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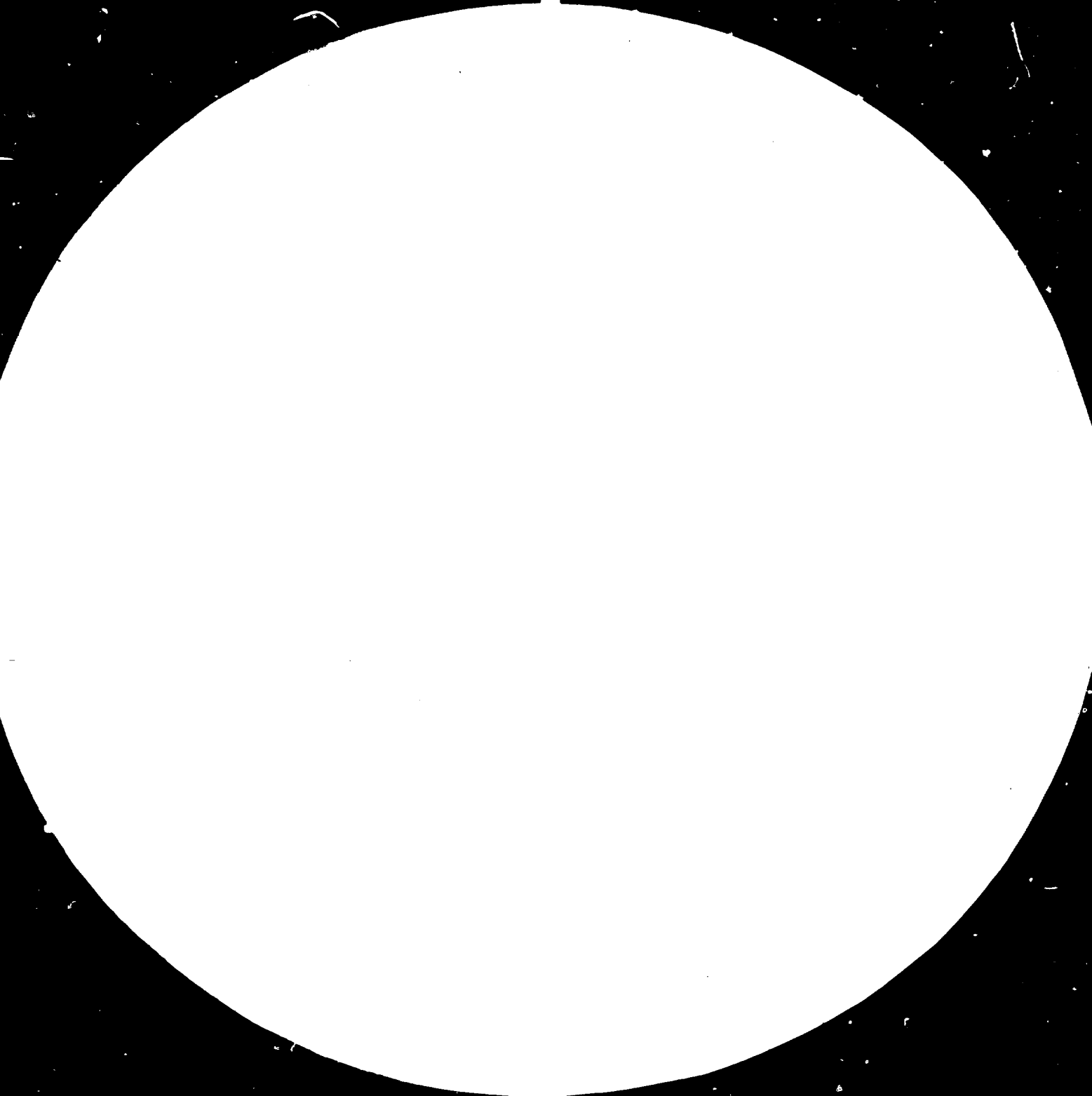
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BENTONITE - BINDING CLAY

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I. Summary

Bentonite is used at present in many industrial branches and its localities may be found in almost all parts of the world.

The aim of this lecture is to set out bentonite characteristics and to show possibilities of bentonite for industrial use. Properties of bentonite are described and methods for their determination are shortly mentioned. A review of world bentonite localities is given together with basic information about them.

Bentonite extraction and its beneficiation is described, too. The extraction and the beneficiation is discussed from the point of view of different mechanization grades.

The industrial use of bentonite is based above all on its adsorbing and rheological properties. The adsorbing properties of bentonite are applied in oil refinery - use of bentonite in natural condition or in activated state is discussed as well.

The application of bentonite in chemical industry is mentioned - bentonite is used either as a carrier of catalysts or as a catalyst itself.

A packing technique exploits the good adsorption ability of bentonite for drying of air and industrial gases.

Further application of bentonite is known in agriculture - bentonite helps improving soil structure or it is used as a carrier of pesticides and insecticides.

A food industry uses bentonite in breweries, sugar and wine production.

Rheological properties of bentonite are exploited chiefly in foundries, for so called "green moulding process". Requirements on bentonite for foundry purposes are given here, too.

The application of bentonite in further industrial branches i.e. in civil engineering, drilling processes and cosmetic and pharmaceutical industries is described, too.

A minor application of bentonite is known in paper industry, paint and varnish industry, textile industry, water treatment and others.

II. Definition and Properties of Bentonite

Bentonite is a clay rock with a dominant content of mineral montmorillonite. Big specific surface, colloidal properties and an ability to interchange ions are characteristic for bentonite.

Bentonite was found out and used at first in England for cleaning of woolen cloth after fulling and for decolorizing of oils and fats.

