

Applied clay mineralogy today and tomorrow

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ABSTRACT: The clay minerals kaolin, smectite and palygorskite-sepiolite are among the world's most important and useful industrial minerals. Clay minerals are important in a number of geological applications such as stratigraphic correlations, indicators of environments of deposition and temperature for generation of hydrocarbons. In agriculture, the clay minerals are a major component of soils and determinant of soil properties. The clay minerals are important in construction where they are a major constituent in brick and tile. The physical and chemical properties of the clay minerals determine their utilization in the process industries.

What about tomorrow? Processing techniques will be improved and new equipment will be available so that improved clay mineral products will be available. Pillared clays and nanocomposites will become important. Further developments in organoclay technology and surface treatments will provide new usages for these special clays. Tomorrow will see further growth and utilization of the clay minerals.

Clay minerals are some of the most important, if not the most important, of our industrial minerals. Millions of tons are utilized annually in a large variety of applications. These applications include uses in geology, the process industries, agriculture, environmental remediation and construction. This paper focuses on the major applications of the clay minerals today and looks into the future growth and applications of certain specific clay minerals.

Why are certain clay minerals used in specific applications? The reason is that the physical and chemical properties of a particular clay mineral are dependent on its structure and composition. The structure and composition of kaolins, smectites, and palygorskite and sepiolite are very different even though they each have octahedral and tetrahedral sheets as their basic building blocks. However, the arrangement and composition of these octahedral and tetrahedral sheets account for major and minor differences in the physical and chemical properties of kaolin, smectites and palygorskite.

Table 1 shows some of the properties of kaolins, smectites and palygorskites that account for many of their applications

The important characteristics relating to the applications of clay minerals are particle size and shape, surface chemistry, surface area, surface charge, and other properties specific to particular applications, including viscosity, colour, plasticity, green, dry and fired strength, absorption and adsorption, abrasion and pH. In all applications, the clay minerals perform a function and are not just inert components of the system. There are several articles and books that discuss clay mineral applications and, although some are historical, they are essential to our present understanding of how and why the clay minerals have such an extensive industrial utilization. Some of these are Anonymous (1955), Pask & Turner (1955), Murray & Lyons (1956), Grim (1962), Clem & Doehler (1963), Haden (1963), Jordan (1963), Konta (1995), Murray (1963, 1984, 1991, 1986), Nahin (1963), Smoot (1963), Ovcharenko *et al.* (1964), Bundy *et al.* (1965), Siddiqui (1968), Grimshaw (1971), Grim & Guven (1978), Robertson (1986), Galán (1987, 1996), Elzea & Murray (1994), Heivilin & Murray (1994), Pickering & Murray (1994), and Keith & Murray (1994).

TABLE 1. Some properties of clay minerals that can be related to their applications.

Kaolin	Smectite	Palygorskite
1:1 layer	2:1 layer	2:1 layer inverted
White or near white	Tan, olive green, white	Light tan
Little substitution	Octahedral and tetrahedral substitution	Octahedral substitution
Minimal layer charge	High layer charge	Moderate layer charge
Low base exchange capacity	High BEC	Moderate BEC
Pseudo-hexagonal flakes	Thin flakes and laths	Elongate
Low surface area	Very high surface area	High surface area
Very low absorption capacity	High absorption capacity	High absorption capacity
Low viscosity	Very high viscosity	High viscosity

Specific applications are discussed under the headings kaolins, smectites, and palygorskite and sepiolite. The last section covers growth of applications for tomorrow.

KAOLINS

Kaolins are rocks that are comprised largely of one of the kaolin group of minerals which are kaolinite, halloysite, dickite and nacrite. The most common kaolin mineral is kaolinite; this mineral's physical and chemical properties, and its applications are discussed in this section. The other members of the kaolin group are relatively rare, although some occurrences of halloysite (Murray *et al.*, 1977), dickite (Sudo & Shimoda, 1978), and nacrite (Hanson *et al.*, 1981) are being, or have been, mined. The term 'China Clay' is, and has been, used as a synonym for kaolin.

For most industrial applications kaolin must be refined and processed from the crude state to enhance its whiteness, purity and other important commercial characteristics. Common impurities in kaolins are quartz, micas, illite, montmorillonite, goethite, hematite, pyrite, anatase, rutile, ilmenite and trace amounts of tourmaline, zircon and other heavy minerals, most of which can be removed by wet processing.

