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USE OF ZEOLITE IN AGRICULTURE AND ENVIRONMENTAL PROTECTION. A SHORT REVIEW

In recent years there has been an increasing interest in the possibility of the use of natural aluminosilicates in agriculture and environmental protection. Zeolites are a large group of (cluster silicates) aluminosilicate minerals with different chemical composition. Due to their unique physical and chemical properties (high sorption capacity and ion-exchange, ion-exchange selectivity and structural thermal stability), they can be used for example in the production of mineral fertilizers. Zeolites can also be used as a medium of the active substances i.e. pesticides, herbicides, fungicides or pesticides. Their addition increases plant production levels and biological activity of the soil. Also zeolite's excellent sorption properties can be used for the remediation of soils contaminated with heavy metals. The history, structure, properties and application of natural zeolites is presented in this publication, based on the relevant literature.

Key words: zeolite, agriculture, remediation

Останніми роками зріс інтерес до можливості використання природних алюмосилікатів у сільському господарстві та охороні навколишнього середовища. До найважливіших скелетних алюмосилікатів належать цеоліти. Цеоліти – це велика група мінералів з різним хімічним складом. Завдяки їх унікальним фізичним і хімічним властивостям – високій сорбційній ємності та іонообмінності, селективності іонообміну і структурній термостабільності вони можуть бути використані, зокрема, у виробництві мінеральних добрив, а також як носії активних речовин – засобів охорони рослин, тобто пестицидів, гербіцидів чи фунгіцидів. Їх додавання збільшує виробництво рослинної продукції та біологічну активність грунту. І навіть більше, хороші сорбційні властивості цеолітів можуть використовуватись для рекультивації ґрунтів, забруднених важкими металами. Подано огляд літератури на тему історії, структури, властивостей та застосування природних цеолітів.

Ключові слова: цеоліти, клиноптилоліт, сільське господарство, відновлення.

Introduction

The first zeolitc mineral, stilbite, was discovered in 1756 by Swedish chemist and mineralogist Axel Fredicka Cronstedt. He noted that during heating, this natural mineral intensively loses water and named it using the Greek words: *dzeo* boil and *lithos* stone, rock. (Polat et al., 2005). Currently, there are over 40 known types of natural zeolites, but only seven of them (clinoptilolite, chabazite, mordenite, erionite, ferrierite, analcime, philipsite) are being exploited. Among natural zeolites most common and most studied mineral is clinoptilolite; not only because of its high occurence in nature and the lowest price, but also because of its unique physicochemical properties (Hubicki et al., 2000). Rich deposits of the clinoptilolite, the so-called clinoptilolite tuffs are present, among the others, in the Carpathian Mountains. It is estimated that there are deposits of the natural zeolite of over a billion tonnes in the village Sokirnica (Vasylij et al., 1998). Clinoptilolitee tuffs contain from 70 to 90 % of clinoptilolite and have a clear color with a tinge of white, gray, green or pink depending on the presence of impurities. Associated minerals are montmorillonite, seladonite, chlorite, cristobalite and pyrogenic minerals - quartz, plagioclase, biotite and K-feldspar. Currently, there are three ways of classifying zeolites. The first method is based on the topology of the framework (the three letter code), (Meier et al. 1996). The second way is classification in terms of the so-called "Secondary bulding units" (SBU’s), (Breck 1974). The third scheme is similar to the classification type SBU (Breck 1974) including the chronology in which zeolites were discovered (Baerlocher et al., 2007).

