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Industrial Minerals and Rocks

(Nonmetallics other than Fuels)

Fifth Edition
Volume 1

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The term clay is somewhat ambiguous unless specifically defined, because it is used in three ways: (1) as a diverse group of fine-grained minerals, (2) as a rock term, and (3) as a particle-size term. Actually, most persons using the term clay realize that it has several meanings, and in most instances they define it. As a rock term, clay is difficult to define because of the wide variety of materials that compose it; therefore, the definition must be general. Clay is a natural earthy, fine-grained material composed largely of a group of crystalline minerals known as the clay minerals. These minerals are hydrous silicates composed mainly of silica, alumina, and water. Several of these minerals also contain appreciable quantities of iron, alkalies, and alkaline earths. Many definitions state that a clay is plastic when wet. Most clay materials do have this property, but some clays are not plastic; for example, halloysite and flint clay.

As a particle-size term, clay is used for the category that includes the smallest particles. The maximum-size particles in the clay-size grade are defined differently on various grade scales. Soil investigators and mineralogists generally use 2 micrometers as the maximum size, whereas the widely used scale by Wentworth (1922) defines clay as material finer than approximately 4 micrometers.

Some authorities find it convenient to use the term clay for any fine-grained, natural, earthy, argillaceous material (Grim, 1968). When used this way, the term includes clay, shale, or argillite, and some argillaceous soils.

Even though no standard definition of the term clay is accepted by geologists, agronomists, engineers, and others, the term is generally understood by those who use it. Clay is an abundant natural raw material, and it has an amazing variety of uses and properties which will be discussed in this chapter.

Clays rank among the leading industrial minerals in both tonnages produced and total value. Their importance is indicated in Table 1, which lists the 1978, 1979, and 1980 production and values according to the US Bureau of Mines (Ampian, 1980).

Statistical data summarizing world production of kaolin, bentonite, and fuller's earth are compiled by the US Bureau of Mines (Ampian and Polk, 1981). The total world bentonite production in 1980 was 6,625,264 st, of which the United States produced 4,184,619 st. The total fuller's earth produced in the world in 1980 was 1,952,600 st, of which 1,534,000 st was produced in the United States. The total world kaolin production in 1980 was estimated at 22,971,000 st. Approximately 13 million tons of this total was produced in two countries, the United States and the United Kingdom. World production data on ball clay, fire clay, and miscellaneous clays are not available.

As industrial minerals, clays are a complex group that consists of several mineral commodities, each having somewhat different mineralogy, geologic occurrence, technology, and uses. In this chapter these commodities are organized as follows: (1) bentonite and fuller's earth; (2) kaolin, ball clay, halloysite, and refractory clays; and (3) miscellaneous clay and shale. Bentonite and fuller's earth are grouped together because they are closely interrelated. Though bentonite is a term based on mineral composition and fuller's earth is a term based on use, the two are virtually inseparable, because much, but by no means all, clay sold as
fuller's earth is actually bentonite. The overlapping of the two terms is particularly evident where both bentonite and nonbentonite fuller's earth are used for the same purposes or products, such as in drilling muds, bleaching or clarifying fats and oils, and carriers for insecticides and fertilizers. Kaolin, ball clay, halloysite, and bentonite and nonbentonite fuller's earth are grouped together because they consist mainly of minerals of the kaolin group. Miscellaneous clay and shale is the final major type referred to as common clay in some publications, such as in drilling muds, bleaching or clarifying fats and oils, and carriers for insecticides and fertilizers. Such a grouping of several fine-grained materials of the type referred to as common clay in some publications is the principal source of the vast amount of new information on the mineralogy, geology, and technology of clays that has become available in recent years. One of the principal sources is The Clay Minerals Society, which has organized a professional and scientific society that has published its own journal, Clay Minerals, since 1965. This professional and scientific society was organized in 1963 from an informal group of clay mineralogists that met in 1962 to present papers at the First National Clay Conference in Washington, D.C. The society is an affiliated society of the Mineralogical Society of America and the Geological Society of America.

The scientific and technological publications pertaining to clays are so numerous that to cover all the material in the format used for other chapters would require a book. Therefore, the authors have attempted to summarize the subject matter and wherever possible have indicated by bibliographic reference where more detailed information is available. For example, the reference to Bicker (1970) is to a bulletin containing only brief summary information on the economic geology of bentonite in Mississippi, but that bulletin contains references to virtually all published reports on bentonite in that state.

The remaining parts of this introduction will be mainly an outline of some of the major advancements in the broad field of clays since the 4th edition of *Industrial Minerals and Rocks* (Patterson and Murray, 1975) and acknowledgment to those who have helped in preparing this chapter. Our intent is to note where some of the contributions, mainly in clay mineralogy, have been made, so that those who are interested can find detailed information not included in this report.

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Definitions and Classifications

The term bentonite was first proposed in 1898 by Knight (1898), a year after he had named this clay taylorite; taylorite was found to be diagenetic. Another recent volume by Weaver and Pollard (1973) contains information on the chemistry of clays, including oxide data and structural formulae.

A great deal of information on the geology, technology, and uses of clay has also been published by various provincial, state, and federal geological surveys, bureaus of mines, and other agencies. Most of these organizations and some of the major reports are listed by Hoy in Part 3 of Volume I and will not be repeated here; however, reference to some of the more important articles will be made in discussions in the following sections of this chapter.

Many changes have taken place in the various clay industries in recent years. Several of these have come about because of technological advancements, changing economic conditions, new uses, shifts in demand, and increases in both domestic and export markets. The changing conditions, particularly increasing freight rates, the energy crisis, other production and marketing costs, and the pressures brought about by governmental controls and mining laws resulting from requirements and restrictions related to environmental considerations, have motivated the formation of organizations to look after the interests of some of the clay-producing industries. One of these organizations formed recently is the Absorbent Minerals Institute, having headquarters at No. 1 Illinois Center, 111 E. Wacker Drive, Chicago, IL 60601. This institute was formed mainly to represent the producers of absorbent granules and other fuller's earth products. A similar organization, the Bentonite Producers Association, was organized in 1971 in Casper, WY, and represents the interests of the producers of bentonite. The kaolin industry organized the US Clay Producers Traffic Association which was incorporated in 1953 in New Jersey. In addition to these organizations dealing specifically with clays, the clay industry and other mining industries formed mining associations in many states, including Georgia and Texas in 1972, in order to protect their interests against restrictive state and federal legislation.

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usually a tuff or volcanic ash; and it often contains variable proportions of accessory crystal grains that were originally phenocrysts in the volcanic glass. These are feldspar (commonly orthoclase and oligoclase), biotite, quartz, pyroxenes, zircon and various other minerals typical of volcanic rocks. The characteristic clay-like mineral has a micaeous habit and facile cleavage, high birefringence and a texture inherited from volcanic tuff or ash, and it is usually the mineral montmorillonite, but less often beidellite.

The difficulty in applying the foregoing definition to bentonite as an industrial mineral commodity is that it is based on origin and is restrictive to an ash, tuff, or volcanic glass parent material. Therefore, bedded deposits consisting of the clay minerals required by this definition but having uncertain origin or parent materials cannot properly be called bentonite. Furthermore, many deposits in the western United States and in other countries that have formed from rocks other than the types required by the definition are being mined and sold as bentonite.

Perhaps the best definition of bentonite as an industrial mineral is one given by R. E. Grim in a plenary lecture at the International Clay Conference (AIPFA) at Madrid, Spain, June 27, 1972. According to this redefinition, which will be used in this chapter, bentonite is a clay consisting essentially of smectite minerals (montmorillonite group of some usages), regardless of origin or occurrence. This definition solves the problem of the difference between the geologic and industrial usages of the term and overcomes the difficulty in assigning a name to smectite clay that formed from igneous rock other than ash, tuff, or glass, or those of sedimentary or uncertain origin. However, bentonite, when used with this meaning is still a rock term (consisting of more than one mineral), and it will not be possible to distinguish it from fuller's earth in many instances.

One way of classifying bentonite is based on its swelling capacities when wet or added to water. Bentonite having sodium (Na⁺) as either the dominant or as an abundant exchangeable ion typically has very high swelling capacities and forms gel-like masses when added to water. Bentonite in which exchangeable calcium (Ca²⁺) is more abundant than other ions has much lower swelling capacities than sodium varieties. Some calcium types swell little more than common clay, and most crumble into granular masses in water. Intermediate calcium-sodium bentonites, the so-called mixed types, tend to swell moderately and to form gel of lesser volumes than equal masses of the sodium type. Bentonite, because of the general relationship of swelling and exchangeable ion characteristics, is commonly divided into the high-swelling or sodium, low-swelling or calcium, and moderate-swelling or intermediate types. The term sub-bentonite (Davis, Vacher, and Conley, 1940) is used inconsistently in industry for the low or moderate-swelling varieties. The authors believe the use of this term should be discouraged because of its implication of a low quality or low value and the lack of a mineralogical or use basis for it.

In the United States bentonite is also classified by geographic location and the uses for which it is sold. Inasmuch as most of the low-swelling calcium type occurs in states bordering the Gulf of Mexico, this variety is commonly called Southern bentonite. The largest high-swelling sodium bentonite deposits and the major producing districts are in Wyoming and adjacent states. Therefore, this bentonite is commonly called Wyoming or Western type. Such terms as dril ling mud bentonite, foundry bond bentonite, and tatonite bond bentonite relating directly to use are applied in marketing. Other terms including high and low-yield bentonite, high and low-gel bentonite, and high and low-strength bentonite are also used to distinguish different grades.

The varied classifications notwithstanding, bentonite occurs in so many different varieties that some cannot logically be classified according to any of the foregoing groupings. One of these types is hectorite, which is a high-swelling lithium-bearing variety of smectite occurring mainly in California and adjacent states. It is, therefore, not a Wyoming type, and it occurs even farther west than the so-called western bentonites. Others are bentonites having magnesium (Mg²⁺) or hydrogen (H⁺) as the most abundant or dominant exchangeable ion. These types are neither sodium nor calcium varieties, and apparently some are low swelling, whereas others have rather high-swelling capacities.

Still another type of bentonite, the so-called potassium type, K-bentonite, or metabentonite, occurs in Ordovician and other Paleozoic rocks at many places in Appalachian and Mississippi Valley regions and elsewhere. This bentonite, which is generally thought to have formed from volcanic ash, consists mainly of illite and mixed-layer minerals. Smectite minerals are ordinarily present in only minor quantities. Because of its mineral composition, this bentonite contains appreciably more potassium than most other types.
The meta prefix originates from the idea that this bentonite was altered by low-grade metamorphism or diagenesis. Apparently, the only attempt to use K-bentonite in the United States was when five or six carloads were mined near Dayton, Rhea County, TN, about 1928; this bentonite was used for purifying lard (Gildersleeve, 1946), and no further mention of this type will be made.

The term fuller's earth is more or less a catchall for clay or other fine-grained earthy material suitable for bleaching and absorbent and certain other uses. It has no compositional or mineralogical meaning. The origin of the term dates back into antiquity; it was first applied to material used in cleansing and fulling wool, thereby removing the lanolin and dirt from it. When in the latter half of the last century it was found that some earths used for fulling would also serve in decolorizing and purifying mineral, vegetable, and animal oils, the term fuller's earth was modified to include this usage.

Extensive use of fuller's earth in processing mineral oils in the first half of this century and the virtual end of its use in fulling fiber led to the general application of the term, fuller's earth, as meaning primarily earth used in petroleum processing. Further modification of the meaning came about as other uses developed for the earth and replaced oil processing as the major use. The term fuller's earth is retained, however, for fine-grained materials used for many purposes. Most of these uses require absorbent properties—in one form or another, but the properties required for some uses, such as certain drilling muds and fillers, are other than absorbency and, therefore, result in further modification of the term.

The classification and understanding of fuller's earth are also complicated by several terms having more or less duplicate or overlapping meanings. When applied in the oil-processing sense, fuller's earth has the same meaning as naturally active clay. Fuller's earth and other clays which are treated with acid or otherwise altered to improve their desirable properties are called activated clay (Torok and Thompson, 1972). The terms bleaching clay and bleaching earth are applied mainly to both naturally active and activated clay, but they also include activated bauxite (Rich, 1960). Both naturally active and activated clays are included under the term absorbent clays (Nutting, 1943); therefore, this term has nearly the same meaning as bleaching clay. The term absorbent clay is applied to fuller's earth used for a wide variety of absorbing purposes which are different from that of processing oils.

History and Use

Bentonite: Bentonite mining began on the Taylor ranch near Rock River, WY, in 1888. This bentonite reportedly was shipped crude to Philadelphia where it sold for $25 a ton and was used in making cosmetics. A mine was opened in the Upton, WY, district on the western side of the Black Hills in 1903. The early method of drying was to rake the bentonite by hand over steel plates heated by wood or coal fires.

The date of the first mining of southern bentonite is somewhat conjectural because of the confusion between the terms bentonite and fuller's earth. One fuller's earth deposit near Gonzales, Texas, that is almost certainly bentonite was mined as early as 1906, and another deposit in that same state mined during the Civil War (Lang et al., 1940) may also have been bentonite. Large-scale mining of calcium-type bentonite began in Mississippi in the early 1930s (Bicker, 1970), and bentonite deposits were used as fuller's earth in several states about this time.

The value of bentonite as foundry-sand bond was recognized in the 1920s, and the iron and steel foundries have since been major consumers of bentonite. Bentonite was first used as drilling mud in the late 1920s or early 1930s, and bentonite is still one of the most efficient materials for drilling muds where the rocks penetrated contain only fresh water. The high-swelling Wyoming bentonite is the most efficient type for drilling mud, but the high-viscosity properties of hectorite make it useful in muds (Larsen, 1955). Some Texas bentonite is also used for drilling muds, particularly in shallow wells, and commonly it is treated with soda ash, polymers, or other chemicals to make it suitable for this use. Low-quality bentonite when sold for use in drilling mud is commonly classified merely as clay rather than bentonite (Anon., 1972d).

Bentonite production remained small during the first few decades of mining, and the first yearly total sufficiently large to be separated from miscellaneous clays in the US Bureau of Mines statistics was in 1930 when production was only a few thousand tons. Demands for bentonite increased during World War II, but a yearly total of 1 million tons was not reached until 1950. More than 2 million tons was produced in 1966, and the peak production year to date was 1978, when 4,467,605 tons were sold or used by producers. Bleaching clay (oil
refining, filtering, clarifying, and decolorizing), drilling mud, iron-ore pelletizing, and foundry-sand bonding have been the major uses of bentonite since World War II (Fig. 1). Beginning about 1950, steel companies used Wyoming-type bentonite as a bond for pelletized taconite ore. This use grew rapidly, and in recent years approximately one-third of the national production has been used for this purpose.

In addition to the major uses, bentonite is used in many miscellaneous products, and hundreds of patents for speciality uses have been issued or applied for. The speciality uses include filtering agents (one of which is a high-value product for clarifying wine, and another is a less costly one for treating waste water), water impedance (preventing seepage loss from reservoirs, irrigation ditches, and waste-disposal ponds, and seepage through basement walls, tunnel walls, and other structures), ingredients in cosmetics, animal feed, pharmaceuticals, colloidal fillers for certain types of paints, an additive to ceramic raw materials to increase plasticity, fire-retarding materials, and for many other purposes (Papin, 1964). The white bentonites occurring in Texas and Nevada and imported from Italy are particularly suitable for many of the speciality products, and a great deal of research evaluating them for many uses has been done. One of the unique uses of high-swelling bentonite that is likely to increase is in the "slurry trench" or "diaphragm wall" method of excavation in construction areas of unconsolidated rock or soil (Blackman, 1969; Lang, 1971). In this method, the trench or hole being excavated is filled with bentonite slurry and the earth being excavated is removed through it. A thin filter cake on the walls of the excavation prevents loss of fluid, and the hydrostatic head of the slurry prevents caving and running of loose soils, which makes costly shoring unnecessary. Considerable quantities of bentonite were once used in making catalysts for petroleum re-

FIG. 1—Bentonite sold or used by domestic producers for specified uses (Ampian, 1980, 1983).
Clays

Fuller’s Earth: Published reports give rather confusing accounts of the discovery of fuller’s earth in the United States. Several states that fuller’s earth was discovered in this country in 1893 near Quincy, FL, by the Owl Commercial Co. (predecessor of the present makers of White Owl Cigars) during an attempt to burn brick from clays on tobacco property. The clay was not suitable for making brick, but an Alsatian immigrant employed as a farm worker recognized that it was similar to fuller’s earth mined in Germany. His observation led to development of the first mine near Quincy two years later and to the use of this clay in processing mineral oils. Fuller’s earth had been mined on a small scale, however, in Arkansas in 1891 (Meyer, 1913), and tested for use in the refining of cottonseed oil.

Both of these reported discoveries are related to the use of fuller’s earth in processing oils and fail to note its earlier use for other purposes. Clays and other earthy materials were undoubtedly used by the early settlers from Europe in cleansing wool and other materials. Little effort was made to search the historical records and to document this, but it was found that soldiers stationed near Perth Amboy, NJ, used Woodbridge fire clay for cleansing buckskins during the Revolutionary War (Cook and Smock, 1878). Fuller’s earth associated with an iron-ore bed near Kent, CT, had been mined in the early 1800s (Silliman, 1820), and fuller’s earth near Falls City, Texas, had been used to bleach sugar during the Civil War (Lang et al., 1940). Also, American Indians were reported to have used bentonite in cleansing blankets, and they probably dug it for other cleansing purposes before the Columbian period.

The use of fuller’s earth in the refining of oils continued to be the major one for many years. The demand for fuller’s earth for processing mineral oil increased rapidly in the first part of this century and reached a peak of approximately 517,000 tons in 1930; this was 91.1% of the total United States production that year. The production of fuller’s earth for this purpose began to decrease thereafter, especially when activated bauxite was introduced in 1937 and magnesium silicate in 1940 as more efficient substitutes. The market for this use was also depressed by improvements in refining methods, which produce oils requiring little purification or bleaching. In recent years, the production of fuller’s earth for use in refining mineral oils has maintained a rather uniform rate of 35,000 to 40,000 tpy. The use of fuller’s earth in processing animal and vegetable oils has never been a major one and has decreased to the point where it is included as a part of the miscellaneous uses in the US Bureau of Mines Minerals Yearbooks.

Palygorskite (attapulgite) fuller’s earth was first sold for drilling mud in 1941. The market for this use expanded slowly and has maintained a level of 7 to 10% of the total United States production during the last few years. Most of the fuller’s earth sold for drilling mud comes from the southern part of the Meigs-Attapulgus-Quincy district of Georgia and Florida. Palygorskite clays produced in this area are superior to most other fuller’s earth for muds used in drilling salt formations, but because of high water loss, they are inferior to bentonite where the rocks drilled contain no saltwater.

Fuller’s earth was used in significant quantities as a carrier for insecticides and fungicides by 1950, and the market for this use has grown at a rather uniform rate since that year. In 1979, nearly 14% of the fuller’s earth produced was used for this purpose.

The use of fuller’s earth granules for absorbent purposes began during the 1930s, but this use did not expand significantly until the World War II period when fuller’s earth was used as an absorbent for greases, oil, water, chemicals, and other undesirable substances on the floors of factories, filling stations, canning plants, aircraft hangars, decks and engine rooms of ships, and other installations. The absorbent granules are porous and ordinarily weigh less than 30 lb per cu ft. Because of their light weight, size, porosity, and absorbent properties, the granules are suitable for many uses, and since World War II many different markets for them have developed (Fig. 2). Among other uses, they are now sold for litter and bedding for poultry, pets, and other animals, and as a soil conditioner in greenhouses and for golf courses. In 1982, 895,700 tons of fuller’s earth were sold for absorbent and filtering uses; this tonnage was nearly 53% of the total fuller’s earth produced in the United States that year.

The foregoing discussions apply only to those uses consuming sufficient quantities of fuller’s
earth to be classified separately by the US Bureau of Mines in the Minerals Yearbooks. In addition, smaller quantities of fuller's earth are or have been produced for many miscellaneous uses. According to Oulton (1965), more than 90 different grades of fuller's earth are produced. Some of these grades are used for pharmaceuticals designed to absorb toxins, bacteria, and alkaloids; for treatment of dysentery; for purifying water and dry-cleaning fluids; dry-cleaning powders and granules; for the manufacture of NCR (no carbon required) multiple-copy paper; for the manufacture of wallpaper; and as extenders or fillers for plastic, paint, and putty. Fuller's earth mined near Ellenton, FL, was used for making lightweight aggregate for the construction of concrete barges during World War II (Calver, 1957; Greaves-Walker, et al., 1951). Still other uses of fuller's earth and its suitability for uses in new products are outlined by Haden and Schwint (1967), Haden (1972), and Haas (1970). One special use of fuller's earth is as a carrier of platinum catalysts that are made in the United Kingdom from sepiolite clays mined in Spain. Other uses of sepiolite fuller's earth (Chambers, 1959) are similar to those of the palygorskite (attapulgite) type mined in the United States.

Some reports also note that fuller’s earth is used in making cement. Probably the basis for these reports is the mining of the Twiggs Clay Member of the Barnwell Formation near Clinchfield, GA, and the use of the clay in making portland cement. It is used for this purpose mainly to obtain the desired chemical composition in the clinker from which the cement is made. The classification of this clay as fuller’s earth results from the fact that the Twiggs Clay Member is mined for fuller’s earth, and this unit is widely known in Georgia as a source of fuller’s earth.

Product Specifications

Product specifications have been tentatively standardized for bentonite and (or) fuller’s earth sold for drilling mud, foundry-sand bond, absorbent granules, and oil bleaching and will be outlined in the many specifications prepared individually with each agent. Drilling mud specifications for (or) fuller’s earth are prepared in the US Bureau of Mines for specified uses. In suspension properties, fuller’s earth should be suspended in 350 cc of water according to API standards or specificat Another use of fuller’s earth is the filtration of water when testing to petroleum. According to API specifications, fulling at 60% weight maximum. Per API drilling mud specification, a fulling agent must be made with a requirement of 75% to 85% fulling at 60% weight maximum. Yield is a test requirement, 10% of the test weight in barrels of bars. 40 barrels of grit test must be made of the agent.

Ful Sullivan (grit test) should not be tested with a coarser ground specified. The fulling at 350 cc of water should still be tested, and the test must be made through a 100 mesh screen (API STI). Fuller’s earth is one of the few agents that will fulfill the specifications, and it has no palygorskite.
be outlined briefly. Specifications for most of the many other products made from these clays are prepared to meet the requirements of the individual customer, and they commonly vary with each.

**Drilling Muds:** The most critical specifications for bentonite and palygorskite (attapulgite) fuller’s earth for drilling muds are the suspension properties, wet-screen analysis, and moisture as shipped.

**Suspension Properties**—The test for suspension properties involves the preparation of a suspension consisting of 22.5 g of bentonite in 350 cc of distilled water. The suspension is aged and the viscosity determined and yield point calculated from dial readings at 300 and 600 rpm with a direct-indicating viscometer, according to procedure and equipment requirements outlined in American Petroleum Institute specification API STD 13A, 5th edition, 1969. Another important suspension requirement is the filtrate test, which is a measure of the volume of water lost from the prepared suspension when tested in a pressurized filter press according to procedure outlined in American Petroleum Institute specification API RP 13. According to these specifications, to be drilling-mud quality, a bentonite must have a dial reading at 600 rpm of 30 minimum, a yield point pounds per 100 sq ft of 3 times plastic viscosity maximum, and a filtrate volume of 13.5 maximum. Palygorskite (attapulgite) prepared for drilling mud must fulfill the same viscosity specification as bentonite, but the suspension is made with water containing 40 g of salt (NaCl) per 100 cc of water. Yield point and filtrate requirements are not ordinarily specified for palygorskite-type drilling muds. Many companies still use a yield specification for bentonite. Yield is a term used in earlier American Petroleum Institute specifications for the number of barrels of 15 centipoise viscosity mud that can be made from a ton of bentonite. The yield requirement is ordinarily 90 bbl per ton minimum.

**Wet-Screen Analysis**—Wet-screen analysis (grit test) is a measure of the material in bentonite or palygorskite (attapulgite) mud that is coarser than 200-mesh US Series sieve. The specified test is made by mixing 10 g bentonite in 350 cc water containing 0.2 g dispersing agent, stirring, aging, stirring, and washing through a sieve with a specified spray system (API STD 13A). The residue on the sieve is then dried, weighed, and the percentage of the original bentonite is determined. Bentonite to fulfill the specifications for drilling mud must have no more than 2.5% residue (grit) and palygorskite no more than 8% residue.

