CHAPTER 12.18

Kaolin

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Kaolin is clay composed of kaolin minerals that is naturally white or nearly white, or that can be beneficiated to white or nearly white. Commercial kaolin deposits are classified as primary or sedimentary. Primary deposits include residual weathering horizons, or hydrothermal alteration zones along fracture networks, hosted in feldpathic igneous rocks such as granite or feldpathic metamorphic rocks such as gneiss. Sedimentary deposits include concentrated kaolinitic clays deposited in fluvial, deltaic, or transitional marine environments, and include kaolinized sediments that were originally feldspar grains, mica grains, or rock fragments that contained labile minerals such as feldspar. Sedimentary kaolin deposits have a continuum of mineral content and textures ranging from bauxite to kaolinitic sandstone to plastic clay (Figure 1).

GOALS OF KAOLIN PROCESSING

Commercial kaolin deposits are mined and processed for wide range of uses (Table 1). Kaolin mined in the United States during 2013 was used as white pigments for paper and paint (55%); as ceramic raw materials (11%); as refractories (10%); as fillers for rubber, plastic, caulk, and sealants (7%); as fiberglass raw materials (5%); as catalysts for oil and gas refining (3%); and for other applications (9%) such as inks, cosmetics, animal feed, pesticides, pharmaceuticals, fertilizer, and roofing materials (Virta 2015). Kaolin processing is designed to obtain physical and chemical properties needed by customers within each market segment (Table 1) by providing products with consistent quality from specific ore types. Specified ranges of major oxides are needed for kaolin products supplied to the ceramics, refractories, fiberglass, and catalyst markets. Coating pigments are typically specified for their degree of whiteness (brightness and shade of color), particle size (wt % <2 μm), and rheological properties of mineral-water slurry and low abrasivity.

ECONOMIC CONCERNS

According to the U.S. Geological Survey (USGS), kaolin is produced in 60 countries (Virta 2015). The largest kaolin-producing countries in 2012 were the United States (23%), Germany (17%), China (12%), Brazil (7%), Iran (6%), Turkey (5%), United Kingdom (4%), Korea (3%), Vietnam, Czech Republic, and Mexico (each with 2%) (Anon. 2015). The largest kaolin-producing companies are Imerys, KaMin, Thiele, BASF, AKW, and Sibelco (Patel 2014). These companies mine large-volume kaolin ore deposits with uniform physical and chemical properties that are used for large-volume applications such as paper pigments. Deposits in Georgia (United States), northern Brazil, and Cornwall (United Kingdom) have the quality and large volume of ores that can be successfully developed for pigments in the context of extremely competitive market conditions, technological complexity of kaolin processing, demanding product specifications, high capital investment needed for facilities, and access to global transportation infrastructure.

The value of kaolin products relates to the beneficiation method, market, grade, and product form. The USGS provides data on total value and volume of Georgia (United States) kaolin produced by different beneficiation methods (Figure 2). The production tracked by the USGS is for kaolin beneficiated by airfloat, water-washed, delaminated, and calcined process methods, to be discussed in more detail later in this chapter. The USGS numbers show gradual increases in airfloat and hydrous (water-washed and delaminated) kaolin value per short ton over the past 20 years. Calcined kaolin values show high volatility because the product mix they represent is very broad in terms of markets served (Table 1), degree of wet and dry processing, and range of packaging and bulk shipment options.

Euromoney Institutional Investor, the publisher of *Industrial Minerals*, tracks prices for some grades of kaolin. In August 2015, its website showed that prices of no. 1 coating kaolin fob (free on board) Georgia were between $149/t and $209/t, prices of Brazilian coating kaolin slurry were between $242/t and $295/t CIF (cost, insurance, and freight) Europe, and prices of bagged <75 μm kaolin for sanitaryware

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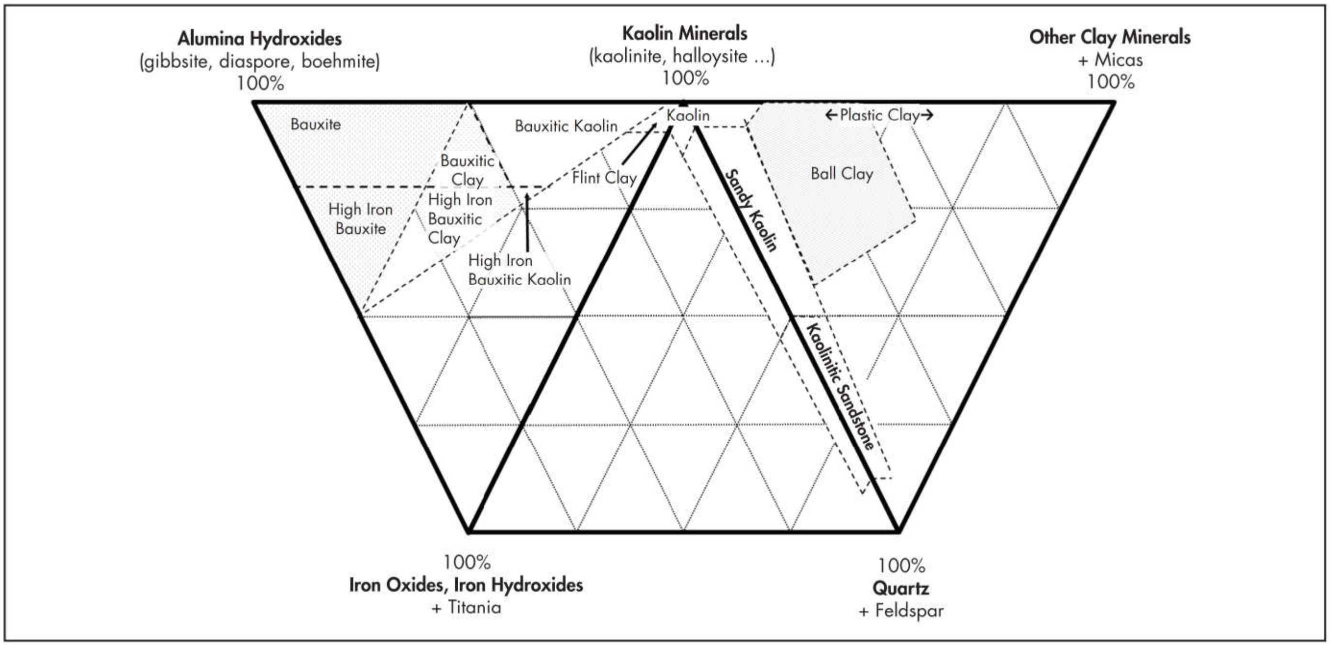


