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PRODUCTION AND APPLICATION OF NON-METALLICS IN AGRICULTURE

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ABSTRACT

Non-metallic minerals and rocks play an important role in the development of agriculture as far as plant growing and animal breeding are concerned. They are applied as fertilizers, sorbents and carriers of chemicals.

Non-metallic sorbents, such as bentonites, zeolites, perlites, tuffs and tuffites, marls and others, according to the conditions of application, soil, climate, quality and quantity of dosage, increase the outputs of both plant growing and animal breeding.

Main data are given for each selected non-metallic sorbent as far as its geology, mineralogy, up-grading and quality requirements are concerned. Practical examples draw the attention of developing and least developed countries to start practical experiments.

The application of non-metallic sorbents in agriculture is so important that special UNIDO meetings and technical workshops are expected to be organized soon.

The UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Minerals Based Industries, being experienced in the extraction, up-grading and application of non-metallic sorbents in agriculture, is ready to extend and transfer the wide know-how developed in Czechoslovakia during the recent two decades to developing and least developed countries.

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INTRODUCTION

The whole history of mankind has a contact linkage with the development of agriculture and the production of victuals can be regarded as one of the fundamental constraints of the further growth of population that depends principally on food, energy and environment.

The considerable development of agriculture, especially in last decades, attributed to the scientific efforts in the field of chemistry and biology and also to the development of machinery and chemical industries, has probably been arriving at the limits given by the limited area and limited rehabilitation capacity of the soil. Available data concerning the application of industrial fertilizers, insecticides, etc., demonstrate stagnating yields despite of the growing consumption of fertilizers. According to statistics, the consumption of fertilizers in the U.S.A. grew by 400% in 1950 - 1972 but outputs increased only by 70% which demonstrates the constant overdosing of fertilizers without making use of them for plant growing. Other industrially developed countries are also huge consumers of industrial fertilizers. The world consumption of nitrogen can serve as a probation. 25% of nitrogen were applied in countries of C.M.E.A., 17% in west European countries and 22% in North America while the Asia consumed only 23%, South America 4% and Africa 3%. Consequently, the systematic care of the soil is a conditio sine-qua non of the growth of agricultural production. Apart from the quantitative protection of exploitable area, a due attention must be paid also to the quality of the soil which is a fundamental prerequisite of the intensification of the agricultural large-scale production. Both on all-world and national-wide scale, there is an urgent need of reclaiming a vast portion of agricultural sandy and sandy-argillaceous soils.

The objective is to raise the yield potential of deficient soils which is low due to the low content of clayey particles and mainly of humus. The fertilization should be carried out by progressive reclaiming methods based on the research of actual conditions, influences on hydrolimits and further physical and biochemical properties of soil.

The most consequential critical properties of deficient soils are insignificant water retention and water leakage enabling the previous nutrients - humus and components of industrial fertilizers - to escape from the soil without being exploited.

The efficiency of the accomplished land reclaiming depends on all accompanying conditions that influence directly the stabilization of physical, sorbent and biochemical equilibrium. These conditions consist especially in grain-size distribution of the soil and its humus content, in the action of climatic influences during the vegetation period, influence of irrigation, influence of species of the grown product and, in a decisive degree, in the level of concurrent manuring of the soil.

Research concerned with raising yields of main products - cereals, potatoes, sugar beet, maize, paddy - has brought along the knowledge of needs and possibilities of systematic maintenance of soils. Traditional methods of reclaiming soils based on drainage and purposeful irrigation, application of clays and marls in soils experienced already in the past, continue.

Obtained experience and progress of the research of non-metallic minerals and rocks have opened the prospects and possibilities of their further utilization in agriculture. It has appeared that the application of non-metallic minerals and rocks in the agricultural large-scale production is feasible. Developed countries with highly developed agricultural production have increased the extraction and final production of non-metallics as raw materials for the production of industrial fertilizers. A wider field of agricultural utilization of non-metallic minerals exists.

In general, non-metallic minerals and rocks take up an important role both in plant growing and animal breeding as they are applied as fertilizers, sorbents and carriers of chemical and biological matters. This paper brings forward a series of new information on the utilization of selected non-metallic minerals and rocks in agriculture.

Bentonites, zeolites, perlites, tuffs, tuffaceous rocks, marls and others, such as diatomaceous earth and tripoli, are of significance to the agricultural large-scale production, both the plant growing and animal breeding. Their most significant function is that of sorbents.

Non-metallic sorbents function in two ways. On one hand, they reduce the wash-out of fertilizers, enhance water retention and rehabilitate the soil from the point of view of the ion exchange. On the other hand, they deliver nutrients direct to plants which increases the yield by 10 to 40% depending on the kind of plant, humus content. acidity and grain size distribution of the soil and the climatic conditions. Besides, they reduce penetrating chemicals to the subsoil waters and many a time to the atmosphere. It has been recognized that the presence of sorbents in soils seems to be of the same importance as the photosynthesis and a series of their properties is regarded as miraculous.

As far as the animal breeding is concerned, the addition of sorbents substitutes for 5 - 15% of fodder. Other functions are in decelerating nutrient circulation in the digestive tract of animals and by it, better utilization of albumen and other nutrients. Sorbents as dietetic additives in animal feeding reduce the occurrence of diarrhoea and some other diseases.

Non-metallic minerals and rocks applicable in agriculture do exist in the majority of developing and developed countries. Consequently, the UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Minerals Based Industries evaluated the broad Czechoslovak experience and took into consideration the published results of other countries in producing this paper as the first evaluation of the application of selected non-metallic sorbents in agriculture. The paper can concurrently be regarded a guide for developing countries to start intensifying the agricultural production by means of available non-metallic minerals.

Due to the limited extent of this publication, the UNIDO-Czechoslovakia Joint Programme has not been in the position to present all the favourable experiments and results achieved in agriculture. Therefore, the UNIDO-Czechoslovakia Joint Programme is ready to assist other countries in consultations, training programmes, evaluation of selected non-metallic minerals and rocks in order to promote not only the industrial exploitation of local non-metallic natural resources but also the intensification of the agricultural production and to contribute to solving environmental problems.

CONCLUSIONS AND RECOMMENDATIONS

1. Non-metallic minerals and rocks play an important role in agriculture as fertilizers, sorbents and carriers of chemical and biological matters.

2. The application of non-metallic sorbents both for plant growing and animal breeding has very favourable results.

3. The most important non-metallic sorbents for agriculture are bentonites, zeolites, perlites, tuffs and tuffites, marls and others, such as diatomaceous earth and tripoli.

4. Some of non-metallic sorbents are represented in the majority of developing and developed countries.

5. Depending on the conditions of application, soil, climate, quality and quantity of dosage, the non-metallic sorbents being applied show the following increase in the yield compared with original conditions without sorbent dosing:

a) Sorbents for plant growing

Applied sorbent	Type of soil /% grain < 0.01 mm/ % humus/	Dosage /t.ha^{-1}/	Tested plant	Increase of output /%/
bentonite	9.2/1.3	20	potatoes	18.6
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
zeolite 50	N.A.	16	capsicum-tomatoes	33
zeolite 80	N.A.	16	paddy	40
tuff	N.A.	20	maize	32.4
tuffites[3/]	tuff	20	maize	from 7.9-30.6

b) Sorbents for animal breeding

Applied sorbent	Substitution for corn in fodder /%/	Tested animal	Increase of weight per day
bentonite	3	bulls	0.1 kg
zeolite 80	10	pigs	0.17 kg
zeolite 60	5	pigs	0.1 kg
zeolite 80	2	cocks+hens	1.5 - 1.7 %
zeolite 90	9	poultry	1 - 3 %

Note: 1/ Zeolite index marks the percentage of clinoptilolite

2/ Not available.

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

6. Non-metallic sorbents act positively against different diseases of the digestive tract since they regulate the transit of the albumen through the body.

7. Aside from the direct economic influence on the agriculture, the non-metallic sorbents affect the national economy by decreasing the imports of food and fodder for animals and by increasing the chance of each country to accelerate the production of food for its own nation.

8. As far as the environmental problems are concerned, the non-metallic sorbents applied in farming decrease the penetration of chemical fertilizers into the subsoil water and atmosphere.

a) Sorbent additives to the fodder contribute to recovering animals without applying antibiotics which are detrimental to the health of people consuming meat of the treated animals.

b) There are indications that the chemical fertilizers applied in farming, mainly nitrates, phosphates and cadmium which is associated as trace element to nitrates, influence the carcinogen effect of different crops and water.

9. In order to exchange experience in the field of the application of non-metallic sorbents in agriculture, it is recommended to arrange an ad hoc experts' group meeting for participants from developing and developed countries.

10. Such experts' group meeting will be the necessary basis for organizing an international seminar as the mean of the transfer of technology and evaluation of important questions concerning various territories and countries such as

    a) evaluation of geological reserves of different non-metallic sorbents,
    b) testing, evaluation and classification of non-metallic sorbents in the connection with local conditions in agriculture,
    c) determination of necessary refining and up-grading of existing non-metallics for the application in agriculture,
    d) evaluation of local conditions in agriculture from the point of view of plant growing and animal breeding,
    e) conducting pilot tests on the application of non-metallic sorbents in agriculture of selected developing countries,
    f) preparation of feasibility studies on commercial and economic evaluation of the application of selected non-metallic sorbents in selected countries and evaluation of projects from the point of view of environment.

11. The presented paper brings forward the information necessary not only for the preparation of experts' meetings but also for the start of practical applications of non-metallic sorbents in agriculture.

12. The UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Minerals Based Industries, being experienced in the extraction, up-grading and application of non-metallic sorbents in agriculture, is ready to extend and transfer to developing and least developed countries the wide know-how developed in Czechoslovakia during the past two decades.

I. CLASSIFICATION OF NON-METALLIC MINERALS AND ROCKS APPLIED IN AGRICULTURE

Non-metallic minerals and rocks owing to their properties are widely applied in agriculture. There are many viewpoints of their classification and they are usually classified according to their fundamental functions and the field of utilization on:

Industrial Minerals and Rocks as Fertilizer Minerals

which are the direct condition of farm output. They are divided into:

1. Primary minerals (nitrogen, phosphorus and potassium)
2. Secondary minerals (calcium, magnesium and sulphur)
3. Micro and trace minerals (boron, iron, manganese, copper, zinc, molybdene, chlorine and cobalt)

Industrial Minerals and Rocks as Sorbents

which are not fertilizers but their presence in the soil is indispensable. They are divided according to their activity in the soil and the field of utilization as follows:

1. Sorbents in vegetál production where they are applied for
   - sandy soils (bentonites and marls)
   - argillo-aranaceous soils (tuffs, tuffites, expanded perlite and zeolites)
2. Sorbents in animal husbandry (bentonites and some of zeolites)

Industrial Minerals and Rocks as Carriers

Diatomaceous earth is among others suitable raw material for carrying chemicals to protect plants against insects.

A. INDUSTRIAL MINERALS AND ROCKS AS MINERAL FERTILIZERS

Minerals and rocks as fertilizer minerals creating conditions for yield potential are classified as follows:

1/ Primary Minerals

Chile niter extracted in the nature as a source of nitrogen N as well as the organic fertilizer guano excrement - droppings of sea birds - were replaced by the nitrogen chemical production consisting in fixing atmospheric nitrogen and combining it with hydrogen H_2 to receive ammonia NH_4^+. With further addition of organic and inorganic components, a group of nitrates (urea) arises; these being enriched with carbohydrates and proteins. and an inorganic group of calcium and potassium nitrates and ammonium sulphates. In a concentrated form, it is ammonium anhydride NH_3 with 82% N. Plants can accept nitrogen from the soils only as nitrates NO_3 and as ammonium NH_4^+. if need be.

Apatite - calcium phosphate - $Ca_5(PO_4)_3 \cdot (F, Cl)$ is a source of phosphorus. It is extracted in the nature, sorted, ground and chemically processed on the basis of sulphuric acid and gives a superphosphate of high value (20% P_2O_5). The research in the field of soil reclamation was conducted in 1840 by the German scientist Justus von Liebig. The volume of phosphate world reserves is still sufficient, however, it has not yet been precised. The largest deposits of phosphates are in North Africa, in the U.S.S.R. and U.S.A. Phosphorus is the donor of energy for plants and makes the substantial component of phospholipides and nucleic acids Phosphorus is accepted by plants in the form of phosphates (H_2PO_4).

Potassium salt - KCl - sylvite; Carnallite KCl.$MgSO_4.11H_2O$ and further compounds of potassium as sulphates K_2SO_4 and 2 $MgSO_4$. K_2SO_4 are the main sources of potassium. Plants accept potassium as K anion which has a considerable influence on the exchange of substances in the cellular tissue of plants as regulator and catalyst.

2/ Secondary Minerals

Limestone - in the nature extracted calcium carbonate $CaCO_3$ is classified in a series of quality grades for application in industry and agriculture according to quality standards. The technology of the upgrading process is geared to purity and fine grinding. Limestone is delivered in microground condition and transported on special waggons provided with containers that can be filled and emptied pneumatically. Limestone is a direct and rich source of calcium.

The plants accept calcium as Ca^{++} ion, which acts with the other fertilising components on the nutriment and growth of plants. Calcium is dissolved slowly by the action of water enabling thus an average concentration to be maintained in the soil. In this way, the pH value of the soil is influenced which is very important in the application of the mineral of group I (N, P, K) and of further trace elements. Calcium is an important agent in the reduction of nitrates for the preparation of favourable biologic processes for creation of proteins.

Dolomite - calcium magnesium carbonate $CaCO_3$. $MgCO_3$ is a direct source of magnesium Mg which is an indispensably necessary soil component for nutriment of plants. They accept magnesium as Mg^{+} ion and it plays an important role in the cellular tissue in the photosynthesis and creation of chlorophyl. Magnesium influences the metabolism of phosphorus and water equilibrium needed for proportional growth of plants, their chlorophyl and yield potential. Natural sources of magnesium occur as minerals langbeinite $K_2SO_4 \cdot 2MgSO_4$; kieserite $MgSO_4 \cdot H_2O$; epsomite $MgSO_4 \cdot 7\ H_2O$.

Sulphur - S - calcium sulphate - mineral gypsum $CaSO_4 \cdot 2\ H_2O$ and further minerals containing sulphur as langbeinite and epsomite are sources of sulphur which is accepted by plants in the form of sulphate SO_4^{-} ions. Sulphur is an indispensable soil component for the creation of nutrients - proteins. The first application of sulphur compounds (H_2SO_4) - of the first fuming sulphuric acid in the research of fertilizers took place 130 years ago in conjunction with the industrial production of superphosphate. In chemical processes in the production of industrial fertilizers, the sulphuric acid is used for the neutralization of ammonia. Ammonium thiosulphate $/(NH_4)_2\ S_2O_3/$ is used in the production of industrial fertilizers. Sulphate (SO_4) is a component in processing the combined fertilizing blend NPK.

3/ Micro and Trace Minerals

Micronutrients are indispensable for plants even if their consumption is impalpable. They occur in some soils, however, in some areas they are deficient. For this reason, and always after investigation of the soil, the micro and trace minerals and elements may be proportioned into the soil. They are usually added into combined fertilizing blends. In some cases also the dosing method of nutrients and trace elements may be applied by spraying them into the soil or on the leafage. The character of the soil, its pH value, meteorological and hydrobiological conditions should be taken into account before applying this method. The plants can accept trace elements and microelements only in water suspensions. The trace mineral microelements occur in the nature in dispersive earths, clays, tuffs, tuffites, bentonites and zeolites.

The following minerals containing important elements are extracted on industrial scale:

Iron

Iron accompanies many minerals as admixtures or contaminations. The main following minerals are extracted for the iron component to be obtained: haematite ore - Fe_2O_3, magnetite - Fe_3O_4, limonite FeO(OH) and pyrites FeS. The plants need necessarily iron for the creation of chlorophyl and as catalyst of the metabolism of vegetative tissue with other substances of industrial fertilizers.

Manganese occurs in the nature only as mineral pyrolusite (MnO_2). The carrier of manganese in clayey mineals, bentonites and subbentonites is the montmorillonite component with 0.02 to 0.10% of MnO. Manganese is also significant for the growth of plants, regulator of oxidation - reduction and it completes often the influence of iron. It is also an active component as trace element in combined blends of industrial fertilizers in the form of soluble sulphate or insoluble oxide.

Copper occurs in minerals chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$) and cuprite (Cu_2O). It has a stimulative effect for the nourishment and growth of plants. During the vegetation period, it works as catalyst in the regulation of the metabolism of nutrients N, P, K, Ca. The total influence on the growth of plant has not yet been fully investigated. Many soils - especially the sandy ones with irregular yields - need copper microelements for fertilization and improvement of the yield potential. Copper participates in combined industrial fertilizers as microelement in the form of sulphates or oxides.

Boron is won from the mineral colemanite $CaB_6O_{11} \cdot 5\ H_2O$ or borax $Na_2B_4O_7 \cdot 10\ H_2O$ and from the contaminated components of the production process of borosilicates and glasses. Only 5 to 6% of boron of its world production are consumed in the production of industrial fertilizers in the form of modified boron compounds soluble in water. Boron acts as stimulator in the fertilization of soil, however, certain plants do not stand boron as trace element.

Zinc

Its source is the mineral sphalerite (ZnS). Zinc is included in the blends for soil fertilization as sulphates, sulphides and oxides. It is applied as catalyst for the growth of plants. It acts as a rule jointly with copper components in the creation of micronutrients of many plants.

Molybdenum

The mineral molybdenite (MoS_2) contains this valuable element. The influence of molybdenum in the production of industrial fertilizers is utilized in the reduction of nitrates and plants can receive molybdenum as oxide ammonium molybdate. Molybdenum acts as microelement in a slight quantity with further components during inflorescence and maturing of-products.

Cobalt (Co) is obtained as by-product in the extraction and upgrading of nickel and copper ores. Cobalt belongs to indispensable elements for the growth of plants, however, it is also very important for the growth and health of animals fed by produce and plants.

B INDUSTRIAL MINERALS AND ROCKS AS SORBENTS

There is a series of mineral microelements in natural soils that are mostly represented in soil in water soluble condition. The following elements are concerned: Al, Ba,Br, F, J, Ni, Se, Ti, Pb.

The application of non-metallic minerals for the fertilization of agricultural soils depends on their capacity to deliver nutrient elements in such a form for the plants which is acceptable for them.

The consumption of industrial fertilizers goes on increasing together with incurred costs, however, the achieved yields per hectare are not proportional. The consumption reached its culmination which is accompanied by a series of negative influences on vegetation and life environment.

It may be concluded that further increase of fertilizer consumption in vegetal production which is not biologically and economically substantiated, is detrimental and unuseful. This phenomenon is evident, especially in sandy soils with low water retention and high water leakage.

The fertilizers are washed out by longer rainfalls into subsoil waters during one year without being utilized by plants and damage in this way natural purity of waters.

The determination of optimum quantities of industrial fertilizers for soils of certain categories and achievement of their maximum exploitation is the crucial assignment.

Research results and field tests proved the effectiveness of the application of natural sorbents in soil fertilization. The application of natural sorbents enables substantial reduction of the leakage of fertilizers, nutrients and trace elements from the soil. Mineral sorbents - bentonites prolong the effectiveness and consequent gradual action of organic and industrial fertilizers according to the character of applied soil and dosing by 5 to 7 years.

The revitalization of deficient soils can be carried out by a new reclaiming process applying mineral sorbents. Mineral sorbents are polyfunctional reclaiming materials influencing favourably physical, sorbent-chemical properties especially of lighter sandy soils improving thus their yield potential. The precious property of mineral sorbents is the capacity of retaining a considerable quantity of reversibly found water in molecular lattice. Water, nutrients, components of fertilizers and trace elements important for the growth of plants are retained, gradually released and passed on to plants in a favourably extended effectiveness.

Water sorption creates the sorption complex, linkage of sand grains with organic colloids and other components sets in.

The influence of water received in interlayers brings about the volume increase of the sorbent clayey component - swelling. In the gradual dehydration, shrinkage - contraction takes place accompanied by the thickening of the soil material accompanied with cracking of particles.

Hydrophylic properties of sorbents influence the diminishing of soil pores and changes their number by increasing the total of small pores under 30 μ and decreasing the total of large ones above 300 μ.

Mineral sorbents have an effective influence on setting up a better water regime of soil. The water movement in capillary pores changes favourably the equilibrium of nutrients and microelements and their distribution to the root system of plants.

The delayed action in retaining capillary waters results from the effect of montmorillonite particles in the sorbent on water movement velocity decrease in the soil and is proportional to the quantity (dosing) of sorbent. Mineral sorbent is applied directly - by its influence of mineral composition, by its having increased water content and by regulating temperature conditions of sandy soil.

The concurrent application of natural sorbent with organic fertilizers increases the effectiveness of industrial and natural fertilizers from non-metallic raw materials and minerals.

Sorbents are of great significance as far as the animal husbandry is concerned since they, while added to the feeding stuffs direct lower the consumption of expensive vegetal fodders, improve the utilization of albumen and other nutriments in the digestive tract of animals and have significant dietetic effects.

C INDUSTRIAL MINERALS AND ROCKS AS CARRIERS

In order to protect plants against insects, new methods have been developed based on spraying and atomizing the disinfection from planes. Such methods are preferred as the active substance, being absorbed by the carrier, is distributed by planes direct onto the earth surface where it acts slowly depending on its release from the surface of the carrier.

The U.S.A. started utilizing sorbents as carriers of insecticides, fungicides and pesticides in 1917 - 1920, (published in 1934). The application of sorbents to this end has widened considerably since that time. Farmers in Iowa sprayed pesticides and insecticides on 1.6 million of hectares in 1960.

Sorbents blended with inert granulated carriers protected successfully the germinating plants especially against insects both distributed by planes and from the earth surface. Methods of the preparation of granulated carriers were gradually improved and more efficient raw materials such as attapulgite and sepiolite have been applied.

Standard composition and properties are required to manufacture carriers of chemicals:

- bulk density	510 - 570 kg/cu.m
- pH (suction tension)	6 - 8
- humidity	3 - 7 %
- LHC (liquid holding capacity)	31% min.
- grains (less than 0.25 mm)	5%
- number of granules in 1 kg	11 - 12 millions

Required grain composition:

grains	> 1.68 mm	0%
	> 0.84 mm	0.2%
	0.84 - 0.59 mm	15 - 35%
	0.59 - 0.42 mm	30 - 55%
	0.42 - 0.3 mm	15 - 35%
	0.3 - 0.25 mm	1 - 5%
	< 0.25 mm	1.5% max.
	< 0.15 mm	0.7% max.

D Influence of Agriculture on Environment

The profile of the soil is of fundamental significance to maximum outputs in case of the intensive vegetal production. From the point of view of the optimal delivery of nutrients to plants, nitrogen is ahead of other elements. The form in which nitrogen is supplied to the plant is that of nitrates and, if need be, ammonia which are the only forms of nitrogen accepted by the plant.

The sources of nitrates in the soil if only the natural circulation of nitrogen is taken into account are predominantly the mineralization processes of decay of organic matters contained in both vegetal and animal tissues. Further, the bond of airy nitrogen through the nitrification bacteria in the soil and nitrates created from nitrogen oxides by means of spark discharges or other reactions and taken away by precipitations.

The efforts to enhance the outputs of agriculture led step by step to the deliberate enriching of the natural nitrogen resources in the soil. Natural manure was applied which was primary supplemented by industrial nitrogen-fertilizers but later only industrial fertilizers were applied. Gradually, the dosages of the industrial N-fertilizers have increased. The relative ratio of nitrogen to other principal nutrients such as potassium and phosphorus increased, too.

Gradually, the balance of nitrates in the soil was deteriorated since the utilization of nitrogen contained in nitrates and the decay of nitrates caused by devitrification bacteria was lower than the input of nitrates, coming from both natural resources and, predominantly, from additional resources.

A consequence of this process was the enhanced content of nitrates in the soil, their transfer into water and the consequent enhancing of content of nitrates in some plants, mostly in vegetables.

The mentioned effects can be observed in a series of countries with highly developed agricultural production. A series of works was published which draw the attention to the undesirable influence of the enhanced content of nitrates in both plants and water in the environment.

