The use of Zeolite from Nižný Hrabovec for zeoponic substrates

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Abstract: Zeoponic substrates are artificial soils having zeolites as a major component. Other components frequently added to the zeoponics are apatite-rich phosphate rocks. The possibility of using zeolite from Nižný Hrabovec for zeoponic substrates was investigated in this work. The KOH solution used to prepare K-saturated zeolite has dissolved the weakly crystalline silica phases and thus helped to increase the amount of clinoptilolite. Mixtures of NH_4- and K-zeolites were mixed with deionized water to determine their K^+ and NH_4^+ release and exchange capacity. The highest amount of NH_4^+ was released when the fraction of K-zeolite was 50 and 80 %. Since a phosphate-rich rock is unavailable locally, we have chosen alginite from Pinciná (South Slovakia) as an alternative component for the zeoponic substrates. Mixtures of NH_4- and K-zeolite (1:1) in two fractions (<0.1 mm and <4 mm) were mixed with apatite and alginate in various ratios preparing zeoponic substrates. The ability of the prepared zeoponic substrates to release ions was tested in open and closed water systems depending on the time. The gradual ion release was observed for both zeolite-alginite and zeolite-apatite substrates. This is in contrast with the behaviour of a commercial (Klinofert) zeolite fertilizer and alginite from Pula. These substrates were releasing ions rapidly, and the final concentration of ions was significantly higher than that for the other substrates. The relative phosphate concentration increased with the increasing zeolite : apatite ratio, with a concomitant decrease in the released Ca^{2+}. This trend confirms that zeolites preferentially uptake Ca^{2+} from the solution driving apatite dissolution. The pure alginate from Pinciná released a higher P concentration than the pure apatite. The highest concentration of K^+ and NH_4^+ was released from the zeolite-alginite 5:1 substrate in the water system. The concentration sum of analysed elements was increased with time and with coarser zeolite fraction in zeoponic substrates. The zeolite-alginite or zeolite-apatite mixtures were mixed with quartz sand, and horticulture grass was sown into these artificial soils. The grass production was better with the alginite-based zeoponics. On the other hand, alginite has a low N content, and therefore the plant production on the pure alginite is lower than on the substrates with the alginite-zeolite mixture.

Key words: Nižný Hrabovec zeolite, alginite, apatite, NH_4- and K-clinoptilolite, zeoponic

1. INTRODUCTION

Zeoponic

High cation exchange capacity and selectivity, temperature stability, reversible dehydration and hydration, and low density predetermine zeolites for a number of applications. One of them is the potential to act as a slow-release fertilizer – a fertilizer whose ion release rate is slow. Two primary mechanisms can be employed to achieve the slow release of nutrients using zeolites: ion exchange and a combination of mineral dissolution and ion exchange (Ming & Allen, 2001).

Parham (1984) first used the term zeoponics to describe an artificial soil consisting of zeolites, peat, and vermiculite. Petrov et al. (1982) have successfully applied zeoponics to grow strawberies and peppers. Lai & Eberl (1986) were the first to examine the possibility of achieving slow-release fertilization by zeolite ion exchange (NH_4-, H-, Na-clinoptilolite) and apatite dissolution. Allen et al. (1993) have added K- clinoptilolite to the system. Nutrient release in these systems can be represented by the following simplified chemical reactions in which the chemical formula for fluorapatite is used as the phosphate rock:

$$0.5Ca_5(PO_4)_3F + 1.5H_2O = 2.5Ca^{2+} + 1.5HPO_4^{2-} + 0.5F^- + 1.5OH^-$$

$$(n+m)Ca^{2+} + (NH_4^+)_{2m} - \text{Clinoptilolite} + (K^+)_{2n} - \text{Clinoptilolite}$$
$$= 2mNH_4^+ + 2nK^+ + (Ca^{2+})_{(n+m)} - \text{Clinoptilolite}$$

These reactions will proceed until an equilibrium state is approached. At this point, the reactions stop until another process, such as nutrient uptake by plant roots, removes the reaction products from the system, driving the dissolution and ion-exchange reactions further (Ming & Allen, 2001).

