

CLAY SORBENTS: THE MINERALOGY, PROCESSING AND APPLICATIONS

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ABSTRACT

Clay minerals that are used for absorbent and adsorbent applications are most commonly calcium montmorillonite and palygorskite. Calcium bentonite deposits are found in North and South America, Europe, Africa, and Asia in many locations on the above continents. Palygorskite occurrences are in North America, Africa, Europe, and Asia, but are much less common than calcium bentonite deposits. Because of their high surface area and lattice charge, these two clay minerals are good sorbents.

These minerals are mined and are normally dry processed but calcium bentonite is wet processed to produce high quality acid activated product for clarifying oils. These processes will be described.

Each of these two sorbent clays have multiple applications, the largest of which is cat litter. Other major uses are as oil and grease absorbents, carriers for agricultural chemicals, pesticides, and insecticides, and bonding agents for animal feed pellets. Other applications will also be discussed.

KEYWORDS: absorbents, calcium bentonite, hormites, acid activated clays

1. INTRODUCTION

Sorbent clays, in particular, calcium montmorillonite, palygorskite (attapulgitite) and sepiolite have been used in many industrial, personal and medical applications for hundreds of years (Robertson, 1986). The terms palygorskite and attapulgitite are synonymous, but palygorskite is the preferred name although many industrial concerns use the name attapulgitite because it has been used in their quality and sales literature for many decades. Palygorskite and sepiolite are members of the hormite group, a name proposed by Martin-Vivaldi and Robertson (1971).

Calcium montmorillonites are referred to as fuller's earth in Great Britain and the term is used in the United States to describe any clay material that has sorbent and bleaching earth capability. The name fuller's earth came from the use of sorbent clays in the cleansing of wool to remove dirt and lanolin, a process called fulling (Grim, 1962). The term as now used, has no mineralogical or genesis meaning.

As mentioned above, the most common sorbent clays are calcium montmorillonites and hormites. Calcium bentonite deposits are found on most continents and are much more common than hormite deposits, which are relatively rare in comparison. Both of these materials, i.e. calcium montmorillonite and hormite, are most generally dry processed for most uses. However, a wet process is used to make high quality acid-activated bleaching earth products.

Sorbent clays are utilized for a multiplicity of applications because of their structure and physical and chemical properties (Murray, 2003) which will be discussed later in this paper. Calcium bentonite and hormite deposits that are traded internationally and/or regionally are described. Those that are used locally are not discussed although there are many calcium montmorillonite deposits which fit this category.

2. MINERALOGY, OCCURRENCE AND ORIGIN

Mineralogy - Calcium montmorillonite is the dominant mineral present in calcium bentonites with the amount usually of the order of 70 % or higher. Common mineral impurities that may be present in minor quantities are quartz, feldspar, illite, calcite, mica, opal-CT, clinoptilolite and kaolinite. Many of the calcium bentonites were reported to contain cristobalite, but most of these are misidentified and are opal CT (Smith, 1998).

The hormites are comprised mainly of palygorskite and/or sepiolite. Associated minerals that may be present in minor quantities are quartz, smectite, dolomite, calcite and occasionally clinoptilolite. Some deposits also contain diatoms.

2.1. OCCURRENCE AND ORIGIN OF CALCIUM BENTONITES

Important calcium bentonite deposits are located in China, England, Georgia Republic, Germany, Greece, India, Italy, Japan, South Africa and United States.

China - The calcium bentonite deposits in China range in age from Late Jurassic to Tertiary. The more important deposits are sedimentary (Yuan, et al., 1996) and were derived from volcanic ash and tuffs deposited in lacustrine or shallow marine environments. The largest deposits are located in Zhejiang, Hubei, Anhui, Shandong, Sichuan and Luoning Provinces.

England - The most important calcium bentonite (called fuller's earth) is located near Redhill in Surrey, in the London basin. This bentonite is Cretaceous in age and is believed to have formed by the alteration of volcanic ash (Hallam and Selwood, 1968). Another calcium bentonite of Jurassic age is located in Somerset. This deposit is also thought to have been formed by the alteration of volcanic ash.