After the World War II, the disease which attacks the sucklings and which is caused by high concentration of nitrates in water was described and named "alimentary methemoglobinemy". The children consuming dried milk food which is solved in water containing enhanced quantity of nitrates frequently suffer by this disorder. The nitrates themselves are not toxic but if nitrates are reduced either in or out the body into nitrites, these latter will intensively change the hemoglobin into the methemoglobin which has not power to mediate oxygen to tissues and so called "interior suffocating" sets in. There are literature sources issued in last years reporting this disorder occurred after children had consumed some vegetables, especially spinage or carrot, if need be, carrot juice or brew-up.

It is evident and the published data and direct observations substantiate it, that the increase of content of nitrates in plants and water is of expressive detrimental effect.

In case of the adult people with sufficiently functioning system which converts the created methemoglobin back to the normal hemoglobin, the risk of methemoglobinemy is not great. However, the risks which are more consequential appear. Nitrites, reduced from nitrates, can,under certain circumstances, react with secondary amines and create nitrosamines. The expressive effect causing mutations and carcinoma has been discovered in case of many nitrosamines. By the action of nitrites, the nitrosation of other matters - amides, methyl and ethylurey carbamates, etc. - can set in and the created N-nitroso-compounds are of carcinogen effect in most cases as confirmed by verifications done with animals. These attempts also brought a very consequential finding that these nitrosation reactions can, under certain circumstances, run in the organism. In such a case, the increased supply of nitrates means the enhanced risk of creation of carcinogen N-nitroso-compounds. Reports have been published in different countries which confirm a possible correlation between the higher concentration of nitrates in water and the occurrence of tumors, especially those of stomach.

On consuming nitrates, a predominant part passes rapidly into the blood and it is gradually secreted by urine in the unchanged nitrate form, which is not toxically detrimental to the man. A part of consumed nitrates passes from the blood into the saliva and this can be reduced, in the mouth, into nitrites. In stomach then nitrites can, at concurrent low pH which is favourable for the nitrosation, create nitrosamines and other N-nitroso-compounds. Similar situation can set in in the urinary bladder during different inflammations when the present microflora develops the reduction of nitrates into nitrites and the latter can again transform different matters into the carcinogen N-nitroso-compounds . These processes were also verified on animals and confirmed by a series of authors. The supply of nitrates and nitrites to the human organism is not insignificant and it ought to be reduced and limited.

In addition to the described effects and influence on the human population, further negative influences on the environment and on the agriculture are to be taken into account.The high concentrations of nitrates in fodder or in drinking water developed the recurring poisoning of the animals as shown in literature. The higher supply of nitrates can influence the offspring; born calves had contaminated red blood pigments by 18% of methemoglobin. Neither the fact that removing 1 g of the residual nitrogen from nitrates requires the consumption of 2 - 3 g of energetic nutriments.

These facts must lead to considerations on dosing nitrogen into the soil so that the high crops may have the lowest possible detrimental influence on the environment (Figure 9 describes an experiment with fertilizing potatoes).

The above-mentioned adverse facts on the influence of the enhanced supply of nitrates on the organism are additionally accompanied by further more negative consequences of the increasing content of nitrates in the soil, water and plants. The reduced biological value of the plants is the question related to the cultivation in over-fertilized soils when increased outputs are not achieved but, vice versa, the reduction of valuable matters such as magnesium,potassium pro-vitamin A,vitamin C, etc. is a consequence of the opulent fertilizing.

The higher content of nitrates in the vegetal products is usually accompanied by further unfavourable factors, e.g. reduced resistance against decay during longer storing, reduced sugar content of beet, turbidity of beer, higher content of nitrosamines in beer, lying-down of cereals, higher liberating of tin and lead from containers after canning.

It is apparent from the above-mentioned facts that a way leading to the reduction of the negative effects is the substantial improvement of the balance of nitrate nitrogen in the soil. Above all, the matter of importance is to procure the perfect utilization of the nitrogen delivered from the soil by plants according to their actual requirements. Nitrogen from nitrates must be kept in the soil until it is utilized by the plant and it must be prevented from penetrating into water.

The final concentration of nitrates in the vegetal mass is a result of the mutual action of biological, chemical and physical factors. Biological factors are individualized by the sort, variety and age of the plant. As well, the genetic effects, activity of enzymes, especially nitratereductase are of significance. Chemical factors are displayed by the content of other nutriments in the soil, microelements, pH of the soil and the presence of different activators and inhibitors of the growth. The following physical factors are of great significance: humidity of the soil, temperature, solar radiation and in addition the soil profile and sorption capacity.

Under optimum conditions, the dosage of nitrate nitrogen will have to respond to the requirements of the cultivated plants and it must be at disposal in the vegetation spell. These conditions can be met if either dung is applied which liberates the nitrogen step by step or the industrial fertilizers (granulated) with the reduced break-down are applied or smaller dosages of fertilizers are repeatedly applied. The significant intervention to fulfil the optimal conditions of nitrogen dosage is the improvement of the nitrogen conservation in the soil by the reconstruction of the soil profile.

The reserve of the necessary nutriments in the soil is a "condition sine-qua-non" of the perfect growth of the plant without any doubts. Up to this time this question was simply deciphered by over-dosing of fertilizers. In view of the fact that fertilizing by industrial fertilizers was preferred and the profile of the soil got worsened, the applicatior of more and more fertilizers were unavoidable and these for the sake of the poor retention capacity of the soil percolated and contaminated water comparatively rapidly. Usually in spring before germinating, the enhanced concentrations of nitrates in drinking water were observed which can be attributed to the wash-outs of nitrates as a consequence of the over-applying of fertilizers or incorrect application and unsufficient retention power of the soil (See Table 1).

As far as the content of nitrate nitrogen in the soil is concerned, it is possible to regard higher concentrations as either the over-dosing or the reserve. However, the absolute quantity of nitrogen should not be the principal criterion but the circumstance whether it is retained in the soil and utilized by the plants or whether it is washed-out without being utilized because of the unsufficient retention capacity of the soil.

Another aspect is that of the accumulation of nitrates in some plants. In this case also the velocity of the liberating of nitrates and the capacity of their utilization according to the actual requirements of the cultivated plant are of importance. If the improved soil profile makes possible relatively greater retaining of nitrates in the soil, the quantity of fertilizers normally contaminating water without being utilized can be subtracted and the dosage of fertilizers can be lowered. In view of the fact that, according to different data from literature, the consumption of nitrites delivered by the vegetal food is assessed 2 - 5 times higher than the quantity accepted from water, the reduction of content of nitrates in the vegetal products is of a considerable consequence.

An incidental aspect of the nitrate question which must be mentioned is the capacity of nitrates to bind cadmium, the element which is expressively venomous in the human organism. The reduction of nitrates will proportionally reduce the content of accompanying cadmium.

II. INDUSTRIAL MINERALS AND ROCKS AS SORBENTS

Sorbents are of major significance to both vegetal production and animal husbandry as mentioned above. Non-metallic minerals and rocks utilized in agriculture as mineral sorbents are widely spread all over the world and most important of them are

- bentonites and marls applied to sandy soils
- tuffs, tuffaceous rocks, expanded perlites and zeolites
- for the application in argillo-aranaceous soils
- minerals of major significance to animal husbandry are bentonites and zeolites

A Theory of Experienced Knowledge of Sorbent Behaviour in Soils

Possibilities and techniques of direct application of bentonite for reclaiming soils have been verified and elaborated in Czechoslovakia most thoroughly. Priority has been given to the dosage of bentonite to sandy soils in order to enhance the portion of minerals with swelling capacity (montmorillonite), which are the functioning component of bentonite and which improve in coarse-grained, highly pervious sandy soils their unsufficient water regime (principally absorption power) and small sorption capacity of nutrients. Further, bentonite has been applied in soils when attempts had been made to affect extreme properties of waste dumps which must be recultivated after the open cast mining of coal and other mineral raw materials. Other spheres of possible application of bentonite in agriculture are as follows: the production of beneficiated industrial fertilizers, the granulation (powdering) of mineral fertilizers, the production of organic mineral substrates, the treatment of animal manure and attempts to apply bentonite in feeders, the application of sorbents of the bentonite type for protection of both surface and underground water against contamination by high concentration of industrial and organic fertilizers.

Further, some results reached in Czechoslovakia and compared to available experience in the world are presented.

Essential Technological Experiences based on Practice and Research of Bentonite Application in Soils

The application of bentonite shows the best results in case of the sandy soils containing max. 10% portion of soil in category I (grain fraction under 0.01 mm) or in argillo-arenaceous soils containing max. 20% portion of soil grains in category I and the low content of humus (under 2%). The higher the content of montmorillonite, the higher the effectiveness of bentonites.

Bentonite is applied to soils in raw state, naturally disintegrated, in which it is most efficient. Usually, if bentonite is exposed to weathering, it disintegrates shortly. A contingent artificial beneficiation (drying, crushing, grinding) must not include detrimental heating which lowers the reclaiming effectiveness of bentonite (maximum admissible temperature is 60°C). It is recommended to apply bentonite into the soil through basic ploughing in autumn. The previous scattering (spreading on the surface) can be done by agricultural machines or by explosives ignited under delivered heaps. The recommended dosage is 20 t per hectare. To reach the optimal effect, all principles of proper agrotechniques must be kept up, especially the soil must be sufficiently fertilized. After the reclamation of soil by bentonite, biological amelioration is recommended to be introduced. As the result of bentonite application, the crop enhanced by 20%, the life time of the effect of 7 years and the pay-back period of 5 years can be expected. The cost break-down of the application shows that the cost of transport shares considerably and 50 km distance is limiting. The price of bentonite is the decisive criterion and constraint of the further bentonite application in the amelioration of soils in the contemporary agricultural practice.

The application of bentonite for soil reclaiming has been materialized in Czechoslovakia only on research level and tested on pilot scale.

This intervention (called "bentoniting of sandy soils") has been incorporated into reclaiming programmes subsidized by the Government. It comprises partially or fully metamorphose tuffogenous rocks which have similar reclaiming properties.

Tuffogenous rocks have properties enabling the application both for wider scale of grain categories of sandy soils and in wider scale of dosages. The substantial element of their effectiveness is usually higher content of carbonates and microelements. It determines some specific applications (to acid soils, gardens, in the production of humus substrates, for the recultivation of waste dumps).

Theoretical Regulations of Sorbent Behaviour in Soils

Critical properties limiting the yield of sandy soils are physical and sorption ones. Sorbents as multipurpose reclaiming agents comply with the requirement of the reclamation of both the critical properties of soils.

According to the experience proper, the optimal admixture of the mineral sorbent based on montmorillonite changes by swelling the effective diameter of pores which causes improved water retention. It means that the substantial influencing of the water regime of sandy soil is mediated by the change of the distribution of pore categories. The significance of water bound directly by sorbents is of secondary importance. Mineral sorbent types of tuffogenous rocks act similarly as bentonite if montmorillonite is their principal effective component.

The values of physical properties based on the dimension of surface and the value of hydrolimits related to the immediate water absorption are enhanced by the addition of mineral sorbents in the linear dependence on the dosage. (These properties are as follows: specific surface, water reception, wilting coefficient, minimum capacity of water). The hydrolimits the equilibrium of which is being stabilized on the boundary-line between porousness under tension and without tension (it is the maximum capillary water capacity) indicate, however, a maximum at a certain concentration which is the expression of the optimal ratio of pore categories or the expression of the optimal effective diameter of pores and it expresses principally the accession of easily available water. In case of bentonite, this optimum corresponds to the concentration 0.3 - 0.6% which again corresponds to the dosage 10 - 20 tons per hectare. The lower concentration applies to better bentonites of higher dispersity and higher swelling capacity. The suction tension (pF) of earth rises with increasing tension of bentonite. The higher is the pF of earth, the higher must be bentonite dosage to be effective. On the contrary, the higher is pF of earth, the lower bentonite dosage is sufficient for the application of its influence on further pF elevation. Maximum yields were found with dosage of 0.3 - 0.6% of bentonite. The yield maximum is generalized in the sphere pF 2.5 in which the admixture of bentonite affects the retention of available water. The presence or absence of organic matters significantly affects the efficiency of the mineral sorbent on water regime of sandy soils. The presence of organic matters not only subdues the expressive maximum of conditional capillary soil water in the zone of medium (optimal) concentrations but in addition it eliminates the reduction of soil porousness in case of the application of higher bentonite concentrations, i.e. it decreases the negative effect of bentonite overdosing upon the physical properties of soils. However, organic matters do not influence the optimal dosage of sorbent regarding the physics of soil, if their content in soil is not too dominant. The optimal bentonite dosage enhances the volume of the conditionally capillary pores or the retention of water by 1 - 2% by volume (Figure 8).

10 t per hectare dosage of bentonite was evaluated to be equal to increasing retention capacity of water of sandy earth by 1%. The 20 t per hectare dosage is a limit of conditionally capillary soil water both in the presence or absence of organic matters as with further dosage increase the quantity of water decreases. When organic matters were absent, high bentonite dosing reduced water absorption of sandy soil. Reduced macropores caused lower velocity of water percolation through earth which decreased with the second power of bentonite concentration. Capillary elevation was also affected by bentonite admixture and influence of more factors was observable: anomaly at low dosage, different effect in case of different quantity of tested bentonites, etc. The presence of substance having lower wetting capacity (or greater angle of wetting) makes the capillary lift lower. However, in the application of a swelling mineral, the mechanism of its effect on the lessening of pore diameters acts inversely. Experiments proved that this influence on the effective diameter of pores is decisive within the range of recommended dosing.

Consolidation of sandy earth by sorbents and related change of water regime is connected with increased heat capacity of the sandy earth, higher heat conductivity and with consequent desirable lowered temperature amplitudes, especially in the surface layer. As a practical consequence is the prolongation of the heat accumulation period in the vegetation profile of soil which can cause the retarding of germination. This fact observed during the experiments proper is both a negative phonomenon (shortening of vegetation period) and a positive one (smaller danger of early frosts).

Swelling sorbent could also affect the germination by changed ratio between diffusion pressure in seeds and suction pressure of bentonited soil, if the suction pressure were affected only by bentonite. This phenomenon could only take place at constant and simultaneously critical humidity, which is almost impossible as bentonite enhances retention capacity of soil, reduces permeability and retards desiccation acting thus against the states of critical water undersaturation. This positive effect was confirmed by laboratory and field results. The zone of the increased suction pressure is created only close to the bentonite nuclei which should be consequently as small as possible. If the humidity were too high, this phenomenon could have the opposite effect on bentonite nuclei - dewatering. This is also of significance if bentonite is applied as the carrier of fertilizers.

Relations regarding the changes of water regime of sandy soils by the application of bentonite or other swelling sorbent are considerable and will be applied in all further aspects of this measure also in the transformation of organic matter and in biological activities in sandy soil. Higher occurrence of bulb bacteria and intensification of their activity in a medium with montmorillonite can inter alia be related to the improved water regime. Montmorillonite and illite protect also rapidly reproducing bulb bacteria from high temperature by changing the water regime of cells caused by a montmorillonite (illite) sleeve. This relation creates a prerequisite for the improved development of vetchy plants on sandy soils which is important for the improvement of conditions of the green fertilizing. The results proved the interaction of the sorbent type of bentonite and organic matter. The presence of sorbent increases the accumulation of organic matter and/or reduces mineralization, binds preferrably simple fractions of humus matters. Cation mineral sorbent enhances also the accumulation of bound humus fractions. This confirms the explanation of principal mechanisms binding organic matters on clay minerals either directly by functional groups or indirectly by bridges of chelates creating metals. The effect of trivalent iron in the same role was proved by own tests. The presence of ferric ion decreased the mineralization and increased the accumulation of bound humus fractions. It might have been one of the effects of the tests bentonite exhibiting a relatively high content of trivalent iron. Hence, organic-metal bonds are apparently important and their destruction causes higher extrusion of humus matters. The acidity is applied in such a way that in acidic medium simpler low-molecular fractions are bound that have here a higher affinity to iron. Swelling clays contribute to the stability of humus complexes and Fe. Uncharged organic molecules are bound only physically. It has been verified already by the research of the sorption of nitrogen organic matters on montmorillonite in the cycle Na-, Cu-, Co-, that nitrogen binds groups of NH_2 which are on the outside and inside surface of montmorillonite. Considerable liberating of surface as well as interlayer water sets in in the sorption by which the qualitative change of sorbent surface from hydrophylic behaviour to hydrophobic one takes place. These organic-montmorillonitic complexes are stable, as found up to 200°C.

A practical application of the sorption of organic matters is used e. g. in refining wines and in preventing organic matters from putrefaction. In the application of Ca-montmorillonite, the interlamellarly sorbed oxygen organic matters were bound unchangeably and it was found that only bases had been sorbed inter layers while the organic polyanions had been bound on surface only (basal distances d_{001} remain unchanged).

Dosages 10 - 20 t per hectare of mineral sorbent were most advantageous for affecting positively the dynamics of the transformation of organic parts of soil. It was proved by testing results. Additions 15 - 30 t per hectare of bentonite are recommended as optimal for retention of organic matter in sand and the optimal dosage 10 t per hectare of bentonite for sandy soils from the point of view of humus share. The optimal concentration of bentonite was found 0.5% for influencing positively the creation of biomass which corresponds to round 15 - 20 t per hectare. There are data showing the influence of bentonite on the accumulation of organic matter, likewise data about the influence on increased quantity of bacteria, data regarding the increased mineralization and data showing the improved resistance of sorbed organic matters to the disintegration by microbes. It is apparent that the optimal dosage of sorbent consists in the achievement of the optimal ratio between mineralization and stabilization of organic matter in soil. It is a matter of extraordinary importance for the fertility of sandy soils where 90% of organic residues are mineralized. As the accumulation of organic matter in sandy substrate in the presence of sorbent was proved, there is also a subordinate consequence to the secondary bond of microelements as their existence is directly related to the humus content.

Explicit data given by some authors regarding both the positive and negative influences of sorbent on the transformation of organic matter are to be understood in relation to the incidental conditions under which they were collected. In generalizing, the factor of quantity must not be avoided because it can have a qualitative effect. Own tests proved that bentonite overdosage decreased the creation of humus or reduced it to the creation of simple low-moleculary pre-phases. Others showed that the addition of montmorillonite above 4% caused reduction of biochemical processes. Different effects of different quantity relations have been proved by other authors who demonstrated the optimal bentonite concentration. It was demonstrated by own tests convincingly, too. The overdosage was connected also with the negative effect of dessication of sandy soil and mineralization of organic matter. (See Figure 6)

It may be purposeful to note that apart from the indirect influence of sorbents on microflora, which is made felt in soil medium through the influence of sorbent, there is a direct interaction between sorbent and microorganisms and also direct mutual sorption, which may influence to a considerable extent the system of biochemical changes of organic matter in soil.

However, in the sorption capacity of soil substrate, both the mineral, especially clay component of soil and the organic one, especially humus component of soil, participate. The clay component of soil ranges between 5 to 35% of the soil sorption capacity.

The results proper brought about the finding that the affinity of ions to sorbents is different: for the sorbent based on montmorillonite, the affinity of cations in a series partly dependent on the valency of Na < K < Ca < Al < Fe was confirmed. The affinity of cations to mineral sorbent grows also in relation to the decreasing partial concentration of the relevant cation in the medium. Empiric equations were determined for the equilibrium of exchangeabl pairs Na - K and K - Ca; for the pairs K - Al and K - Fe, a graphic interpolation is easier. The equilibrium constant is not constant in the course of the whole isotherm and the mentioned differences of affinity participate in the non-ideal course. Anions can be linked to mineral sorbent by mediation, especially by bridges of multivalent cations Ca, Al and Fe. In this case, the increased concentration increases the sorption (chemisorption of anions). The anionic capacity of clays in the complex with Fe^{3+} is exhibited especially at low pH.

The admixture of sorbent in soil medium limits the wash-out of inorganic raw materials from the permeable substrate. The most favourable coefficient of retention for bentonite was achieved with dosage of 20 t per hectare (for dosage of fertilizers 200 kg of pure nutrient per hectare in current ratio). The distribution of potassium, one of the main nutrients, is most expressively influenced by the mineral sorbent (bentonite), then the distribution of nitrogen while that of phosporus is affected least.

If these findings are applied to the system of soil medium - bentonite, it may be supposed that the presence of natural bentonite (predominantly Ca, Mg type) retaints before all trivalent ions (Al, Fe) to which it has a higher affinity. In the presence of these ions and K, Na, NH_4, Ca, Mg ions delivered by fertilizing or by liming an equilibrium will be constituted in which the ions will be linked to bentonite in the ratio which will reflect their valency and concentration in the system. The increased affinity of bentonite for ions present in a very low concentration evokes the possibility of intensive retention of multivalent cations of the character of trace elements. The mechanism of the sorption of these elements is combined, however, with hydrolytic process. In principle, univalent cations will be mostly loosened being important for nutriment while the multivalent ones that have inter alia the assignment to create complexes and structures, will be bound more strongly. However, the relative affinity of hydrolytic products $AlOH^{2+}$ grows with the increasing Al hydrolysis and thus - at a greater proportion of their sorption - ther is also the danger of the degradation of sorption capacity. Likewise, clay behaves strangely to the high content of calcium where already the state of aggregation and creation of tectoids appears. But substantially, the summary of phenomena evoked by sorption properties of bentonite in soil medium will be manifested by the protection of nutrients against leakage and by the mediation of their more advantageous distribution and better utilization by plants. The crucial progressive significance of the sorbent reclaiming application consists in strengthening the sorption capacity of soil and intensifying the fertilization which is a basic prerequisite for increasing the production potential of soils. Besides, a higher efficiency of sorbent was ascertained also at higher level of fertilization.

The most efficient dosage in the investigation of the optimum ratio of sorbent dosage to the dosage of industrial fertilizers (200 kg of pure nutrient per hectare) was with regard to the retention of nutrients 20 t per hectare.

The optimum dosage 20 t per hectare represents 10 kval. per ha of sorption capacity (at 50 mequ per gram). It is the increase of only 0.4 me per 100 g which represents about 10% of the sorption capacity of a current sandy earth. But the experiments proved that this dosage influenced most favourably equilibria, limited wash-out and increased yields. It is evidently the consequence of the total influence of sorbent on all factors of soil fertility.

As far as microelements are concerned, they exhibit a very strong affinity to bentonite due to the above mentioned reasons which is practically utilizable in two directions: on one side by the application of bentonite - either by direct application or by the indirect one of carrier fertilizers - the stimulative effect of the microelement applied to this purpose will be prolonged (a week concentration of microelements is introduced into the soil by the application of the bentonite only), on the other side, bentonite limits the toxicity of a surplus of microelements in soil medium. This fact is utilizable for partial protection of soil medium against the detrimental concentration of heavy metals.

The acquired findings on the retention capacity of bentonite with regard to microelements occurring in fertilizers and to microelements, have naturally their significance also for the protection of surface and underground waters.

If the yield increase of agricultural crops is related for simplification only to the sorption capacity delivered by bentonite, the optimum dosage of 20 t per hectare brings about the increase of yields of about 2% per 1 kval of sorption capacity. Also this parameter complies with testing results.

Even though the sorption capacity of sorbent be only one of the effective factors of its complex effect, it is the factor of first-rate significance. The most stable system is created if all charges of sorbent are covered by countercharges of exchangeable ions. It is most easily possible with monovalent (Na) ions and more difficult with possible majority of multivalent ones. This phenomenom as well as other reasons of disequilibria as e. g. reduction or selective sorption, may give impulses to a series of soil processes and influence the connection of structurally chemical state of soil sorbents with the state of technological properties of soil and naturally also the possibility to create complexes. On the contrary, the quality of sorbed substances may be changed by their sorption.

The primary reason of the sorption, i. e. the mobility of electrons in molecules and their transfer in the realization of sorption, gives the solution for further important connections, i. e. the possibility to utilize sorbents as electronexes (redoxites) to treat or influence the redox-potential of soil medium.

The results of the sorbent stability study on the basis of montmorillonite in soil medium concluded that the factors disturbing the stability of the natural sorbent of bentonite type are especially washing-out by water, high temperature, acidic medium, medium saturated with K ions or NH_4 and hydrolytic products Al.

