The factors affecting these laboratory tests were studied until optimum procedures were established and good reproducibility was obtained.

The ignitibility behavior of eleven coals, ranging in rank from low volatile bituminous to high volatile C bituminous, has been examined by these two methods.

No correlation between the volatile content of the coals and either their ignition point temperatures in air or oxygen, or their crossing point temperatures in oxygen, was found. Results with the inflammability apparatus showed, however, a definite decrease in ignition temperature with decrease in particle size.

The following conclusions were drawn from the study:

1. The ignitibility of a bituminous coal is determined not by its total volatile content, but rather by the surface properties of both the original and the partially charred or carbonized particles.

2. Differences in the ignitibility of the bituminous class of coals are less marked than has sometimes been supposed; provided that sufficient oxygen is available, bituminous coals over a wide range of volatile contents will ignite at much the same ambient temperature when projected into a suitable hot environment in the size consist used for pulverized fuel firing.

3. The ignitibility of a cloud of coal dust particles increases as the particle size decreases. Particle size is more important in the ignition process than the influence of volatile content.

This work is being continued. Next, a wide variety of Pennsylvania bituminous coals will be tested and finally an attempt will be made to correlate laboratory results with plant performance.

Desulfurization of Bituminous Coal during Carbonization

The production of low-sulfur cokes is an important industrial problem. Research in this area in the Department of Fuel Technology is

being directed toward an understanding of the chemical changes that occur during coking, and also toward finding additives that will evolve much of the sulfur as gaseous products. It has been found that a considerable part of the sulfur retained in the coke comes from a reaction of hydrogen sulfide with the hot coke, and that hydrogen or hydrogen-producing gases such as ammonia reduce the retained sulfur. Currently, organic additives are being studied for possible sulfur-reducing properties.

Three cokes, prepared at 500°C, 700°C, and 900°C, were reacted with hydrogen sulfide at temperatures ranging from 500°C to 1000°C. The 500°C coke was found to be the most reactive of the three. The reaction temperature at which the most extensive fixation of sulfur occurs is between 600°C and 700°C. In the coking process, it is established as probable that both pyritic and organic sulfur forms contribute to sulfur fixation. The principal end reaction in all cases appears to be one between hydrogen sulfide and carbon. In cokes prepared at temperatures below 700°C, free sulfur apparently reacts rapidly with the carbon of the coke, so that no free sulfur is detected. The less reactive, higher temperature cokes contain some free sulfur.

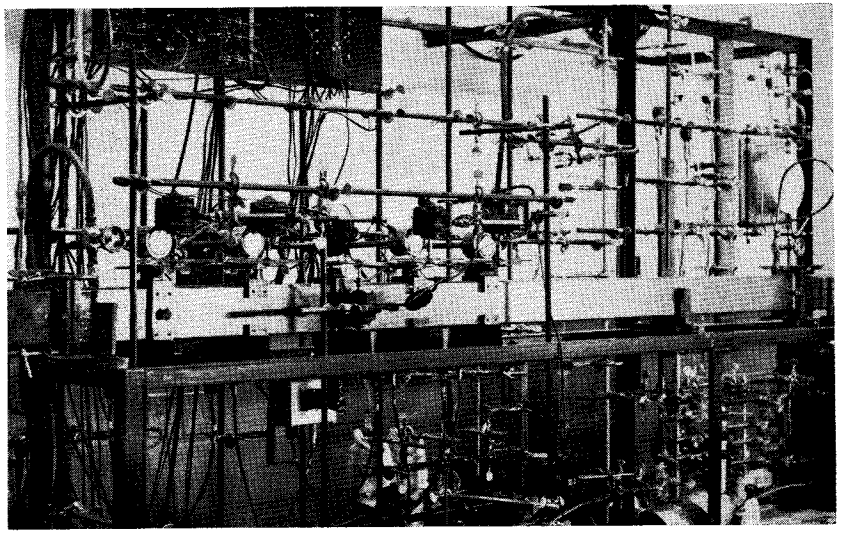
ANTHRACITE RESEARCH

Combustion of Pulverized Anthractie

An apparatus for studying the role of flame radiation in ignition and propagation of flame through finely divided fuel suspensions is described briefly under the section on bituminous coal research. A high-intensity carbon arc lamp adjacent to the combustion chamber serves as a high-flux external radiation source. A radiometer measures this flux, which impinges upon the fuel suspension. An air permeability apparatus has been built for giving gross information on particle sizes, and this will be supplemented by electron microscopy. Concentrations will be measured by a combination of collection procedures and photoextinction. The principal emphasis in the early experiments will be upon: (1) ignition by radiation; (2) rate of flame propagation with and without radiation; (3) effect of fuel type; and (4) effects of particle size and concentration.

Kinetics of Volatile Matter Release from Anthracite

In an effort to understand the mechanism of thermal decrepitation of anthracite, the kinetics of volatile matter release when anthracite is heated to elevated temperatures has been studied. Since hydrogen is the major constituent of the volatile matter, its rate of release under isothermal conditions has been studied in some detail for a series of coals. The rate of hydrogen release appears to follow a zero order law during the initial stages of reaction, where the surface coverage



Shock tube for kinetic measurements on fast gaseous reactions.

is greater than 95 per cent. When the surface coverage falls below 95 per cent, however, a gradual deviation from zero kinetics was observed, and in this range the volume of hydrogen evolved was found to be proportional to the logarithm of time. The effect of particle size on the rate of hydrogen release from different anthracites was found to be complex. For some coals the rate of hydrogen release increased with increasing particle size, while for other coals the rate decreased.

Investigation of the Removal of Mineral Matter from Anthracite by High-Temperature Chlorination

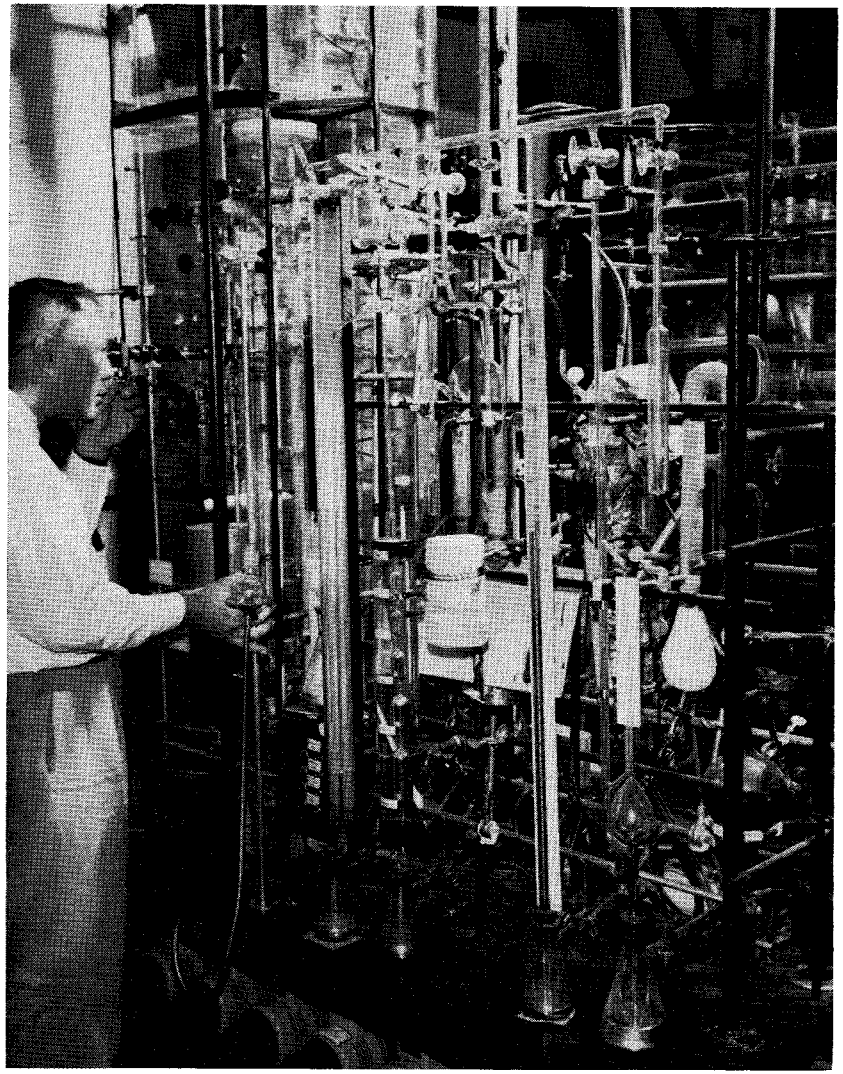
A 42 x 65 mesh fraction of anthracite, containing 7.6 per cent mineral matter as ash, has been treated for one hour with chlorine at temperatures from 700 to 1400°C and atmospheric pressure. This treatment resulted in a marked decrease in ash content, with a maximum removal of about 80 per cent at chlorination temperatures above 1000°C. The effect of chlorination on the resultant surface areas and electrical resistivities of the anthracite have also been studied. Work with different particle sizes of anthracite, soak times, chlorine pressures, and pretreatment conditions is in progress.

