CLAYS, SURVEY

1. Introduction

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. Clay is a natural earthy, fine-grained material comprised 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 the clay minerals also contain appreciable quantities of iron, alkalies, and alkaline earths. Many definitions include the statement that clay is plastic when wet, which is true because most clays do have this property but some clays are not plastic, eg, flint clays and halloysite (1). As a rock term many authors use the term clay for any fine-grained natural earthy argillaceous material (2) that would include shale, argillite, and some argillaceous soils. As a particle size term, clay is used for the category that includes the smallest particles. Soil scientists and mineralogists generally use 2 μ as the maximum particle size. On the widely used Wentworth scale, clay is any material finer than 4 μ (3). Even though there is no universally accepted definition of the term "clay", geologists, agronomists, ceramists, engineers, and others who use the term understand its meaning.

Because of the extremely fine particle size of clays and clay minerals, they require special techniques for identification. The optical microscope generally cannot resolve particles below 5 μ. The most useful instrument for identification and semiquantification of clay minerals is X-ray diffraction (4). Other methods of identification used are, differential thermal analysis (5) electron microscopy (6), and infrared (ir) spectroscopy (7). Identification and quantification of the clay and non-clay minerals present in a clay material are important because the uses and engineering properties are controlled by the specific clay minerals present and the type and quantity of non-clay mineral present. As pointed out by Grim (1), the uses and properties of clay are dependent on the clay mineral composition, non-clay mineral composition, presence of organic material, the type and amount of exchangeable ions and soluble salts, and texture. The major clay mineral groups are kaolins, smectites, illites, chlorites, and palygoskite-sepiolite.

Clay is an abundant natural raw material that has an amazing variety of uses and physical properties. Clays are among the leading industrial minerals in both tonnage produced and total value. Clays and clay minerals are important to industry, agriculture, geology, environmental applications, and construction. Clay minerals are important indicators in petroleum and metallic ore exploration and in reconstructing the geological history of deposits. However, clay minerals may be deleterious in aggregates and in oil reservoirs.

There are several scientific groups whose work is devoted to the study of clays and clay minerals. These include AIPEA (Association Internationale pour le Etude des Argile), Clay Minerals Group of the Mineralogical Society of Great Britain, CMS (The Clay Minerals Society), European Clay Minerals Society, Clay Minerals Society of Japan, Australian Clay Minerals Society, and Czech National Clay Group. Major publications include the *Proceedings of International Clay*

Conferences published by AIPEA; *Clay Minerals* published by the Mineralogical Society of Great Britain; *Clays and Clay Minerals* published by CMS: *Clay Mineral Science*, published by the Clay Society of Japan; and *Applied Clay Science* published by Elsevier. CMS sponsors an annual clay conference; The European Clay Minerals Society sponsors a meeting every 2 years; and AIPEA holds an international clay conference every 4 years.

2. Occurrence and Geology of Major Clay Deposits

Some clay deposits are comprised of relatively pure concentrations of a particular clay mineral and others are mixtures of clay minerals. Kaolins, smectites, and palygorskite-sepiolite can occur in relatively pure concentrations whereas illite and chlorite usually occur in mixtures of clay minerals and non-clay minerals such as shales, which are the most common sedimentary rock. Each of these will be discussed under the headings kaolins, smectites, palygorskite-sepiolite, and common clays.

2.1. Kaolins. Kaolins are hydrated aluminum silicates. Kaolin is a mineral group consisting of the minerals kaolinite, dickite, nacrite, and halloysite. Kaolinite is the most common of the kaolin group minerals. The term kaolin is derived from the Chinese word kauling, which in the Chinese language means high ridge. At Jauchian Fu in China, kaolin was mined for centuries from a hill or ridge. The term china clay is synonymous with kaolin and has two connotations. One refers to the use of kaolin in fine china ceramic products and the other makes reference to the fact that kaolin was first mined in China and thus is called china clay.

Kaolin, in addition to being a group mineral name, is a rock term and is used for any rock that is comprised predominantly of one of the kaolin minerals. Kaolin deposits are classed as primary or secondary (8). Primary or residual kaolins are those that have formed by the alteration of aluminous crystalline rocks such as granite and remain in the place where they formed. The alteration results from surficial weathering, groundwater movement below the surface, or action of hydrothermal fluids. Secondary kaolins are sedimentary rocks that were eroded, transported, and deposited as beds or lenses in association with other sedimentary rocks. Most secondary or sedimentary kaolins were deposited in deltaic environments.

The most common parent minerals from which kaolin minerals form are feldspars and muscovite. The transformation of potassium feldspar into kaolinite results from weathering or hydrothermal alteration, which leaches potassium and silica according to the equation:

$$\underset{\text{Potash Feldspar}}{2\mathrm{KAlSi_3O_8}} + \underset{\text{Water}}{3\mathrm{H_2O}} \rightarrow \mathrm{Al_2Si_2O_5(OH)_4} + \underset{\text{Silica}}{4\mathrm{SiO_2}} + \underset{\text{Potash}}{2\mathrm{K(OH)}}$$

The potassium must be flushed out of the system in order for kaolinite to form, otherwise the mineral illite may form. Granites and rhyolites (Fig. 1) weather readily to kaolinite and quartz under favorable conditions of high rainfall, rapid drainage, temperate to tropical climate, a low water table, and

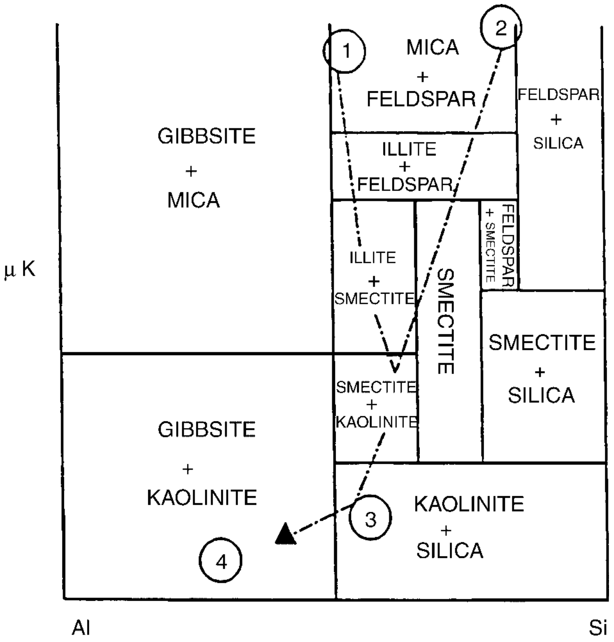

Fig. 1. Phase diagram on weathering of granite. Alteration products of mica (1) and feldspar (2) are smectite and kaolinite and (3) to (4) results from intense weathering in tropical climates.

adequate water movement to leach the soluble components. The more immobile components are alumina and silica, whereas alkalies and alkaline earths are mobile (9). Plagioclose feldspars are relatively unstable and alter before either potash feldspar or muscovite (10).

Kaolinite is the dominant kaolin mineral in secondary or sedimentary deposits. Dickite, nacrite, and halloysite are more commonly found in hydrothermal deposits (8). Kaolin deposits occur on every continent but relatively few are mined and processed for industrial use. Some of the more important and largest deposits are described and discussed below.

The largest kaolin-producing district in the world is located in Georgia and South Carolina in the United States. These deposits are late Cretaceous and early Tertiary in age (11) and occur in lenses and beds in relatively coarse sands. The kaolin was derived from granitic rocks, phyllites, and schists on the Piedmont Plateau (12). The deposits are concentrated in a belt ~30 km wide extending from central Georgia northeast into South Carolina (Fig. 2). The deposits are located south of the fall line, which is the boundary between the crystalline rocks of the Piedmont Plateau and the Coastal Plain sedimentary rocks.

These mineable deposits range in thickness from 3 to 15 m and extend laterally from a few hundred meters to kilometers in length and width. The Cretaceous age kaolins are relatively coarse with a particle size ranging between 55 and 70% finer than two micrometers whereas the early Tertiary kaolins range from 85 to 95% finer than 2 μ. The relatively coarse Cretaceous kaolins are called soft

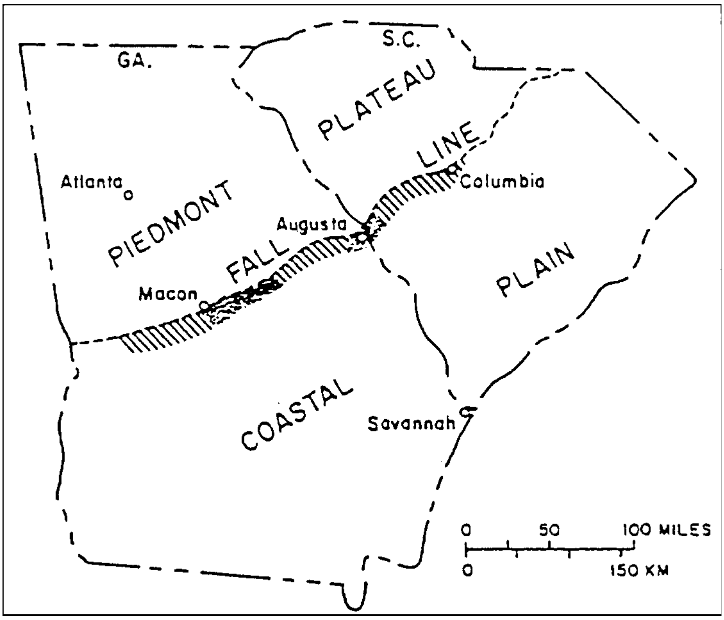

Fig. 2. Location of kaolin deposits in Georgia and South Carolina.

kaolin and the fine Tertiary kaolins are called hard kaolin (8). The Georgia and South Carolina kaolins contain ~85–95% kaolinite. Other minerals present in these Georgia and South Carolina kaolins are quartz, muscovite, biotite, smectite, ilmenite, anatase, rutile, leucoxene, hematite, goethite, and trace amounts of zircon, tourmaline, kyanite, and graphite.

