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INTEGRATED UTILIZATION
OF
BENTONITES

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ABSTRACT

This paper shows the necessity of the integrated view on the bentonite exploitation. Aside the known traditional applications of bentonites the new developments show new ways of bentonite utilization possibilities which are interesting not only from the entrepreneurial point of view but which also influence the national economy.

Bentonite, as a rock, was underestimated in the past. New up-grading and refining methods of bentonites have brought this rock to the new position, in which it has played an important role in agriculture, environmental protection and in different new industrial applications. Economic aspects and the anticipated development in bentonite up-grading and exploitation possibilities have shown that bentonites have a better future in the years to come than they have ever had in the past.

Attention is to be paid to bentonites especially in developing countries which did not pay too much attention to non-metallics and to bentonites earlier, but which can start new industrial ventures in this respect with a relatively low capital. Therefore, this paper brings a comprehensive description which will provide the reader with necessary information on bentonites which are as industrial rocks important not only for the industrial development of new ventures but which can also lead to the diversification and expansion of existing plants, as their integrated utilization leads to different applications which extend the existing bentonite market.

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I. INTRODUCTION

1. The Role of Bentonite in National Economy

Bentonite as a clay rock belongs to the group of non-metallics, its decisive properties are represented by the mineral montmorillonite $Al_2O_3 \cdot 4\ SiO_2 \cdot H_2O \cdot n\ H_2O$.

Montmorillonite is a clay mineral of high dispersion, the particles of which have large surface and high ability to bind water. It is composed of very fine grained and soft crystals of monoclinic system.

Industrial exploitation of bentonites in more advanced developing countries as well as in developed ones is known in traditional technologies, such as a binding agent in the foundries and metallurgy, as a viscosifier, fluid loss reducer and suspension agent in drilling, as a filler in pharmaceutical and cosmetic industries, paper industry as well as a binder in building materials and chemical industries. Less information is available on the possibility to apply bentonites as fillers in the textile, paper and ceramic industries. A lack of information usually exists on the sorption capacity and ion exchange of bentonites. Therefore, the <u>integrated approach</u> for the justification of the exploitation of local bentonites is very important. It is to be underlined that bentonite is one of the most important non-metallic raw materials which require the comprehensive evaluation of their quality and up-grading possibilities according to the requirements of end-users, because different applications can be supplementary to those known already in view of bentonite exploitation.

Not too much attention was paid in developing countries to bentonite occurrences during the old colonial time and in the period close to it. Geological prospection, drilling and evaluations did not recognize bentonite and montmorillonite as a useful rock or mineral for the national economy contribution due to the lack of information and lower industrial development. Later on, however, the development of different activities created the need to import bentonites in order to apply them in the traditional way. Furthermore, new developments of the last two decades have shown that bentonite can play an important role in non-traditional activities with the direct influence on the national economy. Among others let us specify animal husbandry, purification of different types of waste waters and their recycling, nuclear industry and others.

The new possibilities of the bentonite exploitation have brought them to the new position among industrial minerals and rocks and a lot of studies have been made on their purification, up-grading and activating technologies.

There are different grades of bentonites found in the nature. The most important aspect of the bentonite quality is the content of montmorillonite. Those countries, owing deposits of bentonite with the content of montmorillonite higher than 85%, do not need any up-grading, such as Wyoming bentonites in the USA. However, lower content of montmorillonite in the raw bentonites is the most frequent case in the nature. Then the tests, conducted with such bentonites, will determine the most economic and suitable up-grading methods to be applied in order to meet requirements of end-users.

Another aspect is related to the type of bentonites. Montmorillonite shows many interesting properties, which are unique in the group of clay minerals and non-metallics.

The ion-exchange, sorption capacity and swelling, reaching the surface of 1 gram of bentonite higher than 800 sq.m are the most interesting ones.

Since the genesis of bentonites resulted into different types of bentonites, the integrated evaluation of natural bentonites is very important. Meanwhile the sodium bentonites are good because of their binding and dispersion capacity, the calcium bentonites can be applied as soil reclaiming agents as their sorbing capacity is high enough and the calcium regulates jointly the acidity of the soil. Applying different up-grading methods, new types of bentonites can be created, which do not appear in the nature. Such bentonites are acid, aluminium, iron, magnesium bentonites and others.

The methods of digging and extraction of bentonites are quite simple. Mostly the open-cast mining is applied as the cheapest mining method. In many countries, sun drying brings sufficient results to sell bentonites in a disintegrated form. If different types of activation, drying and fine grinding are to be applied, then a feasibility study is recommended to be conducted with the evaluation of the entrepreneurial approach as well as with the view to the national economy.

In general, the important factors, influencing the national economy, are the following ones:

Reduction of imports as well as the export possibilities of bentonites which bring direct savings in the foreign exchange balance aside the increased employment and exploitation of locally available raw materials, which also reflects different types of taxation.

The influence of bentonite exploitation on the national economy can also be demonstrated through the agricultural sector. Application of bentonites as the sandy soil reclaiming agents brings, due to their retaining ability, the increased yield of farming, lower water consumption by irrigation and decreased need of chemical fertilizers. Different developing countries suffer from the food shortage, the other import sometimes more than one half of food consumed locally, in extreme cases the great majority of food. Limitation of water resources and of irrigation possibilities in countries with low rainfall does not allow to expand fields and, sometimes, creates difficulties to the industrial development.

Water, which is short in the majority of different world territories, is the most important component from the point of view of environment, as being used as the simpliest sewage. Therefore, the engineering environment has developed different methods for the purification of contaminated waters. Bentonite, in an effective way, cleans different types of contaminated waters, which can hardly be purified by other methods.

Bentonite, being used in agriculture and environment, is the clay rock, extracted from the earth. Therefore, its application back to the soils and waters does not jeopardize the environmental balance. Bentonites, saturated with different particles from the purification processes and leaving the process as rejects or litters, can be exploited in other processing representing low and non-waste technologies. Such bentonites can be applied as an ideal component of composts in agriculture, of clay ceramics products or cement clinker in the silicate industry or of fuel in such cases when fat or different organic matters are removed from contaminated waters.

Bentonites, however, show the direct influence on the environment in other ways, too. Applying properly bentonites to roots of different types of trees, costs of the irrigating water,needed to keep the decorative tree growing sink down to one half, meanwhile the fruit trees jointly bring much higher harvest. In some countries considerations are being made to apply bentonites into the soil in order to decrease its erosion. Bentonites, if deposited in the depth, can create a protective layer against the penetration of underground corrosive or salty waters.

The foregoing examples show that the exploitation of bentonites influences not only the national economy of any country, but jointly can be interesting from the entrepreneurial point of view. Bentonites create the entrepreneurial possibilities as such or support the development of different other industrial activities. The integrated approach to the bentonite exploitation brings a new view in which also the marketing possibilities are gradually being extended.

Bentonites are those raw materials which are relatively cheap being sold for 30 and more US $ per 1 ton FOB depending on the level of dressing. Their transport costs play high proportion of their CIF price. Therefore, exploitation of locally available bentonites usually leads to economic ventures depending on the quality of local raw ore and on the size of the market.

The feasibility study, however, is to be conducted for each particular venture, as the entrepreneurial conditions as well as their influence on the national economy can vary not only between different countries but also between different developing ventures.

The UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Minerals Based Industries in Pilsen has large experience from the point of view of different possibilities of the exploitation of locally available bentonites. Its activities in selected European as well as in developing countries have shown good examples of the integrated exploitation of bentonites. The recommended start-up, followed by the UNIDO-Czechoslovakia Joint Programme in Pilsen,is related to the testing, classification, up-grading and application of bentonites in different ventures as well as in conducting appropriate feasibility or case studies. Since the economy of the venture is very much influenced by the grade of entering local raw bentonites, the first recommended step is the testing, classification and up-grading evaluation.

2. Purpose and Scope of Study

The purpose of this study is to show the reader that the importance of non-metallics has grown in general, as they can economically be exploited in different ways. Bentonite, a non-metallic rock, has a unique position among non-metallics. In spite of the fact that bentonites have been known during about last hundred years, their higher importance to the development has been recognized during the last one or two decades. Aside the traditional exploitation of bentonites new ways of bentonites up-grading are being developed which change the behaviour of raw bentonites very much in such a way that new applications are realized.

Therefore, this paper is aimed at drawing the attention of managers and of technicians in existing plants as well as in the plants newly established that bentonite is a valuable rock with its boom which will grow in the years to come. New up-grading possibilities are increasing the demand of non-traditional sectors as well as new applications are extending the market, enabling the integrated utilization of different grades of raw bentonites.

The publication is not a scientific paper which would describe, in a theoretical way, the reasons of different bentonite behaviours under different conditions. However, it is a paper which gives the reader a rounded picture on bentonites as on a complex, starting with the description of bentonites as of an industrial rock, explaining the extraction and up-grading possibilities in view of bentonite industrial application. The integrated exploitations are divided into the sector of industry, environmental protection as well as of agriculture. Selected economic aspects and anticipated development of the bentonite exploitation can also be appreciated by different entrepreneurs, who consider to develop the business on bentonites.

The publication, however, will also be useful to the teachers, trainers and trainees of technical universities and engineering schools as providing the reader with the information on the basic testing and up-grading possibilities as well as on the wide range of bentonite applications in different people's activities.

It is to be mentioned that the bentonite technologies are still being developed and, therefore, the information, provided in this publication, is not the final one. Also the limited extent of the paper did not allow the writers to explain all details on bentonites as they felt it should be done. Therefore, any additional information can be obtained from the UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Minerals Based Industries in Pilsen, since this Programme has sponsored the edition of this publication.

II. BENTONITE - INDUSTRIAL ROCK

1. Geological Origin

Bentonite is a clay rock with dominating mineral montmorillonite. It originated by argillation and alteration of effusive rocks particularly andesites and rhyolites and their pyroclastics. Principally bentonite originated in alkaline milieu to the contrary of kaolin whose metamorphosis is confined to acidic environments. Bentonite differs from kaolin by its appearance. It occurs usually in lumps and has typical conchoidal fracture. Its colours are various with yellow, red and grey tints. Bentonite is greasy if touched and swells in water creating a thixotropic gel as a consequence of interlayer water adsorption.

The argillation of effusive rocks may have 5 basic forms:

a/ argillation in alkalic marine environments

which occurred immediately after the deposition of volcanic ash which probably contributed to the alteration of heating water of shallow basins,

b/ argillation by long-term action of ground water

penetrating water affected the deeply burried tuff layers; liberated silica built-up silicified zones beneath bentonite,

c/ hydrothermal argillation

which ran either in depths or in small alcalic lakes with hot bottom springs (hectorite in California), d/ argillation by weathering surface tuffs

The volcanic origin of the parent rock may be inferred from the angular forms of non-clay minerals, such as chip-like relics of volcanic glass and from reduced content of SiO_2.

e/ rewashing

If originated bentonite was rewashed in alkaline environment montmorillonitic clays originated which are difficult to be distinguished from residual bentonites. The denomination bentonite applies usually to montmorillonitic clays, as well.

The bentonite deposits show a character of stratigraphically relatively constant horizons, layers or lenses which contact the underlying beds sharply and pass upwards gradually (genetic type e/), or inversely (genetic type d/), or contact sharply both overlying and underlying beds (genetic types a/ and b/). The areal extent, particularly of altered pyroclastics,is usually large and the thickness is in the order of meters. The shape of hydrothermal deposits is irregular.

2. Occurrence and Distribution in the Nature

As mentioned above bentonite-type rocks have a close contact with the products of past volcanic activity. The deposits are usually secondary, only rarely primary. The properties of bentonites depend largely upon the content and kind of accessory minerals. The most frequent accessory materials are beidellite, notronite, kaolinite, quartz, diatomite, limestone and organic matters. Bentonite occurs most frequently as Ca- or Mg-bentonite or mixed, rarely as Na-bentonite. The substituted ion has a decisive effect on the bentonite properties. E. g. the Na-ion influences very distinctly the rheological properties of bentonite. This ion-exchange capacity and the admixtures are origin of the great variety of bentonites which differ not only among deposits but also within one deposit.

Bentonites are mined in 35 countries (M. Kužvart in Academia ed. 1984). M. Gregor (1969) gathered information on total of 58 different geological occurrences excluding Europe. 19 of the 58 geological occurrences were deposited in the USA, 18 in Central and South America, 8 in Africa (mainly north).

As for Europe, the USSR, Greece, West Germany, Great Britain, Italy, Hungary, Yugoslavia, Czechoslovakia and Romania are notorious for larger deposits of bentonites.

The largest world's reserves of bentonites were geologically verified to occur in the USSR, namely in Ukraine (Chaerkasy 1.5 - 8 m thick layers in the Miocene), the Crimea (Kurtsev deposit), the Transcarpathian region, Azerbaidzhan, Kazakhstan, altogether 16 different mineable localities.

In the USA large deposits of bentonite and fuller's earth are excavated. Two types of bentonites are distinguished in general: strongly swelling Na-bentonites and Ca-bentonites. At the foothill of Black Hills along the boundary between Wyoming, South Dakota and Montana, a marine complex of Cretaceous clayey shales (formerly called the Benton Group after Fort Benton in Montana) extends at a length of ca 250km. It is deformed into a brachysyncline dipping towards the north-east. The complex contains 15 - 20 layers of strongly swelling montmorillonite bentonite with admixtures of mica, feldspar, gypsum, salts and shreds of volcanic glass.

The layers are 1 cm as far as 2.5 m thick (in average 1 m). Every bentonite layer is underlain by a silicified bed for which the migration of silica dioxide during alteration is responsible. The bentonite is mined mainly near Clay Spur, Wyoming. The ratio of exchangeable Na/Ca cations rises towards the outcrop as does bentonite quality.

Deposits of less swelling bentonites and fuller's earth are exploited along the Mississippi river, in Alabama, Kentucky and in Arizona. A hydrothermal type deposit is near Hector in California.

In Greece bentonite deposits on Milos Island have thickness of as much as 30 m. In Japan, the Hojun bentonite deposit is built up of 15 beds thick 1 to 1.5 m. Important deposits of high-quality bentonites occur in East Bavaria (the FRG) which are regarded as standard of bleaching earth (Tonsil A C).

Palygorskite - containing bleaching clays occur in the Meigs-Attapulgus-Quincey area in Georgia and Florida, USA, in the form of lenses in Miocene Howthorn Formation devoid of volcanic ash.

Other occurrences are the Eocene marine sediments at Pout near Mbour in Senegal, in Ukraine where bleaching clays alternate with bentonite, and in Mudh in India. The only mixed deposit of sepiolitic fuller's earth is in Vallecas, Spain in a Tertiary evaporate formation. A mineable Pleistocene deposit is near Ash Meadows in Nevada, USA.

Occurrence in Africa

In Algeria deposits at Mostaganem and Marina are exploited to supply the production of about 100 000 tpa of bentonite and fuller's earth. Bentonites were also mined in Mozambique (Luzinda Mine at Maputo), Namibia, Zambia, Tanzania (Sinya, Amboli at Namanga). There are industrially important deposits in Egypt (El Fayoum), Tunisia and Kenya.

Occurrence in Asia and Oceania

Bentonites are mined and processed in Australia, Burma, China, India, Iran, Israel, Japan, New Zealand, the Philippines. Large deposits of good quality bentonites are situated in China, however, statistics about outputs are not available. In India there are significant deposits of bentonites in the states of Bihar, Gujarat, Jammu, Kashmir, Assam, Uttar Pradesh. The largest exploited deposit is in the Katch and Bhavnagar districts in Gujarat which is claimed to be the world's largest natural sodium bentonite deposit outside the USA. In Iran, deposits at Mehrejan and Zarrin were exploited in 1970's. The largest Asian producer of bentonites is Japan with a large number of mining operations, especially on Honshu and Kyushu. In the Philippines significant ventures were in operation excavating thousands of tonnes of bentonite and associated clays from the deposits situated at Northern Leyte, Batangas and Nueva Erija. There is also an underground mine at Merida, in Leyte.

Europe

Cyprus - the largest mined deposit with reserves over 20 million tons is in the area of Troulli in the Larnaca District. Other large deposit was opened at Limassol.

Czechoslovakia - the best quality bentonites are deposited especially in the North-Bohemian Brown Coal Basin, localities Braňany, Vysoké Třebušice, etc. which are excavated and converted into Na-activated bentonites to supply especially foundry industries and animal feedstock granulation. There are tens of deposits of montmorillonite clays spread over the whole Czechoslovakia which are mined and supplied for local building materials industries and as soil conditioners without processing.

West Germany - the largest producer of bentonites in Western Europe has the important deposits in Bavaria, especially at Moosburg near Munich and at Landshut. The world renown standard of bleaching clays is the brand Tonsil.

Greece - bentonites are deposited on islands of Milos, Chios and Kimolos whereby most of processed bentonites exported into Western Europe and Canada are exploited on Milos.

Italy - most bentonites are mined at Mediterranean islands as with Greece, Sardinia with several deposits in the west of the island, the other important island sourse is the isle of Ponza. The mainland deposits occur at Arsiero, Puglie and Maglio di Sopra.

As mentioned above the largest deposits in the world are in the USSR. In Europe bentonites are deposited, mined and processed also in France (Bergerac), Hungary (Mad and Istenmezeje), Poland, Romania, Spain (provinces of Almerica and Madrid), Turkey (Akdogmus, Pertik, Kaspinari Cankiri, Balikkesir), the United Kingdom (deposits Redhill, Bath, Maidstone in Kent, Woburn in Bedforshire, the well-known underground mines are at Combe Hay), Yugoslavia (Ginovci).

America

Argentina (Neuquen Province), Brazil (Boa Vista in Paraiba State, smaller deposits are especially in Minas Gerais), Mexico (Tlaxcala, Morelos, Durango) the USA - The largest capacity mining the fine Na-bentonite at Clay Spur (Black Hills, Wyoming) was mentioned before. Other reserves of this bentonite outcrop also in younger formations in the Bighorn Mts of Wyoming and at scattered locations in Montana. The calcium bentonites are deposited in beds of Cretaceous age in Mississippi and Alabama whilst calcium bentonites of Tertiary age are mined in South Texas.

3. Mineralogy and Chemistry

Bentonite as a clay rock is characterized by dominating share of the mineral montmorillonite which is classified as clay mineral.

The term clay mineral is of technological origin. Kaolinite, montmorillonite, and clay micas were considered to be clay minerals. Typical feature of clay minerals is laminated structure consisting of layers of tetrahedrons $(SiO_4)^{4-}$ and octahedrons $/Al(OH)_6/^{3-}$ or $/Mg(OH)_6/^{4-}$.

This structure criterion was generally accepted to classify clay minerals. Consequently, the term clay mineral includes minerals which have not typical properties of clays, plasticity, sorption capacity, etc. Table 1 shows a typical classification of clay minerals.

Mineral montmorillonite belongs to the silicate group montmorillonite-saponite which is also known as "smectites". The structure of montmorillonite was not understood exactly because of very small dimension of crystals. The known models are derived from information on structure of other laminated silicates. The model elaborated by Hofman, Endell and Wilm in 1933 which is generally accepted as correct is derived from the structure of pyrophylite. They supposed that montmorillonite three-layer mineral is of identical structure (Figure 1) with the difference in the distances of layers which depend on the relative humidity of milieu and on the depositing of layers.

The oxygen skeleton of the structure of all the smectite silicate group is approximately the same. The classification of minerals within this group is based on differences in the chemical composition. The classification is based on the work of C. S. Ross and S. B. Hendricks (1945). The ratio Si : Al in dioctaedric minerals of the group can vary from 2 : 2 to 6 : 2. Each mineral having the ratio Si : Al 5 : 2 and the below idealized formula is montmorillonite:

$/Si_8/^{IV} /Al_{3.33}M_{0.67}/^{IV}O_{20}(OH)_4$ where M is either Mg^{2+}, Fe^{3+}, Li^+, etc.

Beidellite has formula:

$/Si_{7.33}Al_{0.67}M_{0.67}/^{IV}/Al_4/^{VI}O_{20}(OH)_4$

Nontronite contains cations Fe^{3+} in the octahedrons instead of Al_4 so that its formula differs from beidellite as follows:

$/Si_{7.33}Al_{0.67}M_{0.67}/^{IV}/Fe_4^{3+}/^{VI}O_{20}(OH)_4$

Trioctaedric member of smectite group is saponite of the below idealized formula:

$/Si_{7.33}Al_{0.67}M_{0.67}/^{IV} /Mg_6/^{VI}O_{20}(OH)_4$

while hectorite does not contain Al:

$/Si_8/^{IV}/Mg_{5.33}Li_{0.67}M_{0.67}/^{VI}O_{20}(OH)_4$

Chemisms

The basic cell of pyrophylite which is the accepted model for the montmorillonite structure contains:
8 atoms of Si, 4 atoms of Al, 24 atoms of O, 4 atoms of H

The structural montmorillonite model is based on the presumption that the distance between layers is varying dependent on the humidity of milieu and on the presence of exchangeable cations. Further it is believed that the exchangeable cations penetrate into interlayer space and equalize the negative charge which arises by the substitution $Al^{3+} \rightarrow Mg^{2+}$ in octahedrons and $Si^{4+} \rightarrow Al^{3+}$ in tetrahedrons. The quantity of exchangeable cations per a basic cell is 0.66 (Hendricks, 1942).

Some authors are of opinion that the swelling power of montmorillonite is derived from the presence of hydroxyl groups on the surface of molecules. They do not suppose any substitution and the ion exchange is confined to the positions of dissociated OH groups bound to $/SiO_3OH/^{3-}$ in tetrahedrons.

The presence of Si^{4+}, Al^{3+} and Fe^{3+} was proved for the tetrahedrons. In the octahedrons there occur currently Al^{3+}, Fe^{3+}, Fe^{2+}, Mg^{2+} and more rarely Ti^{4+}, Cr^{3+}, Zn^{2+} and other cations.

The representation of different oxides in smectites is very various. Ross (1945) collected analyses of 54 samples of minerals of series montmorillonite-beidellite which were of the following chemical compositions.

Chemism of montmorillonitic clays

(M. Gregor, R. Čičel, Bentonit a jeho využitie, SAV, 1969)

Component	montmorillonites beidellites /%/
SiO_2	44.02 - 54.58
Al_2O_3	11.66 - 31.30
Fe_2O_3	0.06 - 8.65
FeO	up to 1.4
MgO	0.16 - 8.61
CaO	up to 3.28
K_2O	up to 2.25
Na_2O	up to 3.80

4. Technological Properties

The origin of most interesting properties of montmorillonite is developed from the following specific factors:

a/ immense relative surface,
b/ electrically charged particles,
c/ chip-like form of particles.

The immense relative surface and electrically charged particles are bearers of excellent sorption capacity. The electrically charged particles are responsible for ion-exchange capacity and the chip-like form of particles for rheological properties.

Adsorption

The term adsorption means entrapping molecules of fluid phases on the contact surface of solid phase.

The adsorbed molecules build up a mono- or multi-molecular layer on the surface of solid phase and the bond of molecules to the surface is through either attractive van der Waals' forces or saturation of free valences of solid phase surface.

The first case is called a physical adsorption and it can be characterized by a tiny energy of bond and non-specification. The second phase is known as a chemisorption which has a character of surface reaction /i.e. it is specified/ and the bond to the surface is much firmer.

As was mentioned above each particle of montmorillonite which consists of several three-layer structures has both outside and inside surface. The overall surface is immense and accounts for 750 - 800 sq.m per gram. This large surface is a bearer of significant adsorption power of montmorillonite.

The surface of montmorillonite adsorbs in a selective manner small polar molecules which can access both outside and inside surfaces. Non-polar molecules are adsorbed only on outside surface. The chemisorption of montmorillonite is closely related to its catalytic efficiency in the processes of cracking, polymerization, isomerization, hydration and similar reactions which are catalyzed by acids. The catalytic effect of montmorillonite is explained, akin to other alumosilicates, by the existence of surface sources of protons, i.e. active centres which have character of acceptors of electron pairs. All alumosilicates are characterized by isomorphous substitution of aluminium for silicon. Because the valences of both the elements are unequal substituting aluminium brings a negative charge which is equalized by a monovalent cation or proton occupying the neighbourhood. The centre occupied by the proton behaves as an acid which acts in a catalytic manner due to its acidity.

On contacting with saturated steam montmorillonite adsorbs about 0.5 g H_2O/g. If Na-montmorillonite is contacted with liquid water it adsorbs as much as 10 g H_2O/g and converts into a thixotropic gel of about 20-fold volume. It has been proved that montmorillonites with monovalent inter-lattice cations swell without limits. The swelling of crystals converts into macroscopic swelling, i.e. swelling of particle aggregates. The water films wrap the particles or fill in the voids between plate-like particles. This second phase of swelling is called "osmotic swelling". Montmorillonite behaviour is almost similar if affected by molecules of polar organic matters with organic cations which are adsorbed both on outside surface and inter-lattice voids. Montmorillonites containing adsorbed polar molecules are often called "montmorillonite organic complexes".

Cation-exchange

The inequality of valences caused in isomorphic substitution of aluminium for silicon in the tetrahedrons or magnesium for aluminium in octahedrons is equalized by cations on the surface of layers. These cations are mobile in water suspensions and are attracted by Coulomb's forces to the surface of silicate layers which have a negative charge. But the thermal movement acts contrary with tendency to equalize the concentrations through whole the volume of liquid.

Suppose all the charges on the montmorillonite surface are equalized by Na^+-ions and this Na-montmorillonite is suspended in a solution of potassium salt. The concentrations are forced to equalize between the dispersion

milieu and montmorillonite complex (so called micelar solution). A part of Na^+-ions from the micelar solution is exchanged with K^+-ions from the outside solution.
Schematically:

$$\text{Na - montmorillonite} + K^+ \rightleftarrows \text{K - montmorillonite} + Na^+$$

The balance is dependent on concentration of cations in the solution and properties of changing ions.

In strong acid milieu all the exchangeable cations will be replaced by H^+-ions. Such an H - montmorillonite can be considered a weak acid and the ion exchange which occurs on adding NaOH solution into the suspension of H - montmorillonite can be looked upon as a neutralization of SiOH groups. This process is expressed by the titration curve of montmorillonite which is of course typical for weak acids. The quantity of acid groups expressed as the consumption of NaOH in miliequivalents related to 100 g of montmorillonite at reaching the inflex point of the titration curve is so called "montmorillonite sorption capacity". Its value is usually 80 - 100 mval/100 g.

Rheology

Montmorillonite is of laminated structure consisting of tetrahedron and octahedron formations of oxygen anions tied up with cations inside these spatial formations. The ratio between tetrahedrons and octahedrons is 2 : 1. There are situated molecular water and ions of alkali or alkaline earths in inter-layer spaces. These spaces, similarly to crystal edges, are sources of such properties as the exchange and adsorption of ions and swelling in water and other solvents. The lamination of atoms affects also macroscopically the behaviour of thin leaf crystals. The crystals, depending on ions and quantity of bound water, can mutually shift their faces or they can be oriented "edge to face" or "edge to edge" as in Figure 2. It is obvious that this system makes possible to build up spatial formations of honeycombed structure which are very solid in suspensions or, vice versa, sediments taking up comparatively small room which have arrangement "face to face". By this mechanism, rheological and thixotropic properties can be controlled.