Source: Pruett 2016

Figure 1 Classification of kaolin and kaolin mineral-bearing rocks based on their mineral content

Table 1 Uses of kaolin and properties important for specified use

Properties	Refractory	Fiberglass	Ceramic	Catalyst	Rubber	Plastic	Pigment, coating	Pigment, filling	Specialty
Chemistry, major oxide	x	x	x	x					
White or near-white			x				x	x	
Refractive index							x	x	
Particle size, fineness, and range			x		x	x	x	x	
Particle shape, platy or delaminated						x	x	x	
Surface area (5–25 m^2/g)					x		x	x	
Abrasiveness, soft (2.5 Mohs)							x	x	
Hydrophilic, readily make-down			x				x	x	
Insoluble, wide pH range							x	x	See Murray 2007.
Surface charge, low (meq/g)			x		x		x	x	
Low viscosity, clay-water slurry							x	x	
Plasticity			x						
Conductivity, low (heat, electrical)	x					x			
Refractory, high melting temperature	x		x	x					
Stability, form (heat, chemical)			x				x	x	
Calcined/sintered mineral content	x		x	x	x	x	x	x	
Cost	x	x	x	x	x	x	x	x	

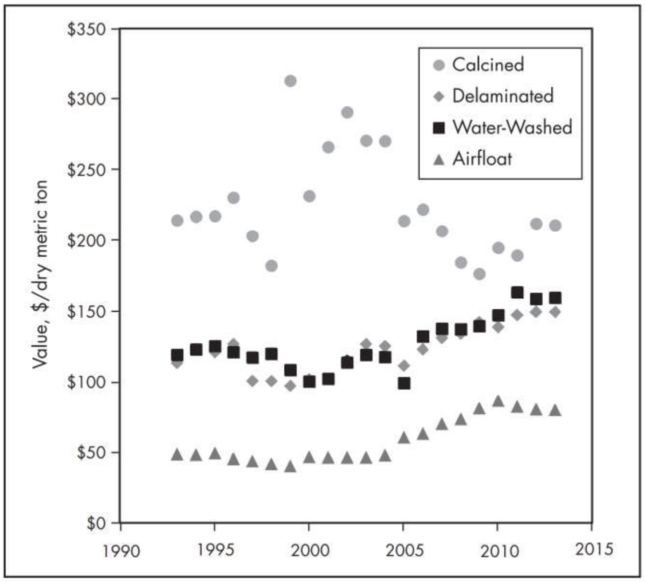
fob Vietnam were between \$198/t and \$209/t (*Industrial Minerals* 2015).

EXAMPLES OF KAOLIN PROCESSING OPERATIONS

Kaolin operations are categorized by dry and wet process. Dry processes include airfloat and calcined operations. Wet processes include water-washed, delaminated, and calcined operations. The distinction between dry and wet process operations is whether the kaolin is made-down into slurry with water at any point prior to shipment of final product. The general advantage with the dry process is in the lower energy and fewer chemicals needed to produce finished product. Typically, the dry process has one energy-intensive step to dry product from a moist crude or plastic state containing less than about 20% moisture. The energy intensity of wet processing kaolin is described in Pruett (2011), and it often involves dewatering and drying slurries containing between 30% and 80% moisture unless the product is shipped as slurry. Dry processed kaolins can be chemical free. Wet processed kaolin need chemicals for dispersion, beneficiation, preservation, and tailings treatment. The advantages of wet processing kaolin are the degree of purity that can be reached by removing impurities, the degree of particle engineering that can be achieved by size separation and grinding, and the overall consistency of the product blend.

Airfloat Operations

Airfloat processing was developed in the 1920s to simply dry and remove oversized grit (>45 μm) particles from kaolin used for paper filling and ceramic applications (Henry and Vaughan 1937; Pruett 2000). Dry processing for pigment and ceramic grades prior to the airfloat and wet processes often involved hand sorting the ore to remove iron-stained gangue, then drying the sorted ore on racks prior to bulk shipment (Smith 1929). The airfloat operation comprises the unit operations of mining and crude ore selection, hauling, storage, blending, feeding and crushing, drying, milling and classification, and bulk loading or packaging (Figure 3; Buie and Schrader 1982).



Data from USGS [illegible]

Figure 2 Average Georgia and U.S. kaolin values by process

Water-Washed Operations

The water-washed operation can comprise multiple unit operations to obtain high-purity pigments (Figure 4), or the operation can comprise a few unit operations such as blunging kaolin ore and degritting the kaolin slurry prior to loading the slurry into a railcar for shipment to some markets. Water-washing kaolin has been practiced for centuries, initially to separate clay-sized kaolin mineral particles from sand-sized quartz and mica particles from primary kaolin ore (Chen et al. 1997; Thurlow 2001). The first major sedimentary kaolin water-washed operation began production in 1908 at Dry Branch, Georgia, United States. Today the water-washed kaolin operation is the principal manufacturing platform for high-purity kaolins having tightly controlled particle size distributions and high brightness.

