

BENTONITE PROCESSING

OPLEMENJIVANJE BENTONITA

ANAMARIJA KUTLIĆ, GORDAN BEDEKOVIĆ, IVAN SOBOTA

*University of Zagreb, Faculty of Mining, Geology, and Petroleum Engineering,
Pierottijeva 6, HR-10000 Zagreb, Croatia*

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Sažetak

Bentonit ima vrlo široku primjenu. Između ostalog, primjenjuje se za izradu nepropusne zaštite u podzemnim odlagalištima visoko radioaktivnog otpada u granitima zbog njegovog svojstva absorpcije vlage. U ovom radu opisuju se karakteristike i oplemenjivanje bentonita.

Abstract

Bentonite has wide variety of uses. Special use of bentonite, where its absorbing properties are employed to provide water-tight sealing is for an underground repository in granites. In this paper, bentonite processing and beneficiation are described.

1. Introduction

Bentonite is naturally occurring industrial rock, characterized by the property of absorbing water and by capacity for base exchange; both properties are significantly greater than that of plastic clays and kaolin; in certain bentonites water absorption is accompanied by a considerable increase in volume and formation of gelatinous mass (Johnstone and Johnstone, 1961).

Bentonite is processed to give sodium and calcium montmorillonite, activated clays and organo-clays all of which have different properties that can be applied in wide range of uses and application. Foundry, pelletizing, construction – civil engineering, environmental markets, drilling, oils and food markets, agriculture, pharmacy, cosmetic and medical markets, detergents, paints, dyes and polishes, cat litter, paper, ceramics, catalyst are uses and applications reported by European Bentonite Association.

Special use of bentonite, where its absorbing properties are employed to provide water-tight sealing is for an underground repository in granites (Chegbeleh et al., 2008). In repository, compacted bentonite is used in buffer zone which is designed for containment of radioactive materials over long time period, as protection against minor rock displacements, impermeable barrier to the mass transport by ground water, protection of chemical buffering

and retardation capacity, conduction of heat from the radioactive canister to the surrounding rock. In mixtures with other materials, bentonite is used as backfill that is low in permeability and its purpose is to maintain mechanical stability of underground constructions (tunnel, buffer).

Aim of this paper is to describe the bentonite beneficiation process.

2. Bentonite

Bentonite is term that was first used to designate particular, highly colloidal, plastic clay found near Fort Benton in the Cretaceous beds of Wyoming, USA, which possesses unique characteristic of swelling to several times its original volume when placed in water and that forms thixotropic gels with water even with small content of bentonite (Grimm, 1953). Later the term is used to describe plastic clays, generated by alteration of volcanic tuff and ash, with dominant content of smectite minerals, usually montmorillonite, named after the deposits in Montmorillon, France (IMA Europe, 2011). Smectite mineral are individual crystallites, majority of which are smaller than 0.002 mm.

Two types of bentonite are generally identified. The first group has extensive water absorption properties, accompanied by swelling and ability to remain suspended in water dispersion for long periods of time. The se-

cond group are bentonites which do not show swelling properties to any extent when wetted, and do not remain suspended in thin water dispersions (Johnstone and Johnstone, 1961). The swelling type or sodium bentonite (Na bentonite) has a single water layer particles containing Na^+ as an exchangeable ion. The non-swelling or calcium bentonite has double water layer particles with Ca^{2+} as the exchangeable ion. Those ions are sometimes found exchanged by Mg^{2+} or Fe^{2+} . In the trade, swelling type, the sodium bentonite is termed as bentonite, and the non-swelling type as fuller's earth (Sinha, 1986).

2.1. Properties

Montmorillonite group of clays have great power to absorb moisture, especially the sodium bentonite. Raw ore may contain as much as 40 percent moisture, which is climate depending. For example raw ore mined in India (Rajasthan and Gujarat) have only 10-12 percent moisture content. Due to high water content, mined ore may not show the swelling properties until dried to 5% water content (Sinha, 1986). Release of moisture causes loss of volume and mass that must be taken into account in plant design stage.

Dry bentonites have color range from cream to olive green. Specific gravity of dry bentonites is between 2.4 and 2.8 (Johnstone and Johnstone, 1961).

In water dispersions, bentonites tend to rapidly break down into very small particles. Sodium bentonite from Wyoming gives 60-65% particles smaller than $0.1\mu\text{m}$, about 90% particles are finer than $0.5\mu\text{m}$ and about 97% will pass a $44\mu\text{m}$ sieve. Calcium bentonites are also dispersed in water but particles are coarser than those of the swelling bentonites. (Johnstone and Johnstone, 1961).