Another region where large sedimentary deposits of kaolin occur is in the lower Amazon area of Brazil (13). A large deposit is mined adjacent to Jari River on the border of the states of Para and Amapa (13). This deposit is fine in particle size similar to the Tertiary deposits in Georgia and South Carolina. This deposit is 40 m thick and extends over an area of 60 km^2. This fine particle kaolin was derived from crystalline rocks on the Guyana shield and is Pliocene in age. Kaolinite is the major mineral present ranging between 80 and 98%. Other minerals present are quartz, gibbsite, rutile, anatase, tourmaline, zircon, and goethite.

Another district in Brazil where kaolin deposits occur is in the Rio Capim basin located south of the city of Belem, which is the major port city on the lower Amazon River. These Capim kaolins are relatively coarse, similar to the Cretaceous kaolins in Georgia. These kaolin deposits are associated with low lying plateaus in the Rio Capim basin and are believed to be Tertiary in age. These coarse kaolins are excellent in quality and the kaolinite content ranges from 65 to 80% with quartz as the predominant non-clay mineral present. Minor quantities of anatase, rutile, zircon, tourmaline, and goethite are also present. It is believed that the Rio Capim kaolins were derived from granites and gneisses northeast of the Capim Basin. The Capim kaolin deposits are in the state of Para (Fig. 3).

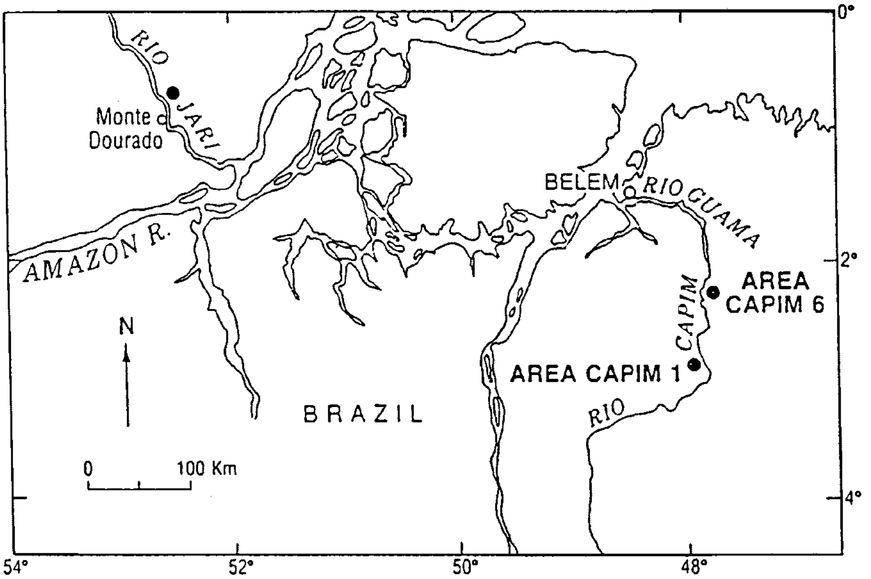

Fig. 3. Location of Jari and Capim kaolin deposits in Brazil.

Large primary kaolin deposits occur in the Cornwall district of southwest England. These kaolins were formed by the alteration of large granite bodies by warm acidic hydrothermal solutions migrating upward along faults, fractures, and joints (14). These solutions altered the feldspars in the granite leaving quartz, mica, and tourmaline relatively unaltered. Superimposed on the hydrothermally altered granite is additional alteration by surface weathering (15). Drilling has shown that kaolinization exists at depths >250 m. The kaolinite content of these altered granites ranges between 10 and 20%. The kaolinite is recovered by hydraulic methods that washes the kaolinite from the soft granite leaving quartz, mica, unaltered feldspar, and other minerals in the residue.

The Czech Republic is the principal producer of kaolin in Eastern Europe. The majority of the deposits are located in the vicinity of Karlovy-Vary, Pilzen, and Podborany. The kaolin primarily occurs as a weathering crust on crystalline rocks of the Bohemian Massif (16). The crystalline rocks where the kaolin deposits occur are granites and gneisses in which the feldspar is almost completely kaolinized. The major non-clay minerals are quartz and mica.

Both primary and secondary deposits are mined in eastern Germany. Near Dresden are two large primary deposits at Caminau and Kemmlitz (17). These kaolins are similar to those in the Czech Republic and are the result of the weathering of the Bohemian Massif, which extends into this area of Germany. The largest secondary deposit is in Bavaria near the village of Hirschau. Kaolin is the altered product of feldspar contained in a Triassic age arkose (18). The deposit extends for ~15 km and ranges in thickness from 3 to 8 m. The kaolinite content in this arkosic sand is ~10% ± 5, with quartz being the dominant non-clay mineral present.

Kaolin occurs in Spain in two areas, a primary kaolin is mined near Galicia in northwest Spain and a secondary kaolinitic sand is mined in the state of Guadalajara east of Madrid (19). This secondary kaolin is a minor constituent (10–20%) of a friable white sand used for making glass.

Near Proyanovski in Ukraine there is a large primary kaolin deposit (13). The major non-clay minerals are quartz and mica. There is also some smectite in the lower portion of the deposit. In some areas of the deposit it is 30 m thick.

Both primary and secondary deposits of kaolin occur in Australia (20). The largest primary deposits are near Pittong, north of Melbourne, where the kaolin is a residual weathering product of granite. The major non-clay minerals are quartz and muscovite. The sedimentary deposits of probable early Tertiary age occur below the extensive bauxite deposits on the Cape York Peninsula in northeastern Australia. The kaolinitic sand, which contains from 40 to 60% quartz, is located on the western margin of the Cape York Peninsula near Weipa and Skardon River.

Several kaolin deposits are mined in China. Both primary and secondary deposits occur mainly in south China (21). The largest primary kaolin deposit is located in the Suzhou district southwest of Shanghai and is the result of both hydrothermal and weathering alteration of granites and other acid igneous rocks. This kaolin contains both kaolinite and halloysite along with non-clay minerals quartz, mica, alunite, smectite, and pyrite. Another primary kaolin deposit is located in the Longyan region in southern Fujian Province. This residual weathered kaolin is comprised of kaolinte and halloysite along with some illite and small amounts of quartz, feldspar, and mica. A large secondary kaolinitic sand deposit is located at Maoming in southwestern Guanzhou province (22). The kaolinitic sand is comprised of about 80% quartz and 20% kaolinite.

Other kaolin deposits of local importance are located in Argentina, Brazil, Chile, Egypt, Indonesia, India, Korea, Mexico, Portugal, Tanzania, South Africa, Suriname, and Venezuela (11,23).

Halloysite, a kaolin group mineral, has an elongate, tubular shape and has a higher degree of hydration than kaolinite. The only halloysite deposit currently mined is located in New Zealand ~240 km north of Auckland. The deposits were formed by hydrothermal alteration of rhyolite volcanics of Pliocene or Pleistocene age (24). The other kaolin group minerals dickite and nacrite are relatively rare. There is one hydrothermal deposit in Japan with lenses of pure dickite at the Shokozan mine in the Hiroshima prefecture (25). Relatively pure nacrite lenses were reported in one deposit in Nyarit, Mexico (26). Generally, halloysite, dickite, and nacrite occur in minor quantities mainly in hydrothermal deposits although they can also occur in some secondary deposits.

There are special types of kaolinitic clays that are used primarily for ceramics. One of these types is ball clays. Ball clays are secondary and are characterized by the presence of organic matter, high plasticity, high dry and fired strength, long vitrification ranges, and light color when fired. Kaolinite is the principal mineral constituent of ball clay and typically comprises 70% or more of the minerals present. Other minerals commonly present are quartz, illite, smectite and feldspar, as well as lignitic material. The three largest areas of ball clay occurrences are in western Tennessee and Kentucky in the United

States (27), southwest England near Devonshire (28) and Germany (18). A second type of secondary kaolinitic clays used for ceramics is called refractory clays or fire clays. These kaolin clays are used in the manufacture of products requiring resistance to high temperatures (27). Major areas of occurrence of refractory clays are Missouri, Kentucky, Ohio, and Pennsylvania in the United States (27), Australia (20), Argentina, Mexico, China, and India. The refractory clays in Missouri and Kentucky are called flint clays, which are dense, brittle, fine particle size kaolinite (29). Flint clays also occur in Australia and China.