**Moisture**—The maximum moisture content of bentonite when shipped from the plant where it is processed is 10% and that for palygorskite is 16%.

**Foundry Sand Bond:** Tentative specifications for Western bentonite for bonding foundry sand are outlined in Steel Founders Society of America SFSA Designation 13T-65 issued in 1965. This specification requires the following characteristics and properties for Western bentonite, as tested by methods described in the specification: (1) water content shall not exceed 12% or be less than 6%; (2) pH value shall be equal to or greater than 8.2, (3) calcium oxide content shall not exceed 0.70%, and (4) the liquid limit shall not be less than 600 or greater than 850. Each foundry has its own green, dry, and hot-strength specifications for bentonite, which vary with the type of metal, size of castings, and foundry production procedures. Methods of testing strengths of bentonite-bonded sands are outlined in detail in publications of the American Foundrymen’s Society (Anon., 1962a, 1963). The tests require the preparation of a specified mixture of bentonite, standard testing sand, and water; the preparation of test cylinders; and testing strengths with approved apparatus, according to controlled procedures.

**Iron-Ore Pelletizing:** Specifications for bentonite used for pelletizing taconite-type iron-ore have not been standardized, and several tests are used (Sastri and Fuerstenau, 1971; Wake- man, 1972). As green pellets must be capable of withstanding handling, compaction, and drying and the dry pellets must be even stronger, mixtures of bentonite, iron ore, and water are commonly tested for water-drop strength, wet-compression strength, plastic deformation, and dry-compression strength.

**Absorbent Granules:** Most absorbent granules marketed are prepared to fulfill the requirements outlined in Federal Specification P-A-1056A, Absorbent Material, Oil and Water (for floors and decks), outlined for purchases by the US General Services Administration. A similar set of specifications is outlined in the American Society for Testing & Materials (ASTM) Standard: C 431-65 Standard Methods for Sampling and Evaluation of Sorptive Mineral Products Used as Floor Absorbs. The size and absorbent characteristics required of granules as outlined in the federal specification are listed in Table 2.

The specifications require that absorbent granules consist of a uniform mixture of minerals of the silicate type. They also must be clean, uniform, and free of lumps or foreign
matter, and no more than 10% of them can pass through an 80-mesh sieve in the attrition resistance test. The attrition-resistance test is made by shaking with steel balls on a screen, according to a specified procedure.

**Fuller's Earth for Bleaching Oils:** Test methods for evaluating bentonite and other types of fuller's earths for bleaching soybean and cottonseed oils are outlined in the American Oil Chemists Society AOCS Official Method Cc 8b-52, revised April 1952, and AOCS Official Method Cc 8a-52, corrected 1958. These specifications contain instructions on bench-type tests, including stirring time, heating rates and temperatures; approved equipment; quantities of raw oil and clay required; methods of color determinations; and so forth. They also require the comparison of the material tested with an official natural bleaching earth approved by the American Oil Chemists Society. The color determination of the bleached oils and their comparisons with the oil bleached by the official earth in the same test are the basis for purchase specifications.

**Mineralogy:** The principal clay mineral in bentonite is smectite, according to the definition used in this chapter, and many fuller's earth deposits also consist chiefly of this mineral. The term smectite is applied as a group name, and montmorillonite is a mineral species name. This usage conforms to the growing acceptance of the term smectite and does away with the confusing use of montmorillonite as both mineral species and group names. Montmorillonite, including both sodium and calcium varieties, is the most common member of the smectite group occurring in bentonite. However, saponite, a magnesium smectite, and hectorite, a lithium-bearing magnesian variety, are the major minerals in some bentonites.

Smectite minerals occur in extremely small particles (Fig. 3); therefore, detailed information on them is difficult to obtain and is, in part, based on theoretical considerations. As the mineralogy of this group of clays is complex, the reader is referred to authoritative books and other references given in the introduction for detailed information on them, and only the following brief summary will be given here.

According to the most generally accepted structure, smectite consists of two silica tetrahedral sheets with a central octahedral sheet. The theoretical structural formula is \((\text{OH})_2\text{Si}_2\text{Al}_2\text{O}_5\cdot n\text{H}_2\text{O}\), and the theoretical composition without interlayer material is \(\text{SiO}_2\), 66.7% \(\text{Al}_2\text{O}_3\), 28.3%; and \(\text{H}_2\text{O}\), 5%. However, smectite always differs from the foregoing theoretical formula and composition (Table 3) because of substitutions of various ions for silicon in the tetrahedral coordination and for aluminum in the octahedral sheet. Furthermore, the substituted ions are thought to be commonly of different valence than the theoretical ion replaced, which results in an unbalancing of the charge in a unit of smectite. This charge deficiency is balanced by exchangeable ions, which vary considerably and result in further differences in the compositions of smectite. Cations which are exchangeable in bentonite include sodium, calcium, potassium, magnesium, lithium, and hydrogen. The exchange capacity of most bentonite is within the range of 60 to 150 milliequivalents per 100 g.

Unit layers of smectite are thought to be stacked with the oxygen layer of one silica tetrahedral sheet adjacent to the similar layer in the neighboring unit. Only a very weak bond exists between neighboring units, and water or other polar molecules can enter between unit layers causing the lattice to expand in the c direction. This expansion by polar molecules and the collapse of expanded units with heat, which can be recognized by X-ray diffraction methods, is applied in studying smectite and distinguishing members of this group from other clay minerals.

The ion-exchange characteristics have an important role in controlling or influencing the physical properties of bentonite and the fuller's earths. In general, those bentonites that have ion have colloidal properties and other clay minerals valuable in providing thixotropic or other characteristics.

The type role in clays is usually a result of the properties that are not dominant, as pointed out by the types that have moderate strength.

FIG. 3—

* Bentonite (API standard, E.I. Du Pont).

**TABLE 2—Characteristics of Absorbent Granules**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Maximum</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matter retained on a No. 6 US Standard sieve</td>
<td>1.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td>Matter retained on a No. 30 US Standard sieve</td>
<td>99.0%</td>
<td>52.0%</td>
</tr>
<tr>
<td>Matter retained on a No. 40 US Standard sieve</td>
<td>99.8%</td>
<td>73.0%</td>
</tr>
<tr>
<td>Matter retained on a No. 60 US Standard sieve</td>
<td>100.0%</td>
<td>90.0%</td>
</tr>
<tr>
<td>Ability to absorb lubricating oil (per gram of sample)</td>
<td>-</td>
<td>0.8 ml</td>
</tr>
<tr>
<td>Ability to absorb distilled water (per gram of sample)</td>
<td>-</td>
<td>0.9 ml</td>
</tr>
<tr>
<td>Solubility in distilled water</td>
<td>1.5%</td>
<td>-</td>
</tr>
</tbody>
</table>
Clays


that have Na⁺ as the dominant exchangeable ion have very high swelling capacities and colloidal properties, and those in which Ca²⁺ is the dominant ion tend to swell little more than other clays. Because of their high colloidal properties, high-swelling sodium bentonites are valuable as drilling muds and other uses requiring thixotropic suspensions. The calcium varieties usually have little value for such uses without beneficiation by the addition of soda ash or other chemicals, and even when so treated, are not ordinarily as efficient as the sodium types. The type of exchangeable ion also has a major role in controlling the bonding characteristics. As pointed out by Grim (1962), sodium bentonites have very strong foundry sand bonding properties after drying (dry strength), but only moderate strengths when moist or wet (green strength). Calcium bentonites, on the other hand, have high green strengths and low to moderate dry strengths. However, part of these differences in bond strengths may be due to particle size or other characteristics, and there is some evidence that the dry strength of some calcium bentonites can be increased by lengthening the mulling (mixing) time in the preparation of foundry sand.

All bentonites contain mineral impurities, which vary considerably in type and quantity present. A few are contaminated with minor quantities of clay minerals other than smectite, such as kaolinite and illite. The common non-clay minerals in bentonite include those listed in the older definition by Ross and Shannon (1926), and minor quantities of most of the accessory minerals in volcanic rock also may be present. Selenite is abundant in many deposits, and some beds contain carbonate veins and concretions. Zeolite minerals and opal, cristobalite, or other forms of poorly ordered

<table>
<thead>
<tr>
<th>Minimum</th>
<th>0.0%</th>
<th>52.0%</th>
<th>73.0%</th>
<th>90.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8 ml</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9 ml</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
silica are present in some bentonite deposits in western United States and at several other places in the world. Some deposits are contaminated with incompletely altered parts of the rock from which they formed. The vitric latitic tuff remaining in the bentonite at Cheto, AZ (Sloane and Guilbert, 1967), is an example of this type of material.

The principal fuller’s earth deposits other than the bentonite type consist of palygorskite (attapulgite) and sepiolite. According to Bradley (1940), palygorskite has an ideal formula of \((\text{OH}_2)_n(\text{OH})_n\text{Mg}_{10}\text{Si}_{24}\text{O}_{68}\text{H}_2\text{O}\), but substitution of Al\(^{13+}\) for either Mg\(^{2+}\) or Si\(^{4+}\) takes place. It consists of two silica chains linked in amphibolelike structures and has both monoclinic and orthorhombic symmetry (Christ et al., 1969). Sepiolite, \((\text{Si},\text{Mg})_2\text{O}_8(\text{OH})_2(\text{OH})_6\text{H}_2\text{O}\), is thought to have three pyroxene-type chains (Grim, 1968), and, therefore, the unit cell is somewhat larger than for palygorskite. Both palygorskite and sepiolite typically occur in fibrous and elongate lathlike particles. Sepiolite is also the mineral forming meerschaum (see “Meerschaum”).

Other nonbentonite fuller’s earths include an uncommon type of rock called opal claystone (Heron, et al., 1965). This rock is more than three-fourths opal or another form of poorly ordered silica, and the remainder is montmorillonite and other mineral impurities. It was mined in South Carolina in the early part of this century and used for bleaching oil, and it is the raw material to be mined near Rimini, SC, to supply a fuller’s earth plant under construction in 1972. Nonbentonite clays that have been used as fuller’s earths in the past include the Anna kaolin in Illinois, halloysite in Utah (Schorter and Campbell, 1940), and glacial clays in Massachusetts. In addition to these nonbentonite clays, there are extensive deposits of fuller’s earth consisting of very impure montmorillonite that are not ordinarily thought of as being bentonite. Two such deposits are the Porters Creek Clay (Paleocene) in the Mississippi Embayment region and the

### TABLE 3-Chemical Analyses of Clays

<table>
<thead>
<tr>
<th>Clay Type</th>
<th>Al₂O₃ (%)</th>
<th>Fe₂O₃ (%)</th>
<th>MnO (%)</th>
<th>CaO (%)</th>
<th>TiO₂ (%)</th>
<th>SO₃ (%)</th>
<th>H₂O (%)</th>
<th>Total C (%)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite, blue-gray, clay spur bed, Belle Fourche, SD (Foster, 1953)</td>
<td>19.92</td>
<td>7.93</td>
<td>0.14</td>
<td>8.56</td>
<td>38.46</td>
<td>37.02</td>
<td>99.71</td>
<td>99.89</td>
<td>100.21</td>
<td>99.47</td>
<td>99.56</td>
<td>99.85</td>
<td>100.59</td>
<td>100.47</td>
<td>100.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bentonite, Polkville, MS (Ross and Hendricks, 1953)</td>
<td>24.32</td>
<td>7.93</td>
<td>0.14</td>
<td>8.56</td>
<td>38.46</td>
<td>37.02</td>
<td>99.71</td>
<td>99.89</td>
<td>100.21</td>
<td>99.47</td>
<td>99.56</td>
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<td>100.59</td>
<td>100.47</td>
<td>100.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bentonite, Cheto, AZ (Kerr et al., 1950)</td>
<td>24.32</td>
<td>7.93</td>
<td>0.14</td>
<td>8.56</td>
<td>38.46</td>
<td>37.02</td>
<td>99.71</td>
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<td>100.47</td>
<td>100.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bentonite, Chambers, AZ (Kerr et al., 1950)</td>
<td>24.32</td>
<td>7.93</td>
<td>0.14</td>
<td>8.56</td>
<td>38.46</td>
<td>37.02</td>
<td>99.71</td>
<td>99.89</td>
<td>100.21</td>
<td>99.47</td>
<td>99.56</td>
<td>99.85</td>
<td>100.59</td>
<td>100.47</td>
<td>100.21</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Bentonite, blue-gray, clay spur bed, Belle Fourche, SD (Foster, 1953)
2. Same as 1 but oxidized to olive green (Foster, 1953)
3. Bentonite, Polvilius, MS (Ross and Hendricks, 1954)
4. Fuller’s earth, Combe Hay, Somerset, United Kingdom (Kerr et al., 1950)
5. Bentonite, Chambers, AZ (Cheto) (Kerr et al., 1950)
6. Hectorite, Hector, CA (Kerr et al., 1950)
7. Palygorskite (attapulgite), Attapulga, GA (Kerr et al., 1950)
8. Halloysite, Eureka, Utah (Kerr et al., 1950)
9. Kaolinite, Mcgon, GA (Kerr et al., 1950)
10. Kaolinite, St. Austell, United Kingdom (Kerr et al., 1950)

**Twigs Clay Deposit**

**Occurrence:**
Jurassic age, mainly in California, Utah, and the States and deposits made up of palygorskite younger. Also, high-swelling clays produced have high swelling age, and many deposits have come from the Shale. This clay is commonly in Miocene and Miocene bentonite clays, in the Pleistocene, and in Pliocene age, and it is also present in the Tertiary age. The deposit is a clayey shale, suitable for bodies along the fault zone. Some miles, and in particular one to more than a mile in diameter, the deposit is in contact with the one with another rock, hydrothermally altered or shaped in one direction. Mostly low-swelling in bedrock, the soap-like to surface tends to crack, when the clay becomes hard, bluish gray to the surface. Typical of these deposits, the bluish slabs are cracked, and the surface seems all bluish gray.

Most bentonite clays occur in a cracked, bluish gray to bluish slabs are cracked, and the surface seems all bluish gray.
Twigs Clay Member of the Barnwell Formation (Eocene) in Georgia.

Occurrence: Though bentonite deposits of Jurassic age are extensive in western United States and elsewhere in the world, virtually all deposits mined to date are of Cretaceous age or younger. All but a very minor tonnage of the high-swelling Wyoming-type bentonite produced has been mined from beds of Cretaceous age, and more than three-fourths of the total has come from a single formation—the Mowry Shale. The Southern or calcium bentonite is mainly in formations of Cretaceous, Eocene, and Miocene age. The abundant miscellaneous bentonite deposits, other than the high-swelling type, in the western states are mainly of Tertiary age. Deposits scattered through Nevada, California, Oregon, and Idaho are mainly in upper Tertiary rocks, and many are thought to be Late Miocene or Pliocene in age. The widely known Cheto bentonite near Chambers, AZ, is in the Bidahochi Formation of Pliocene age, and deposits mined in western Oklahoma are also in Pliocene rocks. Deposits in the Ash Meadows district, NV, occur in rocks mapped by Denny and Drewes (1965) as Pleistocene in age, and if this age assignment is correct, they are among the youngest bentonites in the world.

Most bentonite occurs in beds or lenticular bodies aligned along a definite stratigraphic zone. Some beds extend for more than 200 miles, and other deposits, particularly the lenticular ones, are only a few hundred yards in diameter. Deposits mined range from about 1 to more than 30 ft in thickness. Bedded deposits ordinarily have a characteristic sharp contact with underlying rocks and a gradational one with overlying strata. Deposits formed by hydrothermal processes tend to be irregularly shaped and to grade into the host rock in all directions.

Most bentonite, including both the high and low-swelling types, has a characteristic waxy or soaplike texture. Parts of deposits near the surface tend to be light-yellowish green or gray when the natural moisture is present and to become lighter in color when they dry. Deposits under considerable overburden tend to be bluish green. The change to lighter shades near the surface is related to the oxidation of iron. Typical outcrops of high-swelling bentonite have a popcornlike or frothy texture caused by alternate swelling and drying of the bentonite. Outcrops of low-swelling types commonly have a cracked appearance thought by some to resemble alligator hide.

Most bentonite in North America and elsewhere includes an opal claystone that is more than form of poorly inder is montmorillon. It in the early part ool oil, and in the past ool oil, halloysite in ill, 1940), and in addition to these are extensive selves of these not ordinarily Two such de-lay (Paleocene) region and the

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where occurs in sedimentary rocks and was formed in place from volcanic ash or tuff. Some deposits have been formed by hydrothermal alteration of volcanic or other igneous rock, and other deposits of nearly pure smectite may be accumulations that were transported and deposited in marine or alkaline lake water with only minor postdepositional alteration.

The extensive palygorskite (attapulgite) fuller's earth deposits in the southern part of the Meigs-Attapulgus-Quincy district, Georgia and Florida (Fig. 4), occur as tabular lenses and discontinuous beds in the Hawthorn Formation of Miocene age. This clay is green and bluish gray, and most of it has a waxy or soaplike texture.

In addition to the deposits in the United States, palygorskite fuller's earth is also mined in the following regions: (1) Pout district near Mbour, Senegal (Wirth, 1968); (2) Ukrainian district, USSR (Ovcharenko et al., 1967); and (3) Muh district, India (Siddiqui, 1968). The Senegal deposits are in marine beds of Early Eocene age. The Ukrainian palygorskite is interbedded with bentonite. Deposits in India occur between fossiliferous limestones and apparently are marine in origin.

Insofar as the authors are aware, the only sepiolite fuller's earth mined at the time this report was written is in the Vallecitas and another district in Spain (Anon., 1972b). However, economic sepiolite deposits have been discovered recently in the Ash Meadows district, Nevada (private communication). The Spanish deposits occur in an evaporite sequence of Tertiary age. The Nevada deposits are closely associated with calcium, sodium, and magnesium bentonites of Pleistocene age.

Origin: The evidence for most bedded bentonite having formed from volcanic materials transported considerable distances in the atmosphere was presented by several geologists early in the century, including Hewett (1917), Wherry (1917), and recently by Slaughter and Earley (1965). This conclusion is based primarily on the purity of smectite, on the fact that the nonclay minerals in bentonite are angular and of the type occurring in volcanic rock, rather than mixtures of rounded grains characteristic of detrital sediments, and on the presence of relic shard textures in many bentonites (Ross and Shannon, 1926). Ample evidence supports the conclusion that the parent ash of most bentonite was deposited under marine conditions, but a few deposits apparently accumulated in alkaline lakes (Papke, 1969). As would be expected, different bentonites have
formed from volcanic rock of somewhat different types, and the most common parent materials range from andesite to rhyolite in composition. Opinions differ concerning the process and time of alteration of the ash. Several authors have noted that change in ash would have begun with its contact with water, but when the alteration was completed is questionable. Papke (1969) believes that one type of bentonite deposit formed in alkaline lakes soon after deposition and another type formed more slowly as the result of alteration by ground water. Alteration by ground water requires burial by younger rocks and probably regional uplift and a considerable interval of geologic time. In the authors' opinion, changes have taken place in bentonite deposits throughout virtually their entire geologic history. Some deposits may have been altered extensively before burial beneath younger rocks. However, the prominent cherty zone below several beds points to the downward transport of silica by ground water from altering deposits; this must have taken place after burial.

Bentonite formed by hydrothermal activity occurs in Nevada (Papke, 1969), California (Kelley, 1966), Spain (Anon., 1972b), and elsewhere. Deposits of this type commonly are associated with other minerals known to have formed by hydrothermal processes. They also tend to occur in irregularly shaped bodies rather than in beds, and they ordinarily grade into the host rock through partially altered zones. The distribution and shape of bentonite formed hydrothermally are commonly controlled by fault zones, joints, and other geologic features providing access for heated water.

Alteration of volcanic ash or tuff in restricted alkaline lakes heated by hot-spring activity is also thought to have formed bentonite (Ames et al., 1958). The hectorite deposits in California probably formed this way, and this clay passed through an intermediate stage in which most of the ash was altered to zeolite. A magnesium bentonite called amargosite formerly mined near Shoshone, CA, also formed by the alteration of vitric volcanic material by hot springs (Sheppard and Gude, 1968).

Though the authors have doubts about the theory, some bentonite deposits are thought to

FIG. 4—Map showing bentonite and fuller's earth districts in the United States.

Distri
have been deposited mainly in the form of smectite minerals. According to this explanation, origin of smectite minerals, having formed by weathering of volcanic or other igneous rocks, were transported, separated from impurities, and deposited. This theory has been applied to explain the origin of deposits in India (Siddique and Bahl, 1965), the USSR (Tazhibayeva and Galiyev, 1972), and Nevada (Papke, 1969). Bentonitic fuller's earth deposits in the United Kingdom were thought by Robertson (1961) to have been transported from smectite-rich soils on the European landmass. Such soil would have formed mainly on nonigneous rocks.

As most fuller’s earth deposits are bentonites, they have the same origins; however, some fuller's earth consists of minerals other than smectite and may be of quite different origin. The palygorskite (attapulgite) fuller’s earth deposits in Georgia and Florida are one type that probably formed in a different way. These deposits have been investigated by several geologists and mineralogists, and no one has found convincing evidence of any volcanic materials having ever been present. The first author has investigated these deposits in detail and believes that the palygorskite in them formed in place from seawater evaporating in a tidal-flat environment. This theory is essentially the same as the “neo-formation” idea of Millot (1964).

**Distribution of Deposits**

**North America: United States**—**Southern Bentonite and Fuller's Earth**—Southern of calcium bentonite is now mined in Texas, Mississippi, Alabama, Oklahoma, and Louisiana (Teague, 1972). Undeveloped bentonite deposits occur in South Carolina (Robinson, Buie, and Johnson, 1961). At present, at least 17 different bentonite mining operations are active, and 11 plants are processing bentonite. One of these plants is in Alabama, four are in Mississippi, one is in Louisiana, and five are in Texas. The bentonite deposits in Texas (Fig. 4) are mainly in an extensive belt in the Coastal Plain region. Valuable deposits occur in formations ranging in age from Late Cretaceous to Miocene (Hagner, 1939; Maxwell, 1962; Fisher et al., 1965). The bentonite is mined intermittently near Mineral Springs, Lincoln Parish, LA (Gann, 1971). Deposits also were formerly mined in the Vernon Parish (Welch, 1942), which is in the west-central part of Louisiana. The Vernon Parish deposits are in the Fleming Formation (Miocene) which also contains bentonite in Texas. Most of the bentonite produced in Mississippi is mined near Aberdeen, Monroe County, where the American Colloid and International Minerals & Chemical Corps. operate plants. Bentonite is also mined intermittently in Smith County, and clay that is presumably bentonite is produced in Pearl River County. The deposits mined in Monroe County are in the Eutaw Formation of Late Cretaceous age. Deposits mined in Smith County are in Oligocene rocks, and the deposits in Pearl River County are of Miocene age (Bicker, 1970). The bentonite processed near Sandy Ridge, AL, occurs in the Ripley Formation (Upper Cretaceous) (Monroe, 1941).

Fuller’s earth is produced mainly in the southern states; and the Meigs-Attapulgus-Quincy district, Georgia and Florida (Fig. 4), is the leading fuller’s earth-producing district in the United States. The deposits mined in this district occur in the Hawthorn Formation of Miocene age. Those in the northern part of the district consist chiefly of diatomaceous montmorillonite containing minor quantities of other clay minerals and clastic nonclay mineral impurities. Some of the deposits in the southern part of the district are the purest palygorskite (attapulgite) mined in the world. The fuller's earth mined in central Peninsular Florida also occurs in the Hawthorn Formation, and this clay consists chiefly of montmorillonite.

Large deposits of fuller’s earth occur in the Twiggs Clay member of the Barnwell Formation of Eocene age. These deposits crop out in a belt extending across central Georgia seaward from the fall line. The Twiggs Clay member is now mined and processed by the Georgia Tennessee Mining Co. at Wrens, GA (Patterson, 1972), and it was formerly mined at several other places in this state. The Twiggs Clay member consists mainly of montmorillonite and cristobalite (Brindley, 1957) or opal (Carver, 1972).

In 1973, five plants were actively producing fuller’s earth from the Porters Creek Clay of Paleocene age. This formation extends from west-central Alabama across the northeastern part of Mississippi, the western parts of Tennessee and Kentucky, southernmost Illinois, and into southeastern Missouri. Most of the Porters Creek Clay consists of a mixture of montmorillonite and other clay minerals, and much of it contains appreciable quantities of cristobalite and nonclay mineral impurities (Sims, 1972).