The principal reasons for water-washed kaolin processing are the benefit of complete particle dispersion in the water medium, the option to add chemicals that improve the clay's performance in terms of brightness and rheology, and the better mixing of particles from different ore sources to improve product consistency. The initial steps of mining, transport, storage, and feeding ore into the operation are similar in dry and wet processes (Figures 3 and 4). The blunging or mixing of the kaolin ore with water to form slurry with the aid of mechanical shear, pH adjustment, and chemical dispersants begins the wet part of the process. Degritting the slurry to remove coarse particles >45 μm typically follows the blunging unit operation. When the kaolin is in slurry form, it can be stored in tanks and then transported by pipeline from the mine product tanks to the beneficiation unit operations. Beneficiation can take several forms and form multiple sequences to optimally improve product purity using high-intensity wet magnetic separation, flotation, selective flocculation, ozone bleaching, and acid-reductive leaching, and change the particle size distribution to improve functional performance by blending and centrifugal classification (Murray 2007; Thurlow 2001). The

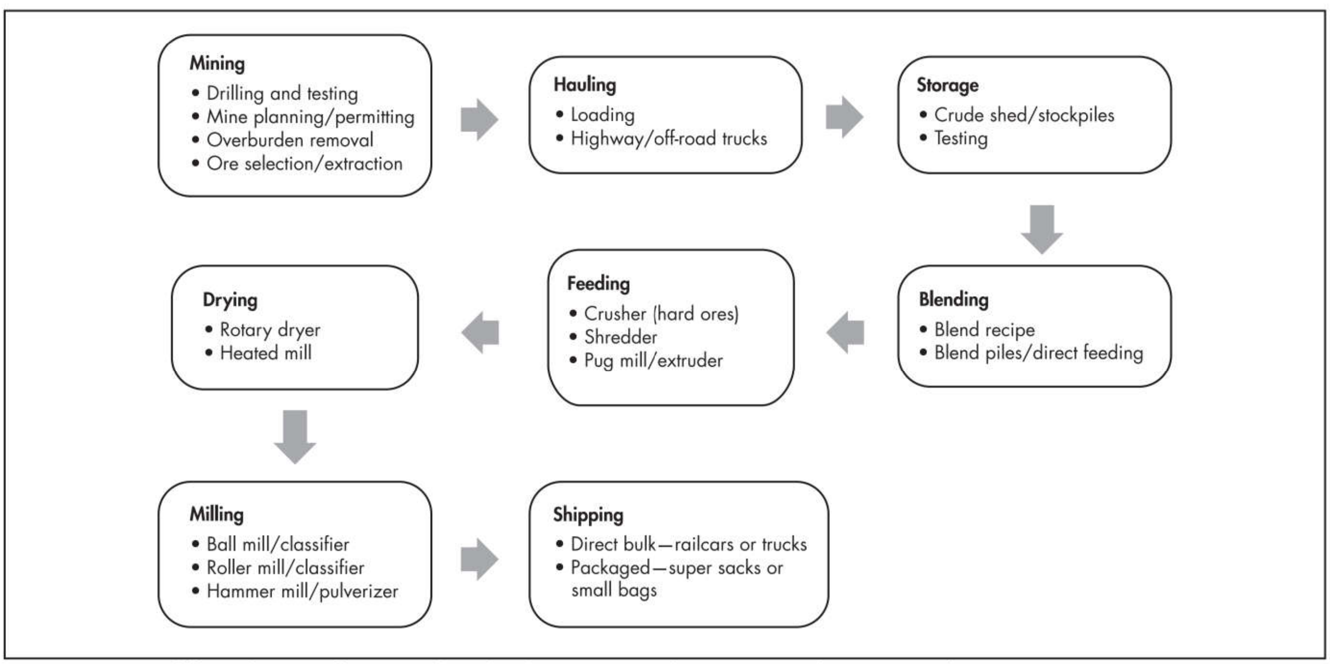


Figure 3 General flow diagram for an airfloat kaolin operation showing typical sequence of unit processes

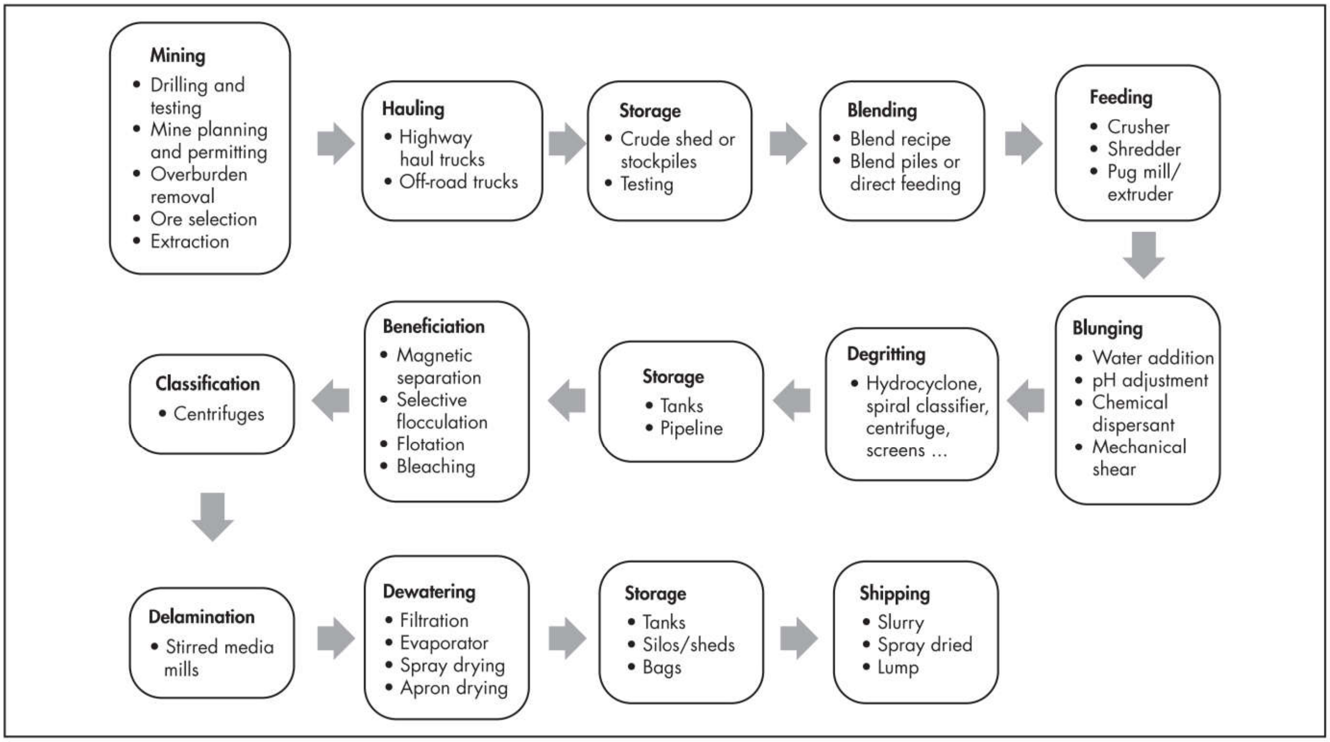


Figure 4 General flow sheet for a water-washed kaolin operation used for manufacturing paper coating pigments

beneficiation and classification processes operate more efficiently at low slurry solids, typically 15%–40%. Dewatering using filters and evaporators is needed to increase slurry solids to 60% or higher for high solids slurry shipment or to more efficiently feed drying equipment at the downstream portion of the wet process.