2.2. Smectites. Smectite is the name for a group of sodium, calcium, magnesium, iron, and lithium aluminum silcates. The group includes the specific clay minerals montmorillonite, saponite (magnesium smectite), nontronite (iron smectite), beidellite and hectorite (lithium smectite). Bentonite is the rock in which these smectite minerals are usually the dominant constituent. The term bentonite was first suggested by Knight (30) and is the term used today to describe the industrial minerals in which a sodium or calcium montmorillonite is the major mineral constituent. The term bentonite was defined by Ross and Shannon (31), who restricted the term to a clay material altered from a glassy igneous material usually volcanic tuff or glass. Wright (32) suggested that bentonite was any clay dominantly comprised of a smectite clay mineral and whose physical properties are dependent on this clay mineral. Grim and Guven (33) used Wright's definition and today some authors use Wright's definition and others use Ross and Shannon's.

Bentonites in which the smectite sodium montmorillonite is the major mineral component normally have a high swelling capacity (34). The best quality and largest sodium bentonite deposits are located in South Dakota, Wyoming, and Montana (35). These high swelling clays are sometimes referred to as Western or Wyoming bentonites. The bentonite beds are Cretaceous age and are in the Mowry formation (35). There are several bentonite layers in the Mowry and the thickest and most extensive is called The Clay Spur Bentonite Bed (Fig. 4), which extends west from Belle Fourche, S.D. across Wyoming to Greybull and then north across Montana into Alberta, Canada. A thickness of 4 m has been reported (36). The sodium bentonite in the Mowry formation was formed by the alteration of volcanic ash. The major mineral is sodium montmorillonite and the non-clay minerals are quartz, opal CT, zeolite, feldspar, and mica (31). Locally secondary calcite and gypsum may also be present.

Bentonites in which calcium montmorillonite is the major mineral component commonly have a low swelling capacity (34). These calcium bentonites are sometimes referred to as southern or sub-bentonites. Large deposits of calcium bentonites occur in Mississippi and Texas (33). In Mississippi the calcium bentonite is in the Eutaw formation of Upper Cretaceous age (37). It is mined in Itawamba and Monroe Counties where it is as much as 4 m thick. Quartz, feldspar, and mica are the major non-clay minerals present. It is presumed that this bentonite is an altered volcanic ash that was deposited from major volcanic eruptions in early Cretaceous time in central Mississippi. Another calcium bentonite is mined in Tippah County near Ripley from the Paleocene Porters Creek formation for its absorbent properties (38). The Texas calcium bentonites occur in a belt, which parallels the present Gulf Coast in late Cretaceous and Tertiary sediments. They are best developed in the Jackson and Gueydan formations of

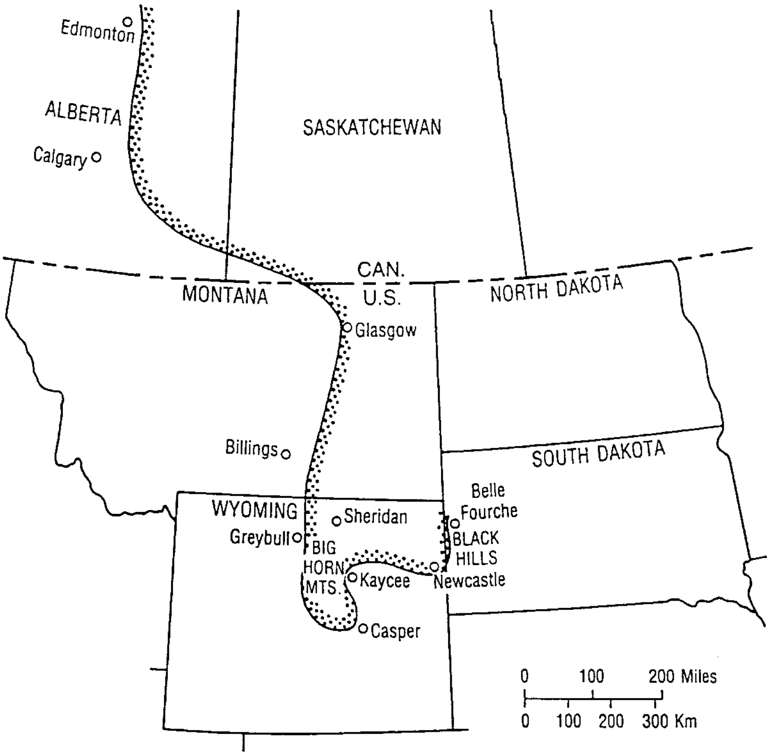

Fig. 4. Location of the clay spur bentonite bed.

Tertiary age in Gonzales and Fayette Counties, which are directly east of San Antonio (39). The calcium bentonites in these two counties range from 0.5 to 3 m in thickness. The color of these bentonites varies from white to yellowish green to dark brown almost chocolate colored. Some of the white bentonite in Gonzales County contains kaolinite (40). The major non-clay minerals are quartz, opal CT, feldspar, and mica. These bentonites are reworked volcanic ash that was deposited in lagoons and small depressions along the ancient Tertiary shoreline.

Other calcium bentonites in the United States occur in Alabama, Arizona, and Nevada. The best known and most extensively mined deposit is near Cheto, Arizona. At this location, a 5 m thick ash bed in the Pliocene Bidahochi formation has altered to calcium montmorillonite (41). This bentonite is very light gray and contains a small percentage of kaolinite. Quartz, mica, feldspar, and opal CT are the non-clay impurities. In Nevada, there is a calcium bentonite in the Amargosa Valley ~100 miles north of Las Vegas (42). This bentonite is Pliocene in age and is white to light gray. The non-clay minerals in this clay include quartz, mica, zeolite, opal CT, calcite, and dolomite. A calcium bentonite is mined at Sandy Ridge in Alabama from the Ripley formation (43).

Calcium bentonites are produced in many other countries including England, Germany, Italy, Greece, Hungary, Republic of Georgia, India, Argentina, Japan, China, Malaysia, and Brazil. The more important of these are the Redhill Surrey deposits in England of Upper Cretaceous age (44); the German bentonites north of Munich (45); the calcium bentonite on the Island of Sardinia in Italy of Miocene age (46); the Pliocene calcium bentonite on the island of Milos in Greece (33); the Askana bentonite deposit in the Republic of Georgia near Tbilisi (33); the bentonite deposit near Neuquen in Argentina (13); and the lower tertiary age bentonite in The Barmer district of Rajasthan near Akli in India (47).

Some less common bentonites including hectorite and saponite are mined in the United States. Hectorite, a lithium montmorillonite is mined near Hector, California and is hydrothermal in origin. It was formed where siliceous lithium and fluorine solutions reacted with carbonates (48). Saponite, the magnesium montmorillonite, is mined in the Ash Meadows area in the Amargosa Valley in Nevada. The saponite is Pliocene in age (42). The most comprehensive description of many of the bentonite deposits of the world may be found in the book by Grim and Guven (33).

2.3. Palygorskite and Sepiolite. Hormite is a group name that has been used for the minerals palygorskite and sepiolite. However, the International Nomenclature Committee (INC) has not yet accepted this name. Attapulgite and palygorskite are synonymous but the name palygorskite was used first so the INC discourages the uses of attapulgite as a mineral name. Palygorskite and sepiolite are hydrated magnesium aluminum silicates that have an elongate shape. Because of their large surface area, they are sometimes referred to as sorptive clays called Fuller's earth. Fuller's earth is a term used for clays and other fine particle size earthy materials suitable for use as sorbent clays and bleaching earths. The term was first used for the earthy material used in cleansing and fulling wool, thereby removing the lanolin and dirt, so this clay acquired the name Fuller's earth (49).

Palygorskite deposits are relatively few in number. Deposits are located in the United States near the Georgia–Florida border in the vicinity of Quincy, Florida and Attapulgus, Georgia; in Senegal east of Dakar; in China at Mingguang in Anhui Province and in Xuyi in Jiangsu Province, and in Ukraine (18). Sepiolite deposits are located in Spain, Somalia, and Turkey. Sepiolite is very similar to palygorskite but normally has slightly higher magnesium content and a somewhat different crystal structure.

The palygorskites in Southeastern United States are Miocene age and were deposited in marine lagoons (50). The deposits range in thickness from 0.5 to 3 m or more and are gray or tannish brown in color. These deposits are mixtures of palygorskite and smectite with the palygorskite content highest in the southern part of the district where the deposits are predominantly palygorskite. In the northern part of the district near Meigs, Georgia (51), the deposits are approximately evenly both smectite and palygorskite. Minerals other than palygorskite include smectite, quartz, and dolomite.

