Lempung Perindustrian dan Mineralogi Lempung

Introduction

Clays are secondary minerals that have formed through the weathering and hydrous alteration of certain parent rocks and their constituent minerals. Common igneous and metamorphic rocks such as granites, gneisses and schists contain minerals such as feldspars, hornblendes, micas and other complex alumina silicates. Silica and alumina are necessary precursors (originator) to the formation of clay minerals.

Long periods of physical weathering breaks down the rocks into finer, grain sizes and allows an accelerated rate of chemical weathering ore mineral decomposition to take place. In some cases, the decomposition takes place in situ and the alteration products may accumulate at the site of origin or be carried away by water and winds. Often fine grained weathering products (mixed sands, etc.) will be transported from the site of origin, redeposited as clastic beds and later subjected to chemical weathering and alteration. Clays formed at the site of the parent rock are called primary clays even though they are secondary in origin after other minerals. These formed after transportation and redeposition of rock and mineral fragments or transported as clays from the original site of origin are called secondary clays. Tapah and Bidor, as an example industrial clays are secondary in that they or their immediate precursors have been transported and redeposited.

Usually secondary clays are mixed with other minerals such as micas and quartz which are more resistant to weathering. Sometimes, as in the case of the upper beds of the many clay formation, reworking by stream and wave action will separate the clay from the unweathered grains, break the latter down to finer grain sizes and carry the clay away to be redeposited after as distinct beds. Such a process is believed to have given rise to the important deposits of plastic ceramic clays in many part of clay deposits.

Clays that remain mixed with quartz sand grains and other minerals may also be of economic significance. The lower beds of some clay formation, are also known as kaolinized sands, are an example. These beds would contain an average of 50 per cent kaolin which can be separated, purified and used in a variety of industrial applications.

Occasionally the parent material may be completely weathered to clay minerals. Such is the case with the bentonites, which were formed as a weathering product of volcanic ash deposited during, an example, in the late Cretaceous period.

Clay such as kaolin can formed 30 to 50 million years ago by movements of the earth's crust, causing collisions between the land masses, like in India. This contributed to the formation of numerous geological faults, one of the smaller ones of which is found like in Rajasthan and North Gujarat (India), where tertiary sediments were preserved. These are now formed as Primary China Clay. China clay has been formed originally at North Gujarat and Rajasthan by weathering of granite masses. Having been washed away and transported by rivers, 20 MICRONS' site called MAMUARA is where they eventually are deposited.

These deposits are called Secondary China Clay and the largest of these reserves as in India are found in Kuch Region.

Description of Clay Minerals

Clay is a general term for a highly variable group of natural materials that are soft, earthy, extremely fine grained, usually plastic when moist and consisting of one or a mixture of various clay minerals and impurities. Alkalies such as sodium, lithium and potassium and alkaline earths such as magnesium, calcium and barium are often present in the molecular structure of clays and have a significant effect in the physical and chemical properties.

Clays occurring in nature rarely comprise pure, single clay minerals. They usually contain a variety of non-clay impurities such as quartz, calcite, mica, feldspar and pyrite, among others.

Most clay minerals involve two basic types of units in their atomic structure. The manner in which theses units are combined and the type of exchangeable atoms that are present will play a very significant role in the type of clay mineral that forms. The major clay resources are: (*refer appendix*)

- kaolinite
- halloysite
- momtmorillonite (bentonites)
- illite
- smectite
- vermiculite
- chlorite
- attapulgite
- allophane

The most important commercial clay minerals include the kaolinite, montmorillorite and illite clays.

- kaolinite types of structure are highly variable in composition and properties. The variations allow them to be used for a number of applications including fired and unfired products.
- montmorillonite structure (bentonites) are of two important commercial varieties. Swelling and non-swelling bentonites are utilized in many ways.
- illite structure are most frequently found with other clays. They are of limited commercial value except for the fact that they are part of the agricultural soil.

Major Classification of Commercial Clays

Six types of clays are available in the world market, namely

- Ball clay
- Bentonite
- Common clay
- Fire clay
- Fuller's earth, and
- Kaolin.

Clays Composition

Ball clays consist primarily of koalinite with minor to major amounts of illite, chlorite, smectite minerals, quartz, and organic materials.

Bentonite comprise smectite minerals (usually montmorillonite) with minor amounts of feldspar, biotite, and quartz.

Bentonite is a soft clay substance that belongs to the clay minerals group. This group is complex and consist of several mineral commodities, each having somewhat different mineralogy, geological occurrences, technology and uses. They are all natural, earthy, fine-grained minerals of secondary origin and composed of an alumina silicate structure with additional iron, alkalis and alkaline earth elements.

Clay minerals are classified into two broad groups:

1. specialty groups - in which bentonite is included, and
2. kaolinitic clays, which include ball clay, fire clay (refractory clay), stoneware clay and kaolinite.