Georgia Republic - The best known calcium bentonite deposit is in the Askana area. This bentonite was formed by the alteration of andesite - trachyte tuffs of Eocene age (Grim and Guven, 1978). Rateev (1967) believes that the Askana bentonite is hydrothermal. A second important calcium bentonite is the Gumbri deposit of Cretaceous age (Dsotsenidze and Matchabely, 1963). This deposit was formed by submarine alteration of volcanic glass.

Germany - Calcium bentonite deposits near Moosburg and Landshut in Bavaria are important commercial bentonites in the European and world markets. The bentonites are Upper Miocene in age and are relatively pure calcium montmorillonites. These bentonites are found in small basins thought to be ponds or lakes into which acid vitreous tuffs were deposited and altered (Grim and Guven, 1978).

Greece - The largest and best known calcium bentonite is located on the Island of Milos. This bentonite is Pleistocene in age and was formed from pyroclastic flows (Christidis, 2001). Both deuteric and hydrothermal activity were important in the formation of the bentonite.

India - The major bentonite mining area is located in Kutch (Crossley, 2003) and in the Barmer district of Rajasthan (Siddiquie and Bahl, 1965). The deposits in both of these areas are Lower Tertiary in age. Siddiquie and Bahl (1965) suggest that these bentonites formed by the weathering of Precambrian igneous and metamorphic rocks followed by transport and deposition in embayments. There are no relict ash structures in the bentonite nor any Tertiary volcanic activity in the area.

Italy - Important calcium bentonite deposits are located on the Island of Sardinia (Carta et al., 1977). There are two types of deposits on Sardinia, a sedimentary bentonite of Miocene age and a hydrothermally altered trachytic tuff (Annedda, 1956). The sedimentary bentonite is a marine altered volcanic ash.

Japan - Calcium bentonites of Miocene and Pliocene age formed by the alteration of volcanic ash, pumice

and tuff are located in Yamagata, Gumma and Nagano Prefectures on the islands of Honshu and Hokkaido (Sudo and Shimoda, 1978).

South Africa - There are two locations in South Africa where calcium bentonites are mined and processed. These locations are at Plettenberg Bay and Albertinia on the Indian Ocean. These bentonites are Tertiary in age. There are no relict structures in these bentonites nor is there any evidence of volcanic activity in the region (Grim and Guven, 1978). They are sedimentary and are gradational with overlying soft shales.

United States - Several localities in the United States are important producers of calcium bentonite. These are at Cheto, Arizona; Gonzales, Texas; Itawamba and Monroe Counties in Mississippi; Bloomfield, Missouri; Olmstead, Illinois; Middleton, Tennessee; Ripley, Mississippi; Sandy Ridge, Alabama; and Ochlocknee and Meigs, Georgia. Absorbent clays are mined and processed at each of the aforementioned locations.

At Cheto, Arizona, the calcium bentonite is white and is Pliocene in age. A volcanic ash of latitic composition was deposited in depositional traps which were altered to predominantly calcium montmorillonite (Kiersch and Keller, 1955).

At Gonzales, Texas, the calcium bentonites are Tertiary in age. In this locality, volcanic ash was deposited over a large area and subsequently devitrified in both shallow marine and lacustrine environments (Roberson, 1964). The color of these calcium bentonites varies from chocolate brown to olive to white.

The calcium bentonites in Itawamba and Monroe Counties, Mississippi, are Upper Cretaceous in age and are sedimentary in origin. The precursor of these bentonites was a volcanic ash which erupted in Cretaceous time near Jackson, Mississippi (Merrill, 1983). The calcium bentonites located in Bloomfield, Missouri; Olmstead, Illinois; Middleton, Tennessee; Ripley, Mississippi and Sandy Ridge, Alabama are all Paleocene in age. These clays are sedimentary and were deposited in the large Mississippi embayment which covered the area in Paleocene time (Thomas and Murray, 1989).

The absorbent clay at Ochlocknee and Meigs, Georgia, is a mixture of calcium montmorillonite and palygorskite with a ratio of about 60 to 70 % calcium montmorillonite and 30 to 40 % palygorskite. These clays are Middle Miocene in age and are sedimentary (Merkl, 1989).