Ming et al. (1995) improved the zeoponic system by substituting phosphate rock with synthetic hydroxyapatite. In addition to Ca and P, synthetic hydroxyapatite has Mg, S, and plant-essential micronutrients incorporated into its structures (Golden & Ming, 1999).

Several wheat crops grown on zeoponic substrates have suffered from Ca deficiency. The supply of calcium can be increased by adding another Ca-bearing mineral, such as calcite, dolomite, or wollastonite (Beiersdorfer et al., 2003; Gruener et al., 2003). Lancellotti et al. (2014) successfully presented using animal bone ash as an alternate P source in the zeoponic mixture.

The development of zeoponic substrates has emerged as one of the leading research topics in the area of using natural zeolites in the agricultural and horticultural industries. Both the Russian Space Agency and the U.S. National Aeronautics and Space Administration (NASA) have been conducting investigations on growing plants in space using zeoponic substrates (Ming & Allen, 1999). Zeoponic substrates may have advantages over hydroponic culture systems, which require sophisticated control and monitoring systems to maintain the nutrient levels

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and control pH. Commercially, zeoponic materials are being used as slow-release fertilizers for golf greens, potting soils for horticultural plants, and soil conditioners (Ming & Allen, 1999).

In this work, we have tested the potential of the Nižný Hrabovec zeolite for zeoponic application. We are also addressing the question of the substitution of phosphate rock by alginite. Slovakia has no known economical accumulation of phosphate rocks, but alginite is known to occur in larger quantities in southern Slovakia. The alginite from Pinciná is not a satisfactory replacement for the phosphate rocks as P source, as it contains only 0.15 to 1.64 wt% of P_2O_5 (Vass et al., 1997). On the other hand, other plant-essential nutrients are significantly more abundant in alginite than in phosphate rocks. Alginite is a rock rich in algal organic matter with a significant amount of clay fraction. The mean content of clay minerals on the alginite deposit are following: illite 35 %, kaolinite 15 % and smectite 10 %. The most common non-clay mineral is quartz followed by feldspars, carbonates, and cristobalite (Vass et al., 1997). This makes alginite potentially useful replacement of phosphate in zeoponic.

Nižný Hrabovec deposit settings

The Nižný Hrabovec zeolite deposit occurs in rhyodacite volcanoclastic rocks (Hrabovec tuff) of the Lower to Middle Badenian age. The Hrabovec tuff builds an 11 km long and up to 120 m wide belt between the villages of Pusté Čemerné, Nižný Hrabovec, Kučín, Majerovce, and Vranov in the East Slovak Neogene basin (Slávik, 1967; Varga, 1984; Baňacký et al., 1987; Baňacký, 1988). Nižný Hrabovec zeolite is a light-green, fine-grained rock. The originally vitreous material was altered to a zeolite, mainly K-, Ca-clinoptilolite. Less abundant minerals are cristobalite, quartz, intermediate plagioclase, K-feldspar, biotite, and traces of zircon and apatite (Šamajová & Kraus, 1977; Kozáč et al., 1982; Šamajová 1997, Tschegg et al., 2019, 2020). The recent whole-rock chemical analyses determined the zeolitic tuff as rhyolitic with a generally high-K calc-alkaline affinity (Tschegg et al., 2019). They presented essentially homogeneous clinoptilolite tuff compositions in spite of two clinoptilolite forms. The coarse-grained tabular clinoptilolites up to 30 μm replaced glass shards and grew into open pore spaces and almost submicroscopic clinoptilolites in the matrix (Tschegg et al., 2019, 2020). Nižný Hrabovec deposit is the largest zeolite quarry in Europe (estimated 150 Mt of clinoptilolite tuff), operated by the company Zeocem, a. s., Bystré, with a production of ~170 kt of zeolite in 2018 (Tschegg et al., 2019). Many possibilities of Nižný Hrabovec zeolite application have been tested since the 1980s. Zeolite found its use mostly in the building industry, agriculture, and environmental protection purposes, but also in other areas such as pet litter and pharmacy (e.g., Kozáč et al., 1982; Kozáč, 1989; Janotka et al., 2003; Reháková et al., 2004; Janotka & Krajčí, 2008; Chmielewská, 2014; Izzo et al., 2019; zeocem.com).