New deposits of bentonite were found at the end of 19th century in USA. One of the deposits was near Fort Benton that has given the name to this clay rock.

Bentonites arised from volcanic rocks like basalt, diabas and from volcanic ash. The conversion of these materials into bentonite took place under alkanin conditions. The level of conversion influenced properties of bentonite, content and kind of concomitant substances. Concomitant substances are clay minerals i.e. illite, beidellite, nontronite, kaolinite, further quartz, limestone, organic matters and others.

The most important mineral present in bentonite is montmorillonite. Its formula $Al_2O_3 \cdot 4SiO_2 \cdot H_2O \cdot nNH_2O$ is not absolutely accurate. The ratio of Si to Al may fluctuate.

Silicon in a structure may be substituted by aluminium, aluminium by magnesium or by iron. It results into free valences where further ions may be bonded. The elastic bond between structural units enables substantial swelling, high viscosity and thixotropy of diluted suspensions.

Concomitant substances and possibility of substitution of ions produce a very wide variety of kinds of bentonites not only from different deposits but sometimes from the same one.

Chemical composition of bentonites is variable. The content of individual oxides usually lies between following limits:

Al_2O_3	11 to 22%
SiO_2	48 to 56% (sometimes even more)
Fe_2O_3	0 to 5%
MgO	4 to 9%
CaO	0,8 to 3,5%
H_2O	12 to 24%
K_2O	upto 1%, very rarely upto 5%
Na_2O	upto 6%

Depending on the chemical composition Ca-bentonites, Mg-bentonites and rarely Na-bentonites can be distinguished.

Basic properties of bentonites are strength and impermeability even at a high moisture content, plasticity in a wide moisture range, high viscosity and thixotropy of suspensions and absorption ability.

Identification of bentonite is done on the basis of qualitative and quantitative identification of mineral montmorillonite. For this purpose the following methods are used:

- a) X-ray analysis
- b) differential thermal analysis
- c) quantitative chemical analysis
- d) determination of exchange capacity of ions
- e) determination of optical properties
- f) determination of specific surface
- g) determination of shape and orientation of particles by electron microscopy

X-ray analysis is the most accurate method for the identification of clay minerals at present. It enables relatively accurate quantitative determination of clay minerals. Differential thermal analysis may be used in such a case only if montmorillonite is present in the tested sample in dominant amount among other clay minerals. If this condition is not met, the determination is practically impossible. DTA gives the picture of the character of the sample (endo- and exothermic reaction in dependence on the temperature, etc.)

Quantitative chemical analysis, exchange capacity of ions, determination of specific surface are the methods that help to evaluate the suitability of bentonite for different industrial uses. These methods are combined with the tests suggested and used in individual industrial branches.

III. Main World Localities of Bentonites

Bentonitic rocks are very closely connected with products of volcanic activity. The localities of bentonites are most often of secondary nature with different contents and sorts of concomitant matters.

The world's biggest localities of bentonites occur in the Soviet Union. Reserves of bentonites are estimated to amount milliards of tons. They are spread almost in all areas of the Soviet Union. The thickness of layers differs from 1 to 27 metres, the area of deposits in tens of square kilometres.

Though the reserves are so enormous they are exploited only partly, however the extraction has an increasing tendency.

Bentonites in the Soviet Union are used mainly in drilling process and for refining of mineral oils. Smaller part of bentonites finds their use in foundries as a binder and in another industrial branches.

Chemical composition of Soviet Union bentonites varies in different deposits, the composition of one of the most important deposits in Georgia is as follows:

SiO ₂	56,94%
Al ₂ O ₃ +H ₂ O	15,46%
Fe ₂ O ₃	2,57%
CaO	1,36%

MgO	2,59%
Fe ₂ O	0,14%
K ₂ O	1,06%
H ₂ O	13,46%
L.I.	6,09%

This bentonite, similarly as the bentonites from almost all the other deposits, is a Ca-Mg bentonite.

Bentonites in the USA are found in many places. Deposits of bentonites are almost all of secondary nature with the exception of the deposits from Wyoming and Arkansas which are primarily sedimented. The quality of these deposits is excellent.

The layer thickness of bentonite deposits varies from several centimetres to 4 metres. The colour of bentonites is yellow or red-brown. It changes depending on the depth from light grey upto light green. Concomitant minerals are calcite, quartz and pyrite.

Chemical composition of some American bentonites is given in table No. 1.

Table No. 1

Chemical composition of USA bentonites

Locality	S.I.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O
	%	%	%	%	%	%	%
Wyoming	6,95	64,38	17,20	8,27	1,91	1,91	1,83
Florida	10,00	62,27	11,76	7,43	3,59	1,89	-
Georgia	6,00	72,00	10,76	6,00	3,34	2,65	4,36
Dakota	8,80	55,45	18,58	3,82	3,50	3,46	-

The biggest consumption of American bentonites is in drilling processes followed with foundries, production of bleaching clays and other branches of industry.

In Europe widely known bentonite deposits are in German Federal Republic, Italy, Hungary, Poland, Yugoslavia, Rumania, Austria, Czechoslovakia, Spain and less known deposits are in some other European countries, too.

The most important bentonite localities in German Federal Republic are near Munich. These bentonites are exploited mainly as bleaching clays. The thickness of bentonite layers changes from several centimetres to 2 metres. Sometimes the thickness may be even 3 - 4 metres.

The contents of montmorillonite is 60-90%, silica sand, mica, calcite, dolomite, Feldspar and clay minerals such as illite and kaolinite occur as concomitant minerals.