These minerals rarely occur in a pure state, occurring with quartz, calcite, dolomite, feldspar, gypsum and iron oxide.

Bentonite is a soft clay substance composed essentially of clay minerals of the montmorillonite group and is formed from chemical weathering of volcanic materials such as tuff or glass, volcanic ash, other igneous rocks, or from rocks of sedimentary origin. The nature of the weathering environment and the original composition of the volcanic material will generally determine the type of bentonite that forms.

Its color ranges from white to light olive green, cream, yellow, earthy red, brown and sometimes sky blue when fresh but yellowing rapidly with exposure to air. When wet it is highly plastic and slippery. Bentonite feels and appears greasy or waxy.

There are two basic types of bentonite depending on whether they contain sodium or calcium in the crystal lattice.

1. **swelling bentonites** - sodium bentonite contains sodium in the platy molecular structure; has strong swelling properties (ability to swell to many times its dry volume when wet) and possesses a high dry-bonding strength
2. **non-swelling bentonites** - calcium bentonite contains calcium in its structure; has a far lower capacity to swell when wet and usually exhibits greater adsorptive characteristics.

Bentonite, an important industrial clay, is made up mainly of the mineral smectite (montmorillonite) and formed by the alteration of volcanic ash. One of its most important uses is as DRILLING mud in the petroleum industry--it removes drill cuttings from the hole, forms a filter cake on the wall of the hole to prevent drilling fluid loss and keep groundwater from entering, cools and lubricates the bit, and keeps barite (a weighting agent) in suspension in order to prevent blowouts.

Bentonites are also used as bonding clays in foundries; as bonding agents for taconite and iron ore pellets; as adsorbents; as decolorizers for fats and oils; and as liners for ditches and ponds to prevent water loss. In addition to fine particle size, bentonites have the unique capability of swelling when they become wet.

Common clays contain illite and chlorite as major components. Most other clays consist of mixtures of illite (a hydrated potassium-iron-aluminum silicate), CHLORITE, kaolinite, and smectite.

Fire clay comprises mainly koalinite, halloysite, and/or diaspore.

Fuller's earth consist primarily of attapulgite or montmorrilonite clays with quartz.

Kaolin comprises primarily kaolinite or kaolin group minerals.

Uses for Clay and Classification

Clays play a very important role in many industries. Colour, plasticity, mineral composition, absorption qualities, firing characteristic, and clarification properties are a few of the characteristics used to distinguish between the different clay types.

Their use depends upon their physical and chemical properties. Clays can be divided into three categories (depending on their uses):

1. firing (pyrometric) properties
2. physical, non-pyrometric properties
3. chemical properties

Major Market of Clays

Clay Types and Uses	
Ceramic Clays (kaolin type)	**common and face bricks, chimney flue linings, sewer pipe, stoneware and earthenware pottery, fire brick, other refractory products**
Kaolin Clays (related uses)	**production of aluminum; kaolin fibres for high temperature insulation; porcelain, as a component in portland cement; synthetic zeolites; as a filler for paper, paint, adhesives and caulking; production of wall and floor tiles; rubber, adhesives, sealants; extender, whitening and reinforcing agent**
Non-kaolinitic Clays (bentonites and glacial lake clays)	**production of lightweight aggregate as a substitute for gravel in concrete products**

Major market (in the world trend) for individual clays were :

Ball clay : Pottery and miscellaneous ceramic (14%), sanitaryware (22%), and floor and wall tile (35%);

Bentonite : Absorbents (25%), drilling mud (17%), foundry sand bond (20%), and iron ore pelletizing (14%)

Common clay and shale : Brick (55%), cement (18%), and lightweight aggregate (17%).

Fire clays : Refractories (72%).

Fuller's earth : Absorbants (75%).

Koalin : Paper coating and filling (60%)..

Clay Products and Consumption:

Ball clays : . Ball clays are usually much darker because they contain more organic carbonaceous material. These fine-grained refractory bond clays have excellent plasticity and strength, and they fire to a light cream to white color. For these reasons, ball clays are used extensively in CERAMICS in whitewares, sanitary ware, and wall tile, and as suspending agents in glazes and porcelain enamels.

Water slurried ball clay (sanitaryware industries), airofloat and shredded (unprocessed) ball clay. The principle ball clay market, in general, in decreasing order, were floor tile and wall tile, sanitaryware, and refractories.