2.2. OCCURRENCE AND ORIGIN OF HORMITES

Important hormite deposits are located in China, Senegal, Spain, Ukraine and United States. All these deposits are predominantly palygorskite except for the large sepiolite deposit in Spain.

China - Palygorskite is mined and processed in an area in Eastern Anhui Province and Western Jiangsu

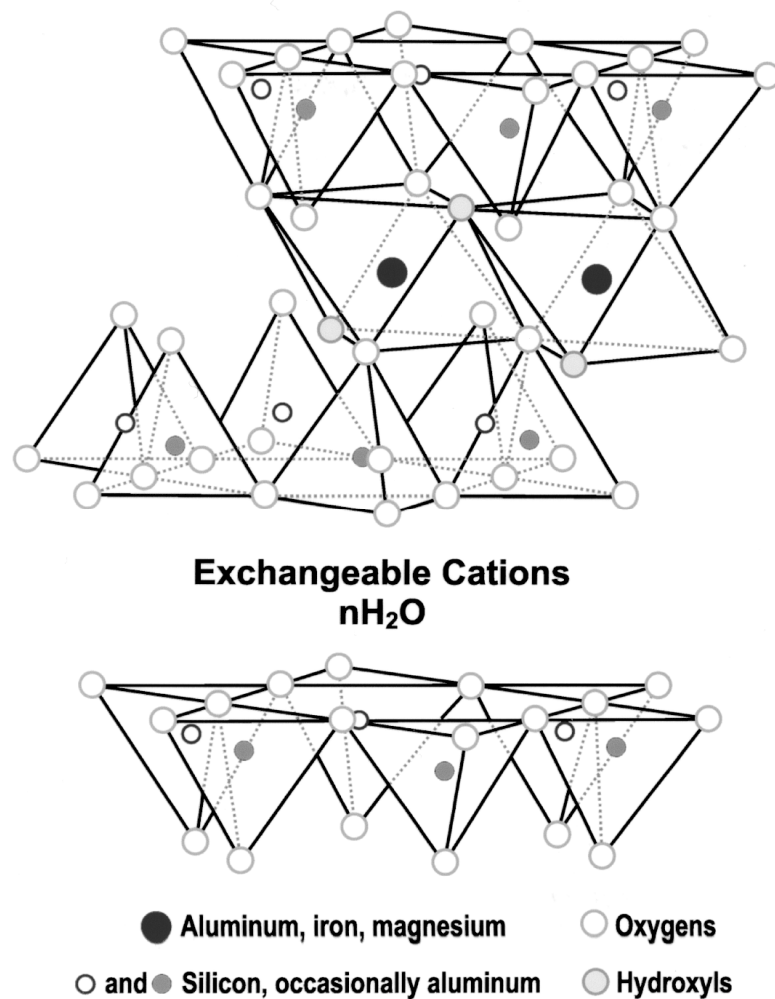


Fig. 1 Structure of calcium montmorillonite

Province about 160 km north of Nanjing. The largest production is from a deposit in Anhui Province, which is Middle Miocene in age as are the deposits in Western Jiangsu Province. These palygorskites are altered basaltic ash which was deposited in lacustrine basins (Zhou and Murray, 2003).

Senegal - Palygorskite is mined near the town of Thies approximately 100 km east of Dakar. The age is Eocene and the deposit is sedimentary in origin (Wirth, 1968). The palygorskite beds extend south-southwest from Thies about 100 km.

Spain - The largest commercial sepiolite deposit in the world is located at Vicalvaro near Madrid. The sepiolite is Tertiary in age and formed in an evaporitic sequence in a lacustrine environment (Huertas et.al., 1971). Other locations in Spain where hormite clays are produced are located near Toledo, Torrejon el Ruhe, Lebija, Almeria, and Maderuelo (Griffiths, 1991).

Ukraine - Palygorskite is mined near Kiev in the Cherkassey district and is lower Miocene in age (Ovcharenko et.al., 1966). The palygorskite is sedimentary and occurs between layers of calcium bentonite.