5. Review of Applicable Bentonite Properties

Whether a certain bentonite is utilizable in praxis or not depends on the content of montmorillonite that is the bearer of desirable bentonite properties.

Even though other accompanying minerals share in the bentonite overall quality, they have only minor effects because the complex bentonite efficiency is a function of montmorillonite. Therefore, the quality of bentonite is directly proportional to the content of montmorillonite so that the exchange capacity fixed as described above suffices to express the quality of bentonite.

In case of some special uses, for instance as catalysts in petrochemistry, other properties are looked for which result from chemical composition and physical structure under conditions of catalysis and the significance of montmorillonite content is rather subdued. However, in general, it is valid that the less montmorillonite the lower is the total exchange capacity and the lower is the quality of bentonite.

The looked-for properties of bentonite can be broken down into two groups; in the first one, there are properties resulting from crystallography of bentonite whereas the second one comprises properties resulting from physical-chemical composition.

Properties resulting from structure of crystals

- binding power
- sorption capacity
- dispersivity
- filling properties
- electro-static properties

Properties resulting from physico-chemical composition

- ion exchange capacity
- catalytic properties
- capacity to create organo-derivates
- capacity to create new crystalline phases
- possibility to produce special chemical matters and building materials

The above variety of technological properties brought bentonite into tens of national economic sectors as useful material. It can be useful to review concisely principal uses altogether with a property or a group of properties which make bentonite useful or indispensable for a particular end-use:

Foundries - bentonite is used to bind foundry sands

Civil-engineering - bentonite has found various applications owing to its binding and filling properties. It is used for insulations, in grouting and jetting of different foundations.

Building materials - bentonite is mainly used as cement clinker additive and component of various clay building materials.

Metallurgy - bentonite is used both for its binding capacity and ability to create new crystalline phases. The iron ores, especially unusable fines are pelletized by bentonite which enhances also their reduceability.

Ceramics - bentonite is used as plasticizer and agent enhancing green strength of ceramic bodies.

Food processing - the selective sorption capacity of bentonite is exploited to decolourize edible oils and refine wines and juices.

Oil well drilling - bentonite is an important component of drilling fluids which have various functions in oil rigs.

Textile industry - fulling of woollen fabrics was probably a first use for bentonite. Its sorption capacity and electrostatic properties are utilized also for textile thickening and antistatic finish.

Oil refining and other chemistry - all properties of bentonites are exploited for various purposes. Bentonite is used as cracking catalyst, bleaching agent to refine oil and grease, carrier of pesticides and insecticides, plastics filler and dessicating agent of gases and vapours, component of thixotropic varnishes and lutes.

Paper industry - special duplicating non-carbon papers, ink encapsulating are main fields for bentonite.

Agriculture - bentonite is used for its sorbent capacity as soil conditioner to reclaim arenaceous soils and improve ecological balance, as mineral additive to forage and for food granulation.

III. EXTRACTION AND UPGRADING OF BENTONITE

1. Extraction

A great part of bentonite deposits in the world are of secondary origin. The material in secondary deposits is of higher purity in comparison with primary deposits because of separation of clastic materials during the natural washing and transport.

The bentonite deposits show a character of stratigraphically relatively constant horizons, layers or lenses, the thickness of which is usually several meters.

The overburden of secondary deposits is usually composed of clays and bentonite material of lower quality and its thickness varies from centimeters to tens of meters. The underlayer is being formed of parent rocks, which may be partly bentonized, or of bentonite of marginal quality or other rocks.

As bentonite is a clayey rock, extraction methods applicable for soft materials, such as clays and brown coal, are used to mine bentonite.

The economy of extraction depends on many factors and local conditions, such as ratio between overburden and exploitable layer, thickness of the layer, homogeneity of deposited material, transport and energy resources and costs and, of course, on the quality and quantity of bentonite in the deposit as well as on its location.

The access to the deposit and possibility of using cheap and effective transport are very important factors of the economy of extraction. For example, the transport by sea of Greek bentonite to Eastern Canada is more economical than railway transport from Wyoming, which is much closer to the spot of consumption. (M. Kužvart, Industrial Minerals and Rocks, Academia, 1984)

Open-pit mining

Quarrying from open face is the most frequent extraction method to win bentonite. It is generally applied when sufficient layer of bentonite of required quality is situated under adequate overburden. (Photo 1)

The overburden is removed by means of shovel excavators, scrapers and bulldozers. In large quarries with thick layer of overburden it is possible to use bigger mechanisms, such as digging wheel and bucket ladder excavators. The stripped surface of bentonite layer is then cleaned by grader to reach as pure as possible bentonite deposited.

The extraction proper of bentonite is carried out usually by smaller machines, such as shovel excavators and bulldozers, because these machines enable to extract material selectively which is difficult when larger digging wheels or bucket ladder excavators are used. (Photo 2) As the bentonite layers are often composed of several relatively thin particular layers of materials and the thickness of these layers varies along slope wall, it is economical to mine selectively. If there are relatively small inclusions of impurities in a large deposit of quite homogeneous material, selective extraction of these impurities may be economical (sometimes even by underground mining) followed up by a large scale mining by means of heavy excavators.

Generally, caterpillar excavators are more suitable than truck excavators because of possible low bearing power of bentonite rock, mainly in rainy weather. As the bentonite is soft rock usually blasting is not used in quarrying operations.

The extracted material is transported by means of trucks, dampers or belt conveyors to the beneficiation plant or to warehouses.

If the quarried material is contaminated with large stones or sand it can be economical to separate these admixtures from the excavated rock direct in the quarry in order to reduce the quantity of transported material. A case study is to be made to evaluate the best extraction and up-grading process.

Underground mining

As the cost in underground mining is often prohibitive for the comparatively cheap materials like bentonite, this method is generally applied only in special cases when deposits of high quality bentonites are located under thick layer of overburden, or if there is sufficient local market for bentonite which cannot be supplied by imported bentonites at competitive prices.

The thickness of overburden is usually in the order of tens of meters and therefore the mining through the inclined adit from the slope is possible and preferred to shaft mining.

Bentonite deposits are generally located in soft rocks and for this reason usually no blasting is necesary for mining. The mining methods are similar to those of coal mining.

The underground mining is used for winning bentonites of the highest quality in Wyoming, Bavaria and Hungary. This method is used only rarely as being costly and technically demanding considering the low price of bentonites and, therefore, it is not recommendable for initial phases of bentonite processing in developing countries.

2. Up-grading

The up-grading methods consist usually of the three following steps:

1/ Separation of undesirable impurities that decrease the relative content of montmorillonite in the rock and contract its usability.

2/ Physico-mechanical beneficiation which means bringing the rock into suitable and desirable forms without changing its natural chemical character.

3/ Chemical-mechanical activation which means a reasonable control of the chemical and mineralogical properties of material with the aim to accommodate the properties of bentonite in maximum degree to the purpose of its utilization.

Usually, the chemical activation is proceeded by appropriate physical-mechanical treatment both in one technological process.

Separation of impurities

The material can contain a considerable amount of parent rock or other rocks (in secondary deposits) in the form of stones, boulders and pebbles or sand.

Different ways of separation of these impurities are applied in accordance with their granularity and percentage.

The largest stones and boulders of as far as 120 mm diameter are separated by means of grates, pebbles can be separated in special drum push-through separators.

Non-plastic admixtures such as limestone, rock gypsum and coarser particles of sand can be separated by screening. The raw material is pre-dried and crushed to the grain size of several centimeters. As the material is not dried completely, the bentonite, which is plastic material, agglomerates into the largest pieces and its dry portions are concentrated in the finest fractions while non-plastic impurities pass into the medium grain size fraction.

For example, Egyptian bentonite containing about 8 per cent of gypsum was pre-dried in the open air, crushed and then screened through the sieves with mesh diameter 0.6 mm, 2 mm and 20 mm. The fraction over 20 mm contained about 30 per cent of original content of gypsum, the gypsum content in medium grain size fractions was about 200 per cent of original value and the finest fraction was of almost the same gypsum content as the original material as it is shown in the following table:

Results of sieving of Egyptian bentonite

Fraction	Per cent	Gypsum content /%/
20 mm	59	2.4
2 - 20 mm	31	16.6
0.6 - 2 mm	6	13.7
0.6 mm	1	10
Losses	3	

Source: U.S. Felix, A. K. Ismail: Terminal Report on Activation of El-Fayoum Bentonite, Cairo, 1986

This process of course depends on many factors, such as moisture of material, hardness and brittleness of components, plasticity of bentonite and other sorbents which can vary in wide ranges for each individual raw material. For this reason it is necessary to find optimum conditions for separation of non-plastic admixtures from the point of view of moisture, grain size, drying conditions and mesh diameters of used sieves.

If the raw material is dried thoroughly and milled to the grain size of several millimeters, the bentonite as a soft material is more concentrated in the finest grain size fraction, while non-plastic materials, which are more resistant to disintegration, remain in coarser fractions.

If the impurities occur in the raw material in the form of sand, the washing of material is suitable method for this beneficiation. The process is then similar to washing of kaolin.

The raw material is blunged in water in propeller or drum blunger and the boulders, pebbles and sand are separated by means of rotary drum screen separators and vibrating screens. The finest fractions of sand can be separated in hydro-cyclones. The resulting slurry of washed bentonite is then concentrated by sedimentation. Various synthetic flocculants can be used to intensify the sedimentation process. The concentrated slurry resulting from sedimentation process can be dewatered by filter-press or directly dried in spray-driers.

As the montmorillonite is strongly swelling mineral, the bentonite slurries are usually thixotropic and viscous, although they contain relatively high quantity of water. The rheological properties of bentonite slurries depend in high degree on the cationic cycle of montmorillonite. The swelling of montmorillonite and delamination of its crystalline structure in water results into very fine dispersity of bentonite particles in slurries.

Natural bentonites where montmorillonite is in calcium or magnesium cycle, can be blunged into stable slurries of rheological properties suitable for consequent handling with concentration of solid phase between 200 and 300 grams in one litre of charge. If the montmorillonite is present in alkaline (sodium or potassium) cycle, the slurries are very thixotropic and the suitable content of solid phase in slurries is much lower, usually between 50 and 100 grams in one litre.

These extraordinary rheological properties of bentonite suspensions brings about specific problems in wet processing of bentonite.

If bentonite slurry is dewatered by filter-pressing, the filtering resistance of filter-press cake is much higher than that of other ceramic raw materials, such as of kaolin. For this reason the production capacity of filter-presses for bentonite slurries is several times lower than in case of kaolin, however, the highest filtering presses are applied. The moisture of resulting filter-press cakes is relatively high (from 50 to 60 per cent) and there is often semi-fluid zone in the center of cake. Though energy intensive the spray-drying of bentonite slurry is preferred to since it is technologically simpler than filter-pressing.

To reach one ton of bentonite with moisture content about 10% (usual moisture content of "dry" bentonite), it is necessary to evaporate about 2 500 kg of water in the case of spray drying, while when filter-press is applied, the quantity of evaporated water is only about 1 000 kg.

On the other hand, the heat efficiency of spray driers is much higher than that of driers which are applicable for drying of filter-pressed bentonite, such as belt driers or rotary driers.

Also the granulometric composition of spray dried material is advantageous for further utilization and it can be controlled in quite wide ranges, while bentonite produced by filter-pressing and drying must be subsequently attrited to the final granulometry.

The washing of bentonite is much more expensive in comparison with other beneficiation processes as well as with washing of other ceramic raw materials.

From the point of view of economy this process is pertinent in such cases when it enables to win material of extraordinary quality or when no other sources of good raw material which does not require the washing, are available in economical distance from the place of consumption.

As the spray drying of bentonite is troubled with high wear of equipment not speaking of high energy demand, in the countries favoured with sunny and dry weather the drying in the open air with drying-up on belt or other driers will suffice for further processes.

As the wet up-grading method enables to reach the highest beneficiation of raw material, it is very advantageous in such cases, when there is possibility of direct use of slurry in subsequent industrial activity without necessity of its drying.

This method is applicable in situations when the slurry is consumed in economical distance from the place of its production. The fact that for each ton of bentonite in slurry it is necessary to transport about 2.5 tons of water must be taken into consideration. It is also possible to transport raw bentonite to the spot of its consumption and to wash directly before its application. The transport costs of raw bentonite will probably be lower than costs of slurry transport and in addition further economy is reached by avoiding necessary storing tanks. However, it is to be born in mind that the waste from the washing process must economically be disposed of.

The washing of bentonite is also applied as a first step of up-grading process when specially activated bentonites are manufactured by wet method, such as for example acid bentonites for bleaching purposes (bleaching earth), for catalyzers or, in some cases, of bentonites for wastewater treatment.

Physico-chemical activation

In many industrial applications bentonite is possible to be applied in natural mineralogical form. For this purpose, bentonite is homogenized, dried and milled to the required grain size.

Raw material from quarry or mine is transported to the homogeneization stock-piles when the primary homogeneization is accomplished by means of controlled depositing by bulldozers and charging suitable parts of material to the technological line. The homogeneity is controlled by moisture content and mineralogy.

Raw bentonite from homogeneization stock piles passes through the grates, where disintegration of largest pieces of rock occurs, to the dozer. (Photo 3) Different types of dozers, such as drum or chamber dozers, are used. The dozing rate is controlled in accordance with input moisture, to get dry, but not overheated material in the output and to ensure regular operation of technological line.

The first technological operation is primary disintegration. Material passes through the pan-mill, push-through mixer or clay cutter, where it is diminished to the pieces under 2 cm in diameter which are suitable for following drying.

On condition of favourable climate, when raw material excavated has low content of moisture, or when material is dried naturally during homogeneization in stock piles, the jaw crusher or roller mill can be used for primary disintegration.

Pre-crushed material is then dried and milled to the final grain size. The drying of bentonite is the most important operation in whole the process. The extraordinary properties of bentonite, such as high plasticity, sorption capacity and ion-exchange capacity have their origin in crystalline structure which is given, beside others, by presence of lattice water and molecular water in interlayer spaces. This inter-layer water is bound very slightly and it loosens at low temperature between 80 and 120°C. It was proven that this water liberated even in water milieu. When water suspension of bentonite was boiled (100°C) for 30 minutes, bentonite plasticity and sorption capacity were reduced by about 20 - 30%.

For this reason it is important to control drying process very thoroughly and to ensure that temperature of bentonite will not exceed 80°C.

Bentonite is usually dried in co-current rotary driers or air-stream driers. The driers are heated by combustion gases of gas or oil fuels. The inlet temperature of combustion gases must not exceed 450°C to prevent from a thermal deactivation of heated bentonite.

Outlet moisture of bentonite at these drying conditions is about 8 - 12%. This value is sufficient for predominant part of applications, if bentonite is to be used for dessicating purposes, its moisture has to be about 1%.

The dried bentonite is milled in different types of mills to the final grain size.

Attrition mills, pan-mills and edge-runner mills are applied most frequently. Mills are provided with air-classifiers and separators of waste, cyclones, slot classifiers and sleeve filters.

The milling is often joined with drying (or final drying) to one operation. The raw bentonite is in this case pre-dried from natural moisture of about 35 per cent to moisture cca 20 - 25% in rotary drier or other equipment and then it is dried and milled in drying mill, which can be of different construction (hammer mill, rod-disintegrator, vibrating mill, pan mill, etc.)

The drying mills are heated with hot combustion gases from combustion chamber, the fuel is usually gas or oil. The drying gases are utilized also for air classification of milled bentonite.

The dried and milled bentonite is stored in bins or packed in paper bags. As it is in powder form, it enables transport by air. During storage and transport the material must be appropriately prevented from humidity. If the washing of raw material is applied as the first step of up-grading, then the spray drying is the most used method because it gives pulverized product without milling and attrition.

Figures 3, 4 and 5 show typical technological arrangements of production of dried milled bentonite.

3. Chemical-mechanical Activation

The technological properties of bentonite can be in a great extent influenced by chemical activation. The chemical activation consists in controlled ion-exchange of "foreign" ions in defect points of crystalline lattice of montmorillonite. The ionic radii and valence of the foreign ions differ from those of regular ones and therefore they are more or less slightly bound and also interchangeable with other cations. Generally, the smaller the cation, the stronger its bond to crystalline lattice. Small ions, such as sodium or ammonium ions, can replace very easy calcium and magnesium ions in natural bentonites.

As the ion exchange occurs between solid phase - montmorillonite, and liquid phase - water solution of activating inorganic salt, always an equilibrium is established during the ion-exchange process. This equilibrium can be influenced by an anion of activating salt. If the insoluble salt is formed from the original cation of montmorillonite and anion of activating salt the ion-exchange runs almost quantitatively. For example, if the natural bentonite is in calcium ionic cycle and it is to be activated in sodium cycle, the activation with sodium carbonate is more effective than with sodium hydroxide, because calcium carbonate is much less soluble than calcium hydroxide and, thus, the concentration of Ca^+ in liquid phase is much lower in this case. On the other hand, it is almost impossible to reach good ion-exchange with sodium chloride, because of high solubility of calicum chloride.

In strongly acid milieu, the montmorillonite is always in H^+ cycle.

Sodium activation

As the sodium cation has very small ionic radius, it penetrates very easy into crystalline layers of montmorillonite and thus opens its structure. This delamination of montmorillonite results to considerable changes of properties of bentonite. The natrified bentonite has extraordinary high plasticity and binding capacity and its water suspensions have thixotropic and geleous character even with low content of solid phase. As mentioned before, the water suspension of about 50 grams of bentonite in one litre has geleous character and it does not flow.

The extraordinary rheological and technological properties of sodium bentonite are the reason of its wide applicability in industry. The sodium activation is the most applied up-grading method for bentonite.

There is practically only one activating agent for sodium activation - sodium carbonate. In comparison with other sodium components it has many advantages, especially:

- low price
- good solubility in water
- relatively low corrosion
- good activation efficiency (due to creation of insoluble calcium and magnesium carbonate)

There are principally three possible technologies for sodium activation of bentonite:

a/ <u>Dry technology</u> where dried bentonite is milled jointly with sodium carbonate and activation occurs mostly during application.

b/ <u>Wet (or paste) technology</u> when raw bentonite is moistened with water solution of sodium carbonate to the form of plastic paste and activation occurs during kneading.

c/ <u>Activation in slurry</u> when sodium carbonate is added to the water suspension of bentonite and activation occurs in slurry.

a/ <u>Dry technology</u>

This technology is the most simple modification of sodium activation but the product is not of comparable quality with the other technologies.

The technological process is almost the same as drying and milling of natural bentonite. The raw material is coarsely disintegrated in the pan mill and dried in the rotary drier to the moisture about 12%. Then it is fed through the belt balance to the mill. Sodium carbonate is dosed by another belt balance to the same mill, the weight ratio between bentonite and sodium carbonate varying from 100 : 2 to 100 : 5 in accordance with the quality of raw material and application requirements.

The joint milling to the grain size of about 60 - 80 micrometers ensures thorough mixing of both components. As the material fed to the mill has a very low content of water, the amount of liquid phase on the surface of crystals is small and ion-exchange occurs in low degree. The manufactured product is actually a mixture of natural bentonite and sodium carbonate. The activation proper does not occur until application when bentonite is mixed with water. Because the activation process is more intensive at higher temperatures this process does not lead to the product of as high quality as the wet process.

On the other hand, in this process there is no handling with solutions of sodium carbonate or with alkaline wet material almost avoiding problems with corrosion of equipment.

b/ <u>Wet technology</u>

The wet technology ensures a thorough homogeneization of components and activation, that is ion exchange of Ca^{2+} and Mg^{2+} ions for Na^{+} ions during technological process.

Raw bentonite passes through the grates and it is fed to the wet pan mill or passed through mixer, where it is moistened with water solution of sodium carbonate to the form of plastic paste with moisture content of about 35 per cent. (Photo 4)

The paste is then kneaded in two axis mixer or, better, in pug mill and then it is extruded in the form of noodles of about 1 - 2 cm in diameter. The steam curing of material during kneading can advantageously increase the quality of the product.

The granulate from kneading machine is then fed to the rotary drier, where it is dried by combustion gases from the combustion chamber, which is heated with oil or gas. (Photo 5)

The combustion gases flow co-currently with dried material to prevent overheating of bentonite and its consequent deactivation. The temperature of dried material must not exceed 80°C.

An elevated temperature during drying positively influences the activation process. The dried material from rotary drier then enters to the mill, where it is milled to the grain size of about 60 - 80 micrometers.

The product of wet activation process is of high quality, because in addition to the chemical activation of sodium ions, the mechanical kneading supports delamination of crystalline structure of montmorillonite.

There are also other simplified modifications of wet process which are in fact compromise between wet and dry process. If the raw material in the stock pile is wet enough (about 30 per cent), it is possible to doze sodium carbonate in crystalline form to the pan mill on the beginning of the technological line or, in the most simple case, it is possible to mix raw bentonite with solid sodium carbonate directly in the stock pile.

Due to high moisture content of raw bentonite and good solubility of sodium carbonate, the reaction sets in already in the stored material and is usually accomplished in the pan mill and drier.

The ion exchange takes place in all phases of the process when bentonite is saturated with soda solution. The elevated temperature during drying, mainly at the beginning of the drying process when the moisture content is high enough, accelerates the ion exchange. If the dried material is milled to fine powder under 40 - 60 micrometers the quality of the product is comparable with that of wet process. The production costs are much lower, mainly due to lower heat consumption and simpler equipment in technological line.

c/ Activation in slurry

There is also theoretical possibility of carrying out the natrification process in a slurry, mainly in such cases where the washing of raw material is a primary step in the beneficiation of bentonite. It is possible to add sodium carbonate to the slurry of blunged bentonite and to homogenize it in a propeller mixer or better in a ball mill where ion exchange sets in concurrently with a thorough dispergation and mechanical delamination of montmorillonite.

Unfortunately, this process, which could be very attractive from the point of view of technological equipment, is usable only in rare cases. The main problem of activation in slurry is on the fact that the slurries of alkaline bentonites are strongly thixotropic and they are geleous even at low content of dry material and thus the maximum content of dry material in water suspension of alkaline bentonite which allows the slurry to flow is about 50 g per one litre. The filter-pressing of this slurry is almost impossible due to fine dispersity of alkaline bentonites which results into extraordinary high filtering resistance. Drying such slurries in spray driers is usually uneconomical due to high amount of evaporated water. It is necessary to evaporate about 19 tons of water to win one ton of dried product.

Because of the above disadvantages the activation in slurry is usable only when the slurry can be consumed directly on the spot of its preparation. Natrified bentonites must be protected against air moisture during despatch and transportation. Waterproof bags (Photo 6) or tanks are usually used for this purpose.

Acid activation

Acid activation of bentonite consists not only of replacement of exchangeable ions with hydrogen ions H^+. Dissolving of compounds of aluminium, magnesium, calcium and iron is of great importance in this process.

Al_2O_3, Fe_2O_3, MgO, CaO and other components are dissolved during acid curing. Also crystalline water is liberated. The dissolving of some oxides and water liberation opens the crystalline structure and results into creation of pores of diameter 1 - 6 nm. Silicon dioxide, remaining in the crystalline lattice is, to a small degree, transformed into geleous form.

The complex of acid activation is not yet fully understood and is matter of many investigations. Generally, it can be said that during leaching of bentonite in strong inorganic acids the dissolution of some components results into significant increasing of specific surface area and porosity of the treated material. These structural changes result into enhancement of sorption capacity. Also selectivity of sorption for different materials can be, to a certain degree, controlled by dimension of pores.

The quantity of dissolved material is quite high. To win 1 ton of dried acid activated bentonite (which is often called bleaching earth in accordance with its main application) it is necessary to work about 2 tons of raw bentonite and consumption of 32-per-cent hydrochloric acid is about 1.5 ton.

Hydrochloric acid is most frequently used for leaching bentonite. The good solubility of all leaching products is the main reason for use of hydrochloric acid. Chlorides of iron, calcium, magnesium and aluminium are very easy to solve while calcium sulphate is insoluble and solubility of ferric sulphate is limited and its sensitivity to hydrolysis during washing is very high.

Consequently, the leaching in hydrochloric acid is preferred to leaching in sulphuric acid, however, the application of hydrochloric acid is accompanied with certain technological difficulties, such as high volatility of hydrogen chlorid and its corrosivity and irritable smell. The disposal of acid waste waters from hydrochloric acid activation is more difficult in comparison with wastes from sulphuric acid activation. There is no insoluble salt of hydrochloric acid and, therefore, no precipitation method is applicable to liquidate effectively chlorides while most of sulphates are easy to precipitate with lime.

On the other hand, the quality of product is much higher if hydrochloric acid is used for leaching and also hydrochloric acid is usually cheaper than sulphuric acid.

The technological process can vary according to local conditions and possibilities but it always consists of the following basic steps:
- blunging of raw bentonite
- leaching in inorganic acid
- separation and washing of sludge
- dewatering of sludge
- drying and milling
- liquidation or recycling of acid wastes

Raw material is blunged usually in propeller blungers to the form of dense viscous slurry. The propeller blungers are most suitable because they enable to prepare slurries of higher content of solid phase. The pebbles and coarser grains of sand are separated from slurry by sedimentation in the blunger, finer sand particles are separated by screening of the slurry through vibrating screen. The mud is then pumped to the leaching tank. The leaching tank must be protected against corrosion because the leaching is carried out in strongly acid milieu of hydrochloric or sulphuric acids. Sooner pitch-pine wood was preferred as the construction material for this purpose. Presently, the stainless steel, rubber-coated steel, reinforced plasts and glass are used as the construction material. The leaching tank is equipped with low-speed paddle-wheel agitator and can be heated. The most simple is heating with live steam which requests to bring only the steam to the bottom of the tank by means of stainless tube. After filling the tank with slurry from blunger, a defined amount of hydrochloric or sulphuric acid is added to the slurry. The content of the tank is continuously agitated. Then the acidity of slurry is checked and if it is adequate to the required value, the live steam is brought to the leaching tank. After reaching the boiling point the agitation is stopped and content of tank is left to leach without agitation for about 24 hours.

Then the slurry is thoroughly mixed and the content of residual free acid is checked. This acid content indicates the degree of leaching. As soon as material is leached sufficiently, the mud is dewatered and washed with water. This operation can be carried out in different ways. The mud can be dewatered by filter-pressing and filter-press cakes are then washed with soft water directly in the filter-press. The required level of residual free acidity is 0.03 - 0.05% in properly washed material. This residual acidity is checked by laboratory testing, when 20 grams of washed product (calculated as a dry material) is neutralized with 1 - 2 drops of 0.1 molar solution of NaOH (indicated with methyl orange). Higher acidity deteriorates the quality of product but too intensive washing can also be detrimental to the output quality due to ion exchange of hydrogen ions in activated bentonite with magnesium and calcium ions from washing water.