Structure and properties of zeolites

Zeolites are minerals naturally formed in the reaction of volcanic ash with surface water or groundwater. They can also arise in the non-volcanic environment during an interaction between the saline soil particles with strong basic solutions (Gworek and Suchard-Kozera 1999; Kumpiene 2010). They are crystalline, hydrated aluminosilicates of metals, including calcium, magnesium, sodium, potassium, strontium and barium. Due to their inner structure they are characterized by unique physicochemical properties: high and cation exchange sorption capacity, ion-selectivity, molecular sieving, catalytic activity and high thermal stability up to 750°C (Hubicki, 2000, Pitcher et al., 2004). The general chemical formula of zeolitesis written as [Barrer 1978, Chen 1978]:

$$Mx/n[AlxSiyO_2(x+y)]\cdot pH_2O$$

where M is (Na, K, Li) and/or (Ca,Mg, Ba, Sr), n is cation charge; y/x = 1–6, p/x = 1–4.Other formulas are also being used e.g. using patterns of oxide (Ciciszwili G.W. et al., 1990):

$$M_{2/n}O\ Al_2O_3xSiO_2yH_2O$$

for example for clinoptilolite: $(K,Na,1/2Ca)_2O\ Al_2O_3\ 10SiO_2\ 8H_2O$

The primary building unit of zeolite framework istetrahedron, the centre of which is occupied by a silicon oraluminum atoms, with four oxygen atoms at the vertices.Substitution of Si^{4+} by Al^{3+} provides the negative charge of theframework, which is balanced by monovalent or divalentcations located at the surface. The aluminosilicate framework,definingthe structure type, is the most stable component.

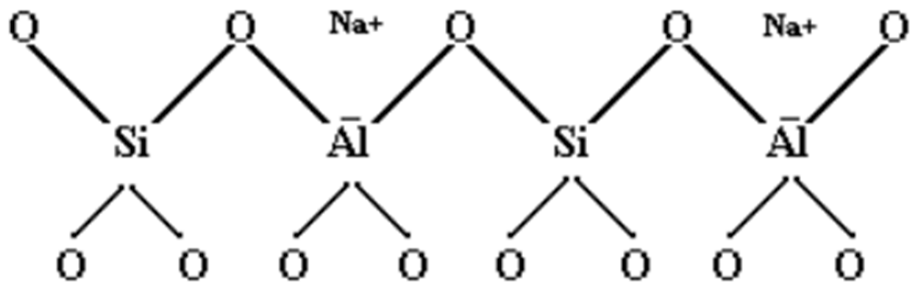

Fig.1. Schematic structure of the natural zeolite (Ciciszwili G.W. et al., 1990)

In natural zeolites, the molar ratio of silicon to aluminum (Si /Al) in the crystal is in the range 1 to 6 and is called a zeolite module. The Lowenstein rule determines the lower limit of the module. According to this rule AlO_4 tetrahedrons cannot be combined with other tetrahedron AlO_4 by mutual oxygen atom, and at the Si /Al ratio = 1 where AlO_4 and SiO_4 tetrahedrons form alternately the mineral skeleton (Barrer, 1980). In the clinoptilolite upper limit of Si / Al ratio reaches a value of 5÷6. Clinoptilolite is characterized by high thermal stability, which increases with the rise of their module. Clinoptilolite specific density is in the range 2,02-2,25 g/cm^3, and its hardness on the Mohs scale ranges from 3.5 to 5.5 (Brzychczyk., 2008). Zeolites have a high porosity. The porous structure of the zeolite crystals allows the selective penetration of particles of a certain size, dehydration and hydration of the crystals, the exchange of water to other molecules and the exchange of ions to different ones (while maintaining the condition of electroneutrality). For this reason, zeolites are well known as molecular sieves (Ceynowa J., 2005). In contrast to other known absorbents such as activated carbon or activated alumina, zeolites have a regular, replicable structure of internal pores and channels from 0.3 to 0.15 nm (Żygadło et al., 2010). Apart from high porosity zeolites are characterized by well developed surface area (about 200m^{2}g^{-1}). Moreover zeolites are capable to exchange ions with external medium,which is the most significant characteristic of zeolite. The equilibrium ion exchange isexpressed by the following equation(Pollard et al., 1992)

$$z_B A^{z_A^+} + z_A B L_{z_B} \Leftrightarrow z_A B^{z_B^+} + z_B A L_{z_A}$$

where z_A+ and z_B+ are the valences of the respective cations, and L is defined as a portion of zeolite framework holding unit negative charge. The ion-exchange behavior of natural zeolite depends on several factors, including the framework structure, ion size and shape, charge density of the mineral network, ionic charge and concentration of the external electrolyte solution (Bish and Ming, 2001).