Average chemical composition is as follows:

SiO ₂	57.5
Al ₂ O ₃	21.25
Fe ₂ O ₃	5.15
MgO	2.15
CaO	4.55
K ₂ +Na ₂ O	1.65
L.I.	8.25

From the chemical analysis it is obvious that they are Ca-Mg bentonites.

The colour of bentonites from these localities is very different i.e. from light yellow to yellow, red-brown upto green, blue and dark purple.

Hungarian bentonites are concentrated into two areas. The bentonite deposits near Hungarian capital Budapest are the product of weathering of volcanic ashes while in the other area the deposits arised from rhyolitic lava as a result of thermal water aggressivity.

Industrial use is in the production of bleaching clays, foundries and in drilling process.

Chemical analyses of Hungarian bentonites show the following composition:

SiO ₂	60 - 72%
Al ₂ O ₃	8 - 20%
Fe ₂ O ₃	1 - 3,5%
CaO	1,5 - 3,5%
MgO	0,5 - 3,0%
L.I.	3 - 10%

In Poland there are several localities of bentonites the most important one being at Radzionkow. Bentonite from this locality contains from 25 - 80% of montmorillonite.

Yugoslavia is a country with relatively rich bentonite deposits. Bentonite is extracted in several localities and exploited for the production of bleaching clays and Na-bentonite.

Ample deposits and production of bentonite exist in Italy. Bentonite is dressed mechanically and chemically. Italy is one of the world exporters of bentonites.

Bentonites have been located in Czechoslovakia at a number of places. The deposits, industrially usable, are in the north-west part of the country.

Chemical composition of bentonite from the locality near Branany shows the following values:

SiO ₂	39 - 47%
Al ₂ O ₃	14 - 22%
Fe ₂ O ₃	13 - 20%
TiO ₂	2,1%
CaO	2,8 - 6,3%
MgO	2,3 - 3,7%
L.I.	11,4 - 14,0%

Average thickness of bentonite layer is 8 metres, maximum thickness reaches as much as 27 metres. Bentonites from this locality are light green to brown green. The content of Fe₂O₃ is relatively high nevertheless the quality is fully suitable for foundry purposes.

Ample deposits occur also in eastern Slovakia where bentonite for foundries and food industry is produced.

Besides Europe bentonites have been located in North Africa in Algeria and Morocco, in South Africa near Johannesburg, further in India, China, Japan, Australia, Egypt and in some other countries.

Bentonite is used today in about thirty fields of the industry and its importance still keeps growing.

As it can be seen from this short review findings

of bentonite clays are extended all over the world.

IV. Extraction and Refining of Bentonites

The method of bentonite extraction depends on geological conditions of a deposit. Bentonites are mainly extracted from open quarries. The extraction of bentonites from shafts is less usual.

Bentonites in some deposits may contain sand and small stones. Removing sand and stones is necessary in such a case. It is done directly in the mining place by means of washing.

Bentonites are extracted by different kind of excavators such as shovel excavator or digging wheel excavator.

The quality of bentonite in the deposit very often varies. It is therefore necessary to guarantee a homogenization of raw material either at the extraction or at the stockyard.

A selective way of bentonite extraction can be used if the quantity of mined bentonite is not too high and/or if the mined bentonite is of a very good quality. The degree of a mechanization of extraction works is not too high in this case. The manual way of extraction may be also used.

The extracted bentonite is transported at the stockyard by lorries or by a system of conveyor belts.

Further beneficiation of bentonites depends on the kind of use. Crushing, drying and milling is used often as a satisfactory way of bentonite beneficiation.

Bentonites are beneficiated by a chemical way such as natrification by soda solution or by percolation with acids.

Bentonite is mechanically processed by pan mills, clay crushers or rolls.

Drying of bentonite is very important part of bentonite beneficiation. There are different kinds of driers, such as drum driers, rotary driers, belt driers. Bentonites can also be dried in the form of suspension in spray driers.

The temperature of the drying medium at the inlet must not exceed 500°C , otherwise a dehydroxylation of the lattice of bentonite could happen. The outlet temperature is not higher than $110 - 120^{\circ}\text{C}$.

The dried product is milled at the required fineness. The milling equipment used for milling of bentonite are hammer mills, rolls and disintegrators or other types when drying and milling is combined in one operation as for example in vibrating mills or attrition mills.

Bentonite dried in spray drier from solution need not be milled. The fineness of dried product is convenient.

A frequent way of the beneficiation of bentonite is natrification. The process of the natrification may take place in a dry or wet way. The natrification in the wet way is preferred because the process of cation exchange is more effective than in the case of dry way. Sodium carbonate is used as a natrification agent. Its advantages are low cost and a considerable reaction rate.

The wet natrification is carried out usually at a temperature range from 40 to 100°C .

The bentonite in the pasty state with sodium carbonate

solution is kept at the above mentioned temperature and kneaded. The wet natrification is rather more expensive than the dry one, nevertheless, the quality of wet natrificated bentonite is substantially increased and its price may be double.

Further, an example of modern plant for the processing of bentonite is given.

The capacity of plant considered is 200.000 tons of milled bentonite per year, out of which 150.000 tons is activated i.e. natrificated bentonite and 50.000 tons non-activated bentonite. The consumption of raw bentonite ranges from 260.000 to 270.000 tons per year, extraction capacity being 300.000 tons of raw bentonite per year.

Bentonite is extracted by hydraulic shovel excavator and transported by lorries to a feeder, which batches the bentonite over conveyor belt to cutter clay crushing rolls. Bentonite partially beneficiated in the cutter clay crushing rolls goes further to the stockyard.

The stockyard is situated very close to the plant. The capacity of the stockyard is 120.000 tons that is sufficient stock for the production.