Activation of Anthracite

Activation of a selected anthracite (42 x 65 mesh) with carbon dioxide was studied using fluidization techniques. Reaction temperatures were varied from 800 to 950°C. The percentage of burn-off ranged from zero to 60 per cent of the devolatilized anthracite. For the

activated anthracites, the pore structure was determined and correlated with adsorption characteristics for carbon tetrachloride vapor. The apparatus shown in Figure 8 has been used extensively in this work. The optimum burn-off was about 50 per cent (on a mineral matter free basis) over the temperature range 850 to 950°C, as judged by maximum surface area production and capacity for carbon tetrachloride adsorption. Under these conditions, the product is found to compare favorably with vapor phase active carbons now used commercially.

Fig. 8—Helium density and low-temperature gas adsorption apparatus used to study the physical structure of activated carbons.



The Effect of Heat Treatment on the Structure of Anthracite

The effect of heat treatment conditions (maximum temperature, soak time, and rate of heating) on the structure of anthracite is being investigated. The change in crystallite size distribution and orientation is being studied by X-ray diffraction. Concurrent with this study is a study of the rates of diffusion of different gases through anthracite. Data on diffusion coefficients, and their change with temperature, will make possible the calculation of the predominant molecular pore sizes and their lengths in anthracite.

Reaction of Anthracite with Free Radicals

Studies are under way on the reactions of anthracite with oxygen and hydrogen radicals. The reactions are being conducted at temperatures below 200°C so that the structure of the anthracite is not changed by thermal treatment. At higher temperatures, where anthracite is commonly gasified with molecular species, appreciable shrinkage of the pore structure occurs, resulting in the obtaining of a less reactive material.

Stoker Combustion of Anthracite

A cross-flow type, commercial-size stoker was used in a study of anthracite combustion problems. The questions investigated were: (1) The drainage rate of water in rice size anthracite; (2) The effect of moisture upon the feeding rate of rice size anthracite; (3) The effect of a modified grate and windbox upon combustion rates.

The results may be briefly summarized as follows: It appears that surface moisture up to 3 per cent has no appreciable effect upon the feeding rate of the Fire-Jet stoker. A moisture content of 5 per cent will reduce the flow of coal as much as 16.6 per cent with one coal, and as little as 5.3 per cent with another. Coals carrying 4 per cent moisture were only slightly affected: 5 per cent to 7 per cent. The drainage behavior was similar in all three coals tested. With 3 per cent moisture, practically no drainage occurs up to 17 hours. It requires about 16 to 17 hours for 5 per cent moisture coals to drain to 3 per cent.

The combustion rate for this modified 36″ wide grate was increased from 135 lbs. per hour to 190 lbs. per hour and, even with wet and poorer grades of coal, a minimum rate of 160 lbs. per hour can be maintained. The combustion efficiencies obtained in these tests were excellent despite the very high burning rates.

CARBON RESEARCH

Character of Organic Binders

Some 25 coal-tar pitches have been coked and graphitized. The reactivity of the cokes and graphitized carbons to carbon dioxide and air has been determined. For 23 of the samples, the reactivity of the

coke to carbon dioxide is lower than the reactivity of the graphitized counterpart. In the case of air reactivities the result is reversed; all the graphitized carbons have a lower reactivity to air than do their coke counterparts. In the case of delayed petroleum coke, the reactivity of the coke to both carbon dioxide and air is considerably greater than the reactivity of the graphitized material. On the basis of reactivity results and physical measurements on the cokes and graphitized carbons, it is concluded that the effect which heat treatment has on reactivity is dependent, to a considerable degree, upon the original extent of intimacy and dispersion between the carbon and metal impurities in the raw material.

Effect of Metallic Impurities on the Gasification Rate of Carbon

A long-range program aimed at determining and understanding the effect of metallic impurities on the gasification rate of carbon is continuing. Pelletizable graphite of the highest obtainable commercial purity is used as the base material, to which impurities are added either in particle form or in solution. A study has been completed on the effect of iron on catalyzing the reaction of carbon with carbon dioxide. The addition of only .05 per cent iron is found under favorable circumstances to catalyze the gasification rate some 150-fold. However, the catalytic activity of the iron can be markedly reduced if the sample is heat-treated in an inert atmosphere at higher temperatures before reacting in the temperature range 950-1200°C. The reduction in catalytic activity is related to the diffusion of carbon into the iron. At present, this problem is being studied by following the effect of heat treatment and reaction on the magnetic susceptibility and thermoelectric power of the samples.

The effect of the addition of boron to carbon on gasification rates with carbon dioxide is also being studied. Preliminary results show that when boron is added in amounts up to 1 per cent, and no heat treatment above reaction temperatures (1050 or 1100°C) is performed, an inhibition of the gasification rate occurs. It is thought that this inhibition is a result of physical coverage of the carbon surface by boron particles. There is some indication that boron is oxidized and slowly lost from the samples at gasification temperatures.

The oxidation of thin films of carbon is also being studied. In this work, relatively thin films of metal or metal oxides are coated with carbon by evaporation. The effect of metal substrate and thickness of carbon film on its reactivity is being investigated.

Reaction of Highly Homogeneous Carbon Surfaces with Oxidizing Gases

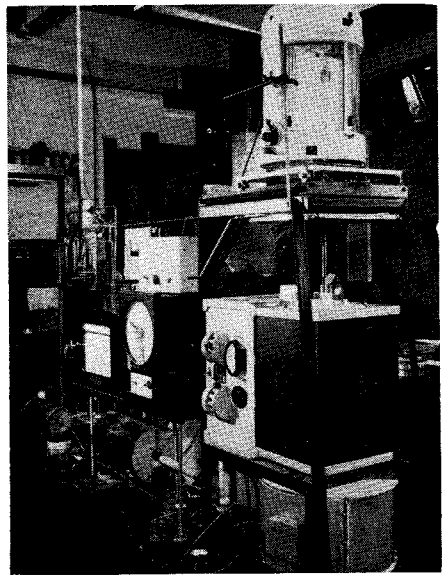
One of the difficulties in predicting the reactivity of carbons to oxidizing gases has been the heterogeneous nature of most carbon surfaces. This research uses graphitized carbon blacks which have essentially 100 per cent of their surface composed of basal plane structure.

One study examines at low pressures (< 100 microns), the build-up and stability of carbon-oxygen complexes on the surface as a result of the carbon-oxygen reaction. The effect of temperature and amount of carbon-oxygen complex on the product carbon dioxide-carbon monoxide ratio is also being examined. In another study, the change in structure of graphitized carbon blacks with oxidation to high burnoffs is being investigated. Here, the opening up of edge surface as the reaction proceeds through the interior of the particle is of particular interest. The amount of edge surface area (high-energy site area) is being measured by low temperature adsorption of nitrogen at very low relative pressures.

Release of Chemisorbed Gases on Graphite by Thermal Treatment

The sorption of hydrogen on selected types of nuclear and spectroscopic graphite has been studied. On nuclear graphite, the desorption of hydrogen over the temperature range 1035 to 1375°C follows the Elovich equation. The activation energy for desorption over the coverage range, 0.32 to 0.68, decreases linearly with increasing coverage. Isotherms for sorption of hydrogen over the temperature range 920 to 1495°C are of the Temkin type. From the maximum amount of hydrogen adsorbed, it is concluded that the adsorption of hydrogen occurs on carbon atoms at the edge of crystallites and that significant intracrystalline sorption does not occur.

Apparatus for studying the reactivity of carbon to oxidizing gases at atmospheric pressure.



Mechanism of Pyrolysis of Organic Compounds to Produce Graphitizable Carbon

The mechanism by which benzene is pyrolyzed at 1200°C has been established to involve rupture of the ring producing a molecule each of acetylene, diacetylene, and hydrogen. Of the two organic products, diacetylene carbonizes much more rapidly than acetylene. However, both acetylene and diacetylene are converted partly into the other hydrocarbon, creating a very complex decomposition pattern. Calculations of the bond orders and total π-electron energies of various possible decomposition products have been made to gain a better understanding of the mechanism of decomposition. Both benzene and diacetylene decompose following first order kinetics. The decomposition of acetylene, however, accelerates with time under the conditions used. This is of interest because of the explosive behavior of acetylene under other circumstances. Diacetylene forms a polymer on standing which has unusual properties.

Formation of Carbon Films by Pyrolysis of Gases

The deposition rate of carbon films formed by the thermal decomposition of carbon suboxide, C_3O_2, is being measured in a flow system. The aims of the work are: (1) to study the type of carbon formed from this molecule, which may decompose into CO and monatomic carbon; (2) to use the kinetic data as a tool for obtaining the decomposition rate of C_3O_2; and (3) to use the highly uniform and very thin films of carbon formed in the process to obtain data on gasification rates of such films. In addition, the possibility of using C_3O_2 decomposition to reduce the porosity of carbons will be explored.