Bentonite : Bentonite is a smectite clay formed from the alteration of siliceous, glass-rich volcanic rocks such as tuffs and ash deposits. The term of Bentonite encompasses a number of different products, two natural and three treated. The major mineral in bentonite is montmorillonite, a hydrated sodium, calcium, magnesium, aluminum silicate. The sodium, calcium, and magnesium cations are interchangeable giving the montmorillonite a high ion exchange capacity. Commercially natural Bentonite is classified into two groups, sodium based and calcium based. Sodium based has predominantly exchangeable sodium ions, and has the ability to absorb large quantities of water accompanied with considerable swelling, and on shearing gives thixotropic solution. Calcium based Bentonite has predominantly calcium exchangeable ions, and when wetted exhibits low swelling and does not form homogeneous solution. The three treated products include sodium-exchanged Bentonite, acid activated Bentonite, and organophyllic Bentonite. Swelling-bentonite, non-swelling bentonite. Blended varieties : preblended bentonite-based foundry sand additive for metal-casting industry. Nanocomposite -ultrafine montmorrilonite products (nylon packaging and engineering resin products. The packaging products act as a barrier film for oxygen and carbon dioxide. Composites made using nanocomposite technology have higher tensile modulus, flexural modulus, and flexural strength, allowing for lighter and thinner part). Major market for bentonite were drilling mud, foundry sand bond, iron ore pelletizing, and pet waste absorbents, waterproofing and sealing (99% swelling bentonite). Other application includes animal feed, civil engineering, pharmaceutical, waterproofing, and water treatment. Non-swelling bentonite mainly used in decreasing order are in foundry sand, clarifying, decolorizing, and filtering of oils and greases, miscellaneous absorbents, chemical manufacturing, animal feed, and desiccants.

Bentonite thickens, swells, gels, bonds and lubricates in aqueous systems. Bentonites have a very small particle size and extremely high surface area. Some is white bentonite, hydroclassified and dried to produce high purity suspending agents, emulsion stabilisers nad rheology modifiers for aqueous applications. In addition heavy metal and bacteria content are maintain at very low level for pharmaceutical and personal care application, household cleaning, ceramics and agricultural application. White bentonites, depending on their purity, range in price from $200 to $1,500 per ton.

Two value added products are processed, one from sodium bentonite and one from calcium bentonite. Organoclays are produced using sodium bentonite as the base. Organic compounds are reacted with the high exchange capacity sodium bentonite where the organic is exchanged for the sodium. Organoclays are used in oil base paints, in high temperature grease, in oil base drilling muds, and several other niche markets. The price of organoclays ranges from $1,500 to $4,000 per ton. Calcium bentonite is acid activated to produce bleaching clays which are used to clarify edible oils and beverages. Acid activation increases the surface area and pore volume thus improving the clay=s performance in removing color bodies and impurities from liquids. The total world volume of the bleaching clay market is estimated at about 850,000 tons. The price ranges from $250 to $600 per ton. A potential new value added growth market for montmorillonites is nanoclays. A nanoclay is clay having nanometer-thick platelets that can be chemically modified to make the clay complexes compatible with organic monomers and polymers. The properties of a polymer, which limits its use, are stiffness and /or strength in durable applications and gas barrier performance in packaging materials. Heat distortion temperature is also a limiting factor for polymers in many products. All the above properties can be significantly improved through the use of nanoclays. The market potential for nanoclays is very large.

Suspending
Effective dispersion and hydration using high shear colloidal mixers achieves a bentonite slurry capable of effectively suspending dense particles.

Typical Applications:
Drilling Muds, Refractory Paints, Emulsion Paints, Agricultural Sprays, Pumpable Solids and Pharmaceutical Lotions.

Plasticising
Bentonite clays with their colloidal like behaviour impart improved plasticity to solids/aggregates by providing mobile contact points between larger grains.

Typical Applications:
Clay and Cementitious Grouts, Plasters, Pastes and Polishes.

Thickening
Viscous suspensions can be achieved at addition rates exceeding 3% bentonite in water.

Typical Applications:
Adhesives, Paints, support fluids for diaphragm and slurry walls.

Sealing
In contact with water bentonites swell to form an impermeable mass which resists water and leachate flow. Pre-mixing with selected sands or soil achieves maximum economy and performance.

Typical Applications:
Ponds, Ditches and the sealing/capping for Landfill Sites.

Bonding
The coating of sand grains and subsequent mulling with appropriate amounts of water produces a mouldable mass having flow properties.

Typical Applications:
In the green sand process for the production of metal castings particularly in iron foundries.

Binding
The use of mixes having high bentonite: water ratios improves pressing and extrusion characteristics.

Typical Applications:
Briquetting, crayons, iron ore pelletising, extruded animal feed pellets.

Emulsification
Bentonites have a high surface area often exceeding 100 sq metres per gram. Oils can be added to aqueous clay gels and emulsified by high speed agitation.

Typical Applications:

Bitumen, Asphalt, Soaps, Detergents.

Water Treatment
Bentonite concentrations as low as 20 - 80 ppm dispersed in water act as excellent coagulants in waste effluents. Subsequent flocculation and settling is achieved by 1 - 2 ppm dosages of a suitable polymer.

Typical Applications:
Sewage treatment, Paper Mill effluent and process water recycling.
Clarification of effluents containing oil impurities.