The found proportions of irreversible fixing of potassium and amonium ions by the sorbent based on montmorillonite allow the optimistic conclusion that in current conditions of agrotechnics, a serious deterioration of applied sorbents will not take place. Some authors recommend ammonium form of sorbent for sorbent fertilizers. Its mobility is decreased by biologic sorption. The authors derive their recommendation from the existence of ammonium mineral sanidine. Ammonization should contribute to the increased sorption of nutrients and water holding capacity. But the effectiveness of bentonites will be more expressively influenced by acidic medium which can in a longer action disturb partly the structure of clay mineral and espesially decrease its sorption capacity by the creation and fixing of hydrolytic products, especially of Al. A significant decrease of sorption capacity was observed especially in the conditions of dynamic leaching. The wash-out of mineral sorbents will also not threaten substantially their effect in soil especially in the case of Ca - Mg bentonites and those containing admixtures acting against peptization. The fertilization with industrial fertilizers increases the concentration of the original electrolyte which contributes to coagulation. It is sufficient to observe the following principles for the elimination of potential danger of disturbing the effectiveness of-the above factors. For the soil reclamation, the sorbents with higher calcium content and in the form of carbonates if need be, should be used, the soil reaction should be maintained on the desirable level by liming and the application of bentonite to soil by means of a technology enabling it by way of regular yearly ploughing.

The acidic medium can disturb not only the structure proper of clay material but also the created complexes or those being in the stage of creation and organic - metallic linkages. The ferric ion in an acidic medium combines with low molecular compounds or fulvoacids that have a higher affinity to

Fe ion and are mobile. It is a mechanism known from the process of subzolization. On the contrary, in the medium saturated with bivalent ions, also the complex creating power is strengthened and the bond between matured humin acids (rich in Fe) and clay particles, especially in case of swelling clays. It underlines the significance of soil reaction which can to a considerable degree limit directly or indirectly the effect of sorbent in soil. On the other side, the fact should be taken into account that mineral sorbent itself, especially in the Ca-Mg cycle, as are Czechoslovak bentonites, regulates to a considerable extent the reaction of soil medium both with the contribution of bivalent cations or admixture of carbonates if need be and especially by the increased stabilization of soil.

The bond of large organic molecules has considerable positive significance for the structure and technological properties of soil, but it limits the exchange of small inorganic cations and limits partly in this way also the assignment of sorbent in this direction. The binding of organic matters to the surface of soil changes also the character of clay sorbent from hydrophylic to hydrophobic behaviour or moves it at least in this direction which has its significance for all the other effects of sorbent, especially the physical ones. Some assumptions should be mentioned here that organic matters acting for many years on montmorillonite make it liable to genetic changes with the possibility of creating a mineral of a different type. A finding is important for all phenomena threatening the stability of clay sorbent that more perfectly crystallized bentonites are more reactive, easily fix ions and molecules and change properties.

Practical experiments proved the effect of mineral sorbent based on montmorillonite still after 7 years after the introduction. On the other hand, agressive factors of soil medium can reduce the effect of sorbent by one third of the input effect.

The action of sorbent in actual conditions of soil and contemporary agrotechnics

The results show that the sorbents of bentonite type have a better effect in lighter soils with lower humus content that the production curve reaches its maximum in the range of dosage 13 - 23 t per hectare, that the absolutely highest yields were achieved in most cases with dosage of 20 t per hectare, that the optimum of this dosage is justified by the effect of mineral sorbent on physical and sorption properties and by economic limits. It was also found that the reclamation effect of bentonite appeared more distinctively at higher level of fertilization, without watering and with roo crops. (See Figure 4)

It may be analogically deduced from the thesis of equilibrium which is supposed to be the optimum of ecologic factors, that the reclaiming matter will be the more effective the more distant are the ratios from the optimum. This thesis confirms also the regularity of optimum sorbent dosage as means to the approximation of the state of ecologic factors to the equilibrium and confirms also the relativity of optimum dosage as the expression of achieved equilibrium at the given state of ecologic factors. This theory roofs also the partial findings on different behaviour (effect) under different accompanying circumstances. The sorbent dosage itself becomes then one of the factors as it changes quantitative ratios of the ongoing processes (e.g. mineralization and retention of organic matter, sorption and leakage, water reception and distribution). As every deviation from the equilibrium of ecologic factors means according to this theory the reduction of the production capacity of soil, the incorrect dosage of reclaiming substance must also have the same implication. This circumstance explains summarily on the one side the decreased effect of sorbent in overdosing and underdosing, but it explains also the phenomenon of different optima of dosing under different circumstances. The optimum dosage is consequently the result of synthesis of particular effects of sorbent as polyfunctional reclaiming matter on the physics of soil (0.3 - 0.6 %),on the sorption (5 - 12 kval per ha), on the biology of soil (0.5 - 0.6 %) and of starting conditions (grainage, humus content) and of accompanying circumstances (precipitation, watering, fertilization, ecologic demands of crops). An important correction factor is the quality of applied sorbent; its intensity of effect drops (optimum dosage grows) in a series starting with bentonites with perfectly crystallized montmorillonite.

One of the fundamental prospective contributions of sorbent application is the extension of possibility to increase dosage of industrial fertilizers in light soils or limit the luxurous vegetable consumption in case of intensive fertilization. It is well known that without the upgrading of the starting basis, i.e. without the reclaiming measures of this type, the possibility of increasing dosage of industrial fertilizers in lighter sandy soils as one of the main intensification factors would be limited. A further not less prospective effect of sorbents is the enhanced exploitation of fertilizers including the organic ones and a substantial contribution to the protection of underground water purity against contamination from high fertilizer dosages. The application of sorbents contributes also to the levelling of lands.

Various reaction of different crops to the soil reclamation by a sorbent (bentonite) can be explained by different ecological demands of these crops that react then differently to the effect of sorbent on the change of equilibria in soil medium. E.g. the connection of the strong influence of sorbent on the limitation of potassium losses entails an expressive reaction of potatoes, the connection of diverse influence on the demands of grain and straw brings about different effect of sorbent on dynamics of phosphorus and nitrogen and on different agrotechnics for autumn and spring crops if need be. It was found by own analyses of cereals that the ratio K : Ca and N : P in the plant grew also with the increasing dosage of bentonite.

It may be expected that like in fertilization, the systematic application of sorbent will call forth the need of adjustment of some further agrotechnical standards, e. g. those of the density of sowing. It was further found by an informative experiment that apart from a slower germination also an intimation of richer shoots of cereals took place.

The application of sorbent to wood degraded soils (subsoils on sandy substrates) is a new element in the reclamation of these soils because sorbent substitutes partly for the destructed sorption complex, limits leaching and improves the function of liming in these soils and reduces the mobility of active organic substances or fulvoacids acting thus against degradation.

A special case is the action of sorbent in critical situations. E. g., the simplified relation of the montmorillonite based sorbent to suction pressure could have in cases of strong saturation by water, a negative effect if this phenomenon acted by itself. Actually, the total sorbent effect of this type acts against the critical state: by swelling, by which the suction pressure of earth increases and pores contract, the water holding capacity increases and water permeability decreases which already acts prospectively against the states of soil undersaturation by water. In a similar way, the cases of nutrient shortage could be considered, especially those of cation character and specifically those of strong affinity to sorbent. In principle, however, also this critical situation is rather unique as the mechanism of equilibrium formation in the complicated soil system considerably limits the possibility of such a critical situation. Nevertheless, it is recommended to eliminate the application of sorbents to unsufficiently fertilized soils, especially by cations. From the viewpoint of irreversible fixation, it is not recommended to manure the bentonited soil in the sequence K after NH_4. Drying strengthens the fixation of these cations.

The above situations limit the framework of external factors limiting the effect of sorbent. The group of internal limiting factors includes on the contrary overdosing, underdosing, a too high $CaCO_3$ content, a rather strong and selective sorption power, mass and compacting effect.

The acquired findings on the effects of sorbents allow the deduction that the contribution of sorbent to soil medium can be also understood as the contribution of potential energy to the system. This increase of potential energy is proportional to the whole surface of sorbent and can be utilized for the intensification of processes in soil and in conjunction with them also in plants. Consequently, this measure can be understood as the elevation of energy potential of soil.

Some authors hint to oxidation effects in the introduction of montmorillonite into the medium. A connection was assumed between the creation of oxidation products of organic bases in their sorption on montmorillonite with simultaneous reduction of trivalent intercrystallinely bound iron. This phenomenon was confirmed by coloured oxidation reaction of diamines sorbed on the surface of montmorillonite and is explained by the loss of electrons from diamines.

This phenomenon offers possibilities for the interaction of montmorillonite with biomass or organic matter in soil medium. Own tests proved that respiration (production of CO_2) in anaerobic medium, when checked without bentonite as well as with 0.5% of bentonite, was not recorded but was found in an insignificant measure at 5% of the Vysoké Třebušice bentonite.

It was also found that clay stimulated the growth of bacteria by the increased redox-potential of medium. Also own tests proved that the composition of humus acids in reduction medium was of a higher quality in the presence of bentonite than without it.

All these experiences confirm a certain form of oxidation effect of the montmorillonite based bentonite in medium. They contribute to the opinion that the admixture of bentonite (montmorillonite) means the introduction of a matter capable of taking electrons from medium which is in fact given already by its character of catex (acceptor of electrons), donor of protons. This mechanism can be realized also through the system $Fe^{3+} \rightleftarrows Fe^{2+}$.

3 Sorbent Application to Animal Husbandry

Exact function of sorbents added to animal fodder is not theoretically and satisfactorily explored. Especially, their dietary and antibiotic-like effects require thorough physiological and biochemical exploration. A hypothesis is upheld that the property of some sorbents to absorb NH_4^+ ion gives them the ability to keep nitrogen in digestive tract of animals which causes slower liberation and thus better utilization of NH_4^+ ions that are created from fodder in digestive tract where the animal proteins are generated. Other precious effect is the ability to lower toxicity of NH_4^+ when fodder additives of non-protein type such as urea are added.

Practical experiments with sorbents, especially natural zeolites, exhibit considerable effectiveness of fodder admixtures containing sorbent. Zeolite dosages favourably affect digestive disorders at changing sorts of fodder in different year`s periods. Animals with digestive disorders accompanied with diarrhoea recovered by means of 15% of zeolite additives in some days. Chicken fed on fodder containing 5% of clinoptilolite and mordenite gained on weight by 8% more (two-month testing period) than the tested species from the compared group.

Excrements of animals were less odorous in all tested cases. As well, sorbents positively influenced animal offspring when applied before litter. In case of 600 g clinoptilolite dosage per day for 35 days before litter, born piglets were heavier than those of compared group, they did not suffer from diarrhoea and their health was excellent.

These experiments prove that dosing sorbents into fodder contributes to curing animals without applying antibiotics which unfavourably influence the quality of meat. Higher productivity, higher earnings, substitution for antibiotics and better quality of meat are positive factors accompanying sorbent applications to animal husbandry.

The best results were obtained in using synthetic zeolites but some of natural zeolites absorbing NH_4^+ ion such as chabazite and clinoptilolite showed the same effects.

Most of authors had taken note of positives and negatives of sorbent influence on animal husbandry and have stressed that taking into consideration all the relations between aminal health and applied sorbent, its composition and purity are of paramount importance. Studying properties of sorbents and composition of fodder before the application is unavoidabl

Review of results obtained by sorbent application in animal husbandry

Application of zeolites

The tests were primarily aimed at:

- weight gains of livestock by zeolite addition to feeding stuffs,
- dietary effects on sick animals suffering from either acidosa or alcalosa.

The results of tests conducted on research scale are very promising.

Zeolite was a very good medium in curing digestive disorders in fardering bags of cattle. Dosage 3.45 g of zeolite per 1 kg of weight of stock influenced quickly the content of propion acid in . rumen and acidobazal state of blood and tested animals recovered rapidly. 2 months taking tests of feeding pigs by 5% zeolite admixture to feeding stuff showed 25% higher weight gains in comparison with pigs fed on unadjusted fodder. In addition, excrements were of drier and finer consistence without characteristic smell. Addition of 5% zeolites to feeding sick pigs influenced positively their health conditions, they recovered quickly while 40% of pigs from the compared group perished.

Other tests on pigs of German race Landrase weighing 40 - 100 kg showed 30.8% weight gains at shortened feeding period by 27.7 days in comparison with controlled group. Thus,the reduction of feeding stuff by 19.2% per 1 kg of weight gain was reached.

In addition, diseases such gastroeneritis, bronchopneumonis and rachitis did not occur while pigs of the controlled group suffered from those diseases and some animals had to be excluded from tests.

120 piglets were parted into two groups and subjected to testing feeding during 80 days. 4% additive of zeolite to feeding stuff caused 18.5% higher weight gains.

Zeolites were of significant effectiveness in poultry breeding. Zeolites containing 60 - 80% of clinoptilolite were added to feeding stuff up to 10%. Better health prosperity of the poultry and increased laying of eggs were a consequence of the zeolite action. Less diseases of digestive tract and sped-up breeding accompanied by lower smell of excrements were results of optimal zeolite admixture.

Some more examples:

Clinoptilolite added to feeding stuff of turkeys was subjected to test. Effect of 4 samples of clinoptilite and 1 sample of mordenite was evaluated. Mineralogical composition fluctuated from 40 to 90% of clinoptilolite and capacity of the ion exchange from 0.25 to 0.9 mea/g. From 1 to 3% higher weight gains were obtained with clinoptilolite from Shewill, Oregon.

Thickening poultry excrements by clinoptilolite additions was tested. Poultry excrements are valuable manure delivered either unprepared or dried and activated. These beneficiation procedures are accompanied by offensive odor and contamination of water and atmosphere. The production of good-quality fertilizers based on poultry excrements blended with natural zeolite - clinoptilolite was developed. Effect of the high capacity of cation exchange between clinoptilolite and ammoniac NH_4 caused the high content of nitrogen, potassium and phosphorus - 4.3%, 4.2% and 1.5% respectively - in the final product. 2 years`stock was not detrimental. 1.6 kg - 2.5 kg of powdered clinoptilolite spred on 1 sq.m. of the floor of a hen-house caused absorbing odors and hens laid 2 - 3% more eggs.

Application of bentonite

Bentonite can be used in animal husbandry to a considerable extent as admixture in feeding stuffs, as admixture in industrial production of granulated fodder and as mineral sorbent for thickening excrements.

Bentonite as admixture in feeding stuffs

The experiments with bentonites from the north-bohemian area were performed in Czechoslovakia in the year 1974 with .. one-year duration of production verification. The physiological substance of higher utilization of nutriments and vitaminous and mineral components during digestion, which is dependent on the rumen biochemistry, was taken into account during experiments. Composition of the feeding ratio pollard - 95% + bentonite "Sabenil 650" - 5% proved to be successful with favourable results. The group of young bulls, fed on this feeding mixture, had the weight addition per day and animal 0.10 kg higher than the group fed on pollard only. The health condition of bulls was excellent.

Bentonite proved to be useful as additional material (3 - 5%) for feeding stuffs enriched chemically. Moreover, the content of iron compounds in bentonite enabled to exclude the dosage of Ferronat (iron additing medicine). The high content of Fe_2O_3 in bentonite had a prophylactic effect in cases of dietary disorders, especially when the type of fodder is changed and during disorders of acido-basic stillstand.

Bentonite as binder in industrial production of granulated fodder

The beet or cane molasses are used preferably during the production of granulated feeding stuff in the amount from 3 to 10%. Sulphite waste liquor substitutes for the lacking molasses very often but it is of an expressive bitter taste. High sorption ability, resistance against overmoistening and resistance against mould are making the bentonite favourable for the use in production of granulated fodder. The significant presence of biogenous elements improves the value of feeding stuff. The pH-value of conditions in digestive tract of animals is regulated by the use of Ca-Mg bentonites.

The bentonite, used in the technology of industrial production of granulated fodder, improves the physical state of granules without the use of molasses. Granules are resistant to cracking and easy to storing after they left a production line. The nutrient content is preserved. Up to 5% of suitable type of bentonite can be used in mixing formula. Moreover, the cost reduction up to 35% is reached in comparison with the technology using sulphite waste liquor.

Bentonite as mineral sorbent for modifying excrements

The excrements of husbandry animals have unfavourable influence on the environment. They have deleterious effects, contain great portion of fluid component and undesirable substances. Bentonite can be advantageously used for thickening the excrements and their use as high valuable fertilizers. Sorption capacity of bentonite works effectively on bonding of NH_4 and on reduction of a bad-smell of excrements. It lowers the risk of penetration of fluid excrements to a free water and affecting the environment. Bentonite is an outstanding additive to excrements making them consolidated and appropriate to composts. 25% of bentonite, 20% of expanded perlite and 55% of liquid excrements can be mixed in cess-pools (sorbents are simply strewn over) and an easily transportable and thickened compost additive is obtained. (Admixture of the expanded perlite is avoidable).

III. OCCURRENCE OF NON METALLIC SORBENTS

Non-metallic minerals and rocks occur opulently all over the world. They have been utilized for many purposes for ages and nowadays they are indispensable in many branches and industries as raw mateials, catalysts, carriers, filtering materials, fillers, etc., either refined and upgraded or non-treated in a natural form. Their application in agriculture or in the production of victuals has been mainly known indirectly as raw materials for different industrial products used in agriculture. One reason of this publication is to indicate the immense significance of non-metallic minerals and rocks to agricultural applications in fertilizing vast portions of deficient soils, increasing outputs of animal husbandry and last but not least in solving environmental problems. It is important to realize possibilities of non-metallic minerals and rocks from the point of view of their agricultural applications in the whole complex of their actions. E.g. a favourable function of perlite is to prevent water evaporation which is of importance to irrigation projects, especially in arid regions. Consequently, a review based on available information on world occurrences of principal non-metallic minerals and data concerning productions, if need be, is presented that the reader may get information not only on applicability but also on the wealth of non-metallics all over the world which is promising from the point of view of agriculture since locally available raw materials can be utilized most economically.

Zeolites

- Crystalline hydrated alkaline aluminosilicates with ion exchange capacity and interconnected cavities in the structural lattice
- They occur in regions with ancient volcanic activity where volcanic glass was atterrated by water
- The world`s largest deposits can be listed as follows
  Itaya (Fukushima, Japan) - thickness 100 m
  Bonie (Arizona, U.S.A.)
  Czechoslovakia`s reserves are assessed 40 million tons, projected production for agricultural use is 400 000 tons in 1985.
- New deposits can be discovered in all the regions where homogenous fine-grained rocks occur in volcanic complexes.
- The dominant mode of winning is that of open cast mines.
- Vast reserves are in the U.S.A., Japan, F.R.G., Italy, Yugoslavia, Hungary, Bulgaria, Mexico.
- They are currently utilized in the production of pozzolanic cements, light-weight aggregates, fillers for paper-making, oxygen separation from air, animal fodders, agriculture, gas adsorption and catalysis.

Bentonite

- It is montmorillonite-rich clay of high sorption capacity, of cation exchange capacity and of swelling, plastic and bonding capacities.
- It occurs in places with argillized andesites, rhyolites and rhyolitic tuffs.
- World`s largest deposits are in the U.S.A. (Black Hills, Wyoming) and Milos Island (Greece).
- Potential spots of occurrence are in any volcanic areas near the sea shore.
- It is usually won from open cast quarries by bulldozers.

- World's reserves are assessed 1 milliard tons. Czechoslovakia's reserves are assessed 250 million tons for applications to soil and 25 million for industrially benefitiated additives to feeding stuffs.

Production of bentonite (thousand tons)

Country	1971	1972	1973	1974	1975
U.S.A.	2 385	2 495	2 974	2 934	2 929
Italy	297	275	299	344	288
Greece	213	375	289	384	427
Rumania	120	120	63	63	63
Czechoslovakia[+]	117	137	134	113	101
Argentina	86	87	90	113	116
Hungary	71	79	72	72	88
Mexico	57	38	46	61	33
Poland	50	50	50	50	50
Spain	38	43	45	76	60
Brazil	28	38	40	71	117

[+] Czechoslovakia's production in 1980 - 135 thousand tons, projected for 1985 - 600 thousand tons for soil, 250 thousand tons for fodders.

- This material is utilized for refining oil, for bonds of foundry sands, for filtering of vegetable oils, wine, sewage waters, reclaiming soils, etc.

It cannot be detrimental to show the review of denominations of bentonite according to their origin in various states since apart from the prevailing denomination "bentonite", a whole series of mostly local denominations was or is still used. It is due to the fact that bentonite is a very broad term. It comprises rocks of different mineral composition with various admixtures of clayey and non-clayey minerals of various physical and chemical properties.

Natural Bentonitic Earths in Different Counstries - Denominations

Active clay - Czechoslovakia
Amargosite - U.S.A. - California
Ardmorite - U.S.A. - South Dakota
Argile smectique - France
Askangel - U.S.S.R. - Georgia
Bentonit - Czechoslovakia
Bergseife - German Democratic Republic, Federal Republic of Germany
Bhakri - Pakistan
Clayoid - U.S.A. - Wyoming
Confolensite - France
Floridin - U.S.A. - Florida
Fuller's earth - England
Geolith - Greece
Gilabi - U.S.S.R. - Azerbejdjan
Gumbolit - U.S.A.
Gumbrin - U.S.S.R. - Georgia
Isarit - German Democratic Republic, Federal Republic of Germany
Khajru - Pakistan
Kil - U.S.S.R. - Crimea
Mud of Denver - U.S.A.
Multani mitti - Pakistan
Nalčikin - U.S.S.R. - Caucasia
Oglandel - U.S.S.R. - Turkmenia
Otailite - U.S.A. - California
Sabz - Pakistan
Saponite - U.S.A. - Wyoming

Savon de montagne - France
Shoshonite - U.S.A. - California
Soap earth - U.S.A. - Wyoming
Steargilite - France
Volclay - U.S.A. - Wyoming
Walkerde - German Democratic Republic, Federal Republic of Germany
Terra cimolia - ancient Roman term
Terra sarda - - " -
Terra sexum - - " -
Terra umbrica - - " -
Terre à foulon - France
Terre à laver - - " -
Terre decolorante - - " -
Terre de charge - - " -
Terre de suspension - - " -

Review of some industrially upgrade bentonitic earths

Bentonitic raw materials are industrially upgraded for different purposes and designated with commercial denominations. Their composition is mostly not indicated. Many of them are replaced with synthetic sorbents.

Absohclay - U.S.A. - Wyoming
Askanit - U.S.S.R. - Georgia
Bentogel - Romania
Bentol - France
Benton - England
Benton CF - France
Bentonil - France
Bolus alba - - " -
C - clearbenton - - " -
Clarsil - - " -

Clarsol	-	France
Franterre	-	- " -
Geko	-	Federal Republic of Germany
Gelisol	-	France
Ivegel	-	Hungary
Sabenil	-	Czechoslovakia
Seasil	-	France
Silenite	-	- " -
Tixoton	-	Federal Republic of Germany
Tonsil	-	- " -
Trasgel	-	Romania
Ultrasile	-	France
Valaisite	-	- " -

Diatomite

- It is low density sedimentary rock consisting of fossilized shells of siliceous algae-diatoms. Mineralogical composition - opal.
- It occurs in place containing beds of sedimentary origin with tuffs and tuffites of contemporary volcanism, mostly Neogene and Quarternary.
- World's largest known deposit is in Lompoe (California, U.S.A.) - thickness 250 m
- Potentially, it can be discovered in areas geologically composed of Neogene and Quarternary strata with volcanic ash.
- Diatomite rock is bulldozered and the raw material is treated by drying, coarse grinding and calcining.
- Diatomite is utilized for filtration processes, as filter, mild abrasive material, as source of silica, for production of insulating building materials, light-weight fireclays and adsorbents.
- Potential reserves of diatomites or diatomaceous rocks are known to be:

Africa - Nigeria (Polishum), Rep. of South Africa (Ermelo
and Prieska districts)

Latin America - Brazil, Chile, Colombia (Quesnel), Costa Rica,
Mexico

Asia - Turkey, Korea, Japan

Production of diatomite /thousand tons/

Country	1970	1971	1972	1973	1974	1975
U.S.A.	542.1	465.6	522.6	552.5	602.5	519.3
U.S.S.R.	371.9	310.0	380.0	390.0	400.0	410.0
France	172.4	168.5	70.0	200.0	205.2	210.0
F.R.G.	91.6	66.5	58.0	52.5	47.7	54.6
Czechoslovakia	87.0	89.0	80.0	10.0	14.0	16.0
Italy	59.9	49.6	50.0	81.1	90.0	90.0
Denmark	19.9	20.0	20.0	20.0	20.0	25.0
Spain	18.1	18.3	19.2	19.4	27.3	30.0
World total	1682.4	1548.5	1542.4	1633.0	1697.0	1632.0

Perlite

- It is acid volcanic glass with 2 - 5% of molecular water with system of concentric spherical cracks, expands ("pops") when rapidly heated to 760 - 1200°C with a tenfold increase of volume (artificial pumice is formed).
- Originally, it occurs where rhyolite intruded under thin cover or effused under lake waters.
- The largest known deposit is in Socorro (New Mexico, U.S.A.) thickness 150 m, diameter of the round body 600 - 800 m.
- It may occur in regions of acid volcanism and contemporaneous fresh water sedimentation.
- It is mined in open cast quarries by occasional blasting, treated in expansion furnace near the quarry.