All the above characteristics had the effect that zeolites are been used in various areas of human life where chemical and physicochemical processes are taking place.

The use of zeolites in agriculture

Natural and synthetic zeolites due to their unique physicochemical properties, have found wide application in many fields related to agriculture. They are being increasingly used in the production of mineral fertilizers with slow release and as carriers of active ingredients of herbicides, fungicides and pesticides.

One of the main advantages of using zeolite additive to fertilizers is their beneficial effect of retention of nutrients in the soil (Anonymous, 2004a). The nutrients are released gradually, not only in the first year of the vegetation period but also in the second or the following years. The most important nutrients necessary for proper growth and development of plants, are nitrogen, potassium, calcium and magnesium. They affect not only the size of the crop but also its quality. Zeolites have the ability to retain nutrients in the topsoil, which are slowly and gradually leached from the soil. This allows the use of smaller doses of fertilizer, which is associated with a reduction in the cost of crop production (DeLuca DK, 1997). The addition of zeolite to the fertilizer has a significant impact on the content of assimilative forms of nitrogen in the soil, especially on light and sandy soils (Polat et al., 2004). Because the soil doesn't absorb nitrates, these are washed out from the soil. The form of nitrogen that takes the longest to leach from the soil is an amide.The fertilizer of high nitrogen concentration in the form of an amide is urea (about 46 % by weight), which is used for the production of mineral fertilizers for several reasons. Firstly, the nitrogen of the urea is gradually taken up by plants. Secondly, the use of ammonium forms conducts the development of the root system as well as supports the downloading of phosphorus, sulphur and boron elements that stimulate normal growth anddevelopment of plants. Urea is used in the production of fertilizers with slow and controlled release. Zeolites are being used to produce this type of fertilizer. Production of the fertilizer consists of heating the zeolite to 400 ° C. During this process the water contained in zeolite's pores vapours and is being replaced by urea. The fertilizer of this type can consist of about 17 wt% of nitrogen. Urea, which is being closed on zeolites tubular takes a slow conversion to ammonium ions. As a result the nitrogen is slowly delivered to plants and it remains longer in the topsoil (Kowal, D., 2009).

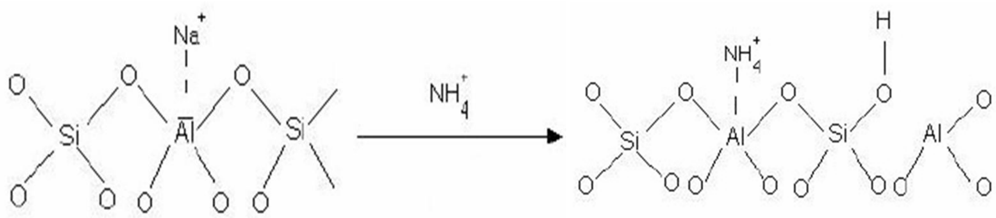

Fig.2. Scheme ion exchange of ammonium ion for sodium

Another advantage of zeolites is their ability to hydrate and rehydrate which may have a significant impact on maintaining proper water balance in the soil and prevent drying of soils and soil-like substrates. Due to high porosity, zeolite can store large amounts of water. This is particularly important during events of water deficit. Drought contributes significantly to the reduction of crop production, especially during active growth (Phillips 2006). The use of zeolite in drought periods has a significant effect on essential oil yield of Medicinal Peppermint (Ghanbari and Ariafar 2013). The addition of zeolite had a positive effect on physicomorpological characteristics of Moldsvian Balm (Gholizadeh et al. 2010).

An interesting application of zeolites is the production of antibacterial agents. They are obtained by introducing Ag^{+} ions into zeolite structure. Antibacterial activity is due to slow release of the active oxygen. Studies have shown the efficacy against bacteria such as Pseudomonas aeruginosa, Escherichia coli, Staphylococcus aureusm (Yoshihiro I. et al. 2002).