After washing the filter-press cakes are dried in belt or etage driers. Other types, such as rotary driers, are usable as well. Material is dried to the residual moisture content of about 8 per cent, maximum temperature of drying bentonite must not exceed 120°C. A higher drying temperature and lower final moisture content result into the product desactivation. Alternatively to filter-presses dewatering and washing can be carried out in battery of decanters. The slurry after leaching is diluted with soft water thoroughly mixed and then left to settle to thicken. The densified mud after sedimentation can be dewatered in the centrifuge and then once more mixed with washing water. The washing is repeated 2 or 3 times and slurry from the last sedimentation is then dried in the spray drier at similar conditions as in other drying process of bentonite, e.g. maximum drying temperature 120°C and residual moisture content of about 8 per cent.

Technological schemes of both the described processes are shown in Figures 6 and 7.

The acid activation brings forth a problem of acid waste water treatment which can be regarded as a major trouble. Waste water from leaching and washing contains certain quantity of hydrochloric or sulphuric acids which can be partially recycled to leach the following charge. On the other hand, this water contains leaching products which makes impossible a recirculation of whole the volume of leaching lye. For this reason only a part of acid washing waters can be recycled to the blunger and the mother liquid from filter-pressing or from the first decantation must be neutralized in the neutralization tank.

The neutralization is usually carried out with lime. The neutralization has to be controlled to reach pH values between 7 and 8, when predominant part of leaching products, such as ions of aluminium and iron, is in insoluble form of hydroxides. If sulphuric acid is used for leaching, also ions of calcium are precipitated during neutralization to the form of calcium sulphate.

Owing to the above reactions the wastes from leaching with sulphuric acid are easier to dispose of in comparison with the hydrochloric acid when waste water contains more soluble products and consequently more salts.

Other activations

In addition to alkaline and acid activations, there are also requirements for activation in other ion cycles, such as Al^{3+}, Fe^{3+}, Mg^{2+}, Ca^{2+}, etc. These types of bentonites are usable mostly in waste water purification and in the production of catalysts.

Generally, there are two ways usable for special activation, differing in the purity of product.

a/ Direct activation

The activation with water soluble inorganic salts of activating ion is a simpler way. It resembles the alkaline activation.

The ion exchange equilibrium between natural montmorillonite and activating ion is established during activation process. Almost all free Ca^{2+} ions in montmorillonite crystalline lattice can be replaced with activating ions if the activating salt is sulphate. In this case the ion exchange equilibrium is advantageously deviated to the side of activating ion because of creation of insoluble calcium sulphate from sulphate anion and calcium ion loosened from bentonite.

All processes suitable for alkaline activation, such as dry process, paste process and slurry process, are applicable for this type of activation with other ions. The slurry process is more suitable than in case of alkaline activation, because water suspensions of bentonites in non-alkaline cycles are not so thixotropic and geleous and it is possible to prepare these suspensions with good rheological properties containing about 300 grams of bentonite in one litre.

The direct activation is quite cheap and simple process but on the other hand, its product is always equilibrium mixture of different ionic forms of montmorillonite, activating salts and by-products of activation. The position of equilibrium depends on concentration of activating ion, type of anion, pH value and, if bentonite is in water suspension, also on concentration of suspension. If these conditions are changed during the application of bentonite, also equilibrium position is deviated and bentonite can change its properties. This phenomenon is advantageously utilized in the case of waste water treatment with specially activated bentonites.

The quantity of applied activating salt varies in dependence on ion-exchange capacity of bentonite and required degree of activation, usually it is from 0.2 to 0.6 mols of activating ion per one kilogramme of bentonite.

b/ Full ion exchange

To reach full ion exchange and to win pure bentonite in defined ion-cycle without activation of by-products, it is necessary to apply more demanding process than direct activation.

The acid activated bentonite in which all exchangeable ions are replaced with hydrogen ions is used as a raw material for further activation. The acid bentonite is blunged to the dense slurry about 200 - 300 grams of bentonite in one litre and then the water soluble salt of activating ion is added to the slurry in the solid form or as highly concentrated solution. The dose of activating agent has to be several times higher than the ion-exchange capacity of acid bentonite in order to reach the highest possible replacement of hydrogen ions in bentonite with activating ions. As the hydrogen ions are released from the crystalline lattice to the water phase during activation, the water phase becomes acidic. Higher acidity of water phase then decelerates the ion exchange and it can deviate ion exchange equilibrium position to the acid form of bentonite. For this reason the pH value of the slurry has to be kept as close as possible to the neutral milieu but, on the other hand, it must not exceed the value at which the hydrolysis of activating ions occurs. This value depends on the character of activating ion and on its concentration in water phase and it can be calculated from the solubility product of appropriate hydroxide. For example, at usual concentrations of activating ions about 1 mol in one litre of water phase the recommended value of pH is for

Al^{3+} ions	under 3.5,
Fe^{2+} ions	under 5,
Fe^{3+} ions	under 1.6.

The pH value cannot be controlled by adding ammonium or alkaline hydroxides since there is a danger of binding this ion to the crystalline lattice of montmorillonite. For this reason only hydroxides of appropriate activating ions such as $Fe/OH/_2$, $Fe/OH/_3$, freshly precipitated and washed $Al/OH/_3$ in quantities which are able to be dissolved in free acid can be used to control pH value.

After dosage of activating agent the slurry is heated to the temperature of about 80 to 100°C and kept for several hours at this temperature to accomplish the ion exchange. Then the slurry is dewatered and washed in the same manner as in the p[illegible]tion of acid bentonite. The mother liquor from dewateri[illegible]s not contain any impurities from activation besides enhanced acidity and so it can be recycled to the blunging of acid bentonite after adjustment of pH. Also washing water can be reutilized in the same way.

If the special activation of bentonite is carried out in the place of the production of acid bentonite, it is advantageous to use the dewatered and washed acid bentonite before drying because of energy saving in drying process.

The dewatered specially activated bentonites can be dried in the way usual for other types of bentonites. Spray driers, belt driers, storey driers as well as drying mills can be used for drying. The maximum temperature of dried material must not exceed 80 - 100°C according to the type of bentonite.

c/ Organobentonites

If bentonite is to be applied in milieu of organic liquids, such as in dye industry, etc. it is necessary to modify its surface with organic compounds in order to reach high affinity to the organic liquids and very low affinity to water.

The organic modification of bentonite is carried out by reaction of alkaline bentonites with hydrochlorides of organic amines in which the carbon chain in akyl group has at least 10 atoms.

The reaction occurs in water suspensions according to the scheme:

Na-bentonite + alkylaminohydrochloride --- alkylammonium bentonite+NaCl

The organic modification of sodium bentonite is carried out in the similar way to the special activation of acid bentonite. The modifying agent is added to the water suspension of alkaline bentonite. Then the slurry is heated and the reaction is accomplished at elevated temperature in several hours. Then the slurry is dewatered and the product is dried and milled. The dried and milled product has hydrophobic character, but it has very good affinity to the organic liquids.

Review of Bentonite Up-grading Process

There are demonstrated diagramatically the particular up-grading processes with the link-up to the end uses in Figure 8.

IV. INDUSTRIAL UTILIZATION OF BENTONITES

1. Foundry and Metallurgical Industries

Binding power is the essential property of bentonite utilized in foundries and metallurgy. Foundry moulding sands consist essentially of synthetic mixtures of sands and clays. The synthetic mixtures are predominating in this field because they can be prepared to meet very precise specifications. Synthetic moulding sands consist of carefully sized sand and their bonding agent is a suitable binding clay, in most cases bentonite. Furthermore, bentonites are also used to recover molding sands. After sieving and dedusting, the small amount of the binding clay which has been destroyed by burning is replaced by new bentonite. In core sands, green strength is often generated by the addition of a small amount of bentonite. Thus, the use of bentonite in foundries may be divided as follows:

a/ Bentonite as the elementary binder for synthetic moulding mixtures for moulds and cores cast without drying (green process) and/or for moulds predried on their surface. These bentonite mixtures are used for casting steel, cast iron and in other branches of metallurgy, such as in casting non-ferrous metals (Al, Mg, Cu) and alloys. (Photo 7)

b/ Bentonite as the auxiliary binder in mixtures containing water glass (its content being 4 - 7%). The content of bentonite accounts for 4 - 5% of the mass and ensures the demanded value of green compression strength usually from 17 to 28 MPa and better disintegration of mixtures after casting. Moulding mixtures of bentonite and water glass harden spontaneously in the air. These mixtures are used for green self-hardening of partly dried moulds in steel foundries, less often in grey cast iron production. (Photo 8)

c/ Bentonite as the corrective agent for conditioning and "activation" of natural moulding sands which exhibit a certain degree of binding activity due to the content of natural clays. By adding 0.3 - 3% of bentonite to the moulding mixture either fresh or after recirculation the binding power will be enhanced as required and the fluctuation in the clay content in the mixture will be balanced. These mixtures are used in grey cast iron foundries.

d/ Bentonite is also applied as the admixture enhancing insufficient binding power of core mixtures with organic binders. The addition of bentonite usually does not exceed o.8% in the mixture and improves the green strength.

e/ Small amount of bentonite (about 2 - 5% of the total) is also added as the dispersion agent for water protective paints used for dried and partly-dried moulds and cores. Bentonite addition prevents relatively heavy particles of grog itself (silica powder, fireclay, milled corrundum, graphite, coke, magnezite, etc.) from sedimentation.

Bentonite used as the binder influences more or less the following properties of the moulding mixtures:

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

Green compression strength as the most important property of moulding sands is given by the content of the plastic binder, i.e. of bentonite. In most foundries the green compression strength values reach up to 35 - 55 MPa. They vary according to the moisture content. From relations among green compression strength, moisture content and permeability ensues the rule - the most suitable bentonite mixture is that with the maximum permeability. Proper determination of the moisture content plays an important role. Moulding mixture with the highest green compression strength for the certain type of bentonite exhibits rather low moisture content and permeability. Thus, this mixture is too dry and moulds and cores have their surface with edges and corners very friable, resulting in casting's defects.

Gases and fumes are evolved during the casting process in quantity depending on the type and amount of binders used. Bentonite itself does not increase the quantity of gases.

Dimensional stability of moulds in the casting process is another factor which may be influenced by bentonite. Binders shrink within the casting process and silica sand changes its dimension positively. These facts are of principal significance concerning prevention of scabs formation.

Scabs are serious defects in foundry processes. The formation of scabs occur within the temperature range 300 - 600°C due to the quick and irregular quartz volume changes at 573°C. For preventing from scabbing,utilization of bentonites with the highest possible compression strength is desirable, e.g. natural Na-bentonite or Ca-bentonite activated with soda fulfil these requirements.

Permeability is another property to be checked in case of moulding sands. It may be defined as the ability to permit the free circulation of air and other gases during casting.

Different binding strength of bentonites is required for various cast materials:

Casting	Green compression strength /MPa/	
steel	machine moulding:	about 40
	hand moulding:	45 - 50
grey cast-iron, non-ferrous metals, light alloys	machine moulding: /small castings/	25 - 35
	machine moulding: /bigger castings/	30 - 40
	hand moulding:	40-55

Requirements on bentonite used in foundries differ in many ways. For example, for green moulds (without surface paints) bentonite should exhibit the following properties:

- high binding power (plasticity, high content of montmorillonite with high sorption capacity, etc.)
- low sensitivity to an excess of moisture (green compression strength must not decrease substantially if the moisture content is two - three times higher than the optimum value)
- resistance against friability during drying
- resitance against repeated heating within the temperature range from 300 to 600°C
- low content of Fe_2O_3 (max. 12%) and no carbonates
- fine granulometry

The standards of bentonites for foundry purposes usually specify values of cation exchange capacity, green compression strength determined on standard bentonite moulding mixture, permeability of the mixture, fineness of milling and the moisture content of the supplied bentonite. All these properties do not cover all the conditions to which bentonite and moulding mixtures are exposed. Moreover, there are not direct relations among bentonite properties. According to local conditions, the suitability of bentonite for foundry and properties which are of the greatest importance may differ considerably (Figure 9). Climate conditions play an important role, too. In countries with a high relative humidity, e.g. during the rain season, many problems with drying and hardening of moulding mixtures containing bentonite and other binders (water glass) may occur. The same mixture which exhibits excellent compression strength values in countries with mild climate may fail in hardening in tropical countries. It is therefore recommendable to evaluate bentonites and all the moulding process under the conditions corresponding to the production conditions as closely as possible.

Bentonite is thus an indispensable binder used in foundries. All efforts of bentonite beneficiation aim at reliability of the casting process and the high quality of cast products. (Photo 9)

In metallurgy, bentonite is also used for iron pelletizing. This is a comparatively new method, having developed significantly only in the past 35 - 40 years. Iron ore pellets have several advantages over iron ore prepared in the ordinary way. From the producer viewpoint it enables to extract and market low-grade and friable ores which under other circumstances would have been unmarketable. For the consumer, iron ore pellets have proved to be excellent blast furnace feed, mainly because of the high iron content, but they also improve handling procedures and there is probably less wastage in the form of the dust. Other advantages include high physical strength, good reducibility, and homogeneous chemical composition, all of which are important in blast furnace technology.

The main reasons for using bentonite are the high green strength resulting from its plasticity, and the high dry strength resulting from its capacity to absorb and to give off moisture. In principle the pelletizing process appears simple but in practice it requires very closely controlled conditions.

Concerning the technology of pelletizing, iron ore is firstly finelly ground to about 80% under 0.044 mm. After upgrading it is dewatered, often in a filter-press, and thoroughly mixed with about 0.5 - 2.5% of bentonite of grain size under 0.1 mm, to which a highly critical proportion of water is added. The mixture is then charged to ball drums (or discs) and rolled into small balls. The action of bentonite is to coat the iron ore particles with a thin film of a highly plastic clay so that they act as nuclei which "snowball" as they tumble, by attaching further layers of feed or smaller balls, until finally the spherical-shaped pellets are formed. When balling is complete, the pellets are carefully dried to avoid decrepitation, pre-heated and then fired at temperatures above 1000°C under oxidizing conditions which promote crystal growth and oxide bridging and thus develop the necessary pellet strength.

Granulometry is of decisive effect on pellet strength and on kinetics of their make-up in green state. The finer are the ore particles the higher is the strength of pellets;

0.2 mm grain size is often taken as the upper limit. However, provided the distribution curve of bentonite grain size is deviated towards finer particles, even coarser particles of ore (larger than 0.2 mm) can be utilized for pelletization.

The wettability of inputs is to be as high as possible since the optimal strength of hardened pellets is affected by a proper utilization of the surface tension of the liquid contained in pores. Consequently, optimal humidity content of particular raw materials is individual and it must be proved. The mineralogical composition of the treated ore influences the strength of hardened pellets.

The main quality requirements on pellets are: sufficient compression strength, shock and abrasion resistance. From the point of view of the firing process, pellets should be porous to draw off vapours and should be thermal shock resistant. As for the process proper running in blast furnaces, important factors are: kind and share of ferric components (magnezite and haematite ore are of widest use), character of slag and the way of filling in the intergranular space.

In general, almost each bentonite used by foundries suits to pelletizing requirements.

2. Ceramics

The small addition of bentonites increases the plasticity of different ceramic green bodies and also increases the green strength. The amount of bentonite added into the ceramic body differs considerably. Technological tests and evaluation have to be done to determine the optimum content of bentonite in different ceramic bodies.

Thus, for instance, if added in the quantity from 2 - 5% bentonite only enhances plasticity and improves workability and mechanical strength of products in green state. Bentonite can also be used for the preparation of casting bodies, however, worse filtering capacity of suspension and/or prolongation of body solidification in the plaster moulds is a consequence which limits the bentonite share in the composition. The addition has a great influence on the viscosity of ceramic bodies in correlation with dispersion electrolyte dosage. Products demanded for whiteness, such as unglazed products and those provided with translucent glazes require bentonites with a low content of chromatogenous oxides of Fe, Ti and Mn (1.5 - 3%). Other chemical, physical and mechanical properties should be well defined, e.g. montmorillonite content and dispersity. Homogeneity and non-variability of bentonite properties are other of important factors.

Natrified form of bentonite is added to special bodies for production of electroporcelain (capacitors, steatite products). It is recommended to use maximally 5% of bentonite admixture as the thixotrophy of the body could then increase.

For application in the ceramic industry, good swelling bentonites containing 4% of alkaline oxides at least are required.

The application of bentonite as a plasticiser is fixed by the following quick test. 10 g of a finely ground bentonite is mixed with 100 ml of distilled water and let to stand overnight after vigorous shaking. The good alkaline bentonite swells forming the gelatinous slurry which must not liquefy during a short period of shaking. To reach these properties unsuitable types of bentonites can be treated with soda for the total conversion of clay into the Na-form.

Sodium bentonite is generally considered to be the most suitable type for utilization in ceramic industry. It is strictly recommended to grind bentonite together with the mixture of raw materials in order to prevent from rise of clusters with the air occluded.

However, the application of bentonite to ceramic production is limited and bentonite additives must be kept under a strict control since the content of minerals montmorillonite and illite enhanced above the optimum are detrimental resulting into cracking during drying. In many African countries, such as Egypt, Libya, Somalia and others, where bentonitic clays are frequently used for the production of bricks, crockery and other ceramic ware, the manufacture is troubled by the above mentioned incidental circumstances. Bentonite for instance worsens filtration of a slurry and increases its viscosity. These problems can be solved using spray drying instead of filter-presses or by an addition of deflocculants. The content of chromatogenous oxides has to be as low as possible otherwise the body colour can be affected.

Due to its outstanding rheological properties, bentonite is also of use in the preparation of enamels and glazes. The addition of clay during the grinding of the crushed enamel maintains the enamel powder in suspension, whereas if diluted by itself it would rapidly settle at the bottom. The control of viscosity and thixotrophy leads to a uniform deposit on vertical and curved surfaces, drying without runs and homogeneous firing.

All these facts show that use of bentonite in ceramic industry deserves proper attention.

3. Civil Engineering

In this field the properties of interest are the following: plasticity, fine particle size, impermeability, swelling, chemical stability and thixotrophy. These specific properties can be exploited in different industrial branches, mainly for foundations of buildings, water systems construction (Photo 10), pargeting facades, etc. Bentonite is also applied as a component of many building materials, such as concrete aggregates and clinker. It is used in a form of water suspensions and pastes.

The diaphragm-wall technique is considered to be the most important application of bentonite in civil engineering. Basically, it is a method of constructing a reinforced concrete wall in the ground to great depths without a casing - a bentonite slurry in suspensions of 3 - 10% is used to hold open the excavation and to stabilize its earth walls until, and during, the introduction of concrete. Just as when used in drilling mud fluids, the bentonite slurry exerts a certain lateral pressure on the whole inner surface of the excavation, penetrates the pores of the soil to form a stabilizing gel, and deposits an impermeable membrane ore "case" on the sides. By this method, fast construction is possible and great savings can be made. Initially a 2 ft. deep pilot trench is dug and faced with concrete on both sides. This acts as a guide for the excavator and as a reservoir for the slurry. Mixed on the site, the slurry is introduced while the earth is being dug. Trenches are usually 2 - 5 ft. wide and dug in sections, or "panels" of 5 - 20 ft. length, each of which is sealed at either end by steel tubes. If steel prefabricated cages for reinforcement are required, these are lowered into the bentonite suspension when the trench has been sunk to the required depth. It only remains to pour in the concrete through a pipe, this displaces the slurry which is then pumped away to waste and/or stored for re-usage. As the concrete sets, the steel retainers are removed leaving a vertical joint against which the adjoining panel is cast. The common applications of diaphragm walls have been works in cut-offs under damps and embankments, temporary works in place of sheet piling, or bored piles, permanent works for retaining walls, load-bearing constructions, shafts, deep basements, underpasses, tunnels, river and dock walls and shaped piles.

Bentonite suspensions should fulfil the following qualitative requirements: enhanced density, a certain degree of viscosity, a thixotropy. Concerning bulk density, it usually ranges from 1.05 to 1.20 metric ton/m^3. In order to prevent the considerably thin bentonite suspension from escaping to permeable layers, enhanced thixotropy is required - it is good enough to use about 6 - 10% of the good quality sodium bentonite (e.g. 60 to 100 kg for 1 m^3 of water). The consumption of calcium bentonite is much more higher. Bentonite suspensions are often stabilized by means of different chemicals (polymers, lignosulfonates, phosphates, starch, soda, water glass, etc.) Alkality of bentonite suspensions should be kept in range from pH = 7.5 (better pH = 9) up to pH = 12.

A similar approach to diaphragm walling is adopted in bored piling, in this instance, the cutting tool bores into the ground, lubricated by the slurry which also prevents cave-in. Sometimes it is necessary to waterproff sub-surface structures - for instance when underdipping new buildings or sinking shafts through waterlogged strata. Here grouting techniques are employed: a fluid is injected into the ground which fills the voids, solidifies and thus stabilizes the ground. Bentonite is a valuable partner in cement grouting as it can penetrate and seal pores under 0.01 mm for which cement-and-water alone is often too coarse. For this purpose, bentonite prepared by wet-milling is able to fill in pores wide 1.10^{-3} - 1.10^{-4} mm. Generally speaking, bentonite-and-cement based water grouts are used in rock and open soil environments, sodium silicate or phosphate bentonite grouts can be used for a variety of strata from fine sand to gravel and when ground waters are lime or salt contaminated. Because bentonite can easily be washed out by strong streams of water, the bentonite grouting must be protected by different linings. Utilization of bentonite in this field results generally into lowering production costs.

In sinking caissons - watertight casings used in laying foundations under water - a 10 - 12%-suspension of bentonite effectively acts as a lubricant between the caisson exterior surface and the soil walls to reduce friction. A cutting edge attacked to the caisson facilitates its emplacement while the bentonite suspension is circulated. Thixotropy suspensions should exhibit their bulk density minimally 1.15 tonne/m^3 for which the concentration of bentonite in suspension given above is high enough. In case that it is impossible to reach the required value of bulk density by adding bentonite and clays, some finely ground heavy minerals, such as barytes can be added. The viscosity of suspension plays also an important role as bentonite particles should penetrate into the pores only to depth of several centimeters.

Bentonite was also involved in the development of a new method and machine for tunnelling through soft ground. The device uses a cutter which revolves in a sealed chamber (the "shield"), containing a slurry of bentonite under pressure. As a cutter penetrates the face, the slurry deposits a clay cake on the tunnel walls, sealing it and preventing collapse. As tunnelling progresses, cast-iron tunnel supports are inserted as the rear of the machine; these also act as a solid base from which the machine can propel itself forward. The spoil is removed by a specially designed extraction device at a controlled rate and pumped to the surface, where it is separated from the slurry in cyclones. The slurry after cleaning is then returned to storage for pumping back to the shield at the tunnelling face. The whole process reduces expenses of tunnelling, particularly in the different ground conditions for which it is designed.

Bentonite suspensions are often used for cheap sealing subsurfaces without demanding for time and hi-tech equipment. In this way, irrigation systems made in sand sub-surfaces are sealed to reduce water losses by percolation processes. The process itself is very simple, being only based on sprinkling powdered bentonite into standing or slow water flows of irrigation runners.By stream of percolating water it is pulled down into bottom and walls of the chamber. Bentonite fills in all pores sealing them. The consumption of bentonite is very low (about 2 - 2.5 kg per sq.m) but the service life is not too long. The same method is applied to seal different pipes and tanks made from reinforced concretes. During pressure tests, water is added by 1 - 5% of finely milled bentonite which seals fine pores in few minutes.

Bentonite is also applied as the compacting agent for gravels and soils. The addition of bentonite to sand-gravel alluvial permits the attainment of high compacting values. Very small amounts, of the order of 0.1 - 0.5 wt%, are sufficient to obtain better results than by increasing mechanical compaction. Thus, impermeable systems with a rigid framework of sand-gravel materials can be obtained which do not present the dangerof compacting during consolidation. In case of rammed water dams, the sealing suspension consisting of 15 kg of bentonite and 0.3 kg of soda per 100 l of water was used. The service life is long enough as proved by an example of the dam perfectly waterproof after 13 years of service.

Small quantities of bentonite can be added to concrete mixtures resulting in their higher binding capacity, strength and water-resistance.(Photo 11) For different types of bentonite different optimal dosage can be found, maximum being about 2 wt.% by which the concrete strength is enhanced by 5 - 15% compared with the untreated concrete. According to the experimental data the use of Ca-bentonite (0.75 - 2.0%) is of great advantage (see Figure 10). Calcium bentonite does not evoke ion exchange which would reduce the active calcium content.

As a cement additive, bentonite improves workability so that cement slurries can be pumped over longer distances. It also suppresses bleeding, which is a defect characterized by separation of mixing water. For clinker firing, bentonite is added in quantity 1 - 2% of the charge. Higher strength of granules which do not disintegrate during pre-heating is reached when bentonite is added. This results into regular operation of kilns.

There are many other fields of utilization of bentonite in the construction industry. A relatively new one is the hydrotransportation of solids. This technique could be used in, for example, mines to transport material to the surface. On the other side, 3 - 4% of bentonite (based on the asphalt content) can be added to asphalt emulsions particularly used for road construction in order to stabilize the system.

4. Drilling Activities

Bentonite performs a variety of functions in drilling fluids and acts as a viscosifier, fluid-loss reducer, suspension agent, etc. Drilling fluids or "mud" is the term used to describe the fluid that is continually recycled through the bit in the rotary drilling holes for oil and gas exploration. (Photo 12) These fluids have to be carefully formulated to perform their essential functions:

1. Lift the cuttings to the surface.
2. Control the well pressure.
3. Seal the formation with a filter cake to isolate formation fluids from the well bore fluids.
4. Protect and not react with the formation to excessively change the mechanical properties of the rock being drilled.

The formation of the fluid to carry out these functions requires that certain properties of drilling fluids have to be controlled. These are:

1. Viscosity which is adjusted to ensure that the cuttings are transported to the surface and that the fluids gel to suspend weighting material;
2. Density which is adjusted either by suspending finely ground minerals or by adding salt to form a dense brine;

3. Fluid loss control which is obtained by the addition of both relatively large particles to block the pores to prevent loss of whole the mud and colloidal materials such as clays or polymers to form a low permeability filter cake;
4. Inhibition which is controlled either by adding salts or polymers to a water based fluid or by formulating the fluid with oil as the continuous phase.

Following two raw materials can meet all the above mentioned requirements: montmorillonite and barytes. Wyoming bentonite which is rich in montmorillonite viscosifies the fluid and also forms an impermeable filter cake . Finely ground barytes could also be added to increase the density of the fluid.

Other minerals have found a market in drilling fluids but their use is not so significant as barytes and bentonite. Calcium carbonate, iron oxide and ilmenite are used as "weighting agent", to increase the density. The organo-bentonite is a special surfactant - treated clay used to viscosify oil based fluids. Attapulgite and sepiolite are fibrous clays that have application as viscosifiers for brines. Mica is used as a larger sized solid to block pores and prevent wholesale loss of fluid.

