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Industrial Clays Case Study

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<i>Industrial Clays</i>	2
Kaolin	2
Bentonite	5
Palygorskite - Sepiolite	7

Industrial Clays

Kaolin

Kaolin is a soft, white plastic clay consisting mainly of the mineral kaolinite which is a hydrated aluminum silicate $Al_2 Si_2 O_5 (OH)_4$. It is formed by the alteration of feldspar and muscovite. Kaolin deposits are classified as either primary or secondary. Primary kaolins result from residual weathering or hydrothermal alteration and secondary kaolins are sedimentary in origin. Kaolin is an important industrial mineral, which is used in many industrial applications.

Three kaolin production areas dominate the world markets. These are the sedimentary kaolins in Georgia and South Carolina in the United States; the primary kaolins in the Cornwall area of Southwestern England; and the sedimentary kaolins in the lower Amazon basin in Brazil. These kaolins are of high quality in that they have high brightness and relatively low viscosity at high solids concentration (70%). This means that they can be used for paper coating which is the largest application. Other kaolin deposits, which are regionally important, are located in Australia, Argentina, Czech Republic, China, France, Germany, Indonesia, Iran, Mexico, South Korea, Spain, Turkey, and Ukraine. The physical and chemical properties of kaolin has led to its 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.

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%

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

The major world production in tons is as follows: *

USA	8,870,000	MEXICO	490,000
UK	2,300,000	TURKEY	450,000
Brazil	1,700,000	Spain	400,000
Czech republic	1,049,225 (beneficiated)	Argentina	300,000
Czech republic	5,183,000 (raw)	France	300,000
Iran	900,000	Ukraine	300,000
Germany	700,000	Indonesia	250,000
South korea	670,000	Australia	250,000
China	600,000		

*USGS

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

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.

A major value added product produced by the US kaolin industry is calcined kaolin. 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% TiO₂ in paper coating and filling formulations and also in paint formulations without any significant loss in brightness and opacity. Calcined kaolins are 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 (Al₂Si₂O₅) and SiO₂. 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 is an excellent ceramic raw material and is a necessary ingredient in most white ware and sanitary ware applications because it fires white, is plastic, and has good shrinkage and strength properties.

Over 400,000,000 tons of kaolin has been produced from the deposits in Georgia in the USA. Within the next few years the kaolin production in Georgia will be downsized because of the depletion of reserves. The same is true in England but fortunately there are several hundred million tons of high quality kaolin reserves in Brazil, which will become the world production leader in this century.

Critical issues involved in the mining of kaolin varies with the geographic location of the deposits. Major issues in mining the kaolin in Southwestern England are the disposal of the waste material produced in the processing and the disposal of the 80 to 85% of the host rock from which the kaolin is extracted by hydraulic methods. Another problem is the depth of the ore body as mining progresses because these deposits are funnel shaped and become smaller in circumference with depth. Another issue with the English kaolins is their relatively high viscosity in comparison with the Georgia and Brazil sedimentary kaolins. As the paper coating machines run faster in order to produce more coated paper to improve productivity, the viscosity becomes more critical.

In Georgia, most of the low overburden kaolins have been mined. This means that as the overburden ratio increases, the cost of mining increases. Another critical issue is that the availability of high quality, low viscosity kaolins are rapidly disappearing so the industry must devise methods to improve the viscosity in order to use marginal reserves of high viscosity kaolins.

In Brazil, a severe problem is the heavy rains, which flood the mines during the rainy season. Also the remoteness of the mines from population centers creates difficulties in labor and management turnover.

Kaolin is an environmentally safe material with no adverse health problems as long as the fine particle dust is controlled. The open pit mines in Georgia and Brazil are reclaimed, so that the land can be used for agriculture, forestry, or recreational projects.

Kaolin particularly that which is used for coating paper is traded in a global market. Kaolin which is used for ceramics and fillers is usually restricted to regional or local markets. The paper coating kaolins are produced by large global companies but the ceramic and filler grade kaolins are produced by smaller companies who employ local marginalized people who are dependent on them for their livelihood. Kaolins are currently and in the future a large contributor to the economy of developing countries such as Brazil, Argentina, Tanzania, Indonesia, Suriname, and India. Paper is a very necessary commodity and as a country develops, more kaolin will be needed to improve the printability of the paper particularly for color printing. China is a good example where 15 years ago there was no paper produced in China that could be used for color printing. Today China is the 3rd largest producer of paper and large quantities of kaolin are imported to produce high quality coated paper for internal consumption.