Absorption

When used in powder or granular form bentonites possess good adsorbing and absorbing abilities. Formerly used as the prime means of absorbing oils from wool (fulling process) until the advent of soaps and detergents. Possess good decolourising ability. .

Common clay and shale : Most of these type of clays were mined for manufacturing of structural clay products, such as brick, cement, clay pipe, drain tile, lightweight aggregate, and sewer pipe. About 90% was used to manufactured brick, lightweight aggregate, and cement. Common clay were used most frequently in the manufacture of heavy clay products, such as building brick, drain tile, flue lining, lightweight aggregate, Portland cement, sewer pipe, structural tile, and terra cotta.

Fire clay : Fireclays are soft, plastic clays used primarily in making REFRACTORY MATERIALS that will withstand temperatures of 1,500 degrees C or more. The most common fireclays, under clays, occur directly under coal seams.

Fire clay mostly used for refractories manufacturing, mainly firebrick. Some of the common refractory products manufactured from fire clay are firebrick and block, grogs and calcines, high-alumina brick and specialities, refractories motars and mixes, and ramming and gunning mixes.

Fuller's earth : Fuller's earth is term used for highly absorbent and natural bleaching clays. Fuller's earth is used to describe calcium Bentonite in the UK and some other countries, but the USA it is used to describe any natural material able to decolourise and bleach oils, and absorb water Fuller's earth mainly attapulgite, and grade from attapulgite-rich to montmorrilonite-rich, an important gellant-grade.

The major uses for attapulgite (*Palygorskite*) and montmorillonite varieties of fuller's earth, in decreasing order, were pet waste absorbents, oil and grease absorbents; Portland cement manufacture, fertilizer carriers; animal feed; filtering, clarifying, and decolorizing of oils and grease animal feeds, desiccant; and pesticide carrier.

Attapulgite and Sepiolite

Attapulgite and sepiolite are hydrated magnesium aluminum silicates, consist of long, tubular particles are thin elongated chain type structure. When dispersed in water these elongate crystals are inert and non-swelling and form a random lattice capable of trapping liquid and providing excellent thickening, suspending, and gelling properties. These clays do not flocculate with electrolytes and are stable at high temperatures, which make them uniquely applicable for many uses.

There is a definite overlap in the use of term fuller's earth with both attapulgite and calcium Bentonite (highly absorbent and natural bleaching clays).

Attapulgite (palygorskite) : It is used as a saltwater drilling mud; in adhesives to control viscosity; as a thickener in latex paints, liquid suspension fertilizers, and pharmaceuticals; and as pet litter, oil adsorbent, carriers for agricultural chemicals, flatting agent in paint, and anticaking agent. Accounted for more than 60% of the sales are adhesive and pesticide carriers and all of the sales for asphalt tile, drilling mud, gypsum products, paint, pharmaceuticals, roofing granules, and textiles. Major market for montmorillonite variety of fuller's earth are for animal feed; Portland cement manufacture; clarifying, decolorizing, and filtering oil and greases, desiccant; oil and grease absorbent.

Sepiolite another variety of clay, has nearly the same physical properties as attapulgite, but a higher magnesium aluminium and iron content than palygorskite and has slightly larger unit cell size. Often used in industry as absorbent and adsorbent for pet litter, industrial absorbent, pesticide carrier, soil conditioner, cigarette filters, solvent cleaning, bleaching earths, filler for rubber, binder etc.

Both mineral are mainly used in drilling muds, paints, liquid detergents, adhesives, car polish, flexiographic inks, cosmetic, floor absorbents, potting mixes, oil-spill clean-up material. These clays are also utilized as carriers for fertilizers, pesticides, or hazardous chemicals, decolorize various mineral, vegetable and animal oils, as receptor coating on carbonless copy paper, and pet litter.

These clays are relatively unaffected by electrolytes their viscosity is retained whereas bentonites flocculate and lose their high viscosity. Both minerals are used as a binder for pelletized animal feed. Studies have reported increased feed efficiency and improved digestive hygience. Another use is as an additive in cement where because of its elongated shape and absorbency it strengthens the resulting concrete. The prices per ton range from US90 to as much as $800 for very fine highly refined material.