Kaolins are most often formed by the alteration of Al silicate minerals in a warm, humid environment. Feldspar is the most common source mineral. Kaolins which have altered *in situ*, either by weathering or by hydrothermal alteration, generally retain the texture and form of the parent rock and these are referred to as primary kaolins. Those kaolins which have been deposited by

sedimentation in fresh or brackish water environments are called secondary. Both types of kaolin are mined and used commercially.

Kaolin occurrences are common and known on all the continents of the world except Antarctica, but commercially viable deposits are relatively few in number. The best known and most highly utilized deposits are primary kaolins in the Cornwall area of southwestern England (Bristow, 1977), the sedimentary kaolins in Georgia and South Carolina in the United States (Pickering & Murray, 1994) and the sedimentary kaolins from the Amazon region of Brazil (Murray, 1981).

As mentioned in Table 1, kaolinite is classified as a two-layer clay, i.e. a sheet of silica tetrahedra combined through octagonal hydroxyls which are shared with an alumina octahedral sheet (Fig. 1). This structure has little substitution of other elements, but there may be some Fe substituting for Al and some Al possibly substituting for Si. Because of this limited substitution in the kaolinite layer, the charge on the kaolinite layer is minimal thus accounting for the low cation exchange capacity. Some charges occur on the edge of the kaolinite crystal due to broken bonds (Grim, 1962). Absorption, which is related to surface area, is another property that is important in many industrial applications. Kaolinite has a relatively low surface area and a low surface charge compared to smectites and palygorskite and sepiolite, so it exhibits low absorption and adsorption. Electron micrographs of kaolinite show that in general it has relatively sharp crystalline morphology which exhibits a pseudo-hexagonal shape (Fig. 2).

Kaolinite is white or near-white in colour which is another important attribute that relates to its chemical composition. One of the more important

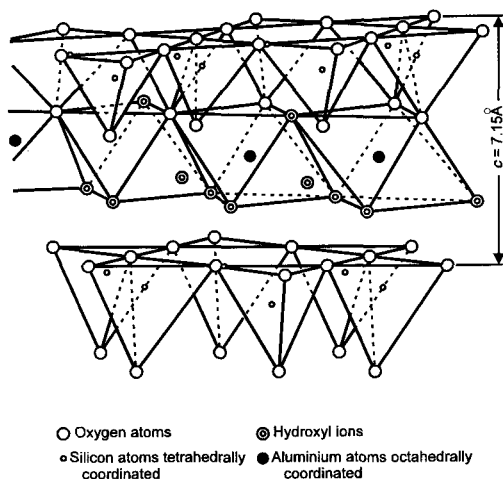


FIG. 1. Kaolinite structure.

properties that many kaolins exhibit is that they have good flow properties when present in large amounts in water. This is particularly important in one of the major uses of kaolin — the coating of paper. The reasons that kaolin has good rheology are that it has little or no charge deficiencies in the structure, has a low surface area, exhibits a good crystalline morphology and its particle size is fine with a broad particle size distribution.

Kaolinite is soft with a hardness of ~ 1.5 on the Mohs scale which means that relatively pure kaolins are not abrasive. This property is very important in many industrial applications. Because kaolin is softer than almost all materials with which it comes into contact, the wear and tear on equipment is minimal.

Relatively pure kaolins are refractory and melt or fuse at a temperature of $\sim 1850^\circ\text{C}$. In most instances, kaolins and particularly ball clays, which primarily comprise kaolinite, are plastic and fire to a white or near-white colour. These properties, in addition to low shrinkage, make kaolins very important ceramic raw materials. Ball clays generally are naturally much finer in particle size than kaolins and thus have higher plasticity and higher modulus of rupture than kaolins. One of the major reasons why a ball clay is added to a ceramic body is to confer green and dry strength.

Kaolinite is hydrophilic and, with the addition of a small amount of chemical dispersant to negate the edge charges due to broken bonds, will disperse readily in water. Therefore, kaolins are used

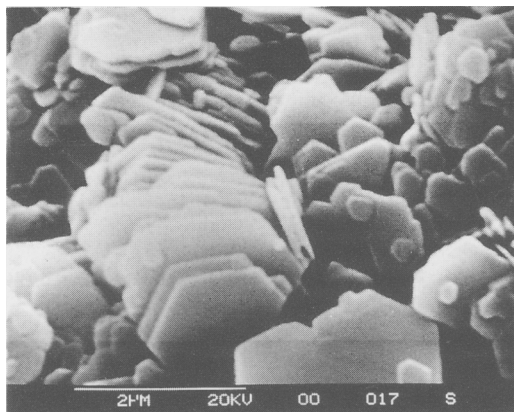


FIG. 2. SEM of kaolinite (Capim River).

extensively in water-based paint and paper-coating formulations. The dispersion of kaolin particles in a water-based system is essential in order for the kaolin to impart the properties of printability, smoothness and opacity to a coated sheet of paper (Murray, 1984).