United States - Large deposits of palygorskite are mined in Northern Florida near Quincy and extend north to the vicinity of Attapulcus, Georgia. These deposits are Miocene in age and were formed in starved lagoons rich in magnesium in which palygorskite was precipitated.

3. STRUCTURE AND PHYSICAL AND CHEMICAL PROPERTIES

Calcium montmorillonite is a 2:1 layer mineral in which an aluminum octahedral sheet is sandwiched between two silica tetrahedral sheets (Fig. 1). There can be considerable substitution in the octahedral

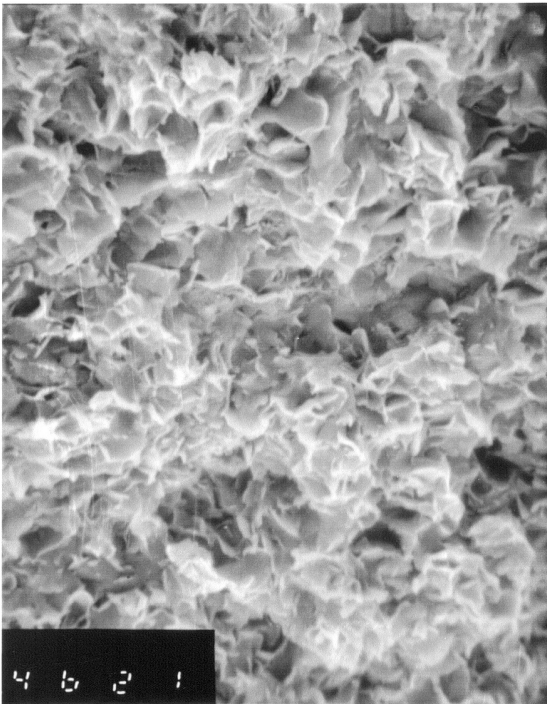


Fig. 2 SEM of calcium montmorillonite

sheet of Fe^{3+} , Fe^{2+} and Mg^{2+} for Al^{3+} which creates a charge deficiency on the layer. Also, there can be some substitution of Al for Si in the tetrahedral sheets, which again creates a charge imbalance. The charge imbalance is balanced by calcium ions adsorbed between the unit layers and on the edges. Table 1 lists the physical characteristics of a calcium bentonite which are related to their absorbency.

Fig. 2 is an electron micrograph of a calcium montmorillonite.

Palygorskite and sepiolite are also 2:1 layer clay minerals, but with a different arrangement of the silica and alumina sheets. Fig. 3 shows the structure of palygorskite. The palygorskite is structurally similar to that of sepiolite which has a slightly larger unit cell. Both minerals consist of double silica tetrahedral chains linked by octahedral oxygen and hydroxyl groups containing aluminum and magnesium ions in a chain-like structure. Fig. 4 shows the elongate nature of palygorskite and sepiolite is quite similar in appearance. Table 2 shows the physical and chemical characteristics of palygorskite and sepiolite (Hormites).

Both palygorskite and sepiolite have 2:1 inverted structures, i.e. the apices of the silica tetrahedrons are regularly inverted along the a-axis. This results in parallel holes or channels throughout the structure, which gives these minerals a high surface area. The water in these channels is called zeolitic water and is expelled at a lower temperature than the dehydroxylation temperature.

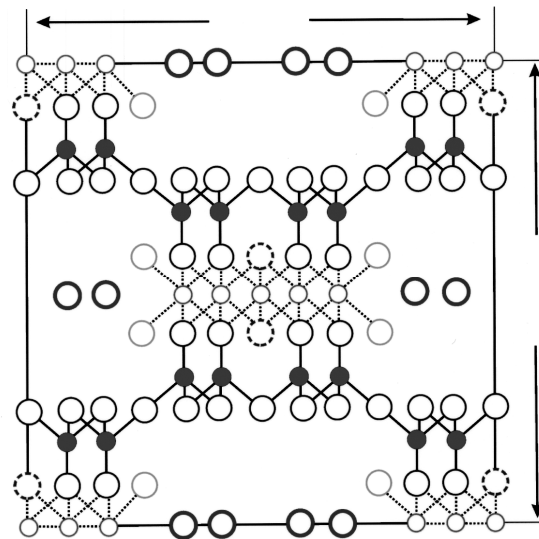


Fig. 3 Structure of palygorskite

Table 1 Characteristics of calcium montmorillonite absorbents

2:1 layer clay minerals
Considerable lattice substitution
High layer charge
Medium cation exchange capacity (40 to 70 meq/100 g)
Fine particle size
High surface area (50 to 80 m ² /g)
High sorptive capacity