The required bentonite must have good swelling properties such that it will show gelation at concentrations of about 5% solids. Both natural and synthetic sodium bentonites are used for this purpose. Wyoming type "swelling" bentonite is a typical example of the natural product and natrified fuller's earth of the synthetic one. Sometimes the gelation properties of both are further improved by adding water-soluble organic polymers to produce "extra-high yield bentonites". The whole field of drilling fluids is highly technical and complex and the specifications for drilling grade bentonite are consequently very tight.

The drilling fluid contains from 6 to 8% of sodium bentonite. In case of the calcium type its concentration in the suspension must be considerably higher and from the economy point of view, use of sodium bentonite is preferred.

Thermal stabilization of bentonite suspension seems to be very important. During the drilling of the rock into the depth 4,000 - 6,000 m, the suspension is heated up to 100 - 250°C. By heating the suspension, particles coagulate irreversibly in the electrolyte-rich brine resulting in an enhanced viscosity and thixotropy of the system degrading thus bentonite decisive properties. Bentonite suspensions have to be protected by means of deflocculants (either organic or inorganic), such as lignates, complex phosphates and protective colloids, such as derivatives of cellulose, polysaccharides, polyacrylates and alginates. It is to be mentioned that calcium bentonites exhibit better protective properties against enhanced temperature and electrolytes.

To prevent from increased adhesion of the bentonite particles on the drilling rods, the suspension is to be treated in such a way in order to minimize the friction and the adhesion ("sticking effect"). That is why the mineral oil in quantity 5 - 15 wt% is often added to the suspension in the presence of an emulgator with amphiphatic structure.

There are many methods of evaluating the efficiency of drilling muds that are mostly based on pressure filtration and evaluation of viscosity under extreme conditions. For the evaluation, API (American Petroleum Industry) and OCMA (Oil Companies Materials Association) standards are used.

The composition of usual bentonite drilling mud is as follows:

Composition of drilling fluid

Component	wt%
liquid phase	90 - 94
sodium-bentonite	6 - 10
protective colloids	0 - 0.2
deflocculants	0 - 0.8
emulsifiers	0.05

5. Chemical Industry

Bentonite plays and important role in chemical industry. It is predominantly used for:

- bleaching of industrial oils, fats and waxes
- reclaiming used lubricants
- manufacture of catalysts
- manufacture of catalysts carriers
- special purposes

a/ Bleaching of industrial oils, fats and waxes

The refining of oils, fats and waxes is based on the selective adsorption of variety of impurities by bentonites which are often called "bleaching earths". Those impurities involve a large scale of different compounds from proteins, fatty acids, gums to dark pigments and traced metals. The resulting products are clear light liquids with better stability and odor.

The bleaching character of bentonite is given mainly by its sorptive properties. Acid-activated bentonites find their utilization in this region predominantly as their sorption capacity and resulting decolorization effect are higher than those of calcium and sodium types.

Bleaching of oils is one of final steps of the refination process. During application of the sorbent, rests of asphalt and bituminiferrous substances are removed. This results in improving chemical stability against oxidation and better deemulgation properties. Mineral oils are treated by two different processes, which are called percolation and contacting.

Using the percolation method, oil is filtered through the sorbent layer of a certain thickness till the sorption capacity of the filling is exhausted. The filters for percolation are of a cylindrical shape of about 3 meters in diameter with the conic bottom on which the perforated or screened bed is situated. The sorbent layer is about 3 - 6 m high. During the process, temperature about 35 - 95°C is maintained. Higher temperature increases the decolorization effect to a certain extent and it has to be used for highly viscous oils and paraffins. Oils for treatment should not content more than 0.1% of water in order not to deteriorate the bentonite activity.

The percolation process can be used either as discontinuous (Figure 11) or continuous (Figure 12) one. Percolation is exploited mainly in case of special oils of the highest quality and natural-occurring bleaching earths are the best suitable materials here. For common grades of oils and paraffins, contact method is more suitable exploiting acid-activated bentonites above all.

Contacting is conducted by the discontinuous cold process or by the continuous hot one. The discontinuous process is preferred in case of smaller amount of light oils (5 - 50 t) to be refined at contacting temperatures from 100 to 110°C. About 0.5 - 10% of the sorbent is added to the heated oil in the suitable vessel and the mixture is stirred intensively at given temperature which is usually 85 - 95°C for oils and 105 - 110°C for paraffins. The contacting period is about 30 minutes for oils and 60 minutes for paraffins. The oil-bentonite mixture is then filtered either on filter-presses or on rotating vacuum presses.

During the continuous process, bleaching earth is dosed automatically to the separate mixer provided with a mechanical stirrer or directly into the oil stream preheated on 85 - 95°C. The mixture of oil and bentonite is then pumped through exchangers into the tube kiln where will be heated on the demanded contacting temperature, e.g. 250°C. From the kiln, the mixture enters the column which serves as the reaction chamber. The mixture (oil and the bleaching powder) is removed from the bottom of a column and it is pumped further through exchangers and coolers into filter-presses. Here the oil is separated from the bleaching earth at 80 - 95°C. This process which is conducted at elevated temperatures (220 - 280°C, upper limit about 390°C) is called hot contacting.

Determination of the bleaching earth ability to decolorize oil is usually done by the comparison of two bleaching clays. From the economic and technological point of view, the sorbent should possess small retaining capacity for the treated oil and good filterability.

b/ Reclaiming used lubricants

Application of bentonites for this purpose is of increasing importance. Many industrial lubricants may be simply regenerated by treatment with a bleaching earth at about 80 - 110°C. Oil from internal combustion engines requires more comprehensive treatment, however, in order to remove water, residual additives, degradation products, unburnt fuel and other contaminants. The process of oil regeneration involves drying the oil by air blowing at 110°C, cooling to about 50°C, and reacting with sulphuric acid to remove residual additives and other degradation products. The resulting acid tar precipitate is removed by settlement perhaps aided by centrifuging. Activated clay is then added to the oil before heating to 200 - 300°C, and steam is passed through the oil to aid in the removal of volatiles as well as provide an inert blanket over the oil. After 10 - 30 minutes of activation at maximum temperature the mixture is cooled to below 100°C, and spent bleaching earth removed by filtration. The resulting oil is able to be re-used as a base blending stock. About 3 - 5% of activated earth is used in the regeneration process although higher doses may sometimes be needed.

c/ Manufacture of catalysts and catalysts carriers

Petrochemistry is the domain of bentonite application for manufacture of catalysts and their carriers. As seen from the Table 2, bentonite participates in variety of different chemical reactions like polymerization, izomerization, cleavage, desalkylation, etc. From all these processes, catalytic cracking in Table 2 is of the greatest importance. Bentonite here acts as the cracking calatyst resulting in high-octane petrol.

Natural and acid-activated calcium bentonites have also been used as catalysts for alkylation of phenols and as promoters for polymerization reactions. Nowadays, bentonite has gradually been replaced by silica and alumina catalysts which can guarantee a higher standard of purity. Silica and alumina are catalysts of the widest use now and bentonite thus is applied in some special cases only.

Assessing of bentonite suitability for the function of a catalyst carrier is based on:
- chemical analysis
- differential thermal analysis
- sorption capacity
- X-ray diffraction
- activity test

The most reliable determination of suitability is the testing on the experimental equipment having similar conditions to those in production. For purposes of catalyst carrier, mainly acid-activated bentonite is used.

d/ Special purposes

Bentonites are outstanding raw materials for preparation of different lubricants and greases. These agents are used in many processes characterized by extreme conditions such as high temperature and pressure, high speed, etc. The preparation of lubricants and greases is mainly based on properties of hydrophobized bentonite which forms a stable gel when mixed with oils and other lipophilic substances.

For these purposes, bentonite must not content any hard mineral particles and must be able to exchange interlayer cations. Hydrophobization of bentonite is made simply by exchanging inorganic cations (preferably Na^+) for organic ones. Properties of organobentonites can be "tailor-made" using suitable organic compounds. Bentonite greases prepared in such a way are known under the name "bentons" and exhibit good lubricating properties within the temperature range from 60 to 200°C, sometimes up to 300°C. They have also a good mechanical and anti-oxidation stability.

There are many other application of bentonites in the chemical industry (as a binder for molecular sieves, production of printing inks) where special activated grades are exploited in a very small amount.

6. Fillers

a/ Dye industry

Bentonites and mainly organobentonites are used mainly as special thickeners, pigments and fillers in the dye industry. The capacity of bentonite to make up gel structure in some organic solvents, such as aceton, esters, organic acids and alcohols, is exploited for the manufacture of thixotropy laquers where the viscosity depends on shear-stress, i.e. on the velocity of deformation (Photo 13).

The addition of quite small quantities of organobentonites to liquid organic systems will significantly influence their rheological characteristics. Viscosity will increase, the flow properties will change since the system become thixotropic and levelling on horizontal and running or sagging on vertical surfaces will be different. In addition solids in the liquid can be suspended, and penetration into porous substrates is controlled.

The only trouble with bentonite is lack of sufficiently white raw material for light dyes. There are only few deposits of naturally white bentonites. If there are light parts in a dark bentonite deposit, they should be extracted selectively since application for dye industry is very profitable.

b/ Paper and textile industries

The auxiliary filler of the technical paper is the principal need for which bentonite is used by paper industry. Bentonite increases stability and homogeneity of the principal filler (usually kaolin), and of the glues, it enhances retention of the kaolin suspension in paper. It was proved that addition of 10% alkaline bentonite enhances the kaolin retention from 45 to 60%, in case of 100% addition of bentonite it raises up to 84%. Quality and technology can be improved by this means. Bentonite is applied for the production of technical isolation papers with better stability against influence of acids, fats and higher temperatures. As an additive to sodium hydroxide, bentonite is used for whitening of spoils in recirculation processing. Organobentonites are sometimes recommended to be applied as fillers into the paper mass.

At present, bentonite finds its utilization as an important component for direct-duplicating papers which use spreads rapidly. One blank paper has its back side coated with microscopic elastic bubbles containing leucodyes which are colourless. The other paper which will become the duplicate is provided with the layer of a special-treated bentonite on the front side. By the sorption-catalytic effect of bentonite and the pressure of a pencil the casing will crush and the leucodye is liberated. On the front-coated paper it reacts with the developer resulting in a visible coloured copy.

In the textile industry, bentonite is applied in several ways: as thickener for yarn dressing and as washing and degreasing detergent for wool cleaning. Further on, it is applied as the active component of textile soaps and as the antistatic agent for synthetic fiber processing. Some alkaline bentonites can substitute for starch and other components in thickeners. Other applications of bentonite in the textile industry involve:

1/ Strengthening of the caproate fiber
Addition of 1% of organobentonite increases the fiber strength by 10 - 12% at 20°C. Non-modified bentonite acts in the opposite manner.

2/ During the alkaline scour of wool the bentonite addition enables reduction of lye concentration.

3/ Removing of carbon from nylon knitworks.

Bentonite was also successfully used for the treatment of wastewaters from wool processing.

7. Cosmetics and Pharmaceutical Industries

Bentonite is largely exploited for the preparation of different cosmetic products, such as soaps, creams, greases, pastes, powders, etc. in which non-stable fats may be partly replaced. It is often a component of tooth-pastes and depilatories. As being compatible with many chemicals (boric acid, phenol, iodine, sulphur) its application in cosmetics is really wide-ranged (Photo 14) Bentonite also plays an outstanding role in soap manufacture. According to given data, an alkaline-activated bentonite may replace from 25 to 50% of fatty acids salts in the soap and binds moreover M^{2+} cations responsible for water hardness. Disintegration washing and cleaning agents on the bentonite basis are also well known.

In the last 30 - 40 years, bentonite begun to be also exploited in pharmacy due to its colloid and rheological properties. It is utilized both as the medicament itself, e.g. adsorbent, antacid or as an auxiliary substance (emulsifier, stabilizer) for preparation of ointments, pills, pastes, etc.

Owing to the fact that water suspensions of bentonite containing more than 10 wt. % of dry matter solidify resulting in formation of the gel substance, preparation of various dermatologic and cosmetic ointments on this basis begun to spread. Bentonite itself is compatible very well with majority of medicinal components which are added into ointments. Bentonite-containing ointments exhibit a good adhesion to the skin and suit also considering their covering possibility. Compared with fatty and/or paraffin ointments the bentonite ones are advantageous as being removable only by lukewarm water from the skin. Bentonite ointments were successfully applied for treatment of chronic surface wounds.

The centre of bentonite exploitation in pharmaceutical industry is principally in an external domaine. In general, bentonite was utilized in the following medical preparations:

1/ Ointments
2/ Medicaments and preventive agents against scalds
3/ Skin protective agent against irritating compounds
4/ Lubricating agent for introducing probes into the human body
5/ Sorbent for digestion disorders

In the last time, organobentonites were successfully proved for the preparation of ointments. Thus, organobentonite denoted as BENTON 34 with the structure of dimethyldioctadecylamoniumbentonite differs from the natural and natrified one as it neither hydrates nor swells in water and is almost hydrophobic.

Some factors influence negatively the application of bentonite in pharmacy. This is linked mainly with a relatively large surface area which could cause a irreversible adsorption of some preparations or some medicaments could be desactivated. It is valuable generally that the bentonite content up to 1% in medicaments can call forth a big reduction in cationic preparations effects.

8. Food Industry

In the food industry, the main areas of bentonite usage are refining of edible oils and fats, sugar refining, breweries and wine production.

The refining of vegetable and animal oils for edible purposes involves the removal of a variety of impurities followed by decolourisation and finally deodorisation (Photo 15).

If hydrogenation is to be performed, this is carried out prior to the final deodorisation stage. It is the purification and decolourisation stage of the refining process that employs an activated bleaching earth which is later removed from the oil by filtration. Two refining processes are available for the production of edible oils - physical or steam refining and chemical refining. Physical refining is used particularly for palm oil although its use is apparently extending into other areas, such as animal fats, coconut, palm kernel, soya, rape and corn oils.

In the sugar refining process, bentonite applies its sorption and flocculation properties. If added in the form of 3 - 6% suspension to the sugar cane juice (the optimal ratio 1 : 1000), the clarification effect of lime and phosphoric acid at pH = 7 - 8 will be expressively better. Moreover, the evaporation ability of juices is enhanced. This procedure is exploited successfully in plenty of sugar factories in Puerto-Rico, Mexico, Middle and South America. In breweries bentonite is applied in the same style.

The most promising application of bentonite seems to be for clarification of wine (Photo 16). Mainly sodium bentonite suits well for these purposes. The colloidal impurities in wine carry positive charge which can be coagulated by stirring a small amount of a electronegatively charged bentonite into the wine. The clarification power of bentonite is also used in the treatment of cider, vinegar, fruit juices, liquor and honey.

9. Environmental Protection - Wastewater Treatment

Bentonite as the sorbent and flocculant

Application of bentonite in wastewater purification technologies is well known for a long time. Generally, it has been used mainly as the auxiliary flocculant or as the "weighting" medium for acceleration of the sludge settlement.

There are many sorbents which have been utilized for this purpose in praxis having different clarification efficiency, accessibility and cost: charcoal (active carbon), hydroxides Al, Fe, Mg, turf, sawdust, bark, slag, aluminosilicates, etc. Some of these materials exhibit only good sorptive properties, some of them are excellent flocculants, too. It is just the case of bentonite which may be used for simple and efficient removal of pollutants from wastewaters.

High blunging and swelling ability given by the presence of montmorillonite forms favourable conditions for good sorption capacity. As many of wide-spread purification methods cannot guarantee high reliability of purification and removal of key contaminants, polluted waters have to be submitted to pre- and post-treatment by means of other methods. Use of various chemical substances and flocculants shows the principal disadvantage in possible secondary contamination of water and sludge (organic monomers, metallic ions) regardless considerably high costs assuming their big quantities. Application of inert materials of the carbon type fails sometimes in case of polar substances. These are excellently sorbed on ion-exchangers but this method seems to be rather expensive in case of large volumes of wastewater which are to be treated. Moreover, the regeneration of ion-exchangers proceeds either by unreasonably high doses of reagents or is impossible when strong bonds between contaminants and the treating agent has been formed.

For purposes of wastewater treatment bentonite has been applied either simple or in compositions with other reagents (it is more common case). Organobentonites found their application nearly exclusively in technologies concerning removal of organic wastes from waters. Bentonite itself without any other additives was successfully used for treatment of wastewaters originated during the wool processing. Application of bentonite is equal - as for the resulting effect - to the former utilization of iron (III) sulphate, calcium hydroxide or organic polyelectrolytes. In addition, bentonite is cheaper and the technological process independent on the pH value of the system within a wide range. Thus, the content of contaminants was reduced by 63% (given as the decrease of chemical oxygen demand - COD). By the similar way organic dyes were taken away from textile wastewaters resulting in more than 98% efficiency. Pollution of water with organic polyelectrolytes was excellently diminished using bentonite in various cationic cycles. A marked dependence between the bentonite ionic cycle and the type of polyelectrolyte (cationic, anionic, non-ionic) was observed.

Briefly summarized, the application of bentonites for wastewaters purification is based on the following properties:

- high value of the specific surface area (up to 800 sq.m per 1 gram),
- ion-exchange capacity (Na^+, H^+, Ca^{2+} ... - bentonites),
- flocculation activity
- role of the "weighting medium" in sedimentation processes (bulk density about 2,200 $kg.m^{-3}$).

The application itself depends on many factors, such as on properties of bentonite, its activation, pollution characteristics and on the content of suspended matter in the treated water. Bentonite is a very suitable agent especially for wastewaters polluted with a higher amount of insoluble, suspended or floated substances. On the contrary, when soluble substances are predominating contaminants, sorption and flocculation processes are less effective.

According to laboratory and pilot-plant tests from the last few years, the most promising results were obtained for the following types of contamination:

- dissolved or emulsified oil matters
- dispersions of organic polymers (washing wastewaters)
- wastes from food processing (milk and meat processing)
- washing waters from cattle husbandry.

Wastewaters with chemical pollution

Outstanding results were achieved by the application of bentonites on waters polluted with organic polymers (acrylate dispersions). These systems are represented by macromolecular compounds which are very hardly degraded within natural conditions. Effluents from the production of acrylic acid and/or its derivatives belong to very unpleasant sources of contamination. Washing and diluted production wastewaters contain 0.1 - 2% of solids, their COD values reaching up to 20,000 mg O_2/l or even more. Structures occurring most often are polystyrene, vinylacetate,esters of acrylic acid, acrylonitrile and monomers. In order to get suitable dispersions, various surfactants are often used. Some of copolymers of acrylic and meta-acrylic acids find their usage in textile industry as sizing media.

Although there are many methods suitable for treating these wastes, mainly by means of inorganic electrolytes like $FeCl_3$, $AlCl_3$, $CaCl_2$....., higher salinity of effluent has often been observed. For flocculation of these wastes, magnesium, aluminium and iron-activated bentonites gave the best results. The dose of activated bentonites used was in range of 5 - 20 grams per litre of wastewater and the sedimentation rates of sludge achieved up to 5 m/hr. By this method, the total clarification of the system to transparent state succeeded (Photo 17), cleaning efficiency being expressed as the difference of COD values before and after the treatment reached 95 - 99%. During the cleaning process, a favourable effect of increased temperature on the flocculation activity was also noticed. Flocks formed at higher temperatures are bigger and can be separated by the simple filtration on screens.

Similar results were achieved for wastewaters polluted with water-soluble dyes, pastes and sizing agents on the acrylate chemistry basis.

Oil containing wastewaters

Bentonite seems to be an excellent clarification agent considering wastewaters polluted with oils, petrol and other types of non-polar liquids containing hydrocarbons. While hydrophobized perlite is a suitable sorbent for removal of oil spills or layers of oily products on the water surface, bentonite exhibits a very good cleaning efficiency in case of oils dissolved or emulsified in the bulk water phase. During the purification process, flocculation, sorption and "weighting" properties of bentonites are of the greatest importance. After the addition of activated bentonite, the emulsion is broken and bentonite with the sorbed contaminants flocculates and settles down rapidly. Bentonites activated into aluminium and iron cycles are used predominantly for this type of pollution. Advantageous seems to be utilization of a very small amount of organic polyelectrolytes from the point of view of better floccules characteristics and sedimentation rate of the sludge.

For wastewaters containing oils in the concentration range 65 - 200 g/l, more than 95% decrease of the chemical oxygen demand was achieved using doses about 5 g/l of aluminium bentonite and 5 g/m^3 of anionactive polyacrylate. In case of the less polluted wastewaters which were characterized by the content of oily substances 6 g/l, parameters of water after cleaning were excellent reaching less than 0.1 mg/l of oily substances (Photo 18). Similar results were obtained using different iron-activated bentonites.

It was proved that the sludge containing bentonite with an oily matter bound on the surface might be utilized as an additive into the red-brick body in amount of 5 - 10% of the total mass. This re-use of wastes serves as a good example of the complex environmental engineering.

Other types of wastewaters

Bentonites either natural or activated may be utilized for other types of wastewaters characterized by the presence of emulsified and finely dispersed liquid and solid pollutants. The efficiency of the whole cleaning process depends on many impacts but the ratio between soluble and insoluble contaminants is the most important factor. Bentonite was successfully used e.g. for treatment of biologically polluted waters from food industry and exploited for thickening of municipal digested sludges from sewage plants (Photo 19).

Application of bentonites for other types of wastewaters

Type of wastewater	Dose of bentonite /$kg.m^3$/	Dose of flocculant /$g.m^{-3}$/	Treating efficiency /%/ +/
waters from meat processing	2 - 5	-	50 - 60
waters from cattle breading	3 - 10	usually not necessary	70 - 80
waters from yeast and vinegar production	3 - 5	-	25 - 30
digested sludges from biological sewage plants - mechanical dewatering	15 - 30	80 - 120	95 ++/

+/ Given in terms of COD decrease of wastewater after treatment.

++/ In terms of decrease of the dry matter content.

10. Agriculture

Soil Fertility - Basis of Agricultural Production Development

Any society taxes the agricultural sector heavily in order to secure the elementary sustenance of all its inhabitants. To meet such a pretentious objective, it is necessary for agricultural science and praxis to orient attention, first of all, on increasing the soil fertility and its effective exploitation.

The soil fertility is a result of the process of transforming rocks and mineral matters in upper layers of the Earth Crust. Oxygen, silicon, aluminium and iron are the basic elements of the Earth Crust, i.e. they also form a substantial part of soil. Their share represents 92.5%. Owing to the activity of living organisms, the content of carbon in soil has increased 20-times, that of nitrogen 10-times, in compariosn with the Earth Crust. This process confirms the fact that plants assist in the accumulation of biologically important matters in soil, however, very slowly. On using fertilizers and appropriate agrotechniques this process can substantially be accelerated. The application of fertilizers brings about not only enhanced crops but, concurrently with the enhanced activity of plants and microorganisms, the process of accumulation of organic matters and biologically important elements is speeded up which affects significantly the soil fertility. Therefore, no more new is the recognition that simultaneously with the growth of yields, the soil fertility increases, too.

The second principle of improving the soil fertility is a proper alternation of cultivated crops which is one of the biological principles of each agriculturalist.

An enhanced application of industrial fertilizers eliminates partially the influence of pre-plants, since the soil possesses a higher stock of prompt available nutrients. On solving the sowing sequence, cereals are the most demanding from this point of view. Pulses - beans, peas and root-crops - potatoes, turnip, sugar-beet, are suitable pre-plants for cereals, especially for spring barley and winter wheat. Multiannual forage crops, represented mainly by lucerne and clover, are the most significant plants of the sowing sequence with respect to the influence on soil. Their root system interferes with a considerable depth thus enhancing the microbiological activity of soil.

In connection with further development of the vegetal production and thus with the complex solution of the problem of cereals, there arises a task to prosecure a sufficient and quality fodder for the livestock. Let us realize that more than a half of vegetal outputs is exploited in animal husbandry for the transformation into animal proteins. Especially the organism of cattle has all the necessary presumptions to consume large quantities of voluminous fodder and its effective transformation into proteins.

The main sources are to be looked for in securing the maximum efficiency of existing agricultural land and effective exploitation of all products raised up on it. The agricultural land is and is still going to be for a long time the main source of mankind sustenance. In average developed countries, 0.5 ha provides nourishment for one inhabitant.

However, it is a regretable fact that the area of agricultural land per capita is ever-decreasing in all countries in connection with expanding construction activities and development of further industrial branches. On the other hand, the calls for nourishment grow substantially due to the prolongation of human life and increasing population. The situation in foodstuffs is going to be very earnest and there is no other way out but creation of permanent prerequisites for securing sufficient food supply through the application of modern science and technique.

Soil Reclaiming by Bentonite

The maintenance and enhancement of soil fertility as the main production means is a fundamental and permanent task of all those engaged in the agriculture. This objective is ever more and more aggravated by the competing requirements for environmental protection and, on the other hand, for higher inputs of fertilizers and energy.

A majority of soils (especially the sandy ones) is characterized by:

1. High water permeability, low water holding capacity
2. Low natural reserves of nutrients, weak sorption complex

The improvement of this unfavourable state of sandy soils can be reached by using proper sorbents (matters of high sorption, i.e. water receptivity). The application of non-metallic sorbents has been a subject of research and practical experiments for more than 20 years.

The effect of bentonite depends direct on the type of soil. In case of sandy soils (from slight clayey ones up to considerably clayey sandy soils), the addition of bentonite always results in a considerable enhancement of outputs. Other heavier soils respond on the bentonite addition unreliably. Instantaneous physical conditions and the humus content are of concern.

The bentonite concentration of 0.3 - 0.6% in the top-soil profile is the most suitable one, i.e. about 10 - 20 tonnes per ha. The grain size of the bentonite applied should not surpass the grain size of the main fraction of the ammeliorated soil. Otherwise, bentonite granules could display their dessicant effect. Crude bentonite does not need any other but mechanical upgrading. Its forced artificial dessication could have an extensive negative influence on its efficiency. Under common circumstances, its application is effective for several years. The depth of bentonite ploughing-in is the same as in case of current soil management. It is recommended to avoid bentonization by matters which increase peptization and to select bentonites of a sufficient calcium content in its exchangeable or carbonate forms. Otherwise, the sufficient supply of calcium should be secured by a parallel measure, i.e. liming.

The favourable influence of bentonite in soil ceases around the 6th - 8th year after application. Bentonite firmly binds humus and thus creates a favourable soil structure. In case of soils containing more than 3% of humus the bentonite effect is low since the higher portion of humus blocks the bentonite function in soil. It is caused by an unfavourable influence of bentonite on humification processes.

Bentonites affect the fertility of arenaceous soils significantly because:

1. They reduce the wash-out of fertilizers, improve the ability of water retention and rehabilitate the soil

with respect to ion-exchange.