The particle shape of kaolinite is an important factor in its industrial utilization. Kaolinite particles that are $\sim 2 \mu\text{m}$ thick are thin plates that orient on a coated surface because of their flat two-dimensional nature. This orientation gives a gloss or sheen to the coated surface and, in the case of coated paper, makes for excellent print quality.

Although there are other specific properties that could be enumerated, it can be seen that kaolin is one of the most versatile of the industrial minerals in its diverse application because it is chemically inert over a pH range of 4 to 9; is white or near white in colour; has good covering or hiding power (opacity) when used as a pigment or extender in coating and filling applications; is soft and non-abrasive; is fine in particle size; is plastic, refractory, and fires to a white or near white colour; has low conductivity of both heat and electricity; is hydrophilic and disperses readily in water; is relatively low in cost.

Some of the many uses of kaolin are shown in Table 2. The largest user of kaolin is the paper industry where it is used both as a filler in the sheet and as a coating on the surface of the sheet. Some properties that are important to the paper maker are dispersion, rheology (both low and high shear), brightness and whiteness, gloss and smoothness, adhesive demand, film strength, ink receptivity, and print quality.

TABLE 2. Industrial uses of kaolin.

Paper coating	Cement	Food additives
Paper filling	Pencil leads	Bleaching
Extender in paint	Adhesives	Fertilizers
Ceramic raw material	Tanning leather	Plaster
Filler in rubber	Pharmaceuticals	Filter aids
Filler in plastics	Enamels	Cosmetics
Extender in ink	Pastes and glues	Crayons
Cracking catalysts	Insecticide carriers	Detergents
Fibreglass	Medicines	Roofing granules
Foundries	Sizing	Linoleum
Desiccants	Textiles	Polishing compounds

Another very large user of kaolins is the ceramics industry, particularly in whiteware, sanitaryware, insulators, pottery and refractories. Both primary and secondary kaolins can have excellent ceramic properties (Murray, 1986). A kaolin which does not have the physical and chemical properties for use in a paper-coating application can have excellent ceramic properties. Halloysite, one of the kaolin minerals, is used as an additive in high quality dinnerware to provide translucency and strength. The major source of halloysite is on the North Island of New Zealand (Murray *et al.*, 1977).

A treatment that is used to produce special value-added products from kaolin is calcining. Calcining involves heating to high temperatures to drive off the structural water and to reorganize the Al and silica into new high-temperature crystalline phases. One product is heated to a temperature range of 650–700°C which is above the normal dehydroxylation temperature of ~550–570°C. At this temperature, the structural hydroxyl groups have been driven off as water vapour. The kaolinite (which is called meta-kaolin at this point) is bulky and has properties that make it an excellent dielectric which is used as a filler in electrical wire coatings. A second type of calcined product is heated to ~1050°C, which is above the temperature where the meta-kaolin is reorganized to form mullite, spinel and cristobalite. These mullite and/or spinel needles that appear on the surface of the former kaolinite particle (Fig. 3) are excellent light scattering points which gives the product a high degree of brightness and good opacity. This product is used as an extender for TiO₂ in many applications in order to reduce formulation costs particularly in paper coating and filling, and in

paints. Another use for this product is as a very fine abrasive particularly in automobile polishes and cleaning compounds. A third calcined product is one which is heated to as much as 1300°C to produce a refractory grog which can be added to refractory mixes to reduce shrinkage and increase the refractoriness.

Another special process that is used to change the surface chemistry of the kaolinite is surface treatment. As mentioned previously, kaolinite is hydrophilic and can be easily dispersed in water. Ionic and/or polar non-ionic surfactants can be applied to the surfaces of the kaolinite to modify them to produce particles which have hydrophobic or organophilic characteristics. These surface-modified kaolins are used extensively in the plastics and rubber industries to improve the dispersion and produce more functional fillers.