Table 2 Characteristics of hormites

2:1 layer clay
Elongate thin particles
Some lattice substitutions
Fine particle size
Moderate layer charge
Medium base exchange capacity (30 to 40 meq/100 g)
High surface area (150 to 300 m ² /g)
High sorptive capacity

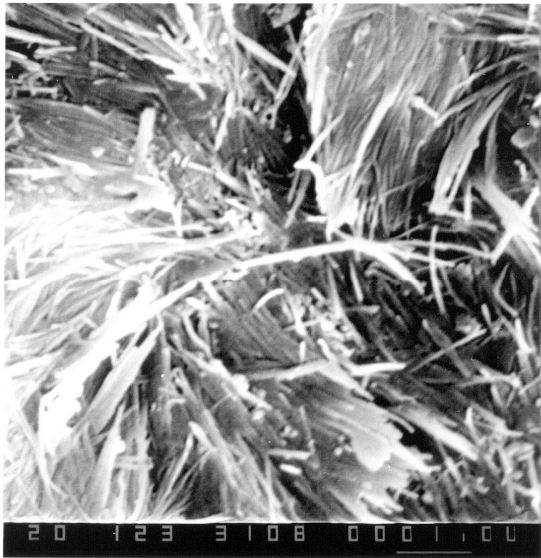


Fig. 4 SEM of palygorskite

4. PROCESSING SORPTIVE CLAYS

Calcium bentonites are dry processed for most applications. The dry process is shown in Fig. 5. The bentonite is mined and transported into crude clay storage sheds in order to maintain adequate inventory in case of inclement weather or equipment breakdowns at the mine. From the storage shed, the bentonite is fed into a hopper, which feeds a shredder or crusher to reduce the size of the crude lumps to about 2 cm. These lumps are conveyed to a rotary dryer. The crude clay lumps are dried to a moisture of 6 to 8 %. From the dryer, the dried clay can either be fed into a roll crusher or to a pulverizer. The roll crusher cracks the dried lumps into a granular form

Typical flow sheet for dry processing Ca-Montmorillonite

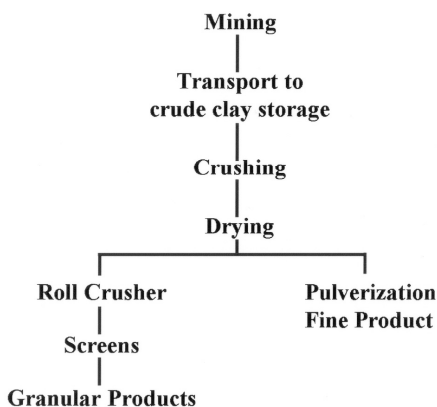


Fig. 5 Dry process flow sheet for calcium bentonite

and these granules are screened to produce 16/30; 30/60; or 60/90 sizes which means that in the case of the 16/30 mesh size, the granules pass through the 16 mesh screen and are retained on the 30 mesh screen. The finer granules are sized similarly on the finer screens. From the screens, the granules are ready for packaging or bulk loading or can be fed into a high heat dryer to reduce the moisture to less than 1%.

These granules from the high heat dryer with very low moisture are sized similar to those with the higher moisture. The granules from the high heat dryer have a higher sorptive capacity and are commonly used as carriers for agricultural chemicals and pesticides.

The dried lumps from the rotary dryer can go directly to a pulverizer to produce very fine products usually less than 200 mesh and less than 325 mesh. The finely pulverized bentonite is bagged and shipped.