GASEOUS COMBUSTION RESEARCH

Carbon Monoxide Combustion

The inhibition of premixed flames of CO and gaseous oxidizers by halogens has been studied, with these results: chlorine and bromine reduce the burning velocities of hydrogen-containing carbon monoxide flames supported by air, oxygen, and nitrous oxide, with the qualification that if the hydrogen content is low, the effect of chlorine upon nitrous oxide-supported flames can become an acceleration caused by chlorine catalysis of nitrous oxide decomposition. Measurements of the reduction of burning velocity by chlorine over a wide range of CO-air compositions show that the relative inhibition (relative to no halogen) is, at most, weakly dependent upon CO-air ratio or hydrogen content. The effect of CCl_4 is identical to the equivalent amount of Cl_2. A lower limit to the chain length in the absence of inhibition is established to be 55, with the probable actual chain length appearing to be more like 1,000. The "radical-free" contribution to the burning

velocity appears to be less than 1 cm/sec, if it exists at all. A theoretical analysis leads to some information on the rate constants of the main inhibition reaction, which is the removal of OH radicals by HCl.

The effect of hydrogen upon the combustion of carbon monoxide has been examined, with the result that the laminar burning velocity of H_2-free CO-air flames is established to be less than 5 cm/sec, and is probably close to zero. Flames of CO containing less than 150 ppm H_2 are extremely sensitive to secondary atmospheric moisture, which diffuses into the combustion zone and accelerates the burning process. Nevertheless it has been possible to demonstrate that such CO-air flames, allowing for the moisture diffusion, have an unusual dependence of burning velocity upon mixture composition, with a maximum near stoichiometric.

Reactions of Free Radicals Generated by the Sodium Diffusion Flame Method

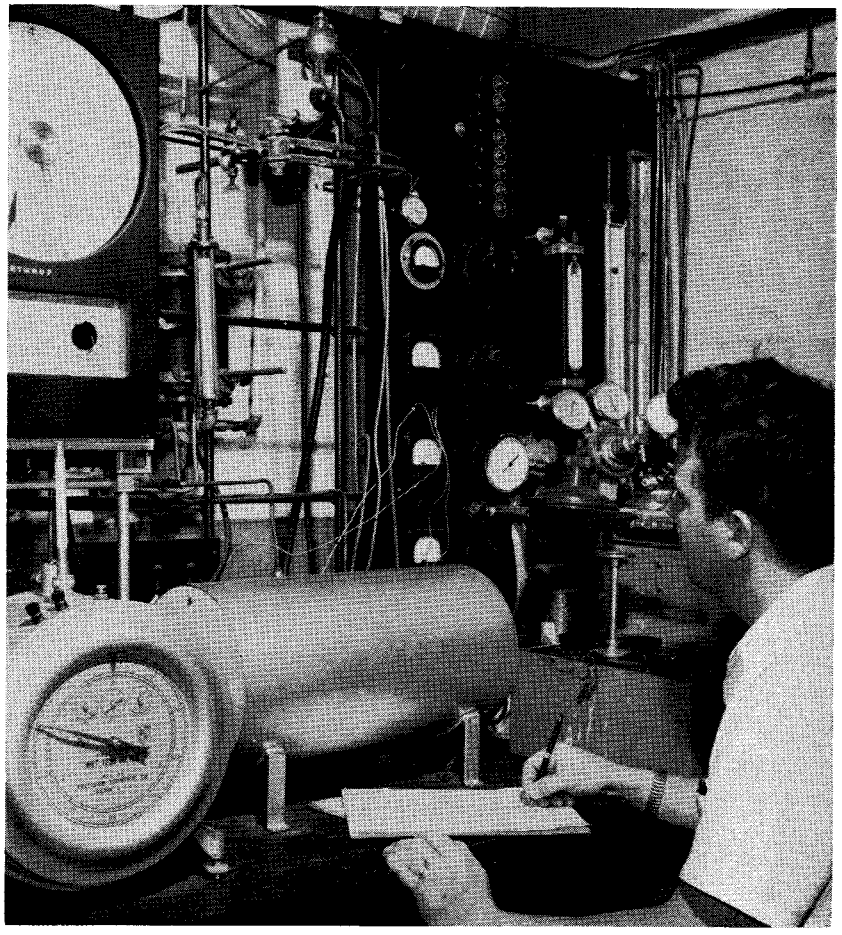
The gas phase reaction of alkali metal vapors with halides is a versatile means for generating radicals in wide variety. Work is under way in which potassium vapor is reacted with small alkyl halide molecules to produce such species as C, CH, CH_2, and CH_3. Products of the secondary reactions of these radicals with each other, and with additives, are being examined by trapping and vapor chromatography. Spectroscopic methods for examining the reaction zone are being investigated.

High Temperature Reactions in Shock Waves

A study has been completed of the thermal decomposition of nitrosyl chloride, ONCl, using a laboratory shock tube equipped to follow the change in light absorption behind primary shock waves in mixtures of ONCl in various dilutions with argon. The temperature range covered was 880°K to 1350°K. Combination of the results with published data at low temperatures permits a quite complete understanding of the decomposition kinetics of this molecule over a 1500°K temperature range.

A single-pulse shock tube is being used to measure the decomposition behavior of the rocket fuel, hydrazine (N_2H_4), at temperatures in the 1000°K range. In a third shock tube, work is commencing on the very unstable molecule, diazomethane.

In work related to the shock tube experiments, a critical review has been made of the bond-dissociation energies of C-C and C-H bonds in small hydrocarbon molecules. An analytical study has been performed on the early stages of competitive, consecutive gaseous reactions. The temperature dependence of the optical absorption in nitrosyl chloride is being examined by means of Sulzer's theory. It does not appear to be amenable to such an approach. Calculations are in prep-



Apparatus used to study the rates of diffusion of gases through porous carbon bodies.

aration for the shock-driver gas interface tailoring conditions in a single-pulse tube. Finally, a comprehensive review is in preparation, covering the entire subject of shock-tube chemistry.

Atom and Free Radical Propellants

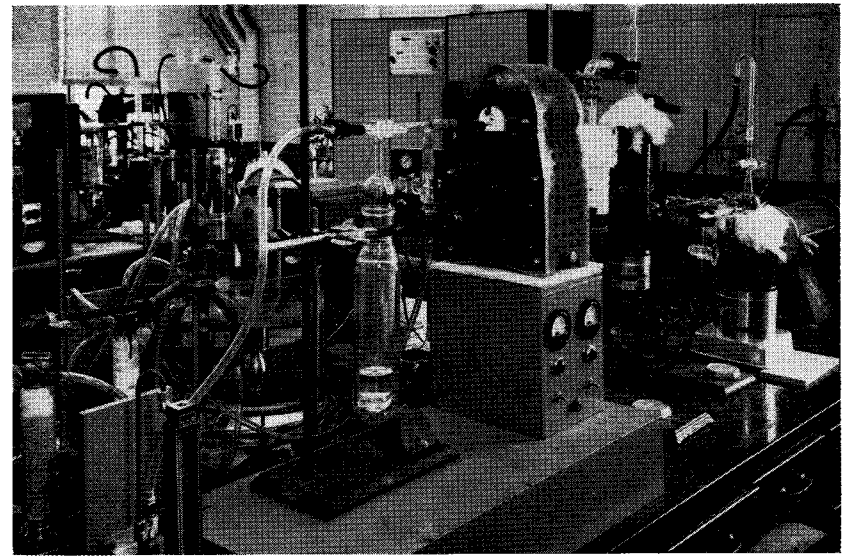
The simplest type of free radical propellant, namely one composed of H atoms in a cold matrix of H_2, has been examined theoretically as to its burning rate. It was found that the expression for the burning rate is similar to gas-phase thermal theories of flame propagation, but there are fewer approximations required. It shows a linear dependence of burning rate upon H atom concentrations in the solid. The theory is readily applicable to other free radical propellants.

FUEL CELLS

The direct conversion of combustion energy to electrical energy, using the fuel cell, is an increasingly important area of study in fuel technology. Most current research effort is devoted to developing fuel cell devices for a variety of special applications. The Fuel Technology Department is carrying out research on the physical and electrochemical basis of simple laboratory cells.

Investigations of current-voltage relations of a low-temperature hydrogen-oxygen cell have been made. These relations have been considered with respect to the kinetics of gas adsorption and electrochemical reaction, and a general theory to explain the effect of different electrode catalysts has been developed. Some aspects of the experimental results are still unexplained, and further work is in progress. The effect of physical properties and activation of carbons used for electrodes is being studied. Recent publications include a theory of the hydrogen-oxygen cell and general review articles on fuel cells.

Further investigations concern the kinetics of ion regeneration for redox fuel cells. A theoretical study has shown that the most important parameter in ion regeneration is the limiting reaction rate available per unit reactor volume. Limiting rates are being determined as functions of concentration and temperature for several systems.



Flow systems for study of high-temperature decomposition of benzene, acetylene, and diacetylene.