- World's largest reserves are in the U.S.S.R. - 500 million tons (1970).
- Perlite is utilized for filtration, for the production of adsorbents, insulating materials, light-weight aggregates, refractories and in agriculture.
- Potential reserves of perlite are known to be:
  Africa - Algeria, Morocco
  Asia - Philippines (Legaspi City, Luzon - 9.9 million tons,
  Polique Bay - 33 million tons)

Production of perlite (thousand tons)

Country	1969	1971	1972	1975
U.S.A.	427	449	567	464
Greece	120	160	N.A.	161
Italy	N.A.	100	N.A.	150
Hungary	60	N.A.	N.A.	72
Mexico	11	9	N.A.	15
Turkey	N.A.	9	N.A.	12
China	N.A.	30	N.A.	N.A.
Japan	N.A.	60	N.A.	100
Czechoslovakia	N.A.	N.A.	N.A.	140

IV. NON-METALLIC SORBENTS IN AGRICULTURE

A/ Bentonite

The denomination of the rock bentonite is rather wide and not accurate term comprising rocks of various mineral compositions. Bentonite is a clayey rock consisting of the mineral montmorillonite.

Different species of montmorillonite and different quantities of admixed clayey and non-clayey components determine a series of physical and chemical properties of this rock.

The designation bentonite was introduced by the American geologist W. C. Knight in 1898 according to the name of fortress Fort Benton in the region Rock Greek in Wyoming - U.S.A.

The fundamental component was denominated montmorillonite by A. Damour and D. Salvetat in 1847. It was a clay mineral occurring in France near the town Montmorillon.

Montmorillonite and its related minerals composed of very fine crystalline particles are distinguished by a large surface. It was identified as mineral by the Swedish mineralogist A. Cronstedt in 1788.

The internal crystalline structure of these secondary water holding aluminum - calcium - magnesium silicates (aluminosilicates) is of a layer structure character. There are structural gaps between the particular layers of the crystalline lattice, into which water molecules, ions with hydration coatings and organic substances can penetrate.

Raw and upgraded bentonites were denominated with regard to the application of bentonitic clays which caused a mess in the indications regarding occurrences, quality, production, possibilities of application in various states and continents.

The first detailed classification of bentonite rocks based on the study on exchange of bases was elaborated in 1923 by C. W.Davis and H. C. Wacher who classified bentonites in four classes that, however, do not comprise all varieties indentified till now.

1. Alkaline bentonites (typical Na bentonites) containing easily exchangeable alkalies; they are not disturbed by hydrochloric acid.
2. Alkaline subbentonites containing exchangeable alkalies and being not resistant to hydrochloric acid.
3. Alkaline earth bentonites containing exchangeable alkaline earths Ca - Mg; they are resistant to hydrochloric acid.
4. Alkaline earth subbentonites containing exchangeable alkaline earths; they are not resistant to hydrochloric acid.

J. N. Wilson presented in 1934 a simplified classification of bentonite rocks taking, however, into account only raw materials with at least 75% of montmorillonite or beidellite. He distinguished only two groups according to the liability of being disturbed by sulphuric acid according to Petérfi's thixotropy:

1. Bentonites proper with thixotropic properties
2. Subbentonites that do not create suspension in water but break down into powder.

The American geologist P. G. Nutting elaborated a new classification in 1943:

1. Effective strongly swelling bentonites with the capacity of retaining a multiple water volume and to create in water stable thixotropic emulsions but without a significant capacity of ion exchange. Swelling can be further increased by natrification. These bentonites are resistant to chemical breakdown so that they are liable only to mechanical weathering by erosion.
2. Ineffective bentonites, but very pure clays activable by natrification.
3. Effective and highly activable mostly beidellite clays of the floridin type and like fuller`s earth with high content of bound potassium.
4. Effective clays insignificantly affectable by acidic processing. They possess durable properties like floridin and English fuller's earths.
5. Effective clays the activity of which is decreased by acidic processing; they have permanent properties as fuller`s earth.

For a simplified orientation, the following classification may be applied:

1. Strongly swelling bentonites - stable, holding multiple water volume - belonging to groups 1 and 2. Application after natrification: industrial application - compacting and consolidation of non-plastic raw materials; applicable in agriculture.
2. Non-swelling bentonites - capable to hold water only in the order of tenths of the total volume, being without thixotropic properties, but with ion exchange capacity. They correspond to groups 1,2,3 as fuller`s earth purifying and bleaching clays.

Geology

It is most probable that the creation of clay minerals of montmorillonite nature has continued on the earth surface since the Archean. According to the theory of the academician Oparin, these effective minerals must have acted on the earth still before the creation of life as catalysts.

The earliest montmorillonites and their deposits (bentonites) were subjected to various changes, mainly to the regional metamorphosis. For this reason, only few deposits of earlier geological ages are known. As the earliest ones are supposed to be the bentonites of the earlier Paleozoic Systems of the Ordovician Period (U.S.A., Canada, Sweden) and of Silurian Period (English Wales). The bentonites from the later superficial Carboniferous Period in the Polish Upper Silesia and those from the basal Perm - Třebeč near Rakovník, Brandov in Krušné Hory (Czechoslovakia) and occurrences in Saxony (F.R.G.) -belong to the later Paleozoic Era.

More deposits of bentonites are known from the Secondary Era, however, many have not yet been discovered.

West German occurrences in the western part of the Schwabish Jurassic System are of Triassic Age. The median and superficial Jurassic System in the eastern part of Schwabish Jura and the median Jurassic System in England are of Jurassic Age. More bentonite deposits of Secondary Age belong to different grades of the Cretaceous System. Classic deposits are in France, England, Belgium and in the U.S.A., namely in Wyoming and Dakota. Further deposits are in the U.S.S.R. the Cremean kil and the Georgian gumbrin, other occurrences are in Azerbejdjan and Armenia.

The Tertiary Period is the richest in bentonite deposits. The occurrences from Eocene and Oligocene epochs are in the northamerican state Mississippi, in North Caucasia (U.S.S.R. - bentonite called malakin) and in Georgia (U.S.S.R. - bentonite askangel). Later tertiary deposits are in Both German states, Hungary, Rumania, Bulgaria, Greece, Yugoslavia, Austria, Italy, France.

Northwestern Africa has also extensive deposits. North America has occurrences in California, Texas, eastern maritime states, U.S.S.R. - Ukraine, Eastern Volga region, Kazachstan, Far East.

Extensive bentonitizations stem from earlier Quarternary Period (so called gumbodzil). They are of the interglacial age between Mindel and Riss and are situated in the northeastern U.S.A. and in Canada.

Czechoslovakian deposits are of different geological ages, they are of the Neogene System and partly from Pliocene.

Mineralogical and chemical composition

Montmorillonite - Al_2O_3 - $4SiO_2 \cdot H_2O \cdot nH_2O$ - is a substantial constituent of natural sorbents - tuffs, tuffites and originated from them bentonites. Montmorillonite is a clay mineral of high dispersion the particles of which have large surface and high ability to bond water. It is composed of very fine-grained (5 - 0.5 um) and soft (Mohs' hardness = 1) crystals of monoclinic system $(Ca, Mg, Fe^{3+})_2/(Si,Al)_4O_{10}/OH/_2 \cdot nH_2O$.

Its chemical composition fluctuates on the average:

SiO_2	49 - 56%
Al_2O_3	21.4%
MgO	4.3 - 9%
CaO	1.8 - 3.5%
Na_2O	0.3%
H_2O	21.3%
Fe_2O_3	1.4%
NmO_2	0.2%

Water in clay minerals containing montmorillonite

Inner crystal structure of these watered aluminosilicates is stratified containing water as essential constructional element in several forms:

a) bonded in the form of H_2O molecules,

b) bonded in the form of OH groups.

Water bonded in the form of molecules escapes when heated at the temperature 250 - 300°C. Water bonded in the form of OH groups escapes at temperatures above 200°C. Water in the from of molecules is devided according to its character to:

a_1) water in pores among particles and adsorbed in the surface of particles

a_2) water contained in interlayers of minerals.

Water in interlayers, except the water near the surface of particles, has all the qualities of common water of liquid state. The expansible structural spaces lie between individual layers of crystal lattice. The molecules of water, ions with hydration coverings, organic and inorganic substances, nutrients and trace microelements can penetrate to these structural spaces.

Montmorillonitic minerals, tuffs, tuffites and bentonites for fertilization of sandy soils in agriculture, used without thermal treatment, avoid the escape of bonded water. The amount of absorbed water is varying. This water by its affection mediates the important process of swelling.

In connection with the description of crystal structure of montmorillonite (see Figure 3), the different structure of kaolinite should be mentioned. Kaolinite is a part of fine-grained clays in crop land. It has the plane of chain Al-OH connected by oxygen compounds with one plane Si - O - Si, whilst montmorillonite has two such planes. It means the ratio $SiO_2 : Al_2O_3$ is 2:1 in kaolinite and 4:1 in montmorillonite.

Free bonds and expansion of interlayèr spaces in consequence of water fixation enable the swelling of montmorillonite. Montmorillonite is assessed as high active clay constituent of a crop land due to the ability of water adoption and release. Kaolinite is, on the contrary, ineffective constituent and in higher concentrations reduces the swelling of montmorillonite.

Each particle of montmorillonite, consisting of several elementary groups of three layers, has outer and inner surface. Area of the surface can be calculated from dimensions of elementary particle, determined roentgenographically and from its weight, determined by chemical analysis. Calculated area of complete surface is 750 - 800 m^2g^{-1}. From complete area, the outer surface of particles can be determined by the use of the curve of particles dimensions. The outer surface of particles is for montmorillonite 30 - 50 m^2g^{-1}. This large specific surface is the substance of high adsorption capacity of montmorillonite. Surface of montmorillonite sorbs selectively small polar molecules which are able to reach outer as well as inner surface of particles. Non-polar molecules are physically adsorbed in the outer surface of particles.

The distance of layers in dry montmorillonite is 9.5 Å, in the ambient with 99% of relative moisture content about 20 Å. This dimension corresponds to four molecule layers of water. Montmorillonite accepts water up to the amount of 0.5 g per 1 g of particles and parallelly enlarges its volume by about 100%.

Adsorption of pure liquids

Na-montmorillonite accepts up to 10 g water per 1 g of particles at the direct contact with liquid water. It is changed to thixotropic gel and its volume is enlarged 20 times.

Adsorption from solutions

Adsorption of dissolved substances occurs on the surface of montmorillonite, especially the adsorption of substances with polar molecules of inorganic and organic ions and macromolecular substances.

Important index, expressing sorption ability of a material is sorption capacity. It is the quantum of sorpted cations in 100 g of the material. The sorption capacity is expressed in miliequivalents. In the case of compact structure of a colloid element or inexpansible gaps of a crystal structure, the sorption is possible only on the surface of elements. The sorption capacity grows if the interlayer gaps are expansible due to penetration of cations into these gaps. The quantity of penetrated cations depends on the size of hydrated cations. Hydration is a fixation of water molecules by intensity of an electric charge. The elements with an electric charge are surrounded by water molecules. The electric attraction decreases with the distance from the charge holder and gradually the attracted water molecules pass into the free water. The hydration capacity, i. e. the size of water cover around cations, depends on the radius of sorpted ion. The smaler is the radius, the larger is the water cover. The sequence of the ion sorption is determinated by the ionic potential. Ionic potential is calculated from the element valency devided by its radius. Ions with the lowest ionic potential are sorpted most easily. Ions with the highest potential stay in solution, where they create complex anions. The lowest ionic potential has Ca: 0.61. Other elements from the lowest to the highest ionic potential: Rb, K, Na, Li, Ba, Sr, Cs, La, Mg, Zr, Al, Ti, Nb, Mo, P. B, S, C and N (33.33)

The sorption capacity of first-rate bentonites is 60 to 100 miliequivalents of exchangeable ions per 100 gramms. The lower limit of agricultural bentonite is 20 - 25 me per 100 g.

The important technological qualities are connected with the sorption capacity. Besides volume changes (swelling, shrinkage), it is also plasticity. Figure 7 presents the dependence between the sorption capacity and plasticity - ability of bonding sandy component of the soil - expressed by Rieke's number.

Beneficiation

The process differs according to the further use of bentonite. The bentonite for fertilization of sandy soils can be used without industrial upgrading, whilst the bentonite for application in animal husbandry and in industrial production of granulated fodder needs the industrial upgrading to reach perfect homogenization.

Mining of bentonite without industrial upgrading

The way and technological process of mining depends on local conditions and on geological situation of strata deposition, i.e. overburden and layer proper of mineral sorbent.

The mining of bentonite for the fertilization of sandy soils must be efficient and simple in order to reach favourable economic relations. The important precondition is a low thickness of overburden. The deposits of bentonite for fertilization of sandy soils are suitable only in cases of easy surface mining. The longwall method is the most suitable, especially in regions with occurence of sandy soils which need the amelioration by bentonite.

Deeper deposits of agricultural bentonites are acceptable only as interlayers or underlayers of more valuable industrial bentonites, quartzites, etc. and they must be mined out anyhow.

The next sources of agricultural bentonites are so called dumped earths - remainders of bentonites which don`t satisfy the standard of industrial bentonites. This material is usually contaminated by carbonates which is favourable for agricultural bentonites. The admixtures of bivalent iron and other toxic elements are undesirable. Indecomposed volcanic admixtures and coal particles are not injurants.

It is necessary to solve the shortest possible transport from mining centres to ameliorations in regions with sandy soils to lower the transport cost.

Opening of a deposit is preceded by geological prospecting and determination of technological process of mining, from which the type of used mining machinery results. Before the stripping starts, the preventive water drainage (drains, sewers, etc.) should have been done.

Mining process

The stripping of overlaying waste rocks is conducted by bulldozers and mobile excavators with direct loading on lorries and transportation to a dump. The mining proper is then conducted by the same machinery.

Technological process of mining must be accordant with regulations for raw material mining in open bearing and is controlled by mining inspection. The extracted bentonite is transported by lorries to a depot, established on the open area with solid subgrade. The lump bentonite can be stored up to the height 0.7 - 1 m. It is mixed roughly and levelled by the shovel loader and then left to weather effect.

A natural disintegration of a lump bentonite occurs as an effect of the weather - precipitation, frost and sunshine. Considerable homogenization of bentonite is reached by its stratification and mixing on the open-air depot. Thus the fluctuating quality of bentonite from various places of the deposit is eliminated.

The natural disintegration and drying of bentonites can be used in areas of mining with occurence of sandy soils as well as for the preparation of composts in these areas.

Basic properties of bentonite for fertilization of sandy soils:

1. The most important property of bentonites, used in agriculture, is the swelling, i.e. volume expansion in contact with water which must be higher than 10%.

2. Complete sorption capacity should be in the range from 20 milligramequivalents per 100 grams to 40 milligram-equivalents per 100 grams.

3. The disintegration of lump bentonite on the open area lasts in average from several months to one year. It can be intensified by mechanical turning upside-down during the period.

Mining and industrial upgrading of bentonite for agriculture

The mining is similar to that of bentonite used without industrial upgrading (points 1 to 6 in Figure 1). The extracted bentonite is transported by lorries to dumping grounds and to homogenization stocks. The raw bentonite is transported from stocks to a feeding hopper (7) which is the beginning of technological line. Raw material is transported by inclined belt conveyor (8) through the feeder (9) and by another conveyor (10) to the pug mill (11) of raw bentonite. At the same time, the precise dosage (1 to 3%) of pulverized soda (Na_2CO_3) is added to the mill by the turnstile from the storage tank of soda (12). The activated mixture from the pug mill enters the worm blender (13) where the next mixing and heating by the steam is carried out. The mixture of bentonite and soda enters by the inclined belt conveyor (14) the parallel-flow rotary drier (15). The parallel flow is used to avoid breaking of material structure by overheating.

Dried bentonite from the drier falls to the set (16), consisting of elevator, crusher and belt conveyor, leading into the fine-grinding mill (17). The mill is equipped with screens, efficient air technique, cyclons, separation filter, magnetic filter of the grist. and belt conveyor which transports finally upgraded bentonite to the storage bin (18). The ground and dried bentonite is discharged from the storage bin through the set of belt conveyor + packing machine (19) into bags or through special filling equipment to a tank wagon (20) (See Figure 1).

Agricultural applications

The practical effectiveness of known theoretical regularities of the effect of artificially introduced sorbents in soil was verified by precise operation experiments in field conditions. In this part, the summarized findings on production effectiveness of the method applying bentonite as representative of montmorillonite based sorbent - for direct fertilization of soils are presented.

Field experiments with bentonite took their course in 1964 - 1967 and 1973 in five main areas of light soils in Czechoslovakia and comprised soil sorts ranging from sandy to earthy soil. The precise field experiments were carried out on the surface of more hectares, they were based on and evaluated according to statistical principles and they helped to solve the forthcoming practical problems.

Operational and economic issues were then solved on the basis of experience from the precise field experiments on the localities of light soils in Czechoslovakia by means of pilot experiments.

The field experiments were based on the principles for statistical evaluation and yields were evaluated by the methods of variation or covariation. The results of field experiments including the description of accompanying circumstances were mostly published (Lhotský 1969, 1972; Lhotský et al. 1967, 1973) and therefore only summary and generalizing conclusions are presented.

Theoretical knowledge was verified by field experiments and it was found that the reclamation effect of bentonite depends on the accompanying conditions that also influence the stabilization of equilibria in soil medium, namely grain size distribution of soil, humus content in soil, level of the present manuring of soil, influence of meteorological character of vegetation period, influence of watering and influence of the sort of cultivated plants.

In the course of experimental years, the dependence of yields of different crop and under different accompanying conditions was on one side statistically provable, on the other side sometimes under the influence of accompanying conditions and even under the statistical conclusive limit but in general with evident positive trend of the bentonite dosing.

Production function, optimum dosage and influence of starting soil conditions

The general average of the exact field experiments for the whole experimental period of 4 years, for all crops and without regard to other factors determines the effectiveness of particular dosages of bentonite and determines thus its production function.

Indexes of bentonite effectiveness in average from all precise field experiments

	Dosage of bentonite per hectare /t/				
	0.5	2	5	20	50
All parameters	100.8	108.2	113.0	119.7	113.0
Conclusive parameters	105.2	112.1	120.5	134.1	125.4
Parameters for main products	101.0	108.1	114.6	121.6	114.8

General averages determine univocally in investigated intervals 20 t per hectare as the most effective dosage. In the second and third place, there are the investigated dosages of 5 t per hectare and 50 t per hectare. The difference in technical effectiveness between the second and third place was relatively close. Lower dosages were not effective enough.

Apart from general averages, there is a differentiation in the effectiveness of bentonite on yields and in the sequence of dosages of particular localities. If the differentiated parameters of the effectiveness of bentonite dosages are related to the initial soil relations of each locality, a significant dependence of bentonite effectiveness on soil sort and on humus content in soil is obtained. This dependence can be simplified as indirect dependence of bentonite effectiveness on the content of grains of first category and on the content of humus in orable land as represented in Figure 5 . It is a quadratic dependence, analogous for both parameters, for both soil properties. The influence of 10% of grains of the first category is adequate to the influence of 1% of humus, 25% of grains of first category to 2% of humus, etc.

Bentonite in fact acts more expressively in lighter soils with lower content of grains of first category (in sandy soils) and with a lower humus content. With high humus content and with higher content of grains of first category (earthy soils), also the amount of optimum dosage is changed in indirect proportion to these factors, i.e. it decreases. The determination of 20 t per hectare as the optimum effective dosage from tested dosages, which by the way corresponds to theoretical knowledge, relates according to the results of field experiments to sandy and argillo-arenaceous soils (up to 20% grains of the first category) or to light soils with humus content up to 1.5%.

If the yield indexes of sandy or argillo-arenaceous localities are evaluated according to the preceding finding, the resulting production curve, i.e. the effectiveness of bentonite, is substantially more expressive than showed the general average of all localities (Figure 4).

The evaluation of the production curve is based on the generally accepted principles on the delimitation of the optimum intensification factor for the demarcation of the zone of advantageous dosages of bentonite on the basis of a continuous production curve.

To this purpose, the increment curve (the first derivation of production curve) and the curve of so-called unit production were applied. The values of the latter curves were obtained according to the formula

$$UP = \frac{\text{increment } \%}{\text{dosage}} \; . \; \text{lifetime}$$

The life time was supposed to be one year for the dosage 0.5 t, two years for 2 t, five years for 5 t, eight years for 20 t and ten years for 50 t. These data are based on practical experience from field experiments.

The optimum zone delimited in this way (6 - 23 t per hectare) is confirmed by actual findings from precise field experiments (dosages 5 and 20 t per hectare). The extent of these advantageous dosages of bentonite for the fertilization of sandy soils is decreased to 20 t per hectare with regard to purposeful life and to economic viewpoint which was fully verified in practice.

Interaction with other intensification factors

The following dependences ensued from the interaction of effects of mineral sorbent (bentonite) with other intensification factors in polyfactorial field experiments:

a) The effect of mineral sorbent increases at higher level of mineral fertilization. The sorbent also increases the exploitability of mineral fertilizers and prolongs their subsequent action.

b) The simultaneous application of organic manures jointly with bentonite raises the effectiveness of both components. This dependence is direct and is limited (according to the results of model experiments) by the upper limit of the dosage of organic manures amounting to 3% of matter (i.e. about 90 t per hectare) of treated soil. A higher dosage of organic manures exceeds the effect of mineral sorbent. The mineral sorbent prolongs the effectiveness and subsequent action of organic manures.

c) The reclaiming application of mineral sorbent is demonstrated relatively more expressively without watering than with watering which veils to a certain extent the effect of sorbent on physical properties of soil. If the sorbent is applied with watering, its sorption effect is applied to the limitation of leaching of nutrients.

All field experiments are taken into account in conclusions, i.e. in all categories of soils (from sandy to earthy ones) if not stated otherwise.

Indexes of bentonite effectiveness in the interaction with the second intensification factor (100 = checking without bentoni on the given level of the second factor)

Second intensification	Its level	Index of bentonite effect at the dosage	
		5 t per ha	20 t per ha
Fertilizing with mineral fertilizers	100 kg pure nutrient per ha	110.6	114.3
	200 kg pure nutrient per ha	117.6	123.5
Organic manuring (composte)	0	115.9	126.8
	40 t per ha	124.5	145.5
	80 t per ha	130.5	166.5
Watering with spray	without watering	113.8	106.7
	with watering	110.5	106.3

These findings prove that the application of mineral sorbent to light soils entails direct increase of yields by the influence of sorbent but also further increase by the effect of interaction with the second intensification factor (mineral and organic fertilization). The third page of yield consists in the fact that added sorbent itself enables the level of fertilization to be increased even on sandy soils by which the area for the gradation of further intensification factors is extended. The indexes are naturally not comparable among various intensification factors.

Reaction of crops to the reclamation of soils by mineral sorbent

Root crops react most expressively and reliably to the reclamation by mineral sorbent (bentonite) and on the whole, potatoes exhibit the best reaction. The reaction of cereal products and fodder crops is more dependent on accompanying circumstances. Winter crops reacted more readily than spring crops. The effect of bentonite on the yield of straw was in general lower than on the yield of grain but spring crops, on the contrary, showed a higher effect on the yield of straw than that one of grain. Maize reacted relatively expressively to the reclamation by bentonite. The sequence of cereal crops was as follows: maize, rye, wheat, barly, oats. The creation of the matter above the earth was influenced by the sorbent in average less expressively than the main product but the ratios were specific in particular cases.