The Senegal palygorskite (52) deposit is very large extending from Theis south-southwest ~100 km to the Senegal-Barrie border. The deposit is ~50 km west of Dakar and is early Eocene in age and ranges in thickness from 1.5 to 6 m. The color of this clay is light tan to greenish gray. Smectite is a common constituent but is normally present in small amounts. The major impurities are quartz and dolomite.

In China, palygorskite deposits are located near Mingguang in Anhui Province and at Xuyi in Jiangsu Province. At Mingguang, the palygorskite occurs directly under a basalt and ranges from 4 to 6 m in thickness (53). Near Xuyi the palygorskite is very near the surface under a smectite-rich layer. The thickness of the palygoskite is ~6 m. These palygorskites are Middle Miocene in age and the deposits were formed from volcanic ash that fell into a lacustrine environment and altered to palygorskite (53). The palygorskite is exceptionally pure but contains some quartz and smectite impurities.

The palygoskite deposit in Ukraine is in the central part of the Ukrainian crystalline massif along the borders of the Cherkassay and Kiev regions. The palygorskite bed occurs in the middle section of a bentonite and is Lower Miocene in age (54). The thickness of the palygorskite layer is ~2 m. Other mineral constituents are smectite, mica, and quartz.

Sepiolite is mined in Spain near Toledo. The deposit is Tertiary in age and was formed in a lacustrine environment (55). The color of this clay is light tan and ranges in thickness from 1 to 5 m.

In Turkey, sepiolite deposits are found in the vicinity of Eskisehar in Anatolia (56). The sepiolite is white and is interbedded with palygorskite layers.

Some very large deposits of sepiolite occur in Somalia. They are Miocene in age but at present are only used by artists for carving various articles. Sepiolite is mined in small quantities in the Ash Meadows area in the Amargosa Valley in Nevada (57). The sepiolite occurs in 0.3–1 m stringers in saponite clays of lacustrine origin. The sepiolite is brown in color and is Pliocene-Pleistocene in age (42).

2.4. Common Clay. Common clay includes a variety of clays and shales that are fine in particle size. The clay mineral composition of these common clays is mixed but usually illite and chorite are the most common clay minerals present. Kaolinite and smectites are usually present in smaller quantities. Illite is a hydrated potassium iron aluminum silicate and chlorite is a hydrated magnesium iron aluminum silicate. These common clays are used in many structural clay products such as brick, tile, pottery, stoneware, etc (58).

Common clay occurs in rocks ranging in age from Precambrian to Holocene. They include soils, glacial clays, alluvium, loess, shale, schist, slate, and argillite. The mineral composition of these clays and shales is quite variable. In addition to the clay minerals, quartz is the most common constituent along with mica, feldspar, and many other detrital minerals. Common clays are present in every state in the United States and in every country in the world.

3. Structure and Composition of Clay Minerals

Clay minerals are phyllosilicates, which are sheet structures basically composed of silica tetrahedral layers and alumina octahedral layers. Each clay mineral has a different combination of these layers. Chemical substitutions of aluminum for silicon, iron and/or magnesium for aluminum, etc, generates positive or negative charges in the structure. The clay minerals are crystalline and their identification is determined by X-ray diffraction techniques. Grim (2) proposed a classification of four types. (*1*) Two layer types consisting of sheet structures composed

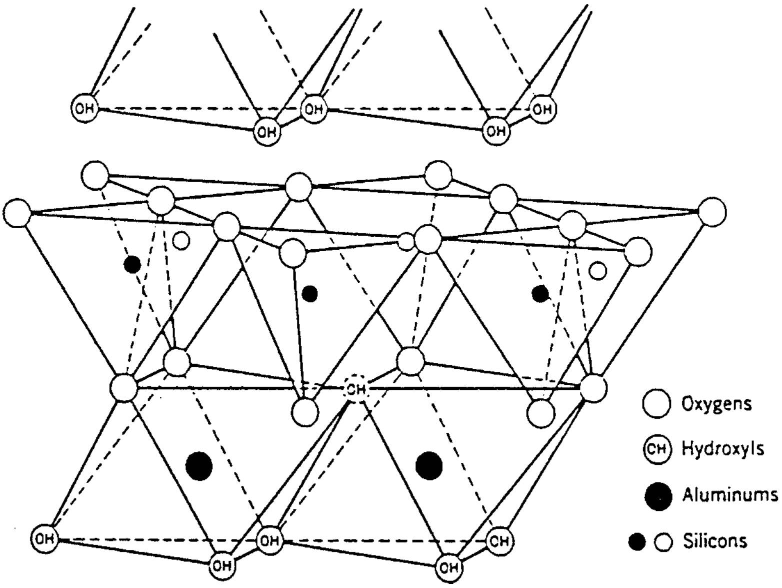

Fig. 5. Diagrammatic sketch of the structure of kaolinite.

of one layer of silica tetrahedrons and one layer of alumina octahedron (termed "1:1 layer types"). (*2*) Three-layer types consisting of sheet structures composed of two layers of silica tetrahedrons and one central octahedral layer (termed "2:1 layer types"). (*3*) Regular mixed-layer types, which are ordered stacking of alternate silica tetrahedral and alumina octahedrals layers. (*4*) Chain structure type, which are hornblend-like chains of silica tetrahedrons linked together by octahedral groups of oxygen and hydroxyls containing aluminum and magnesium ions.

The kaolin minerals (59) are hydrous aluminum silicates with the composition of $2H_2O \cdot Al_2O_3 \cdot 2Si\ O_2$. Kaolinite is the most common of the kaolin minerals. The structure of kaolinite is a single silica tetrahedral sheet and a single alumina octahedral sheet combined to form the 1:1 kaolinite unit layer (Fig. 5). These unit layers are stacked and are held together by hydrogen bonding. Variations in the orientation of the unit layers in stacking cause the differentiation between kaolinite, dickite, and nacrite (60). Figure 6 is a scanning electron micrograph of kaolinite. Halloysite is an elongate kaolin mineral that has a layer of water between the unit layers so the composition includes $4H_2O$ instead of $2H_2O$. Bates and co-workers (61) proposed that halloysite consists of curved sheets of kaolinite unit layers that cause the elongate tubes as shown in Figure 7.

Smectite structures are comprised of two silica tetrahedral sheets with a central octahedral sheet (Fig. 8). The structure has an unbalanced charge because of the substitution of aluminum for silicon in the tetrahedral sheet and iron and magnesium for aluminum in the octahedral sheet. In order to balance this negative charge, cations accompanied by water molecules enter between the 2:1 layers (Fig. 8). Sodium montmorillonite is a smectite that has sodium ions and water molecules in the interlayer and calcium montmorillonite has calcium ions and water molecules in the interlayer. Figure 9 shows a scan-

Fig. 6. Scanning electron micrograph of kaolinite from Georgia.

ning electron micrograph of sodium montmorillonite. Nontronite has iron ions in the structure, saponite has magnesium ions in the structure, and hectorite has lithium and magnesium ions in the structure. Smectites expand when water and other polar molecules enter between the layers.

Fig. 7. Electron micrograph of halloysite.

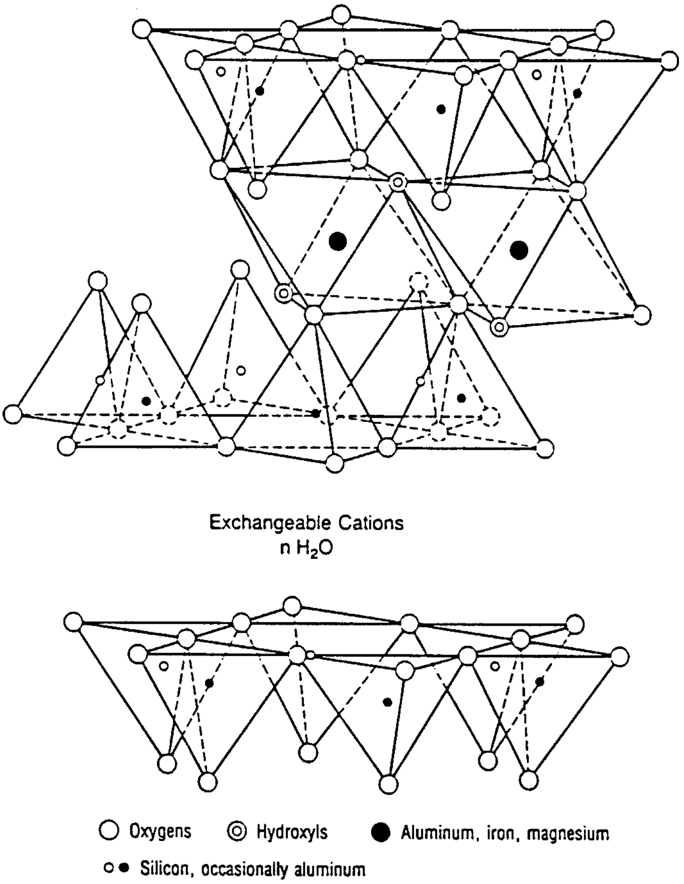

Fig. 8. Diagrammatic sketch of the structure of smectite.