Work is most advanced on the formic acid-titanous-titanyl system. An additional investigation is under way on the topic of possible fuel cell systems for short period, high-power output electrical generation. A preliminary feasibility study is being made.

FUEL REACTIONS RESEARCH

Pyrolysis of Hydrocarbons

The thermal decompositions of benzene, acetylene, and diacetylene have been studied in connection with work on the mechanism of carbon formation. This work is being continued.

Dicacetylene Polymerization

A study is beginning concerning the polymers produced in the exposure of diacetylene to a wide range of environmental temperatures. The study is an outgrowth of research on the mechanism of carbon formation.

Chemical Nature of the Organic Matter of Uraniferous Shales

The recovery of uranium from shales is made difficult by the presence of organic matter which cements the mineral particles together. As part of a program to find more effective ways to recover the uranium from these shales, the reactions of the organic matter with nitric acid have been investigated. This treatment disintegrates these shales very effectively, converting the organic matter to carboxylic acids with interesting properties. As a result of these researches a better knowledge of the chemical nature of the organic matter of these shales has been obtained.

CERAMIC TECHNOLOGY

The research program of this Department falls into five main categories:

(1) Structural studies of minerals, and mineral reactions,
(2) Phase equilibrium studies of oxide systems,
(3) Investigations of magnetic and electrical ceramic materials,
(4) Studies of glasses,
(5) Sintering, grain-growth, and kindred studies.

The marked increase in the research achievements of the Department, which took place around 1955, has been maintained in the biennium under review as shown by the number of publications which have appeared in scientific and technical journals:

Year	1951-52	52-3	53-4	54-5	55-6	56-7	57-8	58-9	59-60
No. of publications	15	9	7	16	22	20	32	27	22

STRUCTURAL STUDIES OF MINERAL REACTIONS

The structural interpretation of the important series of reactions from kaolinite to mullite has been completed and published in a three-part article in the *Journal of the American Ceramic Society*. The ideas developed in this study are now being applied to other mineral reactions in which mullite is the final product, particularly the decomposition reactions of sillimanite, kyanite, and andalusite. An optical study has been made of the movement of the reaction interface between kyanite and mullite, which has enabled the activation energy of the reaction to be evaluated.

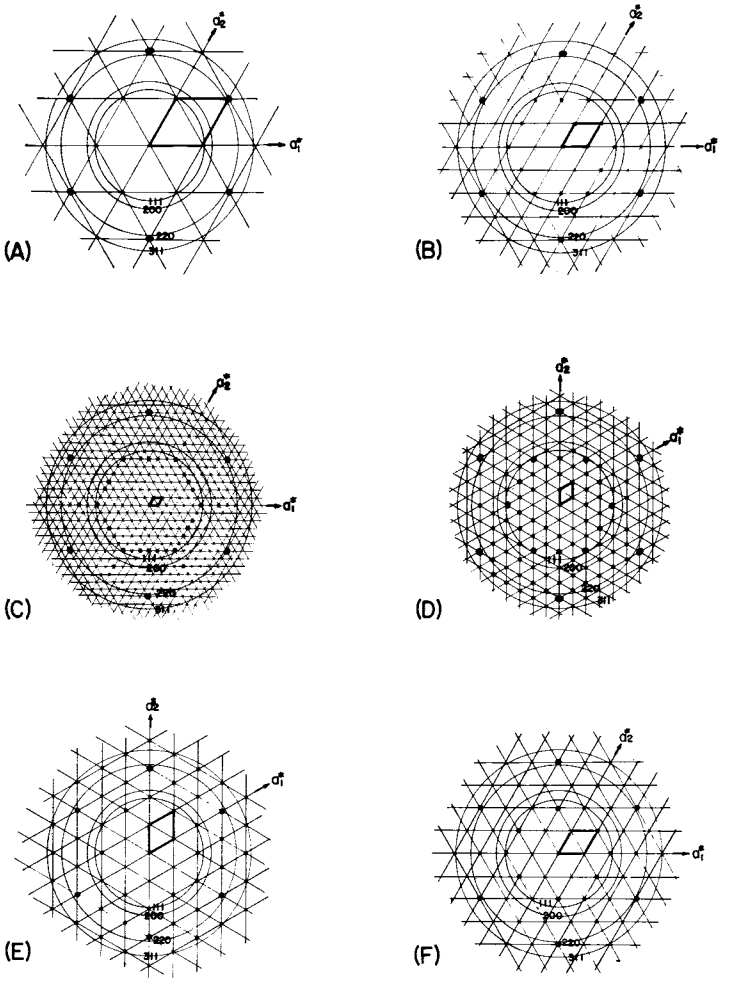


Fig. 9—Single crystal, electron diffraction patterns of transition aluminas: (A) x-alumina at 270° C. (B) x-alumina at 830° C. (C) k-alumina at 1000° C. (D) (?)-alumina at 1030-1180° C. (E) ξ'-alumina at 1180-1350° C. (F) γ-alumina at 1030-1180° C.

The complicated reactions which take place when gibbsite (alumina trihydrate) is heated to form corundum (an important refractory and abrasive material) depend on whether the gibbsite particles are "coarse" or "fine," the division being around 1/10,000 inch. Particular attention has been given to the behavior of "fine" gibbsite, and for such small crystals, electron microscopy and electron diffraction have proved very powerful methods of investigation. Figure 9 shows a series of electron diffraction patterns of single crystals of fine-grained gibbsite heated to various temperatures. By analysis of such diagrams, the atomic rearrangement in the crystal structure of the material can be evaluated. It is seen directly that the thermal transformations occur in a continuous sequence with the atoms at first organizing themselves in a more complex pattern, and subsequently taking up arrangements of lower complexity at higher temperatures.

Studies of the rehydration of magnesium oxide in atmospheres of controlled temperature and humidity are bringing to light the reaction mechanisms involved, which may have important consequences for the behavior of this important basic refractory material. Much progress is likely to result from the study of materials in well-controlled atmospheres, and for this purpose equipment is being developed in which temperature and water vapor pressure can be varied over wide ranges. The broad objectives of this research are to obtain a better understanding of many so-called "meta" phases, i.e., materials not in strict thermal equilibrium, but which nevertheless have considerable metastability and a high energy content.

HIGH-TEMPERATURE REACTIONS IN CLAY MINERAL MIXTURES

The investigations previously reported on reactions between quartz, kaolinite, and mica have been greatly extended. Useful correlations have been established between the ceramic properties of the fired materials, such as their porosity and shrinkage, the initial mineralogy of the materials, and their mineralogy after firing. This work attempts to place a good deal of largely empirical ceramic knowledge on a more systematic basis as a first step towards obtaining a scientific interpretation of the complex ceramic processes. An important consideriation is how far ceramic reactions proceed towards equilibrium. It has been proved that, at least for quartz-kaolinite-mica mixtures, there is a strong tendency towards high-temperature equilibrium. The work is developing in the direction of including feldspars in the initial compositions, and also towards studying various natural clay mixtures. A broad survey has been completed of many shale and clay materials, and work is currently in progress on high alumina clays.

CLAY MINERAL SYNTHESIS AND ALTERATION

Simple equipment has been developed for low-temperature, low-pressure hydrothermal study of the formation and alteration of clay minerals. Under these conditions, reactions are relatively slow compared with those normally employed in synthesis studies where achievement of equilibrium is the primary consideration, and thus it becomes possible to investigate mechanisms of reactions. Kaolinite is the mineral of the kaolin group which is normally synthesized in such experiments, halloysite is rarely, if ever, synthesized. The present experiments have made some progress in this direction, and a fibrous kaolin mineral exhibiting marked lattice swelling and shrinking has been obtained, although it would be premature to call it halloysite. Alterations of alumina minerals and of micas are yielding interesting results, but much remains to be done to clarify the mechanisms of the reactions.

CLAY-ORGANIC STUDIES

The adsorption of organic materials by clay surfaces and the development of new products, such as clay-based greases, give rise to many problems. To obtain a clearer picture of the adsorption process itself, an extended investigation has been made of the reactions between montmorillonites and neutral water-soluble aliphatic molecules. The roles of carbon chain length and of C-H activity have been studied by considering the equilibria of systems composed of clay, water, and organic materials. An infrared study conducted in considerable detail has revealed something of the character of the organic-organic interactions in the clay-organic systems. The modifications of the infrared vibrations resulting from the adsorption process make quantitative I.R. studies of organic adsorption difficult to apply, except when vibrations are used which are unaffected by the adsorption process. An unexpectedly large amount of detailed study has been required in this work.

PHASE EQUILIBRIUM STUDIES OF CERAMIC SYSTEMS

A study of phase relationships in the systems TiO_2-P_2O_5, Li_2O-$Li_2O \cdot B_2O_3$, Li_2O-B_2O_3-SiO_2, Li_2O-Al_2O_3-TiO_2, Li_2O-P_2O_5, and Li_2O-B_2O_3-P_2O_5 has been completed.