2. They supply nutrients direct to plants which increases the output as far as 100% (according to the kind of plant, humus content, pH value, granularity and climate conditions).(Photo 20 - 22)

Apart from the above, they reduce the penetration of chemical matters into subsoil waters and, many a time, into atmosphere. Chemical fertilizers in the agriculture (N and P) together with some trace elements (Cd) are earnestly suspected of influencing the occurrence of carcinogenous effects in some plants and in water.

Exact tests and practical results have furnished evidence that the efficiency of industrial fertilizers is higher by 15 - 25% when applying bentonite simultaneously enabling thus a significant reduction of chemical fertilizer dosage. It necessitates therefrom that consequences of bentonite application with respect to the environmental protection are broader owing to the reduced wash-out of fertilizers into subsoil waters.

The effect of bentonite on the crop yield is also dependent on its quality which is very versatile. Especially, the pH value, humidity, montmorillonite content, sorption capacity, content of bivalent iron and quantity of kaolinite are of concern.

Theory of Bentonite Behaviour in Soil

Bentonite is a clay rock fundamentally containing clay minerals of the montmorillonite group, displaying a high sorption capacity, large active surface and swelling ability. It is a poly-functional soil reclaiming matter influencing positively the physical, sorption, chemical and mechanical properties, especially in case of indigent sandy soils, improving their production ability. On damping, the swelling property of bentonite causes the diminution of soil pores and enables the sandy soil to economize the water consumption. Such effects also influence the enhancement of the maximum capillary water capacity, capillary rise, and the decrease of permeability. Through increasing the content of water, the sorbent affects indirect the regulation of thermal ratios of sandy soils.

The efficiency of mineral sorbent on hydrolimits is also influenced by the presence of organic matters. The hydrolimits, issuing from the direct bonding of water and soil, enhance proportionally to the dosage and organic matters do not affect this dependence. Those are: number of hygroscopicity, wilting point and minimum capacity.

The enrichment of sandy soils by bentonite and regulation of water ratios are connected with the enhanced thermal capacity of the sandy soil, increased thermal conductivity and with the reduction of thermal fluctuations especially in the upper layer, of which the practical consequence is the prolonged time of thermal accumulation in the vegetal profile.

The application of bentonite for soil ammelioration also brings about a new balance of nutrients in a plant. It has been proved that the addition of bentonite into sandy soils causes a change of the following ratios:
- potassium : calcium in favour of potassium,
- nitrogen : phosphorus in favour of nitrogen.

Furthermore, the bentonite additive enhances a stimulation effect of microelements and decreases the toxicity of their excessive concentration.

The influence of soil medium on the efficiency and duration of sorbent effect is of great importance, too.

In soil of slight acid reaction (pH higher than 5), the decomposition of carbonates occurs the released bases of which usually suffice to set the soil reaction right.

In more acid soils (pH 3 - 5), all carbonates decompose and, simultaneously, a part of exchangeable cations is eliminated at a contemporary release of aluminium and magnesium.

Practical applications of theoretical regularities of the efficiency of available sorbents have been verified in agricultural enterprises in Czechoslovakia, China, Ethiopia, Egypt and other countries.

The results obtained have proved that sorbents of the bentonite-type function the most expressively in indigent light soils of a lower content of grains under 0.01 mm and of low humus content as shown in Table 10.

In agricultural praxis there has been proved that bentonites suit well which can be regarded as marginal from the point of view of applications in industries. To the requirements of soil reclamation bentonites reaching at least 20 - 25 mval/100 g of ion-exchange capacity will suffice and contigent Ca-cations are welcome which are undesirable for most of industrial purposes.

It is also possible to use bentonites sorbed with different biological matters coming from different waste-water disposal processes and utilize efficiently such a waste. For greater detail the reader is referred to Chapter IV/9.

Practical Remarks to the Application of Bentonite

The concentration and specialization of agricultural production require a high intensity of fertilization. Principal changes set in with respect to a new technology of animal breeding applied nowadays. On husbanding animals in sheds without littering and removing excrements by water stream, a liquid manure originates the application of which changes substantially the techniques of manuring by organic manures. The concentration of animal husbandry and its economic prosperity under different ecological conditions are dependent on efficient utilization of produced organic manures. New technologies cannot be based on experiences obtained by our fathers since the soil profile, humus content and sorption properties have changed during last 40 - 60 years considerably. New ways are to be sought for the preparation of manures by separation, decantation and filtration of liquid excrements and/or by other suitable methods.

High dosages of pig and cattle excrements without appropriate upgrading and applying scientific methods could bring about undesirable changes of soil profile and, sometimes, substantial detriments to the outputs by enhanced content of nitrates. The nitrate - a salt of nitric acid - is almost non-poisonous. Only the change of nitrate into nitrite jeopardizes the health of people. A high content of nitrates in plants is a consequence of many factors, not only of fertilization. It also depends on the composition of soil, weather, temperature, duration of sun radiation and kind of plant.

One half of nitrates has its origin in the mineralization of organic matters (as far as 200 kg/ha can liberate in soil within a year).

These mutual correlations between soil and fertilization by organic and inorganic matters have already been followed in Czechoslovakia for several years and proper methods of application have been looked for.

The tests and praxis have proved the bentonite dosage of 25 tonnes per one hectare to sandy soils as optimum from the point of view of retention of organic matters in sand and sorption of nutrients delivered by industrial fertilizers.

In general, a conclusion can be drawn that appropriate reclaiming dosages of bentonite in sandy and sandy-clay soils improve their physical sorption for the regulation of nutrient concentration in soil solution. The concentration of soil solution varies considerably in the soil profile which brings about favourable conditions for plant nutrition. The physical sorption constitutes only a small part of overall sorption capacity of soil.

From the point of view of the regulation of soil solution concentrations in plant nutrition, physico-chemical, chemical and biological sorptions are of the greatest importance.

The total sorption capacity depends on the structure and chemical substance of colloidal matters which mediate all the exchange reactions. Two groups of soil colloids are distinguishable from this point of view:

1. Soil colloids of acidic character
2. Soil colloids of altering character which react either as alkalis or acids in dependence on the reaction of soil solution.

The secondary minerals of the montmorillonite group are of significant acidic character. They have an enhanced content of silicic acid and other humic acids bearing a negative charge.

The acidic environment subdues the sorption capacity of cations. The composition of sorbed cations has a great influence on plant nutrition and soil properties. Once the soil sorption complex contains cations Ca and few cations H and no volatile cations Al, the soil distinguishes by good physical and biochemical properties and high fertility. A high portion of H and Al and few Ca and Mg causes worsened physical properties.

The bentonite application is most suitable during the basic autumn ploughing enabling the sorbent to spread over the whole layer of the top-soil.

Bentonite functions more expressively when applied, in a larger dosage especially, during the dry-weather period while its efficiency is lower during the wet vegetal period. The efficacy of bentonite application enhances in connection with the level of fertilization by mineral fertilizers, too. Bentonite improves the exploitability of mineral fertilizers and prolongs their gradual effect. When organic fertilizers are applied together with bentonite, a higher efficiency of both is reached.

In this connection the dosage of industrial fertilizers could be reduced leading to positive impacts on economic aspects and purity of subsoil waters since a considerable decrease in wash-out of nutrients into bottom layers of soil was proven.

The objective of bentonite application for the fertilization of sandy soils is to generate a sorption complex of bond sandy grains and organic colloids and prevent water from quick percolation. 1 g of bentonite can bind as much as 20 g of water forming a stable gel which has excellent binding properties. It is on this fact that bentonite is used in foundries to reinforce sand moulds. A comprehensive quantity of reversibly bound water is a reservoir of humidity in soil available to plants. The reversibility of water bond affects positively the soil porosity since the dessication of gel causes its shrinking and occurrence of hair cracks. The hydrophility of bentonites, evidenced by liberating up to 88 J of hydration heat per 1 g of bentonite, stimulates assimilation processes in plant on damping and acts, to a certain degree, as a thermal regulator in soil.

The mineral sorbent affects the thermal ratios of sandy soils both direct and through an enhanced water content in soil. Theoretical hypotheses have been proved by exact results. Bentonite reduces, first of all, daily temperature alterations during the sun radiation type of climate which is of importance for limiting a detrimental overheating of the soil surface. Bentonite enhances the heat conductivity and heat capacity of soil together with the influence of organic matters.

The main improving effect on soil is, however, that of volume changes. As a consequence of expansion during water reception, the number of capillary pores grows to the detriment of the non-capillary ones which results into a considerably increased quality of physiologically acceptable water for plants.

As a final consequence, it brings about a better water regime and dynamics of microbial processes in soil even at comparatively low dosages of bentonite.

Bentonite Exploitation in Animal Husbandry

Ruminants have a specific digestion system which is, together with its microflora, favourable for consuming voluminous fodder, some synthetic industrial products and different wastes from the industry and agriculture. However, the same microbiological processes of digestion of ruminants are the reason why they exploit the valuable fodder in an ineconomical way. The microflora of rumen has a tendency to digest preferentially easy-digestible glycides, saccharides, and starch as well as easy-digestible proteins, enabling the synthesis of cells of microorganisms, i.e. the nutrition value is frequently lower than in case of fermentation decomposition of such matters in bowels.

However, it does not mean that in case of ruminants only such dosage is economical that consists of voluminous fodder and that easy-digestible and high-energy valuable fodder can be neglected, since those are very important sorts of fodder to reach intensive weight accessions and enhanced production of milk and meat. The dosages should be balanced in dependence on both the production biological and physiological needs of animals and efficient exploitation of fodder. They have to satisfy the physiological and production needs of the organism and to keep up the stability and microbiological activity of digestion processes. From this point of view, the addition of non-protein nitrogen to the fodder dosage of cattle should be considered.

Exploitation of bentonite as additive to fodder

A lack of protein fodder and its unfavourable pricing are the reasons of wide exploitation of the ruminants' ability to convert non-protein nitrogen. A series of nitrogenous matters can serve as a source of non-protein nitrogen.

The application of urea has reached the greatest significance since it is economically efficient and is considered to be a natural substrate for the rumen microflora.

However, the exploitation of nitrogen from the urea displays some known disadvantages and problems, namely

a/ bad taste
b/ toxicity in case of overdosing
c/ inefficient conversion of urea into bacterial proteins, connected with the dynamics of the level of ammonium in the rumen of ruminants.

The level of ammonium released from the urea culminates soon after feeding in the time when there are yet neither enough acceptors nor enough energy for the demanding proteosynthesis.

The optimum supply of nitrogen should reach a certain level to enable the release of such an amount of NH_3 which would simultaneously be exploited for the microbial proteosynthesis. It was verified experimentally that the level of free ammonium of ca 50 - 130 mg in one litre responds this requirement well.

However, the addition of urea into a fodder dosage does not guarantee the requested level of ammonium in the rumen. Since this is the main disadvantage of otherwise suitable application of urea, further research is aimed at finding a way to remove this discrepancy.

There are three possibilities of solving this problem:

1. Additive of easy-cleavable saccharides - in the form of sugar-beet or mollases which is able to prosecure a sufficient amount of energy and acceptors of ammonium in the time period of its enhanced release.
2. The slow-down of the hydrolysis of urea in a mechanical way using a thin layer of emulsified starch enfolding the urea crystals.
3. Substitution of more stable nitrogenous matters for the urea, such as biuret, acetamid.

The control of the level of ammonium in the rumen - transitive bond of ammonium cation to a suitable natural ionexchanger

For this purpose, natural aluminosilicates suit well, such as bentonite and zeolites, which are harmless to the health of people. Bentonite binds and releases ammonium best. Montmorillonite is a substantial part of bentonite. According to mineralogical composition, bentonite contains 40 - 70% of montmorillonite, further mica, quartz, calcite and siderite, 33 trace elements,such as Ni, Ti, V, Mo, Cu, Zn, Co, Ba, Fe, Mg; toxic elements, such as arsen and lead, have not been found.

The additive of bentonite reduces the amount of ammonium one hour after feeding and, on the contrary, enhances it again starting from the fifth hour (experiments with sheep).

On adding bentonite, the fluctuation of the pH value is partly moderated. The concentration of bentonite in the dry matter amounts to 3.5 - 5%. In this way, it is possible to improve the exploitation of nitrogen of the urea and, partially, moderate the danger of toxic effects.

Possibility of rational application of bentonite to fodder of cattle

Biological tests have been conducted to verify the possibility of applying bentonite with urea in the fodder dosage of cattle. 50 bullocs were selected for a comparative test repeated 5-times. They were divided, according to their mass ranging from 250 to 300 kg, into 5 groups, 10 pieces each, so that all the groups were comparative as far as the mass is concerned.

Several Protein Feed Admixtures were compounded to control the test of bentonite efficiency. The admixture with maximum bentonite content had the following formula:

Protein Feed for Cattle Fattening /HZB/

component	content /% wt/
Rape meal	10
Sunflower meal	5
Wheat	30
Barley	29
Wheat brau	11.5

Feed supplement - T	0.5
Mineral	1
Salt	2
Urea	2
Bentonite	8

Parameters of the feedstuff /%/

Dry matter	86.89
Crude protein	20.61
Crude fibre	7.01
Fat	1.50
N-free extract	53.19
Ash	8.24
Starch equiv.	59.67

The above admixture was added to several feed rations which were applied to the tested bullocs. The weight category 250 - 300 kg was fed on the following ration: silage - 19 kg, hay - 1, HZB - 2.5 kg (According to S. Bartoš, M. Macounek et al., in Biol. chem. vet. Prague, No. 4. 1982)

The above mixtures have proved a favourable influence of bentonite additive on the exploitation of non-protein nitrogen and the possibility of substituting for vegetal proteins and, simultaneously, the possibility of reducing the content of nitrogenous matters in fodder dosage of cattle.

The biological tests of the application of bentonite with urea have also confirmed that the application of both components in case of proper incorporation into the fodder dosage, can save a part of extracted bruised corn and thus reduce the costs per 1 kg of weight accession.

Average consumption of nutrients per 1 kg of weight accession:

	with bentonite	without bentonite
dry matter	7.5 kg	7.82 kg
crude protein	0.630 kg	0.741 kg
starch equivalents	4.42 %	4.52 %
costs of fodder per 1 kg of weight accession	100.00 %	105.00 %

Conclusion

The agriculture is still remaining a principal material condition of the life of any society. The actual agricultural production has an important and specific function and, hence, a significant position in the overall reproduction process.

The most important function is the production of food. Through this task this sector is connected with all other spheres of production and non-production activities of mankind. The ratio of the agricultural production to the quantity of exerted labour confirms the fact that the technical development conduces to the accelerated growth of the labour productivity. The production volume in the agriculture per time unit increases.

The nature and its rules represent a space in which the agricultural production develops. However, this natural presumption looses gradually the initial intensity of its influence on the agricultural production in such a range in which particular countries succeed in affecting the natural conditions through technical development. However, the results of scientific-technical development have not yet been reflecting a great deal of the world agriculture. It necessitates therefrom that the influence of natural conditions is decreasing in the developed countries while in the developing countries they are still of decisive character.

The agricultural land fund is the main prerequisite of the development of agriculture. Since the production of food is dependent on the area of agricultural land and its intensive exploitation, it is on each society to devote a special attention to the cultivation and reclamation of agricultural land.

One of the ways of soil reclaiming is a complex system of organic fertilization with the aim to secure a well-balanced level of organic matters in soil. Under actual existing conditions, it would be necessary to add 1.4 tonne of dry organic matter per ha annually into soil. At present, such a demand is met only in countries with a fairly developed animal husbandry where the number of cattle reaches the level of 0.9 - 1 head of cattle per 1 ha of agricultural land in average.

In countries with a lower intensity of animal husbandry there is a tendency to substitute industrial fertilizers for the organic ones. This method can temporarily maintain and, to a certain degree, even enhance the hectare yields, however, at extremely high costs, since the lack of organic matters in soil causes the decrease in soil sorption, worsening of soil structure and its gradual devastation.

A question arises how to follow to keep up and gradually enhance the soil fertility upon the condition of lower additives of organic matters into soil which are short both in the developed and developing countries. (In the former case - because of some new technologies of animal breeding without littering, in the latter case - because of a low number of cattle and its breeding out at grass).

Taking into consideration the conducted agricultural experiments and studies, it can be summed up that the application of non-metallic sorbents in the agriculture is one of the ways how to maintain and enhance the soil fertility.

V. SELECTED ECONOMIC ASPECTS OF BENTONITE EXPLOITATION

1. Bentonite as Commodity

Bentonite belongs to the montmorillonitic clays. There are many commercial and regional denominations for these smectite clays which arise from the traditional use of a clay in a particular region or from the geographical names of regions which have supplied the principal amount of clay. Most of the denominations have no mineralogical significance. In the world trade and industry the attention concentrates on two main types which are sodium andcalcium montmorillonite substantially and generally known as bentonite and fuller's earth.

Most montmorillonites are residual clays occurring mainly in large flat deposits most of which was a product of volcanic ash alteration. Identified world resources of all types of montmorillonite are very large totalling over 5 billion tonnes and are practically inexhaustible.

There are five fundamental forms in which montmorillonite is supplied to consumers. Natural sodium montmorillonite (predominantly in the USA), calcim montmorillonite, acid earth, sodium activated montmorillonite and acid activated montmorillonite. These products are used widely in many applications as shown in Figure 8 where principal applications are listed together with relevant processes to meet the final-use requirements.

Sodium montmorillonite is used mainly in drilling muds, foundry sands and iron ore pelletising. The non-swelling calcium montmorillonite is also used to bind foundry sands and in addition is used as absorbent and bleaching and filtering agent. Sodium bentonite is valued for its thixotropic and binding properties while calcium bentonite and acid activated fuller's earth are used for their sorption properties, catalytic action, bonding power and cation exchange capacity.

The world consumption of bentonites is difficult to estimate because of lack of data from several larger producers, mainly in the USSR and China. During the past two decades the bentonite consumption has almost doubled and was assessed to account for 10 mil. tpa in 1980's. About 40% is consumed in the USA. The pattern of consumption in different countries varies considerably (Table 3). In the USA the consumption in oil well drilling dominates demand while in most European countries and Japan the principal consumer is foundry industry.

In view of very high level of drilling activity in the USA the drilling muds have become the largest world end-use of bentonite which is used to lubricate and seal drill holes. The increase in drilling activity which has resulted in an increase in consumption of bentonite has been partly offset by the development of muds based on competitive materials, either synthetic or other clays, such as attapulgite. However, the affect of competitive materials was small in comparison with the growing level of drilling activity in the world and particularly in the USA.

Bentonite is used as a binding agent in the pelletising of iron ore. The main purpose of using a binding agent is to enable the use of otherwise unusable fines. Pelletisation also facilitates handling, reduceability and can enhance the value of ore by as much as 40 - 50%. Sodium bentonite (either natural of sodium activated montmorillonite) is used for its dry bonding strength and the strength at higher temperatures. There are not important competitive substitutes but the trade was seriously hit by the reduced metallurgical activity in early 1980's. It applies particularly to the USA and Canada which were traditionally large producers of pelletised iron ores. In other countries with easy access to iron ore the production has not been so seriously hit, however, high grade ores are only rarely pelletised.

In most European countries and Japan foundry sands are the main market for bentonite. In recent years the development of high density moulding machines has led to expanded utilization of blended clays to bind foundry sands. Sodium montmorillonite is blended with calcium montmorillonite to achieve optimum properties of hot strength, green strength and dry strength. Consumption of bentonite in foundry industries has fallen off in recent years because of the new technological developments and reduced demand for casting particularly in the automotive industries.

Civil engineering, particularly tunnelling and foundation engineering has recorded a sustained growth of bentonite consumption. This is partly on the expansion of larger ground projects and also on development of new tunnelling techniques.

The main uses for montmorillonite acid earths are as adsorbents for oil and grease and in pet litter. Montmorillonite clays are used in the treatment of both animal and mineral oils and greases as well as vegetable oils. In this field there are several competing materials including non-clay substitutes. There is considerable geographical variation in the consumption of bentonite. In the Mediterranean area clays are used abundantly for clarifying olive oil and bleaching wine and fruit juices. The USA demand for bentonite to process mineral oils is higher than in Europe where solvent extraction techniques are more widespread.

Montmorillonite clays are also used in a number of agricultural applications which include soil conditioning, insecticide and fertilizer carriers and pelletising of animal feedstuff. Recently bentonite has found utilization as efficient thickener to treat municipal, agricultural and industrial wastewaters.

2. Production, Trade and Prices

Production

Most bentonites are mined from open pits though underground mining is also applied in special cases. The quarries use usually modern mining equipment as described in chapter III. The production technology differs according to the chemical character of input and end-use application. If natural sodium montmorillonite or natural calcium montmorillonite is required then the process consists of weathering, drying, crushing and sizing followed by upgrading into granules or powder. If sodium activated or acid activated bentonite is to be produced from calcium montmorillonite some additional operations are necessary. Sodium activated bentonites are formed by adding a small amount of sodium carbonate, usually 2 - 5% to calcium montmorillonite. A number of different grades is prepared by varying the amount of sodium carbonate. Acid activated bentonite is prepared by treating natural calcium bentonite with hydrochloric or sulphuric acid. The processes to produce marketable bentonites are described in detail in chapter III.

No figures are available for some larger producers, especially the USSR and China. In addition trade nomenclatures differ from region to region. In Table 3 there are listed major producers with annual output above 50 000 tons. In addition the following countries are known to produce bentonite, some of them considerable amounts: Austria, Canada, China, Egypt, France, India, Iran, Poland, Philippines, Tanzania and the USSR among others. Table 4 refers mainly to sodium activated bentonites. Table 5 lists major world producers of acid earth. The list os not complete because data for other countries believed to produce fuller's earth are not available or both sodium and acid activated bentonites were summed under one item listed in Table 3, such as Czechoslovakia.

International Trade

The international trade flows are comparatively difficult to trace. Either statistics are not available for larger producers or commodities are agglomerated in published statistics. Some countries publish statistics only for certain grades of bentonite. West Germany, for example, is believed to export large quantities of sodium activated bentonite but the only trade figures available are for "natural bentonite". It is assessed that world actual trade represents about 20% of world bentonite production in early 1980's. However, the available statistics revealed lower figures only 1.6 mil. tons. Since that time the world trade has probably declined due to recession in iron ore pelletisation, especially in Canada that was a large importer of bentonite for this end use. Table 6 shows the principal importers and exporters trading more than 10 thousand tons per year.

The exports are dominated by the USA and Greece while

Canada was the principal importer. Other significant importers are FRG, France, Netherlands and the UK. 40% of the USA exports went to Canada, 13% to Netherlands and 10% to Japan. The second largest exporter is Greece and the principal destination of its exports was Canada and smaller amount went to Italy, France and the Netherlands. Several European countries export to neighbouring countries. For example, the FRG to France, the Netherlands to Belgium and Spain to Portugal. The Scandinavian countries import from the UK. Although there is no bentonite mining in the Netherlands, unprocessed bentonite is imported from Greece and sold to Belgium after upgrading.

The import of Canada which is the largest importer in the world was supplied by the USA (67%) and Greece (33%).

Prices

There are no regularly quoted market prices for montmorillonite clays which are not sold through organized markets like metals or cereals. Prices are published by Industrial Minerals for the UK and by Chemical Marketing Reporter for the USA. These quotations probably reflect prices for relatively small and irregular sales arrived at by negotiations. These negotiations reflect mainly production costs. Major consumers either have their own sources of bentonite or purchase it on long-term contracts. On the other hand, bentonites supplied for adsorbent use, particularly pet litter are sold at retail prices which reflect packaging, marketing and retailer's profit.

The price of bentonite depends first of all on the grade of the material and end-use for which bentonite is supplied. Over the twenty past years the prices have risen as a consequence of higher labour, energy and production costs.

Foundry grades of bentonite are sold for 30 as far as 45 US $/t depending on bagging. Bentonite used for well drilling costs from 45 to 90 US $ per short ton depending upon quality. Crushed and dried bentonite costs about 20 US $ per short ton while bentonite for water and waste treatment costs about 70 US $/t. Prices of bentonites used for iron ore pelletising and animal feeding range around 50 - 60 US $. The above quotations apply to US markets.

The American bentonites sold on UK markets are noticeably dearer. So foundry grade costs about 80 - 90 £ and acid activated bentonite costs around 180 - 200 £ per tonne. Some of the differences can be explained by freight and tariffs. It is to be mentioned that also prices as much as 3 000 US $ per short ton were recorded however, they applied to special purposes and small quantities sold.

Another approach to the prices of bentonite is the value of exports as revealed by international trade statistics but reservation must be allowed for since the commodity classifications differ between countries and the grade is not specified. Further, usually graded material is traded which is reflected in higher values. The reader is referred to Table 7 where FOB values of selected exports are quoted. Table 8 shows quotations of several world suppliers of bentonite.

3. Economic Aspects of Applications

Drilling Muds

The original form of drilling mud was a suspension of bentonite in water known as vanilla mud. The purpose was to seal the walls of drill hole and prevent water loss in permeable formations. Over the years more sophisticated suspensions have been developed to meet demands for drilling deeper holes, offshore drilling and drilling through problematic geological formations. The original vanilla mud has been added by different weighting agents so that some muds are now mixtures of as much as 10 components from which barytes, caustic soda, lignite, lignosulphate share most. Bentonite shares about 10% only. The purpose of drilling mud is:

- to lubricate the drilling bit
- to carry rock cuttings to the surface
- to seal the walls of the hole to prevent from loosing the mud in low pressure formations
- to provide a hydrostatic head of pressure to counterbalance geopressures .uring drilling
- to act as an electricity conductor to facilitate survey

The quality specifications of bentonite used for well drilling are given by the American Petroleum Institute (API) and the Oil Companies Materials Association (OCMA) standards which prescribe viscosity, filter loss, wet screen analysis and moisture content. These standards are best met by sodium-exchanged bentonite not only for quality but also for its favourable price which causes that bentonite shares generally 10% of the mud cost.

It is impossible to get figures of bentonite consumption for all the countries that have oil well drilling activity. From several sources the following figures were gained including the correlation between the length of holes and consumption of bentonite.

Consumption of Bentonite for Oil Well Drilling

Country	length of holes (000 ft)	total bentonite consumption (000 t)	t bentonite per 1000 ft drilled
Canada, 1979	29 382	18 051	0.61
Japan, 1979	312	24 224	77.64
France, 1980	528	14 000	26.52
UK, 1980	1 764	25 000	14.17
USA, 1981	373 526	2 064 000	5.5

Iron Ore Pelletising

Pelletisation of iron ore was introduced in the USA in 1950's to utilize the low grade taconite ores in Minnesota as high grade ores neared to exhaustion. Bentonite is used as binding agent. The advantages of pelletisation are as follows:

- it facilitates the handling of the ore
- iron ore pellets have high strength
- pellets have good reduceability during processing
- pellets have a homogeneous chemical composition unlike lump ore
- pelletising increases the value of the ore by as much as 40 - 50% which can be attractive for developing countries anxious to enhance the value of their exports
- pelletising enables the use of otherwise unusable fines which is the most important point for pelletisation of iron ore

The alternative iron ore upgrading process is sintering which had been established fairly sooner but it can beneficiate only coarser ores leaving thus a good proportion of world's iron ore reserves unused.