2. MATERIALS

The initial materials used for the preparation of the zeoponic substrates were zeolites (NH_4- and K-saturated), apatite, alginites, quartz sand, and a Klinofert fertilizer. The preparation, chemical and physical properties of the initial materials are described below.

Two Nižný Hrabovec zeolite fractions were used in zeoponic substrates. The coarser fraction (< 4 mm) was prepared from zeolite rock in our laboratory by crushing, grinding and sieving. The finer fraction (< 0.1 mm) is distributed by the company Zeocem. Clinoptilolite content ranges between 70 and 80 wt.%. The second most abundant phase is opal-CT and/or opal-C (16–23 wt.%). The remaining phases (plagioclase, dioctahedral mica, cristobalite, K-feldspar, quartz, pyroxene) have content ranging between 0,5 and 3 wt.%. The quantitative mineralogical composition was determined by X-ray diffraction (XRD) analysis using the program RockJock11 (relative errors is approximately ±4–6 %; Środoń et al., 2001; Eberl, 2003; Jánošík et al., 2013).

NH_4- and K-saturated zeolites were prepared according to the procedure of Kozač (1989), and modified to laboratory conditions. Zeolite was first activated by NaCl solution (120 g of NaCl in 1 l of deionized water). Na-saturated zeolite was combined with NH_4Cl solution (110 g of NH_4Cl in 1 l of deionized water) in a ratio of 1 g of zeolite to 5 ml of solution. The mixture was stirred for one hour at 90–100 °C, allowed to cool, and the redundant salt was washed with deionized water (8 times, redundant salt was not detected). NH_4-zeolite was dried at 70 °C. A portion of NH_4-zeolite was used for the preparation of K-zeolite. The NH_4-zeolite was mixed with a KOH solution (115 g of KOH in 1 l of deionized water) in a ratio of 1 g of zeolite to 5 ml of solution. The mixture was stirred for one hour at 90–100 °C, allowed to cool, and the redundant salt was wash with deionized water (at least 10 times). K-zeolite was dried at 70°C. The effect of preparation to both used zeolite was verified by XRD. Any changes were not observed in NH_4-zeolite. The composition was the same as in the initial sample. The significant change was determined at the K-zeolite. The amount of clinoptilolite increased from 75 to almost 90 wt%, and the total amount of opal-C or/and opal-CT and cristobalite decreased from 20 to less than 1 wt%. 2 M KOH solution that was used for K-zeolite preparation dissolved silica phases. The other phases were not affected. The removal of weakly crystalline silica, the second most abundant phase in zeolite from the Nižný Hrabovec deposit, helped to increase the amount of clinoptilolite. The concentrations of predominantly exchangeable cations in solid phases before and after the saturation procedure is shown in Tab. 1.

The second component of the zeoponic substrates was apatite or alginite. We used an apatite sample of an unknown provenience with a particle size of less than 0.1 mm. According to the X-ray diffraction (XRD) and chemical analysis, the sample

Tab. 1. Total amount of selected cations in natural and modified Nižný Hrabovec zeolites.

	Na %	K %	Ca %	NH_4 %
zeolite <0.1 mm	0.34	3.01	1.88	0.03
zeolite 1-4	0.22	2.49	1.59	0.02
K-zeolite <0.1 mm	0.24	7.60	0.40	0.02
K-zeolite 1-4	0.29	8.78	0.19	0.01
NH_4-zeolite <0.1 mm	0.44	0.99	0.26	2.75
NH_4-zeolite 1-4	0.25	0.81	0.16	2.06

consisted of fluorapatite (Vajdová, 2003). Two alginite samples were used, one from Pinciná (Slovakia) and one from Pula (Hungary, Vass et al., 1997).

As an inert component in our zeoponic substrates, quartz sand (0.2-8 mm) from Vyšný Petrovec (Slovakia) was used. In one of the control samples, we also applied a three-component (N, P, K) mineral fertilizer based on natural zeolite-clinoptilolite. We refer to this fertilizer by its commercial name Klinofert-NPK. The fertilizer is produced by the company Zeocem and is intended for the crops of vegetables and small fruits. The manufacturer's recommended rate (80 g/m^2) was used in our experiments.