This differtiated reaction of crops is very well explainable by theoretical findings on the influence of added sorbent to equilibria in soil and to dynamics of nutrients, especially to the ratios N : P and K : Ca and ecological demands of particular crops in relation to the effect of bentonite on equilibria in soil.

Indexes of bentonite effectiveness on the yield of various groups of crops

Group of tested crops	Number of pieces	Index of bentonite effectiveness at the dosage of 20 t per ha
Root crops	10	118.6
Cereals (grain)	10	111.6
Cereal crops incl. maize	11	118.0
Vegetable matter above earth	14	109.8
Winter crops	10	110.3
Spring crops	8	104.9
Grain	15	108.8
Straw	13	106.4

Influence of the other accompanying circumstances on the effectiveness of reclamation by bentonite

The most significant remaining circumstances that were followed in relation to the effectiveness of bentonite are the methods of introducing bentonite into soil and the character of vegetation period. The most suitable method of this transfer appeared to be the basic autumn ploughing which spreads the sorbent in the whole layer of arable land and enables the stabilization of equilibria in the period of rest before the beginning of vegetation. The sorbent introduced by basic ploughing is thus made available by current periodical soil treatment and its contingent migration into the lower soils is eliminated.

The character of the vegetation period will contribute to the effectiveness of sorbent or to the reaction of plants under cultivation. A more expressive effect of bentonite was found in dry vegetation period in the application of a higher dosage while in a moist vegetation period the effectiveness was lower and it was applied also in the zone of lower dosages. The action of sorbent in wet vegetation period is analogous to the action of sorbent in the participation of an exceeding factor as e. g. the watering.

Indexes of effectiveness of bentonite in particular experimental years on sandy localities (P, HP) . 100 = checking without bentonite.

Experimental year	Character of vegetation period	Index of bentonite effectiveness at the dosage	
		50 t per ha	20 t per ha
1964	dry	122.6	131.7
1965	moist	126.6	126.2
1966	moist	107.8	113.6
1967	dry	113.1	132.9

Results of experiments in wood soil

Long-term verification processes on wood soil were based on theoretical findings of the effectiveness of mineral sorbents in soil, on successful results of bentonite application to arable soil for reclamation and also on the orientation experiment with the application of some mineral sorbents (bentonite, basalt tuff, ground tuff), which proved the effectiveness of sorbent on the melioration of properties of sandy substrate and on the improvement of nutriment of wood crops. This experiment is practically one of the first direct applications of effective sorbent in the reclaiming of wood soil.

The field experiments were started with bentonite on sandy soil of podzol type in two north-bohemian localities. The soilforming substrate of experimental soil is formed by secondary rectangular sandstone giving coarse-grained and acidic soils (on the average 5.0% of grain of category I, pH - H_2O 4.5 and pH KCl 3.5). Under the predominant pine corpse, these soils are liable to podzolization which desembocates in these conditions to an expressive production degradation. Under these circumstances, the multilateral fertilization assignment of sorbent known from arable lands receives another meaning, namely hindering destruction effect of the podzolic process.

The effect of sorbent (bentonite) in a long-term experiment on wood sandy soil is documented by a partial result of forest-culture growth in one of tested localities as compared to the effects of current reclaiming processes.

The application of mineral sorbent (bentonite) in the reclamation process in wood sandy soil of podzolic type brought about evidently a further increase of reclaiming intervention (for pine by 22% and for oak by 13%), which equalled the immediate effect of industrial fertilizers. The mineral sorbent in soil has of course a wider and long-term application as the previous chapters have shown.

Forest experiment

Reclamation process	Height of corpse of 8 years (cm) pine	 red oak
Basic reclamation process (ploughing + liming)	192	107
Basic reclamation process + mineral sorbent (10 t per ha of ground bentonite)	232	121
Basic reclamation process + fertilization with industrail fertilizers (N,P,K)	223	111
Basic reclamation process + manuring + mineral sorbent	227	121

Main aspects of bentonite application for the recultivation of dumped waste after quarried mineral raw materials

Bentonite or rocks of bentonitic character, metamorphosed tuffs and tuffites are recommended for the recultivation of dumped waste earths and also as component of applied reclaiming matters. Both the ways of bentonite application aim mainly to the compensation of extreme properties of extracted earths which are often even phytotoxic either by the bentonite proper or more often in the connection with further compensation materials (fertilizers, organic and organo-mineral muds from agriculture and industry, stripped arable land, town wastes, limestone).

The following experiences were gained in the application of bentonite on dumped waste of the North-bohemian brown coal area which was of experimental character: bentonite was applied as basic component of reclaiming matter for dumped waste with extreme properties, that are not currently recultivable (heterogenity, considerable portion of quartz, oxyhumolite, phytotoxic elements, lack of weathered minerals. The reclaiming matter adjusted favourably the pH of the earth, increased its sorption capacity which influenced favourably the nutrient regime and eliminated the liberation of phytotoxic ions from present toxic admixtures (e.g. from pyrite). The combination of required reclaiming mixtures with bentonite has a higher and more durable effect than reclaiming matters proper (e.g. limestone, fertilizers, organic matter). The recultivation for agricultural purposes is accomplished by covering the prepared reclaimed subsoil with a layer of arable soil in usual quantity.

The amount of the optimum bentonite dosage for the adjustment of the properties of extreme dumped earths is verified, preliminary results show that it will be approximately by one order higher than in the application to productive arable soils. The experimental dosages into the extreme dumped earths were between 450 to 900 t per hectare, however, their amount will depend on concrete conditions.

Application of bentonite as admixture to fertilizers

The experiments to utilize bentonite for this purpose were also various. Bentonite admixture was tried mostly as filler in the production of granulated fertilizers and in so-called "powdering" of mineral fertilizers. Experiments geared to the utilization of bentonite in treating organic fertilizers were directed to direct mixing of manure or other excrements of animal husbandry with bentonite or to utilize bentonite as component into composts.

Bentonite for treating hen dirt and for the production of granulated organomineral fertilizer played here the role of dehydrator of wet excrements in processing and binding final granules. The final product contained up to 25% of bentonite. As accompanying component for the acceleration of drying phase, expanded perlite was recommended. The method has not yet been introduced on a large scale. The admixture of bentonite into peat substrate exhibited before all the increase of their sorption capacity which allows a higher content of mineral fertilizers without the danger of their increased detrimental concentration in soil solution. However, the maximum dosage must not be exceeded, overdosing by bentonite initiates the relative deficit of nutrients.

Experiments aimed at the utilization of bentonite (montmorillonite) as component of microfertilizers were carried out, too. Bentonite, in this case, can be applied as a source of microelements being its accompanying components (Cu, Zn, Mn, Zr, Ba, Be, B etc.),as a carrier (sorbent) of artificially added microelements either of one element or their mixture according to the purpose of microfertilizer; as ionex (ion exchange sorbent) and in the same role as regulator of successive harmless release of microelements into the soil solution. The admixture of bentonite was also taken into account for the preparation of concentrated suspension fertilizers of high N, P, K, content.

Very successful is the application of large sorption capacity of bentonites and their property to fix dissociated ions and molecules of polar substances for purification of solutions from excessive concentration of these substances.

The application of bentonite in purifying wines has its tradition, too. The effect of bentonite admixture into the medium for the reduction of salts concentration in leaking solution was experimentally proved; this effect is prospective for the purpose of water purity protection of underground waters in the zones with sources of drinkable waters. The protective effect of bentonite is applicable both to ions from mineral fertilizers (naturally with the activity adequate to the series of affinity to relevant ions) and to organic ions and polar molecules from organic fertilizers (e.g. to humous acids).

It is striking that this capacity of bentonite was so little used even if its real effectiveness is limited before all to strongly permeable (sandy or argillo-arenaceous) soils.

The above effectiveness of bentonite has of course more aspects. Bentonite can sorb in soil also the energetic substrate for microorganisms (and block it thus against degradation), which has both a positive significance (slower mineralization of organic fertilizers) and a negative one (protection against microbial degradation of pesticide residues). There were even found cases of increased infectiveness of vegetal virus after addition of bentonite which blocked evidently the inhibitors of virus disorder.

These results, mostly not exceeding the framework of research, show, however, both great possibilities in the utilization of bentonite and the necessity to verify all - including secondary - effects for rational exploitation of bentonite to the benefit of people.

The unsufficiently explored aspect of energy balance of the enrichment process of soil medium by bentonite belongs here, too, as the addition of bentonite to soil represents actually an energy input of the existing system.

Economic aspect of bentonite application in agriculture

There is a series of factors influencing economy of bentonite applications to agriculture. With regard to the main field of bentonite application in agriculture, i.e. reclaiming soils, farmer may profit from enhanced crop. Other benefits coming from environmental effects, direct savings of fertilizers, etc., should be considered. Economy of soil reclamations was being evaluated in connection with conducted field tests: increase of yields in the conditions of current operation and their financial expression, costs and lifetime of the intervention were figured. The calculation of the economic profitability was based on them. The pilot verification experiments were carried out in 36 localities, their higher yields were proved by the dosage of 10 t per hectare of bentonite as follows: root crops + 17.7%, cereal crops + 4.0%, fodder crops + 5.6%.

The costs incurred with regard to their given conditions were repaid in three years by increased yields of root crops, in 5 years by increased yields of fodder crops and in 7 - 10 years by increased yields of cereal crops.

The decisive cost item is apart from the price of sorbent (extraction cost) before all the transport, it means that economic profitability will depend on the distance of deposit from the place of application.

The price of bentonite is another criterion for practical extension of the method. The price problem still reflects the interest of producer and consumer. The producer would like to valorize the extraction and upgrading costs while the consumer requests raw sorbent either broken-down or partly broken to be suitable for transport. The fact is significant that so-called inpure bentonites of lower quality and with admixtures are advantageous for agriculture. These grades are not accepted by industry and are needed in agriculture (e.g. carbonates).

The transport is the second cost item. Road transport is more advantageous to shorter distances. A rationalization could be achieved by suitable transport optimization programmes.

The operational and technological procedure of soil reclaiming by sorbents in operation conditions was also verified by the Institute for Scientific System of Farming (Ústav pro vědeckou soustavu hospodaření) in 1973. The data on increased yields by verified dosages of bentonites in the actions of the Institute are given below to witness the conformity with own findings. The following average yield increases were achieved by the actions of the Institute in the verification period:

with dosage 10 t per hectare - by 13.1%
with dosage 20 t per hectare - by 19.3%

The highest increase was achieved on potatoes. Average costs of the application of 10 t dosage were repaid in four years. The most effective method of bentonite distribution proved to be the spreading by explosives.

Very good results are being reached in case of bentonite additions to feeding stuffs. According to current practice, 5% of fodder is saved because sorbents regulate the nutrient circulation and in addition, they positively influence the health condition of animals.

Other applications as resistance of bentonite to the aggressive waters are not without significance to agriculture. E. g. agricultural cesspools can be provided with comparatively cheap bentonite sleeves to insulate.

B) Tuffs and Tuffites

Geological occurrences of tuffs and tuffites

Tuffs and tuffites occur in areas of earlier volcanic activity. There are two main areas in Bohemia. Central Bohemian Massif is the area of tertiary volcanic activity where basic basalt effusions prevail as over land deposits.

The majority of tuffs and tuffites found in Czechoslovakia is created by pyroclastic rocks. Volcanic components consisting of clastics of rocks, basalt glass and crystals of minerals were liable to metamorphosis to minerals, carbonates, zeolites and hydrated iron oxides to different extents. Most of the above mentioned tuffs and tuffites are characterized by porosity of different degrees. Main components of the predominant majority of tuffs and tuffites from the above area are minerals of montmorillonitic group containing calcium and magnesium as sorted cations. The second component is represented by the carbonates calcite and dolomite.

Tuffitic rocks are subdivided into two groups according to the content of carbonates. The first group is represented by tuffitic rocks with low carbonate content (up to 2%) with slightly to strongly acidic reaction and with a higher content of montmorillonitic minerals. These rocks have a considerable influence on yield increase in sandy and peaty soils but they require concurrent dosage of lime. The second grou embraces tuffitic rocks of higher and high content of carbonates which are more advantageous by their universal composition and action, but it is necessary to check pH of soil and regulate accordingly the dosing of these tuffs.

Thes tuffitic rocks are also specified from the structural viewpoint. The tuffitic pyroclastic rocks containing a higher content of solid or partly decomposed basalt fragments and crystals of pyroxene and amphibole belong to the first type. Their structure is coarser and the portion of fine particles substantially lower. The second type is represented by pyroclastic rocks which except for a high content of carbonates are similar to bentonitic rocks due to their considerable content of montmorillonitic mineral group. Their structure is substantially finer and the portion of the finest particles significantly higher.

Grain fineness of tuffs is determined by grain size distribution which is significant for the assessment of soil binding capacity. The binding power depends on the quality of the finest portions with grains 0.2 to 2.0 µm. Coarser fractions with grains 0.1 to 0.05 mm are of greater significance for the determination of quantities and sorts of admixtures. The metamorphosed tuffs and tuffites contain more fine portions than kaolinitic clays. Montmorillonitic clays - bentonites and metamorphosed tuffs and tuffites have the finest fractions.

Grain fineness of clayey rocks

Sort	Percentage of grains		
	under 2.0 µm	under 0.5 µm	under 0.1 µm
Kaolin	28 - 80	10 - 35	0 - 2
Clays	75 - 90	45 - 70	5 - 15
Bentonites and bentonitic tuffs fully converted to clays	25 - 95	70 - 95	10 - 60

Mineralogic-chemical characteristics of tuffs and tuffites

The structure of tuffs and tuffites is created by pyroclastic material as sands of various graining and lapilli bombs from concussion eruptions. All components are coated with powdered ash matter.

High content of montmorillonite influences the values of sorption capacity which with tuffs and tuffites reaches the value from 35 to 80 mval/100 g. The contents and sorts of microelements differ slightly in a series of tested samples. It is typical that the most abundant elements are Cu and Sr which occur in the number of 75 analyses in hundredths to tenths of one percent. Zinc is represented in 27 analyses in tenths of one percent. Ba, V, Cr, Co, Ni are contained in all executed analyses in thousandths of one percent.

Nickel is currently present in tenths of one percent in all executed analyses. Molybden was found in a series of analyses in quantity of 0.001 %. A small number of analyses indicated the presence of Ag, B, Ga, Sn, Pb, Be, Zr in the quantity of 0.001 %.

In general, as many as 18 microelements occur. Most frequently, 10 to 11 trace elements are present. Most investigated samples contained high percentages of CaO (up to 25%) and MgO (up to 10%), K_2O content in tuffs and tuffites fluctuates from 0.20 to 3.25%, P_2O_5 content lies between 0.1 and 1.5%. The contents of these compounds would substantially enrich soil reserves with these nutrients.

FeO content of the studied samples was within 0.3 - 1.8%, Fe_2O_3 content occurs between 7.5 and 16.5%. Bivalent iron will then be present in magnetite and primary silicates. Its toxicity is removed by piling and weathering prior to the applications of tuffs and tuffites for soil reclaiming.

Beneficiation

The extraction of tuffs and tuffites for fertilization of agricultural soil is similar to the extraction of bentonite from easily extractable deposits. Tuffs and tuffites occuring in Czechoslovakia predominantly in north-bohemian areas are significant for the utilization in sandy and argillo-arenaceous soils and in peaty soil. It is purposeful to determine the locality for extraction next to the area of application.

Tuffs and tuffites are especially suitable in the recultivation of extensive dumped wastes after coal, kaolin and sand extraction. Prior to planned reclamation actions, it is necessary to explore the localities from the viewpoint of quality, extractability, thickness and capital return and especially with regard to transport and utilization.

The overburden of tuffs and tuffites consists predominantly of sands, stones and various earths, that are transported to dumps. The removal of waste and the extraction proper is carried out by bulldozers and excavators or by mobile excavators loading the material on dump trucks or tipping lorries. Tuffs and tuffites are transported onto a prepared compacted site in a suitable place next to the main road. Here the tuffs and tuffites are deposited to the height of 70 - 90 cm and exposed to weathering, especially to frost, to accelerate the break-down of bulky raw material. In the course of one year, raw material disintegrates, it is then loaded by loaders on trucks and transported to fields.

Agricultural applications

Tuffogenous rocks as tuffs and tuffites of basalt rocks that have become sufficiently clayey have the effectiveness as bentonite. Their montmorillonitic clayey component is very effective. Besides, they contain a higher percentage of carbonates, macronutrients and trace elements.

The tuffaceous structure contributes to better disintegration and consequently to an easier processing and dispersion in soil. These properties make the tuffs and tuffites very suitable as reclaiming matters even for the poorest soils.

The theory of the effects of tuffs and tuffites in sandy soil equals from the viewpoint of swelling, sorption capacity, etc. to that of bentonites. Tuffs and tuffites act in a wide range of applicability together with organic matter in the adjustment of diameter of pores or of the ratio between macro and micropores. They enable in this way the improvement of water sorption, reduction of permeability and retaining of water from precipitation or watering.

The research results of interaction of tuffs and tuffites and soil humus showed the significant application of mineral sorbent in the creation of qualitative humus in unfavourable conditions of overaired sandy soil.. The addition of tuffs and tuffites has substantially improved the accumulation of humus and bound humin acids in the medium of intensive mineralization.

Tuffs and tuffites contain microelements which are gradually released to the soil solution. Carbonaceous admixtures of $CaCO_3$, $MgCO_3$ increase the pH value of the soil solution and intensify thus the creation of complex forming cations. Tuffs and tuffites contribute in this way to the retention of microelements in the permeable sandy soil,

Experiment with tuffite after three years of action

Parameter	Variant			
	Sandy soil		Sandy soil + 3% of peat	
	Prior to reclamation	+ 100q per ha of tuffite	Prior to reclamation	+ 100q per ha of tuff
% CH_1 free humic acids	0.028	0.043	0.056	0.072
% CH_2 humates	0.015	0.023	0.028	0.042
% CH_3 bound humic acids	0.016	0.019	0.018	0.018

Application of tuffogenous rocks - tuffs and tuffites

These reclaiming matters can be advantageously applied for increasing the fertility of acidic sandy soils in areas with occurrence of tuffs sufficiently metamorphosed to clays. They increase in the function of sorbent the effectiveness of fertilization in a similar way as bentonite.

Dosing

The most advantageous dosage is 20 t per hectare which increases yields by 10 to 20% with concurrent application of 40 t of organic manure per hectare, the yield can increase even by 25%.

Procedures

The extraction is substantially identical with that of bentonite. The extracted raw material is loaded by mobile excavators on trucks with carrying capacity up to 15t and transported to the place of destination (up to 50 km) in fields. Tuff is dumped onto 14 piles per hectare and spread by the explosive Permonex or by the agricultural spreader RUR - 5. It is introduced into the soil by the basic autumn ploughing. The duration of dosage effectiveness is 7 to 10 years.

Increasing dosages of tuffs and tuffites raise substantially yields in acidic peaty soil and also in sandy soil, always in a certain dependence on dosage and degree of pH value of soil.

There is a disadvantage in the application of tuffs of low CaO and MgO contents into acidic soils. Additional liming will be necessary for raising the pH value of soil matter to eliminate the long standing action of acidic medium and potential deterioration of the main effective component of these rocks - the montmorillonite.

The advantage of tuffs and tuffites is the property of being active for a longer time interval due to gradual break-down of particles and passing of nutrients, micro-elements and trace elements to soil.

Tuffs and tuffites in the fertilization of sandy soil

Average yields of dry matter of maize from the Locality Okřešice

Experiments E - 1970

Tuff dosage q/ha	Level of mineral fertilization I Dosage of fertilizers	Percentage of yields	II Dosage of fertilizers	Percentage of yields
0	293	100	749	100
50	344	117.4	967	129.1
200	388	132.4	922	123.1
1000	398	135.8	830	110.8

The statistical test showed the best results with the dosage of 200q/ha based on the level of mineral fertilization I. The dosage of 1000 q/ha shows only a low elevation of yields which would not be economic.

Average yields of dry matter if maize grown in peaty soil

Experiments F - 1970

Sort of tuffitic rocks		Dosage 200 q/ha Average yields q/ha	Percentage of yields	Dosage 1000 q/ha Average yields q/ha	Percentage of yields
Checking without tuffites		30.27	100	30.27	100
Tuffitic rocks from various localities	2	54.66	180.6	57.71	190.7
	3	50.59	167.1	59.98	198.1
	6	32.66	107.9	52.50	173.4
	7	33.74	111.5	44.58	147.3

The yields were influenced by dosages of tuffites of different composition from various localities with different contents of carbonates and different values of sorption capacity.

C) Marl

Composition

Marly rocks represent an extensive series of raw materials that occur on all continents in different quantities and compositions. They occur in Czechoslovakia in seven main areas. The total reserves of marls in Czechoslovakia amount to 35 - 40 million cu. m. These raw materials are of considerably different structures and various physical and chemical properties.

Physical and chemical properties

Marls are from the view of parameters of the revitalization effect sorbents of which the clayey and carbonaceous component exert the decisive influence on soil reclamation.

The component of carbonates $CaCO_3$ - $Mg\ CO_3$ has a certain influence on pH value of soil matter which is decisive for the equilibrium in the soil complex.

The clayey component acts as carrier of the finest particles under 0.001 mm.

A substantial majority of microelements is bound in fractions under 0.01 mm. The other microelements as Ti, B, Ba, Cu, Mn are usually bound to coarser fractions. The predominant majority of trace elements is bound in the form of isomorphous admixtures in the structures of silicate minerals or in the sorption complex of clay component.

Typical rational chemical composition in annealed state:

SiO_2	40%
Al_2O_3	10%
CaO	40%
Fe_2O_3	4%
TiO_2, MgO Na_2O, K_2O	5%

The sorption capacity shows values within the range 5.29 - 56.38 mval/100 kg.

The content of $CaCO_3$	1.54 - 66.22% by mass
pH active	6.6 - 8.3
Fraction 0.001 mm	3.92 - 71.38% by mass

The property of clay sorbents to fix ions enables the utilization of their sorbents in the application of artificial or organic fertilizers. It prevents also the nutrients and humus from escaping into underground water. The effect of the action of a series of marls in soil has a direct impact on the economy of the accomplished fertilization process. A higher quantity of kaolinitic clays can reduce the swelling process.

Marls containing soluble carbonates ($CaCO_3$) are more resistant to the influence of soil medium, especially against acidic reaction. Marls are strongly resistant if containg more than 10% of $CaCO_3$, their resistance is lower with $CaCO_3$ content ranging from 2 to 10% and the lowest resistance is shown by marls with $CaCO_3$ content under 2%.

Acidic soils may disturb the structure of marls and wash out succesively effective components of carbonates. In such cases additional liming is recommended.

Main criteria for the aplicability of marls or for the exploitation of their deposits in areas of occurrence

Physical clay content %	Content of carbonates %	suitability
50	50	very favourable
30 - 50	30 - 50	favourable
20 - 30	25 - 30	satisfactory
15 - 20	10 - 25	low
under 15	under 10	very low

Extraction

The utilization of marls belongs to the most ancient methods of agricultural soil fertilization by mineral sorbents. Marls - marly rocks - are sedimented mixtures of clayey minerals with high portion of carbonates $CaCO_3$ - $MgCO_3$, Fe_2O_3. These compounds influence substantially the process of natural break-down and act in this way effectively on the complexes of soil matter.

The main effect of marl is the compaction of sandy soil and consequently the improvement of water holding capacity and sorption power. The quality of marls is given by the content and quality of clay component, carbonates and natural disintegration. High dosages of marls required for the achievement of effects limit their application to the nearest surroundings of deposits. Marls are applicable in natural state immediately after excavation.

The extraction of marls is carried out by the mobile rake of buldozer - mobile excavator - truck as an organized supplying activity undertaken e. g. by machine and tractor stations. The process of excavation is similar to that of bentonites, tuffs and tuffites for fertilization of soils without industrial upgrading. The natural disintegration of lump marl takes place on prepared deposits by the influence of weathering, especially by rainfall and frost.

An important parameter of suitability is the workability of marl in the application to soil which is given by its structural character and which has to be taken into account in the selection of a suitable deposit.

Application in agriculture

The application of marls can be considered for very permeable soils with acidic soil reaction as marls contain a considerable percentage of Ca - Mg component. The effective application of marls will be favourable for sandy soils (terrace sands - average grain size above 0.45 mm) by strengthening the sorption complex with concurrent application of fundamental nutrients to soil. The properties of soils can be applied in the area of Labe Basin (Central Bohemia). The average planned quantity of the opening dosage is 300 m^3/ha.