Acid activated bleaching earth can be processed dry (Fig. 6) or wet (Fig. 7). The acid activated bentonite produced using a dry process is crushed, dried, pulverized and mixed with sulfuric acid. The mixing process must produce an intimate mixture of the clay particles and the acid. Usually about 4% sulfuric acid is mixed into the pulverized clay. This product can be used to bleach certain types of oils where the color of the resulting product is not critical.

The wet process is used to make high quality bleaching earth. The first step in this process as shown in Fig. 7 is to blunge the clay usually at about 15 to 20 percent solids to disperse the bentonite and release the grit sized particles such as quartz, which can then be removed by screening or by a degritting centrifuge or

Dry Process Acid Activation

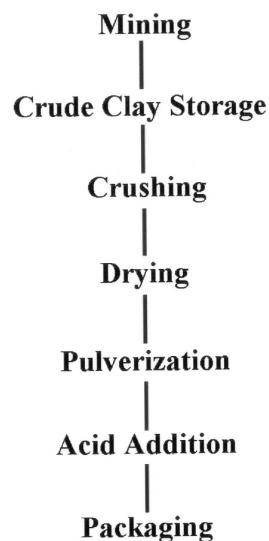


Fig. 6 Dry process for activated bleaching earth

Acid Activation Flow Sheet

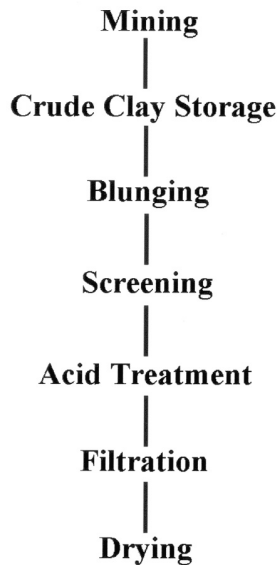


Fig. 7 Wet process for activated bleaching earth

a hydrocyclone. The degrittied clay slurry is then pumped into acid resistant tanks where sulfuric and/or hydrochloric acid are added. The amount of acid is determined from tests by the quality control laboratory to maximize the activity of the clay. The acidified bentonite slurry is heated to a temperature of about 60° C to accelerate the conversion of the calcium bentonite to a hydrogen bentonite. The heated slurry generally remains in the tank for about an hour or less. It is important that the calcium montmorillonite structure is maintained in order to provide an active hydrogenated surface. The heated slurry is then pumped to filter presses that produce a solid cake which is then dried and pulverized. Because of the finer particle size and the acidity of the surface of the clay, this product is superior in clarifying edible oils.

Hormites (palygorskite and sepiolite) are dry processed as shown in Fig. 8. The mined clay is transported to a crude clay storage shed. From the storage shed, the crude clay is crushed and either fed into an extruder or directly into a rotary dryer. The extruder breaks up the bundles of hormite elongate particles which improve the viscosity and absorbent properties. In some cases, MgO is added in the pugger which may result in improved properties. The crushed and/or the extruded clay is fed into rotary dryers, which dry the clay to a moisture content of around 6% or to high heat dryer to reduce the moisture to less than 0.5%. The high heat dryer drives the zeolitic water from the channels in the structure which increases the absorbency of the clay. From the dryers, the clay goes to roll crushers or to pulverizers

to produce ultra fine products. The clay that goes to the roll crushers is screened to produce coarse granular products and medium fine granular products. The pulverizers produce fine products ranging from minus 200 mesh, minus 325 mesh, and by air classifiers ultra fine products less than 10 microns can be separated.

5. APPLICATIONS

The processed calcium bentonite and hormite are used for a large number of applications which are shown in Table 3. The most important use of sorbent clay is for cat litter. The total world market for cat litter is estimated to be about 3,500,000 tons annually.

Other uses include products for absorbing oil and grease spills. Commonly, a granular product is spread on the floor in factories and service stations to absorb the oil. Some sorbent clays will absorb water up to 100% of their weight, thus making it a good anti-caking agent to absorb water vapor, and as a desiccant.

Another large use of these absorbent clays is as carriers for agricultural chemicals, liquid fertilizer and pesticides. The chemical is absorbed on the clay and the treated granules are placed in the ground with the grain seeds such as corn and soybeans.