Illite is a clay mineral akin to mica (62). The basic structure is a 2:1 layer similar to smectite except that more aluminum ions replace silicon in the tetrahedral sheet, which results in a higher charge deficiency, balanced by potassium ions (Fig. 10). These large diameter potassium ions act as a bridge between the 2:1 layers and so strongly bind them together that illite is nonexpandable. The composition of illite is a potassium aluminum silicate with the general structural formula of $(OH)_4\ K_2\ (Si_6\ AL_2)\ Al_4\ O_{20}$. In this structure, iron and magnesium can substitute for aluminum in the octahedral sheet.

Chlorite is a common clay mineral in shales and the structure consists of alternate silica tetrahedral layers and aluminum octahedral layers (Fig. 11). The octahedral layer has considerable substitution of iron and magnesium for aluminum (63). However, the 2:1 mica sheet octahedral layer may have a different composition than the octahedral brucite layer between the 2:1 mica sheets.

Palygorskite and sepiolite have a chain-like structure, (Fig. 12) that consists of inverted ribbons of silica tetrahedral ribbons linked together by aluminum and magnesium octahedrals. The structural formula of palygorskite is

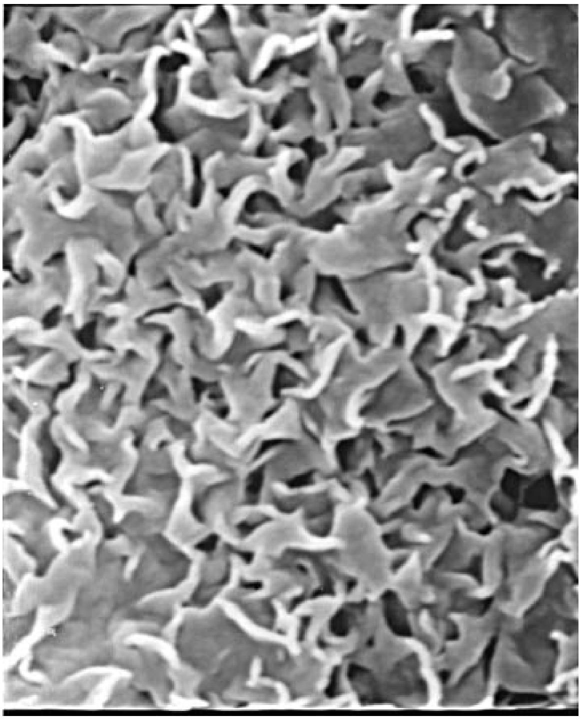

Fig. 9. Electron micrograph of sodium montmorillonite.

$(OH_2)_4\,(OH)_2\,Mg_5\,Si_8\,O_{20}\cdot 4\,H_2O$. The difference between palygorskite and sepiolite is that sepiolite has a higher content of magnesium and paylgorskite has more aluminum as well as a slightly different crystal structure. Figure 13 is an electron micrograph of palygorskite.

Because most of these layer silicates are all made up of 1:1 and 2:1 layers, there are many possible unit layer mixtures of illite, chlorite, and smectite compositions. These mixed-layer clays are relatively common in occurrence. Illite/smectite, illite/chlorite, chlorite/smectite, and kaolinite/smectite have been described. Mixed-layer clays with both random and regular layering were studied by Reynolds (64) and Moore and Reynolds (4).

4. Mining and Processing

Clays of all types are mined principally by open pit and there are very few underground mines. An understanding of the geology and the origin of clays plays an important role in clay exploration. After a clay deposit is discovered, it must be evaluated to determine thickness, quality and quantity. This may be accomplished by testing either core or auger drilled clay (11). The spacing of the drill holes depends on the geologic and surface conditions associated with the

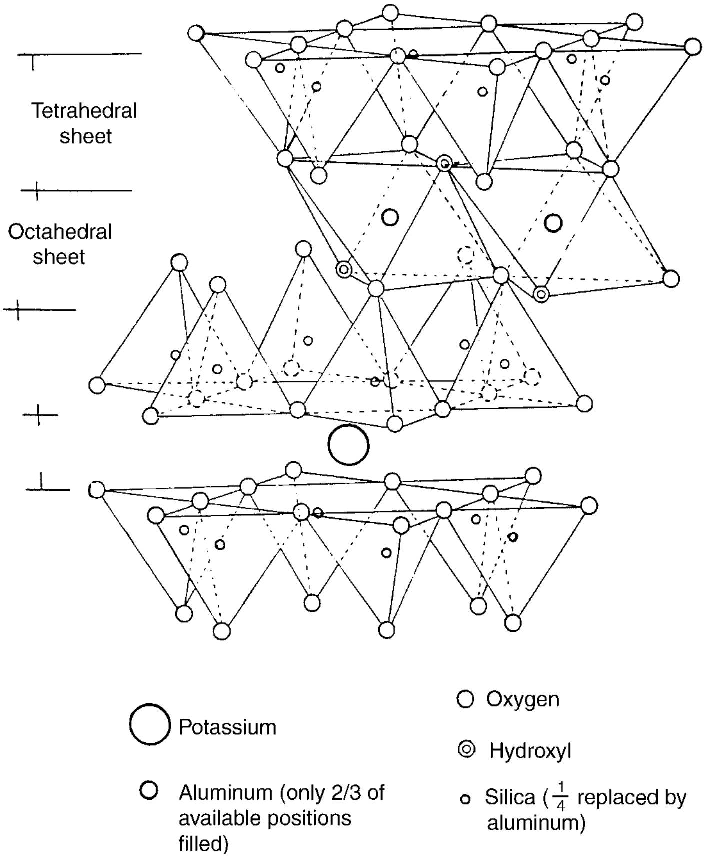

Fig. 10. Diagrammatic sketch of the structure of illite.

particular clay deposit. A drilling pattern used to test a sedimentary clay deposit is very different from the pattern used to evaluate a hydrothermal clay deposit.

Testing the core or auger samples is an important second step in determining the quality of a particular clay deposit. The tests performed to evaluate a kaolin deposit are much different than those performed on a smectite or palygorskite clay deposit. The tests are related to the applications of the clay and to determine the type of processing that will be required to make the final product. General tests that are performed on clays are (*1*) mineralogy, (*2*) percent grit (plus 325 mesh or 44 micrometers), and (*3*) color. Special tests for kaolins are (*1*) particle size distribution, (*2*) brightness, (*3*) low and high shear viscosity, and (*4*) leach response to improve the brightness. Other special tests also may be performed such as magnetic separation, flotation, selective flocculation, and abrasion. Many of these test procedures have been previously described (65). Special tests for bentonites include ion exchange capacity, viscosity, swelling capacity in water, foundry tests, surface area, water and oil absorption, and bulk density. Special tests for paylgorskite and sepiolite include surface area, exchange capacity, viscosity, water and oil absorption, and bulk density. After drilling and testing a mining plan can be designed for obtaining the maximum quantity of clay.

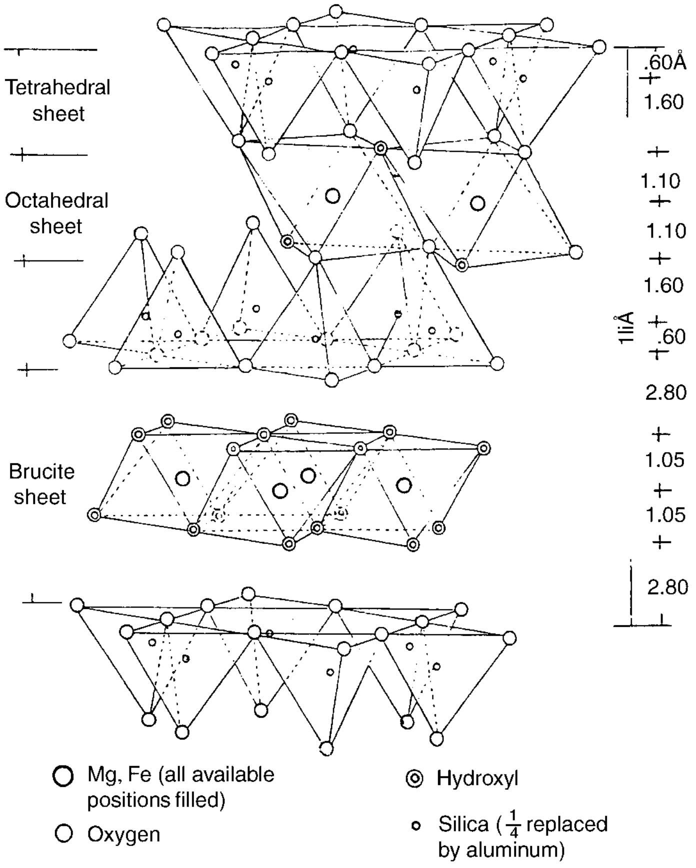

Fig. 11. Schematic diagram of the chlorite structure.