Chemical composition of bentonite and fuller's earth is rarely required for industry purposes, usually the physical properties are the most critical. However, in nature chemical composition of bentonite shows considerable variations (SiO_2 is found to vary in range 45-65%, Al_2O_3 17-25%, Fe_2O_3 up to 12%). Chemical analysis is good indicator of quality. In Table 1 typical analysis of bentonite is shown. It is found that clay turns towards non-swelling if CaO content tends to 1% or more, or if MgO content in form of exchangeable ions is above 2.5%. General rule may be applied: if $\text{Na}_2\text{O}/\text{CaO}$ is more than 4, bentonite is regarded to be of excellent quality; if $\text{Na}_2\text{O}/\text{CaO}$ is 2-3, bentonite is of good quality, and for ratio values 1-2 bentonite is of tolerable quality requiring further processing (Sinha 1986). Chemical analysis however cannot replace physical tests for determination of the commercial quality.

Table 1. Chemical composition of commercial bentonites (Johnstone and Johnstone, 1961)

Tablica 1. Kemijski sastav komercijalnog bentonita (Johnstone and Johnstone, 1961)

Chemical composition in %			
	Wyoming "Volclay"	Panther Creek Mississippi	Ponza, Italy
Silica, SiO_2	64.32	64.00	67.42
Alumina, Al_2O_3	20.74	17.10	15.83
Ferric oxide, Fe_2O_3	3.03	} 4.70 {	0.88
Ferous oxide, FeO	0.46		-
Titanium dioxide, TiO_2	0.14	1.50	-
Lime, CaO	0.50	3.80	2.64
Magnesia, MgO	2.30	0.50	1.09
Potash, K_2O	0.39	0.20	} 1.09
Soda, Na_2O	2.59	-	
Phosphoric anhydride, P_2O_5	0.01	-	-
Sulfuric anhydride, SO_3	0.35	0.20	0.01
Other minor constituents	0.01	8.00	-
Combined water	5.14	64.00	10.88

2.1. Impurities

In all natural bentonites small fragments of other minerals (feldspar, calcium carbonate, gypsum, quartz, etc.) are found. These fragments are termed as "grit", and may constitute 5-10% of prepared commercial bentonites. Gritless bentonites, termed "dust" grades, are produced for certain purposes. (Johnstone and Johnstone, 1961).

2.2. Commercial types of bentonite

European Bentonite Association (EUBA) qualitatively distincts five types of bentonite: calcium bentonite, activated bentonite, natural sodium bentonite, organophilic bentonite and acid activated bentonite.

Calcium-Bentonite or non-activated bentonite is type that is predominantly occupied by Ca^{2+} or Mg^{2+} -ions in the intermediate layers.

Activated Bentonite has initial composition of Ca^{2+} -ions in the intermediate layer replaced with Na^+ -ions in a technical process known as alkali-activation.

Natural Sodium-Bentonite is usually Wyoming-Bentonite, but it is found in other locations also, and is predominantly occupied by Na^{2+} -ions in the intermediate layers. Ca^{2+} or Mg^{2+} -ions can also occur commonly in Na-bentonite in varying concentrations.

Organophilic Bentonite or organoclays have cations in the intermediate layers replaced by polar organic molecules (e.g. alkylammoniumions). They are hydrophobic and can swell in organic solvents.

Acid Activated Bentonite is bentonite whose structure has been partially dissolved by treatment with acids. Depending on degree of activation, original Ca^{2+} , Mg^{2+} , and Na^+ cations are mostly removed, and part of Al, Fe, Mg, Si from the lattice are dissolved. Acid activated bentonite exhibits high surface area $> 200 \text{ m}^2/\text{g}$ and large micropore volume what makes it excellent absorbent.

3. Bentonite processing

Bentonite deposits are usually exploited by quarrying. Extracted bentonite is distinctly solid, even with a high moisture content of approximately 30%. The material is initially crushed or sliced, and, if necessary, activated by addition of soda ash (Na_2CO_3). Bentonite is subsequently dried (air and/or forced drying) to reach the required moisture content. EUBA provides information of moisture content of 15% in dried bentonite, Wyoming Mining Association (WMA) in range 5-20%, and Chinese manufacturer and exporter of processing equipment (SBM Group) in range 6-12%.