Bentonite

Bentonite is a smectite clay formed from the alteration of siliceous, glass-rich volcanic rocks such as tuffs and ash deposits. 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. The industrial bentonites are generally either the sodium or calcium variety. Bentonites are important and essential in a wide range of markets including drilling mud, foundry sand binding, iron ore pelletizing, pet waste absorbents, and civil engineering uses such as waterproofing and sealing. Bentonites have excellent rheological and absorbent properties. Sodium bentonite has a high swelling capacity, and forms gel-like masses when added to water. Calcium bentonite has a much lower swelling capacity than sodium bentonite but this can be improved by treatment with soda ash to produce sodium-exchanged bentonite. Normally these sodium exchanged bentonites do not have as high swelling capacity as the natural sodium bentonites.

The largest sodium bentonite deposits are located in the Western United States in Wyoming, Montana, and South Dakota. These sodium bentonites are also called Western or Wyoming bentonite which means a high swelling sodium bentonite. Other smaller sodium bentonite deposits occur in Argentina, Canada, China, Greece, Georgia Republic, India, Morocco, South Africa, and Spain. Calcium bentonite deposits are much more common than sodium bentonite ones. In the United States calcium bentonites occur in Georgia, Alabama, Mississippi, Texas, Illinois, and Missouri. Elsewhere calcium bentonites occur in England, Germany, Spain, Italy, Greece, Turkey, Georgia Republic, Czech Republic, Ukraine, Japan, Algeria, Morocco, South Africa, China, India, Japan, Argentina, and Brazil.

The world production of all types of bentonite was estimated by the USGS to be 10,226,119 tons, in 2001. The major production by country is shown as follows:

USA	4,080,000	JAPAN	415,115
GREECE	1,150,000	UKRAINE	300,000
CIS	700,000	BRAZIL	275,000
TURKEY	636,273	MEXICO	269,731
ITALY	600,000	OTHERS	1,300,000
GERMANY	500,000		

Bentonite has several important physical and chemical properties which make it important in a wide range of markets. In addition to its rheological and absorbent properties, bentonite has excellent plasticity and lubricity, high dry bonding strength, high shear and compressive strength, good impermeability and low compressibility. In recent years the largest market for bentonite has been absorbent pet litters. Traditional pet litter is a granular calcium bentonite but in the past 10 years a scoopable product line has been introduced. By adding sodium bentonite to the granular calcium bentonite the litter clumps when wetted and these hard clumps can be easily removed from the litter box. Currently the largest market for sodium bentonite is scoopable pet litter, which in the US amounts to over one million tons.

White bentonites are rare and are usually a calcium variety. About 150,000 tons of white bentonite is consumed annually for niche markets including detergents, ceramics, paper, cosmetics, paint, and wine clarification. White bentonite occurrences are in Texas and Nevada in the US, Greece, Turkey, Italy, Morocco, and Argentina.

The FOB price of most bentonites is very low ranging from \$35 to \$110 per ton. 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.

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.

Bentonites are environmentally safe providing dust abatement procedures are used in the processing and handling. In the past, some workers in the bentonite plants have been afflicted with silicosis. However, in recent years, dust abatement, annual lung x-rays, and mandatory dust masks have largely alleviated this problem. The mines are easily reclaimed so that the land is put back into its original form. A good example is in Germany where the overburden is stacked so that it goes back into the pit in the reverse order of its removal so that the top soil is put in place and crops can immediately be grown.

Sodium bentonite produced in the Western United States is used world wide as a drilling mud in oil wells. Calcium bentonite, on the other hand, is produced in many countries including developing countries where it is used in foundries, as an acid activated bleaching earth used in refining edible oils, as a binder for animal feed, and as a sealant for irrigation ditches and earthen dams. There are only two large multinational companies in the bentonite business. In many small and developing countries, local bentonite producers provide the livelihood for many marginalized workers. In India and Malaysia bentonite producers are a major contributor to the economic welfare of their communities. Bentonites are excellent sealants and absorbents so are excellent barriers for landfills and toxic waste repositories.