Raw material is taken out from the stockyard by bucket ladder excavators and by conveyor belts transported for further processing. It is also possible, if necessary, to take out the raw material from different places of the stockyard and to mix it together.

Further processing of bentonite is divided into two production lines. The first line produces non-activated

bentonite and consists of milling equipment i.e. attrition mills. Bentonite is milled and dried at 2 to 8% moisture. The rest on the sieve with openings 0,06 mm must not be higher than 5%. Bentonite beneficiated this way is transported to the bins and filled to the paper bags weighing 40 kg each.

Activated i.e. natrified bentonite is prepared in the second production line. The hot solution of sodium carbonate is used as a natrification agent. The solution is prepared in the blungers, powdered soda is dissolved in water by means of water vapour. The concentration of soda in the solution is 12%, temperature of the solution 80 - 90°C. All tanks and pipelines with the solution are heated.

Raw bentonite determined for the preparation of natrified bentonite goes at first to hammer crusher with rolls, then to box feeders and to the milling equipment, where bentonite is milled to 2 mm grain size and dried from the inlet moisture approximately 30% to the outlet moisture of 15%. The milled and predried bentonite is transported by a system of worm conveyors and by bucket elevators to a blender with two shafts. The solution of soda is added to this blender and simultaneously the water vapour is admitted. Bentonite is kneaded and heated, then pushed through grates to another blender. Hot water is added and bentonite is properly kneaded again. The mass of 80 - 90°C temperature is transported to a worm deairing extruder where it is intensively kneaded and pushed through

a perforated mouth. A cutter placed just after the mouth cuts the mass into pieces of 10 to 15 cm length. The pieces fall to the conveyor belt and are filled to further worm extruder where the last kneading operation takes place.

Bentonite mass has now the temperature from 80 to 90°C, moisture from 33 to 36%. The mass is pushed through the mouth, cut into pieces and by a system of conveyor belts transported for drying.

Natrificated bentonite is dried in belt driers cut into noodles. The dried noodles having the moisture from 8 to 12% are transported by a system of conveyor belts and elevators to the hoppers at the mills. The noodles are milled to the fineness corresponding to the rest on the sieve with the openings 0,06 mm 5% maximum.

An efficient dust exhausting system is installed in the plant. The supposed number of workers is 110, total number of employed people is 135. Out of that there are two shifts at the extraction process and three shifts in the technological process i.e. in natrification, drying and milling processes.

7. Industrial Utilization of Bentonites

Bentonites have found utilization in tens of industrial branches particularly in mineral oil refineries, drilling and drying technology, grey iron foundries, steel foundries, ceramics, chemistry, agriculture, building industry, pharmaceuticals and many others.

The use of bentonite depends on its adsorbing and rheological properties.

Exploitation of adsorbing properties of bentonite will be dealt with first.

1. Using of bentonite in oil refineries

Bentonites are used as a very important agent for refinery of edible, industrial and mineral oils as so called bleaching clays. Bleaching clays have an ability if they are in even small quantity (2 - 3%) added to these oils to adsorb dark colouring substances and phlegmy matters. The oils after adsorption become light and pellucid. Their quality is substantially improved.

Bleaching clays can be divided in two groups:

- a) bleaching clays with good bleaching properties in natural condition only,
- b) bleaching clays activated by reaction of mineral

acids at some types of bentonites, a bleaching activity of these types of clays is often higher than of the unactivated ones.

The determination of suitable clay for bleaching purposes on the base of physical and chemical properties of intended clays is very complicated. There does not exist an exact and uniform criterion applicable for all kinds of bentonites and oils. The best determination of bentonite suitability is empirical testing of ability to decolorize a certain oil.

The bleaching clays belonging to the first group, usable without activation are dressed only mechanically by crushing, drying and milling.

The bleaching clays from the second group must be activated and the activation is usually done by hydrochloric acid or sulphuric acid.

Technology of the activation is following:

The bleaching clay stored for a longer time to improve desintegration is washed into a mud. By sedimentation sand and small stones are removed and the mud is pumped to wooden vessels. The content of vessels is heated by steam. The vessels are provided with paddle wheel-stirrers and acid-proof linings. A certain amount of acid is added to the mud in the

vessel, the whole content is mixed and heated to a boiling point and after that it is left at a standstill for 24 hours. The acidity is checked and if the result is satisfactory the activated mud goes through filter press where it is further washed. The final acidity must be very low. Bleaching clay from filter press is then dried to 5 - 8% of water content and milled.

Finness of milling depends on a sort of oil which is to be processed. For refining of mineral oils bleaching clays with particles under 1,5 mm are used, for other oils the particles of bleaching clay to be used are finer maximum 1% rest on a sieve with 100 op/sq.cm and maximum 12% rest on the sieve with 4.900 op/sq.cm. i.e. particles under 0,6mm and 0,09mm respectively.

For a production of 1 ton of bleaching clay approximately 2 tons of raw clay and 1,3 - 1,5 tons of hydrochlorid acid is needed.

The activation substantially improves bleaching properties, it is supposed that higher activity of bentonite after treatment with acid is caused by enhancing of cation exchange of acid aluminosilicate compound.

The refining of mineral oil and paraffins is done by two different ways so called percolation method and contact method.

The percolation method may be described as filtration at the temperature of 35 - 95°C. It is carried out in a cylindrical vessel where the bleaching clay is placed on the sieve bottom. The refined oil or paraffin flows through by its own gravity. First fractions of refined oils have a better quality while the last ones are of a lower quality.

The contact method is a process in which oils and fine-grained bleaching clay are mixed together and heated upto the temperature of 85 - 110 °C, then cooled down and filtered.