The dosages per hectare may be precised after found results of ameliorations under process including a proper evaluation. The planned service life of this measure is 15 years.

The maximum transport distance from the deposit is 5 km. Transport costs participate by 53% in total costs. The expected return of invested sources will be 6 to 10 years.

The dosing should be based on the supposition that the more coarse-grained and deeper is sandy soil, the higher should be the dosage and on the contrary.

The process of marl spreading

Marl is delivered to fields in autumn or summer and deposited in 14 - 17 heaps per hectare to be spread by explosives. Another method consists in depositing delivered marl into parallel rows which are then dispersed by bulldozer provided with a rack. If the disintegration of soil is sufficient, i.e. if particular pieces do not exceed 10 cm, the marl need not be exposed to further weathering and is applied to soil by autumn ploughing. The disintegration in the soil continues.

The following necessary measures are intensive fertilization with both artificial and organic fertilizers and growing of plants that are not sensitive to liming. It is recommended not to grow potatoes in the first two years after marl application.

D) Zeolite

Geology

Zeolites were defined as a separate group of minerals by Cronstedt in 1956, after the discovery of stilbite. The name is derived from the Greek word for "to boil" (zein) as the zeolites appear to boil when heated. The effect is a consequence of the loss of considerable amount of water.

Zeolite crystals were known to form in the druse cavities in volcanic rocks. The largest deposits, however, have developed by alteration of tuff glass by the action of underground water of atmospheric origin (deposits formed in an open system - type 1) or by the action of connate waters of salt lakes in which volcanic ash was laid down (deposits formed in a closed system - type 2). Zeolites of other genetic types are due (type 3) to hydrothermal activity associated with ore deposits, such as the Tintic deposit (Utah, U.S.A.) or by the effect of recent thermal water without ore accompaniment, for example, in Yelowstone Park (U.S.A.), Wairakei (New Zealand) and Ouikobe (Japan); deposits of this type show a downward zoning with mordenite, laumontite and wairakite zones. Type 4: the following zeolite associations occur (arranged according to increasing depth and decreasing hydration): clinoptilolite - heulandite - analcime; laumontite + albite - (wairakite) - prehnite - pumpellyite - albite (mineral assemblage of the greenshist metamorphic facies follow downwards) in deposits developed in the initial metamorphic stage with deep burial of sediments (4 - 10 km). Zeolites of weathering origin form in salty soils (analcime, chabasite, maholite, phillipsite - type 5). Deep-sea deposits contain, for instance, phillipsite in red clay in the Pacific (type 6).

The first two types of stratiform zeolite deposits are economically most important. The deposits of the first type, formed by hydrolysis of siliceous glasses in thick tuff layers, usually show a well defined vertical zoning (in a downwards direction), glass with chesters of chabasite (clinoptilolite, mordenite, analcime (Nevada Test Site, U.S.A. - thickness 2 000 m).

The deposits of the second type developed from tuffs during diagenesis in salt lakes containing CO_3^{2-} and HCO_3^- ions at pH above 9. Under these conditions, the glass decomposes abruptly, giving rise to zeolites. The pleistocene sediments of Tecopa Lake in California display the following horizontal zoning within one layer, near the shore and mouths of streams - tuffs or clay; in the medium alcaline environment - zeolites (phillipsite, clinoptilolite, erionite); in the center of the lake - potassium, feldspar).

Mineralogical and chemical composition

Crystals of clinoptilolite having dimensions about 15 μm are observable only by reading electronic microscope. Clinoptilolite is that of Ca-K type which necessitates capacity of ion exchange ranging from 86 to 137 mca/100 g of the rock.

Mineralogical composition of zeolite rock

Clinoptilolite	37 - 80%
Amorphous diversified phase	22 - 37%
Feldspars (andesin, labradorite)	7 - 11%
Alpha quartz	2 - 3%
Chlorized biotite	about 1%

Chemical composition of zeolite rock

SiO_2	71 - 72.5 %
TiO_2	0.18 - 0.23 %
Al_2O_3	12.2 - 13.6 %
Fe_2O_3 + FeO	1.1 - 1.7 %
MgO	0.6 - 0.8 %
CaO	2.2 - 2.9 %
Na_2O	0.6 - 1.2 %
K_2O	1.9 - 2.8 %
P_2O_5	0.02 - 0.05 %
SO_3	traces - 0.02 %
H_2O^-	6.3 - 7.5 %
H_2O^- (105°C)	4.5 - 6.0 %

Adsorption of liquids

This type of zeolite adsorbs under standard conditions at 50 % relative humidity about 10 g H_2O/100 g and sometimes up to 16 g H_2O/100 g. E. g. a zeolite from Bulgaria adsorbed 12 g H_2O/100 g and silicagel 14 - 15 g/100 g.

Adsorption of gases

In case of SO_2, NH_3 and CO_2, zeolites adsorb 6 g/100 g under standard conditions. Other standards range from 5 - 15 g/100 g according to the way of application. Zeolite Nižní Hrabovec showed the following values:

- heptane	0°C	1526 Pa - 2.83 g/100 g
- ethanol	0°C	1626 Pa - 6.20 g/100 g
- benzene	0°C	3533 Pa - 6.11 g/100 g

Almost spherical structures compounded of tetrahedrons of SiO_4^{4-} and AlO_4^{5-} (predominantly SiO_4^{4-}) and mutually linked by means of Si - O - Si bond create the crystal lattice. That is a consequence of the presence of comparatively large holes linked by capillars in the lattice which contain monovalent and bivalent cations of alkaline and alkalinized rocks surrounded by water molecules. Molecules of water are bound by Wan der Waal's powers and, therefore, they can be almost driven out by heating up to 350°C. By the mentioned procedure, deterioration of alumosilicate structure does not set in and zeolite is able to absorb water again and get original hydrated state. This phenomenon is characteristic at given temperature for reversible zeolite.

Beneficiation

Methods of upgrading depend on the consistence of rock, humidity of rock and purpose of final application. Predominantly zeolites are won in open-cast mines and quarries. Overburden is usually created by zeolite tuffs and tuffites containing less clinoptilolite, max. 30 - 40%. Excavated rock is conveyed to the sheltered stockpiles for weathering and open-air drying. (In dry and warm regions, the drying of zeolites is sometimes not necessary). Homogenized rock is then crushed (jaw crushers and hammer mills are most frequently used machines) and disintegrated to be efficiently dried in, mainly, rotary driers. Dried ground zeolite is then fed into the fine mill and sorted according to the application.

E. g. demanded grain compositions are as follows:

- waste water purification	- 10 - - 50 mesh
- agriculture	- 10 - - 50
- fillers for tank cleaning in fisheries	- 4 - 1 20
- supplements to feeding stuffs	- 325
- petrochemistry (pellets are shaped)	- 325

Agricultural application of zeolites

An immense series of (40) of zeolitic minerals which occur all over the world is applicable to agriculture. The most important minerals from the point of view of agricultural application is clinoptilolite, others are: analcime, chabasite, erionite, mordenite and phillipsite. Clinoptilolite occurs abundantly and is of very important properties both physical and chemical ones.

It has considerable capacity of ion exchange, capacity of hydration and dehydration, sorption and it also has dietary effects to feeding stuffs.

Examples of application in vegetal production

Zeolite tuffs and tuffites cause neutralization of acid soils and regulate delivering amoniak and other cations from fertilizers. First attempts with clinoptilolite in paddy cultivation were conducted already in 1943. Rice seedlings are cultivated in a blend of soil, clinoptilolite and fertilizer for a certain time. Then they are planted in fields. 5 % higher crop was a result of attempts with zeolite containing 60 - 90 % of clinoptilolite. In case of wheat, zeolite containing 80% of clinoptilolite causes enhancing output by 10 - 15 %.

Very successful resuls were reached with cultivation of potatoes and tomatoes in Sachalin. Two-year tests of zeolite with 50 - 80% of clinoptilolite demonstrated increased output of potatoes by 30 % (400 kg/ha added to standard dosage of fertilizer). When dosage of fertilizer was lowered to 50% and the dosage of zeolite remained the same (400 kg/ha), the output of potatoes was 120%. As well, green-house output of tomatoes was higher by 20 % when 58 g of zeolite per sq.m. were applied.

The results reached in cultivating tomatoes in the U.S.S.R. prove that zeolites considerably influence yield potential if they are used in optimal dosage with fertilizers according to the specific conditions. When tomatoes had been planted in zeolite only, yield was 33 pieces of tomatoes per 1 bush. When blend 1 : 1 zeolite and black soil had been applied, yield was 23 pieces per 1 bush while bushes planted in black soil only bore 18 pieces only. Dosage of 5 tons of zeolite per hectare resulted into 190 kg per hectare higher output of wheat, 20 t/ha showed 270 kg higher output. The optimal dosage was 10 t/ha resulting in 440 kg higher output.

Examples of application in animal husbandry

Attempts conducted in Japan in 1976 in breeding piglets showed that 5 % share of zeolite in feeding stuffs made piglets gain 15% weight compared with the controlled group. Animals having digestive disorder recovered during some days by 15% zeolite admixtures. Zeolite admixtures influenced positively offspring of pigs when dosed before litter. 25 days taking feeding by 600 g clinoptilolite a day before litter made piglets have higher weight in comparison with those of the controlled group. They did not suffer from diarrhoea while animals of the compared group did. The application of zeolite to animal husbandry is deeply explored in the U.S.A.

Clinoptilolite for feeding stuffs of turkey-hens and chickens

Four different samples of clinoptilolite and one of mordenite as additive of fodder. Mineralogical composition varied from 40 to 90% of clinoptilolite and capacity of ion exchange from 0.25 to 0.9 meq/g. The tested animals gained 1-- 3% of weight as a result of the clinoptilolite Sheawille application.

Clinoptilolite for the production of non-odorous fertilizer from chicken excrements

These excrements of chickens are utilized as fertilizer either treated or untreated. The beneficiation procedures are accompanied by offensive odor and a certain contamination of water and atmosphere, too. Technology of the production of valuable fertilizer from chicken excrements was developed. The procedure is based on admixtures of zeolite - clinoptilolite to the fertilizer. This admixture is advantageous for clinoptilolite, has the high capacity of ion exchange in case of NH_4^+ which results in a high content of nitrogen, potassium and phosphorus in the final product - N = 4.3%, P = 4.2% and K_2O = 1.5%. Two-year stock did not cause deteriorating. Atomizing of powder clinoptilolite in ratio 1,500 - 2,500 kg per 1 sq.m. of the floor of a hen-house absorbed the odor of chicken excrements; the laying of eggs was higher up to 2 - 3%.

Zeolite for feeding poultry

Addition of the Sheawille clinoptilolite (Oregon, U.S.A.) to chicken fodder was evaluated in a test conducted in two farms. The addition was 15 kg of clinoptilolite per 1 ton of fodder which reduced the presence of other nutrients by 2%. 6,000 cockerls and 14,000 hens fed on without clinoptilolite and 6,400 cockerls and 25,000 hens were tested (animals were 3 weeks old and the test took 4 weeks). The group fed on the zeolite diet showed 1.5 to 1.7% weight gains. Only cockerls indicated improved efficiency of feeding - 0.03 kg of fodder per 1 kg of weight was consumed less. No differences were found as far as the mortality is concerned.

Economic aspects of zeolite applications

Economy of zeolite applications was not a matter of question in case of the above-mentioned tests. Only one side of all the versatility of locally acting factors was comparatively found in greater detail. It is the question of enhanced revenues for farmers by the increased outputs of the vegetal production and husbandry as well. Other promising aspects can be found in the lowering of farm inputs, such as fertilizers and feeding stuff. As well, positively influencing the health of livestock has economic aspects. In addition to it, industrially won and beneficiated zeolites are raw materials applicable to various industries and other activities so that their production is sure to be a profitable venture if a market exists. Consequently, occurrence of zeolite deposits in a given country has broader consequences than only that of agricultural application since the future of the applications (e.g. for environmental protection) of zeolites is promising.

Some results with direct economic aspects are brought forward:

- Zeolite containing 60% of clinoptilolite in 4 ton dosage per hectare resulted into 30% enhanced output of potatoes.
- Zeolite containing 60% of clinoptilolite, 10 ton per hectare, enhanced output of paprica and tomatoes by 16% at concurrent lowered dosage of fertilizer.
- Zeolite containing 50% of clinoptilolite applied to soil planted with tomatoes (dosage 16 tons per hectare) resulted into 33% higher output.
- 16 tons per hectare of zeolite with 80% of clinoptilolite influenced the output of paddy - 40% more.
- Zeolites in animal breeding showed the following demonstrated results:

Sorbent	Dosage %	Feeding stuff	Animal	Difference
zeolite (80% clinopt.)	10	90% of maize-pulses	pigs	-0.17 kg/day/animal
zeolite (60% clinopt.)	5	95% of current fodder	pigs	-0.10 kg/day/animal
zeolite (80% clinopt.)	2	98% of current fodder	cockerls + hens	-1.5-1.7% of weight
zeolite (98% clinopt.)	9	91% of current fodder	chicken	- 1 - 3% of weight

E) Perlite

Geology

The industrial value and lithological character of perlite was not recognized until the middle of this century. Publications of the 19th century and that published in the first decades of the 20th century mentioned only "glassy rhyolite" or "perlitic rhyolite".

From the industrial point of view, perlite can be described as "any vitric volcanic product with sufficient water content (usually over 2%) to make it expand to a utilizable light-weight material when heated under controlled condition".

The geological determination of perlite is bound to more rigid conditions. For instant, not each expandable volcanic tuff (pumicile) or lava rocks can be regarded as perlite. For the sake of uniformity, it is expedient to use this rock name in the sence of geological determination.

Geologically, the rock consisting essentially of volcanic glass can be described as perlite when it

- takes its origin from a lava of strictly determined chemical composition and water content,
- consolidates under determined physical conditions,
- has the 10 up to 20 fold expanding capacity of original volume in the course of heating.

A set of theories concerning the formation of perlite was composed. The notorious facts or better said, conditions of perlite formation are as follows:

The occurrences of perlite are always confined to areas of volcanism, which yields rhyolite as rocks of rhyolitic-dacitic character. The sudden cooling of lava which prevents from the crystallization of the molten liquid is a prerequisite for perlite genesis. During this process (i.e. the "freezing" of lava) sufficient pressure needs to prevent water from escaping from the stiffening liquid.

The characteristics of the volcanic activity or more precisely said, those of the process of eruption period which make room for the formation of perlite deposits may be described as follows:

During a relatively long period of still stand, the gases of the liquid lava attain a considerable grade of enrichment in the upper part of the volcanic channel. In the initial phase of eruption, the pressure of gases breaks up the mass of earlier volcanites. With the sudden fall of pressure the lava column "bubble over" and enormous masses of pumice are ejected,mixed with rock fragments, originating from sheets of former lava flows or pyroclastics. (The volcanic channel acts as a natural kiln for perlite expansion). By this way, the first phase of eruption is of highly explosive character and produces thick complexes of pumiceous tuffs and pumice.

In deeper horizons of the lava column, the liquid contains smaller amount of gases (and water) while the pressure is higher. During the rapid ascension of this lava, the volatile (mainly water) content has not possibility to escape from the liquid. It may intrude - extruding from the volcanic channel - into the tuffs and pumice series produced by the initial stage of eruption or it may cover the surface of lava-flow.

In the case of extrusion, the cooling and consolidation of lava takes place under pressure. By this way, liquids of high temperatures (1,000 - 1,250°C) are turned into vitritic masses. This is the mechanism - in rough outlines - of the formation of the extrusive type of perlite deposits.

Supposing the weight of a 5-metre thick column of molten rock being equivalent to the pressure of 1 atmosphere, the cover which yields a sufficient pressure for perlite formation must be as the following review shows:

Temperature (°C)	Depths of formation for the phases (metre)		
	pumice	pumice+glasses	glass
900	on the surface	between 0 - 5	under 5
950	above 10 m	from 10 - 48	under 48
1000	above 33 m	from 33 - 64	under 64
1050	above 51	from 51 - 70	under 70
1100	above 60	from 60 - 75	under 75
1150	above 65	from 65 - 80	under 80

The extrusion takes place mainly on the slopes of volcanic cones in the immediate environment of the main volcanic channel. The perlite bodies formed by this way are of limited extrusion, up to several hundred meters in their horizontal dimensions and with an average thickness being 10 - 50 metres. The reserves, however, are adequate to mining on larger scale.

In the cross section of this deposit type the perlite facies of minor parts, the transitional rock types and the "enveloping" breecia (or agglomerates) are always distinguishable.

Lava flows with lesser reserves of heat (temperature of the liquid about 800 - 950°C) may be consolidated into perlite under atmospheric pressure as well. This is the case of the formation of the "lava-bank type" perlite deposits.

The perlitized lava-flows build up thick complexes-- sometimes up to the thickness of 350 metres. In the complexes banks or layers of compact vitritic perlite are alternating with those of pumice bound perlite, lithophysic perlite or even banks or layers of rhyolite representing the changes of water content, temperature and pressure conditions caused by subsequent lava flows in course of the eruption.

Perlite lava agglomerates or lava breccias occur in these sequences always in large masses for the earlier lava flow breaks its way through the older ones. Both clastics and cement of the agglomerates are of perlite, the latter being often pumiceous. In this deposit type, the transitional developing of perlite into rhyolite can be observed, too.

According to the changes of chemical composition and physical state of lava during the series of eruptions, a transitional development may take place between the above-mentioned deposit types.

In the final stage of the volcanic activity, the remaining lavas have only insignificant remains of their original water content. The last products of the eruption cycle are obsidian and rhyolite or some other acidic rocks of the rhyolite - dacite group. Andesites originate from the rest of the magma as well.

Mineralogical and chemical composition

The average amount of silicium dioxide (SiO_2) in the typical perlite is in the interval of 70 - 75 weight % while that of the alumina is generally between 12 - 16 weight %. The sodium and potassium content of perlite is of great importance the viscosity of lava being in proportional relation to the amount of alkalines. The volatiles consisting mainly of water are prevented from escaping by the viscosity of the cooling lava. The same viscosity yields the possibility of the expansion of the rock without disintegration into microscopic drops. The amount total of sodium and potassium (in oxides) is about 6 - 9 weight %.

Other components of the perlite rock, iron, manganese, titan, phosporus and sulphur are present in impalpable quantities and from the point of view of the industrial utilization are neglegible - somewhat higher amount of iron oxides, however, causes undesirable colouring of the products and that of sulphur oxide has detrimental side-effects to kilns.

The most important component of perlite is the water bound to rock texture or "solved" in the volcanic glass. Its behaviour is a determining factor as far as the industrial utilization is concerned.

The water of the perlite rock is present in two forms. The molecules of "textural water" (or water of construction) are set among the silicate tetrahedrons preventing thus the composition of crystal structures, i. e. this form of water content stabilizes the volcanic glass.

The other kind of water content can be mentioned as "molecular water"(or zeolitic, free water) which is concentrated in the submicroscopical or microscopical fissures of the rock texture. It is easy to expel this part of water content from the rock.

There are continuous interferences between the two forms of water, the molecules of the latter enter the volcanic glass. This process results in a slow process of recrystallization.

The above-mentioned composition is characteristic to acidic magmatic rocks (i.e. those consisting mainly of silicium dioxide). Consequently, the perlite belongs to the group of rhyolitic-dacitic rocks or, in broader sense of the term, to the so called "pacific" or "calc-alkaline" province of magmatic rocks. It represents specific rock types which come into being only under strictly determined circumstances. The striking uniformity of mineralogical and chemical composition of perlite deposits throughout the world is a reliable proof of this claim.

The mineralogical character of the perlite rocks can be shortly determined as "volcanic glass with some amount (up to 8 - 10 volume %) of crystallized minerals and other particles (e. g. obsidian fragments and needles)". The characteristical figure for amount of glass is between 90 - 97% of volume, that for the minerals (crystallized fraction) is between 3 - 10% of volume. The bulk of mineral (crystallized) fraction of perlite is composed of feldspars (plagioclase) and also biotite occurs frequently. Other minerals as quartz, apatite and magnetite are extremely rare.

Most of perlites are of grey colour with intensity varying between whitish, silver-grey and dark-grey or black. Bluish or greenish shades of colour are frequent sometimes and russet coloured types occur, too.

SiO_2	12%	MgO	0.2%
TiO_2	traces	CaO	0.68%
Al_2O_3	13%	Na_2O	2.91 - 5%
Fe_2O_3	0.8 - 3%	K_2O	5.02 - 6%
FeO	1.38	H_2O^+	3.18%
MnO	0.02%	H_2O^-	0.36%

Beneficiation

The properties of expanded perlite to adsorb water and nutrients, its stability and resistance against weather and aggressive compounds and the ability to air heavy soils are utilized in agriculture.

The production of expanded perlite (sometimes called Agroperlite) is comparatively intricate procedure and its technology varies according to the required final products and the composition of delivered perlites as raw materials.

Perlites are won from open-cast mines or quarries. Mining methods are notorious and depend on specific circumstances of the mined deposit. In general, the rock is of very hard consistence and mining by means of explosives is frequent. The removed rock is loaded and conveyed to the grading plant.

The first stage of processing perlite can be situated in a separated plant as near as possible to the quarry. Then, perlite is crushed in the jaw-crushers and ground in the hammer mills (other devices can be applied according to properties of the rock). The ground perlite is sorted according to the required granularity of the final products. The finest fractions which are not adequate to further processing are being utilized for other purposes. Granularity of the expanded perlite corresponds to that of the ground perlite. The main phase of further processing is abrubtly heating the perlite to expand. Considerable content of the molecular water and water bound chemically which is abruptly expelled when perlite is heated up to 1000 - 1200°C. The liberating of water makes perlite expand and increase the volume of its particles in pyroplastic state 5 - 20 times. Particles which are spherical and of different size and thickness of wall have a considerable strength and stability after annealing. Bulk density of perlite drops from about 1 kg/litre to 0.08 - 0.15 kg/litre. 7 - 12 cubic metres of the expanded perlite are produced from 1 cubic metre of the ground rock. The process of the production of expanded perlite from crushing - grinding - drying - expanding down to final sorting is drawn in Figure 2.

Application in agriculture

Cultivated plants develop only in soils able to provide them with water, air and nutritive matters simultaneously. About agricultural application of perlite, the first world literature information was uttered in publications of the Perlite Institute (U.S.A.) The experiences with perlite for the Texas floricultures were discussed and proposal was concluded to apply it to ornamental plants and tobacco seedlings. Perlite preparations were applied purely instead of soil, together with high dosage of nutrients.

Since the beginning of the sixties perlite has also been applied in Europe for horticultural purposes - observations were made with strawberry, vegetables and floricultural plants.

Perlite is most suitable for vegetative propagation, for plants cultivated from cuttings, for cultivation and root taking of wine cuttings. It is also used for transport of young seedlings. Experiments were conducted to apply perlite to arable soil for monocotyledonous, dicotolyledonous and hybrid sorts of plants, also for pot plants, for root-taking purposes in nurseries and cultivation of vegetables. The results of laboratory and pilot tests have proved among others for tobacco, that if perlite is applied 15 - 20 cm into the soil layer of the tobacco seedling beds (cultivation area of 25 sq.m. and

140 - 200 litres of perlite) the sprouting occurs 4 - 5 days earlier, there are less weeds, root-taking is more active, uprooting plants is not detrimental and after bedding out larger amount of seedlings develops - 20 - 28% compared to those cultivated in soil without perlite application.

Field tests have shown that the complex effect of the perlite application is best utilized if perlite is applied during the autumn soil fitting. The depth of the ploughed layer is bigger at this time and the soil utilizes winter rains best. Perlite used in any cultivation branch yields better results when its grain sizes are larger (2 - 3 mm diameter) This perlite type should be used for cultivating ornamental plants (e.g. carnation, geranium, chrysantheurim), horticulture (parks and terrain correction) etc.

An indirect agricultural application of perlite was experienced in the U.S.A. Agriculture needs water and a considerable part of it comes from standing waters. On account of evaporation water losses increase significantly all over the world, therefore, numerous solutions were developed to stop it. In the U.S.A, long chain aerylic monomolecular film-like layers were applied, however, they were easily blown away by the wind and perlite was applied to substitute them.