Fuller’s earth used mainly in bleaching animal and vegetable oils is now produced in Texas, and historically this state has ranked...
with the leading producers. The fuller's earth produced in Texas is mined from bentonite beds.

**Wyoming or High-Swelling Bentonite Deposits**—The Northern Rocky Mountains-High Plains region has led the world in the production of Wyoming or high-swelling bentonite since the first mining of this clay. In 1973, 16 plants were processing bentonite in this region. The major producing districts (Fig. 4) are as follows: (1) the northern and western Black Hills districts, Wyoming, Montana, and South Dakota; (2) Kaycee-Midwest, Wyoming; (3) Greybull-Lovell, Wyoming and Montana; (4) Vananda, Montana; and (5) Chinook-Malta-Glasgow, Montana.

Virtually all the bentonite produced in the Northern Rocky-High Plains region occurs in sedimentary formations of Cretaceous age. Most of the bentonite produced in the Black Hills district has been mined from the Clay Spur Bentonite Bed, which is in the uppermost part of the Mowry Shale (Davis, 1965; Knechtel and Patterson, 1962). High-swelling bentonite deposits in the Newcastle Sandstone have also been mined, and a small tonnage has been produced from beds in the Belle Fourche Shale. A bentonite in the upper part of the Pierre Shale was mined on the southern flank of the Black Hills before and during World War II and processed for use as water softener. A very low swelling bentonite having the properties of the southern-type bentonite is now mined on a small scale from a bed in the Pierre Shale in the northern Black Hills.

Most of the bentonite mined in the Kaycee-Midwest and Greybull-Lovell districts occurs in the Mowry Shale, but some beds in younger formations are also mined in these districts (Anon., 1969h). The bentonite produced mainly for taconite-bonding purposes in the Vananda and Chinook-Malta-Glasgow districts, Montana, occurs as extensive beds in the Bearpaw Shale (Berg, 1969, 1970), which is considerably younger than the Mowry Shale.

**Hectorite**—Virtually all the hectorite mined to date has been near Hector, CA, the type locality. The hectorite occurs as a waxy soft nodular layer ranging from 6 to 8 ft in thickness. It is associated with sandstone and clay beds of Tertiary age that accumulated in an alkaline lake environment. The beds below the hectorite contain travertine formed as the result of hot-spring activity (Ames, et al., 1958). The valuable hectorite deposits are overlain by Quaternary basalt.

A large deposit of hectorite has been discov-
posits in Kern County, bentonite near Olancha and probably deposits at other localities in California have been processed for filtering and decolorizing agents in recent years.

**Resources**—Resources of bentonite and fuller's earth in the United States are very large. The reserves of bentonite are at least one billion tons, and the total resources, including all bentonite that will be eventually suitable for one use or another, are considerably larger. This reserve estimate of one billion tons includes very large deposits that have a quality suitable for binding iron-ore pellets but that would be classed as submarginal for drilling mud and several specialty uses. The reserves of very high quality drilling-mud bentonite are limited and are much in demand. Resources of fuller's earth are tentatively estimated at two billion tons. However, almost any figure could be used here, if all the clays equal in quality to the lowest grade material used as bleaching clay in the past were included. A large part of the fuller's earth resources is in the extensive Porters Creek Clay and the Twiggs Clay Member of the Barnwell Formation. These deposits are suitable for use in absorbent granules and certain other fuller's earth products, but they are not used in drilling mud and several of the specialty products.

**Canada**—Bentonite occurs in beds of Cretaceous and Tertiary ages at many places in western Canada (Ross, 1964; Spence, 1924). The major producing districts (Fig. 5) are Onoway (Baroid Canada, Ltd.) and Rosalind (Dresser Industries, Inc.) in Alberta and in the Pembina district (Pembina Mountain Clays, Ltd.) in Manitoba. Bentonite has also been mined near Princeton, B.C., and deposits near Avonlea, Sask. (Anon., 1971), and along the Mackenzie River in the vicinity of Inuvik, N.W.T., have been investigated by industry.

The deposits mined in Alberta are in the Edmonton formation, the uppermost Cretaceous unit in this region. Those mined at Rosa-

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**FIG. 5—Map showing bentonite districts in Canada.**
Industrial Minerals and Rocks

A few thousand tons of fuller's earth are also produced each year. The fuller's earth deposits mined are in La Rioja and Río Negro provinces.

Brazil—A plant processing montmorillonite clays for use as foundry-sand bond was built at Sacramento, Minas Gerais, in 1962 (Anon., 1962). Bentonite has also been found at several other localities in the country.

Peru—Bentonite and fuller's earth occur in the provinces of Pisco, Canete, Paita, and Centralminas Villar, and elsewhere (Cubera, 1963). Bentonite has been mined and used in iron-ore pelletizing in Peru for several years (Anon., 1967), and present production is estimated to be 20,000 tpy (Anon., 1973a).

Europe—Cyprus—A low-swelling calcium bentonite is mined in the Troulli district near Kambia (Anon., 1969). A few thousand tons are produced annually. Part is processed in a small plant at Vassiliki, and part is shipped to Israel for beneficiation and use in several products (Anon., 1970e).

Czechoslovakia—Bentonite occurs in the northwestern, central, and eastern parts of Czechoslovakia (Gregor, 1967). The bentonite is chiefly of the calcium and magnesium types, and it formed from rhylolite tuffs. It is as much as 70% montmorillonite; the nonclay minerals present include cristobalite. Bentonite reserves in Czechoslovakia were estimated to be 10 million tons.

According to Ross (1964), only a very few million tons of bentonite reserves have been proved in Canada. However, the potential resources of bentonite in the country must be very large, considering the large areas now known to contain scattered deposits and the general similarities of strata to Cretaceous and Tertiary rocks in the United States known to contain bentonite.

Mexico—The German firm Süd-Chemie AG with its Mexican affiliate Tonsil Mexicana SA has operated a bentonite plant in Puebla since 1967 (Anon., 1969b), and another plant is active intermittently at Monterrey. Bentonite and fuller's earth also occur in Querétaro, Michoacán, and Guanajuato, and a few of these deposits have been mined on a small scale (Espíndola and Zamora, 1958). Apparently, most Mexican bentonite deposits occur in sedimentary rocks, and some of these are of the nonmarine type.

South America: Argentina—Bentonite deposits are scattered throughout several provinces in Argentina (Bordas, 1947). The principal deposits mined and the 1969 production (Anon., 1971) are as follows:

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<tr>
<th>Principal Deposits</th>
<th>Province</th>
<th>Tons Produced</th>
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<tr>
<td>Rio Chico</td>
<td>Chubut</td>
<td>5,286</td>
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<td>El Alamo y Las Hegueras</td>
<td>Mendoza</td>
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<td>El Catalán</td>
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<td>Del Lago Carrio y Rob</td>
<td>Río Negro</td>
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<tr>
<td>La Emilia y Cristina</td>
<td>San Juan</td>
<td>18,005</td>
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<tr>
<td><strong>Total</strong></td>
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<td><strong>62,139</strong></td>
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The deposits are mostly of Jurassic age (Spence, 1924), and one-third of the bentonite produced in this plant is reported to be available for export.

France—The company Société Française des Bentonites et Déris is the largest producer of bentonite. It operates several plants in France (Anon., 1969). Two of these plants are at Chermont (Anon., 1969). A few thousand tons are produced annually. One of these plants is at Morden, in the Pembina Valley is a low or nonswelling bentonite, which is used for bleaching mineral lubricating oils, and decolorizing animal and vegetable oils.

Other bentonite and fuller's earth deposits in France are chiefly smectite, but those at Morny are mixtures of smectite and palygorskite (Milly, 1964).

Greece—Rather extensive deposits of bentonite occur in the eastern part of the island of Milos (Anon., 1969). The deposits are as much as 10 ft thick. Apparently they formed by the alteration of ash or tuffs of Pliocene age in a marine environment (Wetzenstein, 1972). One plant near deep water operated by the...
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Greek company, Silver and Barytes Ores Mining Co., has a yearly capacity of 200,000 tons. Three other companies are also mining bentonite on this island (Wayland, 1971). The bentonite producers on Milos, bentonite also occurs on Mikenos where three companies have been active in recent years. With production on both islands, Greece ranks among the leading producers of bentonite.

Hungary—Bentonite occurs at scattered localities in Hungary. Recently, bentonite-processing facilities were concentrated at Mod, under the supervision of the National Ore and Mineral Mining Enterprise (Sondermayer, 1967). The new plant is reported to have a capacity for processing 100,000 tpy of raw bentonite. Both natural calcium and sodium-exchanged bentonites are produced for several different uses (Anon., 1970d).

Italy—Italy is one of the leading European bentonite producers. The deposits mined are on the island of Ponza, off the western coast, and on Sardinia. The Ponza deposits are near Cala della Acqua. They are in volcanic rock and were formed by hydrothermal alteration of rhyolite tuffs (Lupino, 1954). The average thickness of these deposits is about 10 m, and 2.9 million tons is estimated to be present (Anon., 1969f). Several grades of bentonite are produced on Ponza, and one of them is a colloidal white bentonite that brings a high price for speciality uses. This white bentonite is one of the few bentonites imported by the United States.

The deposits on Sardinia are mined by Industria Chimica Laviosa SpA, an Italian company (Anon., 1970b), and NL Industries, Inc. (Wayland, 1971). The Italian company is mining the Pedra de Fogu deposits near Alghero, and grades suitable for drilling mud, iron-ore pelletizing, civil engineering applications, water treatment, and wine purification are produced. The deposits mined occur in altered rocks (Pietracaprina and Novelli, 1972). The bentonite mined is the swelling type. It is approximately 70% montmorillonite, and the impurities are chiefly free silica, illite, and calcite. The deposits mined by NL Industries are near Nurallao (Anon., 1969h). These deposits are in Miocene marine sediments, and they are underlain by Jurassic limestone and trachyte flows. This bentonite is sold primarily for drill.

ing muds in countries bordering the Mediterranean Sea and in the Near East.

Poland—Bentonite deposits of Eocene and Miocene age occur in southern Poland; these are processed for use as bleaching clay (Nocwaki and Ciechomska, 1964) and probably for other uses.

Romania—Romania has been one of the major East European bentonite-producing countries for several years. The bentonite is mined underground in the Alba-Iulia-Ocana Mures district (Neacșu, 1969), and apparently it is produced elsewhere. The yearly production of bentonite in Romania is estimated to be more than 100,000 tons (Huvos and Sondermayer, 1968).

Spain—Bentonite and fuller's earth occur at several places in Spain. The most productive bentonite deposits are in the Cabo de Gata region in Almeria. These deposits have formed by the hydrothermal alteration of rhyolite and andesite igneous rocks (Anon., 1972b; Martín Vivaldi and Linares, 1968, 1969). The more intensely altered parts of deposits contain kaolinite, alunite, and jarosite. Other parts contain minor amounts of palygorskite and sepiolite, which presumably indicates an excess of magnesium at the time of alteration. Fuller's earth deposits consisting mainly of sepiolite occur at Vallecas and elsewhere in the Tagus basin (Anon., 1972b; Huertas, et al., 1971). The deposits are in an evaporite sequence of Tertiary age. The annual output of fuller's earth in the Vallecas district is approximately 14 kt. Absorbent granules, insecticide carriers, and materials for other uses are produced.

Switzerland—Bentonite is mined in Switzerland and used in bonding foundry sands (Grim, 1962).

United Kingdom—Calcium montmorillonite clays occur at many places in the United Kingdom, and fuller's earth has been mined since the Roman period nearly 2000 years ago (Anon., 1969f). Fuller's earth districts now active are at Redhill in Surrey, Combe Hay south of Bath in Somerset, and Woburn in Bedfordshire. In addition to these districts, large deposits of calcium montmorillonite have been discovered in the Swindon-Abington district in Berkshire by the Institute of Geological Sciences (Poole and Kelk, 1971; Poole et al., 1971), and other deposits occur near Clophill in Bedfordshire, and Maidstone in Kent.

The deposits in Surrey and Bedfordshire are in the Lower Greensand, which is the upper formation of the Lower Cretaceous Series (Holmes, 1950). These deposits consist of hard bluish-gray clay having a soapy feel. They are in beds of irregular thicknesses, and at
places as many as eight beds of clay are present in the Lower Greensand. Thicknesses of clay mined range from 5 to 8 ft. Most mining is by stripping methods, but deposits in the Combe Hay district are mined underground.

The fuller's earth at Combe Hay district occurs in the Great Oolite series of Middle Jurassic age. These fuller's earth deposits are commonly 6 to 7 ft thick. As in several bentonite deposits in the United States, the fresh clay in the Combe Hay district is bluish green, and the weathered parts of the deposits are yellowish.

Fuller's earth production in the United Kingdom has quadrupled since 1945, and 176,000 tons was produced in 1970 (Anon., 1972c). Probably the biggest market is for foundry-sand bond, and some of the clay is treated with soda ash for this use. Sodium-exchanged fuller's earth is also used in pelletizing animal feeds, iron ore pellets, and for water-impeding purposes. Approximately a fifth of the fuller's earth produced is acid activated; this clay is sold mainly for alkylation catalysts.

USSR—The principal bentonite deposits in the USSR are in the Volga Region, western and central parts of the Ukraine, Transcaucasia Region, Kazakhstan, and Central Asia (Lebedinskii and Kirichenko, 1972; Anon., 1970a). Smaller bentonite resources also occur in eastern and western Siberia, Crimea, and in the northern Caucasus.

Several large bentonite deposits of Lower Miocene age occur in the Cherkassy district (Ovcharenko et al., 1967), which is located along the border between the Cherkassy and Kiev regions in the Ukraine. The deposits consist of five layers having maximum thicknesses ranging from 1.5 to 8 m. Though most of this bentonite consists chiefly of montmorillonite containing minor quantities of detrital mineral impurities, one layer as much as 2 m thick is mainly palygorskite (attapulgite). This palygorskite was discovered during geological studies in 1954, and it is the first fuller's earth deposit of this composition found in sufficient quantities for mining in Russia.

Most bentonite produced in Azerbaijan in the Transcaucasia Region is mined from beds of Cretaceous age (Seidov and Alizade, 1966), but younger deposits are also present in this region. The bentonite in Azerbaijan is interbedded with tuff and calcareous sedimentary rocks and is thought to have formed mainly by the decomposition and alteration of volcanic ash in a marine environment. However, some deposits may have been altered from other rocks by hydrothermal solutions.

The scattered bentonite deposits in Kazakhstan occur mainly in Lower Tertiary rocks (Akhmet, 1963; Tazhibayeva and Galiyev, 1972). They are thought to have altered from hydromica and related minerals in an alkaline and deoxygenizing environment in inland seas in regions of arid climate. The mica minerals apparently were transported from weathered rocks in land areas.

The principal uses of bentonite in USSR are in the manufacture of heavy clay products, drilling mud, and iron-ore pelletizing, and minor quantities are used in purifying oils, water, and wine. In 1967 about 1.5 million tons was produced (Lebedinskii and Kirichenko, 1972), and the total consumption was about 3.4 million tons. Imports to fulfill requirements came from Italy, Czechoslovakia, and Hungary.

West Germany—Lower Bavaria has been a major producer of smectitic fuller's earth and bentonite for many years. The two major producers are Sild Chemie AG, which has a plant at Mooseberg (Anon., 1969k), and Erbsloh and Co., which operates a plant at Landshut (Anon., 1969e). The deposits are mined mainly by open-pit methods, but some underground mining is still done. Both companies produce sodium-exchanged bentonite for use in foundry-sand bonding and for use in several products requiring colloidal properties. Smectite clays are also acid activated and exported to several countries for processing oils and waxes.

Yugoslavia—Calcium-type bentonite occurs in many places in Yugoslavia, and the total resources in the country are very large (Anon., 1969m). The bentonite is processed, including some sodium exchanging, at several places. The three largest producers have a total annual plant capacity of 100,000 tons, of which 30,000 can be acid-activated. Yugoslavia exports bentonite mainly to East European countries, but minor tonnages are also shipped to West European markets. The quantity exported in 1968 was 23,745 tons.

The best quality bentonite in Yugoslavia is in the Ginovci deposits, 81 km northeast of Skopje (Konta, et al., 1971). These deposits are in lacustrine beds of late Pliocene age, and they formed by alteration of dacite tuffs. The bentonite is reported to be more than 85% smectite and contains 1.2% quartz and 0.5% cristobalite. Reserves of the three best grades of bentonite in these deposits are estimated to be 1.4 million tons. The Ginovci bentonite is converted into Bentomak pla.
Africa: Algeria—Calcium-type bentonite is mined in the Marnia and Mostaganem districts of Algeria (Anon., 1969). Algerian bentonite production in recent years has ranged from 25,000 to 38,000 tpy. Part of this clay is processed in a plant at Marnia, and part is shipped across the Moroccan border to a plant at Oudja.

The bentonite in the Marnia district occurs in both altered rhyolite masses and as beds in sedimentary rock of Lower Miocene age (Sadr ans, et al., 1955). Much of this bentonite is essentially pure montmorillonite, but some of the deposits altered from volcanic rock contain traces of kaolinite and some of the transported deposits are 10 to 20% kaolinite.

Kenya—Bentonite in the Athi River valley has been mined intermittently for use as foundry-sand bonding (Thompson, 1952).

Malagasy—Bentonite is produced on a small scale in this country, inasmuch as 99 tons were reportedly to have been exported from that country in 1969 (Anon., 1969).

Morocco—Extensive deposits of bentonite occur in the Camp Berteaux district and other localities near Taourirt in eastern Morocco. This bentonite is the product of the transformation of the glassy materials in volcanic ash. It occurs in beds interstratified with Miocene lagoonal or lacustrine deposits (Millot, 1964). Production in recent years has ranged from 20,000 to 30,000 tpy (Anon., 1969).

Another type of clay consisting mainly of magnesium montmorillonite called ghassoul (rhasoul in French) is produced from deposits in the Tamadelt district in the middle Moulaya valley (Jeanette, 1952; Eyssautier, 1952) and sold for several uses requiring absorbent clay. Ghassoul is a brown to black waxy montmorillonite containing 26 to 28% MgO. It occurs in five separate beds ranging in thickness from 15 to 80 cm.

Mozambique—A bentonite processing plant near Impamputo having a capacity of 24 to 26 tpd began production in 1963. High-quality bentonite also has been produced at Lourenço Marques in recent years, and some of it is marketed in Europe (Anon., 1973a).

Senegal—Large fullers' earth deposits consisting principally of palygorskite (attapulgite) occur in the Pout region and elsewhere in Senegal (Wirh, 1968). The deposits are in lower Eocene sedimentary beds of marine origin. According to the published test data, the deposits in Senegal are not as high grade as some of the best fuller's earth mined in the United States, but they are used for several of the same products. Most of the fuller's earth produced in the Pout region is shipped to European markets.

South Africa—Bentonite is mined in Transvaal and Orange Free State, and it is reported to have been discovered near Plettenberg Bay, Cape Province (Anon., 1972); Woodmansee and Murchison, 1969). Production has increased in recent years and now virtually all of South Africa's bentonite requirements are fulfilled by the domestic output. Apparently, the deposits mined consist chiefly of smectite minerals. The authors are unaware of any development of the palygorskite (attapulgite) deposits at Springbok Flats that are widely referred to in the geologic literature.

Tanganyika—The production of a few tons of bentonite in Tanganyika in 1958 was reported by Ross (1964).

Tanzania—Slatick (1969) noted the production of 203 tons of bentonite in Tanzania and small quantities mined in other years.

Asia: India—Major fuller's earth deposits occur in at least five states in India, and bentonite occurs at several localities. Probably the best known deposits are in the Barmer district, Rajasthan (Siddique and Bahl, 1965). They are believed to be transported clays deposited in a marine embayment during late Tertiary time, and the clay minerals formed by the weathering of igneous rock. Other deposits occur in Tertiary beds in Gujarat and in Mio- cene rocks in Jammu and Kashmir; those in Madras and Bihar are of Jurassic age. Fuller's earth mined in the Muth district is of Eocene age, and it is chiefly palygorskite (Siddiqi, 1968). Indian bentonite is used for drilling mud, foundry-sand bonding, water sealant, and other uses. The deposits in Gujarat are near the coast, and some of this bentonite is sold in Europe and elsewhere. Apparently most of the fuller's earth produced is used domestically for purifying oils and processing fibers.

Japan—Two rather distinct types of smectite mineral deposits occur in Japan (Takeshi and Kato, 1969); one is called bentonite and the other, acid clay. The bentonite is composed chiefly of sodium montmorillonite, and the acid clay is montmorillonite in which H+ has substituted for exchangeable Mg++ and Ca++. Deposits of both types occur at several places in Japan. Bentonite altered from bedded rocks called Green Tuff of Miocene age occur in Hokkaido and several places in Honshu (Takeshi and Kato, 1969; Usasima, Syoya, and Suzuki, 1966). Large deposits formed by hydrothermal
alteration of rhyolite and rhyolitic tuffs occur in Higashikambara-gun district, Niigata Prefecture (Takeshi, 1963). The Teikoku deposit, one of several in this district, is principally sodium montmorillonite. Bentonite formed by diagenic alteration of tuff beds occurs at Usui-gun, Gunma Prefecture, and several places in Yamagata Prefecture (Takeshi and Kato, 1969: Omori, et al., 1961). Several of these deposits contain appreciable quantities of zeolite, cristobalite, and detrital minerals, which contaminate the montmorillonite.

Large deposits of acid clay formed by diagenic processes occur at Tsuruoka-shi district, Yamagata Prefecture, at Kitakanbara-gun, Niigata Prefecture, and elsewhere. Acid clay formed hydrothermally also occurs at several places in Niigata.

The yearly bentonite production in Japan is estimated to be approximately 300,000 tons, and demands are increasing (Takeshi and Kato, 1969). Several companies are now active and are processing bentonite in different ways for domestic markets and export. Japanese bentonite is used for foundry-sand bond, drilling mud, several pelletizing and briquetting bond uses, agricultural engineering, soil-improving agent, additives for ceramic raw materials, carriers for agricultural chemicals, paper making, filler for water-based paint, clarifying and coagulation liquids, making organic-clay bentonite, and for other uses. Acid clay is used mainly to produce activated clay by a sulfuric acid-treatment process. Aluminum sulfate and synthetic gypsum, made with the addition of calcium, are recovered as byproducts of this process. The activated clay is used in decolorizing lubricating oils and other oils and fats, for hygroscopic and absorptive applications, and as petroleum catalyst. Acid clay is also used in the manufacture of globular alumina gel, silica gel, fine powdery silica, filler for noncarbon duplicating paper, and for other uses. The exported Japanese bentonite and acid clay are shipped primarily to countries in southeastern Asia, and petroleum catalysts are apparently the principal products shipped.

Pakistan—Bentonite occurs at several places in Pakistan. Deposits in the Bhirmand district of Azad Kashmir of probable middle Pliocene age have been mined since 1958 (Ali and Shahn, 1962). The bentonite is used for several purposes, including the preparation of surgical dressings. A plant for processing activated bentonite at the rate of 20 tpd was under construction at Gujrat in 1962 (Nawaz, 1962).

South Korea—The Dong Bo Clay Industrial Co. operates a bentonite plant in Seoul (Anon., 1973a). The mines are located in North Kyongsang Province.

Turkey—Bentonite and fuller's earth occur at several places in Turkey. Bentonite has been produced on a small scale for domestic use as foundry-sand bond, wine purification, insecticide carriers, and other uses for several years. In 1973, plans were underway for expansion of mining and processing of sodium bentonite (Anon., 1973). Fuller's earth presumably has been used locally for centuries.


Oceania: Australia—A few hundred tons of bentonite have been produced in Australia in recent years (Kalix, 1971), and there has been intermittent mining of fuller's earth for a long time. The bentonite produced in 1970, the last year for which figures are available, was 136 tons from Nanango Mineral Field and 100 tons from Ipswich in Queensland, and 116 tons from lake deposits at Marahagee and Woodanilling in the southwestern part of Western Australia. In that year, 58,244 tons of bentonite was imported from the United States, and the average f.o.b. value was $23.08 per ton. Considerable interest in bentonite in Australia has developed because of its possible use in pelletizing iron ore and other uses, and it seems likely that valuable deposits will be found. Fuller's earth was mined on a small scale in the Dubbo district, New South Wales, as recently as 1969.