Delaminated Kaolin

Operations that delaminate kaolin are water-washed processes (Figure 4). Delamination was developed to address lower recoveries caused by higher market demand for fine coating kaolin beginning in the late 1930s. The lower recoveries resulted from unused coarse fractions from centrifugation filling tailings impoundments of Georgia coating kaolin producers. The coarse fractions rejected by centrifuge are mostly kaolinite stacks and kaolin agglomerates. Two developments in the middle 1950s enabled these coarse fractions to be used. First was the discovery that coarse platy particles are a good coating pigment for paper (Bundy 1993). Second was the development of delamination. Delamination is the parting or cleaving of kaolinite stacks into individual platelets (Figure 5) by extrusion or by attrition-grinding of clay slurries using stirred media mills (Feld and Clemmons 1963). The grinding media used can be quartz sand or ceramic, which is highly spherical and stronger and more wear resistant than quartz. Media sizes used for delamination are typically about 1 mm.

Calcined Kaolin

Calcined kaolin and metakaolin are thermally processed crude or beneficiated kaolin. The phase changes that occur by heating kaolin to high temperatures include (1) dehydroxilization of kaolinite about 500°C (932°F) to form metakaolin, (2) forming spinel or primary mullite at about 1,000°C (1,832°F) from metakaolin, and (3) recrystallizing the calcined kaolin mass to form secondary mullite above 1,200°C (2,192°F). Metakaolin is used as a pozzolan for cement, to make alum for water treatment, as a pigment for paper, and for a variety of specialty applications. Kaolins that are fully calcined near 1,000°C (1,832°F) are used as pigments and for mild abrasives because of their low concentrations of submicrometer mullite. Low abrasivity and high brightness are important quality parameters for calcined kaolin used for pigments. Kaolins sintered above 1,200°C (2,192°F) are used for ceramics and refractories because of their high mullite content, high strength, chemical resistance, and heat resistance.

Calcined kaolin operations are the extension of either the dry or wet process. Dry process feeds to the kiln can be crushed crude, extruded-milled product, or granulated product as in the case of proppants. Kilns used in the kaolin industry include rotary and Herreshoff. Wet process feeds to a kiln are typically dried with some additional milling or sizing before calcination to either structure the kaolin particles into porous aggregates, as in the case of pigments, or to structure the finished particle into a rounded sphere, as in the case of ceramic proppants (Figure 6). Calcined operations for pigments have milling unit operations after the calciner to produce a fine pulverized form, and some of the milled calcined kaolin can then be reslurried for shipment to pigment customers. Calcined operations for structured particles such as ceramic proppants will have screening unit operations to size the product to meet customer specifications. Most calcined kaolin operations can ship packaged products in super sacks or small bags, or in bulk form as appropriate for the market served.

UNIT OPERATIONS

The unit operations found in kaolin operations are selected and designed based on ore characteristics, product specifications,

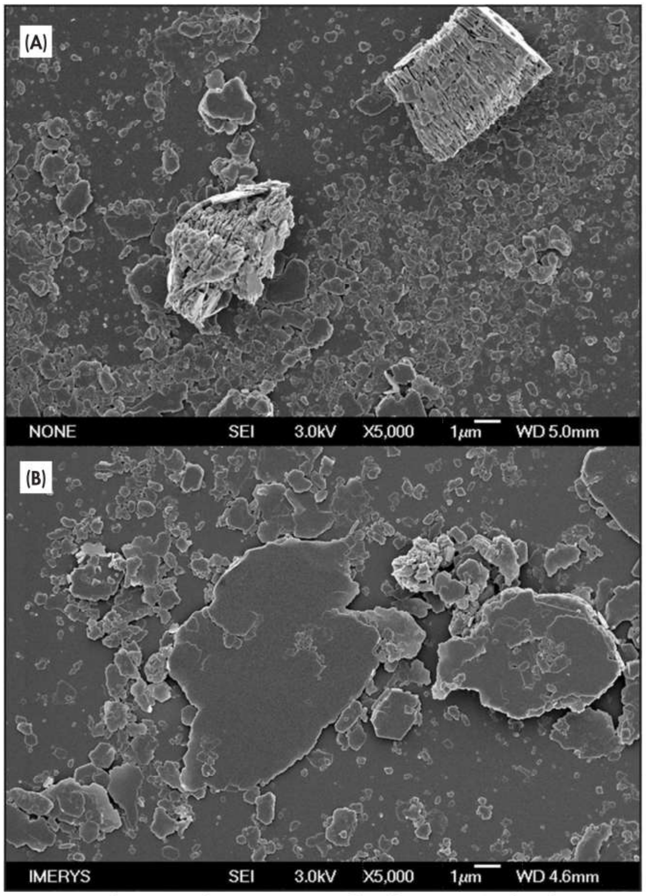


Figure 5 Electron photomicrographs showing (A) kaolinite particles contained in a slurry feeding an attrition grinder that comprise stacks and plates, and (B) kaolinite particles contained in a slurry product from an attrition grinder that comprise plates delaminated from stacks

and cost. Described in the following sections are unit operations typically used for kaolin processing.

Mining and Crude Ore Selection

Kaolin bodies are spatially delineated by extensive drilling and testing of core samples. The drill-hole spacing for exploratory work is typically about 120 m (400 ft), and drilling at 60 m (200 ft) and 30 m (100 ft) spacing typically occurs before stripping to prove reserves, prepare a mine permit, and prepare for mining. After the overburden has been removed, additional drilling at 15 m (50 ft) spacing occurs for mine quality control. The cores retrieved from drilling are described and then split into 0.3–1 m (1–3 ft) interval segments for initial quality testing for key parameters such as grit (>325 ASTM mesh) content, chemistry, brightness, and particle. The initial core intervals having similar quality are then composited into larger contiguous segments that represent one to several meters of a minable kaolin bed. The initial quality parameters are retested on the composites, and additional information is collected on quality parameters important for the intended market, such as brightness and rheology for ores intended for paper pigments, and processability parameters such as brightness response to ozone, magnetic separation, flotation, and leaching. Further details on kaolin testing are provided by Pruett and Pickering (2006).

