Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Current Opinion in Solid State and Materials Science 8 (2004) 397–404
Current Opinion in Solid State & Materials Science

Agricultural and agrochemical uses of natural zeolite of the clinoptilolite type

M. Reháková [a,*], S. Čuvanová [a], M. Dzivák [b], J. Rimár [b], Z. Gavaľová [c]

[a] Department of Chemistry, Faculty of Science, University P.J.Šafárik, 04154 Košice, Slovak Republic
[b] ZEOCEM, a.s., 09434 Bystré, Slovak Republic
[c] Section of Research, CHEMZA, a.s. 072 22 Strážske, Slovak Republic

Abstract

The present paper deals with the agricultural and agrochemical uses of natural zeolite of the clinoptilolite type from the Nižný Hrabovec deposit in Eastern Slovakia. The structure of natural clinoptilolite is ideal for sorption and ion exchange processes. Due to its structure and properties this natural, inert and non-toxic material can be used as a slowly releasing carrier of fertilizer, as well as other agrochemically, pharmaceutically and biochemically active compounds including disinfectants. Natural zeolite can also be used to improve physical properties of soils and for treatment of contaminated soils. It is also suitable—in very small amounts—as additive to animal feed.

Keywords: Zeolite; Clinoptilolite; Agrochemicals; Fertilizer; Animal feed; Contaminated soil

1. Introduction

The increasing demands on environment protection and production of food that does not endanger health require an increase in production of materials to be used in natural based agriculture and horticulture.

As non-toxic, ecologically advantageous and affordable materials, the natural zeolites, due to their structural, ion exchange and sorption properties and also many other characteristics are well suited for agricultural uses—in animal as well as plant production [1–3].

The natural zeolite of the clinoptilolite type is one of the world's most abundantly occurring and most abundantly used zeolitic minerals. At present it is widely used in many fields of industrial technology [1,3,4], agricultural production [1–4], ecology [5–13], but also in other areas such as medicine, pharmacy [14,15].

* Corresponding author.
E-mail address: rehakova@kosice.upjs.sk (M. Reháková).

1359-0286/$ - see front matter
doi:10.1016/j.cossms.2005.04.004

2. The structure and properties of zeolites

Zeolites are a type of inclusion compounds. They are hydrated aluminosilicates, characterised by three-dimensional networks of SiO_4 and AlO_4 tetrahedra, linked by the sharing of all oxygen atoms. The partial substitution of Si^{4+} by Al^{3+} results in an excess of negative charge which is compensated by alkali and earth alkaline cations. These cations are located along with the water molecules in cavities and channels inside the aluminosilicate macroanion framework [16]. The water molecules can be reversibly removed or replaced by other sorbates.

The formulas expressing the general composition of zeolites have been published in many forms. The original textbook version of the zeolite formula

$$\underbrace{M_{m/z}}_{\text{exchangeable cations}}\ \underbrace{[\,mAlO_2.nSiO_2]}_{\text{anionic framework}}\ .\ \underbrace{qH_2O}_{\text{sorbate phase}}$$

was extended by Meier [17] to yield the following formula better suited for describing natural and synthetic zeolites with additives:

$$M_xM'_yN_z[T_mT'_n \cdots O_{2(m+n)-\varepsilon}(OH)_{2\varepsilon}](OH)_{br}(aq)_p \cdot qQ$$

where $\varepsilon = 0, 1, 2, 3\ldots$, M and M′ are exchangeable and non-exchangeable cations, N are non-metallic cations (generally removable on heating), (aq) chemically bonded water (or other strongly held ligands of T-atoms), and Q sorbate molecules, which need not be water. In addition to Si and Al, Be, B, Ga, Ge, P and others can be used as T and T′ atoms.

Three basic properties are characteristic for zeolites: sorption, ion exchange and catalytic.

By replacing metallic cations in the crystalline structure it is possible to obtain modified zeolites [6,8,12,18,19] for specific uses including the removal of NH_4^+ and toxic metal cations from waste water.

Zeolites are capable of sorbing into their cavities or channels different polar and non-polar inorganic or organic molecules [16] but also biochemically, pharmaceutically [14,15,20–22], agrochemically [23–28] effective compounds, odoriferous compounds and others. The process may involve not only individual sorbates but sorbates of more kinds whose dimensions suit the specific zeolite cavities. Combined sorptions [20–22] are also possible in which the zeolite sorbs a certain species of inclusion compounds whose cavities already contain other molecular sorbates. By a sorption of different guest components the physical and chemical properties of the original zeolite are changed. The molecular sorbates may influence exchangeable cations, cause the migration of ionically bonded cations or there may be redox reactions in the zeolite cavities and channels [16,29]. The properties and potential applications of the modified zeolitic forms depend on the way of sorption and on the interaction of the guest component with the zeolite structure.