4.1. Kaolin.

Once drilling and testing have determined the quality and quantity of a deposit, the processing that is required to produce a saleable product is determined. Either a dry or wet process accomplishes beneficiation. The higher quality grades of kaolin that are used in the paper, paint, and plastics industries are prepared by wet processing because the product is more uniform, has better brightness and color, and is relatively free of impurities.

Dry Process. The dry process (66) 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 the quality of the crude kaolin. The general dry process flow sheet is shown on Figure 14. The kaolin is mined by using drag lines, shovels or front end loaders, back hoes and transported in trucks to the processing plant. There it is shredded or crushed to about egg size. After crushing, it is dried, commonly with a rotary drier. After drying, the kaolin is pulverized in a roller mill, hammer mill, disk grinder, or some other grinding device. Commonly heat is applied during the grinding to further reduce the moisture content. The pulverized kaolin is then classified to separate the fine and coarse particles. The finished product can be loaded in bulk bags and shipped by railcar or truck.

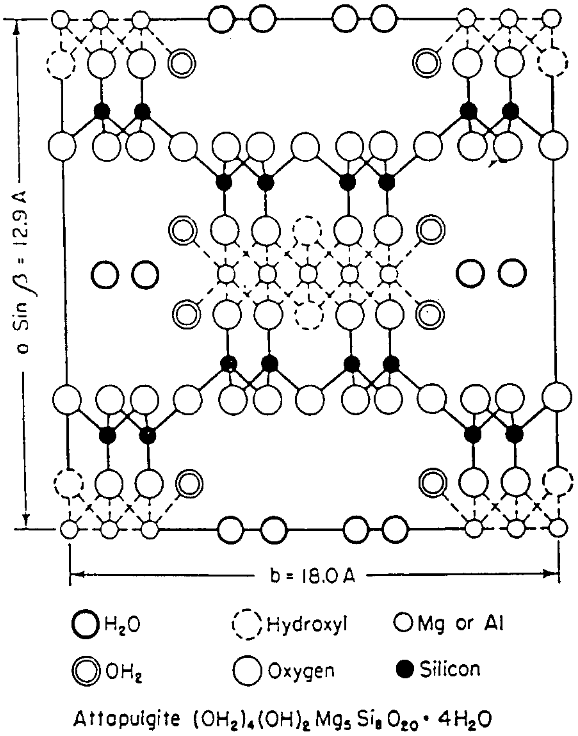

Fig. 12. Schematic diagram of the structure of palygorskite, (attapulgite).

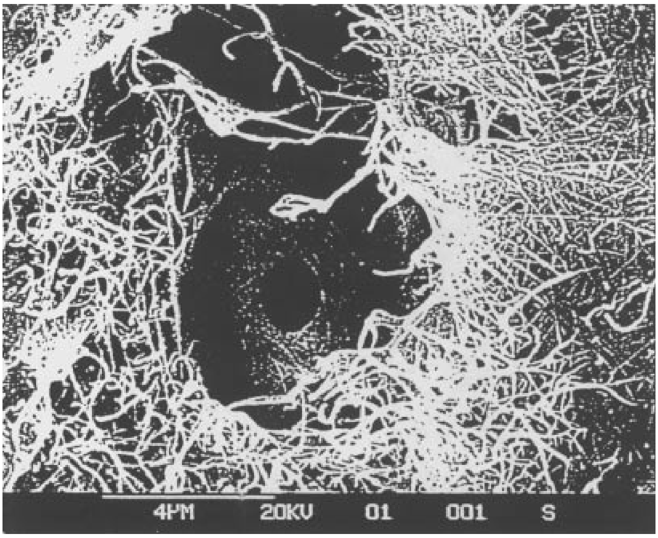

Fig. 13. Elongate particles of palygorskite from Mingguang, China.

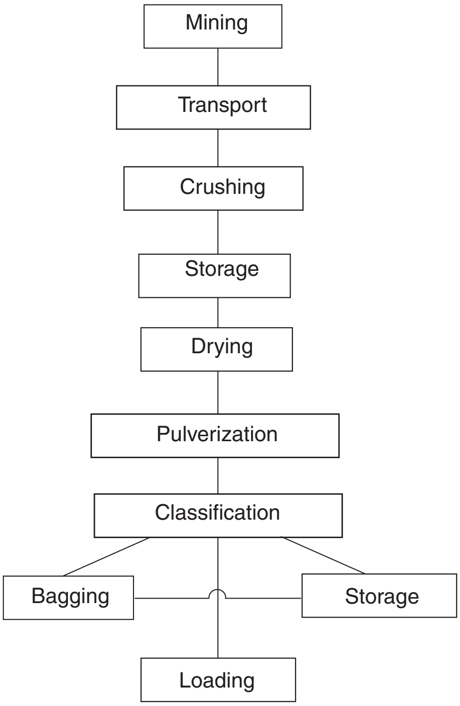

Fig. 14. General flow sheet for dry processing kaolin.

Wet Process. The general wet process flow sheet for beneficiating kaolin is shown on Figure 15. The kaolin is mined with shovels, draglines, motorized scrapers, or front-end loaders and can be either transported to the processing plant or fed into a stationary or mobile blunger. The blunger separates the kaolin into small particles, which are mixed with water and a dispersing chemical to form a clay–water slurry. The dispersing chemical can be sodium polyphosphate, sodium silicate, or sodium polyacrylate, each of which can be blended with soda ash to bring the slurry to a neutral pH that optimizes dispersion and reduces cost. The percent solids of the slurry is normally between 30 and 40, but in some special circumstances it can be in excess of 60 and as high as 70 solids. This clay–water slurry is pumped from the blunger to rake classifiers or hydrocyclones and screens to remove the grit (material >325 mesh). The grit removed from the kaolin slurry is discarded into waste ponds or into mined-out areas. The degritted slurry is collected into large storage tanks with agitators and is then pumped to the processing plant, which may be several miles away. The kaolin slurry is collected in large storage tanks at the plant before it is processed. Although each kaolin producer may process the kaolin slightly differently, the steps in the processing are generally as shown in Figure 15. The first step is to separate the kaolin particles into a coarse and fine fraction through continuous centrifuges. The degritted slurry is then passed through a high gradient magnetic separator prior to centrifugation to upgrade the crude clay by removing iron and titanium minerals. High gradient magnetic separation (HGMS) has

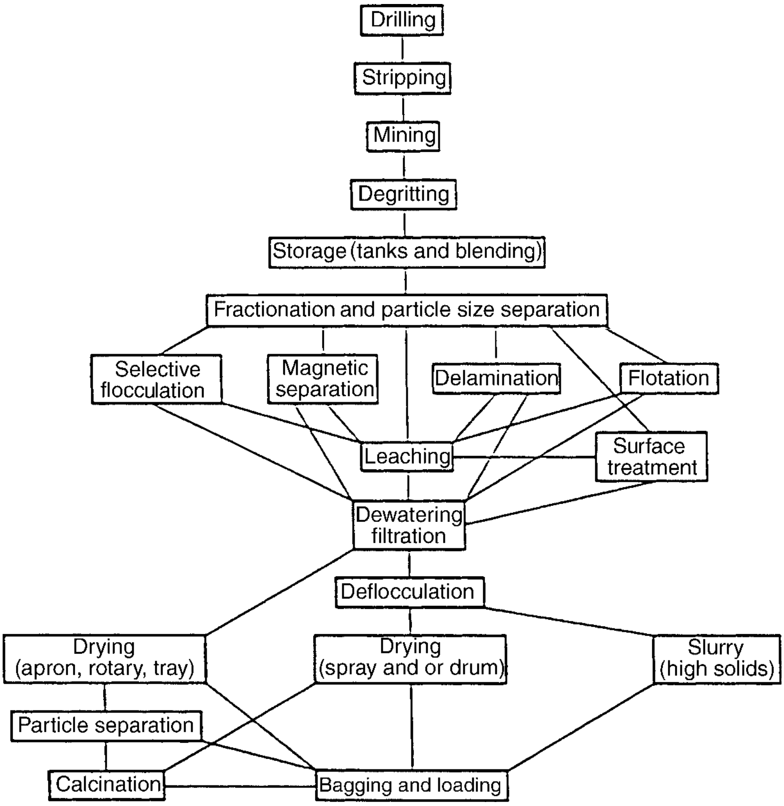

Fig. 15. Generalized flow sheet for wet processing kaolin.

become a standard processing technique in the kaolin industry. The HGMS process (67) uses a canister filled with a fine stainless steel wool that removes iron, titanium, and some mica minerals from the kaolin slurry as it passes through the canister (Fig. 16). The process can be used to upgrade marginal low brightness crude kaolins and to produce high brightness coating clays. It also reduces the amount of chemicals that are needed to leach out the iron in a subsequent processing step. The development of HGMS has dramatically increased the usable reserves of kaolin in Georgia. Superconducting cryogenic magnets with field strengths up to 5 tesla are now being used in addition to the 2-tesla electromagnets. The superconducting magnets use very little power and are effective in removing ultrafine paramagnetic minerals (68). The coarse fraction can be used as a filler in paper, plastics, paint, and adhesives, as a casting clay for ceramics, or as a feed to delaminators. Delamination, a subsequent processing step to produce a special paper coating grade, is described in a following section. The fine particle size fraction is used in paper coatings, high gloss paints, inks, special ceramics, and rubber. As shown in Figure 15, there are many different steps that can be taken after the clay is fractionated. Normally, the coarse kaolin takes one of two routes. (*1*) It can go directly to the leaching department,