Mining method depends on the geology and properties of the ore. The majority of kaolin mined in Georgia (United States) and northern Brazil are from sedimentary deposits. The overburden for these deposits is generally unconsolidated and can be removed by excavators and off-road trucks. Occasional hard layers can be ripped, hammered, or blasted prior to removal. The sedimentary kaolin ores can be mined using a backhoe and hauled to a stockpile or directly to a blunger. Primary kaolin hosted in altered granites such as in Cornwall and Devon (United Kingdom) may also be mined directly from the face by an excavator. Hydraulic mining was commonly practiced in the UK primary kaolins because of the high amount of unaltered matrix; the high amount of quartz, feldspar, and mica particles associated with the kaolinite; and the availability of water. Hydraulic mining involves the use of high-pressure water-jet monitors to wash the mine face to liberate kaolin clay and wash the kaolin into sumps where the kaolin slurry can be pumped to refining operations. Both dry and hydraulic mining require knowledge of the kaolin properties in the ore so that ore quality can be controlled and stockpiles with known qualities for blending can be built.

Crude Transportation and Storage

After excavation, the kaolin is transported from mine to processing plant by two basic methods: as dispersed slurry by pipeline or as solid lump clay by highway haul trucks (Pruett and Pickering 2006).

Dry

Crude kaolin ore is transported from stockpiles at the mine or directly to stockpiles near the plant by highway truck or off-road truck depending on distance and road network. Stockpiles near the plant or near a blunger site can be built on pads open to weather, or they can be built under crude sheds to prevent the clay from becoming too wet and sticky to handle during periods of wet weather. Stockpiles are typically sampled while they are built, after they are built, or both. Stockpile samples are tested similar to crude ore to confirm their quality and provide information to the quality lab for blending.

Slurry

Slurry from hydraulic mining or from blunging operations located near the mine is stored in agitated tanks to prevent sedimentation of coarse particles. Most tanks located between unit operations in water-washed kaolin operations are agitated, including final product tanks. Tanks that do not require agitation are those that contain fine particle size (>95 wt % <2 μm) dispersed kaolins or contain flocculated kaolin for solid–liquid separation or reduced-acid leaching. Transportation between unit operations in a wet plant is by pipeline. Many pipelines in Georgia exceeding 16 km (10 mi) long, and in the Rio Capim area of northern Brazil exceeding 161 km (100 mi) long, connect blunging and degritting operations located near the mine with the main beneficiation operations located near the railroad or port. The quality lab routinely tests the slurry contents of each tank for properties such as solids, pH, brightness, and particle size.

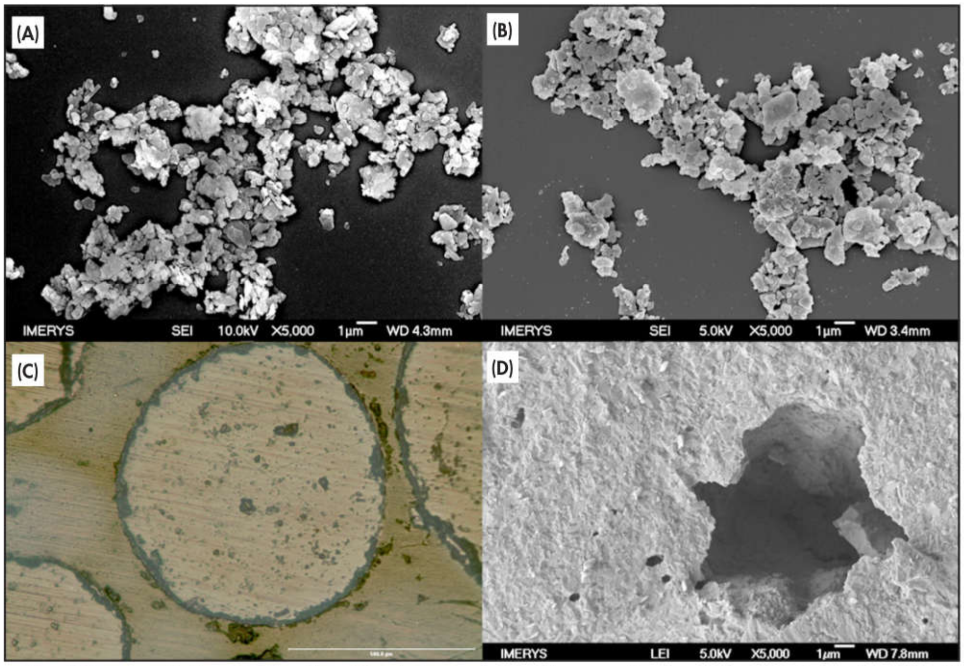


Figure 6 Examples of calcined and sintered kaolin: (A) electron photomicrograph of a pulverized metakaolin pigment, (B) electron photomicrograph of a pulverized fully calcined kaolin pigment, (C) visible-light micrograph showing a cross section of a sintered ceramic proppant, and (D) electron photomicrograph showing porcelain ceramic made by sintering kaolin to mullite

Feed Preparation

Crude kaolin ore from stockpiles must be sized for conveyor handling and to feed blungers. Soft kaolin ores may break down easily when run through a roll crusher. Hard kaolin ores may require a jaw crusher to break down boulder-sized ore into a size range to feed the process. Crushed kaolin can be fed to a shredder to further reduce top size of the ore to smaller than 5 cm (2 in.).

Dry Process

Beyond sizing the kaolin ore for handling in the operation, there is little additional feed preparation required for the dry process other than drying (Murray 1961). A blend pile can be built to help homogenize the feed to the process based on a recipe from the quality lab. Kaolin is typically dried before milling in the airfloat process using a rotary dryer. Some dry process operations can mix the wet crude ore with dry fine materials collected from the downstream process to dry the feed. Dry process calcine operations producing metakaolin for cement or chemicals will combine the crude drying and calcining using a rotary kiln.