3. METHODS

We conducted the following experiments with the prepared substrates (i.e., mixtures of the initial materials):

1. Exchange of cations between the solid and aqueous phase
   a) zeolite only
   b) multicomponent substrates, closed system
   c) multicomponent substrates, open system
2. Plant-growth experiments.

Exchange of cations between the solid and aqueous phase – zeolite only: Mixtures of NH$_4$- and K-zeolites were prepared in the following ratios: pure NH$_4$-zeolite, 4:1, 1:1, 1:4, and pure K-zeolite. Twenty grams of each mixture were then mixed with 200 ml of deionized water. The suspensions were shaken for one hour and then allowed to stand. After 5, 33, and 60 days, the suspensions were filtered, and the concentration of K$^+$ and NH$_4^+$ was determined.

Exchange of cations between the solid and aqueous phase – closed system: NH$_4$- and K-zeolites were pre-mixed in a 1:1 ratio for the preparation of the substrates. Zeolite was then mixed with apatite, alginite, or the Klinofert fertilizers, as specified in Tab. 2. In each case, 6.6 g of a substrate was immersed in 200 ml of deionized water. The conductivity of the solutions was measured every 4 days. After the conductivity measurement, the suspensions were shaken for 1 minute. Portions of the suspensions were filtered after 4 and 32 days, and the concentration of K, NH$_4$, Ca, P, Na, and Mg in the filtrate was determined.

Exchange of cations between the solid and aqueous phase – open system: NH$_4$- and K-saturated zeolites were pre-mixed in a 1:1 ratio for the preparation of the substrates. Zeolites were then mixed with alginite from Pinciná in ratios of 5:1, 1:1, or 1:5. A total of 5 g of the substrate was initially mixed with 150 ml deionized water (pH = 6.18 ± 0.3, conductivity = 3.8 ± 0.5 μS). The conductivity and pH of the solutions were measured approximately weekly for 13 weeks. An open system was simulated by water exchange after each conductivity and pH measurement.

All chemical analyses were performed in the Institute of Laboratory Research on Geomaterials of the Faculty of Natural Sciences, Comenius University in Bratislava. NH$_4$ was analysed by a spectral photometer Spekol 11 (Germany). K, Ca, P, Na, Mg were analysed by an atomic absorbtion spectrometer Perkin-Elmer 1100 (USA). Conductivity was measured by a conductivity meter Metler Toledo MC 126 and pH by a pH meter Mettler Toledo 1120.

Plant-growth experiments: The substrates with compositions listed in tab. 2 were also used in plant-growth experiments. Additionally, each substrate was mixed with quartz sand in three different ratios (4:1, 1:1, 1:4). A total of 53 mixtures were prepared by combining the initial materials. The mixtures were thoroughly homogenized and placed into plastic containers with dimensions of 110 x 58 x 40 mm. Approximately 1 g of horticulture grass seeds were sown into the artificial soil. The

Tab. 2. Solution concentrations of monitored elements after 4 (1) and 32 (2) days of interaction between substrates and water in closed system.