The percolation method is used for high quality oils and it is made with natural bleaching clays.

The oils and paraffins of standard quality are processed by contact method in which activated bentonites are used.

Both processes can be discontinuous or continuous.

Determination of bleaching clay ability to decolorize oil is usually done by comparison of two bleaching clays. The first clay is the tested one with an unknown ability and the other is a standard one. It is to be found out what quantity of bleaching clay is needed to achieve the same decolorizing effect as with the standard one. The colour of oils is measured by a colorimeter.

Decolorizing of edible oils is made by contact method only. The principle of bleaching does not differ too much from the decolorizing of mineral oils. The quantity of bleaching clay needed for proper decolorization varies from 0,3 - 2,0% of clay in relation to the weight of oil.

The activated bleaching clays are mostly used for decolorizing of edible oils. Sometimes a small portion of activated charcoal is added to bleaching clays when a perfect refining of oil is to be reached.

Bleaching clays have substituted chemical decolorizing agents and at present time they are essential in the oil refining processes.

2. Using of bentonite in chemical industry

Bentonites play an important role in chemical processes. They are used either as carriers of catalysts or directly as catalysts.

The bentonites apply mostly in petroleum processing industry. There is a wide range of processes where the bentonites are used but the biggest quantity of bentonites goes to catalytic cracking. Bentonite acts here as a catalyst and the product of this reaction is a high-octane petrol.

A suitability of bentonite for the function of a catalyst carrier is assessed on the basis of chemical analysis (very important is low content of Na_2O , since the Na_2O decreases the activity of the catalyst).

DIA

adsorption capacity

X-ray diffraction

The most reliable determination of suitability is the testing of a catalyst on experimental equipment having similar conditions as in production. This experiment though being very expensive stays for the most dependable one and practically the main criterion for the determination of bentonite suitability.

Requirements on quality of catalyst are very high.

The most important points are:

- a) Catalyst must be of high activity that means the yielding of petrol must be high.
- b) Activity of catalyst is to be kept on constant level - these conditions are reached by periodical addition of fresh catalyst in the quantity of 0,3% per raw material quantity being processed.
- c) Catalyst must be thermally stable - temperature at catalytic craching is 460°C , regeneration of the catalyst requires even 700°C .
- d) Mechanical strength of catalyst is also required - losses of catalyst must not exceed 0,3% per weight of raw material being processed.
- e) Chemical and physical chemical properties of the catalyst must not fluctuate.
- f) A good regeneration ability is required and finally a price of the catalyst should be reasonable.

In the last time bentonite is substituted by kaolin as a craching catalyst. Kaolins have a rather lower catalytic activity but on the other hand lower Fe_2O_3 content in kaolins make them more suitable for processing of crude petroleum with high sulphur content which is now prevailing in the world market.

Another example of the use of bentonite is in the preparation of greases. Greases are used in many machines and equipment working under demanding conditions - high temperatures, high speed, etc. - requiring greases with better properties.

The preparation of greases for extreme conditions is based on properties of hydrophobic bentonite to make a stable gels when mixed with oils.

Bentonite for these purposes must be free from all hard mineral particles and furthermore it is necessary to change a hydrophilic character of bentonite to a hydrophobic one. Hydrophobization of bentonite is made by exchanging of anorganic cations (H^+ , Na^+) for organic ones.

Bentonite greases are prepared on the basis of a bentonite beneficiated in such a way. These greases are known under the name of bentons. They have a very good greasing property within the temperature range from $60^{\circ}C$ to $200^{\circ}C$, in some cases up to $300^{\circ}C$. They have a good mechanical and oxidizing stability.

3. Bentonite in packing technique

Bentonites have a good vapour adsorption ability what enables to use bentonites for drying of air

and industrial gases.

Better drying ability has the bentonite the clay mineral of which is Ca-montmorillonite than bentonite with Na-montmorillonite.

Engineering and electrical products are transported overseas packed in plastic foils and into this packing small cloth bags with drying agent are put. A common drying agent is silica gel which is very expensive and expenses on silica gel may reach even 50% of the total packing cost.

An absorption capacity is a very important property. Silica gel shows absorption capacity of 20 grammes of vapour per 100 grammes of drying agent while bentonite has the absorption capacity rather lower 13 - 14 grammes per 100 grammes. All values are given at 50% relative humidity of air and at the temperature of 25°C.

The cost of bentonite as drying agent if compared with silica gel makes 8 - 10% only.

The absorption capacity of a suitable bentonite is relatively stable even after regeneration.

In Czechoslovakia bentonite is produced as drying agent under the name DEHYDROSIL the properties of which are as follows:

particle size (noodles)	2 - 10 mm
minus mesh material	8 %
bulk weight	0,9 - 1,0 g/cm ³
maximum moisture	15 %
absorption capacity	14/100g

4. Using of bentonites in agriculture

Bentonites are applied in agriculture in two ways depending on their properties. They are products of weathering of rocks and great active components of soil colloids. Properties of bentonite as cation exchange, big surface area, rheological properties, capillarity and others play an important role here.

The presence of bentonite in soil helps improving soil structure. Bentonite is therefore added primarily to a sandy soil, that means into soil with lack of clay colloids.

The second way of use of bentonite in agriculture exploits its dispersion ability and surface activity for a preparation of suspensions of matters for the protection of plants.

As it has already been said bentonite is added in soils where it binds sand grains and together with

organic colloids a sorption complex is formed. Bentonite is able to combine water, i.e. 1 gramme of bentonite may bind as much as 20 grammes of water in a form of stable gel. Water bound this way forms a stock of soil water needed for plants. Bentonite being hydrophilic in contact with water it releases 21 calories of heat of wetting. Bentonite may thus be a thermal regulation of soil and may also influence an assimilation process in plants.