3. The clinoptilolite deposit at Nižný Hrabovec (Slovak Republic)

The East Slovak deposit at Nižný Hrabovec has been investigated geologically in 1974. The mineral clinoptilolite (CT), the principal rock constituent of the volcanic–sedimentary rock, belongs to the heulandite zeolitic group [30–32]. It is isostructural with heulandite.

Detailed mineralogical and chemical analysis [31–33] and the data on physical, mechanical and ion-exchange characteristics (Table 1) of this naturally occurring zeolitic mineral as well as the study of its morphological properties and chemical analysis as compared with other world deposits from the point of view of their identification, genesis and use [34] are well known. The clinoptilolite of Nižný Hrabovec is of the K–Ca (potassium–calcium) type with low content of Fe, Mg and Na ions and other ions in trace amounts [31–33].

The ZEOCEM joint stock company (a.s.) at Bystré has a monopoly on processing natural zeolite and is

Table 1
Data of the natural zeolite of the clinoptilolite type

Mineral composition			
Clinoptilolit	84%	Plagioclase	3–4%
Cristobalite	8%	Rutile	0.1–0.3%
Clay talc	4%	Quartz	traces
Chemical composition			
SiO_2	65.0–71.3%	MgO	0.6–1.2%
Al_2O_3	11.5–13.1%	Na_2O	0.2–1.3%
CaO	2.7–5.2%	TiO_2	0.1–0.3%
K_2O	2.2–3.4%		
Fe_2O_3	0.7–1.9%	Si/Al	4.8–5.4
Physical and mechanical properties			
Softening temperature	1260 °C	Poriness	24–32%
Melting temperature	1340 °C	Effective pore diameter	0.4 nm (4 Å)
Compression strength	33 Mpa	Relative density	70%
Specific weight	2200–2440 kg/m^3	Brightness	70%
Volume weight	1600–1800 kg/m^3	Mohs hardness	1.5–2.5
Appearance and smell	grey-green, without smell	pH	6.8–7.2
Ionic exchange properties			
Total exchange	Ca^{+2} 0.64–0.98 mol/kg	K^+ 0.22–0.45 mol/kg	
	Mg^{2+} 0.06–0.19 mol/kg	Na^+ 0.01–0.19 mol/kg	
NH_4^+ partial exchange capacity min 0.70 mol/kg			
NH_4^+ total exchange capacity 1.2–1.5 mol/kg			
Selectivity			
$Cs^+ > NH_4^+ > Pb^{2+} > K^+ > Na^+ > Ca^{2+} > Mg^{2+} > Ba^{2+} > Cu^{2+}, Zn^{2+}$			

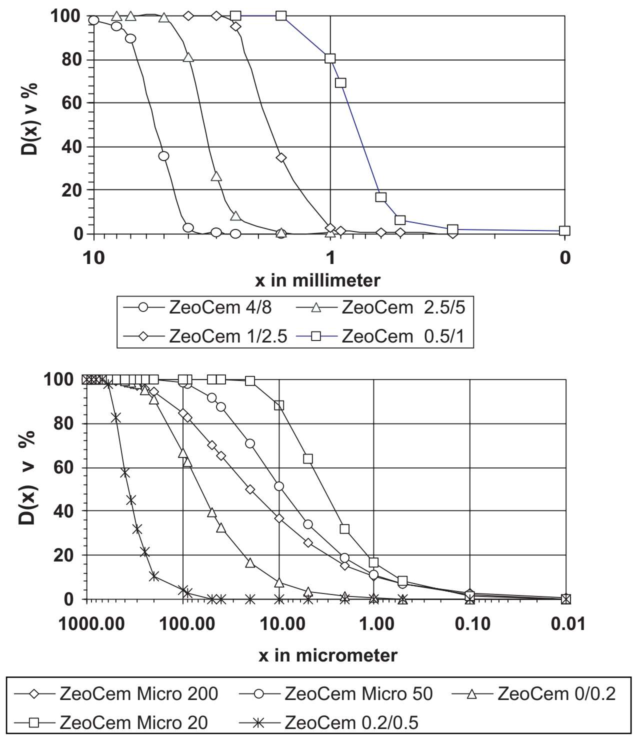

Fig. 1. Granulometric curves of the zeolitic products produced.

one of the foremost producers of zeolite products in the Slovak Republic [31,32]. It has been active in the area of mining and processing natural zeolite since the beginning of the eighties. The natural zeolite which the company mines and processes is used in Slovakia, in many European countries but also in certain countries of Asia and America in various economic fields. More than half the production is destined for export.

The ZEOCEM, a.s. company produces a wide range of products designed for various areas of industry and agriculture. Owing to their high quality, purity and the wide granulometric range (Fig. 1) the company's products are finding enthusiastic acceptance in agriculture (which we will speak about in Section 4), for flue cleaning (dioxins and heavy metals), gas drying, water cleaning and treatment [31,35] as filler in the paper and rubber industries, an additive for adhesives and cleaning and suction agents as well as adhesives and desiccants [31,32].