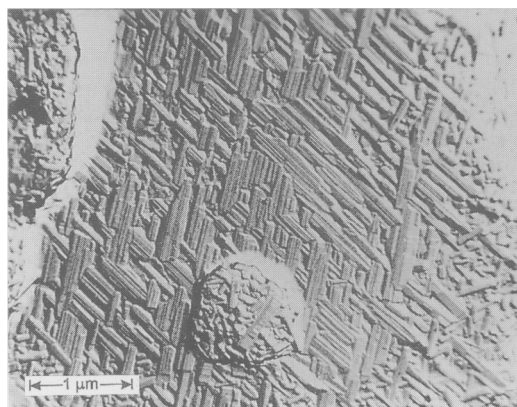


FIG. 3. SEM of calcined kaolinite (Georgia).

Another special application for kaolinite is in the production of synthetic zeolites. Kaolinite can be treated with Na, Ca, Mg and K hydroxides which when heated to $\sim 100^\circ\text{C}$ will convert the kaolinite to zeolite structures with different pore sizes. These synthetic zeolites are used primarily as cracking catalysts in petroleum refining and to remove water from gas streams.

From the above, it can be seen that kaolins are indeed a valuable and versatile industrial mineral. Only a few kaolins in the world can be used for paper coating because of the stringent requirements for low viscosity and good colour. Many more deposits, however, can be utilized for ceramics and filler applications, so a careful evaluation of a kaolin deposit must be made in order to determine whether or not the material can be processed for some industrial use or uses.

SMECTITES

Smectite is the mineral name given to a group of Na, Ca, Mg, Fe, and Li-Al silicates. The mineral names in the smectite group which are most commonly used are Na-montmorillonite, Ca-montmorillonite, saponite (Mg), nontronite (Fe), and hectorite (Li). The rock in which these smectite minerals are dominant is bentonite. The term bentonite was defined by Ross & Shannon (1926) as a clay altered from glassy igneous material, usually a tuff or volcanic ash. Grim & Guven (1978) redefined the term bentonite to be any clay predominantly composed of a smectite mineral, regardless of its origin.

Bentonites which are used industrially predominantly comprise either Na-montmorillonite or Ca-montmorillonite and to a much lesser extent saponite and hectorite. These smectite minerals that comprise bentonites have significantly different physical and chemical properties which dictate their utility to a major degree.

Smectite is a 2:1 layer silicate (Fig. 4) in contrast to kaolinite which is a 1:1 layer silicate. Smectite has two silica tetrahedral sheets joined to a central octahedral sheet. There can be considerable substitution in the octahedral sheet, usually by Fe and Mg for Al, which creates a charge deficiency in the layer (Brindley & Brown, 1980). Also, there can be substitution in the tetrahedral sheets of Al for Si which again creates a charge imbalance. Grim (1962) pointed out that many analyses have shown that this charge imbalance is ~ -0.66 per unit-cell.

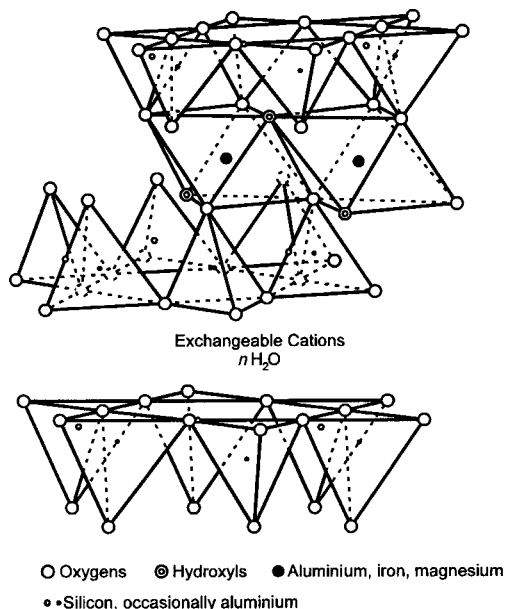


FIG. 4. Smectite structure.

This net positive charge deficiency is balanced by exchangeable cations absorbed between the unit layers and around the edges. Thus, if the exchangeable cation is predominantly Na, the specific mineral is Na-montmorillonite and if it is predominantly Ca, it is a Ca-montmorillonite. Both the Na and Ca ions are hydrated in this interlayer position. Sodium-montmorillonites generally have one water layer in the interlayer position and Ca-montmorillonites generally have two water layers which account for the basal spacing on the X-ray diffraction pattern of 15.4 Å for a Ca-montmorillonite and 12.6 Å for a Na-montmorillonite.