The system TiO_2-P_2O_5 was investigated in the compositional range $TiO_2 \cdot P_2O_5$ to 100% TiO_2. Two compounds exist, $TiO_2 \cdot P_2O_5$ and $5TiO_2 \cdot 2P_2O_5$ $TiO_2 \cdot P_2O_5$ begins to lose P_2O_5 at 1400°C and both fusion and vaporization proceed rapidly at 1500°C. $5TiO_2 \cdot 2P_2O_5$ melts congruently at 1260°C±3°C to a glass which can be retained

in substantial quantities at room temperature. The thermal expansion properties of the two crystalline compounds, and the infrared absorption spectra of several glasses based on the 5:2 composition, were investigated.

Previously, phase relationships in the portion of the system Li_2O-B_2O_3 ranging from $Li_2O \cdot B_2O_3$ to 100 per cent B_2O_3 had been determined. Further work on the high lithia portion of the system ranging from $Li_2O \cdot B_2O_3$ to Li_2O revealed the existence of three compounds: $3Li_2O \cdot B_2O_3$, $2Li_2O \cdot B_2O_3$, and $3Li_2O \cdot 2B_2O_3$. The thermal behavior of the compounds was determined and presented as a phase diagram.

Work was completed on the phase relationships, liquid immiscibility, and thermal expansion properties of glasses in the system Li_2O-B_2O_3-SiO_2.

Compatible phases in the system Li_2O-Al_2O_3-TiO_2 at various temperature levels were determined mainly by solid state reactions for the portion of the system bounded by $Li_2O \cdot Al_2O_3$, $Li_2O \cdot TiO_2$, Al_2O_3, and TiO_2. The existence of a ternary compound, $Li_2O \cdot Al_2O_3 \cdot 4TiO_2$ and nine joins was established. The ternary compound has a lower limit of stability at 1090°±15°C and dissociates and recombines rapidly at 1380°±15°C.

The existence of lithium ortho, pyro, and metaphosphate compounds was confirmed and new optical, X-ray and thermal data were obtained.

The glass forming region in the ternary system Li_2O-B_2O_3-P_2O_5 was roughly outlined and liquidus data were obtained for the three joins $Li_2P_2O_6$-BPO_4, $Li_4P_2O_7$-BPO_4, and Li_3PO_4-$Li_2B_4O_7$. Compatibility relationships for the ternary sub-systems $Li_2P_2O_7$-BPO_4-P_2O_5 and Li_2O-Li_3PO_4-$Li_2B_8O_{13}$ were established. Two ternary compounds with the probable compositions $22Li_2O \cdot 11B_2O_3 \cdot 13BP_2O_5$ and $2Li_2O \cdot 3B_2O_3 \cdot P_2O_5$ were detected.

ELECTRON MICROSCOPE STUDIES OF LIQUID IMMISCIBILITY IN SILICATE SYSTEMS

As an outgrowth of previous electron microscope studies on liquid immiscibility in the simple systems Li_2O-B_2O_3-SiO_2 and Li_2O-TiO_2-SiO_2, which showed that opacification resulted from the development of glass spheres 100-7000 Å in diameter in a matrix glass, work was continued in the more complex systems Li_2O-CaO-TiO_2-SiO_2, Li_2O-Na_2O-CaO-TiO_2-SiO_2 and Li_2O-Na_2O-BaO-TiO_2-SiO_2. The degree and temperature of opacification due to separation of two liquids in these systems indictate that they could be used as bases for the development of opaque glazes.

A large region of two liquid separations in the ternary system PbO-La_2O_3-SiO_2 was outlined using electron microscopy.

FLUORESCENT MATERIALS

Determination of the phase relationships on the $Zn_3(PO_4)_2$-$Mg_3(PO_4)_2$ join by the quench method has enabled the previously designated "gamma zinc phosphate" to be identified as a solid solution of zinc orthophosphate in magnesium orthophosphate. $Mg_3(PO_4)_2$ takes 95 mole per cent $Zn_3(PO_4)_2$ into solid solution at 1000°C. β-$Zn_3(PO_4)_2$ takes a small amount of $Mg_3(PO_4)_2$ into solid solution (about 3 mole per cent at 1000°) and, in order to satisfy the requirements of the Phase Rule, α-$Zn_3(PO_4)_2$ must take a small amount of $Mg_3(PO_4)_2$ into solution.

Data on peak emission and brightness of the β-$Zn_3(PO_4)_2$ solid solution and the $Mg_3(PO_4)_2$ solid solution were obtained, using molar substitutions of manganese as an activator. The brightness of the β-$(Zn,Mg)_3(PO_4)_2$:Mn solid solutions compares favorably with commercial β-$Zn_3(PO_4)_2$:Mn phosphors and the N.B.S. standard. The manganese-activated phosphors near the high zinc end of the $Mg_3(PO_4)_2$ solid solution series are very bright relative to the β-$Zn_3(PO_4)_2$:Mn standard, but they peak near 6280 Å, which may in part account for the higher brightness.

Phase relationships in the systems Li_2O-MgO-P_2O_5, Li_2O-ZnO-P_2O_5, and $Sr_3(PO_4)_2$-$Mg_3(PO_4)_2$ were clarified as a basis for the understanding of the emission characteristics of the compounds and solid solutions which occur.

The influence of firing atmosphere on the luminescence of a large group of spinels activated with Mn^{2+}, Fe^{3+}, and Cr^{3+} was investigated. The colors of the emission spectra were correlated with the oxygen coordination of the activator in the host lattice.

Several methods were developed for the preparation of a yellow-fluorescing rutile form of germania.

SOLID SOLUTION IN MULLITE

A study of the solid solution of TiO_2, Fe_2O_3 and Cr_2O_3 in mullite was made by measuring the changes in lattice parameters and unit-cell volume. Synthetic mullite ($3Al_2O_3 \cdot 2SiO_2$) was reacted with up to 12 weight per cent of the oxides at temperatures ranging from 1000° to 1700°C. The approximate minimum temperature required for the formation of solid solution was 1200°C for Fe_2O_3 and 1400°C for Cr_2O_3 and TiO_2. The maximum amount of solid solution found was 2 to 4 per cent TiO_2 at 1600°C, 10 to 12 per cent Fe_2O_3 at 1300°C, and 8 to 10 per cent Cr_2O_3 at 1600°C. Lattice parameters and unit-cell volumes for each solid solution series increased with increasing amounts of foreign oxide. There was good agreement between the calculated and observed increase in cell dimensions for the iron oxide series.

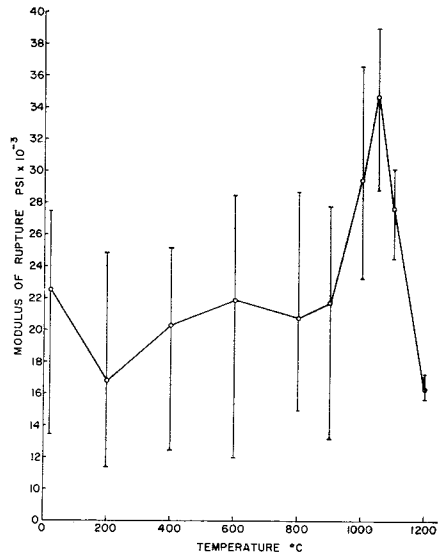


Fig. 10 — Variation of transverse strength with temperature for a refractory porcelain.

Except in the case of titania, there was good agreement between X-ray data and petrographic observations.

STRENGTH AND ELASTIC PROPERTIES OF CERAMIC MATERIALS

The variation of transverse strength and elastic modulus with temperature was determined for two glass-bonded commercial porcelains, one a chemical porcelain composed of quartz, mullite, and glass, and the other a refractory porcelain composed only of mullite and glass. The strength of the refractory porcelain was found to peak rather sharply at 1050°C, giving a value of 35,000 psi compared to 22,000 psi at room temperature and 900°C. The variation of strength with temperature is shown in Fig. 10. A similar effect was observed for the chemical porcelain which gave a strength maximum of 16,000 psi at 700°C.

The elastic modulii of these porcelain bodies decrease rapidly above 600°C. The temperature at which rapid decrease begins appears to be relatively independent of the amount and composition of the glass phase present.

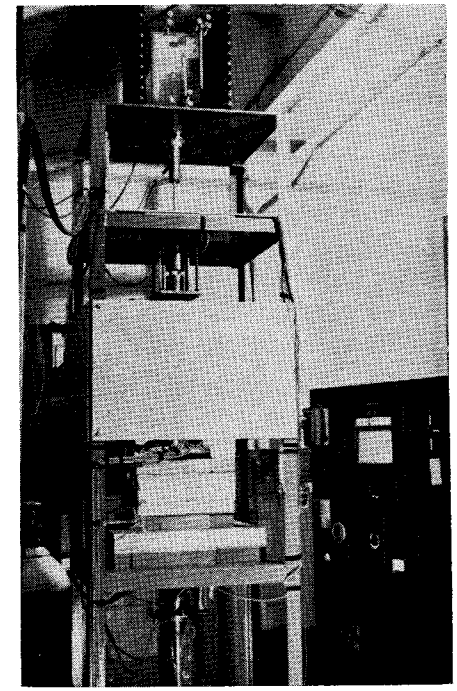
In another investigation of mullite bodies, an attempt was made to sinter relatively pure $3Al_2O_3 \cdot 2SiO_2$ and $2Al_2O_3 \cdot SiO_2$ compositions to low porosites at 1710° and 1650°C, respectively, using an addition of 1 per cent MgO to each body to facilitate the reaction.