Zeolites are also used as a dietary additive to fodder. They help to partially neutralize the negative effects of micotoxins present in the feed. The zeolite action occurs predominantly in the gastrointestinal tract; it consists of disconnection of mycotoxin from the fodder particle and its absorption. Then it is being released with faeces. Adding natural zeolite of the clinoptilolite type to feed mixtures in low doses of about 1–2% influences very important functions heretofore not recorded by other natural compounds (Rehakova et al., 2004).

The use of zeolites in soil remediation

Increase of soil pollution by heavy metals is one of the main problems of modern agriculture. The increased accumulation of metals in soils is highly influenced by human activity and the related development of industry and irrational use of fertilizers. Heavy metals may persist in the soil for hundreds of years, which is associated with the risk of their inclusion in a trophic chain. Methods of the prevention of chemical degradation of soils are a complex and depend on many factors. The main factor determining the solubility of heavy metals in soil is low pH. This is explained by the fact that there is a slow dissolution of the oxides of iron, aluminium and manganese and also the release of heavy metals from the primary and secondary minerals in acidic environments (Karczewska 2002). Another important factor that determines the retention of heavy metal ions is the sorption capacity of soils, which is determined by the number and quality of soil sorption complex.

The ongoing concern in relation to the purity of the soil and the need to restore its original properties forced us to seek new and alternative ways of the soil cleansing. Natural and synthetic zeolites are being used among other additives (Leggo et al. 2006) to reduce the bioavailability of heavy metals in the soil The beneficial effect of zeolite on the pH and increase of soil sorption capacity is being a subject of studies for many years. The use of zeolites in acidic soils cause an increase in pH that significantly affects reduction in heavy metals solubility and bioavailability for plants. Except of ion exchange reactions, the pH increase promotes the adsorption of heavy metals on the surface of zeolites and their oxides precipitation (Yu et al. 2009).

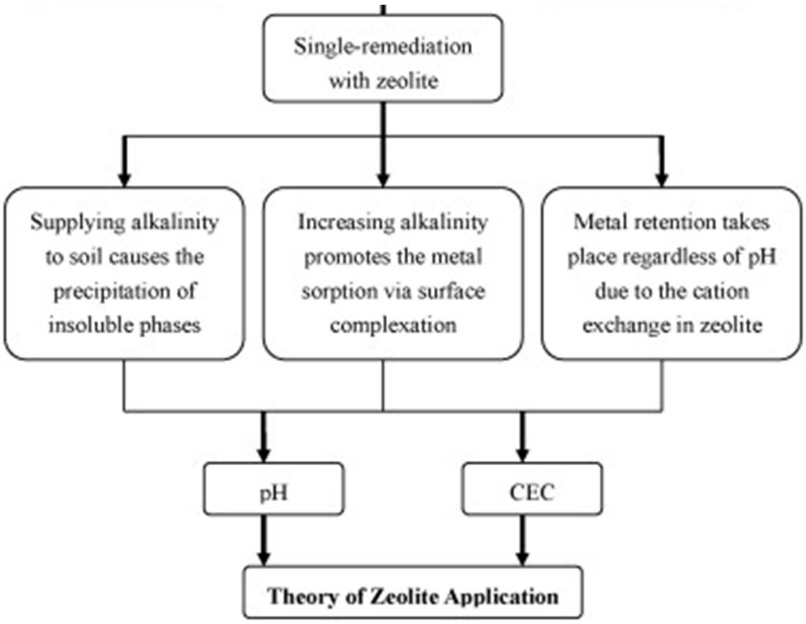

Fig.3. The scheme for the single-remediation of heavy metal-polluted soil with natural zeolite (Wei Shi -Yu et al., 2009)

Until now some studies have demonstrated advantages of zeolite for the remediation of heavy metal-polluted soils. The use of zeolites significantly reduced the uptake of cadmium and lead by wheat (Chen et al. 2000). Studies concerning the effects of various additives on a change of the solubility of lead, cadmium and zinc have shown that zeolites significantly reduced the solubility of lead and cadmium in polluted soils. As a result their content has significantly decreased in lupine white (compared to plants grown without the use of additives (Castaldi et al. 2005).