The high charge on the smectite layer is satisfied by cations such as Na, Ca, Mg, Fe and Li. Smectites have a high CEC which is generally of the order of 60–100 mEq/100 g of clay. These interlayer cations and water layers can be replaced by polar organic molecules such as ethylene glycol, quaternary amines and polyalcohols. This is an important property which can be translated into some very useful organo-clay products. Smectites occur normally as very thin flakes of extremely small particle size (Fig. 5) which give the clay a high surface area when well dispersed. The high charge, CEC, and surface area give smectites a high degree of absorbency for many materials (oil,

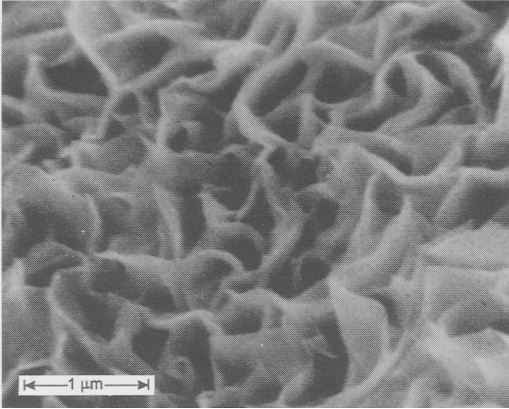


FIG. 5. SEM of Na-montmorillonite (Wyoming).

water, chemicals, etc.); when mixed with water, the high charge and fine particle size give the fluid a very high viscosity. These basic properties of smectite relate to many industrial uses which are described in the following paragraphs.

The colour of smectites can vary from white to tan to brown or brownish green to blue-green. Colour, especially if the colour is white, controls the use in many instances. The many uses of smectites are shown in Table 3.

The primary uses are in drilling muds, as foundry bond clays, for pelletizing iron ores, and as sealants in irrigation ditches, farm ponds, earthen dams, landfill liners, etc. The major Na-montmorillonite deposits are the Western Bentonites which are mined in South Dakota, Wyoming and Montana in the USA (Elzea & Murray, 1990). These are high-swelling clays which will expand up to ten or more times their clay volume when placed in water. This unique swelling property makes them necessary

ingredients in most freshwater drilling muds. These Western (Na) Bentonites yield 100 barrels of mud per ton. Only 5% of this high-swelling bentonite is required to produce the high viscosity, thixotropic fluid with low filter cake permeability that is necessary to meet the American Petroleum Institute (API) drilling fluid specifications. Hectorite is also a very high-swelling clay but because the deposits are relatively much smaller, it is used primarily for special applications where high viscosity suspensions are required. Some Ca-montmorillonite can be treated with a Na compound such as soda ash or Na polyacrylate to exchange Na for Ca to make a drilling mud, but neither the viscosity nor the water loss properties are as good as with the natural Na Western Bentonites.

The major Ca-bentonite deposits in the world are in Texas and Mississippi in the USA, in England, Germany, Greece, Italy, Spain and India. The term fuller's earth is used for any fine-grained earthy material suitable for bleaching oils and absorbent uses. It has no compositional or mineralogical meaning. However, most fuller's earth materials are composed of Ca-montmorillonite and/or palygorskite.

The moulding sands used in foundries consist of quartz sand and bentonite. The bentonite provides bonding strength and plasticity. A small amount of tempering water is added to the mixture to make it plastic. This mixture of sand, clay and water is then moulded around a pattern and is cohesive enough to maintain the shape after the pattern is removed. Then, molten metal is poured into it. The important foundry properties of bentonite are green compression strength, dry compression strength, hot strength, flowability, permeability and durability. These properties vary greatly with the amount of tempering water added (Grim & Guven, 1978).

TABLE 3. Industrial uses of smectites.

Drilling mud	Medical formulations	Crayons
Foundry bond clay	Polishing & cleaning agents	Cement
Pelletizing iron ores	Detergents	Desiccants
Sealants	Aerosols	Cosmetics
Animal feed bonds	Adhesives	Paint
Bleaching clay	Pharmaceuticals	Paper
Industrial oil absorbents	Food additives	Fillers
Agricultural carriers	De-inking of paper	Ceramics
Cat box absorbents	Tape-joining compounds	Catalysts
Beer and wine clarification	Emulsion stabilizer	Pencil leads

Both Na- and Ca-bentonites are used as foundry bonding clays. Calcium-montmorillonite has a higher green strength, lower dry strength, lower hot strength and better flowability than Na-montmorillonite. Blends of Na- and Ca-bentonites are commonly used to gain the optimum properties for the moulding sand which is needed for a particular metal.