The $3Al_2O_3 \cdot 2SiO_2$ body sintered to a porosity of 7.1 per cent and was practically all mullite as determined by X-ray and petrographic examination. The $2Al_2O_3 \cdot SiO_2$ body sintered to a porosity of 10.9 per cent and was composed of mullite (probably a 3:2 mullite) and corundum.

High temperature strength and elastic modulus measurements were made at several temperatures up to 1200°C, and some observations were made on the load-bearing properties, the strain at fracture, and the calculated thermal shock resistance of the sintered mullite bodies.

THERMAL AND MAGNETIC STUDIES OF FERRITES

A detailed study of manganese ferrite ($MnFe_2O_4$) has been completed. The experimental approach used was to measure gain or loss in weight of a sample at high temperatures as a function of temperature and oxygen pressure. A theoretical analysis of the weight changes was then attempted. X-ray lattice constants and line widths



High temperature furnace with atmosphere control for ferrite research.

were measured at high temperatures and on samples quenched to room temperature. The magnetization of rapidly cooled samples was also measured at room temperature and at temperatures below, down to liquid hydrogen.

From the results, four principle conclusions have been drawn: (1) From the phase boundary and weight gain experiments, one concludes that manganese ferrite of varying oxygen content is stable over a broad range of temperatures and oxygen pressures. This is very similar to the behavior of magnetite, $FeFe_2O_4$ or Fe_3O_4, but in direct contrast to that of nickel ferrite. (2) The lattice defects which are associated with the gain in weight are probably cation vacancies. However, a theory of these changes in stoichiometry, assuming a random distribution of the cations and vacant lattice sites, proves to be inadequate. This leads to the conclusion that ionic ordering still exists, even at the high temperatures investigated (1200-1400°C). (3) From the X-ray line width measurements it is concluded that small regions of the manganese ferrite are distorted tetragonally. The origin of the distortion is suggested as trivalent manganese in the B-sites; Mn^{3+} is the only ion present that is known to have a strong Jahn-Teller effect. (4) It is concluded that the variation of the measured values of the magnetization (Bohr magneton number) is due not only to the firing conditions during soaking, but also to the processes occurring on cooling. This applies even to samples which are rapidly cooled.

The formation of cation vacancies upon oxidation has also been studied extensively on a manganese-zinc ferrite. This process, which has a fair rate at temperatures as low as 400°C, consists of two simultaneous changes: (1) Cations diffuse to the free surfaces of the grains where they bind oxygen from the atmosphere and form new unit cells. (2) Some of the Mn^{2+}- and Fe^{2+}-ions inside the grain lose electrons, i.e., change their valency to Mn^{3+} and Fe^{3+}; this compensates for the lost positive charges of the cations which have migrated to the surface and have left a hole (cation-vacancy) behind. The valence change of Mn and Fe is responsible for a decrease of the lattice constant connected with the oxidation. The macroscopic length changes are exactly equal to the changes of the lattice constant. This proves conclusively that the new unit cells formed under process (1) are added on the free surfaces (pores), and not on the grain boundaries.

THEORETICAL ANALYSIS OF MECHANICAL-THERMAL EFFECTS IN ANISOTROPIC MATERIALS

Ceramic materials containing crystals with large anisotropy of thermal expansion have several unusual properties: very low mechanical strength, elastic modulus, and thermal expansion coefficient at room temperature; increase of these properties up to 1200°C; hysteresis character of all property vs. temperature curves, etc. It is thought that all these features are causally related to the anisotropy in that it produces very large internal stresses in a ceramic material upon departure from the firing temperature, which in turn cause ruptures when the stresses surpass the internal strength. Upon reheating, recombinations of the ruptured grains occur.

The problem of the anisotropy stresses has been treated theoretically, using the Laszlo model as a first approximation and leading to a second approximation (normal-stress model). The result is a frequency distribution of the internal stresses. By choosing one single parameter (namely, the ratio internal strength to internal E-modulus), a close fit of the theoretical curve with the experimental expansion curve can be obtained.

NUCLEATED AND CRYSTALLIZED GLASSES

The mechanism of nucleation and crystallization in glasses has been under study using several approaches to the problem.

1. The internal friction of progressively crystallized lithium silicate glasses reveals the formation of a new relaxation process which is believed to be associated with the initial stages of nuclei formation. This relaxation process leads to a high-temperature peak in the internal friction as measured by the torsion pendulum at the low frequency of 0.4 cycle per second. (Figure 11.) It is revealed long before any evidence of crystallization can be detected by other means, such as X-ray diffraction analysis.

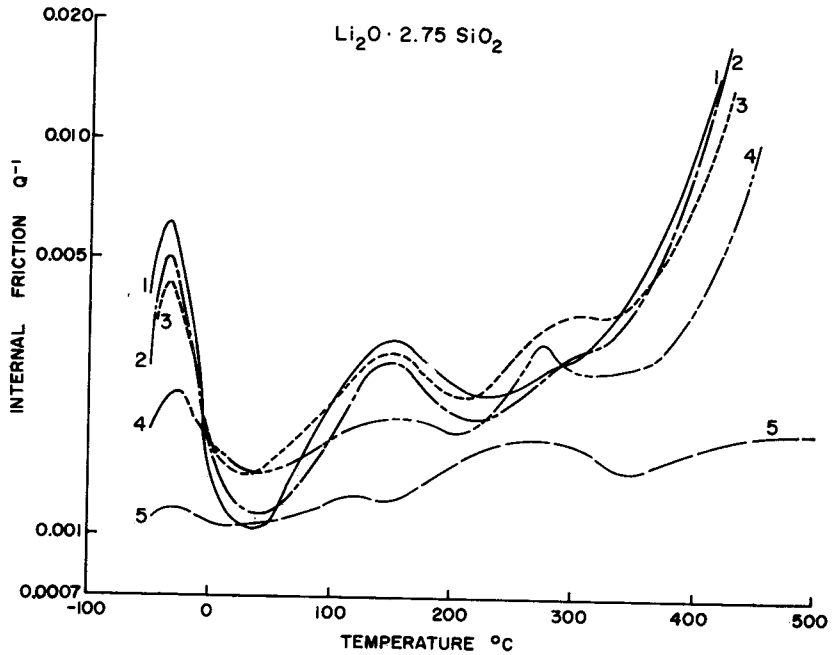
Furthermore, as the glasses become progressively more crystallized, both the low temperature peak (near—30°C) and the intermediate temperature peak (near 150°C) decrease continuously. This indicates that the structural condition in the glass responsible for the low-temperature peak is gradually destroyed as the material becomes more crystalline. In other words, these peaks are characteristic for this composition only in the glassy state. The high temperature peak (near 300°C), however, becomes more pronounced as crystallization progresses.

2. X-ray diffraction studies of the surfaces of progressively crystallized $Li_2O \cdot 4SiO_2$ glasses have been made. A high degree of orientation of the lithium disilicate crystals occurs when no nucleating agent has been added to the glass. The 002 plane of the othorhombic lithium disilicate is always oriented parallel to the surface of the glass. This orientation persists in highly crystallized glasses to the full depth of the sample.

When a nucleating agent such as platinum is introduced, the orientation is completely destroyed at depths as little as 4 microns beneath the surface. This was determined by selectively etching away the surface with HF and X-raying the new surface. With amounts of platinum as small as 0.010 per cent, orientation at the original surface is virtually eliminated. The effectiveness of platinum nuclei in destroying orientation may be attributed in part to the similarity of the 111 plane of the cubic platinum crystal and the 002 plane of lithium disilicate. The random distribution of the platinum nuclei thus become sites for the precipitation of lithium disilicate crystals.

3. Infrared measurements in the region 2 to 25 microns, of the nucleated and progressively crystallized glasses, are being made to

Fig. 11—Internal friction curves for lithium silicate glass fibers recrystallized to various extents.



GLASS	PER CENT CRYSTALLIZED
1	NONE
2	14
3	29
4	55
5	78

VARIATION OF Q^{-1} WITH CRYSTAL CONTENT

follow the structural changes occurring during crystallization. The few relatively broad bands in the glass are gradually changed to sharp bands as crystallization increases, and new adsorption bands appear. It appears that crystallization can be detected by infrared spectra at considerably earlier stages than is possible by X-rays.

SINTERING OF MAGNESIUM OXIDE POWERS

Various mechanisms have been suggested by which finely powdered materials can be sintered into coherent solids, that is to say, the particles join together without melting occurring. Herring showed theoretically that, from measurements of the shrinkage at constant temperature of a powder compact containing particles of essentially one size only, it might be possible to distinguish between four possible sintering mechanisms. An attempt has been made to apply these ideas to magnesium oxide compacts made of three different particle size fractions when fired at temperatures between 1150 and 1700°C. The results are still not wholly conclusive, but at present they point towards surface migration of atoms as the most probable sintering mechanism for this particular oxide.