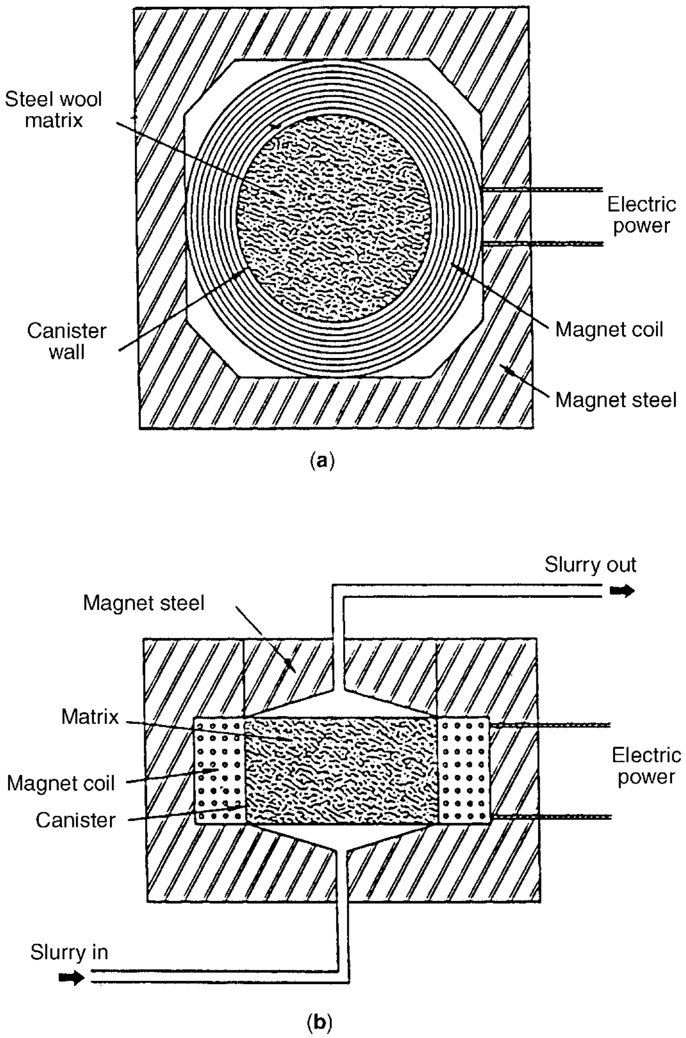

Fig. 16. Diagrammatic sketch of a high gradient magnetic separator. (**a**) Top view, (**b**) Side view section through magnet.

where it can be chemically treated to solubilize some of the iron if the brightness needs to be upgraded, or it can be flocculated so that the dewatering step is facilitated. (*2*) It can go through magnetic separation and into the delaminators or directly to the delaminators and then to the magnetic separator or to the delaminators without any magnetic separation step. In the leaching operation, the kaolin slurry is acidified with sulfuric acid to a pH of ~3.0 to solubilize some of the colloidal iron. Sodium dithionite, a strong reducing agent, is then added to reduce the iron to iron(II) state, which is more soluble and forms a clear iron sulfate that is removed with the filtrate in the dewatering step. In some cases, the iron in the kaolin is in a reduced state rather than the normal oxidized state. Usually, such kaolins are slightly gray. These gray kaolins are treated with a strong oxidizing agent, such as ozone or sodium hypochlorite, prior to acidification and the normal reduction leach procedure. To facilitate flocculation prior to dewatering, in many cases alum is added along with the sulfuric acid. At this point in the process, the kaolin slurry is between 20 and 30% solids and is flocculated. This flocculated slip is then dewatered, which raises the solids to >60%. The dewatering is accomplished by large rotary vacuum filters or plate and frame filter presses. The dewatered filter cake is then prepared for drying by using rotary, apron, drum, or spray dryers. Most of the clay that is shipped in dry bulk form is spray dried in a dispersed state. The usual process is to take the filter cake, which is flocced, and disperse it by adding a long- chain sodium polyphosphate or sodium polyacrylate.

This dispersed high solids slurry (>60%) is fed into the spray dryer, where it is sprayed or atomized and dried to meet the final moisture specifications, which normally range from <1% to as high as 6%. This dispersed clay slurry can also be dried by rotary drum dryers for some special uses that require the flake form. Slurry clay, which is normally shipped in tank cars or trucks at 70% solids, is produced by evaporaters or mixing the dispersed clay from the filters with enough spray-dried clay to bring the final solids to 70%. About 80% of all shipments of coating and fine filler clays to the paper industry is now being shipped in slurry form. If the filter cake is to be dried with rotary or apron dryers, then the filter cake is extruded into noodles ~3/8 in. (1 cm) in diameter and fed into the rotary dryer or onto an apron dryer. The final moisture from these dryers is generally ~6%. This type of clay can be shipped in lump form, or if necessary in powder form, using hammer mills swept with hot air. The final moisture of this disintegrated kaolin can be <0.5%. It is commonly referred to in the kaolin industry as "acid clay" because the pH is ~4.5. The wet processes are used on the sedimentary kaolins in Georgia and Brazil.

Primary kaolins such as the English china clays produced in the Cornwall district of southwest England are wet processed in much the same manner as the Georgia kaolins except for the mining methods. The kaolin content of the weathered granites ranges from 10 to 20%. Mining uses high pressure hydraulic monitors that play a stream of water on the mine face, washing out the fine particle kaolin and leaving the coarse quartz and mica residue. The fine kaolin is suspended and is transported in small rivulets to a collecting basin in the bottom of the open pit. This slurry is pumped to large thickeners, where the clay slurry is concentrated, and then processed generally following Figure 15.

Special Processes. Several special processes are used to produce unique and special quality grades of kaolin. One of these special processes is delamination, which is a process that takes a large kaolin stack and separates it into several thin, large-diameter plates (Fig. 17). These thin, large-diameter plates have excellent covering power on rough base sheets of paper and are also used to produce high quality lightweight coatings. The process of delaminating involves attrition mills into which fine media, such as glass beads or nylon pellets, are placed along with the coarse kaolin stacks and intensely agitated. The fine media impact the kaolin stacks, separating them into thin plates (69). The brightness and whiteness of the delaminated kaolin is very good; the clean newly separated basal plane surfaces are white because they have been protected from ground water and iron staining. The delamination process has enabled the

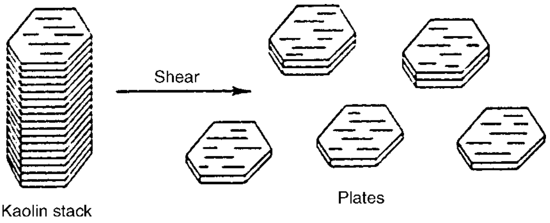

Fig. 17. Diagrammatic representation of delamination of a kaolin stack into large thin plates.

kaolin industry to convert low priced coarse clay into a higher value special coating and filler clay. Another special process is ultraflotation, which is a flotation process to remove iron and titanium contaminants to make a 90% brightness kaolin product (70). Selective flocculation (71–73) is another special process that produces a 90% brightness kaolin product by selectively removing iron and titanium impurities.

Calcining is another special treatment that is used to produce special grades. One grade is thermally heated to a temperature just above the point where the structural hydroxyl groups are driven out as water vapor, which is between 650 and 700°C. This procedure produces a bulky product that is used as paper coating additive to enhance resiliency and opacity in low basis weight sheets. A second grade is thermally heated to 1000–1050°C. By proper selection of the feed kaolin and careful control of the calcination and final processing (74), the abrasiveness of the calcined product can be reduced to acceptable levels. The brightness of this fully calcined, fine-particle kaolin is 92–95%, depending on the feed material. It is used as an extender for titanium dioxide in paper coating and filling and in paint and plastic formulations.

Another special process is *surface treatment*. Kaolin is hydrophilic and can be easily dispersed in water. Because of the nature of the kaolinite surface, it can be chemically modified to produce hydrophobic and organophilic characteristics. Generally, an ionic or a polar nonionic surfactant is used as a surface-treating agent. These surface modified kaolins (75), are used in paint (1), plastics (76), and rubber (77).

4.2. Smectite.

Virtually all bentonite, which is comprised mainly of a smectite mineral, is surface-mined. Bulldozers and motorized scrapers are most commonly used for removing overburden. In a typical open pit, the overburden is removed in panels. The exposed bentonite is then mined by loading the material into trucks with draglines, shovels, or front-end loaders. Once the bentonite is removed, the overburden from the next panel is shifted to the mined-out panel.