In relation to the final application, bentonite is either sieved (granular form) or milled (into powder and superfine powder form). For special applications, bentonite is purified by removing the associated gangue minerals, or treated with acids to produce acid activated bentonite (bleaching earths), or treated with organics to produce organoclays (EUBA). Figures 1-2 show process flow diagram for bentonite processing.

SME Mineral Processing Handbook describes simple processing method. Bentonite is processed first by drying in the rotary kilns to moisture content 5-8%, and then grounded in high speed roller mills followed by classification into the size grades using cyclones and screens (Weis, 1985).

Ring roller mills are size reduction machines embodying functions of size reduction, drying, conveying and beneficiation. Feed size 50 mm is grinded to various size products as fine as 0.037 mm, or to granulation 3.36 mm containing minimum of fines. Wet fed bentonite, moisture content 15-32%, is fluid bed dried to 7-11% of moisture content. Fuller's earth of moisture content 47% is fluid bed dried to 30-35% moisture. Negative pressure air system results in dust free conveying. Liberation and removal of foreign materials such as silica via auxiliary bottom discharge is achieved simultaneously with grinding.

The most important property of the montmorillonite – to regain interlayer water and to expand – is lost if dried (heated) above the certain temperature which are: 105-125°C; 300-390°C; and 390-490°C for Li montmorillonite, H or Ca montmorillonite, and Na montmorillonite, respectively (Grim, 1953). For many sodium bentonites drying temperatures up to 205°C are safe and bentonite may be dried and wetted any number of times repeatedly without losing swelling (colloidal) properties (Johnstone and Johnstone, 1961).

Experience in drying the bentonite commercially has shown that, regaining of interlayer water is difficult in practice if the last trace of interlayer water is removed, but as long as some water remains between the layers, swelling is generally relatively easy (Grim, 1953).

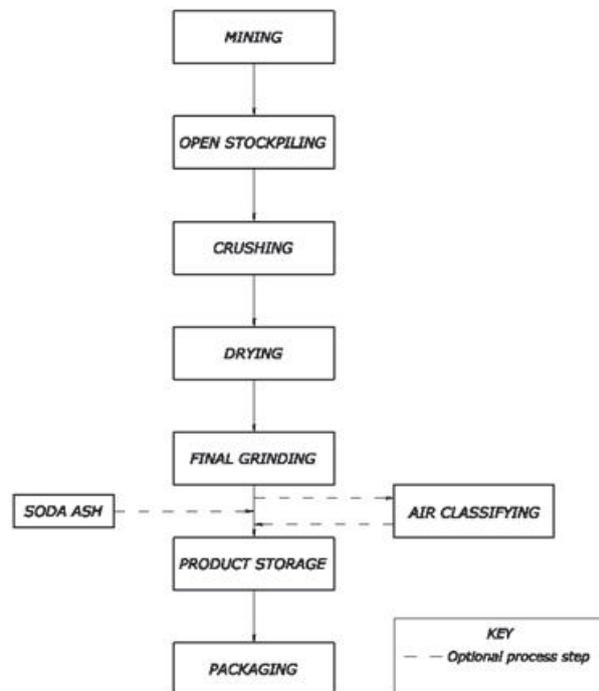


Figure 1. Process flow diagram for bentonite processing (EPA, 2005)
Slika 1. Tehnološka shema oplemenjivanja bentonita (EPA, 2005)

4. Discussion

Processing of bentonite is relatively simple, however, due to its high affinity to absorb moisture; special attention is required in order to select appropriate size reduction device. If the raw bentonite contains significant content of moisture, primary size reduction in crusher that employs impact as the main mechanism of comminution may not be effective. Usually for the primary crushing of wet and sticky material good choice are roller crushers that have specially designed toothed rollers that tear large blocks of clay in small pieces for further processing. But also jaw crusher and cone crusher may be applied.

Next steps in processing of bentonite are drying in rotary kiln and milling. Order of steps depends on the choice of the mill. If the mill is sensitive to the moisture, (i.e. if milling of the wet material is inefficient), crushed material is dried prior to milling. If the chosen mill is of the ring roller mill (Raymond) type or fluid energy mill (Stuivant Micronizer) type that uses air stream or fluidized bed to stimulate drying and conveying, produced material may be of satisfactory wetness for the final product. If not, bentonite may be dried after the milling.