New Zealand—Bentonite mining began in New Zealand at Petone Bay, Hawke's Bay, in 1940, and in recent years it has also been produced in the Harper Hills region of Canterbury. The Harper Hills deposits mined are in lower Eocene beds, and apparently they formed by the alteration of volcanic materials deposited in a marine environment (Ritchie, et al., 1969). Bentonite also occurs in beds of Miocene and probable Late Cretaceous ages in this region. The bentonite mined in the Harper Hills region is a low-swelling iron-rich variety, containing as much as 10% kaolinite clay. New Zealand bentonite is used mainly for foundry-sand bond and as an additive to ceramic material, but it may be suitable for other uses, including pelletizing taconite iron ore.

Evaluation of Deposits

Exploration: The exploration for bentonite and fuller's earth deposits, as for virtually all minerals, requires geologic occurrence testing, and standing of the reviewing agencies on deposits rocks in the field investigatory work and research for many of the beds are often due to the development of the local clay. Bentonite and fuller's earth deposits are not bentonite, as required.

Once locating or drilling widely used overlying equipment a tolyct, only when the top of the auger is approached, is a plottage required.

Testing: The earth is hand recovered also used in hard rock in hand.
minerals, requires first an understanding of the geologic occurrence of deposits, then sampling, testing, and appraising of results. An understanding of the geology of the deposits is essential in the early stages and is gained by first reviewing all published and other information on deposits under consideration or on similar rocks in the region. The second step is geologic field investigations, which may require mapping, but reconnaissance studies have been adequate for many deposits. The Wyoming bentonite beds are generally easy to find in the field, because of their tendency to swell when wet and to develop a “popcorn” or frothy texture caused by shrinkage when drying. The calcium or low-swelling bentonite and some fuller’s earth deposits are not as easy to find as the swelling-type bentonite, and extensive drilling is commonly required.

Once located, deposits are explored by augering or drilling. The auger method has been widely used for bentonite, mainly because the overlying rocks can be penetrated by such equipment and the bentonite sampled satisfactorily, particularly if the hole is cleaned when the top of the bentonite is reached. Power augers are also used in some fuller’s earth exploration, but they have generally been found to be unsatisfactory in searching for palygorskite (attapulgite) type deposits. These deposits are commonly explored with drilling equipment, and a fishtail bit is used to penetrate the solid sand or hard rock in the overburden. A core barrel with a toothed cutting-head is used when the top of the clay is approached, and the clay is sampled with such equipment. A double-tubed barrel has been found to be effective in obtaining more complete recovery in some deposits. Core drilling is also used in exploring for hectorite, because of hard rock in the overburden.

Testing: The testing of bentonite and fuller’s earth is handicapped by the general absence of universally accepted procedures and specifications. As a result, these clays are tested and their valuable properties are expressed in many different ways. Some of the reasons for this are the widely varying properties of the clays and the many different specifications outlined by purchasers for many uses. The purchaser of a single grade of bentonite may require tests of a slurry of different concentrations, preparation procedures, aging, temperature specifications, and even measurements of liquid and plastic limits. Clearly, the absence of standardized test procedures indicates the need for an effort on the part of the American Society for Testing & Materials or another organization, with the cooperation of industry, to establish useful procedures having wide application. Rather than go into details on the many empirical and tentative test procedures that are now in use in evaluating bentonite and fuller’s earth and that are likely to be superseded by more scientific and technically accurate methods, only a few generalized comments on tests will be made in the following paragraphs.

Bentonite and fuller’s earth are tested for use in drilling mud by adding water and mixing slurries of specific concentrations and measuring viscosity, yield, yield point, and filtrate (a measure of wall-building properties), and making a wet-screen analysis, according to standard procedures recommended by the American Petroleum Institute (Anon., 1969, 1969a). The Oil Companies Materials Association (Anon., 1969b) in the United Kingdom also has specifications for testing drilling muds. Tests for foundry sand-bonding properties require preparation of standard mixtures of bentonite and sand and measurements of compression strengths of carefully prepared test pieces in a manner similar to the methods outlined by Fisk (1946), the American Foundrymen’s Society (Anon., 1962; 1963), and the Steel Founder’s Society of America (Anon., 1965a). Tests for taconite pelletizing bonds vary considerably (Davison, 1969), but some require certain strengths in pellets measured by the number of times they can be dropped in specified intervals onto a hard surface without breaking (Stone, et al., 1971; Sastry and Fuerstenau, 1971; Wakeman, 1972). Oil-bleaching tests of fuller’s earth and bentonite are commonly made according to procedures described by the American Oil Chemists’ Society (Anon., 1958). Ross (1964) and Nutting (1943) also have given procedures for evaluating fuller’s earth for use in bleaching oils. Tests for a variety of different insecticide, dust diluents, and carrier uses have been described by Weidhass and Brann (1955). Most tests for absorbent granules are made according to procedures in Federal Specifications P-A-1056A, Absorbent Material, Oil and Water (for floors and decks), available from the US General Services Administration. No standard procedures have been developed for testing bentonite for use in water impendence, but rather detailed procedures for testing bentonites for canal and pond sealants have been described by the Colorado State University Experiment Station (Dirneyer and Skinner, 1968).

As swelling bentonites are generally more...
suitable for uses requiring colloidal properties and low-swelling ones are used in other ways, a preliminary indication of the potential value of bentonite can be determined by a swelling test. Perhaps the most common test is the simple procedure of adding 2 g of dried and ground bentonite to a 100-ml graduate filled with distilled water and determining the volume of the settled bentonite in milliliters (Ross, 1964).

Mineralogical Investigations: In addition to the testing of the type outlined in the foregoing paragraphs, information on the mineralogical and chemical composition of bentonite and fuller's earth is also required. Mineralogical composition, including the purity and undesirable contaminants, is determined in some company laboratories. Other companies obtain information of this type from consultants who are experienced in the use of X-ray, electron microscope, differential thermal analysis, petrographic microscope, and other methods of investigating clays.

Appraisal of Field and Laboratory Results: The final step in the evaluation of bentonite and fuller's earth deposits involves the synthesis of data collected during the field investigations, sampling and testing, and other laboratory programs. Maps are prepared locating drill holes and showing the thicknesses and quality of clay and thicknesses of overburden. Reserves of various grades of clay are calculated, and the mining cost is determined from such maps and from geologic and engineering notes taken during the fieldwork.

Preparation for Markets

Mining Methods: In the United States, virtually all bentonite and fuller's earth are mined by stripping methods. Bulldozers and scrapers or pans are most commonly used in removing overburden, but one company strip mining near Attapulgus, GA, operates a large walking dragline powered by electricity for stripping. In the typical pit, the overburden is removed in panels, the clay mined by loading trucks with dragline or endloaders, and the overburden from an adjacent panel shifted to the mined-out area. One company hauling on privately owned roads operates trucks having 100-ton capacity, but most hauling requires use of public highways and lighter trucks. Thicknesses of overburden removed vary considerably. Most Wyoming-type bentonite mined is under less than 30 ft of overburden, but in a few places overburden is as much as 40 ft thick. The thickness of overburden removed from some southern bentonite deposits is as much as 100 ft (Teague, 1972), and beds of the same thickness have been stripped from low-swelling bentonite in one district in Arizona. The overburden stripped from fuller's earth deposits ranges from a few feet to more than 75 ft.

The rocks overlying most bentonite and fuller's earth deposits are soft and can be loaded directly by self-propelled or pushed scrapers, but in places they must be loosened by bulldozers and rippers before loading. Some of the overburden above fuller's earth near Attapulgus, GA, and Quincy, FL, contains limestone and cemented sandstone that must be blasted. Volcanic rocks above hectorite deposits in California also must be blasted where stripping is done. Bentonite is mined underground by the square-set method in the New Discovery mine near Beatty, NV (Papke, 1969), and insofar as the authors are aware, this is the only bentonite now mined underground in North America. Hectorite in California and bentonite in the Ash Meadows district, Nevada (Papke, 1969), and the Chambers (Cheto) Arizona, district, were formerly mined underground. Early in this century, overburden was stripped from fuller's earth near Quincy, FL, by hydraulic methods, and the clay was transported by trams. Most bentonite and fuller's earth produced in other countries are also strip mined, but underground methods are used in a few places, including the Combe Hay district in the United Kingdom (Anon., 1969f). Deposits in this district are selectively mined by hand, using compressed air picks. The clay is extracted in lumps 3 to 18 inches across, and it is hauled to underground storage facilities in mine cars drawn by electric locomotives. It is loaded as needed from the storage dumps onto trucks and hauled to the plant.

Because of variable physical properties most bentonite and fuller's earth deposits are selectively mined. Bentonite from a single pit or bed may be separated into as many as three stockpiles at the plant, each with different physical properties. Various grades of bentonite suitable for different uses are then prepared from the separate piles and by blending clay from more than one pile. Blending bentonite as it is dumped on stockpiles, using earth-moving or cultivating equipment to obtain a uniform clay, is also common practice. The properties of fuller's earth, and particularly the palygorskite (attapulgite) type, vary considerably, but deposits tend to be more uniform than bentonite. Commonly, an entire deposit will be suitable for one product, and another deposit in the same district may differ in gross and essential use.

Beneficial Both bentonite and fuller's earth deposits are selected to maximize profit by the removal of volatile matter. The Wymani delivered to 30% moisture or calcium-t fullers earth matter and processed in or 8% water may contain moisture fuller's earth. those of be however, buret requires minerals pre-ules when co.

In most pit some sort of chunks before fuller's earth using products. It is fed into a product or in diam and operation in WY and Fuller's earth dryers vary. The desirable colloidal grade greatly if the temperature is kept at temp 100° to 200° in the main kept at temp 1964. Temp. range part of the and the high.

The dried wayson much the product is great or other pulvite and mground to a;
Bentonite and fuller's earth may be loaded directly from piles or delivered to the plant in lumps before drying. One plant processing fuller's earth uses an extruding process before drying to improve properties desired in certain products. In this process the crushed clay is fed into a pugmill, where water is added, and the clay is then extruded as rods approximately ½ in. in diam. Drying in most plants is done by gas or oil-fired rotary dryers as large as 10 ft in diam and 65 ft long. A fluid-bed dryer is in operation in one bentonite plant at Colony, WY, and a similar dryer is used in processing fuller's earth at Meigs, GA. The temperature in dryers varies with the intended use of the clay. The desirable properties of both bentonite and colloidal grades of fuller's earth are reduced greatly if the clay is heated too much. The temperature in dryers processing bentonite is likely to be approximately 800°C at the inlet, 100° to 200°C at the outlet, and 400° to 500°C in the main drying zone. The bentonite itself is kept at temperatures of less than 150°C (Ross, 1964). Temperatures used in processing fuller's earth range from 150° to 650°C. The lower part of the range is used for colloidal grades and the higher part for absorbent granules.

The dried clay is ground and sized in several ways. In some plants, rods in rotary dryers do much of the grinding, but most of the powdered product is ground with roll and hammer mills or other pulverizers, and screened. Most bentonite and much of the fuller's earth used is ground to approximately 90% finer than 200 mesh (US Standard sieve size). Some fuller's earth for special markets is reported to be 95% finer than 10-micrometer particle size. Granular grades of bentonite are also sold, and the wide use of absorbent granule-type fuller's earth requires the preparation of a coarse product. The preparation of coarse absorbent granules is, in effect, a beneficiation process, because much of the fine and medium-grained sand impurities in the fuller's earth are in the size fraction discarded.

Bentonite and some southern bentonite, in addition to being processed like other bentonite, are beneficiated by a hydroclassification process. In this process, the clay is dispersed in water and pumped into a multistage concentrating circuit where nonclay and other undesirable materials are separated and removed. The slurry is then passed through drum or spray-type dryers, and the concentrate is ground. A high-value material is prepared in one plant by centrifuging a dilute slurry.

Transportation: Several types of packaging are used for both bentonite and fuller's earth. For other than bulk shipments, multiwalled paper bags, some of which have plastic liners, are most common. Fiber drums are used for specialty products sold in rather small quantities. Metal drums of 100-lb capacity are required for some uses, particularly absorbent granules used aboard ships and where lengthy periods of storage or repeated handling are necessary. One French company uses the modern containerized method for export shipments (Anon., 1969). Most of the granules sold for animal litter are packaged in 10 to 30-lb paper bags, and packaging is a major item in the cost of the product.

The method of transporting bentonite and fuller's earth depends on use and location of markets. Most of the processed bentonite is shipped by rail in hopper cars, but boxcars and bulk trucks are also used. Bagged bentonite is commonly palletized for shipment by either rail or truck. Trains carrying only bentonite are used for large shipments to distant points and for overseas consignments. Ore carrier-type ships having bentonite as the only cargo are commonly used for Great Lakes and overseas shipments. The bentonite transported this way is only partly dried at the point of origin and is shipped semi-dried. This method makes it possible to load and unload it by bulk-handling equipment, avoiding the costs of bagging, but it requires further drying and grinding at or near the place used. Much of the bentonite used in pelleting taconite ore, as well as...
most of that sold in the European markets, is handled in this way.

Fuller's earth is transported in a similar manner, except that orders are not sufficiently large to permit trainload or some of the other bulk-handling methods. Though some fuller's earth is transported unbagged in special cars, most is bagged for rail transportation. Trucking is also used more extensively in the transporting of fuller's earth than for bentonite, because orders tend to be smaller and are delivered directly to the warehouses of distributors. Granules for this use are commonly delivered by truck to warehouses of the distributing chain store.

Synthetic and Organic-clad "Bentonite"

A plant (Fig. 6) operated by Baroid Div., NL Industries, Inc., at Houston, Texas, making synthetic mica-montmorillonite began production in 1970. An early announcement of this plant indicated that one of the products was hectorite (Anon., 1970). Published mineralogical reports related to the research on the development of this synthetic material refer to a randomly interstratified alumina montmorillonoid (Granquist and Pallack, 1967; Granquist, et al., 1972) and SMM, which stands for synthetic mica-montmorillonite (Wright, et al., 1972). The principal product made in 1972 was advertised in a company pamphlet as BARASYM SMM. It consists of small stacks of thin, parallel, irregular platelets, having an equivalent diameter on the order of 1000A and a thickness of about 10A. This material is recommended for use in catalytic cracking, hydrogenation/dehydrogenation, double-bond isomerization, and disproportionation, and it may be a base for reforming catalysts and a component in hydrocracking catalysts. As a petroleum-cracking catalyst, BARASYM SMM is reported to be intermediate in activity between silica-alumina and zeolitic catalysts, to have a high selectivity for gasoline, and product distribution similar to silica-alumina catalysts.

FIG. 6—Synthetic “bentonite” plant, Houston, Texas (courtesy Baroid Div., NL Industries Inc.).
The company's advertising pamphlet indicates it has typical properties as follows:

Appearance: White, free-flowing powder
Particle size: 20–80 micron microspheres
Density:
  Apparent: 0.6–0.7 g per ml
  True: 2.5 g per ml
Typical analysis: 48% SiO₂
  (as received)
  37% Al₂O₃
  2.6% NH₄
  1.6% F
  12.0% H₂O
Trace analysis:
  10 ppm Ni
  190 ppm Fe
  800 ppm Na
  100 ppm Ca
  250 ppm Mg
  0 ppm SO₃
Surface area: 110–160 sq m per g, dependent on calcination temperature
Saturation volume (calcined 1300°F)
  Ni sorption: 0.27 ml per g
  H₂ porosimeter, 50,000 psi: 0.62 ml per g (excluding macropore volume)
Cation exchange capacity: 1.5–1.6 meq per g
Accessible * surface acidity: 1.8 × 10⁶ sites per g

* To pyridine vapor at 200°C

Synthetic hectorite is also made in the United Kingdom by Laporte Industries, Ltd., and sold under the brand name Laponite CP (Green, et al., 1970). This material is purer than naturally occurring varieties, as it contains no fluorine. It is presumably suitable for some of the same uses that synthetic bentonite was developed for in the United States.

For several years an organic-treated bentonite has been on the market under the registered trade name Bentone (Grim, 1962). This product is processed in such a way that the original inorganic exchangeable ion on the bentonite is replaced by an alkyl amine organic cation. This reaction produces a hydrophobic clay because the inorganic ions that can be hydrated are removed, and a large part of the clay-mineral surface formerly capable of adsorbing water is coated by hydrocarbon chains. Organic-clad bentonites are used in making paint; to gel organic liquids; to produce greases having superior properties. For adherence to metal, ability to repel water, and resistance to high temperatures; and in other products.

Organic-clad bentonite is also made in the United Kingdom and France (Anon., 1970) and in Japan (Takeshi and Kato, 1969). Some of the Japanese product is sold under the brand name Nikkagel. It is prepared by treating bentonite with alcohol under pressure and heat followed by ion exchange with an organic amnonium salt. A product called Organite is prepared by further exchanging Nikkagel with an amine having a benzene nucleus.

Future Considerations and Trends

The overall demands for both bentonite and fuller's earth seem destined to increase at a rate approximately equal to the growth in Gross National Product. According to Cooper (1970), in the year 2000, production of bentonite in the United States is likely to be three to five times the 1968 amount. The growth rate in fuller's earth requirements will probably exceed the rate forecast for bentonite.

Both bentonite and fuller's earth are used in so many different products and in so many ways that there are many possible substitutes for specific uses, and both have lost markets to other materials in the past. One of the most obvious losses of fuller's earth to other materials occurred when the use of synthetic materials in petroleum refining increased before World War II, and more efficient methods of refining were introduced. Bentonite sales have also suffered mildly from the use of oil-based and specialty muds; however, bentonite is likely to remain the cheapest and most efficient material for mud in certain types of drilling for years to come. Bentonite is in some danger of a market loss which may be caused by a breakthrough in the use of another material for bonding taconite pellets. Though the proportion of bentonite added in taconite bonding is small, it is still a contaminant, and some type of bonding material that will burn off completely or even add heat in the steel furnace will continue to be sought.

The manufacture of synthetic hectorite and other montmorillonitelike mineral products in the United States and United Kingdom marks a technological breakthrough. Worldwide markets for organic-clad bentonite and washed or otherwise purified white bentonite for specialty products are also likely to increase with general economic growth and the development of new uses and products.

Rising costs of transportation and fuel are two of the major pressures on the bentonite and fuller's earth industries that are likely to have a significant influence on future trends. The cost spread between rail and ocean transportation is the principal reason for the loss to Greek producers of some of the Wyoming-type bentonite market for bonding taconite ore in eastern Canada. The comparatively low cost of ocean
transportation is also the primary motivation behind an overseas search for bentonite reserves near deep water. Progressive increases in fuel costs, particularly for the low-sulfur type required for ecological reasons, seem to be almost a certain forecast. Fuel shortages have caused temporary shutdowns of some plants, and problems related to fuel supply seemed ominous at the time this article was written.

Kaolin, Ball Clay, Halloysite, and Refractory Clay

Definitions and Classifications

Kaolin: The name kaolin is derived from the Chinese term Kauling meaning high ridge, the name for a hill near Jaucho Fu, China, where the clay was mined centuries ago. Apparently the first to use the name kaolinite for the mineral of kaolin were Johnson and Blake (1867). The term kaolin is now variously used as a clay-mineral group, a rock term (consisting of more than one mineral), an industrial mineral commodity, and interchangeably with the term china clay. The following mineralogical definition by Ross and Kerr (1931) is probably the most widely accepted one:

By kaolin is understood the rock mass which is composed essentially of a clay material that is low in iron and usually white or nearly white in color. The kaolin-forming clays are hydrous aluminum silicates of approximately the composition 2\(H_2O\cdot Al_2O_3\cdot 2SiO_2\), and it is believed that other bases if present represent impurities or adsorbed materials. Kaolinite is the mineral that characterizes most kaolins, but it and the other kaolin minerals may also occur to a greater or lesser extent in clays and other rocks that are too heterogeneous to be called kaolin.

When applied as a term for an economic clay commodity, the foregoing definition must be modified to include some indication of use and to account for the fact that most kaolin now marketed is beneficiated to improve purity and whiteness. The following definition will apply to further discussions of kaolin in this chapter. Kaolin is a clay consisting of substantially pure kaolinite, or related clay minerals, that is naturally or can be beneficiated to be white or nearly white, will fire white or nearly white, and is amenable to beneficiation by known methods to make it suitable for use in whiteware, paper, rubber, paint, and similar uses. The term is applied without direct relation to purity of deposit. Many very large kaolin deposits are essentially pure, and they require little concentration during preparation for market. Most are slightly off-color and require bleaching, and others contain as little as 10% clay that must be washed and concentrated to recover marketable kaolin.

China clay is an ancient term originating from the use of clay, later found to be kaolinitic, in porcelain tableware and art objects in China. This term will be used rarely in this chapter.

Ball Clay: Ball clay is a term apparently originating in the United Kingdom many decades ago from the mining practice of piling out a lump of clay, rolling it into a crude ball, and loading it into a horse-drawn cart or wagon. Ball clay is defined by the American Society for Testing & Materials (Anon., 1971a) as a secondary clay commonly characterized by the presence of organic matter, high plasticity, high dry strength, long vitrification range, and a light color when fired. Kaolinite is the principal mineral constituent of ball clay, and it typically makes up more than 90% of this type of clay. The minor differences between the light fired color required by this definition and the white required for kaolin provide little practical basis for distinguishing these two types of clay. Therefore, ball clay is actually a variety of kaolin, but it is treated as a separate type of clay because of its wide application in marketing and as a use term in the ceramic industries. Ball clay is used in the United States, United Kingdom, India, Republic of South Africa, and a few other countries. Similar clay or clay used in the same products as ball clay is included with kaolin or china clay in most countries.

Halloysite: Halloysite occurs in two forms; one has the composition \((OH)_2Si_2Al_2O_7\cdot 4H_2O\) and the other \((OH)_3Si_3Al_2O_7\cdot 4H_2O\). The hydrated form is generally a dense porcelainlike hard clay that dehydrates at surface temperatures or slightly above to a white or light-colored porous, friable, or nearly cottony-textured material. The dehydrated form is similar to kaolinite in composition and mineral structure, and the hydrated form has a c-axis spacing greater than that of kaolinite. The two forms of halloysite have caused considerable nomenclature problems. The system most commonly used now is to restrict the name halloysite to the hydrated form and to call the dehydrated form metahalloysite. However, some reports use the name endellite for the hydrated form and the name halloysite for the dehydrated form. As virtually all this hydrated will be used for the mineralogical Halloysite, kaolinite, and it is indicated that the name halloysite is accepted by clay industries organizations, and some organizations use it for various purposes.

The fusion refractory clays are listed in the lower cutures (Norton, 1926, Table 4). Table 4 contains the fusion temperatures of refractory clays.
all this clay below the surface occurs in the hydrated form, only the name halloysite will be used further in this chapter, except in the mineralogy discussion.

Halloysite, like ball clay, is a variety of kaolin, and it is included with kaolin in most production statistics. However, the term halloysite is accepted worldwide, and it is used in the clay industries, as well as by mineralogists, geologists, and soil scientists.

Refractory Clay: Refractory-clay includes several varieties of kaolinitic clay that are used in the manufacture of products requiring resistance to high temperatures. The qualities and properties of refractory clays are expressed in terms of pyrometric cone equivalents (PCE) which is a method of designating fusion points. Pyrometric cone equivalent is defined as the number of that standard cone whose tip would touch the supporting plaque simultaneously with that of a cone of the material being investigated, when tested in accordance with the Standard Method of Test for Pyrometric Cone Equivalent (PCE) of refractory materials (ASTM Designation C24) of the American Society for Testing & Materials.

The fusion points of products made from refractory clays range from just above PCE 19, the lower cutoff according to accepted definitions (Norton, 1968), to as high as cone 37 (Table 4). The refractory properties of kaolinitic clays are ordinarily classified, according to suitability for heat service, as low (PCE 19 to 26), moderate (PCE 26 to 311/2), high (PCE 311/2 to 33), and superduty (PCE 33 to 34). A few essentially pure kaolinitic clays have fusion points as high as cone 35, and some refractory kaolins and fire clays containing diaspor, boehmite, or gibbsite have PCE's as high as cone 37.

The principal types of clay included in the refractory clay are fire clay, kaolin, and ball clay. Definitions of refractory kaolin and refractory ball clay are the same as given for these two types of foregoing definitions, except that the adjective "refractory" is added to indicate use. The definition of fire clay used in this chapter is essentially the one by Norton (1968), which assigns this term to all clays that are not white burning and have a PCE above 19. The term fire clay, therefore, excludes most kaolin and ball clay because they burn white, but it does include kaolin and ball clay that are colored when fired. This classification of refractory clay as a group name and the threefold subdivision are by no means universally applied. Other reports, including earlier ones by the authors themselves, have used the terms refractory and fire clay interchangeably.