4. The use of zeolites in agriculture and horticulture

In agriculture as of course in horticulture the natural zeolites are widely used as slow releasing carriers of fertilizers [3,31–33,36–46] as well as other agrochemicals—insecticides, pesticides [23–28], antibacterial agents [48,49], growth stimulators, for improving the fertility and biological activity of the soil, recultivation and increasing the production capacity of acid and devastated soils, increasing the nitrogen balance especially in light and sandy soils [36,44]. They are also used in drying and storage of grain, the care of wines—clarification and fining, the production of hothouse and bark-torf substrates, preparation of substrates for fruit and vegetable storage and others [31,32]. They are also useful from the ecological point of view for removing harmful wastes from the soil—sorption of heavy metals and other toxic compounds [11,45,50].

In breeding of farm animals zeolites may be used [31–33,51–56] as mineral additives to feed mixtures with dietetic and antibacterial effects as well as for facilitating the handling of excrements and litters of the animals. They act as deodorants in reducing the smell and moisture in stables. In fish breeding they are suitable to remove the ammonia in recirculation systems [31].

Zeolite products are also suitable for multistage usage—first as litter for farmyard animals which is then used as natural fertilizer for agricultural plants.

4.1. Zeolites as carriers of fertilizers

Natural zeolites are suitable carriers for fertilizers of various kinds [31–33,36–46]. The nutrients are released gradually, not only in the first year of the vegetation period but also in the second or the following years. Very important is also the hydratation and dehydratation capacity of zeolites which may be used to improve the water balance in the soil especially in the growing of moisture sensitive vegetables, special vineyard cultures and fruit and decorative plants.

Zeolite based fertilizer has several advantages: it is a fertilizer prepared on the base of a non-toxic natural material, it is easily applied at the beginning of the vegetation period yet supplies an even fertilizing effect throughout the whole period. It is ecologically advantageous since the active compounds and nutrients are washed out into the soil slowly and gradually. In case of torrential rains they are not washed out all at once and thus there is no underwater pollution or the pollution of neighboring rivers.

4.2. Fertilizers and other products on the base of clinoptilolite from Nižný Hrabovec

Natural zeolite of the clinoptilolite type from the Nižný Hrabovec locality was subjected to study from the point of view of fertilizer sorption [31,33,43–47] and as a feed additive [52–54] but studies were also carried out with a view to the sorption of other agrochemicals such as insecticides [27,28], growth stimulators [43,47] etc. Study effort was also directed at the possibility of using natural zeolitic materials as solid disinfectants [29] and as a carrier of pharmaceuticals for veterinary pharmacy [20–22].

In the past, zeolitic materials containing insecticides (such as supercypermetrine or pyretroide) were subjected to a study with a view to using natural zeolite as insecticide carrier [27,28]. A product produced at present (by the ZEOCEM a.s. company) is designed for repressive and preventive protection of vegetable products in storage against storage vermin [31,32]. It is effective and ecological. The mechanism of its action is based on the adsorption of the protective wax surface layer of insect cuticle and consequent desiccation. It is selectively toxic for ecto-parasites and storage vermin while at the same time preserving the sanitary qualities of stored products.

A zeolitic material containing iodine and iodide ions was studied with a view to use as a solid disinfectant [29]. It has long been published that redox reactions of ferric and iodide ions produce elementary iodine [57]. Iodine molecules are produced in a redox reaction of Fe^{3+} ions present in the structure of natural clinoptilolite with iodide ions present in modified forms in its cavities and channels ($2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+}$). The iodine may diffuse slowly out from the zeolite channel system. XPS measurements as well as ac and dc conductivity measurements significantly contributed to the characterisation of this zeolitic material and the confirmation of presence of elementary iodine and iodide ions in the channel system [58,59].

Combined sorptions of natural zeolite of the clinoptilolite type with cyclodextrine (CD) [20–22] were studied with a view towards the possibility of using natural zeolite as a slow releasing carrier of pharmaceuticals for veterinary pharmacy. The CD molecules were simultaneously as guest and host components since CD enclosed the salicylic acid or spironolacton.

The use of fertilizers on the basis of natural clinoptilolite as well as other possibilities of application of natural clinoptilolite have been studied in cooperation with practical research workers, mainly with the CHEMKO, a.s. Strážske and ZEOCEM a.s. Bystré industrial enterprises [33,46,47,50].

Years of effort and series of vessel and field tests led to the development of two types of zeolite fertilizers with clinoptilolite content up to 40% (ZEOMIX NPK) [44] and 50% (KlinoFert NPK) [31]. These products are multicomponent fertilizers containing the principal nutrients N, P and K together with other biogenic elements, namely sulphur, magnesium, iron, calcium, manganese, boron and molybdenum. ZEOMIX NPK (developed and produced in Chemko a.s., Strážske) contains 8.5% nitrogen, 6.3% phosphorus as P_2O_5, 6.3% potassium as K_2O, 11% sulphur, 0.1% boron, 0.02% molybdenum. KlinoFert NPK (developed and produced in Zeocem a.s. Bystré) contains nitrogen min 6.0%, phosphorus (P_2O_5) min 4.5%, potassium (K_2O) min 7.5% and sulphur (SO_4^{2-}) min 10%.