Palygorskite (attapulgite) and spiolite deposits are relatively rare in comparison with the other industrial clays. Major deposits of palygorskite occur in US, Senegal, Ukraine, Spain, Turkey, and China. Spiolite deposits occur in Spain, Turkey, and Somalia. The world production of attapulgite is estimated by USGS to be about 1 million tons and spiolite about 400,000 tons. Spain is the largest producer of sepiolite and accounted for about 95% of the world production. US by far are the largest producer of attapulgite, which in 2000 produced 725,000 tons, or 76% of the world production. The total world production of fuller's earth clays including attapulgite, spiolite, and calcium montmorillonite is estimated to be in excess of 3.3 million tons (Murray, H, 2002)

Koalin : A hydrated aluminum silicate. The physical and chemical properties of kaolin has led to it's extensive use as filler, extender, paper coater, ceramic raw material, pigment, and also it is an important raw material for the refractory, catalyst, cement, and fiber glass industries.Various grades of kaolin clays may be distinguished. White kaolin clays are fine in particle size, soft, nonabrasive, and chemically inert over a wide pH range. In looking at usage trends, kaolin based pigments can be grouped into four broad categories: standard hydrous, delaminated, structured and engineered. The categories can be differentiated by particle size and shape, brightness, rheology and other properties. Standard hydrous pigments are beneficiated from kaolin crude to remove impurities, while delaminated grades are processed further to free individual kaolin platelets. Structured grades are created by calcining. Approximately 56% kaolin was water washed (slurried or hydrous kaolin), 17% calcined, 13% delaminated, 11% airfloat, and 3% untreated. Some marketed as pigment-grade (low temperature) and high-temperature (refractory grade, calcined kaolin). Apart from paper, now an important petroleum catalyst. Halloysite is used in the manufacture of petroleum cracking catalysts, speciality cements, china and porcelain. Halloysite clay crystals comprise laths and tubes together with broken fragments of more massive material. While tabular forms are the most common, other morphological types are also known, including prismatic, rolled, pseudo-spherical and platy forms.

There are two broad groups of processed Kaolin clays, calcined and uncalcined. This makes it especially valuable in the paint industry. Chemists are able to take advantage of its new structure properties so the uses for calcined clay are growing. These added values command a higher price that more than offsets the increased processing costs.

The uncalcined clays also have good characteristics that make them valuable as extenders in paints. A feature of the structure of Kaolin clays in that if forms platlets. These platlets act together to effectively reflect the light in a paint formulation.

The major market consumption of kaolin, in decreasing order, were paper coating and filler, refractories, fiber glass, paint, catalyst, and rubber.

Clays in Major Products

Ceramics : All varieties of clays were used in ceramics. Demand for clay in the manufacture of ceramics ranging from china to sanitaryware to roofing granule. The largest ceramic market was floor tile and wall tile (46%), followed by sanitaryware (18%), catalyst (12%), roofing granules (10%), quarry tile (4%), fine china (3%), and pottery (3%).

Ball clay dominated the crockery, electrical porcelain, glazing, and sanitaryware market. Koalin dominated the catalyst market. Ball clay and common clays and shale were the predominant clays used in floor and wall tile manufacture, and ball clays and kaolin dominated the fine china market.

Paper : Their largest consumer is the paper industry, which uses them as a coating to make PAPER smoother, whiter, and more printable, and as a filler to enhance opacity and ink receptivity. Kaolin, the most widely used paper coating pigment in North America, gives papermakers nearly all the finished sheer properties they need at a relatively low cost. Kaolin has good colour and brightness, as well as a fine particle size that aids opacity, gloss and smoothness. As the paper coating machines run faster in order to produce more coated paper to improve productivity, the viscosity becomes more critical. Its platy particles boost ink receptivity and print quality, and it dispersed easily at high solids for good runnability. The brightness of kaolin always higher than standard pigments with an 86 to 88 TAPPI brightness to high-brightness pigments above 90. As shown the largest market for kaolin is paper coating. Kaolin is uniquely suited for this use because of its fine particle size, platy particles, good viscosity, low abrasion, good opacity, white color, high brightness, and good print quality. Several grades which vary in brightness and particle size are available to the paper coater. Prices (FOB) range from 4 to 8 cents per pound. An analysis of a sheet of paper in the National Geographic magazine would show that approximately 35% of the weight would be kaolin.

These are a number of characteristics that are tested in Kaolin. The most important characteristics are the particle size and brightness. The smaller the size, the more costly it is and the greater the number of uses it has. The best grads of Kaolin have a median particle size of 2 micros. One micro is the size of the particles in cigarette smoke. There are grades of 'less than 5 micros', 'less than 10' and so on. Each has its different applications.

The brightness is a measure of the amount of light that the Kaolin reflects back to the measuring instrument. The scale is called the G.E. Brightness Scale and ranges from 1 to 100. Most Kaolin applications require a brightness number over 87. 95 on the brightness scale is a high number for calcined Kaolin clay. Calcined kaolins have a high brightness and opacity and are used to extend titanium dioxide which is expensive ($1.00 per lb.). Titanium dioxide is a prime pigment with exceptionally high brightness and opacity. Calcined kaolin can replace up to 60% T O in paper coating and filling formulations and also in paint formulations without any significant loss in brightness and opacity. The price of calcined kaolin products range from 15 cents to 25 cents per pound. The major competitive mineral is calcium carbonate, which has made severe inroads in paper filling. However kaolin still dominates the paper coating market. Kaolin, or **kaolinite** has been used by blending with plastic clays to increase refractoriness and reduce drying shrinkage in brick production.