Blunging and Slurry Preparation

Feed preparation for the wet process needs to liberate and disperse individual kaolin particles from the ore. Crushed kaolin ore is fed into a blunger (a tank or vat with a mixing shaft) to make clay slurry with water and dispersant chemicals under mechanical shear. The crushed kaolin ore is conveyed to a point where it drops into the blunger. Water is added to achieve target solids of between 30% and 70% (Murray 1980). The mixing shaft has a bottom blade or impeller for breaking up particles under high shear. The slurry must pass through a screen to prevent large lumps of clay from exiting. Downstream in the kaolin water-washed process are two other unit operations having a similar purpose. The reblunger (or repulper) is located after the filters for reslurrying filter cake with dispersant chemicals, but without additional water. The slurry (or reslurry) is located at the load-out to prepare hydrous and calcined kaolin slurries for shipment. Chemicals to disperse, stabilize, and preserve the slurries are added. Hydrous kaolin slurry solids can be raised by adding dry clay. Water is added to make calcined kaolin slurry.

Chemicals are important in the wet process beginning at the blunging unit operation. Kaolinite has a very low surface charge, unlike other clay minerals such as micas and smectite. The charge on kaolinite edges and faces are pH dependent (Yin et al. 2012). At pH <5, kaolinite particles will flocculate because of positive edge charge and negative face charge. Making a high (>50%) solids fluid slurry at low pH and without dispersant is impossible; the kaolin will have a plastic or cake-like texture. At pH >6, kaolinite particles have negative charge on their edge and faces. However, particles will not be fully dispersed until pH is >9, because some ancillary minerals such as anatase have a higher pH zero point charge. A dispersant chemical is used to amplify the negative charge and to prevent particle collision and coagulation. Chemicals used to adjust kaolin slurry pH are inexpensive and have a monovalent cation. Kaolin particles coagulate in water having divalent cations such calcium and magnesium, divalent anions such as sulfate, trivalent ions such as aluminum, and a high ionic strength that depresses the double layer surrounding particles. Typical chemicals used to raise pH during blunging and slurry make-down are sodium carbonate, sodium hydroxide, and ammonium hydroxide. Dispersant chemicals that amplify the negative charge on kaolin particle surfaces include a wide variety of phosphates such as sodium hexametaphosphate and tetrasodium pyrophosphate, sodium silicate, and sodium polyacrylate. The inorganic dispersants are short-lived at low-dose amounts, whereas sodium polyacrylate is a relatively long-lived dispersant and is used to stabilize the dispersion of slurries that need to be transported long distances by rail or ship.

Beneficiation, Wet Process

Impurity removal is one major advantage for wet processing kaolin. The dry process has few opportunities to upgrade ore quality other than by selective mining; by ore sorting; and by separating out large, hard particles. Kaolin, being a clay, has many silt-sized and clay-sized impurities disseminated through the ore and can have iron oxide (hematite and goethite) and iron sulfide (pyrite) aggregates that are fragile and prone to disaggregation and dispersion through the ore when disturbed during processing. Kaolin beneficiation unit operations take advantage of size, magnetic susceptibility, surface chemistry, chemical attack, and thermal attack.

Degritting

Degritting (or desanding) is the first beneficiation step in the wet process following blunging. The objective of this unit operation is to remove most particles that are greater than 44 µm (325 ASTM mesh) that are called grit. Removing grit particles prevents erosive wear caused by quartz particles and prevents sedimentation during periods of reduced flow in pipelines and tanks. The techniques used for degritting depend on the size and amount of unblunged kaolin mineral and non-kaolin impurities greater than 325 ASTM mesh size. Kaolin extracted from primary deposits with a monitor will have desanding performed on the slurry removed from pit by gravel pumps (Thurlow 2001). Kaolin ores that are blunged will have degritting performed adjacent to the blunger and close to the mine for easy disposal of sandy tailings. Some degritting operations have attrition scrubbers to help disperse unblunged clay particles that are rejected in the degritting process by autogenously grinding them with quartz sand in the grit.

Degritting is performed by gravity settling techniques, gravity-assisted classification techniques, and screening. Gravitational processes are most effective for removal of spherical, coarse, and dense mineral grains and rock fragments. Screens are effective for removal of platy-shaped mineral grains such as micas and for removing low specific gravity materials such as vegetable matter. The processes used for refining are a function of gangue material particle size. Process equipment that uses gravitational setline include the bucket wheel desander, spiral (or screw) classifier, dragbox (or sandbox), and hydroseparator. These gravitational processes work best on slurries having low (<30%) solids. Gravity-assisted processes are hydrocyclones and degritting centrifuges. Their advantages are a relatively small footprint and higher separation efficiency for higher (30%–70%) solids and for finer (10–100 µm) particles. Hydrocyclones are typically set up in banks having larger-diameter (≥25.4 cm [10 in.]) cones upstream of 15.2-cm and 10.2-cm (6-in. and 4-in.) banks of cones that make finer cuts. In the case of kaolin deposits with sand and silt content below 15%, a rubber-lined, continuous solid bowl decanter degritting centrifuge can achieve grit levels as low as 0.1 wt % (Adler 1999). Screens having ASTM mesh size ≥325 are used after de-sanding to remove remaining grit. Screens are located throughout the kaolin beneficiation process to remove coarse residues such as scales, paint chips, insect parts, spent grinding media, and so on, that may contaminate the slurry during its processing and storage, prior to loading for shipment. Screens used for degritting are typically rectangular or inclined; those used in process are typically rectangular or round.