In more than 20 years of research and application work in the agricultural area, ZEOCEM has developed many other products. These include mainly ZeoFeed—an ingredient for the production of feeding mixtures with more then 80% of the effective substance (clinoptilolite) [31,32,55,56], ZeoSand and ZeoGravel—a group of ingredients designed to improve soil properties, ZeoClean—a mineral additive for litters designed for use in large scale breeding of farm animals and ZeoCorn—the (already mentioned) preparation for repressive and preventive protection of vegetable products in long term storage against storage vermin. Other products for household (pets etc.) and horticulture are produced under the "Hobby Line" heading [31,32].

ZEOMIX NPK and KlinoFert NPK are second generation fertilizers with interesting effects on the quantity and quality of the harvest of crops treated, the soil environment and certain aspects of the environment in general [43–45]. They act as a growth conditioner. Plants in good condition are better prepared to resist fungoid pathogents during the vegetation period.

Let us mention some of the most recent findings made in the year 2003 with respect to growing of root vegetables, small fruits, onions, grasses and forest trees. The effect of the KlinoFert NPK zeolitic fertilizer was compared to non-fertilized control samples.

The use of the zeolitic fertilizer has led to a significant increase of root biomass in parsley (*Petroselinum sativum*—Olomoucká variety) to 1500 g per meter of root length as compared to 487 g per meter of root length in the control. In the carrot (*Daucus carota*—Tromphy variety) root biomass was 3400 g per meter of root length as compared to 2300 g in the control. The onion (*Allium cepa*–Banco variety) showed 49.5 g root mass as compared to 26.7 g in the control. Significant increase was also found in haulm mass. In strawberries (*Senga sengana*) we found an increase in the harvest of as much as 70% as compared to the control, in addition the condition of the plants was markedly improved as were their taste properties.

In grasses we found a significant increase in the amount of green biomass produced from 5.9 to 8.8 t/ha (metric tons per hectare)—an increase of 49.2%. It should be remarked that the use of the zeolite fertilizer led to an increase of the share of grasses and decrease of weeds.

In forest trees the effect of the fertilizer was tested in replanting the saplings of black pine (*Pinus nigra*) and the European beech (*Fagus sylvatica*) to their permanent place. KlinoFert NPK was applied into the holes during the planting. At the end of the vegetation period the trunk thickness just above the root and tree height were measured. The comparison was repeated for three successive years. The one-time application of KlinoFert NPK has in all three years led to greater trunk thickening and faster growth in length. The use of zeolite fertilizer permitted the saplings to withstand the replanting shock better and their start in the decisive three-year period after replanting was faster.

Some of the results obtained in field tests using the ZEOMIX NPK fertilizer are briefly summarized here [43,44]: using doses of 300 kg/ha (300 kg per hectare) on winter wheat in the course of three years led to stabilization of harvest at 4.0 t/ha with 26% gluten content. Doses of 400 kg/ha for winter rape led to a stable seed harvest of 3.0–3.5 t/ha. Doses of 300 kg/ha for spring malting barley led to good malting quality parameters, mainly the protein content of 11%. Doses of 350 kg/ha for sugar beets led to a significant increase of the root sugar content to between 16% and 18%.

4.3. Dynamics of nutrient release from zeolitic fertilizers

Fertilizers based on the natural clinoptilolite from Nižný Hrabovec were also studied from the aspect of the dynamics of nutrient release. To this end, spring barley (*Hordeum vulgare*) was grown in parallel in experimental vessels with zeolitic fertilizers and compared to those with standard three-component NPK fertilizer (containing nitrogen, phosphorus and potassium).

Already in the first stages of growth slower and more gradual release of nutrients from the zeolitic fertilizers could be observed. In the first days the plants in the vessels with standard NPK fertilizers grew more quickly as compared to those with zeolitic fertilizer. The gradual release of nutrients by zeolitic fertilizers was confirmed by lower biomass values for above-ground plant parts, especially in the first stage of growth, as compared to standard NPK fertilizer. On the other hand, the dry matter content, especially in roots, was higher with zeolitic fertilizers. The deciding result is that the resulting barley biomass after using zeolitic fertilizers has more favorable harvest index (higher grain share) which documents that the use of this type of fertilizer has a positive influence on directing the assimilates to the utility part of the plant.