SURFACE STRUCTURE OF GLASSES

The glass industry has an increasing need for a better understanding of the surface structure of glasses, because this surface structure determines the mechanical performance of the shaped product and the chemical reactivity of the hot glass with vapors, liquids, and solids. Changes in the surface properties of glass as a result of its contact with molding materials and refractories are recognized as important from a practical viewpoint, but the theoretical aspects are not fully understood.

For these reasons the Glass Container Industry Research Corporation has established a research contract with The Pennsylvania State University to aid in research work designed to provide a better understanding of the phenomena. Owens-Illinois has established a post-doctoral fellowship with the aim of studying the low- and high-temperature surface chemistry of glass. Particular subjects of study will be the interaction and rate phenomena of reactions between glasses and other solids, liquids, and gases, and an evaluation of the response of solids in high-frequency fields to their structures.

Also, in order to give the proper theoretical explanation for the phenomena, a new concept for the structure nucleation, and conditions of glass formation is being developed.

The laboratory is equipped with a high-frequency induction furnace, and a unit for dielectric heating with ultra high-frequencies

recently designed for this research and built by Sherman Industrial Electronics Company, Inc.

In addition, the laboratory has a horizontal temperature-gradient furnace, a vertical tubular Globar furnace, and a strip furnace with binocular microscope attachment.

THE EXPERIMENT STATION

The Mineral Industries Experiment Station provides contract administration and accounting facilities, machine shop, thin section laboratory, printing and reproduction, photographic and drafting shop, carpenter shop, and stockroom facilities, for carrying on the research program in the College of Mineral Industries. In addition, it provides a common central laboratory containing the more expensive and sophisticated analytical techniques required in a research program of this magnitude on minerals and materials. These facilities are called the Mineral Constitution Laboratories and comprise wet chemical analysis, emission and absorption spectroscopy in the visual and infrared regions, X-ray powder diffraction, X-ray fluorescent spectroscopy, X-ray single crystal analysis, electron microscopy and diffraction, and mass spectrometric analysis of gases. The Mineral Constitution Laboratories have been operated for about five years as a full-scale experiment to determine whether expensive and complicated techniques can be operated better as a central facility available to all on a rental basis, rather than as separate activities attached to individual departments. These laboratories have been outstandingly successful, although many administrative problems have been revealed through their operation, mainly concerning non-uniformity of use and difficulty in financing. It is believed that they can be solved with consequent benefit to the whole research program, making techniques available which would not otherwise be within the reach of small departments.

The Experiment Station, in addition to the activities already listed, conducts a University-supported program of research in the conservation of Pennsylvania mineral resources (the Mineral Conservation Section) and a program of research supported by the Pennsylvania Coal Research Board on development of new uses for anthracite and bituminous coal (Coal Research Section).

MINERAL CONSERVATION SECTION

During the 1959-1961 biennium the Mineral Conservation Section supported an expanded program of research aimed at the development of mineral resources in Pennsylvania, and at improved methods of extraction and utilization of mineral products. Currently active

research projects are listed below, and many are summarized in previous pages under departmental headings.

Bulletin 73, published in December 1959, comprises Part 1 of an *Atlas of Pennsylvania Coal and Coal Mining* and deals with the bituminous coal fields, the composition and heat value of the coal, and the employment, mining, and marketing factors of the bituminous coal mining industry.

The following projects, with the department indicated in parenthesis, are being actively pursued as part of the program of the Mineral Conservation Section:

Historical Statistics of Pennsylvania's Mineral Industries (Mineral Economics).
Mineralogy and Properties of Pennsylvania Clays and Shales (Ceramic Technology).
Beneficiation of White Clays (Mineral Preparation).
Beneficiation of Ganister for Refractory Brick (Mineral Preparation).
Composition of Limestones and Dolomites (Geology).
Atlas of Pennsylvania Coal and Coal Mining—Anthracite (Geography).
Bituminous Coal Distribution Costs (Mineral Economics).
Geology and Copper Deposits of the South Mountain Area (Mineralogy).
Beneficiation of Iron Ores (Mineral Preparation).
Improved Methods of Strip Mining (Mining).
Exploitation of Thin Seams in Pennsylvania (Mining).
Fracture Trace Patterns in Sedimentary Rocks of Centre County (Geology).
Electrodeposition of Manganese (Metallurgy).
Geophysical Investigations of Iron Ore Deposits (Geophysics & Geochemistry).
Hydraulic Backfilling in Anthracite Mining (Mining).
Activated Carbon Market Survey (Mineral Economics).
Specifications for Mineral Products (Mineral Economics).
Placer Chromite Deposits of Southeastern Pennsylvania (Geology).
Petrography of Catskill Sediments (Mineralogy).
Beneficiation of High-Alumina Clays (Mineral Preparation).
Serpentine and Chromite Deposits in Pennsylvania (Geology).
Beneficiation of Chromite (Mineral Preparation).

MINERAL CONSTITUTION LABORATORIES

ELECTRON MICROSCOPY AND DIFFRACTION

Various departments are currently using the electron microscope and diffraction facilities in the study of clays, gels, shales, electro-

deposited metals, and other materials. Much of the work involves the study of microstructure in solids, where the surface features observed can often be related to the structure of the bulk material, and where the size, shape, and orientation of impurities or extraneous phases can be determined. Electron diffraction is often used in conjunction with such studies to identify secondary phases or impurities, and to determine the orientation of crystals.

Recent electron microscope studies of fired kaolinites show that the mullite phase developed from large, well-crystallized kaolinites is oriented preferentially with respect to the original crystal. This orientation was observed only occasionally on poorly-crystallized kaolinites. Further studies are being made to determine what conditions are necessary for this orientation to prevail in the fired specimen. Other phases of this study showed that mullite from fired kaolinite or halloysites can form with a preferred orientation related to the structure of the platinum foil upon which they are heated. Studies are under way to determine the orientation of the mullite on the crystal lattice of the platinum using X-ray and electron diffraction methods.

The effect of impurities on crystal growth and properties of crystals is of great importance. Methods are being investigated for an evaluation of the effects of impurities on crystals such as $(NH_4)H_2PO_4$ grown from solution. Using the replica technique to study fracture surfaces, it has been possible to detect unique structures for each of the three types of impurities studied to date. These include cations and anions which are adsorbed by the growing crystals, and clay particles which are occluded in part, and which also react with the solution to release aluminum ions, which are in turn adsorbed by the crystal.

These problems require the development of new techniques for preparing and examining samples by electron microscopy which can ultimately be used on other specimens as well. Work has been started on a scheme for using thin nuclear emulsions together with surface replicas for locating radioactive areas in a solid. In the study of $(NH_4)H_2PO_4$, for example, radioactive cations could be added to the solutions from which the crystals are grown and points of adsorption on the crystal faces could be detected. The replica would show the effect of the adsorbed impurity on the growth pattern.

ANALYTICAL SECTION

The Analytical Laboratory is well equipped to handle many types of samples and fills a need for accurate analyses of various materials under study in the exploration and evaluation of mineral deposits. A continuous program of research into methods of analysis is maintained.

New methods must frequently be devised to meet the requirements of researchers who need analytical data in their work.

The Analytical Section works closely with the X-ray and Spectrography Sections, providing them with accurately analyzed samples for standardization; in return, invaluable help with various analytical problems is provided.

A special flame spectrophotometer has recently been put into operation for the determination of lithium, sodium, potassium, rubidium, and cesium. With this equipment the alkali metals can be rapidly determined using very small samples.

The role of classical methods for the analysis of materials has changed greatly in recent years, for with the perfection of various physical methods, routine work is handled to an increasing extent by the new instrumentation. Accordingly, the emphasis in the Analytical Laboratory is on analyses of the highest possible accuracy, the results being often used for the standardization of more rapid physical techniques. New equipment of first-line quality has been acquired and is being used to advantage in this connection.

The facilities of the Analytical Laboratory are available to staff and students engaged in research, providing them with the best possible analytical data for application to their many problems.

X-RAY SECTION

The X-ray Section is equipped with six modern-type diffractometers. Four of these are used to facilitate the identification of the phases formed by nature or by controlled treatments which may vary any combination of the variables of time, temperature, pressure, and composition. Two of these modern instruments are equipped to do X-ray fluorescence analysis which is a physical method of obtaining a chemical analysis. The speed of analysis which is possible with this method opens up a new era of analysis in which thousands of samples can be studied. It is most advantageous to use this fluorescence method when many samples have to be analyzed since it is a comparative method and the necessary calibration curve is usually the most time-consuming part of the whole operation. When possible, it is desirable to work in connection with the Analytical Section to obtain the true chemical analyses in order to prepare the calibration curve.

Several computer programs have been written for PENNSTAC, a modern digital computer, to aid in the interpretation of the diffraction patterns in terms of the lattice spacings and integrated intensities.