Magnetic Separation

The high-intensity magnetic separator (HIMS) was developed in the mid-1960s (Iannicelli et al. 1969) for kaolin beneficiation and is now used in Georgia (United States), Brazil, Cornwall (United Kingdom), and Germany for the removal of iron-bearing discoloring impurities. Magnetic separation of kaolins requires a high magnetic field, high magnetic field gradient, multiple collecting surfaces, long retention time, well-dispersed slurry and flow, and a wet separator (Iannicelli 1976; Mills 1977). The conventional HIMS has an electromagnet surrounding a central canister that is 2.1 m (84 in.) or 3.1 m (120 in.) in diameter with an effective depth of about 51 cm (20 in.). The canister is filled with a matrix of stainless-steel wool with wire diameters between 30 and 180 µm. The field strength of a conventional HIMS is 1–2 Tesla (Stadtmuller et al. 1997). In the 1980s, superconducting magnet technology was deployed on kaolin process applications to lower energy consumption, reduce footprint, and achieve higher field strength up to 10 T. Superconducting HIMS are static canister magnets that are similar to the conventional HIMS and reciprocating canister magnets that oscillate the canister between a fixed magnetic field for processing and out of the magnetic field for flushing. The impurities removed by conventional and superconducting magnets are iron minerals such as hematite, goethite, and ilmentite; and iron-bearing titania minerals such as anatase and rutile.

Flotation

Reverse froth flotation was introduced to Georgia (United States) kaolin processing in the early 1960s to remove iron-bearing anatase using a ground limestone carrier (Greene and Duke 1962; Grounds 1964). Cundy (1976) eliminated the carrier by fully dispersing the kaolin slurry to pH 9, adding a fatty acid (oleic acid) to coat the anatase particle surfaces making them hydrophobic, and adding divalent ions (calcium or barium) to coagulate anatase particles in the conditioning process prior to reverse froth flotation. Yoon and Hilderbrand (1986) developed a noncarrier flotation process using hydroxamate collectors instead of fatty acids. Other impurities that can be removed using reverse froth flotation are graphite and organic compounds (Yildirim et al. 2013).

Selective Flocculation

Selective flocculation is another common method to remove iron-bearing anatase from kaolin. Pruett (2012) reviewed two approaches to selective flocculation used by kaolin producers in Georgia (United States). One approach is to flocculate the anatase by coagulation at moderate pH and separating with the assistance of a high-molecular-weight polymer in a thickener. The second approach is to fully disperse the kaolin slurry at high pH (>9) and add a high-molecular-weight polymer that flocculates out the kaolinite particles in the thickener to separate out dispersed colloidal impurities such as anatase, iron oxides (goethite), and phosphates.

Oxidation

Oxidation will increase brightness and whiteness of some kaolin by chemical or thermal methods. Oxidation acts on organic matter contained in gray-colored kaolin, which may drop brightness 15 (or more) units lower than an equivalent cream-colored kaolin (Schroeder et al. 2004). The chemical method typically uses ozone gas, which is generated by passing oxygen gas or dry air through a high electrical charge that ionizes the gases. The ozone is then mixed with clay slurry in a contact tower to allow the gas to react with the organic matter associated with the kaolin. Oxidizing chemicals such as hydrogen peroxide can also be used to oxidize organic matter in kaolin slurry. The second method to oxidize kaolin to increase brightness is calcination. Calcination to >400°C (752°F) will burn out most organic matter to increase brightness.

Reduced-Acid Leaching

Leaching to remove soluble iron oxides such as hematite and goethite is typically performed at ≤3 pH downstream in the wet process prior to filtration. Sulfuric acid is typically used to lower pH. Sodium hydrosulfite (sodium dithionite) is added to form the chemical-reducing environment that promotes the dissolution of iron oxides and iron hydroxides and reduction of ferric to ferrous iron associated with the kaolinite. Reduced-acid leaching improves brightness and the blue shade of kaolin products derived from oxidized kaolin ores that are cream- or pink-colored. Reduced-acid leaching is performed before dewatering with filters to enable the removal of soluble iron species. Because filtration is performed at low pH to promote kaolin flocculation, other chemicals such as alum and other filter aids are added to the low solids slurry near the addition points of sulfuric acid and sodium hydrosulfite.

Fractionation and Particle Sizing

Particle-size classification is an essential part of the water-washed kaolin process because it was integral to making coating pigments for paper coating (Table 2). The continuous bowl-type decanter centrifuge was a major advance in kaolin processing in the 1930s and enabled the production of 80% <2 µm and finer clays (Murray 1980). The disc nozzle centrifuge is used for classification to the finer cut sizes needed for ultrafine kaolin products. Cut size is the minimum particle size in the sediment underflow or maximum size escaping with the unsettled slurry product effluent (Leung 1998). Separation efficiency is a function of slurry dispersion, viscosity, and solids. Other methods to change the particle size of kaolin products are by blending finer particle size kaolin into the feed and by using stirred media mills to make finer particles.

Table 2 Particles size (equivalent spherical diameter) of paper coating pigment grades

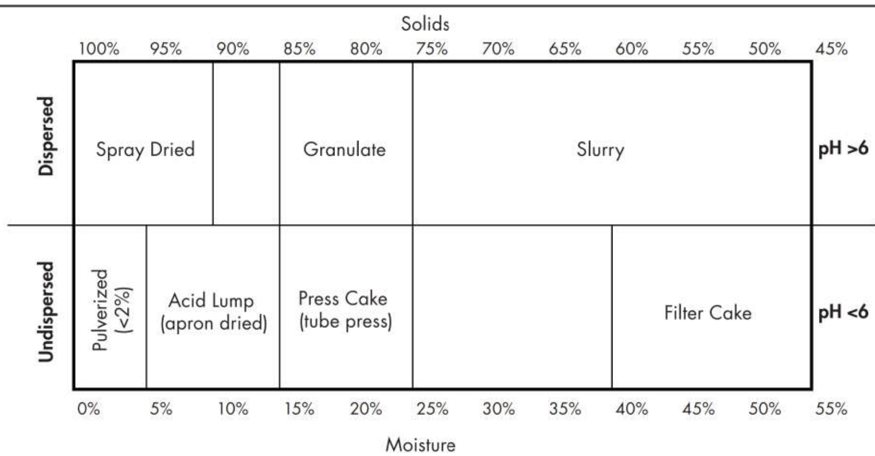
Grade	Wt % <2 µm
Ultrafine	98
Fine No. 1	95
No. 1	90
No. 2	85

Dewatering and Drying

Water removal is required for most water-washed processes that involve beneficiation and particle sizing. The selection of dewatering and dry unit operations depends on the final product form(s) needed by the markets served (Figure 7). Kaolin slurry solids in the process start at the blunger between 35% and 70%, and the solids generally decrease through the process to between 15% and 35% at the leaching stage. Kaolin slurry from hydraulic mining is low (~5%) solids concentration.