Palygorskite - Sepiolite

Palygorskite is a term that is synonymous with attapulgite. The term attapulgite is largely used industrially even though the international mineral nomenclature committee ruled that palygorskite was first used and therefore is the preferred term. Both palygorskite and sepiolite are hydrated magnesium aluminum silicates. Sepiolite has a higher magnesium content than palygorskite and has a slightly larger unit cell size. Both of these minerals are thin elongate chain type structures. 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 makes them uniquely applicable for many uses. The term fuller=s earth is a term used for highly absorbent and natural bleaching clays. Thus the term includes both attapulgite and calcium montmorillonites, so there is a definite overlap in the use of the term fuller=s earth, with both attapulgite and calcium bentonite.

Palygorskite (attapulgite) and sepiolite deposits are relatively rare in comparison with the other industrial clays. Major deposits of palygorskite occur in North Florida B South Georgia in the US, Senegal, Ukraine, Spain, Turkey, and China. Sepiolite deposits occur in Spain, Turkey, and Somalia. The world production of palygorskite (attapulgite) is estimated by the USGS to be about 1,000,000 tons and sepiolite about 400,000 tons. By far the largest producer of attapulgite is the United States, which in 2000 produced 725,000 tons, or 76% of the world=s production. Spain is the largest producer of sepiolite and accounted for about 95% of the world=s annual production. The total world production of all fuller=s

earth clays including attapulgite, sepiolite, and calcium montmorillonite is estimated to be in excess of 3.3 million tons.

The major uses of palygorskite and sepiolite, are in drilling muds, paints, liquid detergents, adhesives, car polish, flexiographic inks, cosmetics, floor absorbents, potting mixes, oil-spill clean up material, carriers for fertilizers, pesticides, or hazardous chemicals, decolorize various mineral, vegetable and animal oils, as a receptor coating on carbonless copy paper, and for pet litter. Because these clays are relatively unaffected by electrolytes their viscosity is retained whereas bentonites flocculate and lose their high viscosity. Both palygorskite and sepiolite are used as a binder for pelletized animal feed. Certain studies have reported increased feed efficiency and improved digestive hygiene. Another use is as an additive in cement where because of its elongate shape and absorbency it strengthens the resulting concrete. The prices per ton range from \$90 to as much as \$800 for very fine highly refined material.

Palygorskite and sepiolite are surface mined in open pits, similar to bentonite. The processing involves crushing, drying, pulverization, classifying, bagging and loading. Palygorskite and sepiolite are both elongate minerals. Palygorskite and sepiolite are both elongate minerals, which have caused some health organizations concern because of the problems with asbestos, which is an elongate mineral. However, numerous tests have shown that neither of these minerals are carcinogens. Again these clays are environmentally safe as long as dust abatement procedures are taken. The open pits are reclaimed back to their original conformation so that crops or trees can be grown and harvested.

Palygorskite and sepiolite, particularly those classified as gel clays, are traded in a global market. Absorbent grades are produced and used in regional and local markets. No large multinational company is involved in the production of these clays. Palygorskite produced in Senegal, Turkey, China, and Somalia contribute a livelihood for many people who are involved in the mining, production, transportation, and marketing of these clays. Palygorskite and sepiolite are excellent absorbents and are essential for use as carriers for fertilizer, insecticides, and pesticides in agricultural applications when blended with bentonite, the material is a superior barrier clay for use in landfills and toxic waste repositories.

Summary Table

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%
Environmental Issues	Dust Abatement and Mine Reclamation	

The industrial clay industries are very important in providing needed employment in many areas. As an example, the kaolin industry in Georgia is a billion dollar industry, the largest mining industry in the state. It provides employment for about five thousand people and is a major contributor to the economy of the counties in which the mines and processing plants are located.

Principal Sources of Authority for data:

Roskill Information Services, Ltd.

US Geological Survey

Industrial Minerals Magazine

Industrial Minerals and Rocks, 6th Edition- Soc. For Mining, Metallurgy, and Exploration