Kaolin

History and Uses: The sedimentary kaolins of the Coastal Plain of Georgia and South Carolina and the residual kaolins of North Carolina have been known since Colonial times. Smith (1929) quotes from Sholes in his chronological history of Savannah, "1741—Porcelain Clay was discovered in or near Savannah by Mr. Duchet, and china cups made." In 1767, Josiah Wedgwood sent Thomas Griffiths to Macon County, North Carolina, to send a shipment of English kaolins in Cornwall were available. In 1768 (Barton, 1966), the English kaolins in Cornwall were discovered, which virtually ended the mining of the Georgia halloysites for more than a century. In 1876 (Smith, 1929), the mining of the sedimentary kaolins of Georgia was started again by Riverside Mills of Augusta in Richmond County. Mining of the Georgia kaolins has been continuous since that time. In addition to the original pottery in Savannah, a second pottery was established near Bath, Aiken County,
thereby effectively lowers paper-production surface, imparting smoothness, gloss, brightness, other materials used in filling and coating. It is opacity, and printability (Bundy, et al., color picture magazines contains as much as Kaolin is less expensive than paper pulp and
sumer of kaolin (Fig. during Sherman's march to the sea (Lang et al., 1963a), and new uses are still being discovered. It is a unique industrial mineral because it is chemically inert over a relatively wide pH range, is white, has good covering or hiding power when used as a pigment or extender in coated films and filling applications, is soft and nonabrasive, has low conductivity of heat and electricity, and costs less than most materials with which it competes. Some uses of kaolin require very rigid specifications including particle-size distribution, color and brightness, and viscosity, whereas other uses require practically no specifications; for example, in cement, where the chemical composition is most important. The better grades of kaolin make up most of the tonnage sold and, of course, have the highest value. Many grades of kaolin are specially designed for specific uses, in particular for paper, paint, rubber, plastics, and ceramics.

The paper industry is by far the leading consumer of kaolin (Fig. 7), and approximately 50% of the total production is used in paper products. Much of the paper used in today's color picture magazines contains as much as 30% by weight of kaolin. Kaolin used in paper fills the interstices of the sheet and coats the surface, imparting smoothness, gloss, brightness, opacity, and printability (Bundy, et al., 1965). Kaolin is less expensive than paper pulp and thereby effectively lowers paper-production costs, and it is cheaper or more efficient than other materials used in filling and coating. It is inert to the other ingredients in paper, is retained well between the paper fibers, is available in large quantity, and the platy structure of kaolinite lends itself to the production of high-gloss papers. The low viscosity of kaolin at both high and low shear rates is a very important property, because at today's very high speed production rates the coating must be applied at high solids content and still give the correct coating thickness and opacity to the paper. High-quality paper coating kaolin flows readily when applied with very high speed coating equipment, giving the paper a smooth and even film.

The rubber industry uses large tonnages of kaolin as a filler or extender in both natural and synthetic rubber (Fig. 7). Kaolin is incorporated in the latex mix to improve properties such as strength, abrasion resistance, and rigidity; furthermore, it lowers the cost. Through the years, two terms, "hard-kaolins" and "soft-kaolins" (Klinefelter et al., 1943), have become commonplace in describing types of kaolin used by the rubber industry. The hard kaolin, though distinctly softer than flint kaolin or flint clay, is a very fine particle-size kaolin that tends to improve the tensile strength of rubber and its resistance to tear and abrasion. The principal products in which large quantities of the hard varieties are used are footwear and cable covers. Soft kaolin lacks the reinforcing properties of the hard kaolins and is used to lower elasticity and improve abrasion resistance, particularly in such products as floor tile and soft rubber goods.

Kaolin is used as an extender in paints because it is chemically inert, has a high covering power, gives desirable flow properties, is low in cost, is white, and reduces the amount of expensive pigment required. In addition, it has very excellent suspension properties and is available in a wide range of particle sizes which can be used in many types of paints. For example, coarse-particle kaolins are used in paints where a dull or flat finish is required, and fine-particle kaolins are used in high-gloss paints. Large quantities of calcined kaolin and water-beneficiated kaolin are used in interior flat wall paints and in metal primers. Water-beneficiated grades of kaolin disperse easily in water and are, therefore, particularly suited to latex paints. Some kaolin is chemically treated to make it organophilic or hydrophobic and thereby is suitable for use in exterior oil-base paints. Calcined kaolin, because of its resistance to abrasion and dry covering properties, is being used in increasingly large quantities by paint manufacturers.

SC, at an early date. This plant was destroyed during Sherman's march to the sea (Lang et al., 1940). However, kaolin mining was active again in Aiken County shortly after the Civil War and has continued with only minor interruptions until the present. South Carolina has ranked as the second leading kaolin-producing state for several decades. Kaolin mining in North Carolina started in 1888 in Jackson County (Parker, 1946), and in 1904, the earliest mines opened in the Spruce Pine district. The first kaolin operation in Vermont (Ogden, 1969) was in the early 1800s, and most of the product was sold in Troy and Albany, NY.

Production figures for kaolin from most areas in the late 1800s and early 1900s are difficult to trace. It is estimated that about 3 million tons were produced in Georgia before 1932 (Kesler, 1956), after which much better statistics have been available. In 1980, total production in Georgia alone was over 6 million tons, and South Carolina ranking second produced more than 657 thousand tons.

Kaolin has many industrial applications (Murray, 1963a), and new uses are still being discovered. It is a unique industrial mineral because it is chemically inert over a relatively wide pH range, is white, has good covering or hiding power when used as a pigment or extender in coated films and filling applications, is soft and nonabrasive, has low conductivity of heat and electricity, and costs less than most materials with which it competes. Some uses of kaolin require very rigid specifications including particle-size distribution, color and brightness, and viscosity, whereas other uses require practically no specifications; for example, in cement, where the chemical composition is most important. The better grades of kaolin make up most of the tonnage sold and, of course, have the highest value. Many grades of kaolin are specially designed for specific uses, in particular for paper, paint, rubber, plastics, and ceramics.

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Kaolin is used in...
Clays 615

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larger tonnages of both natural and kaolin is incorporated and improves properties of in addition, it has properties of and particle sizes which are desired by paint manufacturers. For example, in paints, kaolin is used as a reinforcing agent, and it makes the plastic more durable. Calcined and partially calcined kaolins are used as a filler in PVC wire insulation to improve electrical resistivity. In manufacturing glass-reinforced polyesters, kaolin has helped eliminate flow problems which hindered production of large products, such as automobile body parts and boat hulls. The kaolin actually results in a stronger, more uniform part or body. Plastics are a major area of future growth for kaolin products. They are

Calcined kaolin is an excellent extender for the leading paint pigment, particularly in latex types, and its use reduces costs and simplifies the formulation of the paint. Kaolin is used extensively as a filler in plastics. The desirable characteristics in plastics resulting from the use of kaolin include smoother surfaces, more attractive finishes, dimensional stability, and resistance to chemical attack. Manufacturers of polyvinyl chloride (PVC) use kaolin as a reinforcing agent, and it makes the plastic more durable. Calcined and partially calcined kaolins are used as a filler in PVC wire insulation to improve electrical resistivity. In manufacturing glass-reinforced polyesters, kaolin has helped eliminate flow problems which hindered production of large products, such as automobile body parts and boat hulls. The kaolin actually results in a stronger, more uniform part or body. Plastics are a major area of future growth for kaolin products. They are

used extensively in vinyl floor coverings, and surface-modified kaolin gives improved dispersibility in certain plastic systems, which will greatly increase their usage. Historically, kaolin was first used in ceramics, and this is perhaps still the best known application, even though the total tonnage sold for this use is small compared with that marketed for paper, paint, and rubber manufacturing (Fig. 7). It is used in the manufacture of whitewares, wall tile, insulators, refractories, and in some face brick where a white color is desired. Specifi-
pension properties, color, and water-release characteristics. Kaolin is also used in porcelain, again because of its excellent suspension characteristics and good color.

Kaolin has many other important applications, but in terms of tonnages required compared with the aforementioned uses, they are rather small. Although the following list is not complete, it gives an idea of the extremely wide range of products containing kaolin as a suspending agent, filler, extending agent, or a main constituent because of its chemical or mineral composition, whiteness, particle size, or other properties:

- ink
- adhesives
- insecticides
- medicines
- food additives
- catalyst preparations
- bleaching
- adsorbents
- porcelain enamels
- paint
- roofing granules
- sizing
- foundries
- linoleum
- floor tiles
- textiles

Production Specifications: Paper Filler and Coater—The most important specifications for kaolin used in paper applications are brightness, particle size and particle-size distribution, viscosity, and screen residue. Some purchasers also require tests of abrasiveness. The Technical Association of the Pulp and Paper Industry [TAPP] (Lyons, 1966) has given detailed information regarding the properties and test procedures for kaolin used in paper, and only brief descriptions of the more important tests will be outlined.

Brightness—This test consists of drying, pulverizing, forming a plaque, comparing with a standard of known brightness, and calculating the brightness measured at 457 millimicrons with a reflectance meter constructed, calibrated, and operated according to the requirements of The Technical Association of the Pulp and Paper Industry Standard T452M-48. This test must be very carefully done by an experienced and competent technician in order to obtain accurate and reproducible results. In general, a minimum brightness of 80% is required for filler clay and 85% for coating clays.

Particle Size—Many methods of determining particle size and particle-size distribution are used, but the most accurate is based on the Stokes principle. Size determinations can be made by the application of this principle, because settling rates in fluids are controlled by particle diameters when the attraction of gravity, densities of particles and fluids, shape of particles, and the viscosity of the fluids are identical. Coarse particles, therefore, settle more rapidly than finer ones, and determinations of a given particle size and distribution can be made by the time-rate principle. The time-rate principle is equally valid for settling by gravity or when settling is augmented by centrifugation. A rapid test for plant control consists of the preparation of a standard, dilute deflocculated slip of the clay in question, settling by controlled centrifugal force for predetermined short-time intervals under such conditions as to effect reproducible packing of the sediment, and measuring the apparent volume of sediment at each time interval. Typical particle-size analyses of filler and coating grades are shown on Fig. 8.

Viscosity—Flow properties of kaolin are very important to the paper coater because they affect the functioning of the coating operation as well as the final quality of the paper product. Two viscosity tests are used in the kaolin industry, one to measure high shear viscosity and the other to measure low shear viscosity. Standard procedures and conditions are rigorously followed in making these tests.

Screen Residue—Material held on a 325-mesh screen is regarded as grit or residue. A 100-g sample is thoroughly mixed and dispersed with a dispersing chemical. After carefully determining the weight and percent solids of the dispersed slip, the amount of residue retained on the screens can be accurately weighed and percentages calculated.

Filler for Paint and Plastics—In addition to several of the properties required for use in paper, the kaolin used in paint and plastics must meet certain electrical resistivity specifications. The resistivity test is designed to give an indication of the amount of residual salts that might be contained in the clay. The higher resistivity values reflect a low soluble-salt content. A certain weight of kaolin is added to a specified weight of distilled water. The suspension is boiled for 5 min and reweighed. The loss of distilled water conductivity is conductivity b.

For certain fineness-of-grit and pulp applications, kaolin is sold for paper coating clays rather than as a coating material. The fineness-of-grit measurement is made by the application of this principle, because settling rates in fluids are controlled by particle diameters when the attraction of gravity, densities of particles and fluids, shape of particles, and the viscosity of the fluids are identical. Coarse particles, therefore, settle more rapidly than finer ones, and determinations of a given particle size and distribution can be made by the time-rate principle. The time-rate principle is equally valid for settling by gravity or when settling is augmented by centrifugation. A rapid test for plant control consists of the preparation of a standard, dilute deflocculated slip of the clay in question, settling by controlled centrifugal force for predetermined short-time intervals under such conditions as to effect reproducible packing of the sediment, and measuring the apparent volume of sediment at each time interval. Typical particle-size analyses of filler and coating grades are shown on Fig. 8.

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Clays

After being used in the paper production, kaolin is used in the ceramic industry. The properties of kaolin are essential because they affect the slurry's viscosity and the suspension's stability. The measurement of slurry suspension viscosity is critical. The low shear viscosity is used to measure the suspension's stability. Typical standard procedures are followed in making the determinations.

For certain paint applications, the Hegman fineness-of-grind test specification is important. This test is intended to measure the degree of dispersion and consists of a fineness gage and a scraper. The gage is calibrated from 0 to 8, and the fineness is reported by numbers. The higher the number, the finer the particles and the better the dispersion. Some paint customers specify that a pigment or extender must be finer than a particular Hegman number.

Ceramics—The most important tests for kaolin sold for ceramic products are modulus of rupture, casting rate, pyrometric cone equivalent (PCE), fired color, and shrinkage. The measurement of strength of clay bodies is a basic requirement by the ceramic industry. The modulus of rupture (MOR) is the fracture strength of a material under a bending load. The MOR measurement is made on a long bar of either rectangular or circular cross section, supported near its ends; a load is applied to the central part of the supported span. ASTM has standard methods of test for MOR of ceramics.

Casting rate is important, and fine-grained bodies cast more slowly than coarse ones. Viscosity of a slip must be carefully controlled, for if it is too viscous the slip will not properly fill the mold or drain cleanly. Therefore, viscosity is measured and controlled on shipments of kaolin used in the casting process.

For certain applications, particularly for refractory purposes, the pyrometric cone equivalent (PCE) is measured. The pyrometric cone measures the combined effects of temperature and time (Anon., 1952; Klinefelter and Hamlin, 1957; Norton, 1968). The cones consist of a series of standardized unfired ceramic compositions molded into the shape of triangular pyramids. The sample of kaolin is molded into the standard cone shape and is heated along with several standard cones so that its end point can be determined in terms of an equivalent cone number. ASTM test method C24-56 gives the procedure of making this PCE test (see Table 4).

The fired color of kaolin is also important because some burns white and some burns buff or slightly pink. This is a visual test, and the test specimen, fired to a predetermined temperature, is compared with a standard.

Shrinkage is an important property. Ceramic articles undergo shrinkage at several different points in the manufacturing sequence. During drying, the article will shrink in varying amounts depending upon its composition and the amount of water present. The article shrinks further during firing. Therefore, it is important to know both the drying shrinkage and the firing shrinkage. Linear shrinkage and volume shrinkage can both be measured, al-
through linear shrinkage is more commonly reported (Jones and Berard, 1972).

Miscellaneous Uses and Products—Because of the many different uses of kaolin, the industry is plagued by many different purchase specifications and product requirements. Virtually none of these, except those outlined in foregoing discussions, have been standardized, and purchase specifications are frequently changed. However, the grades of kaolin now marketed by the major producers, those grades described in sales and advertising brochures, can, with or without blending, fulfill a wide variety of specifications.

Geology: Mineralogy—By definitions, the clays discussed in this section consist chiefly of kaolin-group minerals. The members of this group are kaolinite, nacrite, dickite, and halloysite. With the exception of the hydrated form of halloysite, which has somewhat more water, all these minerals have essentially the same composition. Their overall crystal structures are also similar, but minor differences in arrangements of ions in octahedral positions, stacking of unit layers, crystal habit, etc., are sufficient to cause the use of separate names. Kaolinite is, of course, the most common member of the group, and halloysite obviously forms halloysite deposits. The other two members of the group rarely occur in economic deposits.

Structurally, kaolinite consists of an alumina octahedral sheet and a silica tetrahedral sheet. These sheets form triclinic crystals. The theoretical structure formula of kaolinite is \((\text{OH})_2\cdot\text{Si}_4\text{Al}_2\text{O}_8\cdot\text{H}_2\text{O}\), and the theoretical composition is \(\text{Si}_4\text{O}_8\cdot46.54\text{%}, \text{Al}_2\text{O}_3\cdot39.5\text{%}, \text{and H}_2\text{O}\cdot13.96\text{%}\). There is relatively little ionic substitution in the mineral lattice, although there is evidence suggesting minor substitution of iron for aluminum in some kaolinite. The perfection or degree of ordering of kaolinite crystals varies considerably. By interpretation of X-ray diffraction data, Murray and Lyons (1956) have shown that the crystallinity of Georgia kaolin ranges from poorly ordered to very well ordered forms. Other investigators (Brindley and Robinson, 1946; Range, et al., 1969) have found similar variations in ordering in kaolinite from several localities. The more perfectly ordered forms of kaolinite commonly occur in hexagonal or subhexagonal crystals. Growth of crystals along the c-axis into accordionlike or vermicular forms are also common. Fig. 9 is an electron micrograph which shows both the hexagonal thin plates and vermicular stacks of kaolinite.

The clays described in this section contain, in their natural occurrence, a wide variety of mineral impurities. Georgia kaolin generally is 85 to 95% kaolinite, the remainder is mainly quartz, minor muscovite, biotite, smectite, illite, sericite, and traces of zircon, tourmaline, kyanite, and graphite. Kaolin deposits in Latah County, Idaho, contain considerable illite (Hoserman et al., 1960). Kaolinite and halloysite make up from 10 to 40% of residual deposits in the Spruce Pine district, North Carolina. The bulk of these deposits consists of angular quartz, muscovite, mica, and potash feldspar; tourmaline is also present (Bristow, 1969).

Occurrence—Most kaolin is soft and plastic when natural moisture is present or where water has been added to dried material: One way of describing the natural texture is by the colloquial phrase—a good whittling clay—which refers to the ease with which the clay can be carved with a knife. Dry kaolin is ordinarily friable, and a common but not a diagnostic test for it is its stickiness when touched to the tongue. Some types of kaolin, which have apparently been under considerable overburden or which contain introduced silica, are hard and are sometimes referred to as flint-kaolin. Though much more lithified than plastic varities, this so-called flint kaolin is softer than most flint clay referred to in the section on fire clay, which also consists of kaolinite.

Kaolinite and related clays occur in several different types of deposits. Many kaolin deposits throughout the world are in the form of tabular lenses and discontinuous beds in sedimentary rock. Most deposits of this type are of Cretaceous age or younger. The shapes and lateral extent of such deposits vary appreciably. Deposits as much as 60 ft thick are common in some districts, and bodies of kaolin are known to extend laterally for more than a mile. Extensive sedimentary deposits of this type occur in the Georgia-South Carolina kaolin belt (Anon., 1970), Arkansas bauxite region (Gordon, et al., 1958), and Lone district, California (Johnson and Ricker, 1948) [Fig. 10].

Residual kaolin deposits occur in weathered rock, and they are at or very near the surface, except where they formed during ancient weathering cycles and were later buried by younger rocks. Most residual kaolin deposits have formed from igneous rock. The age of kaolin formation is commonly controlled by the age of the present land surface rather than the age of the parent rock. Residual kaolin deposits are generally irregular and range from small lenses to large bodies which were formed during weathering cycles and were later buried by younger rocks. Most residual kaolin deposits have formed from igneous rock. The age of kaolin formation is commonly controlled by the age of the present land surface rather than the age of the parent rock. Residual kaolin deposits are generally irregular and range from small lenses to large bodies which were formed during weathering cycles and were later buried by younger rocks. Most residual kaolin deposits have formed from igneous rock. The age of kaolin formation is commonly controlled by the age of the present land surface rather than the age of the parent rock.
generally irregularly shaped and grade downward into the parent rock through partly altered weathered saprolite zones. They also commonly contain rounded boulders and irregular masses of fresh or only partly altered rock that were originally in the centers of joint blocks or otherwise protected from percolating water. Residual kaolin deposits occur in the Spruce Pine district, North Carolina (Parker, 1946); the Arkansas bauxite district (Gordon, et al., 1958); Latah County, Idaho (Ponder and Keller, 1960); Alberhill district, California (Cleveland, 1957); and elsewhere in the United States (Fig. 10). They also occur in many other countries and are particularly common in Czechoslovakia (Kuzvart, 1969) and Brazil (de Souza Santos and de Souza Santos, 1972).

Some kaolin deposits throughout the world occur in rocks that have been hydrothermally altered. Such deposits are ordinarily in irregularly elongate pods or pipelike bodies aligned along joints, faults, or other permeable zones that allowed movement of warm or hot aqueous solutions. Some deposits of this type also occur in altered tuffs and are bedded. As with the residual type, the age of hydrothermal kaolin formation is not necessarily related to the age of the host rock. Most hydrothermal clay deposits are probably no older than Tertiary, though some occur in rocks that are much older. Insofar as the authors are aware, deposits in the Little Antelope Valley, California (Cleveland, 1957), contain the only hydrothermal kaolin now mined in the United States. It is used for refractory clay. However, kaolin formed by this process occurs at many places in the western states, and deposits were formerly mined on a small scale in several mining districts.

Origin—The two fundamental geologic proc-

FIG. 9—Electron micrograph of Georgia kaolin showing hexagonal thin plates and vermicular forms of kaolinite.
esses that form most of the clay minerals of the kaolin group are weathering (Keller, 1964) and hydrothermal alteration (Sales and Meyer, 1949). These processes under certain conditions remove elements other than silicon, aluminum, oxygen, and hydrogen, the constituents of these clays. The clays form as the other elements are removed from preexisting minerals and possibly by the growth of new atomic arrangements from materials in solution. Though most kaolin minerals form in these ways, the origin of valuable deposits is quite another matter. Certainly, many of the scattered kaolins in western states formed by hydrothermal processes, but few such deposits have been significant sources of kaolin. In the Arkansas bauxite region (Gordon, et al., 1958) and in Latah County, Idaho (Hosterman, et al., 1960), are districts containing both transported clay and residual kaolin formed by weathering of igneous rock. In both districts, the kaolin grades downward through saprolitic zones into parent rock, which is nepheline syenite in Arkansas and granodiorite in Idaho. Also, in both districts, kaolin transported from the residual material occurs in sedimentary rocks—in marine shale in Arkansas and in lacustrine beds in Idaho. However, this explanation of origin is inadequate to account for all the kaolinitic clays in the regions containing these districts. The transported kaolin in Kansas is of Wilc type throughout a much larger area. Similarities, however, cannot all be related to type of kaolin deposit. Similarly, Valley and Ridge type depositions occurred in these districts. Probabilities were mainly of carbonate rock, based on the large deposits of feldspar in the areas enclosing the kaolin from the of the sinkholes.

Strange as it may be, the origins of these deposits are least understood by most geologists. However, others have investigated the kaolin or the material enclosing the kaolin to determine its origin. In the Valley and Ridge districts, the kaolin deposits have been transported from the enclosures of the sinkholes. One of the first geologists to investigate such deposits was Veatch (1909) who studied the deposits in Georgia. His conclusions were that the material enclosing the kaolin is a diagenetic deposit formed by the weathering of carbonate rocks. The greater part of...
Clays of kaolin deposits have been widely studied by many geologists and mineralogists. The origin of kaolin deposits, however, is still a matter of considerable debate. Some geologists believe that kaolin is derived from the weathering of feldspars and other aluminous minerals. Others believe that kaolin is formed from the decomposition of silicate minerals. Yet others propose that kaolin is derived from the alteration of carbonate minerals. The origin of kaolin deposits is still not fully understood and continues to be a topic of much research.

One of the first geologic studies of the Georgia kaolin deposits was by Ladd (1898). He described the kaolin deposits in Georgia and concluded that they were formed by the weathering of feldspar and other aluminous minerals. In contrast, Veatch (1909) concluded that the kaolin deposits in Georgia were formed by the weathering of ancient igneous rocks. Brooks (1927) suggested that kaolin deposits were formed by the alteration of carbonate rocks. Rogers (1937) proposed that kaolin deposits were formed by the weathering of metamorphic rocks.

The greater part of the Piedmont region was a land surface for a very long period of geologic time. Just before the beginning of the Cretaceous, the Piedmont region was uplifted and tilted southeast. Streams rapidly carried the weathered residue to the Cretaceous sea. Veatch postulated that an enormous quantity of sediment was dumped rapidly at the stream mouths, forming extensive sand flats. Fine clay particles were deposited in nonpersistent and lenticular beds of white clay in the deeper and quiet waters near the stream mouths. He considered the Tuscaloosa in Georgia a nonmarine deposit.