Bentonite beneficiation and processing involves relatively simple milling techniques that includes crushing or shredding, drying, and grinding and screening to suitable sizes (Fig. 18). The high swelling Wyoming or sodium bentonites have ~25% moisture. The processed bentonite generally contains only 7–8% moisture, although because bentonite is hygroscopic, it may contain considerably more moisture when used. The raw bentonite is passed through some sort of crushing or shredding device to break up the large chunks before drying. Drying

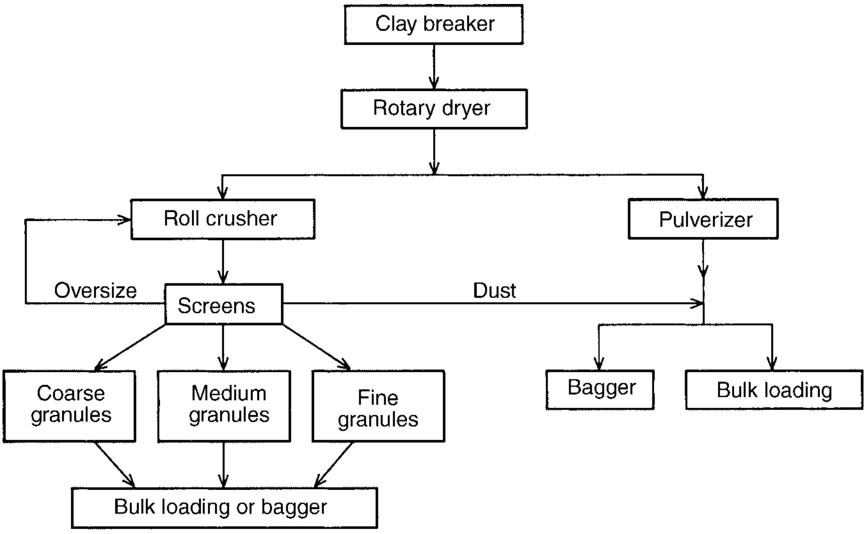

Fig. 18. Flow sheet for processing bentonite.

in most plants is accomplished by gas- or oil-fired rotary dryers, but in one bentonite plant in Wyoming, a fluidized-bed dryer is used. The bentonite properties can be seriously affected by overdrying, so the drying temperature must be carefully controlled. The dried bentonite is ground and sized in several ways. Granular bentonite is cracked by using roll crushers and screened to select the proper size range granules. Most powdered bentonite is ground with roll or hammer mills to ~90% finer than 200 mesh. The bentonite is shipped mainly in bags, but some is shipped in bulk.

Special processing is used in some plants to produce special products. Extruders can be used to pug the clay and mix it with additives that may improve the viscosity and dispersion properties. Some hectorite and Southern bentonites are beneficiated wet. In this process, the bentonite is dispersed in water and degritted by centrifuges, hydrocyclones, settling devices, or screens. The slurry is either filtered and then flash-dried or sent directly to rotary drum or spray dryers.

Organic-clad bentonite is bentonite that is processed to replace the inorganic exchangeable ions with alkylamine cations, which produces a hydrophobic clay (78). These organic-clad bentonites are used in paints, greases, oil-base drilling muds, and to gel organic liquids.

Acid-activated bentonites are special sorptive clays used for bleaching edible oils and decolorizing special lubricating oils. The process flow sheet for acid activation is shown in Figure 19. The process involves slurrying the bentonite in warm water, removing the grit by hydrocylcones, reacting the clay with either sulfuric or hydrochloric acid at elevated temperature, dewatering in plate and frame filter presses, and flash drying. A dry activation process is also used and involves adding a concentrated sulfuric acid to the clay in a blender and pulverizing and drying the acid–clay mixture to ensure uniform distribution of the

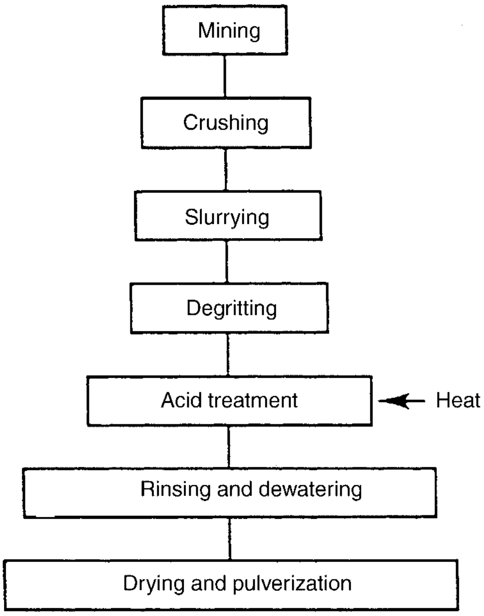

Fig. 19. Flow sheet for the production of acid activated bentonite.

acid. Aluminum, magnesium, and iron octahedral ions are partially removed, resulting in a highly charged particle saturated with hydrogen ions, which makes for a good bleaching and decolorizing clay.

4.3. Palygorskite-Sepiolite. The mining of palygorskite clays is no different than mining bentonites. The processing is also similar (Fig. 20). The clay is shredded or crushed, dried, screened, air-classified, and packaged. Some of this clay is thermally treated to harden the particles to prevent disintegration of the granules during bagging, transport, and handling prior to arrival to the customer. The temperature of this thermal treatment is <400°C so that no structural modification results, but all of the absorbed water is driven from the surface and interior of the particles.

When palygorskite (attapulgite) is to be used for salt-water drilling mud, the clay is extruded at high pressure through small orifices. This shears apart the bundles of palygorskite into individual elongate particles, which produces a higher viscosity. Extrusion with magnesium also produces a gelling quality product.

5. Environmental Considerations

Almost all clays are surface mined, so the industry is required to reclaim the disturbed land in most countries. Common practice is to open a cut and then deposit the overburden from the following panels or cuts into the mined out areas. The land is leveled or sloped to meet the governmental requirements and then planted with grasses or trees. In the processing plants the waste materials,

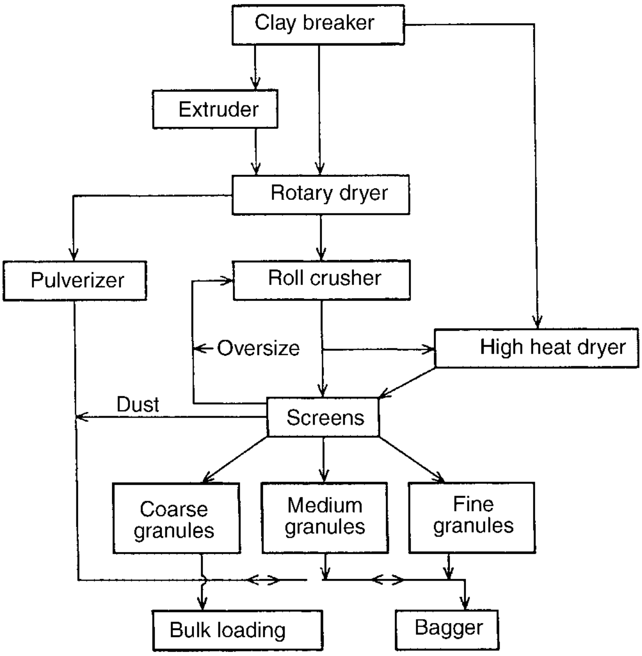

Fig. 20. Flow sheet for dry processing palygorskite (attapulgite).

which include chemicals and separated clay particles or other minerals, are collected in impounds. The clay and other particles are flocculated with alum or other chemical flocculants, and the clear water is released into streams after adjusting the pH to 6–8.

Air quality is maintained in the processing plants by using dust collectors on the dryers and by enclosing transfer points where dry clay may cause dust. In areas such as the bagging departments, the workers may be required to wear dust masks. None of the clays, kaolins, smectites, or palygorskite-sepiolite are health hazards. Any dust, if inhaled in large quantities, can be a problem, but the industries use dust collectors and require workers to wear masks, therefore, no serious lung ailments result. The clays themselves contain no deleterious trace elements or chemicals that are hazardous to human health.

6. Production and Consumption

Clays are one of the most important and versatile industrial minerals. They are used in construction, agriculture, process industries, and environmental applications (79). They are necessary ingredients in many products including kaolins in paper, paint, ceramics and rubber, bentonite in drilling fluids, foundries, and fluid barrier applications, palygorskite-sepiolite in special drilling fluids, carriers for agricultural chemicals, suspending agents in paints and pharmaceuticals, and common clays for making bricks and other structural clay products.

The total kaolin production in the world is estimated to be $\sim 40 \times 10^6$ tons/year; bentonite production about 10×10^6 tons/year; palygorskite-sepiolite about 3×10^6 tons/year; and common clays over 100×10^6 tons/year.

Future research and development efforts will improve current clay products and develop new value added products. There are adequate clay reserves in the world so that tomorrow's markets will continue to be served.

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