The principle of pelletising consists in the tendency of small particles to agglomerate. Hot pelletising starts with drying and grinding of iron ore to the consistency of talcum powder. Then a binding material is added and everything moistened to form a slurry. The mixture is then fed into horizontal rotary drums where it agglomerates to produce small pellets. These green pellets are then fired at high temperatures.

Sodium bentonite, either natural or activated one, is used as the bond because of its highdry bonding strength and the strength at high temperatures. The amount of bentonite added to bind pellets depends on the ore type.

The disadvantage of using bentonite is that it acts as a chemical impurity, reducing the content of iron ore and enhancing the silica content. Using bentonite also needs additional limestone and coke as much as 30 kg per 1 ton charged into blast furnace. Therefore, alternative materials have been tested and some producers use slaked lime, hydrated lime, cement clinker, etc. Despite the alternatives that have been applied none of them has achieved the acceptance of bentonite which is partly on lower prices of bentonite which is even economical when transported for very long distances.

But the consumption of bentonite for iron ore pelletising has considerably declined over the recent years which is not a result of a successful substitute being used but due to the recession in the metallurgical sector in western industrialized countries, especially in the USA and Canada. In Brazil, India, Sweden and the USSR the pelletisation is growing but still it accounts for a small proportion of total iron ore production. World pelletising capacity in 1979 is shown in Table 9 compared with the overall iron ore output.

Bentonite was also tested for pelletising coal with promising resutls and in Brazil it is used for pelletising manganese ore.

Foundry Sands

In most European countries and Japan foundry sands are the largest market outlet for bentonite. To make a foundry sand 4 - 6% of bentonite is added to new silica sand and 0.1 - 1.0% to a returned sand; for high pressure moulding the bentonite content rises up to 8 - 10%.

Specification for bentonite for foundry sands includes moisture content, gelling index, pH value, heating and bonding properties and water holding capacity without flowing (liquid limit). Steel casting is dominated by natural sodium bentonites for its higher liquid limit while iron and non-ferrous castings use sodium activated or calcium bentonites. The proportion of using different bentonites vary from one to the next foundry depending on a complex of technical and economic considerations.

The greater use of high pressure machines and automated processes have led to using blended clays more. Mostly, sodium bentonites are blended with calcium bentonites to control hot, green and dry strengths.

Bentonite for Sandy Soil Reclamation

The conducted experiments and practical experience in the world proved that bentonite brings about not only increased agricultural outputs but also in many cases increased quality of crops, e.g. better flavour of products. In the USSR, great efforts were put into bentonization of soil, the bentonite application yielded the best results in case of cotton and tea in arid regions of Middle Asia and Caucasus sub-tropic belt. Especially, in case of Georgian wine, twofold outputs are ascribed to the effect of bentonite. However, the bentonite found also applications in northern regions of the USSR for the plantation of grain. potatoes, vegetable, flax, sugar beet, maize and apple trees when a shorter vegetal period maturing was experienced.

Identical results are reached in Hungary in planting wine, maize, sunflower, potatoes, tobacco, grain. In case of maize and sunflower, the yield increased by 120 - 160% by bentonite application and in addition to, water percolation was reduced by 85 - 90%.

Many applications of bentonite were carried out in Japan, especially for rice. In France the effect of mineral sorbents on potatoes and wheat was researched in great detail. Among other countries applying sorbents, FRG, Italy and Czechoslovakia are worth mentioning.

The systematic research of bentonization of soils started in Czechoslovakia in 1960's. The first field experiment was conducted in 1960 with very low dosages of bentonite (about 0.5 - 1 tonne per hectare). The results were good ranging between 11.8 as far as 22.2% of increased yields of potatoes and the quality of potatoes was claimed to be better. In the period 1961 - 1963, about 200 separated field tests were conducted on the overall area of 1 400 hectares. In case of arenaceous soils and optimal dosages of bentonite accompanying industrial fertilizers the increases yield accounted for 15 as far as 60% according to the sort of crops, so that the cost returned already in the first year of application. The cost in industrial grade bentonite was three-times lower than the price of the increased output in these years. When raw ungraded bentonite was applied, the price of the increased yield was nine times higher than its cost. Especially, irrigations accompanied by bentonite were economically successful. It was experienced that the sugar beet output was by 90% higher in case of irrigation + bentonite against 74% in case of sole irrigation, so that 23% effect of bentonite. Similarly in case of maize 92.9% against 82.9%, in case of lucerne 34.1% against 16.8% and 16.3% against 8% in case of potatoes.

The experimental results of higher efficiency of bentonite application in dry periods were confirmed by experiments and praxis in Egypt. Conclusions were drawn that mixing sandy soil with local bentonites would improve mechanical, hydrophysical and chemical properties of sandy soils. Consequently, yield and water use efficiency by plants are increased. The reaction of different tested plants was positive, beans and barley yielded twice in comparison with control fields. Bentonite also influenced positively the period of germination, growth of stalks, nutrient uptake, water efficiency. The consumption of irrigation water was cut down by a half. Results of bentonite applications are summed in Table 10.

Other Applications

Civil engineering and building materials

Bentonite is used in civil engineering for diaphragm wall construction, piling, grouting. It is also used for tunnelling. Slurries containing 4 - 8% of bentonite are used for grouting to prevent the movement of water through fissures in rocks and concrete structures. The bentonite slurries are used to seal water reservoirs, ponds and irrigation works. The same slurry can serve as lubricant in sinking caisson and similar foundations. A major use of bentonite in civil engineering is plastic concrete, a mixture of cement and bentonite to form a consistency of hard clay. This concrete is impermeable and capable of moving with the ground. In civil engineering mainly sodium bentonite is used.

Bentonite is used as plasticizer in a great variety of building materials, incl. red bricks, portland cement, gypsum products, paints, pottery and vitrified pipes and tiles. Bentonite has been an important component of thixotropic paints.

Filtering and decolourising of oils and other liquids

Most glyceride oils, i.e. those of vegetable or animal origin, must be bleached before use. Crude fats or oils after mechanical expression or solvent extraction are refined to remove free fatty acids, phosphaticles and impurities. The oils are often used in light varnishes and other industrial end-uses.

These oils are also bleached with calcium or acid activated bentonite at about 1000°C or at lower temperatures under a vacuum. The consumption of activated bentonite varies with the grade and colour of oil but it is usually about 1% of the weight of oil processed. In the USA about 150 000 tons of bentonite and fuller's earth are consumed to bleach the vegetable oils. Other huge producers of vegetable oils are Argentina, Brazil, China, India, Indonesia, Italy, Malaysia, Nigeria and the USSR. Most of developing countries export the vegetable oils in the unrefined state and therefore most of bleaching clays are used in developed countries. This pattern will probably change as developing countries will invest into oil refineries more. The demand for bentonite has risen sharply in Malaysia up to 35 000 tpa because sooner the Malaysian palm oil was refined in Europe. The Philippines and Indonesia will probably follow. The Mediterranean countries use considerable quantities of activated calcium bentonites for decolourising olive oil. Bentonites are also used to filter and clarify mineral lubricating oils (predominantly in the USA) and to clarify wines and fruit juices.

Other uses

Acid activated bentonites are used as adsorbents for oil, grease and pet litter. The use of bentonite for this purpose depends mainly on their local availability because many competitive adsorbents can be used efficiently. For example, the pet litter is the second largest market segment for bentonite (after foundry sands) in the UK. These adsorbents are sold as granules and in consumer's packaging in retail outlets. In the industrial field the adsorbents are sold to shops where spillages are likely to take place, e.g. machine shops, garages and chemical and dye factories.

The use of montmorillonite clays as dry carriers for pesticides, herbicides and insecticides increased considerably in the world in 1970, since the use has grown slowly but steadily. This field is dominated by fuller's earth. For example, in the USA about 92% of montmorillonite clays used to formulate pesticides were acid earth. The annual supply of montmorillonite clays for this purpose accounts for about 70 - 80 thousand tons in the USA and about 60 000 tons in Japan where this is the third largest end-use for bentonites. Other dry carriers frequently used are attapulgite, kaolin, sodium and calcium bentonite.

In Europe there are not used the above non-metallics as carriers because there is generally an adequate water supply and the use of heavy dusts is very limited. In addition dusts are not satisfactory in areas of stronger winds.

There are competitive materials used as carriers and diatomaceous earth is a favoured material but it is rather expensive. Montmorillonite and attapulgite may be used when an insecticide is stable otherwise the clay facilitates its break-down as a catalyst.

Some bentonites are used in the manufacture of oil refining catalysts which is a market of great demand fluctuations because it is linked with new installations. These catalysts are used on once-only basis and their replenishment is a very small market. In the USA the consumption of bentonite for this purpose fluctuates between 2 - 20 thousand tpa.

There are other small volume uses for bentonite which are difficult to get to know from statistics. Either these uses are proprietary in order to protect from competitors or they are included in the item "miscellaneous". Bentonites are added to mineral oils to formulate greases usable at higher temperatures.

Other uses include:

- to enhance opacity of thin papers
- to encapsulate ink in no-carbon duplicating paper
- gelling agents in adhesives
- bentonite is also used in the manufacture of some medical, pharmaceutical and cosmetic preparations
- pelletising of animal foodstuffs

4. Selected National Economic Aspects

It is obvious that merits of development of large-scale exploitation of bentonite in a country can go far beyond the money values of exports and end-product prices. A bentonite exploitation project will touch such national economic criteria as new job creation, foreign currency balance, food production through reclaimed marginal land and ecological aspects.

Especially two application fields are of a greater national economy significance. Firstly, it is a rehabilitation of deficient soils both to enhance their productivity and to maintain the regime and purity of water. Secondly, bentonite as an efficient adsorbent is used in a growing manner for treatment of waste water from different industries, agriculture and human settlements.

The maintenance and enhancement of yield potential of agricultural land is an essential prerequisite of solving the world food problem. In addition, the soil plays a very important role in maintaining the landscape ecological balance since it also controls the regime and purity of water. It is on this recognized complex function of soil that an enhanced attention has been paid to it in recent decades.

A considerable part of the world agricultural fund is taken up by arenaceous and argillo-arenaceous soils which are looked upon as deficient ones. Especially, high water permeability, small water retention, low natural nutrient supply and a weak sorption complex are characteristic of sandy soils. They have thus low natural productivity and fail to retain water. Amelioration of these soils have larger national-wide consequences both for the staple crop and food selfsufficiency and also for ecological balance. According to the present world praxis and research, at least four types of amelioration actions are applied among them the application of bentonite has, under certain favourable conditions, comparatively good economic return. These amelioration actions can be listed:

- reclaiming reconstructions which means reconstruction of soil texture and stratigraphy
- differentiated agrotechniques consisting in special soil preparation, optimization of cultivating schedules, differentiated manuring
- optimization of farming system which includes law provisions to protect soil fund and build-up of appropriate economic environment through incentives and subsidies to maintain the soil fertility
- technical reclamations which consist in reconstruction of water regime, draining, irrigation and applications of amelioration materials, such as composts, organic wastes, mineral sorbents.

To illustrate the efficiency of mineral sorbents, the once-for-seven-year application of bentonite brings about the improvement of soil fertility which corresponds to considerably higher humus content in soil. If organic composts were applied a similar improvement would require the applications of organic matters for 15 subsequent years.

VI. ANTICIPATED DEVELOPMENT

1. Bentonite Survey in Developing Countries

The actual consumption of bentonite depends strongly on the development in a few sectors. This applies mainly to the demand for natural Na- or Na-activated bentonites which are consumed in pelletising iron ore, foundries, oil well drilling and oil refineries.

Since 1982, the pelletisation of iron ore has recorded a decline. The original forecasts from the early 1980's that there will be a sustained growth of iron ore consumption up to about 125% in 1990 were revised. (Industrial Minerals, Nov. 1986) It is supposed that the consumption will stagnate or grow very slowly and the figure 1 000 mil. tons of iron ore in 1990 maximally is accepted. The share of North America will decline to the benefit of Brazil and Australia which, however, need not pelletize.

The forecast for bentonite consumption in drilling fluids are influenced by the situation on the crude oil market as it developed in the mid of 1980's when the prices of crude oil were considerably cut down. This development has resulted into a substantial reduction of drilling activities as documented by figures of bentonite consumption. In 1981, 2 mil. tons of bentonite were consumed in oil well drilling while in 1984 the figure was 1.4 mil. tons only valid for the USA.(Industrial Minerals, Nov. 1986) To describe the future of this very volatile industry is a difficult deal since much depends on the policy and coordination executed by OPEC. A substantial growth of price is not expected because of situation of supply exceeding demand. From the point of view of middle-term horizons this means that higher-cost firms will gradually be driven off the sector and other will merge and reorganize. The result will be a considerable reduction of drilling activities and many rigs in operation will be exhausted within next three years. It is expected that then the demand for will exceed the supply of crude oil resulting into a rapid growth of prices. The experts from oil industry expects this "closing-up of the circle" to set in before 1990. If there are no substantial technological developments introducing new components into drilling fluids the market for bentonite should recover in this time.

The foundry industries are not expected to restore the consumption figures from the end of 1970's. This is put into connection with the developments in the car-making sector - smaller cars with more and more plastics and ceramic materials instead of steel and cast iron.

On the contrary, a favourable future for bentonite is expected in food processing, agriculture and environmental protection. There are many competitive materials for bentonite as adsorbent in the industrialized countries and its consumption is thoroughly dependent on local economic conditions. In the developing countries developments of down-stream processings in food industry and extension of metallurgical and foundry industries can be expected with all the consequences for the sustained growth of demand for bentonite. It applies, e.g. to the down-stream processing of edible oils to enhance their export value. There in arid countries bentonites have good prospects to be used not only due to their fertilizing effect making thus possible to introduce marginal land into the food chain economically but also to maintain the ecological balance. Other sectors will be developed which are traditional consumers of bentonite, mainly, building materials and ceramics, civil engineering, because developing countries plan to diversify their industries. Some developing countries can probably enter the international trade with bentonites because they many have comparative advantages for it consisting in more factors. E.g. a good accessibility to a deposit of good quality bentonites which can, together with a cheap labour, result into competitive prices.

Survey of Bentonites

The purpose of survey of bentonites is not only to identify the material wanted but also to determine conditions for further up-grading and industrial exploitation. Therefore, the survey of bentonites will be based on actual geological prospecting and laboratory and pilot tests to evaluate the industrial applicability of raw material.

The purpose of prospecting is:

- to find the bentonite deposit,
- to determine the type and extent of overburden,
- to describe the dip and strike of strara,
- to investigate drainage conditions,
- to take representative samples.

Office studies

The field works can considerably be expedited and final results enhanced if preparatory studies are undertaken:

- geological and topographical information which can be gathered by referring to any well-drilling records or similar data or by consulting landowners, local geologists and other non-technical people,
- information on geological formations in the area which is also important from the point of view of option

for mining methods,

- considerations of geographic location which is of consequence for further economy and can sometimes make the possible industrial exploitation economically infeasible,
- study of soil conservation and environmental protection laws which may require a certain or complete reclamation of area exploited making thus otherwise good deposits economically infeasible.

Field work

The modern prospecting for non-metallics is based on sophisticated methods of geophysics that include:

- Geoelectrical methods which examine natural or induced electric fields of direct or alterating current and are based on the principle of distinguishing rocks and minerals after their resistivity. They are advantageous for the velocity of measurements and evaluation of results and because a lot of information is obtained. The most used methods among them are symetric resistivity profiling (SRP), combined resistivity profiling (CRP) and vertical electrical sounding (VES).

- Magnetic survey which is based on different susceptibilities of rocks and minerals. Rocks containing magnetic minerals have a higher mg susceptibility and can be distinguished by their measuring. These values can vary considerably depending on the content of ferromagnetic minerals. Therefore, the magnetic properties of the rocks must be established prior to mg measuring.

- Seismic method which is based on recording the velocity of elastic waves propagation which is different for particular types of rocks. E.g. velocity in igneous rocks is 5 - 7 thousand m/sec., in clay 1.5 - 3.0 thousand m/sec. The application of this method has spread very rapidly with the development of light portable devices capable of providing information to a depth of 100 m.

- Gravimetry which is based on studying gravity effects of particular rocks which are direct proportional to the unit density of those rocks. The unit density of a rock depends on the mineralogical and chemical composition of rock-forming minerals, on the texture and structure of rock and on the grade of metamorphism.

- Nuclear methods which are based on measuring natural activity or activation of material examined. The first type includes measuring of total alpha and gamma activity, emanation, beta radiation, gamma spectrometry, etc. The second group uses the effect of artificial sources of beta and gamma radiation of neutrons on the rocks and determines the properties of rocks by measuring the secondary field of radioactivity.

- "Wildcat" prospecting

  The prospecting through walking or travelling about the area may be a successful method to look for surface signs or clay deposits. This method should not be underestimated since such a ground reconnaissance may help to gather information cheaply and conserve cost in subsequent drilling or may help to plan the subsequent works more efficiently.

  - Vegetal growth may indicate the presence of clay, because the clay beds are not favourable to the vegetation, any sudden changes to poor vegetation may be a sign of clay deposit

- Burrowing animals may choose to make their dense under clay strata because the earth will be drier there than in neighbourhood. A line of burrows at a horizon may indicate a clay seam over it.

- Observing appearance of material on the surface since clays have specific textures, colours, etc. Clays found on the surface show a distinctive cracking pattern.

- Earth movements, e.g. fresh landslides may expose clay outcrops, as clays weather rather readily into small particles it is not probable that larger lumps could be found in flows so that it is necessary to collect and sample fines.

Sampling and field tests

Sampling is an all-important task to explore clay deposits. Several types of sampling and equipment are used. If the deposit is exposed to an outcrop then trenches perpendicular to the course of the outcrops are dug. If the clay is too deep for trenching pits are dug. Both trenches and pits are effective methods yielding information and large amount of samples, however, because of hand work of a great extent they can be rather costly.

If a deposit of clay outcrops on the side of a hill and the underground mining seems probable horizontal adits and openings are drilled into the face of the hill.

Usually, due to the depth, topography and consistence of overlying materials the deposit is to be drilled. There are two general types of devices for drilling clay deposits:

- Hand auger capable to be used to a depth of about 9 m at bore diameter about 100 mm. For narrower holes it may go as down as 20 m. They are a powerful tool for remote areas because of easy transportability.

- Powered auger drills which can reach as much as 120 - 180 m depth within 8 hours.

Other drilling methods and devices, such as diamond core barrel drilling, are used to prospect and sample more valuable materials.

During sampling, some preliminary simple tests can be done on the spot.

A simple "hand" test consisting in moistening a handful of clay with a few of water drops to judge the plasticity. Clays are also judged by tasting utilizing the salts accompanying them. Hardness and friability of clays which are important for mining method applied can also be evaluated on the spot. It applies also to upgrading methods. E.g. well weathered outcrop makes possible to suppose a high plasticity of deposited clay.

Laboratory Testing for Regional Activities

A proper survey of bentonites must yield an information valuable for the industrial exploitation decisions. This information can only be obtained in laboratories where representative samples will be analyzed and semi-industrially verified, if need be.

The organization of testing of bentonites is based on the properties of this industrial mineral to be distinguished in view of requirements of end-users. Bentonites can be tested on the equipment and by methods developed to test other clays, kaolins and sands. Such a laboratory aiming at utilization of the above non-metallic minerals and rocks on regional scale will consist of:

- section for preparation and beneficiation of samples,
- section for analytical chemistry,
- section for physical chemistry and mineralogy,
- section for technological tests,
- pilot workshop.

The section for preparation and beneficiation of samples receives, describes and designates samples of won raw material, semiproducts and final products and prepares specification of tests to be carried out. Besides, preparation and beneficiation of samples take place here.

The basic assignment of the section for analytical chemistry consists in analyzing chemical composition of raw materials, semiproducts and final products. This is made by abridged chemical analyses and complete chemical analyses. In supplementary programme some special analyses are carried out.

The section for physical chemistry and mineralogy evaluates by suitable methods raw materials, semiproducts and final products. Samples of raw materials are evaluated from the mineralogical point of view. The results of thermal analyses are combined with data of chemical analyses and mineralogical analyses are determined.

Clays are subjected to granularity analysis. Specific properties as adsorption capacity, specific surface, etc. are determined by physical-chemical methods.

As far as sands are concerned, both sand fractions and clay fractions are assessed from the mineralogical viewpoint. Higher attention is paid to heavy portions of sands (mineralogical quantitative and qualitative analysis of contaminations).

Technological section is engaged in routine tests of clays, kaolins and sands. For clays the basic parameters are determined: humidity, sieve residues after wet screening, drying and firing dilatation, water absorption, firing colour, bending strength after drying, binding power, refractoriness, fusibility, content of water and number of plasticity, rheological properties, bending strength after firing, refractoriness and abrasivity.

Pilot workshop - Samples of clays, kaolins and sands are processed by semi-industrial equipment to verify quality of products. Samples of minimum weight of 50 kg pass through processing lines modelling the actual production conditions. The workshop passes samples of beneficiated semiproducts and final products to the other sections for evaluation.

As far as bentonites are concerned their testing in a regional laboratory should run as follows:
- the appearance of samples is judged
- the content of impurities is fixed by means of washing through screens
- mineralogical composition is analyzed. The most powerful method to describe bentonites mineralogically is the X-ray powder diffraction using the X-ray goniometer. /Zussman 1967, Thorez 1980/. Using the X-ray analysis of clay samples saturated with ethylen glycol or glycerine, swelling clay minerals, especially montmorillonite can be determined.

- Chemical composition is analyzed by classical methods of silicate analysis or by atomic absorption spectrophotometry (AAS) which is capable to identify more than 40 elements of periodic talbe even if they are present in trace amounts. Among these elements there are all those determinable by silicate analysis.
- Thermal analysis is other necessary step to accomplish the information on mineralogical composition by studying the changes in chemical, physical and physico-chemical properties of minerals at increasing temperatures from 20 to 1000°C usually. The differential thermal analysis (DTA) records reactions as deviations from the base line. The deviations indicate the escape of volatile components (H_2O, CO_2, SO_2, F_2, Cl_2 and so) oxidation (C to CO_2, e.g.) the destruction of crystalline phase and the origin of amorphous phase or, vice versa, irreversible changes ($\alpha \longleftrightarrow \beta$ quartz) and melting (solid ⟶ melt). These changes correlated to a standard which is chemically similar to the sample under examination are expressed as a curve. The amount of material under DTA is 0.2 - 1 g. The thermogravimetric analysis (TGA) determines minerals on the basis of the loss of mass as a fuction of temperature. If the reactions of particular minerals do not coincide the contents of mineral can be fixed with accuracy of several per cent. If two decomposition reactions coincide the fractional thermogravimetry (FTG) should be used. The thermal dilatational analysis (TDA) or contraction dilatation thermal analysis (CDTA) enables to study the length changes of heated materials.
- Granulometric analysis is carried out to study the clay particles (0 - 60 μm) and it is a powerful means for the petrographical classification of clays indicating very expressively the technological properties of clays. This analysis can considerably be sped up using the Andreasen sedigraph.

- Sorption capacity determination is a datum which characterizes the quality of bentonites. It is fixed by means of a typical staining method using methyl blue.
- Ion exchange capacity illustrates also the quality of bentonite and is determined by the saturation of NH_4^+ ions, expressed in milliequivalents per 100 g of dry bentonite.
- Binding power determination is of grave importance for bentonites to be used in foundry industries. The test is based on the bending strength of specimen which is made up of standard sand and bentonite under test.
- Plasticity is determined by different empiric methods the most used of them is that according to Pfefferkorn.
- Rheological properties evaluation consists in determining the thixotropy and liquidity of bentonites according to different empiric methods using current equipment (rotary viscosimeters).

The above testing is used to characterize sampled bentonites. To accomplish the information on bentonite it is necessary to examine its behaviour and technological properties during industrial processing. A 50-kg sample is usually verified in a pilot workshop which models the actual condition of a given end-use. The processing of bentonite to suit various industrial end-uses is comparatively simple as is also the pilot plant to verify bentonite technological properties.

The process consists in:
- drying the sample in a chamber drier,
- milling the sample which requires usually a vibratory mill, drum mills for both wet and dry milling,
- blunging the sample,
- kneading the sample; frequent devices are edge-runner mixer, auger two-axis mixer and extruder.

The above equipment is used also for wet and dry mixing.

- screening the sample through a series of vibratory sieves.

2. Up-grading of Bentonites

New developments are anticipated in the field of up-grading methods to utilize bentonite for more specialized end-uses. A considrable development is expected to concern the wet up-grading methods which enable to separate exactly undesirable components, mainly exchanged ions and balast admixtures. The wet processing with the subsequent spray drying will lead to getting a product of controlled granulometry.

Modern refining methods, such as high-intensity electromagnetic separation applied to the slurries, are expected to be applied more widely. To delaminate and adjust the dispersion capacity of bentonites new high-frequency processes based on ultrasound are applicable. Thoroughly new properties of bentonite can be obtained through the application of high-frequency electrical field to the water suspensions of bentonite.

The application of bentonites for the waste water disposal purposes will be influenced by sustained development of special activations both by inorganic and organic matters of surfactant-type to enhance the selective capacity of bentonite for various types of water (sorption of heavy metals, tenzides, organic dyes).

Activation agents are sought for which are both available abundantly and/or are waste in order to solve in an advantageous manner the problem of their disposal and concurrent economical application to refine the natural raw material.

The activation agents will be preferred for the waste water treatment which will not contract the application of waste in the agriculture and industries. This applies to, e.g.,inorganic salts easy to hydrolyze into both insoluble and non-toxic products or to organic matters easy to decay biologically.

For special end-uses the production of organobentonite will develop. Organobentonites are those bentonites which have organic matters anchored to their surface which control the properties of bentonites to be used in compositions with other organic materials.

A thoroughly new way to process bentonite has been put into verification research which is based on biotechnological processes. There exist certain cultures of bacteria which are capable to separate selectively certain components of crude bentonite which results into concurrently enhanced purity of bentonite and its delamination.

3. Non-traditional Uses of Bentonite

Catalysts

A progress can be anticipated in developing a series of new efficient catalysts for a homogeneous catalysis when special activated bentonites can find a wide application field. As an example Cu-bentonite can represent these types which is used for the processing of special chemicals.

Catalyst carriers

Bentonite is expected to be used extensively as a carrier of certain catalysts, especially in petrochemistry for oil cracking mainly.

Waste water treatment

Activated bentonite of special controlled properties will contribute to enhancing efficiency of waste water disposal plants. They will be used for a/ pre-treatment and post-treatment of water in existing facilities and b/ for special selection of contaminants as final step of the process.

Fillers

Bentonites are expected to find an extended utilization especially in the processing of dyes and varnishes as fillers. Both inorganic and organobentonites have prospects.

Encapsulating

Bentonites are considered as incomparable sorbents to produce the non-carbon direct duplicating papers which are demanded in a growing manner. Bentonites can contribute significantly to their improved quality.