Solid–Liquid Separation

Most approaches to separating water from clay use a slurry containing flocculated kaolin to provide an open porous structure and pathways for water to exit. Flocculating the clay to a pH <5, adding alum to coagulate particles, and possibly using a high-molecular-weight polymer to open the floc structure enable good dewatering rates for solid–liquid separation by thickeners, rotary vacuum filters, plate-and-frame filters, tube presses, and centrifuges. Thickeners can increase slurry solids up to 15% (Gwilliam 1971) or higher. Rotary vacuum filters were first used in 1950 to dewater kaolin to cake solids ranging from 50% to 65% solids (Adler 1999; Murray 1980). The plate-and-frame filter has a hydraulic ram to apply between 15 bar (220 psi) and 68 bar (1,000 psi) to achieve maximum cake solids up to 75%–80% (Thurlow 2001). Tube presses apply pressures up to 100 bar (1,450 psi) to achieve cake solids up to 82% (Gwilliam 1971).



Note: Kaolin products with pH >6 and containing dispersant are slurry, granulated, and spray-dried forms. Kaolin products with pH <6 are undispersed and include filter press cake, lump, and pulverized acid lump.

Figure 7 Product forms and moisture content of kaolin products

Dewatering technologies designed for dispersed slips include centrifuges and membrane filters. Dewatering centrifuges can act on fully dispersed slurry, coagulated slurries, or fully flocculated slurries. The disc-nozzle design can increase solids into the range of 30% to 40% (Asdell 1967). Leung (1998) describes a 3,000–4,000 G decanter centrifuge that can take solids into the range of 60% to 65%. Membrane filters can take dispersed kaolin slurry solids from <20% solids to >60% solids (Adler 1999).

An important advantage of solid–liquid separation is the removal of soluble salts from the kaolin. Soluble salts are deleterious to clay-water rheological properties and can be deleterious to brightness. These salts may be inherited from the crude, from process chemicals added during blunging or postblunging, or from ferrous iron released during the leaching process.

Evaporation

High-solids slurries with about 65%–70% solids can be made using a combination of solid–liquid separation and evaporation unit operations such as evaporators or by back-mixing dried kaolin. Evaporators used to dewater kaolin can have direct flame acting on a falling curtain of kaolin slurry, or they have indirect heat-exchange with steam to heat the clay slurry prior to it passing through a low-pressure chamber to reduce boiling temperature (Willis 1987).

Kaolin slurries are dried using spray dryers by Georgia and Brazilian kaolin producers. The product formed from a spray dryer is a bead approximately <1 mm in diameter, showing face-to-face particle aggregation and having moisture content between 1 and 8 wt %.

The rotary, tray, fluid bed, and apron dryers are fed acid-flocculated filter cake or extruded noodles. The product formed from these processes are typically clay lumps or granules. Moisture contents can range up to about 15%.

Milling and Dry Classification

Milling can be performed on dried crude from the dry process, on dried water-washed or delaminated beneficiated kaolin, and on calcined kaolin. The roller mill is used in the airfloat process to reduce particle size to below 45 µm (325 ASTM mesh) and to remove some coarse-particle size impurities such as quartz (Williams 1985). The roller mill is composed of a vertical shaft suspending rollers rotating against the mill wall (bull ring). Air currents lift fine particles upward in the grinding chamber to the whizzer separator. The whizzer allows fines to pass upward, and it throws coarse particles against the wall to drop back into the grinding chamber. Other mills, such as ball mills, cage mills, and hammer mills, work on the same principle of impact grinding to degrade particles and lumps into finer sizes and using air classification to return coarser particles to the grinding chamber. Some mills have separate heat sources to dry the feed to the mill if it has not been fully dried of moisture to aid particle separation and to prevent caking on mill surfaces. The Hegman fineness of grind test is used to determine the top size of particles and effectiveness of the milling.

Finished Product

Each market application has its own specific set of properties measured and reported on the kaolin product certificate of analysis (COA). Pruett and Pickering (2006) discuss the major chemical and physical tests generally included on the COA.

The finished product from all dry and wet operations is generally stored and tested by the quality lab prior to final packaging and shipment. High-solids slurries are stored in agitated tanks. Spray-dried products and lump products are stored in silos, flat stores, or bays. Bulk dry products are loaded directly into trucks, railcars, or ships. Slurries generally need a final chemical treatment of dispersant to maintain viscosity through the logistic chain; biocide to prevent microbiological growth from causing product degradation and contamination to the customer; and thickeners to prevent sedimentation of coarse particles in un-agitated tankers, railcars, and ship holds during transportation.

Kaolin for small-volume and specialty applications or for shipment overseas can be packaged in totes or bags. Totes hold small volumes of finished kaolin slurry. Spray-dried, apron-dried, and pulverized low-moisture products can be packaged in super sacks or small bags. Bagging operations can be manual or completely automated using robots. After the bags are filled, they are typically checked, weighed, pressed to densify and remove excess air, placed on pallets, and then shrink-wrapped.

Environmental and Regulatory Considerations

Addressing liquid, solid, and gaseous effluents is required where kaolin is processed. Water-washed kaolin operations generally need large impounds or thickeners to capture tailing to clarify water reused in the process or released back to the environment. The water needs to be acidified to flocculate out kaolinite particles. The clarified water meeting local turbidity requirements needs to be neutralized to local standards prior to its release into surface waters. Some kaolin ores contain iron sulfides (pyrite) that if heated above 400°C (752°F) release SOx(g) that may require operations to scrub air released from dryers or calciners with lime. Fine dry kaolin is dusty. Capture of dust particles around dry handling areas of the plant and from emission points in the process is an important part of the process design.

Some markets have additional regulatory considerations. The Registration, Evaluation, Authorisation and Restriction of Chemicals regulations require identification of chemical components in products shipped or used in European markets. Some markets require U.S. Food and Drug Administration (FDA) or equivalent compliance. For example, chemicals used for wet processing paper pigments that are retained in the product must comply with FDA food contact rules to be accepted by some paper customers.

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