Smith (1929) concluded that the basal Cretaceous sediments in Georgia were Upper Cretaceous and correlated them with the Middendorf Formation of eastern South Carolina. Smith believed that Veatch's explanation of origin was essentially correct, except that he agreed with Neumann (1927) that the kaolin was deposited in freshwater. Cooke (1943) assigned the basal Cretaceous sediments to the Upper Cretaceous under the name Tuscaloosa, which is still used. Kesler (1963) believes that in east-central Georgia there is no basis for subdividing the Upper Cretaceous, and he found that the kaolin lenses have no preferred stratigraphic position within the formation. Kesler theorized that feldspathic sands were deposited as delta sediments above sea level and were subsequently altered to kaolin. The kaolin was separated from the coarser sediment and deposited at points of lowest elevation. As the kaolin accumulated in the ponds, sand was washed from the margin into and over the edge of each deposit, forming gradational and interfingered contacts.

Bates (1964) reviewed the origin of the Georgia kaolins and summarized the mineralogic and geologic data, some of which support a marine origin and some a freshwater origin. Hinckley (1961) suggested that face-to-face flocculation of kaolin particles in a marine environment would result in the properties that distinguish a so-called "hard" kaolin, whereas edge-to-face flocculation in freshwater would produce a less dense, "soft" clay. Buie (1964) proposed the possibility that volcanic ash was first altered to montmorillonite and then to kaolinite. This is a radical departure from previously proposed theories of origin, and much more detailed field and laboratory work must be done before this hypothesis can be adequately tested. Jonas (1964) concluded from a detailed petrologic study that the originally deposited sediment was muscovite, feldspar, and quartz, and that postdepositional alteration and
Recent studies of spores, pollen, and invertebrate fossils in and associated with kaolin indicate that many of the deposits thought to be Cretaceous are of Eocene age (Buie and Fountain, 1967; Cousminer and Terris, 1972; Scudder, 1969), a possibility suggested by Eargle (1955). The first announcement of the Eocene age for any of the deposits was by Buie and Fountain, who on the basis of paleontological evidence established the presence of middle Eocene strata beneath some of the commercial kaolin deposits and above others. In one of the studies, Cousminer and Terris (1972) concluded through palynological work that some, if not all, of the sedimentary kaolin is middle Eocene in age. Results of palynological studies by R. H. Tschudy of the US Geological Survey on samples collected by Patterson have confirmed that some of the kaolin deposits are of Late Cretaceous age or older, and that some are no older than Claiborne (middle Eocene). Tschudy's work also revealed that sand beds of Paleocene age are present in the kaolin belt. This raises the possibility that some of the kaolin deposits may be of Paleocene age and that kaolin deposition took place during several different intervals of geologic time.

The recent findings on the range in age of Georgia kaolin deposits require some caution; the deposits have had a very complex history and origin, and the theories advanced to date do not provide adequate explanations. Probably the purity of the kaolin is the result of some sedimentary winnowing process, an idea favored by Kesler (1963) and others, as evidence now available suggests that the ultimate source was aluminum silicate minerals in the claystone rocks of the Piedmont region. The major mining and beneficiation activities are in Twiggs, Wilkinson, and Washington Counties, Georgia, and in the vicinity of Aiken, SC. Large reserves of fine-particle-size kaolin have been discovered in the last 10 to 15 years in the vicinity of Wrens, GA, which is in the east-central part of the belt. Other reserves are scattered throughout the belt. Very large potential resources of off-color high-iron clay and deposits under overburden that is too thick to be stripped profitably, at present, are scattered throughout the seaward parts of the belt.

**Major Kaolin-Producing Countries**

**United States—Georgia-South Carolina Kaolin Belt**—The principal reserves and the major kaolin-producing centers in the United States are in a belt extending from Twiggs County in the central part of Georgia to Lexington County in west-central South Carolina. This same belt extends southwest from Macon to Andersonville, GA (Zapp, 1965), and west to Eufaula, AL (Warren and Clark, 1965). The Andersonville and Eufaula districts contain appreciable kaolin resources, but both are centers of production of refractory kaolin and refractory bauxite materials, and no kaolin, as defined in this report, is now produced in either district.

The deposits in the Georgia-South Carolina belt occur in sedimentary rocks a short distance seaward from the crystalline rocks of the Piedmont region. The major mining and beneficiation activities are in Twiggs, Wilkinson, and Washington Counties, Georgia, and in the vicinity of Aiken, SC. Large reserves of fine-particle-size kaolin have been discovered in the last 10 to 15 years in the vicinity of Wrens, GA, which is in the east-central part of the belt. Other reserves are scattered throughout the belt. Very large potential resources of off-color high-iron clay and deposits under overburden that is too thick to be stripped profitably, at present, are scattered throughout the seaward parts of the belt.

**Alabama—Kaolin is mined from the Tuscaloosa Group in Marion County, Alabama (Clarke, 1964). It has been mined in this area for 40 years, and approximately 1 million tons has been shipped. This kaolin is relatively pure and is easily beneficiated by removing quartz and mica. Most of the production from this district has gone into various ceramic products.**

**California—Filler-type kaolin is mined and processed near Ione and Bishop, CA. The Ione clay is sedimentary in origin (Bates, 1945), whereas the kaolin near Bishop is hydrothermal (Cleveland, 1957).**

**Florida—The Florida kaolin is found in sand and gravel deposits of the Citronelle Formation (Calver, 1949). The formation ranges from 20 to 55 ft in thickness, and the recoverable kaolin averages about 15%. The only operating mine is in Putnam County. Most of the production is sold to the ceramic industry. Recently, these kaolinite sediments were named the Fort Preston Formation and dated middle Miocene (Calver, 1949).**
Idaho—Filler-type kaolin is mined and beneficiated in Latah County, Idaho. These deposits occur as residual weathered products of granodiorite and as lacustrine sediments (Hosmer et al., 1960; Ponder and Keller, 1960). Mineralogical analyses show that some of the deposits contain halloysite in addition to kaolinite and that the deposits are variable, some being almost all kaolin and others containing kaolin, quartz, orthoclase, mica, and minor quantities of other minerals.

North Carolina—Near Spruce Pine, a primary kaolin (the term primary kaolin is used here as commonly applied in the kaolin industry for hydrothermal-type deposits and for residual deposits of kaolin formed by in-situ weathering) altered from pegmatite and aplite (Parker, 1946) is mined and beneficiated. This kaolin is a mixture of kaolinite and halloysite and is used primarily by the ceramic industry. These deposits generally contain approximately 40% kaolin and halloysite, so that the mica, quartz, hornblende, and other minerals must be removed by wet beneficiation methods to produce a usable product.

Texas—Near Kosse, Texas, a kaolin deposit of early Eocene age in the Wilcox Group is mined and beneficiated as a filler and ceramic clay (Fisher et al., 1965). Pence (1954) described these deposits as nonmarine in origin. They contain 40 to 70% quartz, and the kaolin is a byproduct of a glass-sand operation.

Other States—Kaolin has been mined in the past or has been reported present in commercial quantities in Arkansas (Tracey, 1944), Illinois (Grim, 1934), Minnesota (Parham, 1970), Mississippi (Conant, 1965), New Mexico (Glassmire, 1957), Vermont (Ogden, 1969), and Virginia (Ries and Sommers, 1920).

Resources/Resources of kaolin in the United States of a quality equal to or better than the lower grade clay now mined are at least 1 billion tons. The one grade of kaolin about which there is concern for long-range supply is the very high grade fine-particle-size white clay suitable as a paper coating and for certain other speciality uses (Buie, 1972). Reserves of this type of clay probably total 100 to 200 million tons. Potential resources of kaolin, including discolored and very sandy clay and that below more overburden than can be profitably stripped at present, are several times the estimated reserves.

United Kingdom—The United Kingdom is second only to the United States as a producer of kaolin or china clay and is the largest exporter of kaolin in the world (Anon., 1972g). China clay is the United Kingdom's chief export, and almost the entire output comes from the St. Austell area of Cornwall. Historically, the china clays in Cornwall were discovered by William Cookworthy (Barton, 1966) in the mid-1700s to be suitable for making porcelain. In Cornwall, an extensive region of kaolinized granite has been formed by hydrothermal alteration of feldspar (Bristow, 1969). The granite masses were emplaced in Permian time and are now exposed over large areas of Devon and Cornwall. The china clay deposits typically occur in funnel or troughlike bodies narrowing downward. Hot acidic solutions are thought to have migrated upward, guided by structural weaknesses such as faults and joints, and then to have been trapped under a roof of relatively impermeable rock. The hot solutions attacked the granite, altering the feldspar and mica to kaolinite. Quartz, tourmaline, and mica are the principal impurities. Drilling has shown kaolinite to exist at depths of more than 800 ft (Bristow, 1969).

In most places, the clay can be mined using high-pressure water jets, but sometimes blasting or ripping is required to loosen the rocks. Selective mining is very important because of variability in the various deposits. Much blending is done to produce a uniform product. As the rock face is washed, the slurry containing the kaolin in suspension flows to the lowest point in the pit. The slurry is then pumped into spiral classifiers which remove the coarse material. After this initial classification, the slurry is pumped to the surface of the pit where hydrocyclones remove finer sand and mica particles. The slurry is then thickened in large-diameter tanks. A series of refining tanks is used to remove the heavier coarser particles. After primary classification, the slurry is fed to centrifuges to separate the remaining kaolin from the filler grade. The kaolin is dewatered by filter presses and is dried. Two new processes have been designed—the tube filter press (Clark, 1968), which utilizes extremely high pressures and produces a relatively dry filter cake that needs little if any additional drying, and a process catalogued as micromineral separation (British Patent No. 1,222,508), which produces a rather clean pure kaolin.

More than 2.7 million tons of kaolin were produced in England in 1970, of which 2.1 million tons were exported (Anon., 1972f). The exports are handled through the ports of Par and Fowey. The kaolin is transported to port by rail or truck. Most ships that transport ka-
Kaolin is produced in several countries around the world. Some of the major producing countries include:

- **United States**: Kaolin deposits are found in several states, with the largest deposits located in Florida. The kaolin is used primarily in the paper, ceramic, and rubber industries. In recent years, the US has been a major producer of kaolin, with production reaching over 100 million tons annually.

- **China**: China is one of the largest producers of kaolin in the world. The country has significant deposits of kaolin, and production is mainly used in the ceramic and paper industries.

- **Brazil**: Kaolin deposits in Brazil are among the largest in the world, with production reaching several million tons annually. The kaolin is used in the ceramic, rubber, and chemical industries.

- **Europe**: European countries such as Germany, France, and Austria are significant producers of kaolin. Kaolin is used in the ceramic, paper, and construction industries.

- **Russia**: Russia is another major producer of kaolin, with production reaching millions of tons annually. The kaolin is used in the ceramic, refractory, and rubber industries.

- **Other Countries**: Kaolin is also produced in various other countries, including Australia, Japan, and South Korea.

The production of kaolin varies significantly from year to year, and the demand for kaolin is expected to increase in the future due to growing demand in various industries.
granitic and metamorphic rocks (Holzer and Wieden, 1969). Most of this kaolin is used in the ceramic industry and as filler in the paper and rubber industry. In 1966, more than 450,000 tons were mined in Austria, but less than 100,000 tons of this was processed using wet beneficiation techniques.

**Bulgaria**—Sedimentary kaolin deposits of probable Pliocene age occur in northwestern Bulgaria (Karanov, et al., 1969). The individual deposits are small because the kaolin is associated with sand which fills sinkholes in a karst area underlain by Lower Cretaceous limestones. The average kaolin content in these sands is about 18 to 25%. The best kaolin has an iron content of 0.6 to 0.8%. The kaolin is used locally in the ceramic and paper industries.

**Czechoslovakia**—Czechoslovakia is the principal producer of kaolin in Eastern Europe. The major deposits are in the vicinity of Karlovy-Vary, Plzen (Pilsen), and Podborany in west Bohemia (Kuzwart, 1969). The kaolin is primary, is of high quality, and is used for the production of fine ceramics, paper, rubber, and refractories. More than half a million tons has been mined, and by 1975, the annual production will probably be as much as 1 million tons. Reserves are estimated to be more than 1.5 billion tons (Kuzwart, 1969).

**Denmark**—A small tonnage of primary kaolin is mined on the Island of Bornholm primarily for the Danish ceramic industry in Copenhagen (Almeborg, et al., 1969). Most of the output goes into the manufacture of low-durcina refractories and glazed heavy-clay products. The quality of the kaolin is not high enough to be used in whitewares or as filler for paper.

**East Germany**—Both primary and secondary kaolin deposits are worked in East Germany (Stör, et al., 1969). The kaolin is mined from an area north of Bautzen, Dresden, and Colditz. The iron content of the various commercial deposits ranges from as low as 0.2% to as high as 2%. Most of the kaolin is used for ceramic purposes, but shipments for paper and rubber filler are increasing. Reserves are estimated to be considerably more than 100 million tons.

**France**—Many small companies produce kaolin from districts in Brittany and around the Massif Central in central France. The deposits in Brittany are of approximately the same age as those in Devon and Cornwall in England (Anon., 1972f). In Brittany, the deposits are all primary in origin: and the deposits around the Massif Central are both primary and secondary (Damiani and Trautmann, 1969). About 80% of the French production is from Brittany and is near the coast. Production is more than 250,000 tpy. Most kaolin is used by the ceramic industry, but its use as a filler for paper, paint, and rubber is increasing because of improved processing techniques now being implemented. France imports about 250,000 tpy, mainly from England and the United States to meet its requirements for kaolin.

**Greece**—Low-grade deposits of kaolin suitable for use in cement, ceramics, refractories, and paper filler occur on the Aegean islands of Milos, Polyaigos, and Mytilene (Anon., 1972f). Reserves are small and production is limited.

**Hungary**—Most of the commercial kaolin deposits in Hungary are confined to an area in the northeast, in the Tokaj Mountains. These deposits are primary and have been derived from rhyolite (Varju, 1969). Secondary kaolin-bearing sandstones are mined and washed at Sarisap in the Visegrad Mountains west of Budapest. The output is small, probably less than 60,000 tpy and is used in ceramics, paper, rubber, and plastics. Reserves are relatively small, so that the kaolin industry in Hungary will probably continue to produce primarily for domestic usage.

**Italy**—Both primary and secondary kaolin deposits are mined in Italy, primarily for the ceramic industry. Production is small and has never reached 90,000 tpy (Moretti and Pieruccini, 1969). The most important areas are in northwest Italy near Brella, on southern Sardinia, and near Rome.

**Poland**—In the Lower Silesia area of Poland southwest of Wroclaw, primary kaolin derived from granite and gneiss is mined for local consumption mainly for the ceramic industry (Anon., 1970h; Gawrons and Kozydral, 1969). Reserves of individual deposits range from 2 million to more than 10 million tons, and total reserves are indicated to be several tens of millions of tons.

**Spain**—Spain has the fourth largest production of kaolin in Western Europe; in 1970, the total was 285,000 tpy (Anon., 1972f). By 1976, according to the National Mining Plan, the production will be more than 500,000 tpy. Both primary and secondary deposits are mined.
in Spain (Martin Vivaldi, 1969). The deposits are widely scattered, but the commercially important production is concentrated in the northwest near Galicia-Asturias and in the east near Cuenca-Teruel-Valencia. The primary deposits of Galicia were formed by the hydrothermal alteration of mylonitized granite; reserves exceed 300 million tons. The secondary deposits in eastern Spain are Cretaceous in age and are principally kaolinitic sands ranging from 10 to 20 m in thickness. Reserves are estimated to be more than 1 billion tons. Most of the production is used by the ceramic industry, primarily in refractories, but as beneficiation techniques improve, more will be consumed in the paper, paint, rubber, and other industries that need filler clays.

WEST GERMANY—The largest kaolin mining district is in the townships of Hirschau and Schnaittenbach in Bavaria (Anon., 1972f). The deposits are sedimentary in origin, derived from decomposed granite in the Nnab basin mountains, and are Triassic in age. These deposits consist of a mixture of quartz, feldspar, and kaolin and are about 40 m thick. The material is wet processed to recover about 10 to 20% kaolin, and the quartz and feldspar are also salable products. Because of the high content of quartz and feldspar, sophisticated hydrocyclone-processing stages are used to make very precise particle separations (Anon., 1972f). Other areas in West Germany where kaolin is worked are Obermenzen near Frankfurt, Hesse, and Westphalia (Lippert et al., 1969).

OTHER COUNTRIES—Small tonnages of kaolin are produced in Romania, Sweden, Portugal, Yugoslavia, and Belgium (Anon., 1973; Maikovsky and Vachtl, 1969b).

AFRICA—REPUBLIC OF SOUTH AFRICA—The kaolin deposits of South Africa have been derived from the weathering of granite, shale, and tillite (Coetze, 1969). Kaolin is mined near Capetown, Grahamstown, and Durban. With the exception of the large deposit of altered tillite near Grahamstown (Murray and Smith, 1973), deposits are small but of good color and quality. The Grahamstown deposit is very large, with reserves in excess of 50 million tons, but the quality ranges from excellent to very poor and it changes in very short intervals both horizontally and vertically. Approximately 50,000 tons are used locally in South Africa, the ceramic industry taking more than 50% of the production. Other uses include insecticides, rubber, paint, plastics, and pharmaceuticals. The large deposit at Grahamstown could be potentially valuable in the future as advanced beneficiaiton techniques become available and water supply to the area is improved. A severe water-supply problem for wet beneficiaiton of kaolin exists throughout South Africa.

SWAZILAND—Kaolin deposits of economic importance are found in the Malilangatsha Mountains of the Manzini district (Hunter and Uri, 1969). Kaolinite dikes ranging in width from 3 to 10 m, 75 m in depth, and as much as 620 m in length have been studied. The kaolin ranges from white to pale red, depending on the iron content. The entire production of some few thousand tons is exported to South Africa.

OTHER COUNTRIES—Other African countries having minor kaolin production include Angola, Arab Republic of Egypt, Ethiopia, Kenya, Nigeria, Tanzania, Malagasy, Mozambique, and Morocco (Anon., 1973; Maikovsky and Vachtl, 1969c). The deposits in the Pugu Hills district near Dar es Salaam, Tanzania, are among those having economic potential. The kaolin is in upper Tertiary sandstone which is 30% white clay (Harris, 1969). Attractive features of these deposits include a location only 50 km from deep water and a possible glass sand coproduct. However, an attempt in the early 1950s to develop and export this kaolin failed.

ASIA—SRI LANKA—The best known kaolin deposit on Sri Lanka is the Boralesgamuwa field, south of Colombo. The kaolin is probably Pliocene or Pleistocene in age, is sedimentary, and occurs in layers and pockets 4 to 19 ft thick (Pattiaratchi, 1969). The percentage of kaolin ranges from 20 to 85, and the major impurity is quartz. The kaolin is used for ceramics, paper, rubber, paint, and as an insecticide carrier. The production is small, about 3000 tpy, and the estimated reserves are about 8 million tons.

INDIA—Kaolin and related clay materials are mined in many locations in India (Arogyaswamy, 1968). The major producing area is in the vicinity of Chaibasa. The deposit mined in this district occurs in weathered granite. High-quality kaolin is also produced in the vicinity of Kundra, Chattanur, and Quilon, Kerala. The kaolin in this region occurs in altered feldspathic granite, and the altered zones are as much as 10 m thick.

INDONESIA—Large residual kaolin deposits altered from granite are known to occur on the islands of Belitung and Banka (private communication). Although the deposits are large, little is known about the quality of the kaolin. There are small wet-processing operations which produce a small industry in Indonesia.

IRAN—Large primary kaolin deposits occur in the central part of the country. The deposits are found in the vicinity of the Persian Gulf and extend towards the Caspian Sea. The kaolin is of Cretaceous age and is derived from the weathering of limestone. The kaolin is used for ceramics, paper fillers, and calcined diatomaceous earth. The production is about 30,000 tpy.

PEOPLES REPUBLIC OF CHINA—Kaolin is used extensively in China, particularly in the provinces of Yunnan and Szechuan. The kaolin is of Mesozoic age and is derived from the weathering of granite. The kaolin is used for ceramics, paper fillers, and calcined diatomaceous earth. The production is about 30,000 tpy.
which produce China clay for the ceramic industry in Indonesia.

**Iran**—The largest kaolin deposit in Iran is in the central part of the country near Simiron (Khadem, 1969). This deposit is the result of deep weathering at a diastem in a Cretaceous limestone sequence. The material is used for fine ceramic and refractory purposes. The reserves are about 15 million tons.

**Japan**—Large primary and secondary kaolin deposits occur in Japan (Fuji, Okamo, and Shimazaki, 1969). The deposits are scattered throughout the islands. The primary deposits were formed by hydrothermal alteration of volcanic and granitic complexes and from in-situ weathering of granite, pegmatite, and volcanic rock. The secondary deposits are lacustrine, of lower Pliocene age, and range from 20 cm to 20 m in thickness. About 200,000 tpy is produced in Japan (Anon., 1972f). The reserves in many deposits range from 5 to 20 million tons.

**Korea**—Primary and secondary kaolins occur in Korea (Heikes and Kim, 1965). Both dry and wet beneficiation methods are used to process the kaolin for the ceramic, refractory, paper, and rubber industries. More than 100,000 tons are mined for domestic and export markets; over half of this is shipped crude to Japan for use as paper filler. The largest deposits, consisting of mixtures of kaolinite and halloysite, are in the Hadong-Sanchong area of southernmost Korea.

**Malaysia**—Residual kaolinite altered from granite is being mined and wet processed to make paper-filler clay (Anon., 1970f) east of Kuala Lumpur. The reserves are large, but present production is only about 5000 tpy.

**Peoples Republic of China**—Kaolin not only was used first in China, but advertisements in recent trade journals indicate that it is still being mined on a large scale and is available for export. Historically, deposits in the Ching-Tae-Chen district in Fuliang, Kiangsi Province, were the principal source of kaolin used in making fine ceramic ware (Pai, 1945). These deposits are associated with Ordovician and Silurian phyllite. The clay is mostly light gray to white, and it is 70% pure kaolinite. Presumably, this district is still in production, but this was not verified. Other kaolin-producing regions in China include Singtze, Loping, Yukan, and other districts in Kaingsi Province, and Tzuhnein, Kaiying, Fengyn, and Chingsing, Hopeh Province. Kaolin in deeply weathered granite occurs at several localities in Kwangtung Province which surrounds Hong Kong. This kaolin from granite may be the clay advertised for export because it is much closer to the ocean than most other deposits.

In addition to the kaolin mentioned in the foregoing paragraph, kaolinitic clays associated with diaspore and bauxitic clays in Carboniferous, Permian, and Mesozoic coal measures occur in Szechuan, Honan, Kupel, and Fukian Provinces and elsewhere. Several of these clays are called kaolins and are used in ceramic products. Residual kaolin formed by the weathering of arkose sandstone occurs in Szechuan Province, and deposits formed from weathered feldspar in granite and pegmatite occur at several places in China.

**Philippines**—Philippine kaolin deposits are primary and are generally small and scattered. Most are hydrothermal in origin, although one deposit called Bukidnon is believed to have formed from in-situ weathering of a dacite (Comski, 1969). The major deposits are on Luzon and Mindanao. The bulk of the kaolin is used in refractories, tiles, and sanitary wares. Very little is used in the paper and rubber industry. The reserves are limited and transportation is costly; these factors and the variable quality of the kaolin make the mining operations very marginal.

**Turkey**—Both primary and secondary kaolin deposits are mined in Turkey, primarily for the Turkish ceramic industry. Approximately 100,000 tons of kaolin are used annually in Turkey by the ceramic industry (Jeyhan, 1969). Reserves, estimated at 2.5 million tons, are mainly in the western half of the country.

**Other Countries**—The production of kaolin has been reported in recent years (Ampian, 1973) in Pakistan, Taiwan, Thailand, and South Vietnam.

**Oceania**—Australia—Most of the kaolin deposits in Australia are primary and have been formed as a result of deep weathering of both silicic and mafic rocks (Gaskin, 1969). Secondary deposits in Western Australia are associated with the coal measures of Cretaceous age. Some of the Australian kaolin is very white and can be used readily as filler and for ceramic purposes (Anon., 1970g), but the viscosity of almost all the kaolin is very high,
which prohibits its use for paper coating. The bulk of the kaolin produced is used for refractories; the rest is consumed by the ceramic, paper, paint, plastics, and rubber industries. Although no precise estimates of reserves have been made, the total amount of kaolin in Australia is known to be very large. At present, more than 100,000 tons is processed in Australia primarily for local consumption, although some is being exported to Japan as paper filler. Most of the deposits mined are within 200 km of the major cities of Melbourne, Sydney, Adelaide, and Perth. Extensive exploration for kaolin is being carried out in Australia by several major companies, primarily because of the lucrative Japanese export market.