Bentonites are used extensively to pelletize iron ores (DeVaney, 1956). Finely pulverized ore concentrates are pelletized to balls of ~2.5 cm in diameter for ease of transport and to produce a superior furnace feed. Bentonite constitutes ~0.5 wt% of the pellets. Because of its superior dry strength, Na-bentonite is preferred for pelletizing ores.

Because of their high swelling capacity, Na-bentonites are used as water barriers. The bentonite is used to prevent the flow of water through earthen structures such as dams, to prevent seepage of water from ponds and irrigation ditches, to contain chemicals in landfills and toxic waste impoundments, and to prevent water from entering basements of homes.

Another use of high-swelling Na-bentonite is in the slurry-trench or diaphragm-wall method of excavation in construction where unconsolidated rocks or soils are encountered (Lang, 1971). In this method, the trench being excavated is filled with bentonite slurry and the earth material being excavated is moved 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 soil which make costly shoring unnecessary.

Calcium-smectites are used as animal feed bonds. In addition to their binding ability, they act as absorbents for bacteria and certain enzymes which promote the growth and health of the animal. Another very large and growing use for the Ca-smectites is as a pet waste absorbent. This market uses granules of Ca-smectite which are treated with deodorants and more recently a percentage of powdered high-swelling Na-smectite to produce clumping cat litter. Some Ca-montmorillonites are acid activated to remove ions from the surface and the edges of the octahedral sheets. This increases the charge on the clay particle and makes them very effective in decolorizing mineral, vegetable and animal oils. The Ca-montmorillonite is generally activated by using either hydrochloric or sulphuric acid.

A process based on the exchange capacity is used to make special products from Na-montmorillonite which are termed organo-clays. In this process, the exchangeable ions on the montmorillonite surface are replaced with alkylamine cations which produce a hydrophobic surface (Jordan, 1950). These organic-clad Na-montmorillonites are used as thickeners in paints, greases, oil-based drilling fluids, and to gel various organic liquids.

Another recently developed concept is to use Na-montmorillonites in plastic compositions called nanocomposites. The Na-montmorillonite is delaminated to produce extremely thin, small particles which can then be treated with organic molecules to cause them to interact with the plastic polymers to produce exceedingly strong and heat-resistant products. These products are now being used in certain automotive plastic components.

Pillared clays are another recent development in which the ions on the Na-montmorillonite are exchanged with specific chemicals such as Al hydroxide which goes into the interlayer position. By controlling the amount of chemical added, pore sizes can be regulated. These pillared clays can be tailored for specific catalyst and absorbent uses.

PALYGORSKITE (ATTAPULGITE) AND SEPIOLITE

Palygorskite and attapulgite are synonymous terms for the same hydrated Mg-Al silicate material. The name specified by the International Nomenclature Committee is palygorskite. However, the name attapulgite is so well established in trade circles that it continues to be used by many producers and users. Sepiolite is structurally similar to palygorskite except that it has a slightly larger unit-cell. Both minerals consist of double silica tetrahedral chains linked together by octahedral oxygen and hydroxyl groups containing Al and Mg ions in a chain-like inverted structure. These inverted tetrahedra occur regularly and cause channels through the structure (Fig. 6). Both palygorskite and sepiolite are elongate in habit as shown on the electron micrograph of palygorskite (Fig. 7).

As mentioned previously, the term fuller's earth is used to describe palygorskite (attapulgite), and smectite clays which have sorptive and bleaching qualities. Thus, there is some confusion in mineral statistics, because the term fuller's earth can be either of these mineral types.

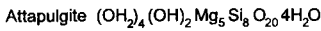
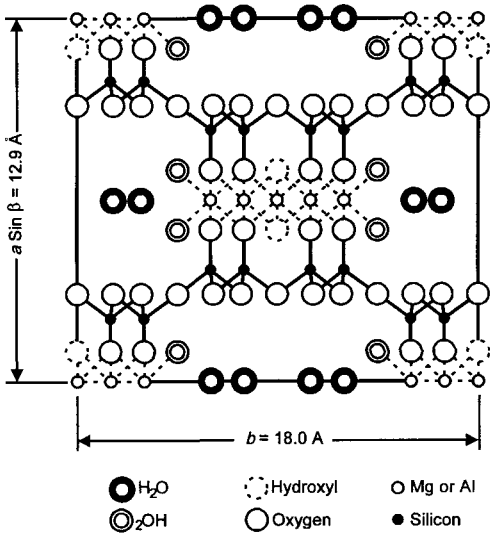


FIG. 6. Palygorskite structure.