Table 2 shows the content of nitrogen, phosphorus and potassium in the plants grown with the zeolite and standard NPK fertilizer. The data shown confirm the gradual release of nutrients, especially nitrogen. In the ear formation phase the nitrogen content was lower (5.6%) with the zeolite fertilizer than it was with the standard NPK fertilizer (8.9%). In the offshoot formation stage the barley with lower nitrogen content does not form too many offshoots of which many would form no ears. The plant cover does not grow unnecessarily dense and does not exhibit the propensity to fungoid diseases. The decisive fact is that zeolitic fertilizer leads to better harvest.

4.4. The use of natural zeolite and zeolitic fertilizer to decrease the residual content of heavy metals and other toxic compounds in plants

The decrease of content of heavy metals and other toxic compounds in plants growing on heavily contaminated soils in industrial areas has been studied using natural zeolite as well as zeolitic fertilizers. The results of study of growing certain agricultural plants in contaminated soils with varying dosages of natural zeolite (CT), zeolitic fertilizer and standard NPK fertilizer confirmed the favorable influence of both zeolite and the zeolite based fertilizer (Table 3). Natural clinoptilolite by ion exchange of heavy metals and sorption of toxic substances into its cavities and channels blocked their reception into the plants.

Table 3 shows the results of vessel experiments in growing the spring barley (*H. vulgare*) in contaminated soils in different variations with additions of CT, zeolite based fertilizer and standard NPK fertilizer. Analysis of plant material showed that the lowest content of heavy metals (Zn, Cu, Pb, Cd and Cr) as well as of PCB (polychlorinated biphenyls) was found in plants grown in contaminated soils with the application of CT. Plants grown in contaminated soils with the addition of zeolitic fertilizer showed a somewhat higher content. The

Table 2
Nutrient content (N, P, K) in plant biomass by phenophase

Fertilizer dose (kg/ha)	Content [wt.%]			
	Growth phase	N	P	K
NPK 150	4 leaves	7.253	0.550	3.59
	offshoot formation	7.193	0.419	2.88
	haulm formation	8.022	0.449	2.58
	ear formation	8.931	0.279	1.78
Zeolitic fertilizer 150	4 leaves	6.049	0.485	4.26
	offshoot formation	5.401	0.376	3.54
	haulm formation	5.388	0.305	3.75
	ear formation	5.605	0.263	3.42

Crop grown: spring barley (*H. vulgare*). Vegetation substrate: soil from the mountainous regions of East Slovakia.

Table 3
Analysis of plant material: spring barley (*H. vulgare*), grown on: contaminated soil (CS) of an industrial zone with variants of application of natural zeolite (CT), zeolitic fertilizer (ZEOMIX NPK) and standard NPK fertilizer (NPK)

CS with added dose [kg/ha]	Content of the elements [mg/kg]					Content of PCB[1] [μg/kg]
	Zn	Cu	Pb	Cd	Cr	
CS	107	33.1	1.34	0.34	7.5	4765
CS + CT 150	52.4	16.3	1.05	0.24	5.2	2524
CS + NPK 150	65.1	31.0	1.42	0.35	5.4	3477
CS + NPK 250	68.8	30.8	1.84	0.36	6.0	3586
CS + ZEOMIX NPK 150	41.9	24.5	0.95	0.30	4.4	2953

PCB[1] = expressed as the sum of Delor 103 and Delor 106.

highest content both of heavy metals and PCB was found in plants grown on untreated contaminated soils.

Analysis of biomass quantity yielded analogous results. The plants that grew best were those growing in contaminated soils with CT added. Good results were obtained also by adding zeolitic fertilizer in low doses (150 kg/ha).

In small plot experiments we investigated the influence of higher doses of CT and zeolitic fertilizers on reduction of intake of heavy metals from contaminated soils. A zeolite of the clinoptilolite type at 600 kg/ha reduced the intake of cadmium from the soil to 0.04 mg/kg in the plants. The effective dose for lead was also 600 kg/ha. Zeolitic fertilizer proved effective in reducing the intake of heavy metals at 700 kg/ha but further increase of dosage led to a negative influence on the resulting plant biomass.

The results show that adding pure natural zeolite of the clinoptilolite type leads to significant decrease of the content of heavy metals and PCB in plants. Good results may be obtained also using zeolitic fertilizer but in that case it is necessary to find the optimum dosage to balance the blocking influence on heavy metal intake with the growth of the plant biomass.

4.5. Zeolites as feed additives

Adding natural zeolite of the clinoptilolite type to feed mixtures in low doses of about 1–2% has influences on very important functions heretofore not recorded by other natural compounds [51–56].

In Slovak Republic the presence of mycotoxins in feed mixtures of both plant and animal origin has been observed. The most abundant types of mycotoxins include the aflatoxins B_1, B_2, G_1, G_2, M_1 and ochratoxin A. They are produced by the toxinogenic phyla *Aspergillus flavus* and *Aspergillus parasiticus*.