Research as well as practical experience have shown that bentonite not only makes the yield of plants higher but also in many cases improves even their quality.

Addition of bentonite proved successful in the growing of cotton and tea in dry areas of the Soviet Union. Good results in the use of bentonite were achieved in growing of cereals, vegetables, potatoes, corn and fruit trees.

Bentonite for agricultural purposes is being defined as: Bentonitic rock with certain content of montmorillonitic clay minerals of total sorption capacity from 20 mval/100 g to 40 mval/100 g.

Bentonites of this, a little lower quality, are available in many countries.

Increasing of capillary voids in soil caused by swelling properties of bentonite as the main effect of bentonite in agriculture can be mentioned. Higher number of capillary voids enables binding of higher quantity of water which substantially improves water regime and microbial processes in soil. The quantity of bentonite needed for this purpose is not very high and relatively good results may be achieved at reasonable costs.

The consumption of bentonite depends on the properties of soil - the more sandy soil the more bentonite is necessary to be added.

Bentonite may be applied directly mixed with fertilizers either solid or liquid.

From an economical point of view the use of bentonite is very effective. It results in higher harvest what above all is important for countries with lack of food and moreover a profit from higher yield out-balances the expenses on bentonite several times.

Bentonites are also used as carriers of agents for plant protection such as pesticides and insecticides. The carriers must be indifferent against these agents, sufficiently mechanically stable during handling, moisture should not exceed 8%, grain size is required to be from approx. 0,25 - 2,5 mm, bulk density 400 - 900 g/l.

Poultry farming uses bentonite for the preparation of granulated fodder where binding properties of bentonite are applied.

5. Bentonite in food industry

The use of bentonite in production of edible oils has already been discussed. Bentonite applies in further branches of food industry e.g. in sugar manufacture, brewing industry, canning industry and namely in the production of wine.

Bentonite was used for clarification and decolorization of sugar cane juices. This process was successfully implemented in sugar manufacture in South and Central America.

The production of sugar from sugar beet as it is known mainly in Europe nowadays does not practically use bentonite. The use of bentonite for decolorization of sugar beet juices brought some technical problems to the sugar production process and was practically without success.

Problems also occurred when bentonite was used for the stabilization of beer. There are agents existing in some countries produced on the basis of bentonite

the use of which is successful. Their effect is based on adsorbing properties - they decrease total content of nitrogen matter. Use of bentonite agents for stabilization is not widely spread, its application has found place in some breweries only.

The production of wine is the food industry branch where bentonite has found its widest application. Bentonite is considered to be the best agent against turbidity of wine caused by proteins. In many countries where the natural wine is produced bentonite is essential.

It applies its colloidal properties and ability to exchange cations. Moreover, bentonite is inert and dissoluble and does not influence the characteristic taste of wine.

A determination of suitability of bentonite is made in the following way:

5 grammes of bentonite is added into 100 ml of water and mixed properly. Bentonite swells, forms hydrogel which is left at a standstill for approx. 2 hours. Then 20 ml of this gel is added into measuring cylinder containing 1000 ml of distilled water and mixed. Mixed suspension must be stable and must not settle down at least for 10 days. The solution i.e.

20 ml of gel in 1000 ml of water is given into another measuring cylinder, acetic acid is added to reach 3,5 pH and further 20 mg of iron trichlorid is added and it is properly mixed, too. Several minutes later precipitated particles settle down to the bottom. The liquid above the precipitated particles becomes clear after 12 hours. If both the described tests were positive it means that the bentonite is suitable for the treatment of wines.

The quantity of bentonite needed for the clarification of wine is determined experimentally. It varies from 50 - 150 g/100 l of wine and depends on the sort of wine and on the quantity of proteins present in wine.

The effect of bentonite depends on the way of application. The application may be following:

- a) The bentonite is dosed into the wine through a sieve and the wine is properly mixed with the bentonite.
- b) The bentonite is spread at the surface of wine and proper mixing takes place after 1 or 2 hours.
- c) A 5% suspension of bentonite in wine is prepared and left at a standstill for 12 - 24 hours and then it is added to the corresponding amount of wine.

The mixing of wine with bentonite must be done very carefully otherwise it could happen that an un-

satisfactory clarification and stabilization would have been reached.

Further the use of bentonite based on its rheological properties will be dealt with.

6. Bentonite in foundries

Bentonite in foundries is considered to be an essential raw material the quality of which could influence the quality of castings. Proper attention must be therefore given to a checking of bentonite itself and to the moulding materials prepared from bentonite.

The use of bentonite in foundries may be divided according to the purpose as follows:

- a) Bentonite as an essential binder for the so called "green moulding process". Sand moulds and cores are made from bentonite mixtures that may be cast without drying. Sometimes if it may be necessary the surface of mould may be slightly predried by a flame. These bentonite mixtures are commonly used in steel foundries, grey iron foundries and for the casting of non-ferrous metal alloys, too.

b) Bentonite together with water glass is a binder in mixtures called "binding mixture with water glass". Adjective "binding" shows that these mixtures possess certain green compression strength usually from 350 to 550 p/sq.cm in contrast to mixtures with water glass that have green compression strength very low (100p/sq.cm maximum) and must be hardened by carbon dioxide. A combination of binders - that of bentonite and water glass - enables to utilize advantages of both the matters. Moulding mixtures of bentonite and water glass harden spontaneously in the air. To speed up the hardening the moulds may be pre-dried. These mixtures are used in steel foundries, less often in grey iron foundries.