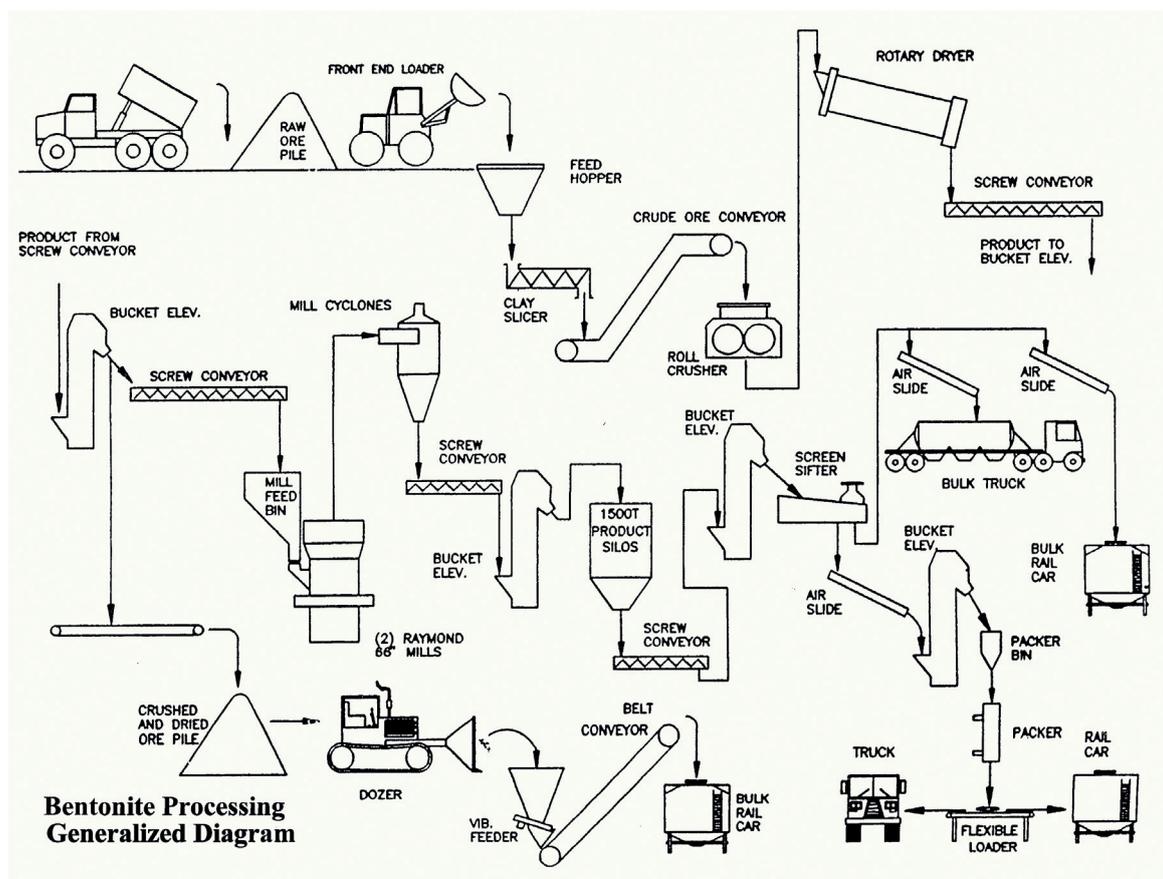


Figure 2. Generalized diagram for bentonite processing (Wyoming Mining Association)
Slika 2. Opća shema oplemenjivanja bentonita prema Wyoming Mining Association

Desirable properties of bentonite are sensitive to high temperatures of drying and to over drying so the optimal dryer needs to satisfy three conditions: temperature of material below 205°C, moving of material in order to promote its dispersed form, and maintain of material for the optimal time in the dryer.

Dried material is sieved, air classified and stored in silo. Small grain class is agglomerated if material of larger grain size required. Agglomeration is achieved by compaction of fines between rollers that have specially designed surface.

5. Conclusion

Processing of bentonite is relatively simple, but some considerations need to be taken into account in plant design stage in relation to water absorption property. This refers especially to the processing of raw ore of high

water content that may cause difficulties in size reduction stage if inappropriate mechanism of comminution is chosen. Drying of bentonite is the second consideration and it may affect the quality of the product because too high temperature of drying can cause the loss of swelling properties; also if all water removed, rehydration may be difficult. The third consideration is related to the storage of dried product.

General procedure for processing bentonite or sodium montmorillonite is given: stockpiling and natural drying; crushing (slicing); drying; milling (grinding) and, if necessary, activation with soda ash; classification; agglomeration. Where local supply of bentonite is required but unavailable, calcium montmorillonite (fuller's earth) may be modified by cation exchange with the soda ash, although exchanged soda bentonite may not have swelling properties as high as the natural sodium bentonite.

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