Depending on weather conditions in the given year a 40–80% contamination of the cereal grain by fungi of the *Fusarium* genus, namely *Fusarium graminearum* and *Fusarium poae*. An effective tool for degradation of the toxins in animal feed was found in the zeolite of the clinoptilolite type from Nižný Hrabovec in the concentration of 0.9–1.7 kg/100 kg of feed. The effect was demonstrated in the improved condition of the animals and weight increases.

In general, in monogastric animals it was found that salts of organic acids were effective as feed additives; this was true especially of calcium formate $(HCOO)_2Ca$ [33,52–54] which has bactericidal and acidifying effects in the feed mixture while at the same time influencing the pH adjustment of the digestive tract and increasing the activity of the enzyme pepsin.

Finally, this leads to increased growth intensity in animals and better feed conversion. To support these positive effects half of the calcium formate was replaced by zeolite from the Nižný Hrabovec deposit which at the same time played the role of carrier for formic acid (HCOOH). In the course of animal digestion process the formate is transformed to formic acid and only in this form can influence the digestion process. The feed additive containing 50% calcium formate, 8% formic acid and 42% of natural zeolite of the clinoptilolite type proved more effective at increasing the growth intensity and improving feed conversion in pigs and poultry [52].

Following are some of the test results for the above feed additive (developed by CHEMKO a.s. Strážske under the trade name of ZEOFORM containing 42% of natural zeolite of the clinoptilolite type) [52–54]. The feed mixture contained 1.5% of the feed additive. After the first month of feed administering the animals in the test group showed a weight increase of 13.4 kg as compared to 8.3 kg in the control group. The daily increase was 0.47 kg in the test group against 0.29 kg in the control group. At the same time the consumption of feed per kg of weight increase was 3.13 kg in the test group and 4.7 kg in the control group.

5. Conclusion

Under the present requirements of ecological agriculture there are wide areas of use for a natural, inert and non-toxic material such as the natural zeolite of the clinoptilolite type from the Nižný Hrabovec deposit. The structure of natural clinoptilolite is ideal for sorption and ion exchange processes. Due to its structure and properties zeolite may be used as a slow-releasing carrier of agrochemicals of various kinds; fertilizers, pharmaceutically and biochemically effective compounds for veterinary pharmacy and also disinfectants. Natural zeolites are effective in improving soil properties and treating contaminated soil. Natural zeolite of the clinoptilolite type is also suitable—in low doses—as a feed additive.

Wide as the contemporary area of practical uses of zeolites may seem, the search for other application possibilities is still going on.

Acknowledgments

The authors wish to thank the Quality Management Section of CHEMZA a.s. Strážske, Laboratory of Analytical Methods for making the analyses of N, P, K, heavy metals and PCB content in plant material and soils. Thanks are also due the employees of CHEMKO a.s. Strážske who in cooperation with TU Nitra, UKSUP Michalovce, Zvolen and Košice realized the vegetable and cereal growing experiments in the years 1993–2003, as well as the Botanical Garden of the P.J. Šafárik University of Košice where a part of the experiments was realized.

The authors gratefully acknowledge the financial support provided by the Scientific Grant Agency of the Slovak Republic (grants no. 1/1385/04 and 1/1373/04).