	Na mg/l		K mg/l		Ca mg/l		Mg mg/l		NH4 mg/l		P mg/l		Total	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
zeolite < 0.01 mm	1.32	3.09	4.79	9.82	0.16	0.16	0.11	0.06	9.86	11.20	1.28	2.20	17.52	26.53
zeolite : apatite 1:1	1.24	3.36	4.61	7.65	0.15	0.15	0.05	0.04	8.05	8.16	0.84	2.07	14.93	21.43
zeolite : apatite 5:1	1.68	3.87	4.56	9.27	0.11	0.20	0.08	0.07	9.36	9.25	1.65	3.74	17.44	26.40
zeolite : apatite 20:1	1.45	2.65	4.92	8.52	0.10	0.15	0.08	0.04	11.33	9.63	1.24	2.90	19.11	23.88
zeolite : alginite 1:1	2.00	2.87	5.68	8.55	0.62	0.91	0.15	0.25	7.45	7.86	1.63	2.23	17.52	22.66
zeolite : alginite 1:5	1.55	2.46	2.53	5.36	1.30	2.32	0.48	0.84	3.94	3.85	0.53	0.88	10.33	15.71
zeolite : alginite 5:1	1.82	3.28	4.76	9.69	0.36	0.43	0.10	0.11	8.86	10.08	2.03	2.33	17.92	25.92
zeolite < 4 mm	2.46	4.04	7.88	12.60	0.15	0.17	0.04	0.07	9.35	14.90	0.63	0.13	20.51	31.90
zeolite : apatite 1:1	1.60	2.61	7.20	8.55	0.16	0.18	0.02	0.04	5.40	9.55	0.90	0.85	15.28	21.77
zeolite : apatite 5:1	1.97	5.81	7.54	11.11	0.10	0.16	0.03	0.06	7.35	11.53	0.67	1.89	17.67	30.56
zeolite : apatite 20:1	2.16	3.76	9.20	11.90	0.30	0.20	0.04	0.06	7.90	14.48	0.93	1.41	20.55	31.81
zeolite : alginite 1:1	1.40	2.66	4.96	8.90	0.64	1.12	0.18	0.28	3.63	5.95	1.27	1.19	12.06	20.09
zeolite : alginite 1:5	1.37	2.75	4.68	7.00	1.60	2.70	0.60	0.85	1.67	2.81	0.31	0.47	10.22	16.58
zeolite : alginite 5:1	2.11	7.35	8.77	33.08	0.29	0.84	0.06	0.24	7.14	15.54	1.53	1.12	19.91	58.18
apatite	1.58	3.66	1.67	3.38	6.00	7.50	0.08	0.14	0.20	0.30	0.48	1.62	10.01	16.60
alginite – Pinciná	2.64	2.94	1.02	1.93	5.73	8.78	1.94	2.98	0.20	0.30	3.63	4.62	15.16	21.55
alginite – Pula	1.62	4.14	1.00	3.80	172.00	252.00	74.80	97.00	1.92	0.30	1.63	3.18	252.97	360.42
klinofert	0.37	1.21	10.20	33.80	3.00	4.30	0.52	0.72	24.60	34.80	5.22	6.23	43.91	81.06

plants were grown in a laboratory and watered regularly with deionized water. The conditions of dry and hot weather were simulated once during the experiment with 6 days of increased sunshine and no watering. The growth of the horticulture grass was monitored by measurements of the stalk lengths and weights.

4. RESULTS AND DISCUSION

Exchange of cations between the solid and aqueous phase – zeolite only

The interaction of zeolites with deionized water documented the different affinity of K^+ and NH_4^+ for the exchangeable positions in the zeolite structure (Fig. 1). The amount of K^+ and NH_4^+ released is not linearly proportional to the fraction of K-zeolite. The concentration of NH_4^+ in the analyzed solution is highest when the zeolite mixture contains 50 or 80 % of K-saturated zeolite (Fig. 1a). When the fraction of K-saturated zeolite is higher or lower, the concentration of the released NH_4^+ falls off. On the other hand, the concentration of the released K^+ relates to the fraction of K-saturated zeolite in the system, albeit not linearly. (Fig. 1b).

Most papers about ion-exchange properties of clinoptilolite have dealt with the sorption and selective sorption of ions but not with the desorption process – the release of the adsorbed substance (see a review by Pabalan & Bertetti, 2001). They documented a relatively high selectivity of clinoptilolite to K^+ and NH_4^+. Kithome et al. (1998) investigated ammonium desorption from a natural clinoptilolite material. They calculated reaction rate coefficients for the adsorption and desorption processes and showed that the rates for those two processes are similar.