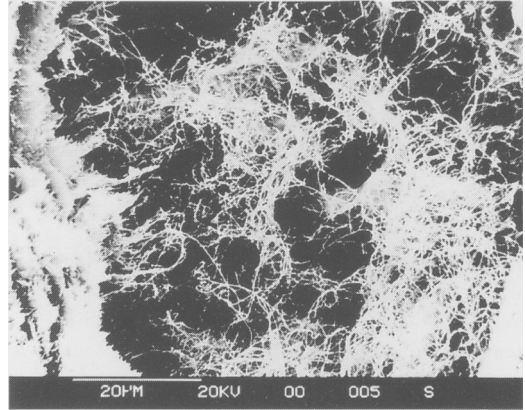


FIG. 7. SEM of palygorskite (Florida).

Sepiolite is normally light tan or cream in colour, whereas palygorskite generally has a bluish-grey tint. They are classed as a 2:1 layer inverted structure (Fig. 6). Ferrous iron commonly substitutes for Al in the octahedral sheet thus producing a moderate charge on the layer. This charge causes these minerals to have a CEC that is intermediate between kaolinite and Na-montmorillonite, usually in the range of 30 to 40 mEq/100 g. Because of the inversions in the silica tetrahedral sheet, the structure has parallel channels or holes throughout, which along with the elongate habit and the fine particle size, give a high surface area. The charge on the particles, the channels through the structure, and the high surface area give palygorskite and sepiolite a high capacity to absorb and adsorb various materials which makes them beneficial for many industrial applications. Also, the elongate

particles cause higher viscosity when it is added to any liquid. It is a physical and not a chemical viscosity, so it is very stable as a suspending medium in many applications such as salt water drilling fluids.

A major occurrence of palygorskite is in the southeastern USA in southern Georgia and northern Florida, where major deposits of palygorskite (attapulgite) occur. The major occurrence of sepiolite is near Madrid in Spain. Two other large occurrences of palygorskite are in Senegal near Theis, ~100 km east of Dakar and in China in Anhui Province, ~120 km northwest of Nanjing. There are also occurrences of sepiolite in Turkey.

The applications of palygorskite and sepiolite are many (Table 4). One of the greater uses is as viscosity builders in saltwater or high-electrolyte content drilling muds. The viscosity and gel strength of the mud are not affected by variations in electrolyte concentration and thus it can be used with salt water or when formation brines become a serious problem, and with oil-based drilling fluids.

TABLE 4. Industrial uses of palygorskite (attapulgite) and sepiolite.

Drilling fluids	Adhesives	Cat box absorbents
Paint	Pharmaceuticals	Suspension fertilizer
Paper	Catalyst supports	Agricultural carrier
Ceramics	Animal feed	Industrial floor absorbents
Asphalt emulsions	Petroleum refining	Mineral and vegetable oil refining
Cosmetics	Anti-caking agent	Tape-joint compounds
Sealants	Reinforcing fillers	Environmental absorbent

Because palygorskite and sepiolite are not easily flocculated, they are used as suspending agents in paints, suspension fertilizers, medicines, pharmaceuticals and cosmetics. In paint, these minerals improve the thickening and thixotropic properties.

Another major use of these minerals is as floor-sweep compounds for absorbing oil and grease spills on factory and service station floors. Granular particles of these minerals are the most effective. Palygorskite and sepiolite are used extensively in agriculture as absorbents and adsorbents for chemicals. The fertilizer, chemical, pesticide or herbicide is adsorbed onto the granular clay particles which are then placed in the ground with the seed or for later treatments using spreaders. The chemical is released slowly to provide the necessary plant food or protection for the growing plant. Finely pulverized palygorskite and sepiolite clays are also used to absorb chemicals which can be dusted or sprayed on the plant or on the surface of the ground.

Another use for fuller's earth materials, which include palygorskite and sepiolite, is as sorbents for pet waste. Granular clay particles are an effective medium for absorbing animal waste, particularly for domestic cats. The clay materials can be treated with chemicals which will prevent odours and bacterial degradation for several days.

Another sizeable use for palygorskite is for tape-joint compounds which are used to smooth the joints in a wall board surface. These compounds provide a smooth, strong, uniform and paintable surface when dried.

Other uses for these minerals are shown in Table 4. Galán described other uses for palygorskite and sepiolite in a recent paper (1996).

GROWTH AND APPLICATIONS FOR THE FUTURE

The future will see further growth in the use of clays in the applications they now serve and will see new utilization, particularly in industrial and environmental applications. The growth of the current industries will create expanded markets for paper, ceramics, plastics, etc. This will cause a demand for exploration for new deposits and improved processing to upgrade marginal quality deposits so that marketable products can be made.