Other uses

Bentonites are used for pelletising the waste from nuclear power plants. They are also anticipated to be more utilized in the chemical industries as carriers of chemicals, e.g. insecticides and mainly as sorbents to reclaim indigent sandy soils in arid regions.

The foregoing examples show that bentonites and other montmorillonitic clays will have good future in the years to come and, therefore, more attention is to be paid to these non-metallic rocks already at present.

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Table 1 Classification of Clay Minerals

Kaolinite Group	Montmorillonite Group	Micaceous Group 3/	Aluminous Group
Kaolinite	Pyrophylite 1/	Muscovite 1/	Gibbsite 1/
$Al_2(Si_2O_6)(OH)_4$	$Al_2Si_4O_{10}(OH)_2$	$Al_4K_2(Si_6Al_2)O_{20}/OH/_4$	$Al(OH)_3$
Dickite	Talc 1/	Bravaisite	Diaspore 1/
$Al_2(Si_2O_5)(OH)_4$	$Mg_3Si_4O_{10}(OH)_2$	$Al_4K_x(Si_{8-x}Al_x)O_2O(OH)_4$	$HAlO_2$
Nacrite	Montmorillonite 2/	Brommallite	
$Al_2(Si_2O_5)(OH)_4$		$Al_4Na_X(Si_{8-x}, Al_x)O_{20}(OH)_4$	
Anauxite	Beidellite 2/	Attapulgite	
$Al_{2-n}(Si_{2+n}O_5)(OH)_4$	Nontronite 2/	$(Mg_5Si_8)O_{20}(OH)_2 2H_2O$	
Endellite	Saponite 2/	Ordovician bentonites	
$Al_2(Si_2O_5)(OH)_4 \cdot 2H_2O$	Hectorite 2/		
Halloysite			
$Al_2(Si_2O_5)(OH)_4$			
Allophabe, Amorphous			

Source: Refractories, JP/290/86

Notes: 1/ These minerals are usually not considered among clays but when finely ground

to be continued ....

behave like clays in ceramic processes.

2/ Formula to be found on pg 20

3/ Most of micaceous minerals are not very specific.

Table 2 Principal Applications of Bentonite in Petrochemistry

Type	Raw material	Product	Principal process	B-ite property	Type of B-ite, reaction conditions
I	butenes	petrol	dimerization of olefins	catalytic	H^+-act., 150°C, 35 atp
II	non-stable unsaturated petrol	stable unsaturated petrol	polymerazation of dienes	catalytic	H^+-act., 200°C, 5-20 atp, gas phase
III	unsaturated detonating petrol	unsaturated non-detonating petrol	izomerization	catalytic	H^+-act., 510°C, 2 atp, gas phase
IV	sulphurous petrol	desulphrized petrol	cleavage of C-S bonds	catalytic	H^+-act., 360-400°C, 3 - 7 atp, gas phase
V	non-stable oil /paraffin/	stable oil /paraffin/	physical adsorption	adsorption	natural or activated, 0.5 - 10% on oil to 100°C
VI	as V	as V	chemisorption	adsorption	as V, 1 - 5% on oil at 200 - 360°C
VII	higher hydrocarbons	high-octane petrol	cleavage desalkylation, depolymerization, isomerization.	catalytic	H^+-act., 460 - 510°C, up to 1 atp, gas phase
VIII	lubrication oils	greases	swelling	thickener	organobentonites

Table 3 Consumption of Bentonite by End Use

	Australia 1980		Canada 1979		France 1980		FRG 1982		Japan 1981		USA 4/ 1982	
	t	%	t	%	t	%	t	%	t	%	%	%
non-iron pelletisation	37000	55.2	265213	78.1	2000	1.2			7688	2.0	800000	21.1
foundries	12000	17.9	51125	5.3	80000	50.0	160000	60.6	145540	37.4	720000	19.0
drilling	7913	11.8	18051	15.1	14000	8.7			33950	8.7	1900000	50.0
chemicals + dye			260									
fertilizers, carriers, soil conditioners			806	0.2			10000	3.8	67027	17.2		
civil engineering					260000	16.3	30000	11.4	97442	25.0		
livestock feed					20000	12.5					140000	3.7
bleaching					10000	6.3	35000	13.3			145000	3.8
absorbents							10000	3.8			225000	5.9
pet litter											280000	7.4
others	10087	15.1	4451	1.3	8000	5.0	19000	7.1	37869	9.7	185000	4.9
Total	567000		339906		160000		264000		389516		3795000	

Source: National Mineral Industry Reviews and other statistics, published /mainly Industrial Minerals)

4/ approx.

Table 4 Selected Countries Producing Bentonite, 1973 - 1980 (000t)

	1973	1974	1975	1976	1977	1978	1979	1980
Argentina	101.6	113.2	116.0	132.3	114.8	107.0	157.4	131.4
Brazil	44.2	77.1	116.8	143.2	108.4	167.6	212.8	248.0
Czechoslovakia	134.0	116.0	159.0	164.0	182.0	182.0	189.0	121.0
Germany, Federal Republic of 1/	600	600	600	600	600	600	600	600
Greece	472.2	384.4	411.0	316.8	557.0	408.7	495.2	501.9
Hungary	73	73	87.9	71.1	80	82.2	72.5	77.7
Italy	299.3	243.9	280	234.6	280.3	235	252	323
Japan 1/	460	452.1	403.7	399.2	399.2	399.2	399.2	399.2
Romania 1/	50	62.8	62.8	63.5	63.5	63.5	65.3	65.3
Spain	47.6	75.9	75.3	108.2	114.6	108.3	120.7	97.7
USA	2787.4	3003.2	2929.5	3193.7	3398.8	4053.4	4011.7	3796.3

Note 1/: USBM Minerals Yearbooks estimates

Source: USBM Minerals Yearbooks

Table 5 Selected Countries Producing Acid Earth 1973 - 1980 (000t)

	1973	1974	1975	1976	1977	1978	1979	1980
Italy	113.6	105.3	70.5	24.9	6.3	-	-	5.4
Mexico 1/	50.3	53.9	38.2	20.1	61.4	40.6	48.8	51.4
Great Britain 2/	185	166	164	201	223	218	220	210
USA 3/	1032.8	1111	1078.7	1217.1	1295.8	1387.7	1422.7	1391.5

Notes: 1/ Sepiolite
2/ Includes calcium bentonite
3/ Includes attapulgite and sepiolite for bleaching

Source: USBM Minerals Yearbooks

Table 6 Selected Exporters and Importers of Montmorillonite Clays (000 t)

Export	1973	1974	1975	1976	1977	1978	1979	1980	1981
Germany F.R. of	31.6	37.3	32.9	44.3	30.5	25.0	26.3	29.8	24.0
Greece	316.7	296.9	336.4	381.6	381.1	331.7	272.2	339.7	N.A.
India	3.5	8.0	15.7	6.2	11.1	15.9	21.8	18.2	8.9
Italy	15.7	24.0	19.3	23.5	18.6	20.2	31.3	19.0	36.3
Netherlands	12.0	18.0	13.0	10.5	18.1	24.9	27.3	36.0	46.6
Spain	15.4	18.6	22.6	26.1	11.9	37.9	39.9	32.6	N.A.
UK	17.4	22.3	15.9	18.4	17.1	17.7	15.9	25.0	N.A.
USA	551.9	698.0	670.9	752.3	755.6	709.9	840.6	1012.4	882.9
Imports									
Australia	63.1	69.1	50.2	63.7	11.8	19.4	N.A.	N.A.	N.A.
Belgium	11.3	17.3	22.6	27.8	26.6	28.6	24.6	38.5	25.8
Brazil	19.3	17.7	13.1	14.0	16.2	14.4	21.6	13.2	N.A.
Canada	367.6	345.2	286.0	366.6	478.1	295.7	612.3	469.5	311.6
France	72.8	124.0	103.8	94.3	91.3	88.5	94.5	18.0	95.0
Germany F.R. of	33.8	107.0	43.5	93.3	77.5	45.9	66.8	78.0	77.2
Italy	25.9	26.8	23.4	42.5	64.6	54.7	29.9	55.4	25.4
Netherlands	42.8	38.4	46.4	35.4	38.3	58.7	64.9	68.9	63.2
UK	53.5	73.4	45.4	48.4	79.0	46.2	75.4	79.2	N.A.

Source: International Trade Statistics

Table 7 FOB Values of Selected Exports of Bentonite and Fuller's Earth (US $/t)

	1975	1976	1977	1978	1979	1980	1981
Belgium (bentonite)	82.6	73.9	80.4	91.7	109.9	108.7	93.8
France (bentonite)	124.6	125.8	125.9	146.3	235.8	189.2	153.6
(fuller's earth)	52.0	49.9	50.0	139.3	102.6	85.7	93.6
Germany F.R. of (natural bentonite)	95.4	92.3	113.7	136.2	150.3	155.5	154.4
Greece (crude bentonite)	12.7	12.7	13.7	16.4	17.2	15.2	-
(processed bentonite)	18.8	17.3	19.6	19.3	22.7	26.3	-
Italy (bentonite)	55.0	80.4	73.2	94.2	80.0	120.1	92.5
USA (bentonite)	62.4	70.6	64.1	65.9	71.4	76.4	82.5
(fuller's earth)	67.2	70.6	67.9	78.7	77.1	88.7	103.6

Source: International Trade Statistics

Table 8 World Prices of Bentonite

Country	Company	Price/t	Application
Argentina	Gaberovich HNOS	$ 65 fob plant	oil well drilling
		$ 55 fob plant	pelletisation/ foundry
	Industrial Petrol	$ 60 - 70 fob B. Aires	all qualities
Brazil	Bentonit Uniao Nordeste	$ 62 - 90 fob Cabadelo	oil well drilling
		$ 72 fob Cabadelo	foundry
		$ 57 fob Cabadelo	pelletisation
Cyprus	Peletico Ltd.	$ 90 fob Larnaca bags	oil well drilling
		$ 72 fob Vassiliko Bay granular in bulk	- " -

Source: Industrial Minerals, November 1981

Table 9 Pellet and Total Iron Ore Output in Major Mining Countries (1979)

Country	mill.t /pellets/	mill.t /usable ore/	%
Australia	7.0	99.8	7.0
Brazil	10.0	91.7	10.9
Canada	30.9	61.3	50.4
France	-	31.7	-
India	4.3	19.7	21.8
Sweden	7.5	26.6	28.2
USA	79.3	87.1	91.0
USSR	37.0	242.0	15.3
Venezuela	-	15.3	

Source: AIOA

Table 10 Increments of Yield by Sorbent Application

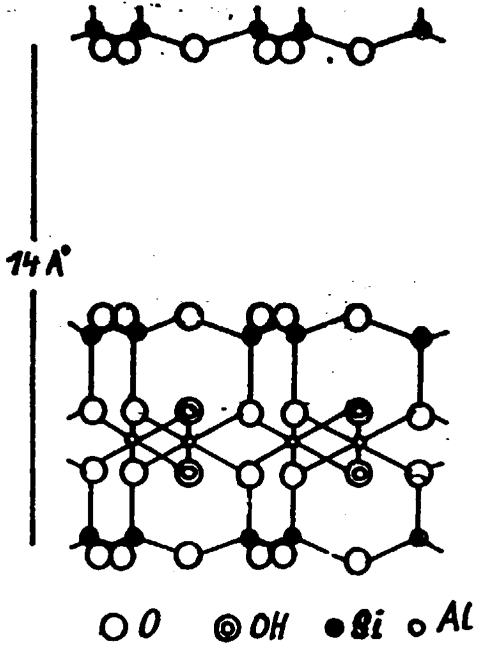
Applied sorbent	Type of soil (% grain 0.01 mm/% humus)	Dosage (t.ha^{-1})	Tested plant	Increase of output /%/	Application in
bentonite	9.2/1.3	20	potatoes	18.6	Czechoslovakia
bentonite	9.2/1.3	20	rye	16.7	- " -
bentonite	11.1/1.7	20	barley	11.5	- " -
bentonite	11.1/1.7	20	maize	8.8	- " -
bentonite	6.4/0.4	20	barley+rye	22.2	- " -
bentonite	6.4/0.4	20	pulses	39	- " -
bentonite	6.4/0.4	20	maize	39.2	- " -
zeolite 60 1/	N.A. 2/	4	potatoes	30	- " -
zeolite 50	N.A.	10	capsicum + tomatoes	16	USSR
zeolite 50	N.A.	16	capsicum + tomatoes	33	- " -
zeolite 80	N.A.	16	paddy	40	Japan
bentonite	sandy soil	20	maize	80 - 90	Hungary
bentonite	desert soil (pure sand)	20	barley	90 - 100	Egypt
bentonite	- " -	20	vegetables	90 - 100	- " -
tuff	N. A.	20	maize	32.4	Hungary
tuffites 3/	turf	20	maize	from 7.9-80.6	Hungary

Notes: 1/ Zeolite index marks the percentage of clinoptilolite

2/ Not available.

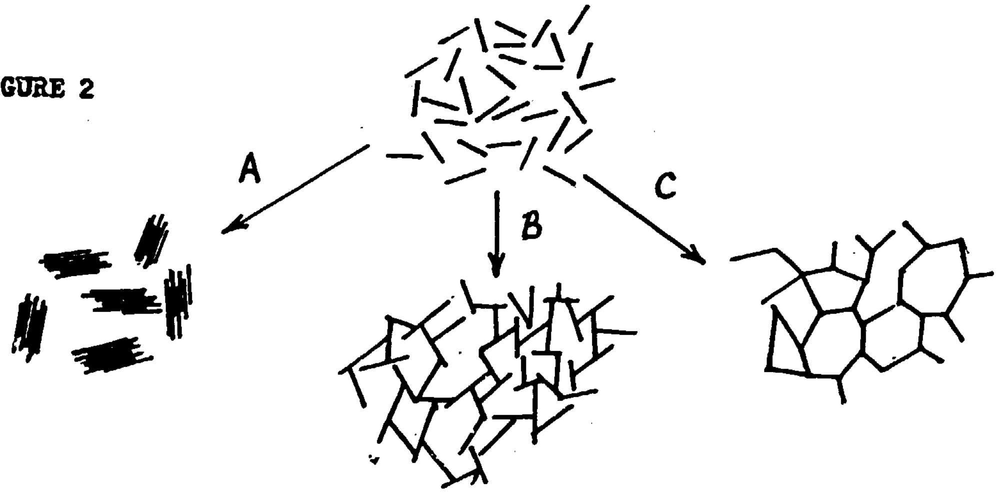
3/ Tuffites of different carbonate content and different sorption capacity.

FIGURE 1



Montmorillonite Structure Scheme (Projection onto plane b c)
Hoffman, Endell, Wilm

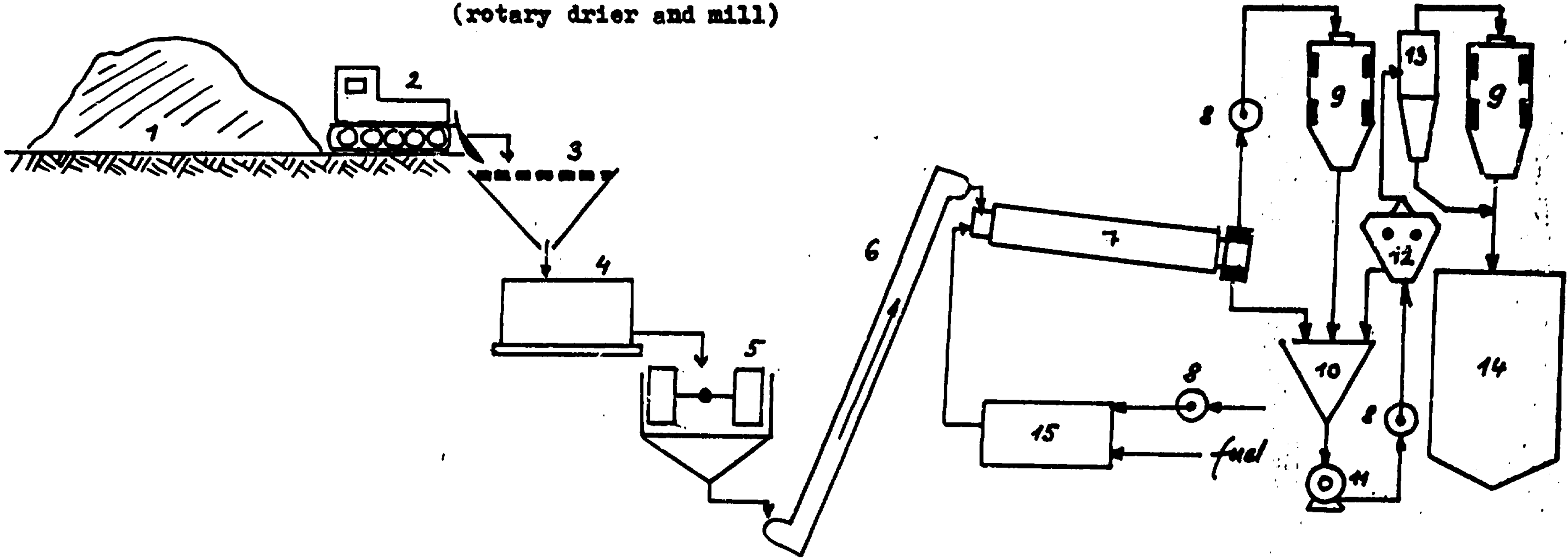
FIGURE 2



Basic Types of Plate Particles Aggregation
A - face to face
B - edge to face
C - edge to edge

FIGURE 3

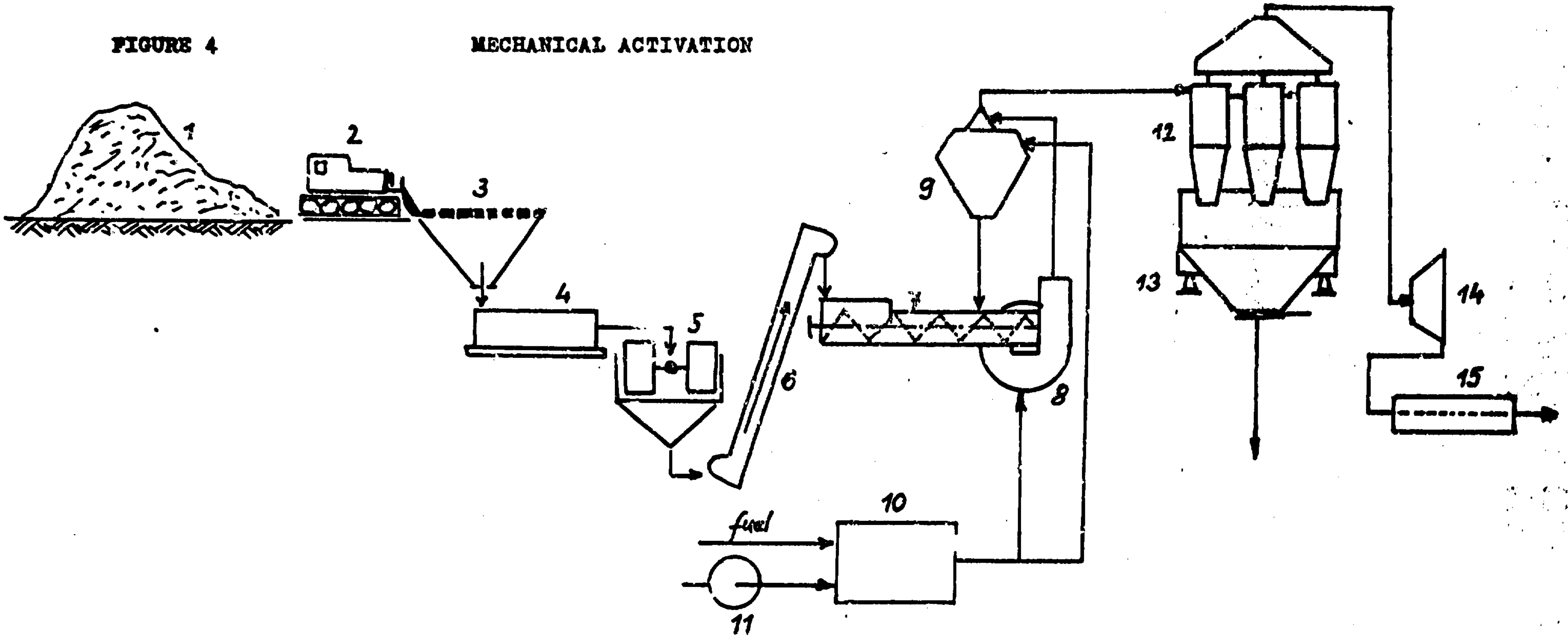
MECHANICAL ACTIVATION
(rotary drier and mill)



LEGEND

1 - stock pile
2 - bulldozer
3 - grates
4 - drum dozer
5 - pan mill
6 - elevator
7 - rotary drier
8 - blower
9 - bag filter
10 - hopper
11 - mill
12 - air classifier
13 - air cyclone
14 - product silos
15 - combustion chamber

FIGURE 4 MECHANICAL ACTIVATION



LEGEND

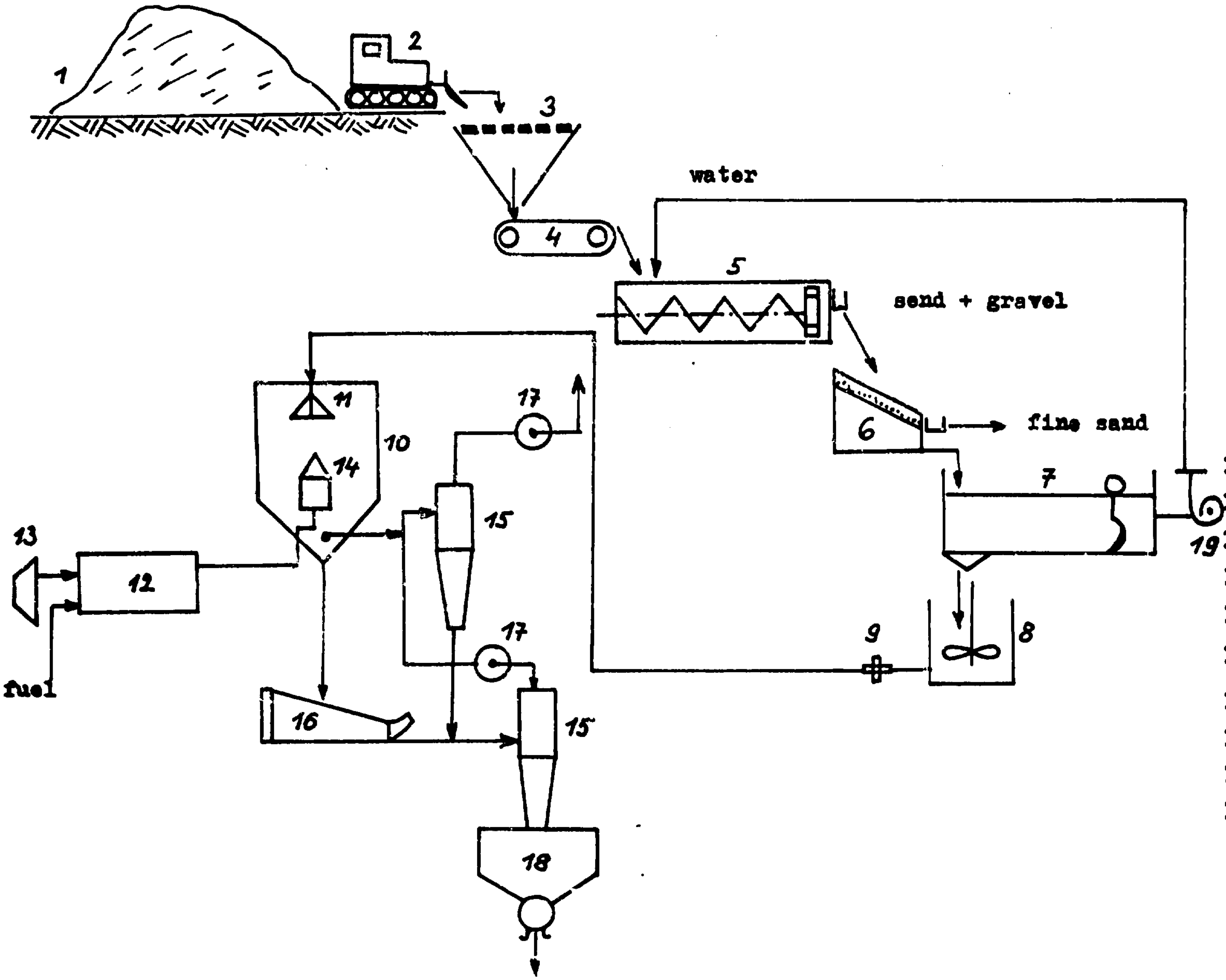
1 - stock pile
2 - bulldozer
3 - grates
4 - drum, dozer