Table 3 Sorbent Applications of Calcium Bentonites and Hormites

Cat box filler	Desiccants
Agricultural carriers	Bleaching oils and fats
Industrial floor absorbents	Dyehouse effluents
Animal feed bondants	Pharmaceuticals
Anti-caking agents	Terpolymer rubber compositions
De-inking paper	Heavy metal absorption

Animal feed pellets are mixed with absorbent clay to form pellets. The clay is more than just a binder because it absorbs bacteria and deleterious enzymes from the animals digestive tract.

Another growing use is as absorbent liners in landfills and toxic waste dumps. The clay absorbs heavy metals and organic compounds, thus preventing the waste from contaminating ground water and surface water.

Another use is to absorb dyehouse effluents to remove the color bodies, thus clarifying the water.

Acid activated bleaching earths are used to refine and clarify edible oils and fats. This use constitutes about 75% of the market for acid activated bleaching earths. The oils and fats that are refined using acid activated clays are palm oil, soybean oil, corn oil, rapeseed oil, sunflower oil, linseed oil, castor oil and tallow and lard.

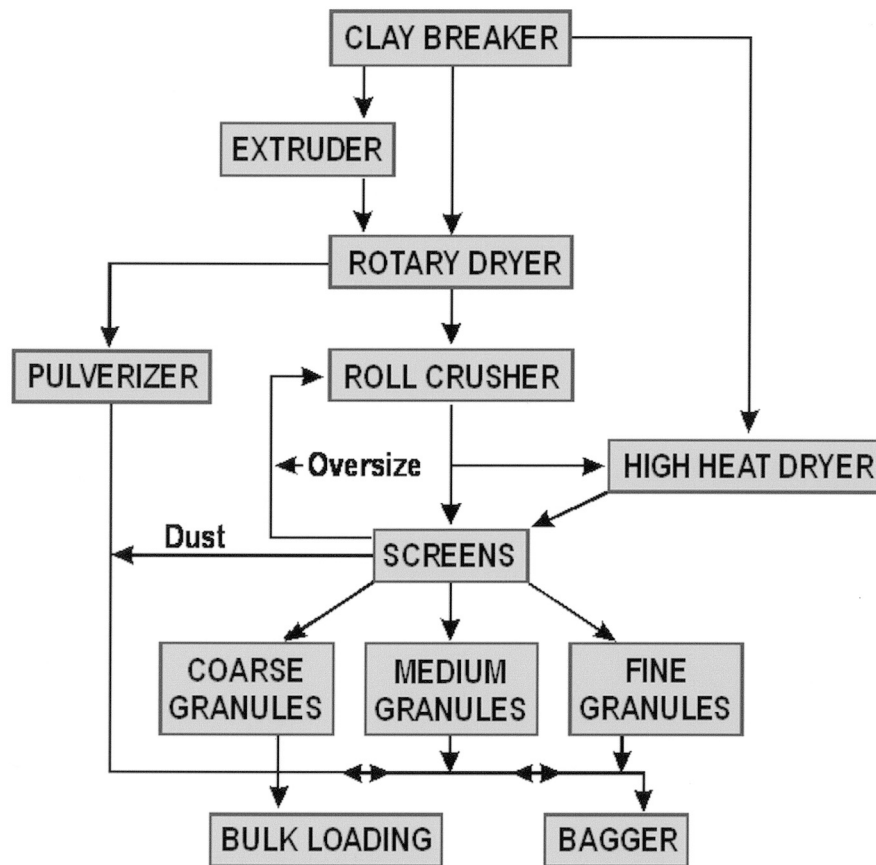


Fig. 8 Dry process flow sheet for hormites

Some sorbent bentonites are used medicinally to absorb bacteria and acids from the stomach and intestines.

6. SUMMARY

Calcium bentonites and hormites are excellent sorptive clays because of their fine particle size, large surface area, moderate to high surface charge, and moderate base exchange capacity. Hormite deposits are rare in their occurrence compared to calcium bentonite. Most of these active sorbent clays are of Cretaceous age or younger. The majority of these clays are dry processed except for high quality bleaching earth which is produced using a wet process. The major use by far is for cat litter with an annual tonnage of more than 3,500,000 tons.

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