A rotating single crystal camera and a Weissenberg camera are available for the intensive study of crystal structures.

High-temperature furnaces are available for special studies of thermal inversions or thermal expansion by X-rays. An automatic balanced filter is available for studies which require monochromatic radiation. An automatic sample changer is available for use with the fluorescence equipment to make possible the analysis of 100 samples for one element. Further automation is being considered to analyze for several elements sequentially.

SPECTROSCOPY SECTION

The Spectroscopy Section is fully equipped for both emission and absorption spectroscopy. Over the last two years, improved equipment has greatly extended the capabilities of the laboratories. A new source unit, a new comparator-microphotometer, and a new arc-spark stand have been installed in the emission laboratory. In the absorption laboratory, potassium bromide optics have been obtained for the

Shown below is the new comparator-microphotometer. The viewing screen is a projection of a master plate, used for identification, and of the unknown plate. By means of a slit of light that scans the analytical line and a detector, the intensity is obtained, thus allowing the quantitative determination of elements.

infrared spectrophotometer. The new optics permits work in the 15-25 micron region, an extension of the previous 2-15 micron range.

The use of controlled atmospheres (carbon dioxide and argon-oxygen mixtures, for example) has greatly improved the precision and accuracy of emission spectroscopy, without adversely affecting the sensitivity. Trace elements, as well as the major constituents, in various rocks, minerals and ceramic materials, have been successfully determined by this means. In many instances, the precision and accuracy is $\pm$ 2-5 per cent of the amount present.

Infrared spectroscopy is becoming increasingly useful in inorganic chemistry, and is currently being used by members of the Geophysics and Geochemistry and Ceramic Technology Departments in identifying compounds and investigating bonding in synthetic and naturally occurring substances. It is anticipated that research will continue in this comparatively new field.

COAL RESEARCH SECTION

The Coal Research Section, a subdivision of the Mineral Industries Experiment Station, serves to stimulate activity in new areas of coal research, to implement negotiations with research-sponsoring agencies, and to expedite investigations once they are undertaken. Exchange of ideas and information among investigators in the various departments of the College is effected through Section-sponsored meetings and other avenues of contact.

The Pennsylvania State University is the logical place for the development of a major center for research on coal and coal products. Its strategic location within the Appalachian coal fields facilitates investigations on virtually all types of coal from peat to anthracite, a situation which is not readily duplicated in any of the other coal-producing areas of this country. This, combined with the facilities of the College of Mineral Industries, would appear to insure the success of a diverse program of research focused on this important energy source.

Ten new research projects have been instituted under the auspices of the Coal Research Board of the Commonwealth of Pennsylvania. There are now a total of twenty-seven investigations being conducted. The projects are carried out as a part of the Section's program by faculty and staff members in the departments of Fuel Technology, Geology, Geophysics and Geochemistry, and Mineral Preparation. Results of considerable significance have already been obtained in several of the programs.

More than twenty Special Research Reports have been submitted to the Coal Research Board of the Commonwealth. These reports

contain in detail the results obtained on a variety of subjects ranging from the radiation chemistry of coal to the grindability of anthracite.

The following is a list of the titles of projects active during this biennium:

RESEARCH ON ANTHRACITE

The Production of Metallurgical Coke from Blends of Anthracite and Bituminous Coal
The Grindability of Anthracite
The Mineral Constituents of Anthracite and Their Relationships to the Chemical Characteristics of Ash
Investigation of the Chemical Nature, Physical Structure, and Distribution of Ash in Anthracite
The Behavior of Petrographically Distinct Anthracite Particles Under Thermal Stress
The Mechanism of the Thermal Decrepitation of Anthracite
Effect of Radiation on the Physical and Chemical Properties of Anthracite
Reaction of Anthracite with Atomic Species
Physical Structure of Anthracites as Affected by Heat Treatment, Oxidation, and Grinding
Use of Anthracite as a Molecular Sieve Material
Factors Affecting Ignition and Burning Rates of Pulverized Fuels, Especially Pennsylvania Anthracites
Streaming Potential Studies of Petrographically Distinct Anthracite Particles for Increasing the Technological Applications and Markets of Anthracite
Studies of Solid State Reactions of Anthracite Coals Subjected to Super Pressures at Moderate Temperatures
To Determine Characteristics of Extremely Fine Anthracite Particles Looking to Increase Markets for a Size that Is Now a Waste Product

RESEARCH ON BITUMINOUS COAL

Correlation of Laboratory Tests of Ignitability, Reactivity, Plasticity, etc. of Pennsylvania's Bituminous Coals with Combustion Performance
Production of Chemicals from Bituminous Coals by the Use of Prehydrogenated Aromatic Fractions
Reaction of Bituminous Coals with Concentrated Surfuric Acid
The Reduction of Sulfur in Coal During Carbonization
Effect of Radiation on the Physical and Chemical Properties of Bituminous Coal and Coal By-Products

The Petrography of the Mineable Bituminous Coals of Pennsylvania and the Mode of Sulfur Occurrence
Preparation of Highly Porous Carbons from Humic Acids Derived from Nitric Acid Treatment of Bituminous Coal
Identification of Basic Chemical Constituents of Pennsylvania Bituminous Coals with the Mass Spectrometer
Factors Affecting Flames of Powdered Fuels, in Particular Pennsylvania Bituminous Coals
Fuel Cell Study
Reaction of Pennsylvania Bituminous Coal with Atomic Species
Reduction of Sulfur in Pennsylvania Bituminous Coals During Preparation
Chemical Structure and Physical Properties of the Macerals of Pennsylvania High, Medium, and Low Volatile Bituminous Coal in Relation to Coal Utilization

PENNSYLVANIA'S COLLEGE OF MINERAL INDUSTRIES

Dedicated to education and research in mineral conservation by which the means may be found to make conservation effective. This includes diligent search for mineral truths and the energetic discovery, maximum recovery, and complete utilization of irreplaceable mineral resources.

FIELDS OF WORK

Earth Sciences: Geology, Mineralogy, Geophysics, Geochemistry, Meteorology, and Geography.
Mineral Engineering: Mineral Economics, Mining, Mineral Preparation, and Petroleum and Natural Gas.
Mineral Technology: Fuel Technology, Metallurgy, and Ceramic Technology.
Solid State Technology: An Interdisciplinary Program in Instruction and Research on Solid Materials.

DIVISIONS OF SERVICE

RESIDENT INSTRUCTION — RESEARCH
EXTENSION AND CORRESPONDENCE INSTRUCTION

RESEARCH: A FUNCTION OF THE UNIVERSITY

The foundations of The Pennsylvania State University are the Morrill Land-Grant Act of Congress signed by Lincoln in 1862 and the 1863 Act of the Pennsylvania Legislature implementing the federal legislation and designating this institution as the instrument of the Commonwealth in carrying out the terms of the federal act.

The spirit of research which permeates the University is in keeping with the purposes of the Land-Grant Act in bringing the methods and procedures of modern science into relation with the agricultural and industrial pursuits of the nation.

The mineral resources of Pennsylvania have always dominated its economy. The advanced stage of their development has brought problems that must be solved if the Commonwealth is to retain her position of economic leadership. In the solution of these problems another resource, scientific and technologic research, is necessary. One of the important functions of Pennsylvania's College of Mineral Industries and Experiment Station is to develop this great resource—research—by educating leaders in technology through graduate instruction and by aiding in the solution of technical problems.

PUBLICATIONS OF THE MINERAL INDUSTRIES EXPERIMENT STATION

Research results of the Experiment Station are disseminated through the following publications: (1) bulletins which present reports of original research; (2) circulars which present reviews of work in the College of Mineral Industries or elsewhere in nontechnical language, reports of certain meetings, and general information; (3) contributions to various technical journals by individual staff members, usually available from the Experiment Station in reprint form.

BULLETINS

Bulletin 72 Proceedings of the Ninth Annual Drilling Symposium. Theme: Exploration Drilling. October 8-10, 1959. Edited by H. L. Hartman. 1960. *Price $3.00.*

Bulletin 73 Atlas of Pennsylvania Coal and Coal Mining: Part I, Bituminous Coal by George F. Deasy and Phyllis R. Griess. 1959. *Price $1.00.*

Bulletin 74 The Use and Interchangeability of Fuels in Pennsylvania by W. Gibson Jaworek and John J. Schanz. 1961. *Price $1.00.*

CIRCULARS

Circular 55 Mass Spectroscopic Analysis of Solids Abstracts for the Years 1953-1956. Edited by L. F. Herzog, II. 1959. *Price 50¢.*

Circular 56 Proceedings of the Twenty-first Technical Conference on Petroleum Production, August 24-26, 1959. *Price $2.50.*

Circular 57 Publications of College of Mineral Industries of The Pennsylvania State University, University Park, Pa., July 1, 1958 to June 30, 1959. *Free.*

Circular 58 Publications of College of Mineral Industries of The Pennsylvania State University, University Park, Pa., July 1, 1959 to June 30, 1960. *Free.*

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