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. Due to its structure and properties zeolite may be used as a slow-releasing carrier of agrochemicals of various kinds and fertilizers. Natural zeolites are effective in improving soil properties and treating contaminated soil. A wide range of applications of zeolite promotes the pursuit of other possibilities for their use.

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1. Anonymous (2004)Manufacture of slow release fertilizers and soil amendment. http://www.zeolite.co.uk/agricandhort.html. 2. Baerlocher Ch. McCusker L.B., Olson D.H. (2007) Atlas of zeolite framework types. 6th revised edition. 3. Barrer R.M. (1978)Zeolites and Clay Minerals as Sorbents and Molecular Sieves. Academic Press. 4. Barrer R.M.(1980) Properties and Applications of Zeolites. Kent, Whitstable. 5. Bish L.W., Ming D.W. (2001) Applications of natural zeolites in water and wastewater treatment. Natural Zeolites: Occurrence, Properties, Applications 45, pp. 519-550. 6. Breck D. W. (1974) Zeolite Molecular Sieves: Wiley, New York, 771. 7. Brzychczyk B. (2008) Modelowanie termicznego procesu utylizacji odpadów z naturalnymi sorbentami zeolitowymi. PhD dissertation Akademia Górniczo-Hutnicza w Krakowie. 8. Castaldi P, Santona L, Melis P. (2005) Heavy metal immobilization by chemical amendments in a polluted soil and influence on white lupin growth. Chemosphere 60(3) 365-371. 9. Ceynowa J. (2005) Katalityczne membrany zeolitowe. Membrany teoria i praktyka. 10. Chen N.Y. (1978) Natural Zeolites. Occurence, Properties, Use. Pergamon Press, pp.421-430. 11. Chen Z.S., G.J. Lee, J.C. Liu (2000) The effects of chemical remediation treatments on the extractability and speciation of cadmium and lead in contaminated soils. Chemosphere 41 235–242. 12. Ciciszwili G.W., Andronikaszwili T.G., Kirow G.N., Filizowa L.D. (1990) – Zeolity naturalne. WNT, Warszawa. 13.DeLuca T.H., DeLuca D.K. (1997): Composting for feedlot manure management and soil quality. Journal of Production Agriculture, 10: 236–241. 14.Ghanbari M., Ariafar S. (2013) The effect of water deficit and zeolite application on Growth Traits and Oil Yield of Medicinal Peppermint (Mentha piperita L.), Int.J.Med.Arom.Plants, 3(1), 33-39. 15. Gholizadeh A., Amin M.S.M., Anuar A.R., Saberioon M.M. (2010) Water stress and natural zeolite impacts on phisiomorphological characteristics of moldavian balm (Dracocephalum moldavica l.). Australian Journal of Basic and Applied Sciences, 4 (10). pp. 5184-5190. 16. Gworek B., Sucharda-Kozera B. (1999) Zeolity – geneza, budowa i podstawowe właściwości fizyczne. Ochrona Środowiska i Zasobów Naturalnych, 17, str. 157–169. 17. Hubick Z., Rudaś M., Jakowicz A. (2000) Chemia i Inżynieria Ekologiczna. 9, nr 5–6, 603. 18. Karczewska A., Kabała C. (2010) Gleby zanieczyszczone metalami ciężkimi i arsenem na dolnym Śląsku - potrzeby i metody rekultywacji. Zeszyty Naukowe Uniwersytetu Przyrodniczego we Wrocławiu 576. 19. Kowal D., (2009) Metody wytwarzania granulowanych nawozów wieloskładnikowych z wykorzystaniem mocznika, PhD dissertation 20. Kumpiene J.(2010) Trace elements immobilization in soil using amendments. W: Hooda (red). Trace elements in soil, str 353-379, John Wiley and Sons. 21. Leggo P.J., Ledesert B., Christie G. (2006) The role of clinoptilolite in organo-zeolitic-soil systems used for phytoremediation. Sci. Total Environ., 363 , pp. 1–10. 22. Meier W.M., OIson,O.H., Baerlocher C. (1996) Atlas of Zeolite Structure Types. Elsevier 4th rev.Edition. 23. Polat E., Mehmet K., Onus Naci A. (2004) Use of natural zeolite (clinoptilolite) in agridulture. Journal of Fruit and Ornamental Plant Research vol.12, 183-187. 24. Phillips, N and Edwards J.,(2006) Cereal seed quality after drought. www.dpi.nsw.gov.au/cereal seed quality after drought. 25. Pitcher S.K.,. Slade R.C.T, Ward N.I. (2004), Heavy metal removal from motorway stormwater using zeolites. Science of the Total Environment, 334-335,161-166. 26. Pollard S.J.T., Fowler