Perlite was first hydropnobized by silicon-perlite grain size 0.1 - 1.2 mm, bulk density 100 kg/m.cub. The perlite can be dumped from sacks directly on the water surface in one spot and the slightest breeze suffices to spread it to cover the whole surface. To substitute the lost perlite (blown away etc.), about 0.2 - 0.25 litre (cub. m.)/week is wanted. If the perlite is highly hydrophobic, the value of perlite consumption can be reduced down to 0.07 litre (cub. m.) /week.

Economic aspects of perlite application in agriculture

Expanded perlite proved to be useful for reclaiming argillo-arenaceous soils because of its light-weight and stability accompanied by weather and aggressive coumpounds resistance. It makes soil airy, keeps nutrients and water. The main field of its utilization in agriculture is that of horticulture, vegetal propagation, planting of ornamental plants, etc. Perlite demonstrated its usefulness to irrigation for it prevents evaporation of water from delivering ponds, etc.

For national economy of a country producing the expanded perlite other aspects of its application are of importance. Perlite is being applied in construction of building for its light-weight and insulating capacity, in the production of refractories, in the production of glass, etc.

It can be said that extraction of perlite and production of expanded perlite is promising venture from the point of view of both national economy and agriculture.

F) Diatomaceous Earth and Diatomite

The diatom sediments are distinguished according to the degree of consolidation:

a/ non-consolidated sediments
b/ consolidated sediments

a/ Diatomaceous earth or kieselgur is an earth which is grey to green or brown and messy in wet state, however, after drying, it becomes light coloured and disintegrates so that it can be rubbed by fingers to powder. The quality of diatoms in the rock fluctuates so that compositions range from the pure diatomaceous earth to those with certain content of clayey admixture up to the diatomaceous clay.
Pure diatomaceous earth is rare, it occurs only in small lenses or thin layers.

b/ The diatomite proper differs from the diatomaceous earth by a higher degree of consolidation. It is designated in literature as polished slates. Another type of consolidated diatomite is the sucking slate which was formed by fine diatom shells being cemented with an opal substance.

It is foliated, porous, sucking greedily water and other liquids.

All technically important properties of diatomites depend on their composition, i. e. on the quality and sort of diatom shells and their purity. Diatomites exhibit their light-weight and porosity, they possess a high sucking and filtering capacity, they are resistant to the attack of acids, to high temperatures, some of them are even refractory. These properties make them a much-sought-for raw material and their application in technical practice is versificated.

Beneficiation methods

The selection of beneficiation methods depends on the sort of diatomaceous earth, its mineralogical composition and physical properties (structure, hardness, etc.) These properties are decisive for both the selection of beneficiation technology and the choice of technological equipment. The upgrading technology depends naturally on the required properties of final product, too. It may be concluded that each diatomaceous earth needs a special beneficiation method for particular kinds of products even if some operations be very similar or coincident. The drying process may be given as example. Some types of excavated diatomaceous earth should be temperately separated and then dried in a rotary drier or a belt drier if need be. Other types of diatomaceous earth require blunging and spray drying. Similar situation may be observed also in the other phases of beneficiation.

Chemical composition and basic physical properties of diatomaceous earth are demonstrated as follows:

SiO_2	45 - 80%	Loss on ignition	0.3%
Al_2O_3	12 - 15%	$K_2O + Ha_2O$	rest
Fe_2O_3	1.5%	Bulk density	$0.3 - 0.5\ g/cm^{-3}$

Application of diatomaceous earth

There are many denominations for the designation of diatom sediments. Unconsolidated rock composed of siliceous shells or envelopes of diatoms is most frequently denominated diatomaceous earth. The consolidated equivalent rock is called diatomite.

In a wider sense of the term, diatomite is a organogenous sediment composed of microscopic shells of unicellular series of diatoms containing higher or lower quantity of another inorganic or organic admixture. Apart from the shells of diatoms, also siliceous spicules of sponges are presented in diatomites of sea origin,also shells of faraminifers and radilaria.

Diatomite is a sedimentary raw material formed from the siliceous shells of diatoms which were microscopic plant organisms living in fresh or salt waters. Because of the cellular nature of diatomite (about 80% porosity) and its resistance to the temperature up to 800°C, diatomite is used as a heat, smell and sound absorbing material, It is used either as powder for loose filling, as calcined and agglomerated material for fluxes, as shaped and fired bricks or as aggregate for light-weight products. Its significant application is that of carriers of chemical and biological matters, too.

V. ECONOMIC ASPECTS OF SORBENT APPLICATION

To judge the economy of sorbent application and to express it financially, all the influencing factors (especially those that act locally must not be avoided) are to be taken into account. In general, the economy must be questioned from minimally three points of view; the first one is that of a contingent producer of sorbents, the second one is that of the national economy and the third viewpoint is the economy of an applying farm.

Production of sorbents

Starting extraction and production of non-metallic raw materials in industrial large scale is a question of large capital expenditures with postponed repayment since preinvestment phases are very long - geological prospection, infrastructure, etc. In addition, if the only demand comes from industries or foreign market, transports are usually long and expensive. It is a frequent case that mining and producing is not feasible due to long distances and expensive transports. Consequently, applications of non-metallic minerals in agriculture can make possible to start mining and production of non-metallics in smaller scale for local market and to invest accrued capital in gradual enlargement of the production. Thus, great capital risks related to the production for far markets could be avoided or lessened. And vice versa, the application of non-meallic sorbents in agriculture can help to enlarge the existing production.

A concise review of current application of some non-metallic rocks and minerals is listed to pour light on the whole developing tree of connected application processes.

Zeolite

is raw material for the production of pozzolanic cements, concrete and light-weight aggregates in civil engineering. It is used for filling paper and as catalyst in chemical industries. Further, it is unavoidable for delivering oxygen from atmosphere, for gas adsorptions, etc.
In agriculture, it can be utilized for reclaiming argillo-arenaceous soils and mainly in animal husbandry for proparation of feeding stuffs.

Bentonite

is material utilized in oil refineries as drill-mud for drilling, bonding agent for foundry sands. It also is utilized for filtering vegetable oils and sewage waters. And wide field of applications is in agriculture; natural bentonite for reclaiming sandy soils and beneficiated one as fodder additive.

Diatomite

is source of pure silica and raw material with wide application in many industries as fillers, as filtrating material, as insulating building material. It is utilized for the production of light-weight fireclays, adsorbents and carriers of other matters. In agriculture, it is utilized as carrier of chemical and biological matters.

Perlite

is utilized in filtration processes, for the production of insulating materials in civil engineering and ceramics as light-weight refractory. It is significant in agricultural applications for transport of seedlings, horticulture, terrain corrections and propagation of plants. Its capacity of preventing water evaporation begins to be utilized for irrigation system.

National economy

Many aspects influence the national economy of a country applying non-metallic sorbents in agriculture. Direct impact is in enhancing agricultural production, lowering costs, etc. An effect of significance is the influence of sorbent applications on the environment and water economy (especially in arid regions). Sorbents prevent leaking different matters as poisons and fertilizers from soil. That they lower consumption and wash-out of industrial fertilizers, it has direct impact to the health of the nation as many matters penetrated from soil to plants, milk and meat are suspected of causing enhanced occurrence of cancer diseases. Widened application of non-metallic sorbents helps with developing other sectors of the national economy - extraction and upgrading - and also with creating jobs. By enhanced production of victuals and fodders, foreign trade balance is sure to be positively influenced. And simultaneously, sorbents help setting environmental questions.

Entepreneurial Economy

Effect of application of sorbents in a farm is touched by many factors which differ according to a given locality. Prices of transport, agricultural products, fertilizers and price of soil and contingent provisions of environmental acts, etc. act together. Thus, economy of any sorbent in a farm is an individual case and it must be calculated separately.

All the economic data regarding the known agricultural applications throughout the world are not available or sufficient to a complex evaluation. One case can be shown:

Attempts with zeolite application to the planting of potatoes in extreme conditions of East Siberia. Dosage of 4 tons of zeolite per hectare at standard dosage of fertilizers resulted into enhanced output of potatoes by 30%. The ratio between the additionally invested money and enhanced revenues was 1 : 5. The important role the prices of products and fertilizers play can be observed on the results of the controlling test. The same dosage of zeolite was applied but the dosage of fertilizers was 50% only. The output of potatoes was higher by 15% in comparison with the state without zeolite application but the ratio between invested additional costs and enhanced revenues from crop was 1 : 7.

It has been experienced that the pay-back period of the investment in sorbent reclamation is 5 years in the worst case and frequently 2 - 3 years.

A concise review of results of different sorbent applications in agriculture is listed. If local variables such as the prices of sorbent, soil, fertilizer, fodder and output are inserted, a picture of the economy of sorbent applications can be attained.

a) Sorbents for plant growing

Applied sorbent	Type of soil /% grain < 0.01 mm/ % humus/	Dosage /t.ha^{-1}/	Tested plant	Increase of output /%/
bentonite	9.2/1.3	20	potatoes	18.6
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
zeolite 50	N.A.	16	capsicum+ tomatoes	33
zeolite 80	N.A.	16	paddy	40
tuff	N.A.	20	maize	32.4
tuffites[3]	turf	20	maize	from7.9-80,6

b) Sorbents for animal breeding

Applied sorbent	Substitution of corn in fodder /%/	Tested animal	Increase of weight per day
bentonite	3	bulls	0.1 kg
zeolite 80	10	pigs	0.17 kg
zeolite 60	5	pigs	0.1 kg
zeolite 80	2	cocks+hens	1.5 - 1.7 %
zeolite 90	9	poultry	1 - 3 %

Note: [1] Zeolite index marks the percentage of clinoptilolite

[2] Not available.

[3] Tuffites of different carbonate content and different sorption capacity.

VI. FINAL NOTE

About one third of the world population suffers from hunger. The extension of agricultural production is, therefore, one of the most relevant tasks to be solved by the whole mankind. The problem is most urgent in developing and least developed countries where the population growth rates are very high. Limited area and limited rehabilitation capacity of high-yielding soil are the most relevant factors of the extension of agricultural production.

The application of non-metallic sorbents (bentonites, zeolites, perlites, tuffs and tuffites, marls, etc.) represents a large possibility of the development of agricultural production, both plant growing and animal husbandry. The non-metallic minerals and rocks are applied as fertilizers, sorbents and carriers of chemical and biological matters. The most important role is that of sorbents. The application of non-metallic sorbents increases the soil yields by 10 to 40%, depending on local conditions (kind of plant, quality of the soil, climate). Moreover, they have some ohter favourable influences, such as reduced penetration of chemicals to the subsoil waters, etc. In animal husbandry, the addition of sorbents to feeding stuffs improves the utilization of nutrients in digestive tract of animals which is reflected in higher weight additions. Sorbents have also dietetic effect. They reduce the occurrence of diarrhoea and some other diseases.

Non-metallic minerals and rocks proved to be useful in the intensification of agricultural production which can be documented by a number of evaluated tests, performed in Czechoslovakia as well as in some other countries. However, their application must be verified for local conditions of a definite region and country.

An aspect of sorbent application in agriculture is of significance. This aspect is the carcinogenic effect of nitrosamines which are reduced from nitrates contained in vegetal products as a results of the contemporary efforts to reach high agricultural outputs by means of opulent fertilizing. The direct correlation between the content of nitrates and the enhanced danger of carcinoma occurrence has been proved above all doubt. In view of this fact, any intervention leading to a reduction of the consumption of fertilizers, and reclamations by non-metallic sorbents are promising, is significant to the health of people.

The UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Minerals Based Industries is ready to assist the developing and least developed countries in consultations, training programmes and evaluation of selected non-metallic minerals and rocks in order to promote not only the industrial exploitation of local non-metallic natural resources but also the intensification of the agricultural production and to contribute to solving environmental problems.

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ANNEXES

Table 1 Relation among output, fertilizers and content of dry matter and nitrates

Plant		Potatoe I							
		1	2	3	4	5	6	7	8
Output	q/ha	243.81	268.96	343.14	364.80	347.74	343.33	357.05	363.58
	index	1.00	1.10	1.41	1.50	1.43	1.41	1.46	1.49
Dry matter	%	22.03	21.43	20.79	19.64	20.34	20.40	20.27	19.71
	index	1.00	0.973	0.944	0.892	0.923	0.926	0.920	0.895
Nitrates	mg NO_3^-/100 g of potatoes	12.27	13.32	13.45	12.87	19.68	17.44	21.17	21.33
	mg NO_3^-/100 g of dry matter	55.70	62.16	64.69	116.45	96.76	85.45	104.44	108.22
	index	1.00	1.12	1.16	2.09	1.74	1.53	1.88	1.94
	kg NO_3^- in output	2.99	3.58	4.62	8.34	6.84	5.99	7.56	7.76
	index	1.00	1.20	1.55	2.79	2.29	2.00	2.53	2.60
Plant		**Potatoe II**							
Output	q/ha	310.46	354.46	376.96	370.73	393.53	393.41	383.95	360.45
	index	1.00	1.14	1.21	1.19	1.27	1.27	1.24	1.16
Dry matter	%	18.34	19.93	17.46	17.38	17.23	16.82	18.08	17.30
	index	1.00	1.087	0.952	0.948	0.939	0.917	0.986	0.943
Nitrates	mg NO_3^-/ 100 g of potatoes	12.37	12.48	11.67	15.20	19.05	19.08	15.05	20.83
	mg NO_3^-/ 100 g of dry matter	67.28	62.62	66.84	87.46	110.56	113.33	83.24	120.40
	index	1.00	0.93	0.99	1.30	1.64	1.69	1.24	1.79
	kg NO_3^- in output	3.84	4.42	4.40	5.64	7.50	7.51	5.78	7.51
	index	1.00	1.15	1.15	1.47	1.95	1.96	1.51	1.96

to be continued ...

Table 1 Continuation

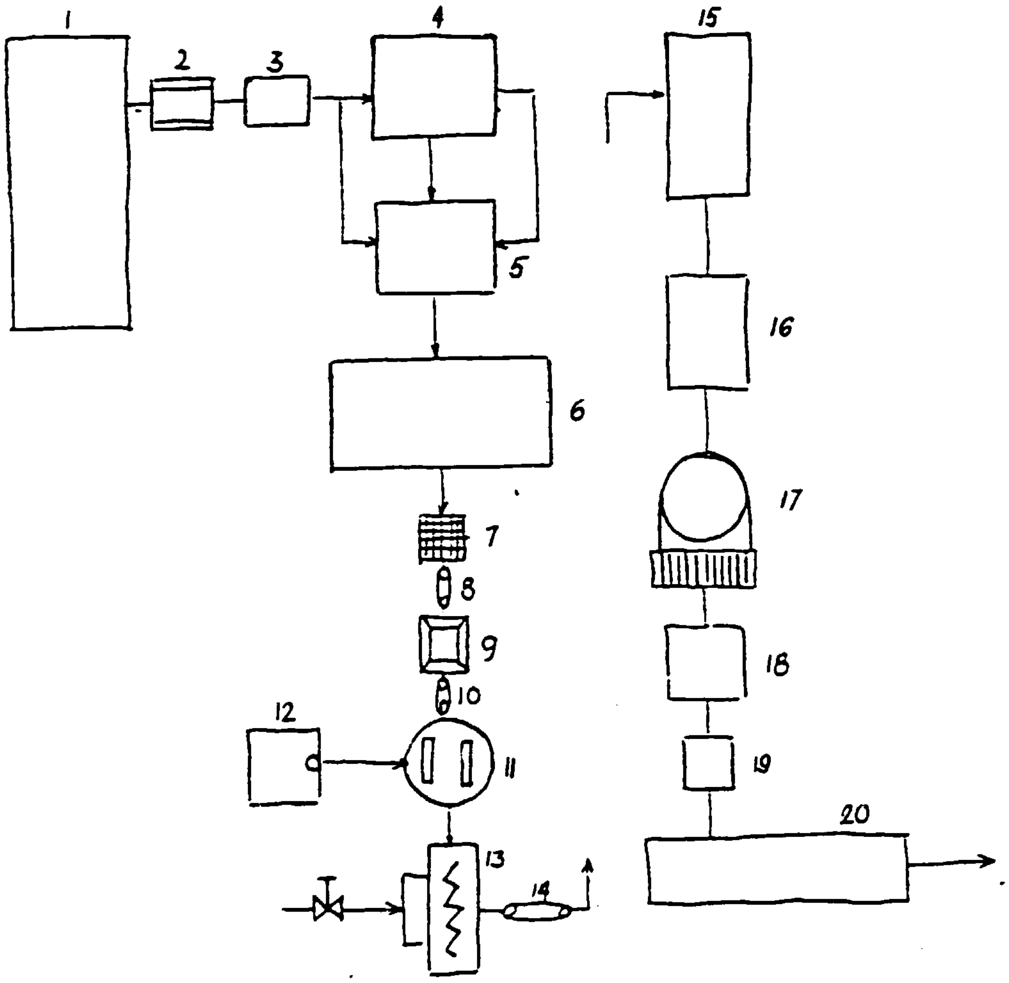
Plant		Potatoe III							
Output	q/ha	279.15	280.86	364.65	348.76	365.57	353.82	357.20	352.07
	index	1.00	1.01	1.31	1.25	1.31	1.27	1.28	1.26
Dry matter	%	24.11	23.76	22.77	22.97	22.40	22.72	22.16	22.20
	index	1.00	0.985	0.944	0.953	0.929	0.942	0.919	0.921
Nitrates	mg NO_3^-/100 g of potatoes	6.72	8.00	9.47	8.45	10.68	10.27	8.72	9.59
	mg NO_3^-/100 g of dry matter	27.87	33.67	41.59	36.79	47.68	45.20	39.35	43.20
	index	1.00	1.21	1.49	1.32	1.71	1.62	1.41	1.55
	kg NO_3^- in output	1.88	2.25	3.45	2.95	3.90	3.63	3.11	3.38
	index	1.00	1.20	1.84	1.57	2.07	1.93	1.65	1.80
Fertilizer dosage									
manure /q/ha/		-	250	250	250	250	250	250	250
N = ammonium sulphate /kg/ha/		-	-	40	80	120	120	120	120
P_2O_5 - superphosphate /kg/ha/		-	-	40	40	40	120	40	120
K_2O /kg/ha/		-	-	80	80	80	80	240	240

Source Czechoslovak Hygiene -1970 /15 , p.g. 205

Source: Czechoslovak Hygiene - 1970, 15, p. 205

Figure 1

Block diagram of mining and industrial upgrading of bentonite

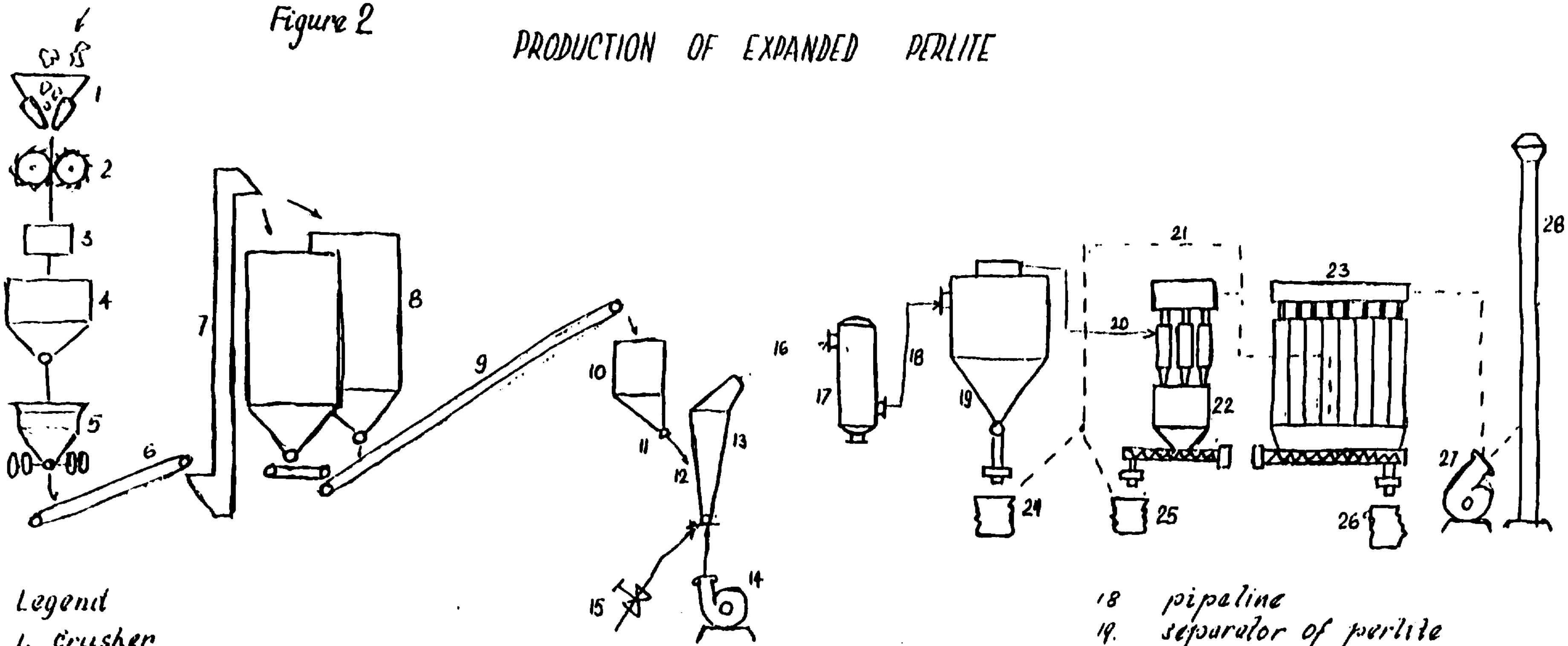


Legend

1. deposit
2. excavator
3. lorry transport
4. stock in quarry
5. stock in mill
6. weathering stock
7. feeding hopper
8. belt conveyor
9 box feeder
10. belt conveyor
11. pug mill
12. proportioner of Na_2CO_3
13 steampreheated worm blender
14. belt conveyor
15. rotary drier
16. elevator, crusher, belt conveyor
17. fine grinding mill
18. silos
19. special filling device
20 warehouse