New Zealand—The only kaolin being produced in New Zealand is in the Northland some 120 km north of Auckland (Bowen, 1969). The deposits are hydrothermal and are mixtures of kaolinite and halloysite. Reserves are estimated to be approximately 20 million tons. The kaolin is wet beneficiated for use as a ceramic whiteware component and as filler for paper and paint. The kaolin is very bright and white but has a high viscosity and is somewhat abrasive, which prohibits its use in paper coating. At present, the entire output of some 5000 tpy is utilized in New Zealand.

Exploration, Evaluation

Exploration in the United States: The principal productive deposits of kaolin were found in the Carolinas and Georgia in the late 19th and early 20th centuries. Most discoveries were in outcrops in stream beds and road cuts. Today, exploration is carried out in geologically favorable areas, taking into account topography and elevation. Geologic and topographic maps, if available, and aerial photographs are used to lay out exploration drill-hole patterns. Most exploration holes are drilled to depths of as much as 200 ft and on 400- to 800-ft centers. Many deposits were missed in the past because only random spot drilling instead of pattern drilling was used. Also, because drilling was limited to 50 or 60 ft, many good deposits at greater depths were not discovered. Auger or fishtail drills are used to the top of the kaolin bed, and then a special core barrel is used to core the kaolin. Cores are difficult to recover, and special care by expert drillers is necessary to get good core recovery. In many areas, two or three kaolin beds separated by sand are penetrated where drilling is as deep as 200 ft.

Many geophysical methods of exploration for kaolin have been attempted, but to date none has been successful (Gross, 1960). Geochemical techniques also have been unsuccessful. The only positive method to locate and delineate kaolin deposits to date is by pattern drilling.

Evaluation of Deposits: After coring the kaolin and recording the thickness of the various strata above the kaolin and the thickness of the kaolin bed, a large-scale map is prepared. On this map, the drill holes are located and the thickness of the overburden and the kaolin are recorded. The cores are sent to the crude evaluation laboratory where the kaolin is prepared and tested.

The cores are cleaned and divided into sections 2 ft or less in length for testing. The reason for splitting the cores into short sections is to be able to spot any lens or section that may be off-color, have high grit or high viscosity, or not meet specifications in some way. The 2-ft sections are dried and pulverized. The pulverized material is then evaluated using the following tests for paper-type kaolin:

1) Percent grit or screen residue
2) Particle-size distribution
3) Low shear viscosity
4) High shear viscosity
5) Brightness
6) Leachability

Grit percentage is determined as explained in the section on end uses and specifications and is an important crude evaluation test. A good rule of thumb is that as much as 5% grit can be handled easily using air-flotation techniques. Much higher percentages of grit can be handled using wet beneficiation methods, but the higher the grit percentage the lower the recovery of kaolin and the higher the cost. Normally in the United States, a maximum of 10 to 15% grit is set for the upper limit of grit percentage, but if the kaolin is of unusually high quality, a higher grit percentage can be tolerated.

Particle-size distribution is important because from this test the percent recovery of coating and filler clays is determined. For many years an important delineation point has been the percent of particles less than 2 micrometers in size (Lyons, 1966). This percentage can vary from as low as 50% to as high as 90% in the Georgia deposits. This is an important test because brightness properties are defined in terms of particle size and distribution. A refractory product requires the particle size to be uniform.

Leachability is another test to determine that the kaolin is suitable for its intended use. The leachability test is used to determine whether the kaolin contains substances that may be harmful to the environment or to the consumer.

Air-Float Characteristics

For air-float clay, the following characteristics are determined: floatability (the percentage of particles that float in air), sinkability (the percentage of particles that sink in water), and the median size of the particles.

After all the tests are completed, the overburden and the core samples are examined to determine the quality of the kaolin. The results of these tests are then used to determine the best method of processing the kaolin and the type of products that can be produced from it.
of sand are pent.

After coring the thickness of the overburden is determined and the kaolin present to the crude kaolin is prepared.

Both low shear and high shear viscosity tests are run on the degritted crude clay and on the coating clay fractions. The upper limit of low shear viscosity that can be tolerated is 800 cps at 10 rpm and a high shear of 300 rpm at 1800 reciprocal seconds. The low shear viscosity is a measure of thixotropy, and high shear viscosity gives an indication of dilatancy (Murray, 1970).

Brightness is measured on the degritted crude clay and on the coating clay fractions. For No. 2 coating clay (80% finer than 2 micrometers) a minimum brightness of 85.5% is required, and for No. 1 coating clay (92% finer than 2 micrometers), 87.0% brightness is required. Brightness determinations are made following procedures of TAPP1 Standard T646.

Leachability is measured on the coating clay fractions to determine the ultimate brightness that can be attained using standard reducing and oxidizing leach procedures. These determinations are very important because they establish the extent of treatment and whether the kaolin can be utilized alone or must be blended to meet brightness specifications.

For air-float clays only grit and brightness are determined. For ceramic clays, grit, brightness, green and dry strength, and fired color are determined. Chemical analyses for iron and alumina are commonly required for kaolin used in a refractory product. Other factors that can be important are the particle shape, pH, percentage of particles less than 0.25 micrometers in size, percentage of nonkaolin minerals, particularly smectite, in some cases total surface area, and the quantity of dispersing agent necessary to attain the lowest viscosity at 71% solids.

After all the tests are performed and evaluated and the overburden thicknesses and the thicknesses of the deposit have been determined, a decision is made whether the deposit is of a quality suitable for any of the present uses for kaolin or a potential aluminum resource, or whether the property should be dropped. The economic limits of the ratio of overburden to kaolin that can be mined economically range between 6 and 8 to 1, depending on the type of overburden, and the reclamation requirements imposed by federal and/or state law.

If the decision is made to keep the deposit for future mining, then additional drilling is done on 200- or 100-ft centers. From this drilling information, additional maps and cross sections are prepared, from which a stripping and mining plan is devised.

The classification of a deposit as potential aluminum clay is of relatively recent practice as a result of the interest in using kaolin as a raw material to produce aluminum. The United States is dependent on foreign sources of bauxite to supply approximately 90% of its aluminum requirements. The purchase of bauxite represents a significant outlay of dollars which contributes to our balance of payment deficits. Kaolin clays in Georgia and South Carolina contain 35 to 39% Al₂O₃ and represent a very sizable resource from which aluminum could be recovered if the economics become favorable. A report by the National Materials Advisory Board (Anon., 1970) reviewed the various processes for extracting alumina from non-bauxite ores. An article (Anon., 1973b) also described a process to make aluminum using high-alumina clay which is chlorinated and reacted with manganese to form aluminum. Coal is used as the fuel.
requirements needed by the beneficiation plant. Detailed maps showing the elevations of the top of the kaolin, thickness of the deposit, all quality determinations, and lateral extent are prepared which are used to control the mining operation properly.

The principal beneficiation steps are shown in Fig. 11. After the kaolin is exposed and tested, the kaolin is mined by shovels, draglines, motorized scrapers, or front-end loaders. The kaolin is either loaded in trucks or dropped into a blunger which disperses it in water with the aid of a dispersant chemical to form a clay-water slip or slurry. This slurry is pumped from the blunger to a degritting station, where, by the use of settling boxes, screens, and/or hydrocyclones, the coarse foreign particles called grit are removed. Grit is defined as that material coarser than about 44 micrometers. After degritting, the kaolin slurry is collected in large storage tanks and then pumped through pipelines to the beneficiation plant.

Two basically different processes are used to produce a salable kaolin product—a dry process and a wet process. The dry process is simple and yields a lower cost and lower quality product than the wet process. In the dry process, the properties of the finished kaolin reflect generally the properties originally found in the crude kaolin. Therefore, deposits containing the desired qualities of brightness, low grit content, and particle-size distribution must be located by drilling and testing. In the dry process, the kaolin is crushed to approximately egg size, dried in rotary dryers, pulverized, and air floated. The air-floating process removes most of the grit.

The wet process (Fig. 11) has been highly developed in recent years to produce kaolin products of uniform and predetermined physical and chemical properties. Crude kaolin of variable quality can be wet processed to produce a uniform high-quality product.

The kaolin slurry is pumped from the mines to the plant, where it is stored in large tanks. Kaolins of various qualities are blended at the mine tanks or in the terminal tanks at the plant to provide a feed for the beneficiation plant that will produce products to meet specifications. The first step in the wet process is to fractionate the kaolin slurry into coarse and fine fractions by using continuous centrifuges, hydrocyclones, or hydroseparators (Fig. 11). After fractionation, the kaolin is leached to remove ferruginous coloring compounds. In this step the kaolin is acidified with sulfuric acid to a pH of about 3.0 to dissolve the iron. A strong reducing agent such as a hydrosulfite is then added, and the iron reacts and forms a soluble sulfate, which is removed during the dewatering step. The dewatering of the flocculated kaolin slip is accomplished by using high-speed centrifuges, rotary vacuum filters, or filter presses. Sometimes the flocculated slip is thickened by using thickeners or centrifuges before filtration. After filtration, the kaolin filter cake can be extruded to needle form and dried in apron dryers or rotary dryers or it can be redispersed to the fluid state and spray dried, drum dried, or shipped in slurry form as 70% solids in tank cars.

The foregoing paragraph is a simplified description of the wet process. Other processes are used to produce brighter and whiter kaolins and to reduce viscosity. Flotation (Greene and Duke, 1962), selective flocculation (Bundy and Berberich, 1969), and magnetic separation (Iannicelli, et al., 1969) are used to remove iron and titanium impurities to produce kaolin in the range of 90% brightness. This kaolin has a blue-white shade.

The most recent development for improving brightness and whiteness is a high-intensity magnetic separator which removes substantial quantities of iron and titanium mineral impurities. The intensity of these newly developed units ranges from 18 to 22 kilogauss. The main feature of the separator system (Fig. 12) is a canister filled with a special type of fine steel wool which provides a uniform magnetic field through which the kaolin slurry is pumped and the magnetic particles retained in the matrix. Periodically, the magnet is deenergized, and a high volume of water under pressure is back flushed through the matrix to flush out the impurities (Oder and Price, 1973).

Delaminated kaolin is produced by splitting apart the larger books or stacks of kaolin (Fig. 13), this yields a product in which the individual plates tend to be wider, thinner, and whiter. The processes used for delamination include wet attrition grinding (Gunn and Morris, 1965) and extrusion (Lyons, 1959). Delaminated kaolin has special application in lightweight paper coatings, in paint films, and in special rubber applications.

Calcination is another widely used process to produce special products from kaolin. When kaolin is heated to approximately 1050°C, it is converted to mullite, silica-alumina spinel, and cristobalite. The product is whiter, brighter, has better hiding properties when used in thin film applications, and is more abrasive.

Other special processes are used to modify...
then added, and reduced sulfite, following the water steps. The kaolin slip is centrifuged, using the centrifuges, and filtered. Sometimes, it is required by using this separation. After this, the kaolin may be extruded in dryers or extruders, or dried, or dried, or used in tank facades.

A simplified description of the processing steps (Greene and Bundy and Greene and Bundy) separation steps are summarized to remove impurities and produce kaolin products. This kaolin is used for improving the clay in high-intensity applications. It has substantial improvement in the mineral industry and is widely used in its applications. The main machinery (Fig. 12) is a thin film of fine steel, a magnetic field that is pumped and arranged in the matrix, and the pressure is back within a thin film out the impurities.

It is split by splitting by splitting, and the impurities of kaolin are separated in which the thinner, and the delamination. Light films, and in thin film, are processed to modify kaolin. When heated to 1050°C, it is transformed into a spinel, and results in thicker, and brighter, having bright in thin film. Figure 11 is an illustrated flow diagram showing kaolin beneficiation methods (Murray, 1963b).
FIG. 12—Diagrammatic illustration of magnetic separator used in removing iron and very fine-grained titanium minerals from kaolin.

the surface of the kaolin chemically to improve its function in many systems, such as ink, rubber, paint, and plastics. These surface-modified kaolins can be hydrophilic, hydrophobic, or organophilic.

Transportation: The kaolin products are shipped from the beneficiation plants in bulk, in covered hopper cars, and in slurry form in tank cars or in tank trucks. Kaolin is also shipped in 50-lb multiwall bags in boxcars or in trucks when the customer cannot handle the material in bulk. Export shipments are made in bulk ore-type carriers in 2,000- to 15,000-ton lots, in either lump or spray-dried form. Some export tonnage is also shipped in special paper bags of 25- to 50-kilo capacity.

Markets and Consumption: The various markets to which kaolin is supplied were discussed in the section on end uses. In 1980, 7,878,993 tons of kaolin were produced and sold in the United States (Table 1). Fig. 7 shows the tons of kaolin sold for use as paper filler and coating, rubber, ceramics, refractories, and other uses for the years 1965-1979. Since 1930, the market for kaolin has increased tenfold. In the 1930s, practically all the kaolin sold to the paper industry was used as filler, whereas today the proportion of filler clay to coating clay sold to the paper industry is approximately 1 to 2. Coating clay has a much higher value per ton than filler clay, and this increase in the use of coating clay has had more effect on the kaolin industry than any other single factor over the past 40 years. In 1980, the total value of kaolin sold was reported at $527,098,609 (Ampian and Polk, 1981).

Exports of kaolin to Europe, Japan, and South America have increased significantly from 1965 to the present largely because of the increasing use of coating clay by the paper industry. In 1980, 1,392,000 tons of kaolin having a value of $133.7 million, was exported (Ampian and Polk, 1981). The largest export tonnages of kaolin are shipped from Savannah, GA, and Port Royal, SC.

Future Considerations and Trends: Cooper (1970) has estimated that the demand for kaolin from the United States in the year 2000 will be five to six times greater than the amount now being sold. He has estimated a high of 23,680,000 tons and a low of 16,710,000 tons. He has assumed a technological and economic breakthrough that will allow kaolin to be used widely depending on whether it is in pulverized, lump, bead, or in some other form. Lump clay will generally weigh 60 to 65 lb per cu ft. Spray-dried clay in bead form will weigh 40 to 50 lb per cu ft. Depending on the fineness of pulverization and moisture content, pulverized kaolin will range from about 35 lb per cu ft for air-floated kaolin to as low as 20 lb per cu ft for very fine particle size finely pulverized kaolin.

Kaolin is supplied commercially in pulverized form, in lump, generally in the shape of small extruded noodles, in spray-dried bead form, in small pellets, or in flake form. The weight per cubic foot of the kaolin will vary depending on whether it is in pulverized, lump, bead, or in some other form. Lump clay will generally weigh 60 to 65 lb per cu ft. Spray-dried clay in bead form will weigh 40 to 50 lb per cu ft. Depending on the fineness of pulverization and moisture content, pulverized kaolin will range from about 35 lb per cu ft for air-floated kaolin to as low as 20 lb per cu ft for some very fine particle size finely pulverized kaolin.

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t is in pulverized form. Lump clay 15 lb per cu ft will weigh 40 lb to the fineness of content, pulverized in boxcars, in slurry form in tanks are made in England, have better color, and have lower oil absorption. Kaolin, however, has better flow characteristics and gives better hiding or opacity. In paper uses, ground calcium carbonate has several disadvantages with respect to kaolin: (1) it is reactive in acid finishes, (2) the ground calcium carbonate particles are too large to produce high gloss, (3) it gives poorer flow characteristics at high solids, and (4) it is more abrasive. Precipitated calcium carbonate is used in coating paper to give higher brightness and better ink receptivity.

Talc competes with kaolin mostly in paint, caulking compounds, and drywall compounds. In paints, talc gives better brightness and flatting in interior paints.

Precipitated silica and silicates give better reinforcement to rubber, produce higher tensile strength, modulus of elasticity, and resistance to abrasion. These materials are also added in paper to improve brightness and to extend the TiO₂ used in paper. However, kaolin is only one-third to one-half as expensive; consequently the precipitated silicas and silicates will be used only in conjunction with kaolin to achieve specific requirements.

Alumina hydrate is used in paper manufacturing to give higher brightness and to extend TiO₂. It is seldom used alone but is blended with kaolin. Alumina hydrate is two or three times more expensive than kaolin.

The drive to produce very lightweight coated paper has led to the development of plastic pigments which are uniform in size, lightweight, and spherical (Anon., undated; Heiser and Shand, 1973). The pigments give some superior properties such as gloss, opacity, and improved printability to coated paper but are much more expensive than kaolin. These pigments will be blended with kaolin to give certain improved properties for particular applications but will not replace kaolin as a coating pigment.

Batt Clay

History and Uses: Probably the first deposits of the material now known as ball clay mined in the United States were those worked near Paris, TN in 1860 for use in a local pottery (Hosterman, 1973). The first clay shipped to out-of-state consumers was that produced in west Tennessee in 1894 by a Mr. I. Mandel. Later, the industry expanded into Kentucky, and the ball clay districts in the western parts of these two states competed with districts in the United Kingdom (Anon., 1969k) for the world leadership in production. In 1981, more than 916 thousand tons of ball clay was produced in the United States (Ampian, 1982). More than 80% of this tonnage was produced by companies active in Tennessee and Kentucky. The other states producing ball clay are Mississippi, Texas, and California (Fig. 10). Ball clay is also produced intermittently in Maryland.

Ball clay is used principally in the manufacture of vitreous china sanitary ware, electrical porcelain, floor and wall tile, dinnerware, and artware (Phelps, 1972). It is also used in refractory products, ceramic glazes, and porcelain enamel slips.

Geology: Mineralogy—Kaolinite is the principal mineral in the ball clay deposits in Tennessee and Kentucky, but other clay minerals are present and nonclay minerals vary appreciably in abundance. The kaolinite in these deposits is fine-grained, and much of it is poorly ordered. The main clay minerals other than kaolin are illite, smectite, chlorite, and mixed-layer clay. Quartz is by far the most abundant nonclay mineral; in some deposits it makes up as little as 5% of the clay, but in others, as much as 30% (Olive and Finch, 1969). The other nonclay minerals ordinarily present occur in very minor or trace amounts and include plagioclase, potassium feldspar, and calcite. Organic matter in the form of black leaf imprints and disseminated lignitic and peaty materials are common in most ball clays.

Occurrence and Origin—Ball clay is extremely plastic. Deposits range from very light gray to nearly black. Most deposits are lenticular bodies varying considerably in size and shape. Some are more than 30 ft thick and extend over areas 1000 ft wide and 2500 ft long, but most deposits are smaller. The physical properties of a typical deposit vary considerably, and layers and pockets mined from a given deposit are commonly separated in different stockpiles suitable for a particular use.

Most deposits in Tennessee and Kentucky are in beds of Claiborne age (middle Eocene), but a few, including one mined, are in Wilcox beds (lower Eocene) (Olive and Finch, 1969). The deposits mined in Texas near Henry's Chapel, northeastern Cherokee County (Fisher
et al., 1965) are also in Wilcox beds. The ball clay mined in Panola County, Mississippi (Bicker, 1970), is in formation of Claiborne age, and the deposits are approximately the same age as younger ones in Tennessee and Kentucky. The deposits mined in Stanislaus County, California, are in beds of Paleocene or Eocene age (Cleveland, 1957). Those mined on a small scale in the Hart district in eastern San Bernardino County, California, are in hydrothermally altered Tertiary rhyolites (Kelley, 1966).

Most ball clay occurs in transported sedimentary deposits, but one minor producing district in California contains hydrothermally altered clay. The deposits in the Tennessee, Kentucky, and Mississippi districts are in sedimentary formations cropping out along the eastern edge of the Mississippi embayment. According to one theory of origin (Olive and Finch, 1969), they accumulated in an elongate broad valley. The abundance of plant remains and organic matter associated with this clay indicates that the depositional basins probably were swampy.

Distribution of Deposits: United States—Any attempt to estimate the resources of ball clay is based on piecemeal information. The reserves, primarily in Tennessee and Kentucky, total probably as much as 100 million tons, and are owned by eight or ten different companies; they are thought adequate to sustain the industry for 100 years (Phelps, 1972). Additional reserves are in the producing districts in Mississippi, Texas, and California. Potential resources of low-grade ball clay, which probably would require beneficiation for market, occur in the vicinities of all of these districts. The prospects are also favorable for the discovery of more deposits of kaolinitic clay having the physical properties of ball clay in several southern states. Furthermore, if the term ball clay is applied to such deposits as the hydrothermally formed clay at Hart, CA, many areas in the western states are likely to contain large deposits.

Other Countries—The principal ball clay deposits in the United Kingdom occur in the Bovey Basin southeast of Dartmoor in Devonshire, the vicinity of Petrockstow in north Devonshire, and in the Wareham and Poole regions of Dorsetshire. These ball clays occur in sedimentary rocks of Tertiary age, consisting mainly of lenticular units of sand, clay, and lignite of probable lacustrine origin (Scott, 1929). The clay is very fine grained plastic kaolin ranging in color from off-white to dark brown and gray. The darker colors, as in the ball clay in Kentucky and Tennessee, apparently are caused by carbonaceous impurities. The deposits are believed to have been transported from altered granite and other igneous rocks. Watts, Blake, Bearne, and Co. is the major producer of British ball clay.

Ball clay occurs at several localities in India (Arjogyswamy, 1968), but production is limited, and in recent years India has been an importer of ball clay. The best quality ball clay produced is in the Than district of Gujarat. Other deposits are mined in two districts in Kerala.

Evaluation of Deposits: The prospecting techniques for ball clay are very similar to those outlined for kaolin. The commonest used tests are very similar to those for evaluating the ceramic properties of kaolin and heat-resistant properties of refractory clays. Chemical analysis for soluble sulfate in ball clays, is commonly required because this material can be tolerated in only very minor amounts in most ceramic products.

Preparation for Markets: Ball clay is mined by stripping methods and trucked to plants. Most plant processing involves primarily drying and grinding to a suitable size. A few plants air-flow part of their output. Ball clay is packaged in paper bags, but some is shipped in bulk carload lots in both crude and processed form. In recent years, some ball clay has been shipped in tank cars. This clay is prepared for shipment by deflocculation in water, and it is shipped as 60 to 62% solids (Phelps, 1972). Such slurries are used by plants manufacturing ceramics by the slip-casting method.

Future Considerations and Trends: The production of ball clay in the United States has grown rather consistently for the last several decades, and continuation of this trend is forecast. Nationwide demands are likely to be 2 to 2.3 million tons in the year 2000 (Cooper, 1970). In general, the ball clay industry faces little competition from foreign sources, and exports are appreciably greater than imports. However, the major districts in Tennessee and Kentucky are in the central part of the country and as rail transportation costs increase, a greater proportion of the demands in the populous coastal region may be satisfied by imports.


defined as a filler (1909). Deposits and used for ma-
else and after World War major source of

Halloysite, a common clastic mineral, is widely used in the production of ceramics. The major source of halloysite in the United States has been the Dragon mine, Tintic district, Utah, where it was mined for use in ceramics and used for making alum about 1912. Halloysite is also used in portland cement in recent years. Other deposits in Idaho consisting of mixed kaolinite and halloysite are used in refractories. Deposits of similar clay-mineral composition in North Carolina (Parker, 1946) are mined for use in ceramics and other products.

Geology: Mineralogy—Halloysite is so similar to kaolinite that the two cannot be distinguished without careful mineralogical work. Very fine tubular structures are commonly observable in electron micrographs of dehydrated halloysite (metahalloysite) and are observed in electron microscopy of samples containing natural moisture. The occurrence of these deposits and the minerals associated with them clearly indicate that they formed by hydrothermal activity. Other deposits have been formed hydrothermally occur in the Terraced Hills, Washoe County, Nevada. These deposits are bedded and are alterable hydrothermally, and several of these deposits have never been advanced, but the extent of the beds suggests that they are of sedimentary origin. Halloysite mixed with kaolinite in the Spruce Pine district, North Carolina (Hunter and Hash, 1953; Parker, 1946) and the Bovill district, Idaho (Hosterman et al., 1960), is mainly residual and formed by the weathering of igneous rocks. Several deposits in foreign countries are thought to have formed hydrothermally, and some are the result of surficial weathering.