c) Moulding mixtures of natural clayey sand which are used in grey iron foundries exist. Illite is the clay mineral present in these natural mixtures most often. The content of clay mineral varies, therefore bentonite is often used in addition of 1 - 3% to improve and stabilize properties of natural sand. Return moulding sand (that is used sand from moulds and cores cast) circulating in foundries loses partially its binding properties, the addition of bentonite helps keeping the green compression strength as well as permeability on the required level.

d) Small quantity of bentonite is added to mixtures of organic binders again to improve their strength in green state. The addition of bentonite usually does not exceed 0,8%.

e) Bentonite is also applied in paints that protect surface of moulds and cores against effects of molten metal. Paints are water suspensions of silica powder, fine milled corundum, chamot, magnesite, graphite, etc. Bentonite is added to this paints in the quantity of 2 - 5%, it prevents relatively heavy particles of grog from sedimentation.

The wide application of bentonite in foundries has enabled the foundrymen to prepare moulding sands of required properties.

Bentonite used as a binder influences more or less the following properties:

- green compression strength
- tendency to drying of surface
- permeability
- development of gases and fumes
- dimensional stability of a mould

Green compression strength is the most important property of moulding sand and depends on plastic properties

of binder, i.e. of bentonite. Green compression strength is expressed in pounds per sq.cm. Values of green compression strength must be so high to enable casting in green state. In most foundries such values of moulding sands lie in a range of 700 - 1100 pounds/sq.cm. A determination of strength is made with specimens of cylindrical shape prepared from a tested moulding sand by ramming. Dimension of specimen are: 50 mm diameter, 50 mm height.

Green compression strength of bentonite moulding mixtures varies depending on moisture. From the relations among moisture, green compression strength and permeability ensues a rule commonly known in foundries - the most suitable bentonite mixture is that with maximum permeability. Moulding mixture with the highest green compression strength attainable with given bentonite has rather low permeability and low moisture. Such a mixture is unusable for foundry purposes. It is too dry and its use could cause a casting's defect. Moulds and cores prepared from this mixture dry very quickly at the surface, edges and corners are friable. Sand grains from moulding material get loosened and enter a casting.

Proper determination of moisture plays an important role otherwise even good bentonite may get deteriorated.

At casting gases and fumes occur whose quantity depends on the kind and amount of binders. Bentonite does not give rise to excessive quantity of gases what is its further advantage.

And, finally, the last property which may be influenced by bentonite is a dimensional stability of moulds at casting process. Binders at casting process shrink, on the other hand silica sand changes its dimensions positively. These facts are of principle significance at prevention of scabs formation.

Scabs are serious castings defects that occur in foundry practice. The formation of scabs occur within a temperature range 300 - 600°C. Irregular and quick expansibility of quartz at 573°C supports scabs forming. An explanation and further causes of scabs forming are far beyond the scope of this lecture therefore it cannot be discussed here, on the other hand if foundrymen want prevent scabing bentonite with the highest possible green compression strength is to be used. The most suitable is Na-bentonite or Ca-bentonite natrified with soda.

At the beginning of this chapter moulding mixture from bentonite and water glass as binders was mentioned and it was said that green compression strength

lies in the range from 350 to 550 p/sq.cm. This mixture may be dried in the open air or by-dried with a flame. The strength is enhanced upto 4 - 6 kp/sq.cm. and moulds treated such a way after casting process produce castings without scabs. These moulding mixtures may be very easily treated in such countries where a relative humidity is low. On the other hand during the rainy season for instance in India all efforts to harden bentonite failed - water glass mixtures were unsatisfactory owing to the high humidity which did not allow drying of the mixture and thereby formation of hydrated glass which is the precondition of hardening.

Required properties for bentonite mixture are different for steel castings, grey iron castings and non-ferrous metal castings.

Steel castings - for machine moulding green compression strength should be approx. 800 p/sq.cm
- for hand moulding a higher green compression strength is required ranging from 900 - 1100 p/sq.cm

Castings from grey iron, non-ferrous metal and iron light alloys - for machine moulding of small castings 500 - 700 p/sq. cm
- for machine moulding of bigger castings 600 - 800 p/sq.cm

- for hand moulding 800 - 1100 g/sq.cm

Permeability is another property to be checked at moulding sands. Bentonite has no influence on the permeability if its content is in the range from 3 to 10% what is the range used in foundries.

Permeability may be defined as an ability of rammed moulding mixture to let gases through it. Permeability is given in normal unit of permeability and the values are to be from 20 n. u. p. for the smallest castings up to 300 for steel castings.

Let us now make a review of requirements how they are specified by foundry experts.

Bentonite should have the following properties for the green moulding:

- a) high green compression strength (good plasticity, high content of montmorillonite and high sorption capacity)
- b) low sensibility to an excess of moisture (i.e. green compression strength must not decrease substantially if the moisture is even two times higher than the optimum value)
- c) resistance against friability at the drying
- d) resistance against repeated heating at temperature range from 300 to 600°C

- e) low content of Fe_2O_3 (maximum 12%) and no carbonates
- f) high fineness of milling

It is not possible to express all these properties in standards because suitable tests do not exist for some of the above mentioned requirements. The standards of bentonite for foundry purposes usually specify a value of cation exchange, minimum of green compression strength determined at standard bentonite moulding mixture, permeability of the mixture, fineness of milling and moisture of the supplied bentonite. All these properties do not cover all the conditions to which the bentonite and moulding mixtures are exposed. Moreover, there are not direct relations among properties of bentonite. The bentonite with cation exchange of 60 mval/100 g may have the green compression strength substantially lower than bentonite with cation exchange of 40 mval/100 g only. The same considerably varied relations were found between cation exchange and decolorizing efficiency. It is therefore recommendable and in practice very often applied to evaluate bentonites under the conditions corresponding as closely as possible to the conditions in the production. It means to stimulate in foundries the conditions of casting process which is difficult and though a number of methods were tried a method reliably evaluating the bentonite for foundry use does not exist until now.