References

[1] Van Bekkum H, Flanigen EM, Jansen JC. Introduction to zeolite science and practice. Amsterdam: Elsevier Science Publisher; 2001.
[2] Allen ER, Ming DW. Recent progress in the use of natural zeolites in agronomy and horticulture. In: Ming DW, Mumpton FA, editors. Natural Zeolites '93. Brockport, New York: International Committee on Natural Zeolites; 1995. p. 477–90.
[3] Colella C. Application of natural zeolites. Handbook of porous solids 2002;2:1156–89.
[4] Colella C, Mumpton FA. Natural zeolites for the third millenium. Napoli: De Frede-Editore; 2000.
[5] Misaelides P, Macasek F, Pinnavaia TJ, Colella C. Natural microporous materials in environmental technology. Dordrecht: Kluwer Academic Publishers; 1999.
[6] Bowman RS. Application of surfactant-modified zeolites to environmental remediation. Micropor Mesopor Mater 2003;61: 43–56.
[7] Chmielewská E. Remediation of specifically polluted waste effluents using natural zeolites. Environ Prot Eng 2003;1:35–42.
[8] Chmielewská E. Adsorption of arzenate and chromate from waters on hydrofobised zeolitic media. Turk J Chem 2003;27(5): 639–48.
[9] Tian WH, Wen XH. Using a zeolite medium biofilter to remove organic pollutant and ammonia simultaneously. J Environ Sci-China 2004;16(1):90–3.
[10] Pilchowski K, Chmielewská E. Adsorptive separation of 1,2-dichloroethane from model waste water on natural clinoptilolite. Acta Hydrochim Hydrobiol 2003;31(3):249–52.
[11] Puschenreiter M, Horak O. Slow-release zeolite-bound zinc and copper fertilizers affect cadmium concentration in wheat and spinach. Commun Soil Sci Plant Anal 2003;34(1–2):31–40.
[12] Gebremedhin-Vaile T, Olguin MT, Solache-Rios M. Removal of mercury ions from mixed aqueous metal solutions by natural and modified minerals. Water, Air, Soil Pollut 2003;148(1–4):179–200.
[13] Ponizovskij AA, Dimoyanis DD, Tsadilas KD. The use of zeolite for detoxication of lead-contamined soils. Soil Sci/Pochvovedenie 2003;36(4):439–43.
[14] Çolić M, Pavelić K. Molekular mechanizmus of anticancer activity of some natural dietetic products. J Mol Med 2000;78: 333–6.
[15] Čolić M, Pavelić K. Prírodní, zeolit klinoptilolit, noví adjuvant u antikanceroznoj terapii. http://www.megamin.hr/naveni-rad-3-hr.htm. 2003.
[16] Schöllhorn R. Intercalation compounds. Zeolites. In: Atwood JL, Davies JED, Mac Nicol DD, editors. Inclusion compounds, vol. 1. London: Academic Press; 1984. p. 260–3 [Chapter 7].
[17] Meier WM. Zeolites and zeolite-like materials. Proc seventh international zeolite conference. Tokyo: Elsevier; 1986. p. 13–22.
[18] Chmielewská E, Jesenák K, Gáplovská K. Arsenate and chromate removal on cationic surfactant-loaded and cation-exchanged clinoptilolite rich tuff vs. Montmorillonite. Collectm Czech Chem Commun 2003;68(4):823–36.
[19] Reháková M, Chmielewská E, Nagyová S. Study of organo-modified forms of natural zeolite of the clinoptilolite type. Solid State Phenomena 2003;90–91:411–6.
[20] Mondík P, Sopková A, Viernstein H, Legéndre B. Cyclodextrins in the role of host and simultaneously guest component. In: Szeitli J, Szente L, editors. Proceedings of the eight international symposium on cyclodextrins. Netherland: Kluwer Academic Publishers; 1996. p. 197–200.
[21] Mondík P, Sopková A, Viernstein H, Légendre B. J Therm Anal 1998;51:1023–37.
[22] Sopková A, Mézeš P. Combination of cyclodextrins with synthetic and natural compounds. J Incl Phenom 1999;33:109–20.
[23] Kam S-K, Kim K-S, Ahn BJ, Lee M-G. Adsorption and desorption of triadimefon by natural and synthetic zeolites. Hwahak Konghak 2002;40(2):265–73.
[24] Tamura K. Spraying zeolite compositions to leaves for promoting plant growth (Japan). Jpn Kokai Tokkyo Koho 2003. JP 2003116350 A2 20030422.
[25] Kim DG, Kim DH, Kim Ych, Park GH, Sung ND, Cho YG. Process for producing pesticide compositions containing zeolite (S Korea). Repub Korean Kongkae Taeho Kongbo 2000. KR 2000058598 A 20001005.
[26] Pursell T, Shirley AR Jr, Cochran KD, Holt TG, Peeden GS, Pace CB, et al. Pesticide carrier. PCT Int. Appl. 2003;WO 2003105582 A2 20031224.
[27] Sopková A, Mezeš P. About the inclusion of an insecticide in zewolitic materials. J Therm Anal 1996;46:471–8.
[28] Sopková A, Janoková E. An insecticide stabilised by natural zeolite. J Therm Anal 1998;53:477–85.
[29] Reháková M. Inclusion compounds of the zeolite type, properties and possibility of their application. Thesis, University P.J.Šafárika, Košice 1997.
[30] Šamajová E. Zeolites in tuffaceous rocks of the West Carpathians (Slovakia). In: Kalló S, Sherry HS, editors. Occurrence, properties and utilisation of natural zeolites. Budapest: Akadémiai; 1988. p. 49–57.
[31] Natural minerals for healthy life. Bystré: ZEOCEM 2004.
[32] ZEOCEM, a.s. Bystré, 2004: http://www.zeocem.sk.
[33] Reháková M, Čuvanová S, Gavaľová Z, Rimár J. Využitie prírodného zeolitu typu klinoptilolitu v agrochémii a v poľnohospodárstve. Chem listy 2003;4:245–324.
[34] Sopková A, Bubanec J. Zeolitické materiály a ich morfologická charakterizácia. Chemický průmysl 1988;38:11–7.

[35] Munka K, Gajdoš L'. Overenie účinnosti filtračného média na báze chemicky modifikovaného prírodného zeolitu Klinopur-Mn pri úprave vody na modelovom zriadení v ÚV Kúty. Výskumný ústav vodného hospodárstva. Bratislava 2004.

[36] McGilloway RL, Weaver RW, Ming DW, Gruener JE. Nitrification in a zeoponic substrate. Plant Soil 2003;256:371–8.