TYPICAL PROPERTIES		CHEMICAL ANALYSIS	
Specific Gravity	2.6	Al2O3	20.5%
% Residue on 325 mesh	0.1	SiO2	56.9
Hegman Gage	7.0	Fe2O3	0.3
Oil Adsorption	49	MnO	0.7
Median Particle Size, µm	2.0	Na2O	0.1
GE Brightness	90+	K2O	1.6
pH 20% aqueous slurry	6.0	TiO2	1.2
Resistivity (ohms)	100K+	CaO	0.9
Hardness (Mohs)	2.9	MgO	0.1
White Undertone	Blue	LOI	17.7

Mining and Process Technology

The mining and processing of bentonites is very simple. The mines are open pit and the bentonite is crushed, dried, pulverized or screened for granular products, classified, and bagged and loaded. For organoclays, acid-activated clays, and nanoclays, a wet process is used. This includes blunging at low solids, screening or centrifuging to remove coarse particles, acid leaching or reaction with organic compounds, filtering, and drying. For nanoclays an intense grinding or shearing is required to delaminate the montmorillonite into very thin flakes before reaction with an organic compound. Palygorskite and sepiolite are surface mined in open pits, similar to bentonite. The processing involves crushing, drying, pulverization, classifying, bagging and loading.

Evaluation of kaolin deposit generally directed at resource definition, mineralogical characterization, sand-clay separation, technology, stratigraphy, other aspects as an example, alumina content for potential aluminum production, refractory materials, and kaolin filler.

All kaolin is mined using open pit methods utilizing shovels, draglines, and backhoes. The normal economic overburden to kaolin ratio is 6.5 to 1 or less.

Two processing methods are used in the production of kaolin - dry and wet.

The dry process is rather simple and a typical flow sheet is as follows:

MINING > CRUSHING > DRYING > PULVERIZATION > CLASSIFYING > BAGGING & LOADING.

The wet process is more complex with a typical flow sheet shown as follows:

MINING
BLUNGING
DEGRITTING
Fractionation and particle size separation.
Selective Flocculation Magnetic Separation Delamination Flotation
LEACHING Surface Treatment
DEWATERING
Apron Drying DEFLOCCUATION High solids slurry
Calcination SPRAY DRYING
BAGGING & LOADING

Tests are conducted to improve the color of the clay, attempting to provide a whiter product. Exploration and evaluation of kaolin resources is conduct as process toward clay deposit development. The kaolinized sand is process to removed foreign materials and particle size classification and upgrading the kaolin to paper filler standards.

Technology in kaolin beneficiation usually related to silica removal, brightening, calcining, and kaolin delamination. The company has achieved a kaolin quality suitable for some applications in the paper industry. The clay occurs in beds up to 30 meters thick and is suitable for various applications. This clay deposites consist of approximately 60 percent kaolin and 40 Per cent Quartz other minor minerals.

Crude China Clay from various pits is normally tested for variations in laboratory and accordingly, crude are selected for particular applications. After excavation from the mines, the crude material is bunged and transferred to factory after degritting.

HYDROUS KAOLIN

While still slurry form, clays with different properties are homogenously blended to achieve final products with specific characteristics. These slurries are further processed for wet grinding, delamination and for particle size classification through hydrocyclones, and finally, through most advanced cryogenic super conducting magnetic separator and flotation for removal of impurities that discolour the products. Chemical bleaching is also done to enhance whiteness & brightness.

CALCINED KAOLIN

Calcination is the process of heating the small particles of Kaolin to about 1800 degrees fahrenheit for about 45 minutes. In other word, calcined kaolins are also produced by heating spray dried fine particle kaolins to temperatures in the range of 1,000 C. The kaolinite becomes anhydrous and transformed to mullite (Al_2 Si_2 O_5) and SiO_2. This process 'pops' the structure of the Kaolin molecule and increases the surface area. The brightness goes up. The reflective characteristics are increased. Rotary calcining kiln removes chemical water from clay crystal and forms porous aggregate structures. These thermally structured calcined clays are used to replace and substitute of TiO_2 - 15 to 25% in many applications.


Summary Table of Industrial Production and growth

Cumulative Total World Production Kaolin	39,000,000 tons
Bentonite	10,226,119 tons
Palygorskite-Sepiolite	1,400,000 tons
World Known Reserves Kaolin	- 1 billion tons plus
Bentonite	- 300 million tons plus
Palygorskite-sepiolite	100 million tons plus
Annual Growth Kaolin	2%
Bentonite	4%
Palygorskite	1%

The total world production is currently estimated to be 39 million tons per year distributed as follows: *

Paper Filling and Coating	45%
Refractories	16%
Ceramics	15%
Fiberglass	6%
Cement	6%
Rubber and Plastics	5%
Paint	3%
Catalyst	2%
Others	2%
Refractories	16%

*Roskill Information Services, Ltd. AThe Economics of Kaolin@ 10th Edition

The Geochemistry of clay minerals

Equilibrium adsorption and ion exchange

The typically small grain size (<2 µm) of clay minerals results in the presence of large surface areas. These surface areas are available for exchange of ions and molecules between the solids and surrounding solutions.