G.D., Sollars C.J., Perry R.(1992) Low-cost adsorbents for waste and waste-water treatment—a review. Science of the Total Environment 116, pp. 31-52. 27. Rehakova M. , Cuvanova S., Dzivak M. , Rimar J., Gavalova Z. (2004) Agricultural and agrochemical uses of natural zeolite of the clinoptilolite type. Current Opinion in Solid State and Materials Science 8, 397-404. 28. Vasylij I., Gomonaj, Golub N.P., Szekeresh K. Y. , Leboda R., Skubiszewska-Zięba J., 1998, Badania nad przydatnością zakarpackiego klinoptylolitu do adsorpcji jonów Hg(II), Cr (III) i Ni(II) z roztworów wodnych, Ochrona środowiska 4(71). 29. Wei-yu Shia, Hong-bo Shaoa,, Hua Li, Ming-an Shao, Sheng D. (2009)Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite. Journal of Hazardous Materials 170, 1-6. 30. Yoshihiro I., Masanobu H. Hiroo T., Tomoko N., Tomomi M., Yasushi K., Hajime H., Masanori S.(2002) Bactericidal activity of Ag–zeolite mediated by reactive oxygen species under aerated conditions. Journal of Inorganic Biochemistry 92(1), 37-42.31. 31. Żygadło M., Seweryn A., Wozniak M. (2010) Synteza zeolitów na bazie popiołów lotnych z wybranych instalacji odzysku ciepła. Archiwum Gospodarki Odpadami i Ochrony Środowiska vol12(1), 15-26

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PRELIMINARY STUDIES OF DYNAMIC PARAMETERS IN MULTI-MATERIAL STRUCTURES WITH THE ADDITION OF ZEOLITE

The aim of this article is to present the results of preliminary research of the damping parameters of vibration in the constructions with the addition of zeolite. The first part of the article deals with the characteristics and application of zeolite. It describes mainly the impact of the addition of zeolite on the concrete parameters. The main part of the article presents the research outcomes of the damping parameters of the three models of plate-beam. The models contain modified binder in which the part of the concrete is replaced by the zeolite (with more than 85% content of the clinoptilolite). The values of the damping coefficients of vibration are determined by the collocation method as well as the method based on the estimation of kinetic energy of the vibrating system. The damping coefficients of the first three models of model vibration are determined.

Key words: damping parameter of vibration, zeolite, clionoptilolite, concrete.

Подано результати попереднього дослідження демпфірувальних параметрів вібрації у конструкціях з додаванням цеоліту. Перша частина статті стосується характеристик та застосування цеоліту, описано вплив додавання цеоліту на конкретні параметри. Основна частина статті – це результати вивчення демпфірувальних параметрів трьох моделей пластини балки. Моделі містять модифіковане зв'язувальне, в якому частину бетону замінено на цеоліт (з понад 85 % вмістом клиноптилоліту). Значення коефіцієнтів загасання вібрації визначаються колокаційним методом, а також методом, основаним на оцінці кінетичної енергії коливальної системи. Коефіцієнти загасання перших трьох моделей вібрації визначаються.

Ключові слова: параметр загасання вібрації, цеоліт, клиноптилоліт, бетон.

Introduction

While designing more complex bridges, overpasses, viaducts with substantial spread and low stiffness, it is significant to determine correctly the dynamic response of the structure. The operation life of