5 - pan mill
6 - elevator
7 - screw conveyer
8 - drying mill

9 - air classifier
10 - combustion chamber
11 - fan
12 - cyclones

13 - product silos
14 - blower
15 - filter

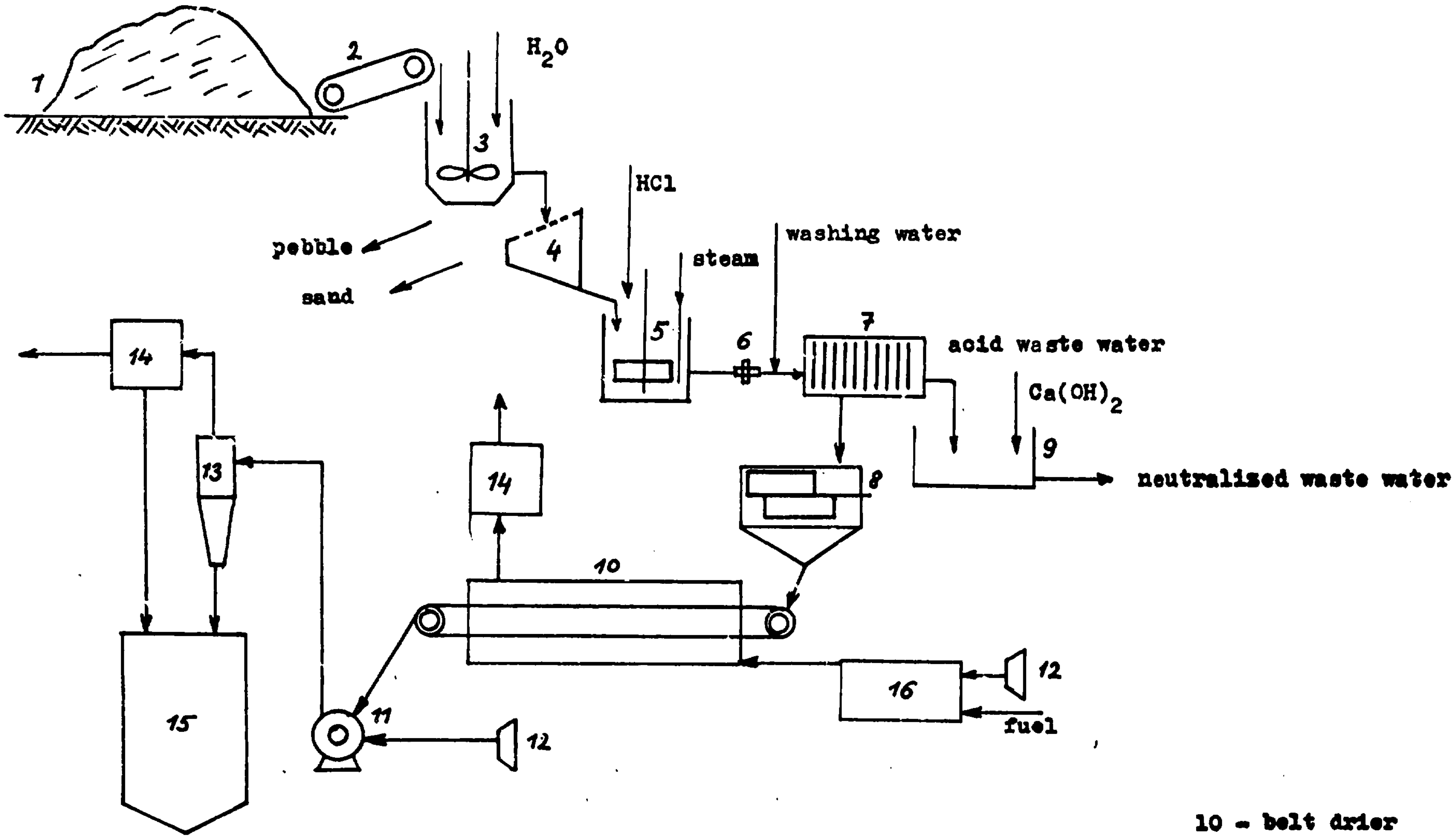
FIGURE 5 BENTONITE WASHING PLANT



LEGEND

1 - stock pile
2 - bulldozer
3 - grates
4 - belt dozer
5 - drum blunger
6 - vibratory screens
7 - sedimentation tank
8 - tank for slurry
9 - dosing pump
10 - spray drier
11 - spraying wheel
12 - combustion chamber
13 - blower
14 - hot air distributer
15 - air cyclone
16 - air ejector
17 - fan
18 - dried product silos
19 - pump

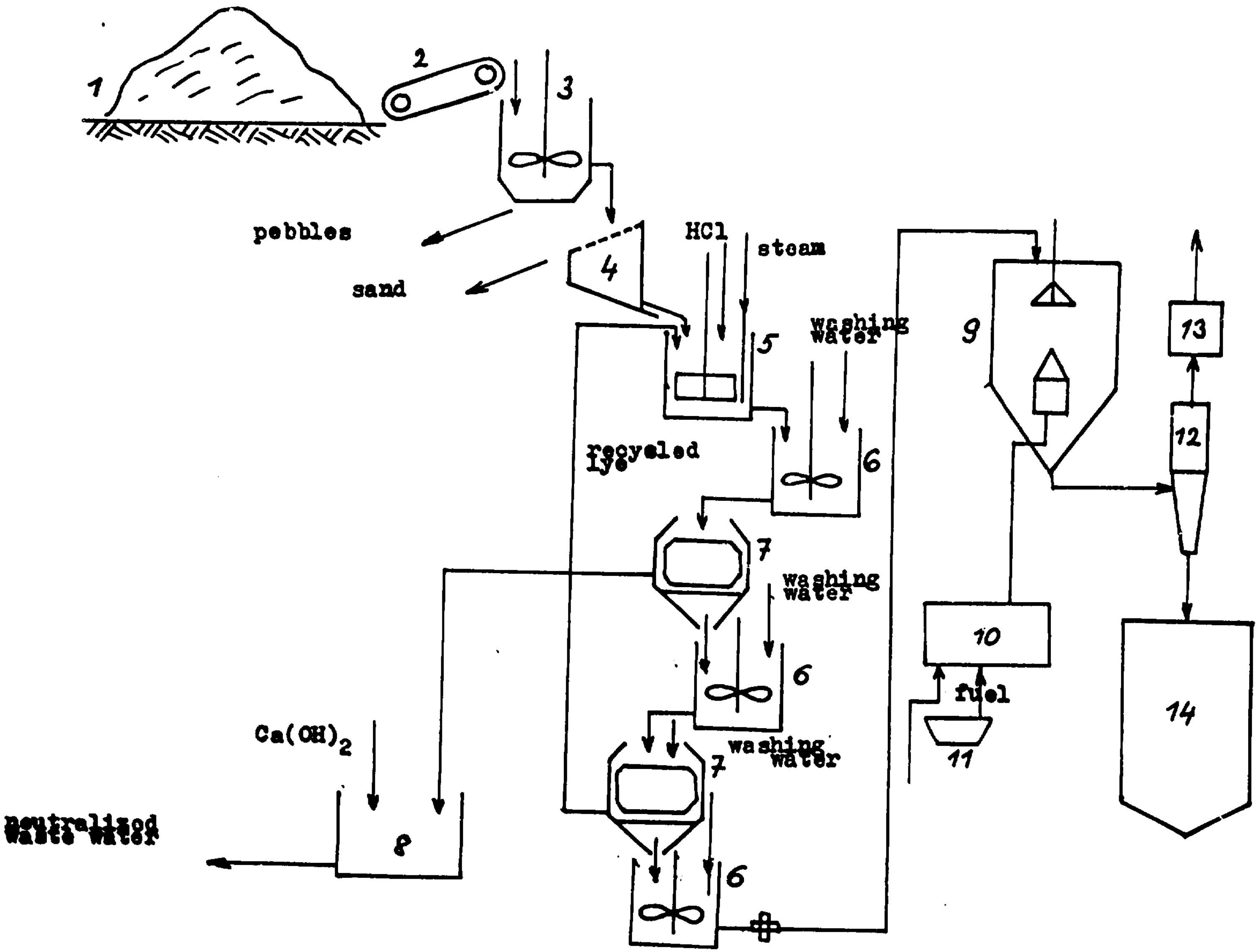
FIGURE 6 ACID ACTIVATION - FILTER PRESS TECHNOLOGY



LEGEND

1 - stock pile
2 - belt conveyor
3 - propeller blunger
4 - vibrating screen
5 - leaching tank
6 - high pressure pump
7 - filter press
8 - pass through mixer
9 - neutralization tank
10 - belt drier
11 - mill
12 - fan
13 - cyclone
14 - filter
15 - product silo
16 - combustion chamber

FIGURE 7 ACID ACTIVATION - DECANTATION TECHNOLOGY



LEGEND

1 - stock pile
2 - belt conveyor
3 - blunger
4 - vibrating screen
5 - leaching tank
6 - decanter
7 - centrifuge
8 - neutratization tank
9 - spray drier
10 - combustion chamber
11 - fan
12 - cyclone
13 - filter
14 - product sile

FIGURE 8 DIAGRAM OF BENEFICIATION PROCESSES AND APPLICATIONS OF BENTONITE

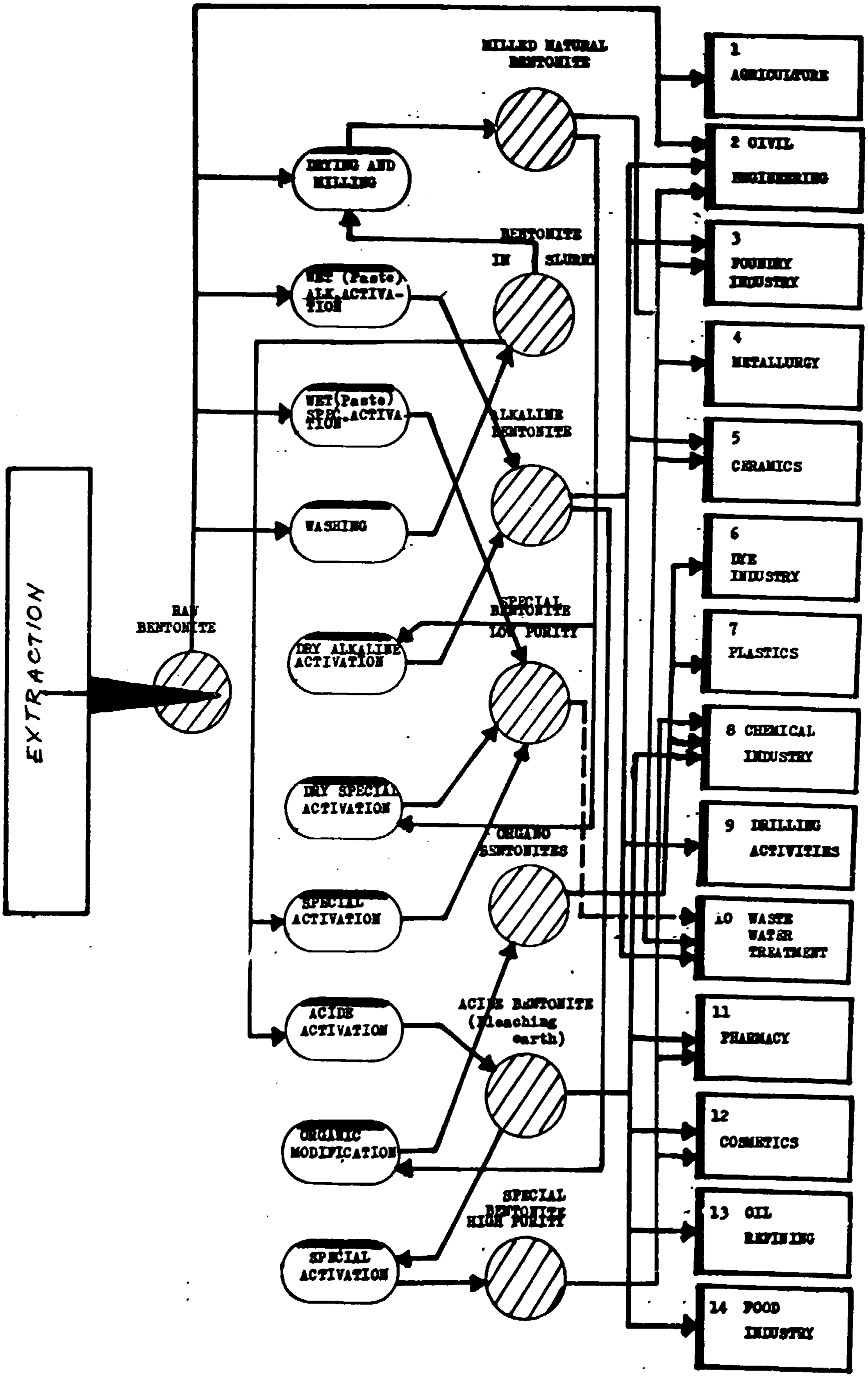
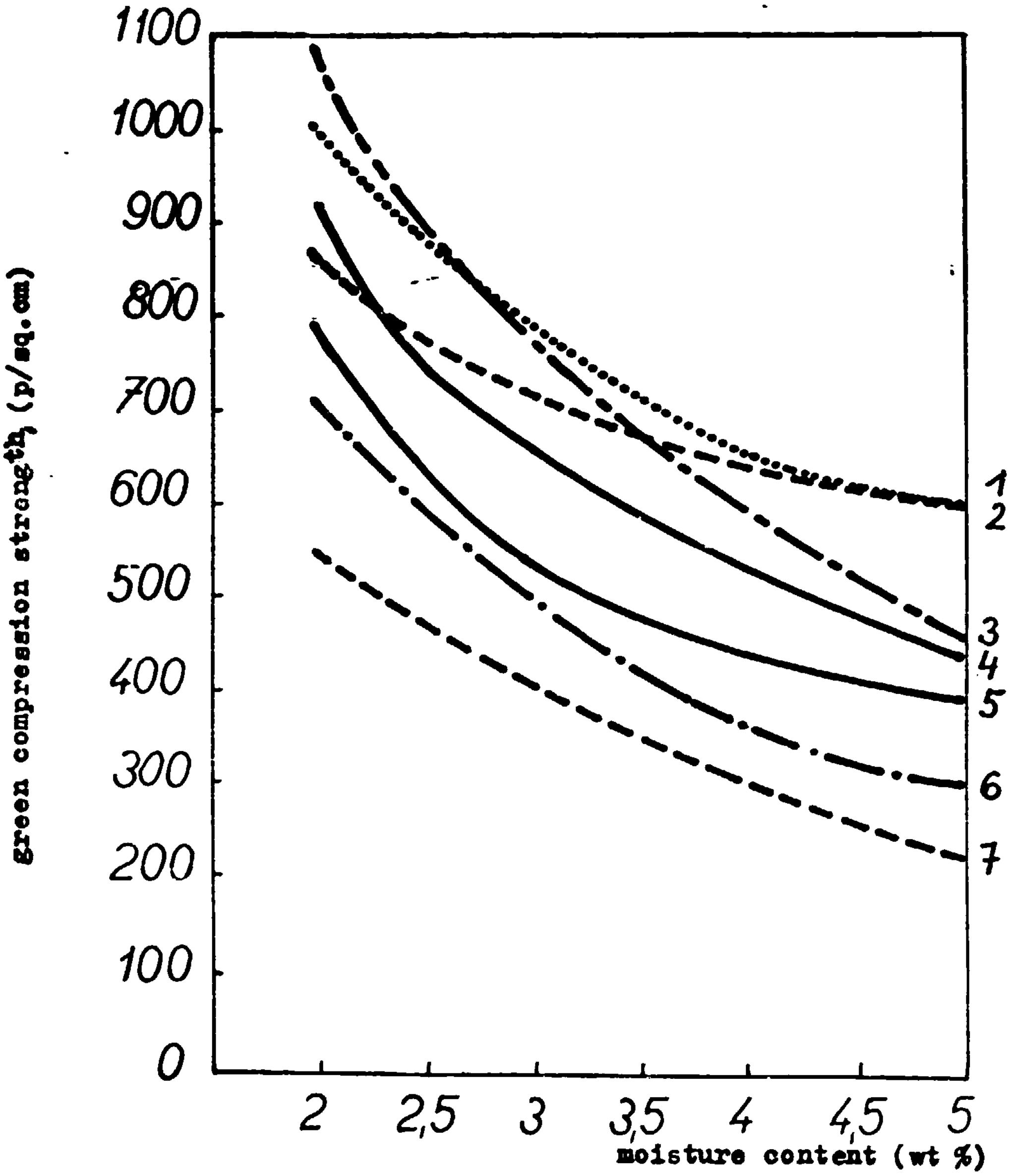


FIGURE 9 DEPENDENCE OF GREEN COMPRESSION STRENGTH ON MOISTURE CONTENT



Dependence of green compression strength on moisture content of different bentonites (mixture with sand 5 : 95). According to reference : Čičel B., Gregor M., Bentonit a jeho využitie, 1969

LEGEND

1 - Italian bentonite, 2 - English Na - bentonite, 3 - English Ca - bentonite, 4 - bentonite from Cyprus, 5 - Wyoming Na - bentonite, 6 - bentonite from North Africa, 7 - bentonite with 8 % of illite

FIGURE 10 INFLUENCE OF Ca - BENTONITE AND Na - BENTONITE ADDITION ON THE COMPRESSION STRENGTH OF CONCRETE

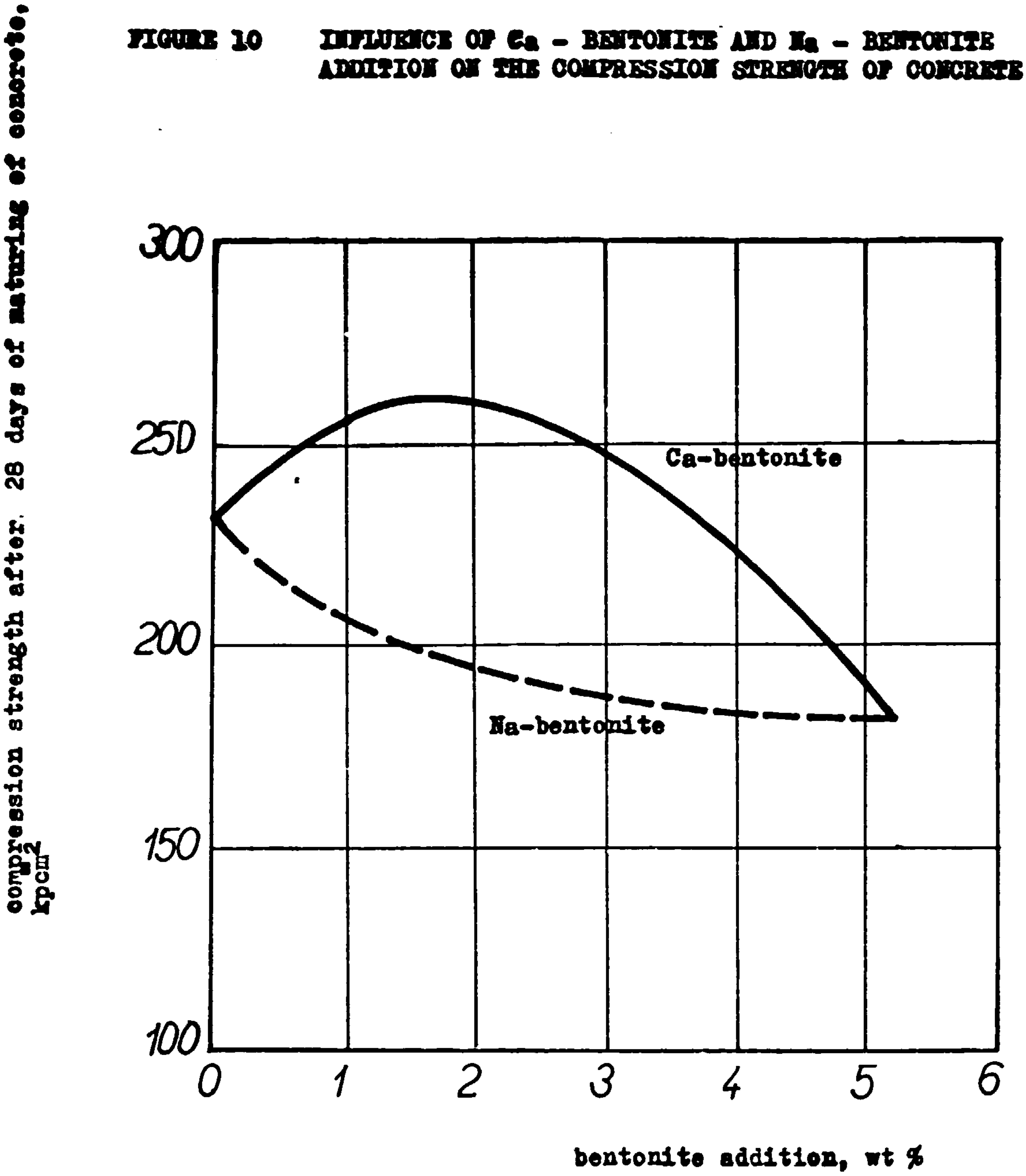
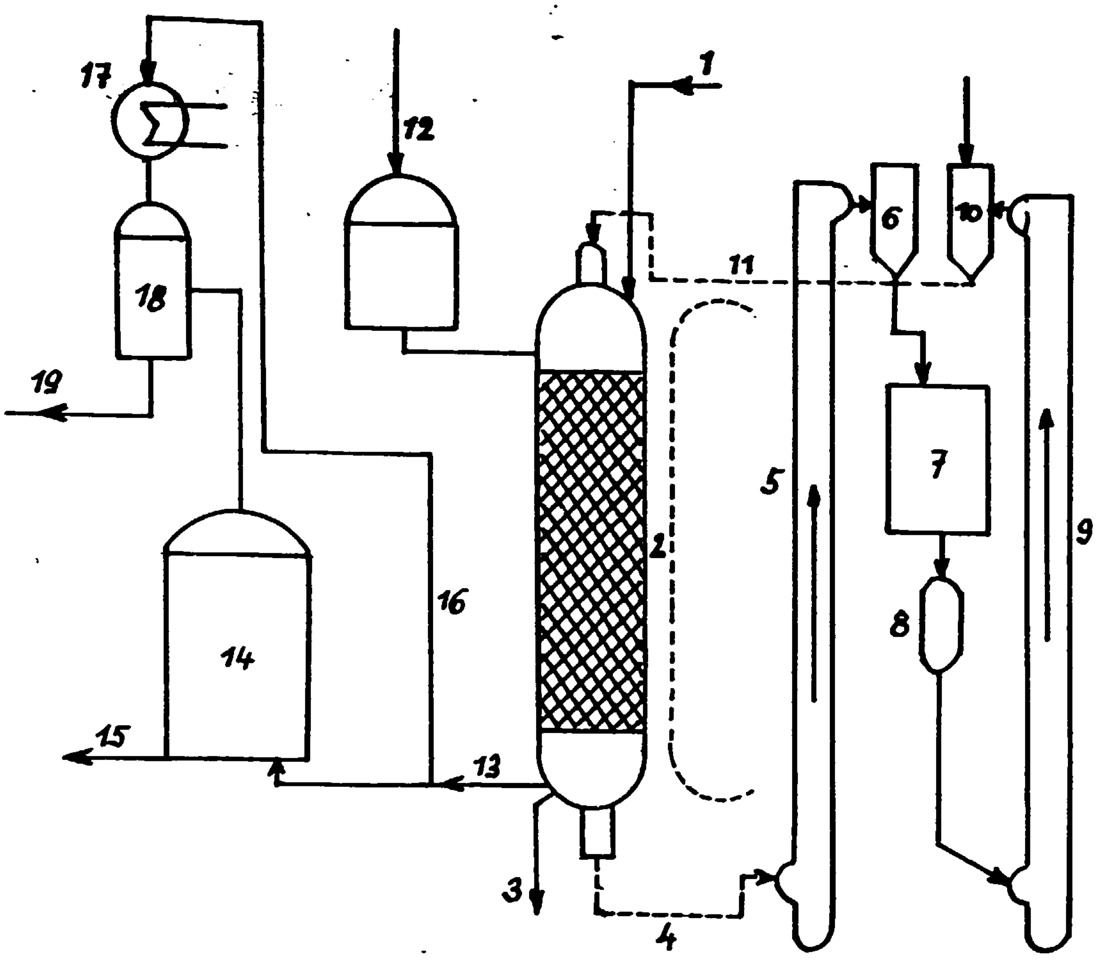


FIGURE 11

DISCONTINUOUS PERCOLATION OF OILS WITH BLEACHING EARTH

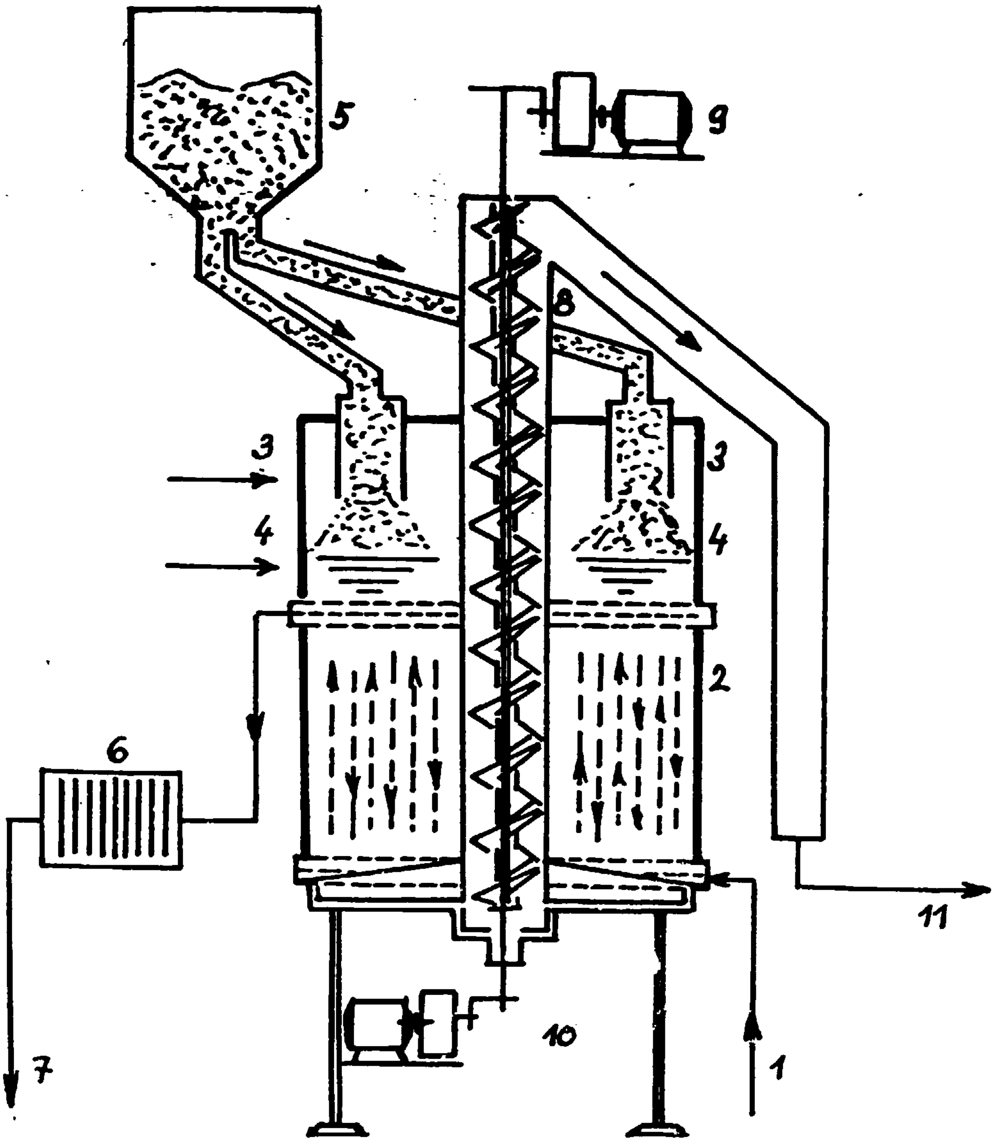


LEGEND

1 - crude oil, 2 - percolator with granuled sorbent, 3 - final product, 4 - transport of exhausted sorbent, 5,9 - elevators, 6,10 - sorbent tanks, 7 - sorbent regeneration, 8 - cooler, 11- - transport of sorbent after regeneration, 12 - tank for washing oil, 13 - used oil, 14 - tank for used oil, 15 - for circulation, 16 - steam, 17 - condenser, 18 - decantation station, 19 - water

FIGURE 12

CONTINUOUS PERCOLATION OF OILS WITH BLEACHING EARTH



LEGEND

1 - crude oil, 2 - percolator with granuled sorbent, 3 - level of sorbent filling, 4 - oil level, 5 - tank for sorbent, 6 - filter press, 7 - filtered oil to the tank, 9,10 - elevator drive, 11 - exhausted sorbent for regeneration