Distribution of Deposits: United States—In the United States, small deposits of halloysite occur at many places in the United States, but known deposits large enough to mine profitably are rare. The deposits in the Dragon mine, Utah, the major producer, are two large pipe-like bodies replacing lower Paleozoic limestone near the contact with monzonite porphyry. The two bodies are separated by a zone of iron-oxide deposits extending along the Dragon fissure (Morris, 1968). The occurrence of these deposits and the minerals associated with them clearly indicate that they formed by hydrothermal activity. Other deposits thought by Papke (1971) to have formed hydrothermally occur in the Terraced Hills, Washoe County, Nevada. These deposits are bedded and apparently altered mainly from tuff. The halloysite in the Gore district, Georgia, is bedded and occurs in the Armuchee Chert of Devonian age (Broadhurst and Teague, 1954). An adequate explanation of these deposits has never been advanced, but the extent of the beds suggests that they are of sedimentary origin. Halloysite mixed with kaolinite in the Spruce Pine district, North Carolina (Hunter and Hash, 1953; Parker, 1946) and the Bovill district, Idaho (Hosterman et al., 1960), is mainly residual and formed by the weathering of igneous rocks. Several deposits in foreign countries are thought to have formed hydrothermally, and some are the result of surficial weathering.
resources of halloysite in the old Gore mining district in Georgia are estimated at more than a million tons (Broadhurst and Teague, 1954), and some use may again be found for these deposits.

Other Countries—Halloysite occurs in many countries, but, as in the United States, most deposits are small; the authors are aware of small-scale mining only in Morocco, Japan, Korea, Czechoslovakia, and New Zealand. The deposits mined in Morocco are in the Maza district about 6 km west of Melilla (Hilali et al., 1969; Martin Vivaldi and Vilchez, 1959). These deposits occur above travertine and are overlain by pyroclastic materials. They are in a bed of Pliocene age, ranging in thickness from 1.5 to 2.5 m. Halloysite mined in Japan includes deposits that formed by hydrothermal alteration of granite and quartz porphyry and others that were transported and deposited in sedimentary basins (Takeshi and Kato, 1969). Hydrothermal deposits occur at the Taishu mine, and white sedimentary halloysite is in the Tajimi and Arikabe deposits. The halloysite mined in Korea is presumably from the San Chong and Tan Song deposits described by Kim and Kim (1964). The halloysite deposits mined in Czechoslovakia are in the Michalovec district in the eastern part of the country (Kuzvart, 1969). These deposits are thought to have formed by the hydrothermal alteration of dacite. They extend over an area 500 m square and are as much as 36 m thick. They occur below overburden 30 to 40 m thick. The halloysite mined is reported to be suitable for use in ceramics, refractories, paper and rubber fillers, and in refining sugar. The deposits in New Zealand occur in the Maungaperua district on the North Island. This clay is mined by New Zealand China Clays, Ltd., and sold for use in paper filler, ceramics, paint extenders, and filler for adhesives and cosmetics. The halloysite is in massive deposits formed by hydrothermal alteration of andesite of middle Cenozoic age (Bowen, 1969).

Several of the kaolin deposits in other countries consist of mixtures of halloysite and kaolinite. One such mixed deposit occurs in altered felsic volcanic rocks in the Burela district, Spain (Anon., 1972b), the principal kaolin-producing center in that country. The kaolin produced contains appreciably more halloysite than kaolinite, but the clay must be considered to be a mixed type. Another mixed halloysite-kaolinite deposit is in the Bukidnon district in the Philippines (Comsti, 1969).

Future Considerations and Trends: Halloy-
site will probably be in demand in the United States for use in petroleum catalysts and other products as long as suitable high-quality deposits can be mined at a reasonable cost. As mentioned previously, known high-grade deposits are limited, and though additional deposits may be found, the point may be reached when it will be cheaper to use substitute materials than to prospect for new deposits. Catalysts made from halloysite are in competition with those manufactured from kaolin and synthetic materials containing alumina and silica.

The products other than catalysts made from halloysite in recent years are all low-value or high-weight items lacking the broad market base of catalysts. All these other products can be made from other clays or other materials, but halloysite will continue to be used for them until reserves are exhausted, cheaper substitutes found, or local markets disappear.

Refractory Clays

History and Uses: The first plant in the United States for making refractory products from clays began operation at Salamander, NJ, in 1825. The refractory industry grew rapidly and expanded from New Jersey to centers in Pennsylvania, the Ohio River valley, Missouri, and to western states.

Refractory clays are used mainly in making firebrick and block of many shapes, insulating brick, saggers, refractory mortars and mixes, monolithic and castable materials, ramming and air gun mixes, and other products. A product called chamotte is used in Europe (Anon., 1972, 1972c) and elsewhere is made by calcining high-grade fire clays and other kaolinic clays. A similar material produced in the United States is called merely calcined clay or calcined kaolin. A related material called mullite refractory is made by calcining bauxitic clay or clayey bauxite. Further fabrication into finished refractory products is required for chamotte and calcined clay. Considerable tonnages of fire clay also have been used in the past in the United States in the manufacture of light-colored face brick, tile, stoneware, and other products.

Product Specifications: The specifications for refractory clays are as many as the different uses. As resistance to heat is the most essential property, many specifications include reference to pyrometric cone (Table 4), indicating the heat duty required. Resistance to shrinkage, warping, cracking, and abrasion is also very important in many products, and expressions of the requirements for these properties appear in some specifications. Restrictions include cutoffs or content of alk constituents in.

Geology: The origin of refractory clay has been considered to apply to fire clay, there are various considerations.

Mineralogy—kaolinite, the various clays consist of the harder and very crystalline kaolins. The kaolinite tends to occur in harder varieties in the country, however, is ordi-

Some of the fire clays contain mineral than kaolinite, products can be made from fire clay, gibbsite, Al₂O₃, clay, that consists of kaolin and minor quan-

Occurrence of acteristics of fire clays range from: Fire clay, there are impurities, semi-hardness, breaks with a shardlike partick limestone. Type hard and has a texture. Such c. birds eye, or nodules.

Most fire clay and deposits ran to Tertiary. Find in rocks of Penn this age occur as mediately below beds. Fire clay c. occurs mainly in
In the United States and other high-quality desirable countries, high-grade refractories and mullite products may be reached by calcining kaolinitic clays or other materials, but for the sake of substituting mullite for kaolinite, the additional cost may be justified. Clay and mullite products can be manufactured in some specifications. Many of the end products must fulfill rigid specifications on dimensions. Restrictions on raw clay commonly include cutoffs on plasticity, impurities, and content of alkalis, alkaline earths, and other constituents that reduce fusion points.

Geology: The mineralogy, occurrence, and origin of refractory kaolin and refractory ball clay have been discussed in the foregoing sections. Therefore, the following discussions will be concerned with these subjects only as they apply to fire clay.

Mineralogy—The degree of ordering of the kaolinite, the principal mineral in fire clay, varies considerably. Most of the kaolinite in the harder and purer varieties of fire clay (flint clay) is very well ordered, and it is even more perfectly crystalline than the kaolinite in many kaolins. The kaolinite in the hard fire clay also tends to occur in coarser particles, and in the harder varieties the grains are interlocking. The kaolinite in the plastic varieties of fire clay, however, is ordinarily characterized by imperfectly crystalline structures. The more disordered form of this kaolinite has been widely referred to as fire clay mineral in an effort to distinguish it from the more perfectly crystallized forms.

Some of the better grades of refractory clays contain minerals that are richer in aluminum than kaolinite, and, therefore, higher alumina products can be made from them. Some refractory kaolin is a mixture of kaolinite and gibbsite, Al₂O₃·3H₂O. The better grades of fire clay, that are exceptionally rich in aluminum, consist of kaolinite and diaspore, Al₂O₃·H₂O, and minor quantities of Boehmite, Al₂O₃·H₂O. Some of the kaolins in these deposits occur as isolated tabular lenses ranging in thickness from 3 to 20 ft.

In addition to the fire clay mentioned in the foregoing discussions, other deposits are scattered throughout the western states (Anon., 1967; Mark, 1963; Van Sant, 1959, 1964).

**Distribution of Deposits:**

**United States—** Fire clay of Pennsylvanian age is widely scattered throughout the Appalachian region and parts of the Mississippi Valley (Anon., 1967). The very high quality diaspore-bearing clay, as well as other grades of fire clay, occur in the Clearfield district, Pennsylvania (Anon., 1964; Bolger and Weitz, 1952) (Fig. 10), and the Ozark region in Missouri (Keller, 1952; Keller et al., 1954). High grade kaolinitic flint clay and semiflint clays are mined in the Olive Hill district, Kentucky (Patterson and Hosterman, 1963); the Clearfield district, Pennsylvania (Anon., 1964; Bolger and Weitz, 1952) (Fig. 10), and the Ozark region in Missouri (Keller, 1952; Keller et al., 1954). High grade kaolinitic flint clay and semiflint clays are mined in the Olive Hill district, Kentucky (Patterson and Hosterman, 1963); the Clearfield district, Pennsylvania (Anon., 1964; Bolger and Weitz, 1952) (Fig. 10), and the Ozark region in Missouri (Keller, 1952; Keller et al., 1954). High grade kaolinitic flint clay and semiflint clays are mined in the Olive Hill district, Kentucky (Patterson and Hosterman, 1963); the Clearfield district, Pennsylvania (Anon., 1964; Bolger and Weitz, 1952) (Fig. 10), and the Ozark region in Missouri (Keller, 1952; Keller et al., 1954). High grade kaolinitic flint clay and semiflint clays are mined in the Olive Hill district, Kentucky (Patterson and Hosterman, 1963); the Clearfield district, Pennsylvania (Anon., 1964; Bolger and Weitz, 1952) (Fig. 10), and the Ozark region in Missouri (Keller, 1952; Keller et al., 1954). High grade kaolinitic flint clay and semiflint clays are mined in the Olive Hill district, Kentucky (Patterson and Hosterman, 1963); the Clearfield district, Pennsylvania (Anon., 1964; Bolger and Weitz, 1952) (Fig. 10), and the Ozark region in Missouri (Keller, 1952; Keller et al., 1954).
These deposits are of several types, and they include transported, residual, and hydrothermally formed clay. Districts in which these scattered deposits occur include several areas in King County and the Castle Rock area in Cowlitz County, Washington; the Molalla and Hobart Butte areas, Oregon; and the Alberhill area, California. Most of these deposits are of Cenozoic age.

Refractory kaolin is produced primarily in the following districts: (1) Georgia-South Carolina kaolin belt; (2) Andersonville, Georgia (Anon., 1972a); (3) Eufaula, Alabama; (4) Arkansas bauxite region; (5) scattered districts in Texas; (6) Latah County, Idaho; and (7) Ione, California (Anon., 1972e). Refractory ball clay is produced primarily in the western parts of Kentucky and Tennessee, but some of the ball clay produced in Texas may be used in refractory products.

The total refractory clay, resources in the United States suitable for low-heat-duty refractory products may be as much as 7 billion tons (Hosterman, 1973). However, the reserves—those clays that can be mined and processed now at competitive costs and are suitable for low-heat-duty products or better—are probably no more than 1 billion tons. The reserves are primarily in the fire clay and refractory kaolin and ball clay districts outlined previously. The remaining resources of high-grade diaspore clay are mainly under considerable overburden in Pennsylvania, and only small resources are present in Missouri. The bauxitic kaolin resources are primarily in the Arkansas bauxite region, and the Eufaula, Alabama, and Andersonville, Georgia, districts. Some deposits also occur in other parts of Alabama and Georgia.

Other Countries—Refractory clays are produced in many countries; however, the information available to the authors on worldwide production is sketchy and incomplete. This is partly because the distinction between fire clay and miscellaneous clay is not made in some countries, and clay used for refractory products is lumped with kaolin in others.

Those countries that produce more than 1 million tons of refractory (fire) clay annually include the United Kingdom, Federal Republic of Germany (West Germany), and Japan. The production in France exceeded a million tons a few years ago but has apparently dropped below this figure in recent years. Other countries producing 100,000 to 1 million tons annually include Argentina, Australia, India, Italy, Mexico, New Zealand, Sweden, the United Arab Republic, Uruguay, and Yugoslavia. Refractory clay is exported from the Peoples Republic of China, which is apparently a major producer. Fire clay is also mined in the USSR, Czechoslovakia, Hungary, Poland, and other East European countries.

As in the United States, fire clay in other countries is in several types of deposits. Kaolinitic fire clay associated with coalbeds of Carboniferous age is mined in the United Kingdom, France, Federal Republic of Germany, and elsewhere. Very high alumina diaspore-bearing flint clays are sources of refractory materials in Scotland, South Africa, Israel, and the Peoples Republic of China. Refractory kaolin is mined in Japan, India, Hungary, Italy, Czechoslovakia, Poland, Sweden, Yugoslavia, Mexico, Argentina, Brazil, Chile, Peru, Republic of South Africa, United Arab Republic, Australia, New Zealand, Iran, and other countries, and most such deposits are of Cretaceous age.

Exploration and Evaluation: The methods used in exploring and evaluating fire clay deposits are in general similar to those used for bentonite and kaolin, except that different drilling and testing procedures are required. Drilling fire clay deposits, particularly those of Pennsylvanian age, ordinarily requires diamond bits and core barrels of the type used for minerals in hard rock. This is because the clay itself and the rocks overlying the deposits are hard. The most common test in the evaluation of fire clay is the determination of PCE (pyrometric cone equivalents, Table 4, p. 613).

In addition to the PCE requirement, fired test pieces also may be tested for such properties as high-temperature stability, hot strength, porosity, and spalling (Anon., 1972h; Norton, 1968). Chemical analyses are also required for some evaluations, and the contents of alkalies, alkaline earths, iron oxides, and a few less common elements are critical, because they act as fluxes when clay refractories are heated.

Preparation for Markets: Fire clay and other refractory clays are mined by methods similar to those used for other types of clay. However, a much higher percentage of fire clay mining in the past has been underground. The underground mining has been required because much of the higher quality clay occurs at considerable depths, and the overlying rocks are too hard to strip profitably.

Firebrick and related products are prepared for markets by grinding the clay, shaping or forming the firebrick or other products, and firing. Commonly several varieties of fire clay and grog (crushed previously fired clay) are blended to make product, and all prepare different clays are ordinarily plastic or plastic fire cl forming and b Most firebrick is mechanical products are intricate by hand.

Most firebrick by gas or oil. A making specially limited market, products are or truck. Heavy or required for one is ordinarily fire in both paper ba Future Consid output of refrac States was 11.8 tion has decrease versals of the the total refrac tion tons valuec This trend in dec has been due ma (1) the develop nuous refractory i basic oxygen pro f furnaces; (2) whereby fire cla brick, stone, nall classified as mis clay.

The decrease is brought about b previous paragrah and markets for made from it can sistently. Deman in the year 200 17 million st (C).

The availability one of the long grade refractory grade diaspore s front that can be are nearing exhaust ing increases cos underground min the production o clays has i
Clays

Miscellaneous Clay and Shale

Miscellaneous clay and shale includes a wide variety of clay and other fine-grained rocks that are used in many ways. Most products made from them are fired and include such things as structural and face brick, drain tile, vitrified pipe, quarry tile, flue tile, conduit, pottery, stone ware, and roofing tile. Very large tonnages of these materials are blistered by firing to form lightweight aggregate, and large quantities are used in making portland cement (see the specific chapters in this volume). Uses not requiring firing of a finished product include fillers for paint and other products and shale and clay used for packing dynamite in blast-holes and for plugging oil and gas wells that are no longer in use. Adobe building blocks are also used in unfired form in several southwestern states.

Properties

Clay and shale are used in so many different structural clay products that they necessarily have a wide range in physical properties. The properties are plasticity, green strength, dry strength, drying and firing shrinkage, vitrification range, and fired color. The properties desired vary with the structural clay product made. For example, a clay used in making conduit tile must be very plastic and have high green and dry strengths and uniform shrinkage, but for drain tile or common brick these properties do not have to be controlled so closely.

Most clays are plastic when naturally wet or mixed with water. Plasticity can be defined as the property of a material to undergo permanent deformation in any direction without rupture under stress beyond that of elastic yielding. Some clay materials are very plastic and are called fat clay; others having little plasticity are called lean clay. The type of clay mineral, particle size, particle shape, organic matter, soluble salts, absorbed ions, and the amount and type of nonclay minerals influence the plastic properties of clay.
Green-strength and dry-strength properties of clay and shale are important because most structural clay products are handled at least once and must be strong enough to maintain shape. Green strength is the strength of the clay material in the wet or plastic state. Dry strength is the strength of the clay after it is dried. Plasticity and green strength are closely related and are influenced mainly by the same variables. Dry strength is dependent on the proportion of fine particles present, the shape of the individual particles, the degree of hydration of the clay fraction, the method of forming the ware, and the rate and thoroughness of the drying. The presence of a small amount of smectite, which occurs in very fine hydrated particles, generally increases dry strength.

Both drying and firing shrinkages are critical properties of clay used for structural clay products. Shrinkage is the loss in volume of a clay as it is dried or fired. Drying shrinkage is dependent on the water content, the character of the clay minerals, and their particle size. Most plastic clays shrink appreciably with drying, which tends to produce cracking and warping. Sandy clay or clay having low plasticity has low shrinkage properties but tends to produce a weak porous body. Smectite minerals in rather large amounts (10-25%) commonly cause excessive shrinkage, cracking, and slow drying. Firing shrinkage depends on the density of the clay, volatile materials present, the types of crystalline phase changes that take place during firing, and the dehydration characteristics of the clay minerals.

The temperature range of vitrification or glass formation during firing is a very important property of clay and shale used in structural clay products. Vitrification is a process of gradual fusion in which some of the more easily melted constituents produce increasing amounts of liquid as the temperature is increased. This liquid produces glass as the material is cooled, and the glass is the bonding material in the final fired product. Some clay has a short vitrification range, and when such clay is fired the temperature of the kiln must be very closely regulated. Clay consisting chiefly of illite, smectite, or chlorite has lower vitrification temperature than kaolinite-rich clay. Some mineral impurities in clay, such as calcite and feldspar, lower vitrification temperatures by acting as fluxes. The degree of vitrification attained also depends on the duration of firing and the temperature. Commonly the degree of vitrification is regulated by the amount of shrinkage and porosity needed in the final product.

Uniform color is an essential property of many structural clay products. The color of a product is influenced by the state of oxidation and particle size of the iron minerals; the firing temperature and degree of vitrification; the proportion of alumina, lime, and magnesia in the clay material; and the composition of the gases in the kiln during the burning operation. High-grade white-burning clay contains less than 1% Fe₂O₃, buff-burning clay ordinarily contains 1-5% Fe₂O₃, and red-burning clay contains 5% or more Fe₂O₃. Other constituents also affect the color, but finely divided iron-bearing minerals generally are the principal materials causing color in fired products.

Occurrence

Miscellaneous clay and shale occur in many types of rocks ranging in age from Precambrian to Holocene. They include glacial clay, soils, alluvium, loess, shale, weathered and fresh schist, slate, and argillite. Some fire clay and kaolin are also included in the miscellaneous clay group, particularly when used in the manufacture of structural-clay products. This group consists of so many different types of rocks that only a few broad generalizations about their mineral makeup are possible. The most common mineral in many of them is one of the members of the mica group, and the dominant one in a given deposit may be illite, sericite, or one of the micas normally occurring in coarser grain sizes, such as muscovite and biotite. In addition to illite, the clay minerals present commonly are kaolinite, smectite, mixed-layer varieties, and chlorite. Some materials in this group actually contain more quartz and other detrital minerals than clay minerals.

Miscellaneous clay and shale are now mined in every state in the United States, except Alaska and Rhode Island, according to US Bureau of Mines Minerals Yearbooks. In 1980, 32.4 million tons of these materials having a value of $114.7 million were produced (Table 1). The states producing more than 1 million tons were Alabama, California, Georgia, Illinois, Indiana, Iowa, Louisina, Maryland, Michigan, Missouri, New York, North Carolina, Ohio, Pennsylvania, South Carolina, Texas, and Virginia. Texas was the leading state in production in 1980, with 3.4 million tons, and North Carolina was second, with 2.8 million tons.

Testing, Processing, and Markets

The testing of miscellaneous clay and shale for most products requires the preparation of test pieces of special firing (Clews, 196). Feltler and Hamlin, tested for such properties as plasticity, cracking, parting, and porosity, soluble salt content, and workability. Miscellaneous clay and shale are face to rural areas. For near population centers has been relocated because of a rise in fuel costs, seems likely to be the industry. Another strong miscellaneous clay and shale for raw materials are facing steeple in the near population centers has been relocated because of a rise in fuel costs, seems likely to be the industry.

Government C Bentonite and Kaol

Most of the bentonite resources in the United States. At
The color of a material's oxidation state, the firing temperature, the pro-
portion of the clay in the firing, and the properties of the clay itself affect the final product.

Fired test pieces are tested for such properties as shrinkage, war-
ping, cracking, permeability, modulus of rupture, crushing or compression strengths. Color and soluble salt content are also important for some products.

Miscellaneous clay and shale is dug from open pits. Pits must be near plants and the digging must be cheap, because both the raw material and finished products are heavy, and the margin of profit is ordinarily low. Most products made from these materials are processed and marketed much in the manner described for refractory clays.

Future Considerations and Trends

The long-range trends in demands for some products made from miscellaneous clay and shale can be expected to keep pace with the growth in the gross national product, but demands for others are likely to fall short of this growth rate. Demands for clay and shale required for portland cement and lightweight aggregate are increasing, and this trend is likely to continue. Though demands for heavy structural-clay products will continue, these materials are facing strong competition from cement, wood, glass, plastics, aluminum and other metals. Growth in demands for structural-clay products is also hampered by the heavy weight of these products, which limits their market range, and by increasing production costs. The rise in fuel costs, which has been forecast, seems likely to be a major problem faced by the industry.

Another strong trend in the industry using miscellaneous clay and shale has been the shift to rural areas. For a long time, plants were near population centers because of transportation costs. Suburban growth in many population centers has forced plants to close or to relocate because of ecological pressures and raw-material supply problems. This trend seems certain to continue until virtually all active plants are in rural areas, which, in turn, tends to favor a substitute material because of increased transportation costs and other factors.

Government Controls and Influences

Bentonite and Kaolin on Public Domain Lands

Most of the bentonite and part of the kaolin resources in the United States are on public domain lands. At the time this chapter was written, bentonite and kaolin deposits on federal lands for which mineral rights were not withdrawn or otherwise not obtainable were subject to the general mining laws. Mining claims could be filed on valid bentonite deposits, and under certain conditions such claims could be patented. The staking and patenting of mining claims on public domain lands are primarily under the jurisdiction of the Bureau of Land Management, an agency of the US Department of Interior. Further information on the staking and patenting of mineral claims on federal lands can be found in Bureau of Land Management pamphlets 0-377-927 and 0-377-930.

Depletion Rates

The following depletion rates were in effect in 1973 (Anon., 1972k): kaolin, ball clay, bentonite, fuller's earth, and fire clay, 14% domestic and 14% foreign; clay and shale used for making brick, tile, and lightweight aggregate, 70 1/2%, both domestic and foreign. The depletion rate for clay used for the extraction of alumina or aluminum compounds was set at 22%, but because no clays have yet been used for this purpose in the United States the rate was not applied.

Tariffs

The statutory rates of duty per long ton for the various classes of clay in effect in 1980 (Ampian, 1981) are listed in Table 5.

Ecology

All segments of the clay industry, like all other mineral industries, face major problems related to the environmental controls, and compliance with regulations now in effect has added significant production costs. Virtually all the major plants producing clay involving a dry-grinding process have installed equipment to control dust emissions in the atmosphere. Not all such equipment has proved effective, and some companies are faced with further expenditures for improving dust control. The control of turbidity and other contamination in water pumped from pits and discharged from washing and other types of plants is also required. This regulation has forced mining to be shut down at least temporarily in flooded fuller's earth pits and adds the costs of maintaining settling ponds to remove the suspended materials in the discharge from kaolin-washing plants. As most clays are strip mined, land
reclamation costs are now a major item. Commonly, as much as $500 per acre is spent in restoring mined bentonite lands in Wyoming, where the value for the surface alone is only about one-tenth of that amount. The restoration of some of the strip-mined land in the Georgia kaolin belt costs as much as $800 per acre, but the average cost is about $300 per acre. The high costs of reclamation in Georgia are due to state laws governing mining that are even more stringent than the federal regulations.

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Bibliography and References


Esquef, J.M., and Zamora, S., 1958, "Informe
104 pp.
Heron, S. D., Jr., et al., 1965, "Clays and Opal-Bearing Claystones of the South Carolina Coastal Plain," Bulletin 31, South Carolina Division of Geology.
Jones, I. T., and Best Enusual Process University Press.


Jeanteau, A., 1952, "Argiles Siltées et Rha


Industrial Minerals and Rocks


Poole, E.G., et al., 1971, “Calcium Montmorillonite (Fuller’s Earth) in the Lower Greensand of the Fernham Area, Berkshire,” Report No. 71/12, Great Britain Institute of Geological Sciences, 63 pp.


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