Exchange of ions involves **adsorption** and **desorption** which are commonly fast (on geological time scales).

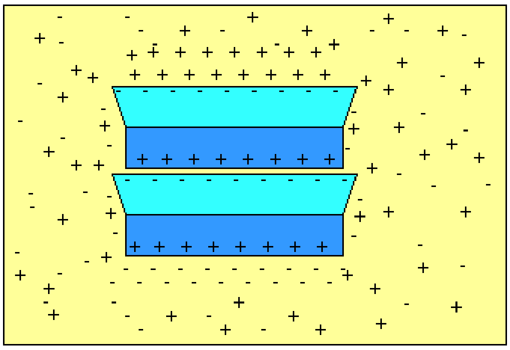
This exchange process can be treated as an equilibrium process.

The kinetics of adsorption in natural environments is poorly understood (implications for waste treatment and disposal).

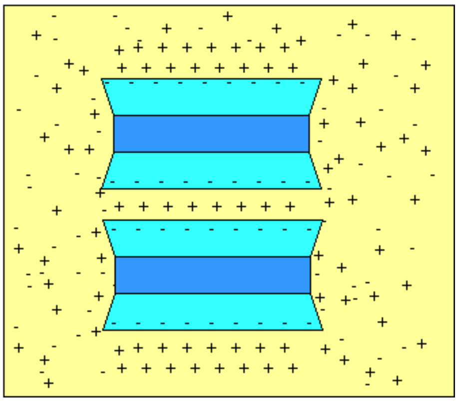
Adsorption takes place because of the attraction of ions to a surface. The strength of the bonding varies from weak van der Waals (physical adsorption) to strong chemical bonds (chemisorption), henceforth simply referred to as adsorption.

This process involves neutral species (H_2O, H_4SiO_4, organic molecules) and ions.

Example of **kaolinite**: Notice in the schematic diagram below that for 1:1 structures, positive ions are attracted to the light-blue tetrahedral basal oxygen surface. At the same time, negative ions are attracted to the dark-blue octahedral hydroxyl surface.



Example of **vermiculite or smectite**. The case for low-charge 2:1 structures is notably different from 1:1 structures. The schematic diagram below shows that 2:1 structures have mostly positive ions are attracted to the light-blue tetrahedral basal oxygen surfaces.



Surface charge properties

One way in which surface charge can develop is by adsorption of an ion where the solid acts as an electrode. (*e.g.*, H^+ and OH^- on the surfaces of clays) .

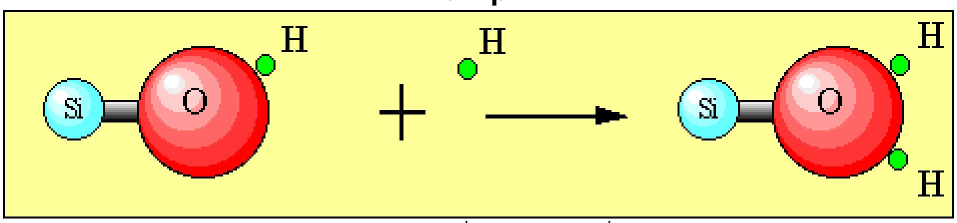
In clay-aqueous systems the potential of the surface is determined by the activity of ions (*e.g.*, H^+ or pH) which react with the mineral surface. .

The simultaneous adsorption of protons and hydroxyls as well as other potential determining cations and anions, leads to the concept of **zero point of charge** or **ZPC**, where the total charge from the cations and anions at the surface is equal to zero.

The charge must be zero and this does not necessarily mean the number of cations versus anions in the solution are equal. For clay minerals the potential determining ions are H^+ and OH^- and complex ions formed by bonding with H^+ and OH^-.

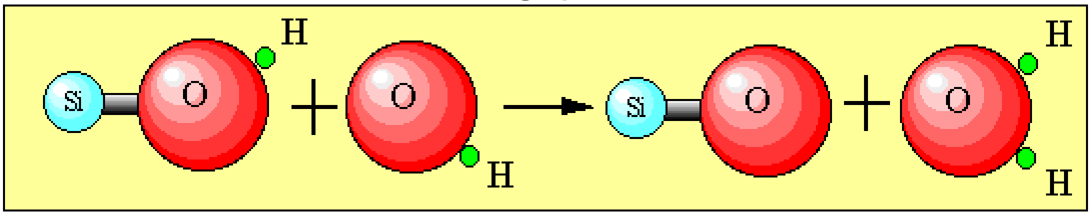
For example on the basal oxygen surface of kaolinite or illite, the O^{2-} ions bond with H^+ to form hydroxyls. These surfaces further react as either acids or bases with other protons or hydroxyls: The surface charge is therefore, pH dependent. The broken Si-O bonds and Al-OH bonds along the surfaces of the clay crystals result in hydrolysis.