The bentonite, nevertheless, is and will be an indispensable binder used in foundries. All efforts are paid to bentonite beneficiation with the aim to give to the foundries a bentonite of such properties that would enable a reliable casting process.

7. Use of bentonite in ceramics

Bentonite is applied as a plastification admixture in a form of a fine dispersed clay in ceramics.

Bentonite if added in a quantity from 3 to 5% only enhances plasticity to improve workability and mechanical strength of products in green state.

Systematic research in the Soviet Union shows the following possibilities of use of bentonite:

- a) A certain type of bentonite may substitute as many as 20% of kaolin in an earthenware body and 6% of kaolin in China clay body without the white colour of bodies being influenced.
- b) The bentonite decreases the temperature of sintering hence it decreases the firing temperature, too.
- c) A wide interval between sintering temperature and body refractoriness enables a production of ware with a low or high porosity.

A similar experience has been met with in other countries, too. These advantageous properties of bentonites enable either to use raw materials of low quality for instance less plastic clays or partially they may substitute high plastic clays.

The use of bentonite brings of course some disadvantages, too. Bentonite for instance worsens filtration of slurry, increases shrinkage and viscosity. These problems could be solved with the use of spray drying in place of filter presses or with addition of deflocculants. All advantages and disadvantages are to be taken into account and it is important to choose an optimum alternative from both technical and economical point of view.

The content of oxides of iron, manganese and titanium must not exceed 3% otherwise the colour of body could be affected adversely.

These facts show that the use of bentonite in ceramic industry deserves proper attention.

3. Bentonite in civil engineering

Application of bentonite in building industry is based on its hydrophilic, thixotropic and swelling

properties. Bentonites are used in a form of suspensions and pastes.

Water suspensions of bentonites enable to seal rocks or huge objects built beneath the subsoil water level. The sealing of rocks and civil engineering works is made in different ways.

Grouting is a process when the suspension of bentonite with water applied to the pervious rock prevents water from seepage.

A cement suspension is used for the same purpose the advantage of bentonite suspension is that it is a better sealing medium than cement suspension. Particles of bentonite are finer than those of cement and in voids and leakages they swell preventing thus the seepage of water.

A resistance of bentonite against water with deleterious effects is higher also than the resistance of cement. Bentonite suspensions on the other hand have a small strength and may be washed away by subsoil water.

A further way of bentonite suspension application is a sealing of bottom and slopes of canals and dams. This application has a big significance at the tightening

of irrigating canals where it prevents the leakage of water.

There are some other technologies of bentonite suspension application but their description is out of the scope of this lecture.

9. Use of bentonite in drilling processes

Colloidal and rheological properties of bentonite suspensions have found a very important application in geological survey.

Drilling fluid is prepared from bentonite and is used for drilling of crude oil, coal, ore, natural gas and mineral raw materials.

The main tasks of drilling fluid are:

1. to consolidate walls in the drill at a time of drilling
2. to slow down the sedimentation of drilled earth
3. to help to transfer the drilled material from the drill to the surface
4. to create a thin, impermeable and elastic layer on the drill surface that prevents the natural gas and water from intruding into the drill

5. to cool a drilling pit and to lubricate drill rods

The drilling fluid contains from 6 to 8% of bentonite if it is sodium bentonite. Calcium bentonite is less suitable for the preparation of drilling fluid. It is necessary, for the preparation of drilling fluid from calcium bentonite, to use substantially higher amount of this type of bentonite to obtain drilling fluid with suitable properties. This influences very unfavourably the use of calcium bentonite in drilling technique and, hence, it is preferred to use sodium bentonite instead.

The consumption of bentonites for drilling purposes is relatively high; in the USSR it amounts to almost one half of total bentonite production and in the USA one third of the total bentonite production.

The amount of drilling works grows and simultaneously grows the consumption of the drilling fluid containing bentonite and the requirements on the properties of drilling fluids are higher, too.

10. Bentonite in pharmaceutical and cosmetic industry

Bentonites may be used in pharmacy and cosmetics either directly or as auxiliary agents. The direct use of bentonite is based on its adsorbent and antacidic

properties. Bentonite is a component of some ointments, pills, pastes.

Water suspensions of bentonite with bentonite content higher than 10% create a gel that enables using such gel as a base for a preparation of ointments. The advantage of bentonite is that bentonite is a very well compatible with almost all other components.

It is also known that for X-ray diagnostic of stomach water suspension of barium sulphate is used. Bentonite is added to this suspension in the amount of 5% what prevents the sedimentation of heavy particles of barium sulphate.

Bentonite is a frequent component of different cosmetic products such as soaps, pastes, creams, etc. Bentonite replaces the part consisting of fats in these products.

The consumption of bentonite in pharmaceutical and cosmetic industries, of course, is not big. The requirements for the quality of bentonite for these purposes, on the other hand, are high.

11. Use of bentonite in other industrial branches

So called organobentonites what are products of reaction between bentonite and suitable organic matter, have found an application in paint and varnish industry.

Bentonite as auxiliary filler may be used for the production of paper for technical purposes. The addition of bentonite enables to increase the amount of filler, i. e. kaolin in the paper mass.

Bentonite in textile industry is used as a washing and degreasing agent.

There are many other examples and possibilities where bentonite may be used and they all identify bentonite as a very important and useful material.