Figure 2

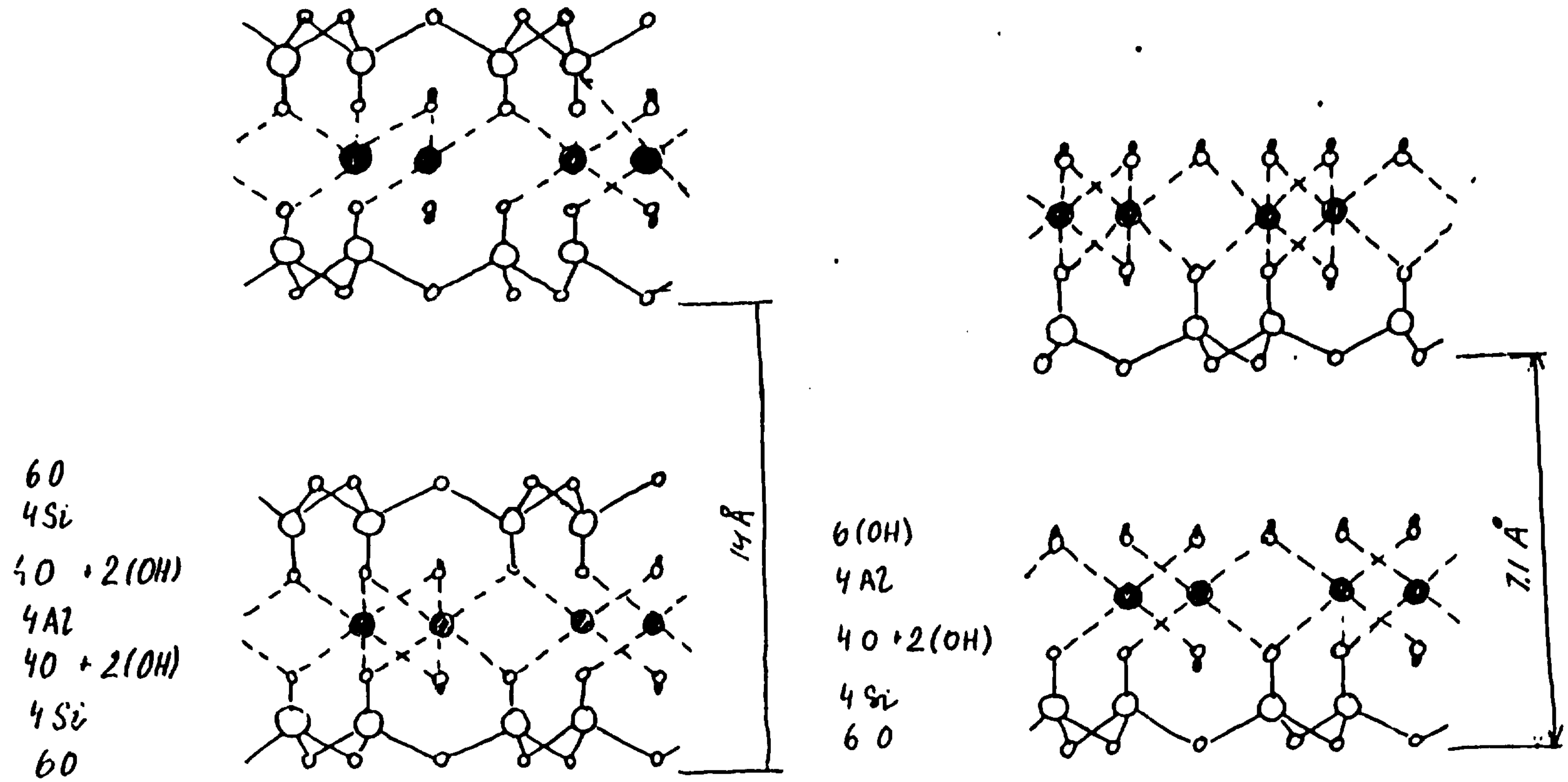
PRODUCTION OF EXPANDED PERLITE



Legend

1. crusher
2. hammer mill
3. vibrating sieves
4. crushed perlite silos
5. crushed perlite transport
6. belt conveyor
7. elevator
8. silos
9. belt conveyor
10. silos
11. rotary vane feeders
12 perlite inlet
13 expander
14. combustion air fan
15. gas inlet
16 expanded perlite exhaustion
17 compensating chamber
18 pipeline
19. separator of perlite
20. pipeline
21. dust collector piping
22. cyclones
23. dust collector
24. · 25 perlite packaging
26. finer perlite packaging
27. dust collector fan
28. chimney

Figure 3   Lattices of montmorillonite and kaolionite

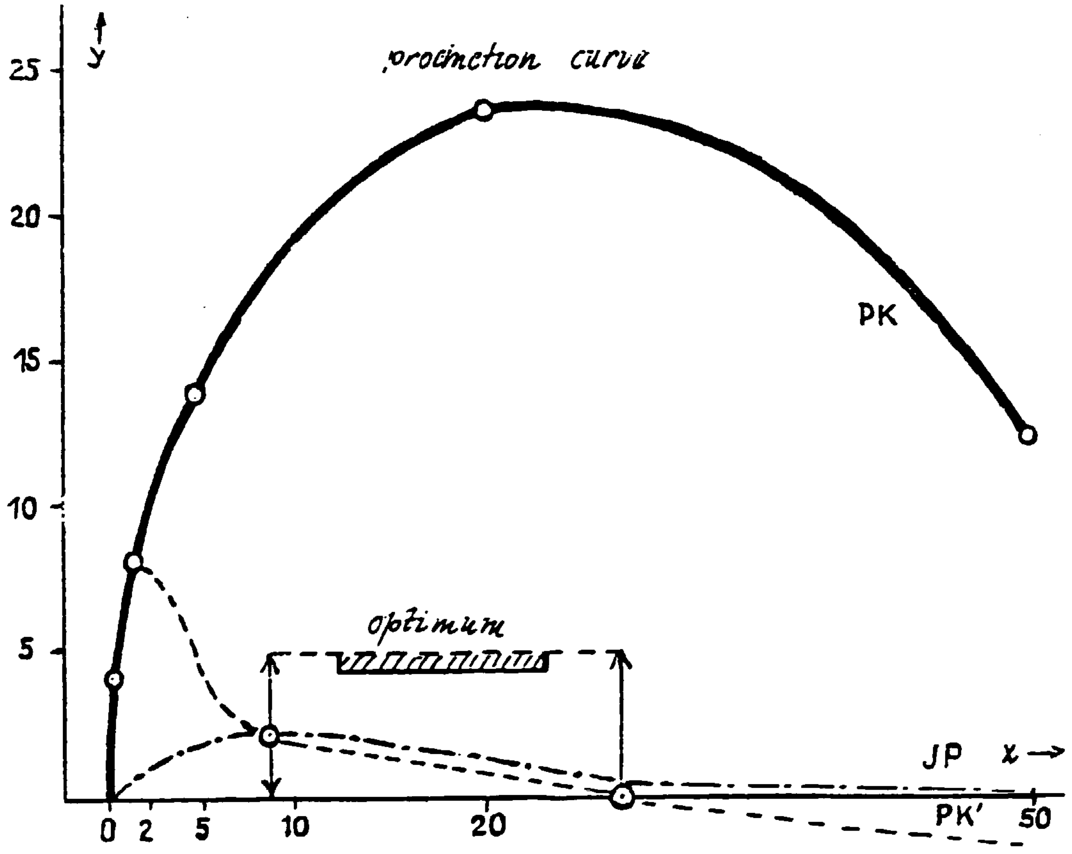


montmorillonite

kaolionite

Figure 4

Dependance of yield increases (sandy and argillo-arenaceous soils) on bentonite dosage including marked interval of optimum



— Legend

- x - tons per hectare
- y - yield increase
- PK - production curve
- PK' - first derivative of PK
- JK - unit increase of yield

Figure 5

– Relation between reclaiming efficiency of bentonite and type of soil and humus content in soil

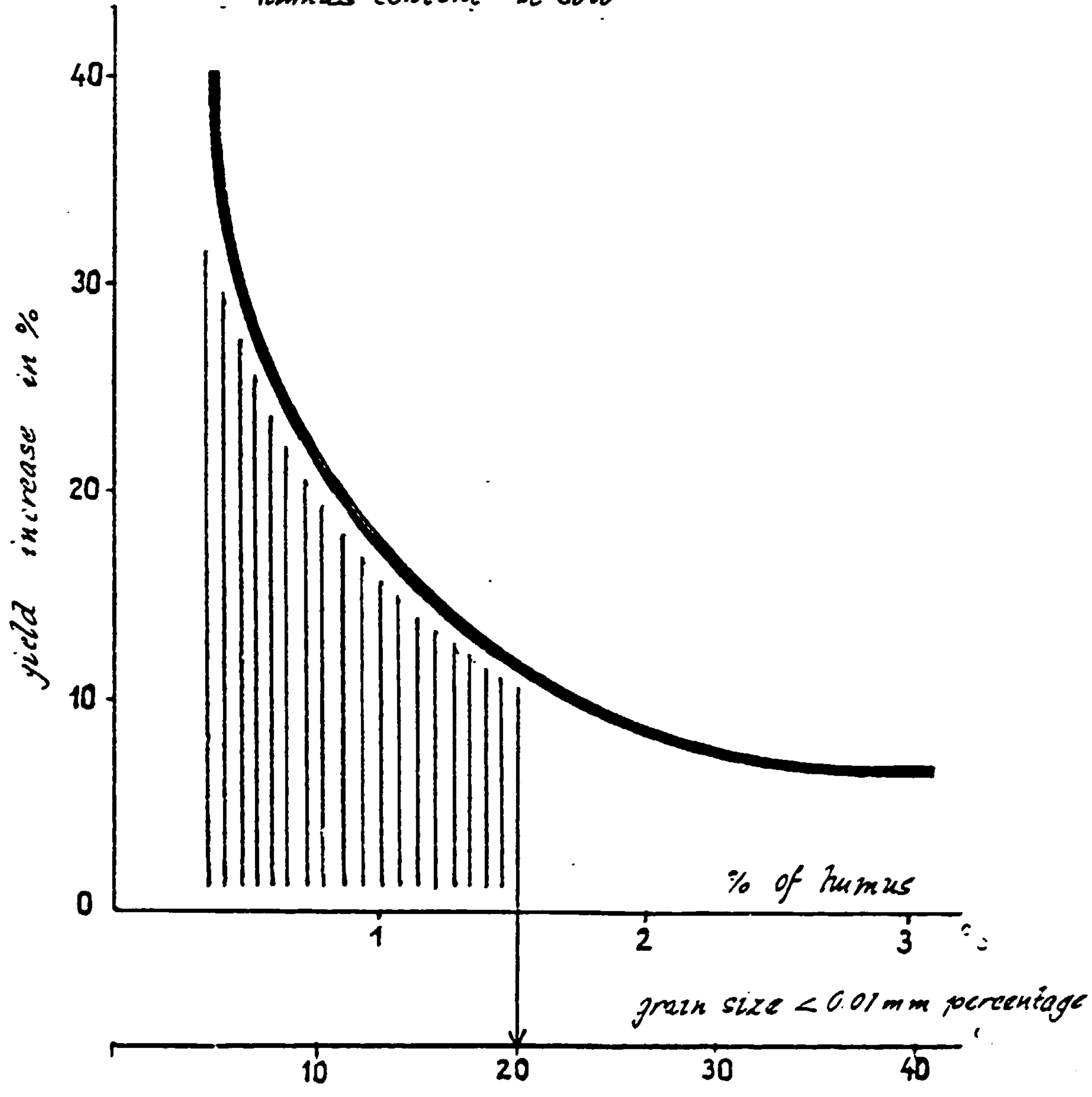


Figure 6

Effect of bentonite on humus retention in sandy soils after four years

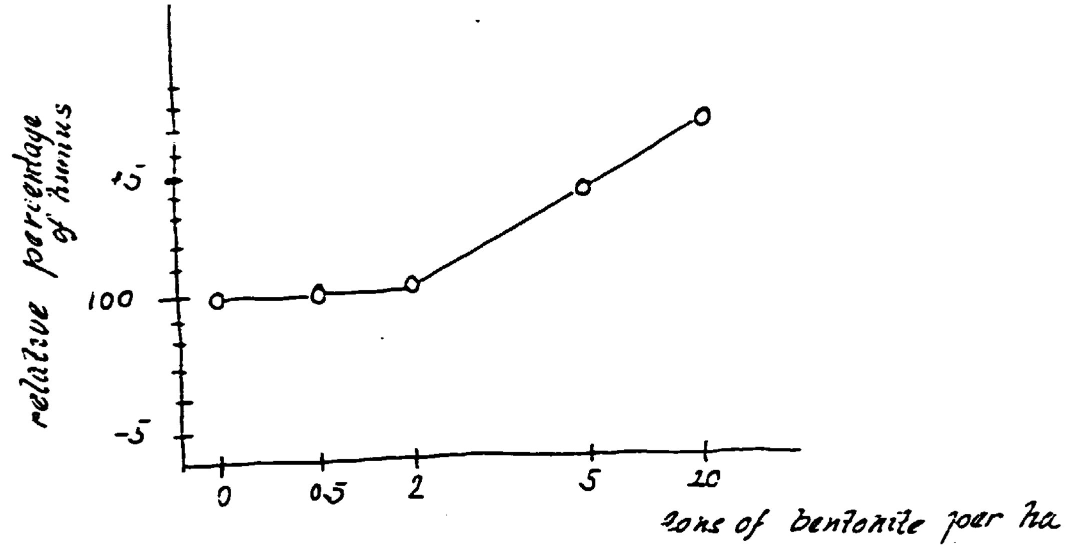


Figure 7

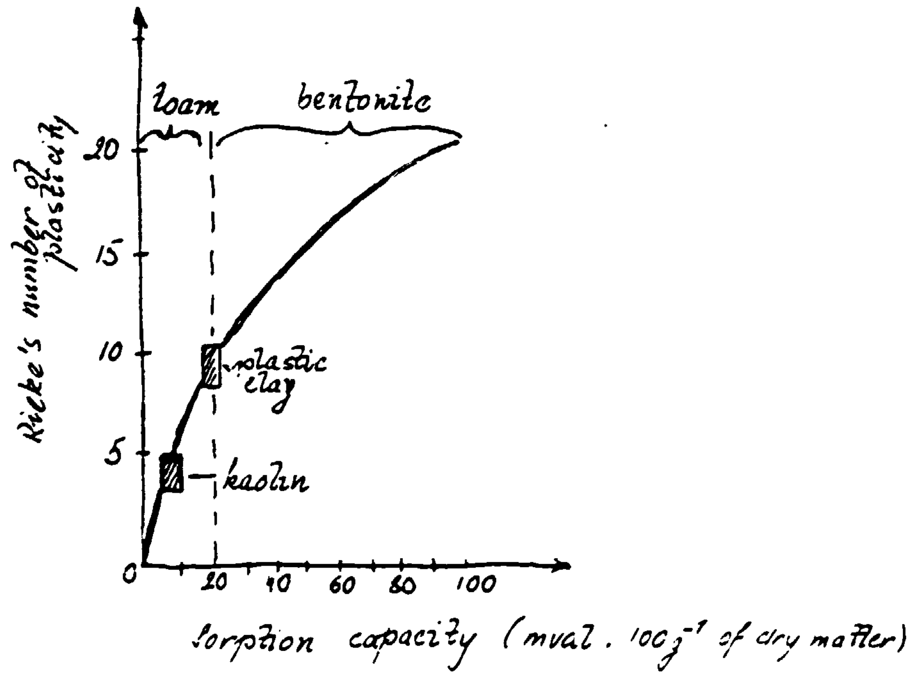


Figure 6

Effect of bentonite on
pore distribution in sandy soil

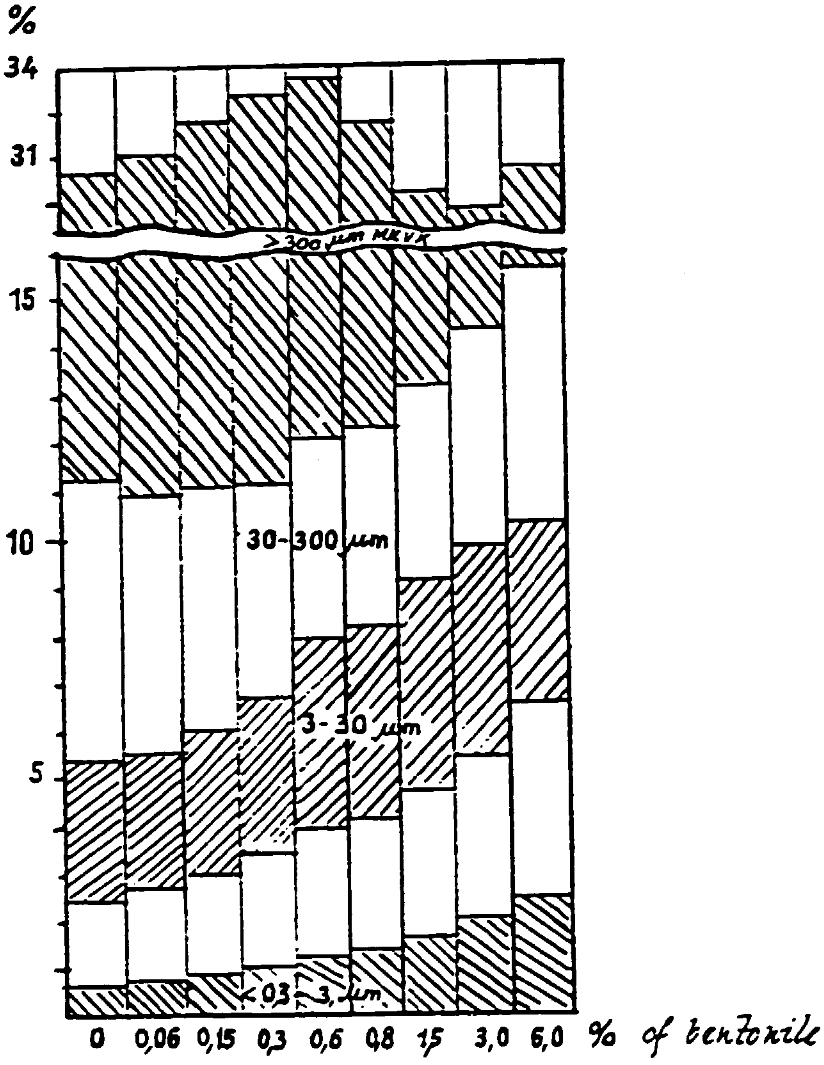
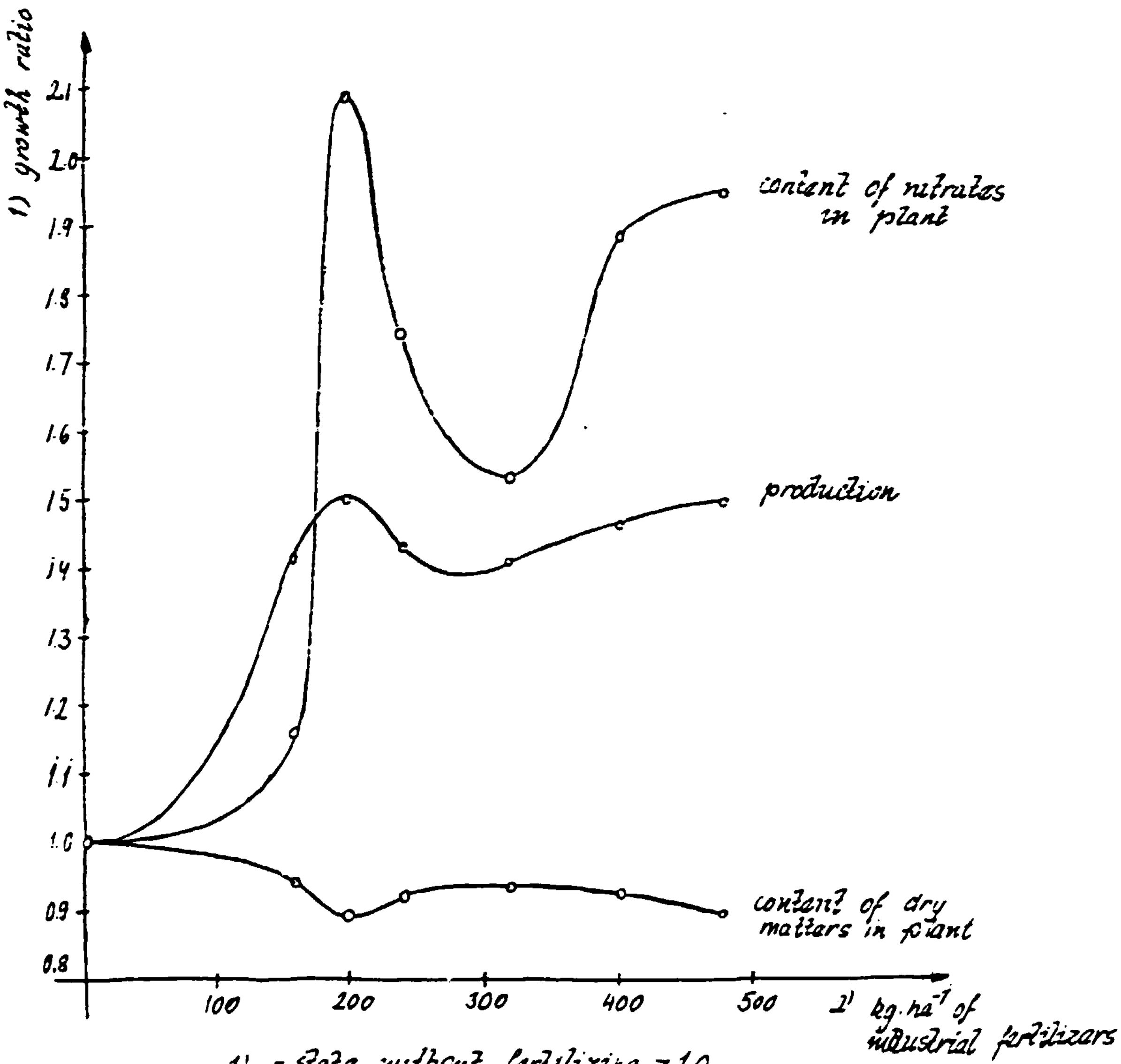


Figure 9

Relation between fertilizing, production growth and content of detrimental nitrates in plant



1) - State without fertilizing = 1.0

2) - mixture of ammonium sulphate
superphosphate
potassium salt

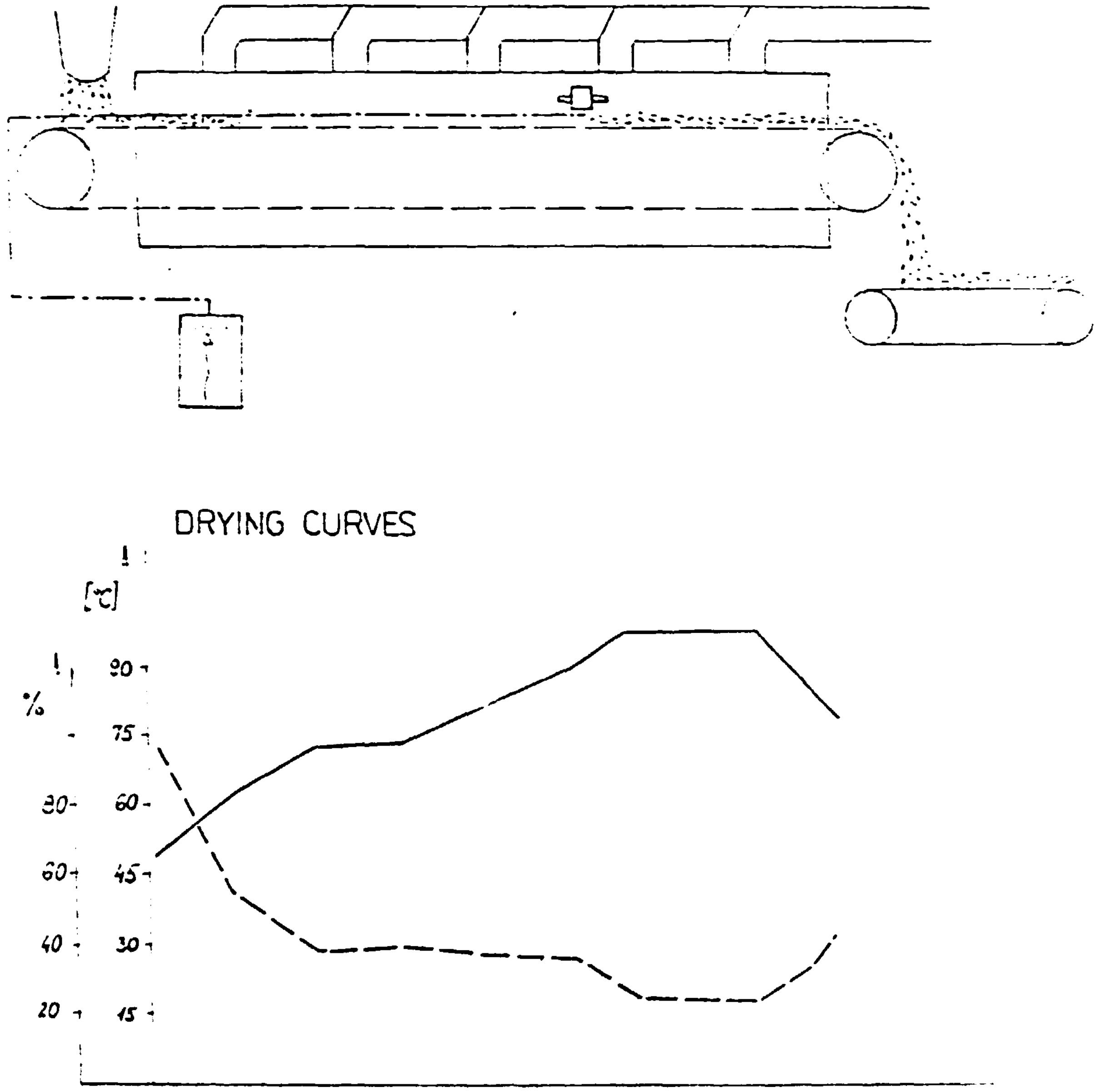


Figure [illegible]   Drying Curves of a Dryer