Low pH



$MOH + H^+ \rightarrow MOH_2^+$

High pH



MOH + OH^---> MO^- + H_2O

The potential at the surface is determined by the activity of these ions given by the Nernst Equation,

where:

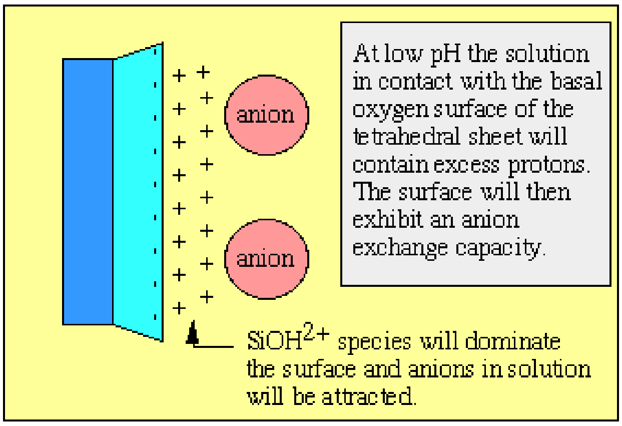
The electric potential (E) is equal to the standard state electric potential (E^o) and the relationship:

$$E = E^o - (RT/nF) \ln (a/a^o)$$

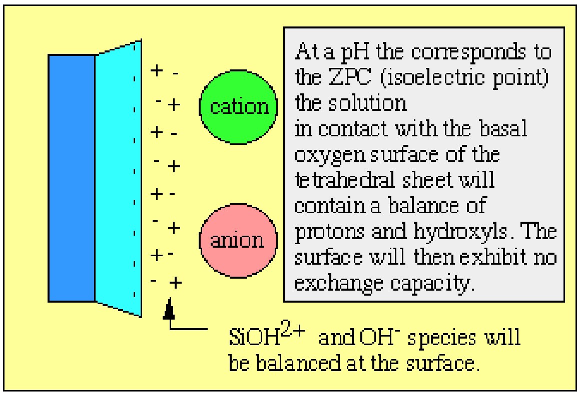
where: F= Faraday constant, n = number of molar equivalents of electrons transferred

The pH that corresponds to the **ZPC** is referred to as the pH_{ZPC} or the isoelectric point.

1. With pH's below the pH_{ZPC} the solid has would have anion exchange capacity.



2. pH's at the pH_{ZPC} , the solid would have no exchange capacity.



3. pH's above the pH_{ZPC}, the solid would have cation exchange capacity.

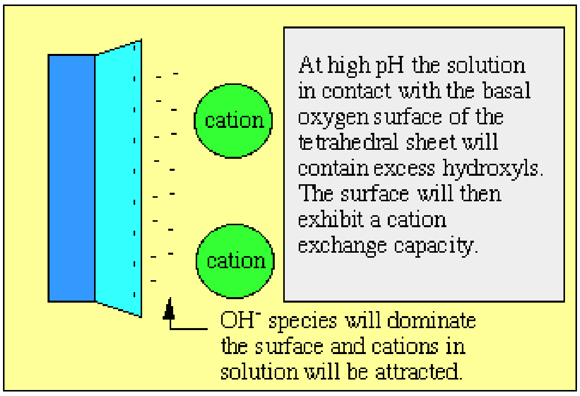


Table of pH for zero point of charge for clay minerals. Note that in Georgia Piedmont soils, the typical pH is below 4, in Georgia estuarine systems typical pH is 7.5.

Mineral	pH_{ZPC}
Gibbsite	10
Hematite	4.2 - 6.9
Goethite	5.9 - 6.7
Na-feldspar	6.8
Kaolinite	2 - 4.6
Montmorillonite	<2 - 3
Quartz	1 - 3

Note that Al and Fe hydroxides have a high pH_{ZPC}. Kaolinite and montmorillonite have low pH_{ZPC}.The ZPC is determined from a titration curve where pH is varied (see figure 3.2 from Eslinger and Pevear).

The adsorption of potential-determining ions results in the development of a **electric double layer.**

inner layer - fixed and contains potential determining ions
outer layer - mobile diffuse layer of freely moving counter ions

There are numerous models devised to predict the distribution of surface-species. The two simplest models that give a reasonable representation of the ion distributions are the **Gouy** and **Stern** models.

See figures 3.3 and 3.4 from Eslinger and Peaver

Potential determining ions need not be protons and hydroxyl.

Organic anions from the dissociation of humic and fulvic acids. Deprotonated carboxyl groups (*e.g.*, $RCOO^-$).