As we have seen historically, improved mining technology and particularly new and improved beneficiation methods have resulted in higher

quality and more uniform clay products. This will continue and will be even more accelerated in the future. In Table 5 is a list of processes that are continually being improved and modified to produce higher quality and new products.

Rather than discuss each of the processes listed in Table 5, magnetic separation and flotation will be used as examples as to how the processes have been continually improved for applications to clays and particularly to kaolins.

High-intensity wet magnetic separation (Iannicelli, 1976) became a standard process in the kaolin industry in Georgia and in England in the early 1970s. These magnets were designed so that the retention time in the magnetic field could be controlled and the field strength set between 0.5 and 2 Tesla. The use of a matrix such as steel wool in a canister in the magnetic field provided a uniform magnetic field throughout the canister. These magnets were 2.1 m in diameter and 0.5 m deep. The throughput could be as high as 100 tons/h in some applications. The purpose of the magnet was to remove coloured impurities, particularly Fe and Ti minerals. Since the first generation of these magnets, there have been very significant improvements in the composition and size of the matrix materials, and superconducting magnets are now available which greatly reduce the power consumption and provide increased field strengths as high as 6 Tesla. Products of very high purity and whiteness are now routinely produced at lower cost and, in addition, marginal crude clays can be utilized to make standard products. These marginal clays were not being mined previously, so the magnet has provided a way to extend the useable reserves of kaolin.

Flotation is another process which has provided a method to produce products with greater purity and higher brightness and whiteness. The first flotation

TABLE 5. Special processes applicable to clays.

Acid activation	Fine pulverization
Air classification	Flotation
Calcination	Granular sizing
Centrifuging	High-heat drying
Chemical leaching	Magnetic separation
Delamination	Organoclaying
Dewatering	Oxidation
Dispersion	Selective flocculation
Extrusion	Surface treatments

process used in the kaolin industry involved the use of calcite particles as carriers in order to float the very fine kaolin clays (Greene & Duke, 1962). Continual improvements in the flotation process, both in equipment (such as column flotation) and flotation chemicals, have improved the recovery and the product quality. Today, products can be made routinely with very low Ti contents, a high brightness and whiteness, and at reduced cost.

Process improvements, more precise identification and quantification of minerals present in minor quantities in a clay which are deleterious to its use, better dispersion techniques utilizing improved process equipment and new chemicals, and other processes will permit the production of higher quality products and the ability to utilize deposits that are not now economic. Also, continued research and development will develop new products that can serve markets not now accessible.

Organo-clays and surface-modified clays will continue to be a significant growth area — organo-clays for the bentonite industry and surface-modified clays for kaolin and palygorskite-sepiolite. The development of new chemicals to clad the montmorillonite will allow market penetration into new areas which need functional fillers. Surface modification of hydrophilic clays can make these clays organophilic and/or hydrophobic so that they can be dispersed in systems other than water and in some instances so that they will react with the medium into which they are dispersed to become an integral part of the system, thus providing a needed function such as strength, heat resistance, etc.

Another growth area for the future is pillared clays (Lussier *et al.*, 1980; Occelli, 1986; Vaughan, 1988a,b). The pillars that are built in the interlayer position can be tailored to produce selective pore sizes, specific absorbent and adsorbent characteristics, and unique catalytic properties. The best clay base for pillaring is a high-swelling Na-montmorillonite.

The field of nanocomposites is a very promising growth area (Bandosz *et al.*, 1994a, 1994b). Ultrafine montmorillonite platelets have been shown to be excellent functional components, in certain plastic composites, to improve their strength and heat resistance. This is a very promising growth area not only for Na-montmorillonite, but for other clay minerals.

Wet processing of ball clays, smectites and palygorskite and sepiolite will be used in the

future to produce improved value-added quality products for specific applications.

SUMMARY

The number of applications for the clay minerals kaolinite, Na- and Ca-montmorillonite, palygorskite, and sepiolite continues to expand. Because of their very fine particle size and physical and chemical properties that are directly related to their structure and composition, clay minerals have the most diverse utilization of the industrial minerals. Their availability as an abundant raw material that can be beneficiated to produce a large number of relatively inexpensive products ensures that market growth will continue for the foreseeable future.

New and improved processing, continued research and development and new market opportunities will lead to expansion into new markets. This will require continued exploration and development of new deposits in all areas of the world. The future for the growth of clay mineral applications is indeed optimistic.

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