[37] Li Z. Use of surfactant-modified zeolite as fertilizer carriers to control nitrate release. Micropor Mesopor Mater 2003;61(1–3): 181–8.

[38] Vasil'ev GV. Complete complex organomineral fertilizer (zeolite-3). Russ. 2004; RU 2223250 C2 20040210.

[39] Bagdasarov VR, Kazachenko AA, Rustambekov MK, Uspenskii BG, Kuznetsova VV, Efremov EN. Prolonged-activity nitrogen-zeolite fertilizer. Russ 2004. RU 2222514 C2 20040127.

[40] Alelishvili M, Andronikashvili TA, Tsitsishvili V, Dolaberidze N. On the possibility of growing cucumber and scallop without application of traditional fertilizers. Chem Environ Res 2003; 12(1–2):121–34.

[41] Hogrebe M. Container for slow fertilizer release in soil to plants. Ger Offen 2004. DE 10240938 A1 20040311.

[42] Janjgava N, Kardava M, Khazaradze N. Efficiency of natural zeolites and organic zeolite fertilizers in garlic growing. Bull Georgian Acad Sci 2003;168(2):305–8.

[43] Rimár J. Možnosti regulácie úrody jarného jačmeňa zeolitovými hnojivami. Agrochémia 1998;3:14–6.

[44] Rimár J, Gaval'ová Z, Zeleňák J. Zvýšenie účinnosti kvapalného hnojiva DAM 390 v kvantite a kvalite úrody plodín Výskumná správa. Chemko Strážske, 2001.

[45] Rimár J, Gaval'ová Z, Zeleňák J. Efektívnost' hnojenia sóje fazul'ovej. Agrochémia 2001;3:23–5.

[46] Sopková A, Bubanec J, Šingliar M, Černaj P, Fabián P. Ekologické hnojivo. ČSPV 1990:6523–90.

[47] Sopková A, Bubanec J, Černaj P, Šingliar M, Mondík P, Budínska V, et al. Hnojivá s vyššou účinnost'ou využívajúce prírodné zeolity. Chemický průmysl 1993;48(68):145–9.

[48] Chen Y, Wang L, Jiang S, Yu HJ. Study on novel antibacterial polymer materials (1) preparation of zeolite antibacterial agents and antibacterial polymer composite and their antibacterial properties. J Polym Mater 2003;20(3):279–84.

[49] Matsumura Y, Yoshokata K, Kunisaki S, Tsuchido T. Mode of bacterial action of silver zeolite and its comparison with that of silver nitrate. Appl Environ Microbiol 2003;69(7):4278–81.

[50] Šingliar M, Sopková A, Bubanec J, Fabián P, Kal'avský F. Využitie prírodných zeolitov v pol'nohospodárstve. Agrochémia 1992;32:91–3.

[51] Zeo agronomic technolofgy. Feed additive. 2004; http://www.zeoinc.com. Animal feeding.1999; http://www.atzzeoliti.it/applications.htm. Rotamin Feed Additive Reduction of the digestion system illnesses. 2004; http://www.rotamadencilik.com/rotamin.html.

[52] Rimár J, Gaval'ová Z. Využitie mravčanu vápenatého ako prísady do krmných zmesí, ale aj ako konzervačných prípravkov pre silážovanie objemových krmív. Výskumná správa. Chemko Strážske: 2002.

[53] Bindas L', Vajda V, Maskal'ová I. Využitie acidifikujúcich látok a zeolitov v chove ošípaných. V. Dni výživy a veterinárnej dietetiky. Zborník z mezdinárodnej vedeckej konferencie, Hrádok: 2002: 188–92.

[54] Skalická M, Koreneková B, Makóová Z, Nad' P. Vplyv aditív na vybrané produkčné ukazovatele hydiny. V. Dni výživy a veterinárnej dietetiky. Zborník z mezdinárodnej vedeckej konferencie, Hrádok: 2002: 237–9.

[55] Koňaková A. Overenie prípravku ZeoFeed na parametre úžitkovosti vo výkrme brojlerových kurčiat Bratislava:Ústredný kontrolný a skúšobný ústav pol'nohospodársky. 2003:protokol 316.

[56] Koňaková A. Overenie prípravku ZeoFeed na parametre úžitkovosti nosníc-biologická skúška. Bratislava: Ústredný kontrolný a skúšobný ústav pol'nohospodársky. 2003: protokol 317.

[57] Pascal P. Noveau traité de chimie minerale, vol. VXI. Paris: Masson et Cie; 1956. p. 542.

[58] Reháková M, Sopková A, Casciola M, Bastl Z. Ac and dc conductivity study of natural zeolitic material of the clinoptilolite type and its iodine forms. Solid State Ionic 1993;66:189–94.

[59] Reháková M, Bastl Z, Finocchiaro P, Sopková A. X-ray photoelectron spectroscopic studies of a iodine doped natural zeolite of CT type and its thermal degradated products. J Therm Anal 1995;45:511–8.