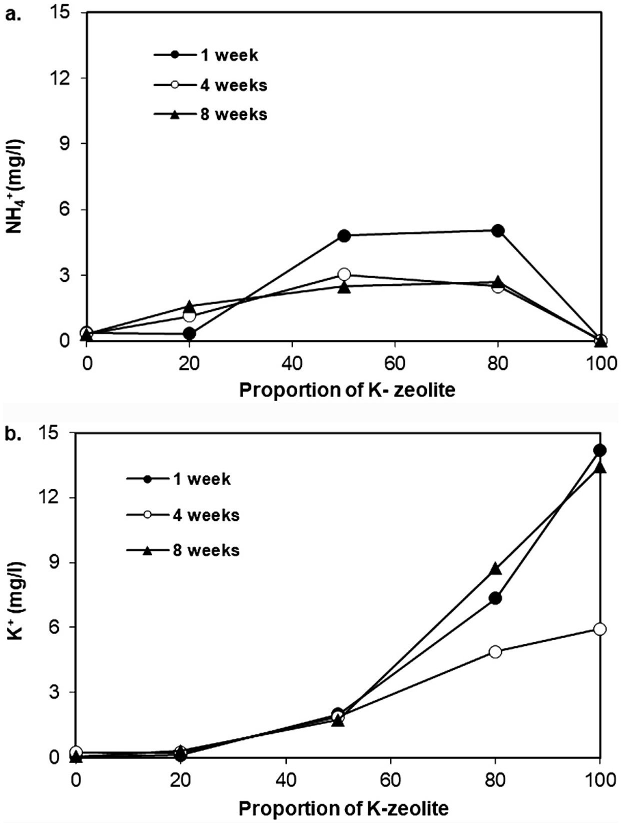

Fig. 1. Dependence of NH_4 (a) and K (b) release from various mixtures of NH_4- and K-saturated zeolites to water solutions.

Because of the similar ionic radii and the same cation charge of K^+ and NH_4^+, one could assume that the adsorption and desorption reaction rates are similar also in the case of potassium. Ames (1960) has already pointed out the competition between K^+ and NH_4^+ for the adsorption sites. Several papers showed that clinoptilolite prefers K^+ over NH_4^+ (e.g. Jama & Yucel, 1989; Casadella et al., 2016). Casadella et al. (2016) even presented that the desorption of NH_4^+ is higher than K^+ after a 24-hours experiment using 1.0 M HCl or ultrapure water at 60 °C. In contrast, some column tests showed a higher affinity of clinoptilolite-reach zeolites to NH_4^+ (Hedström & Amofah, 2008; Chmielewská, 2014). We observed that pure K-zeolite releases significantly more ions into the solution than the pure NH_4-zeolite (Fig.1). It shows higher desorption of K^+ and higher Nižný Hrabovec zeolite affinity to NH_4^+ than for K^+ in our case. The ion exchange in multiple-cation solutions is a dynamic process where the cations could be replaced several times by other cations (Inglezakis et al., 2003). For the above, we explain the observations shown in Fig. 1 as rapid desorption of K^+ from clinoptilolite and subsequent ion exchange of K^+ in the solution for NH_4^+ from the clinoptilolite exchangeable sites, whereas this mutual exchange may take place several times. In other words, the proportion of K- and NH_4-zeolite 1:1 and 4:1 generates an equilibrium state between the effort to bind and release K^+ rapidly and the reluctance to release NH_4^+. This caused more or less equivalent content of K^+ and NH_4^+ in the solution (Fig.1).

Exchange of cations between the solid and aqueous phase – closed system

Two different groups of zeoponic substrates could be distinguished concerning their interaction with deionized water. The first group comprises the Klinofert fertilizer and the Pula alginite. These substrates release ions rapidly, and the final concentrations of the ions were significantly higher than that of the other substrates. In comparison to the other suspensions, those with the Klinofert fertilizer and with the Pula alginite had five and ten times higher conductivity, respectively. The ion concentration in the suspensions with the Klinofert fertilizer and the Pula alginite rapidly reached a plateau and did not vary further (Fig. 2).

The conductivity measurements point to a gradual release of ions for the other substrates (Fig. 2). The shape of the measured curves (Fig. 2) is essentially the same for all substrates, with two exceptions. The two samples with a trend milder than the rest include the pure apatite substrate and the zeoponic with a finer zeolite and alginite in ratio of 1:5. The rate of ion release appears to be also a function of the zeolite grain size. The substrates with the coarser zeolite initial material (< 4 mm) release ions at the beginning of the experiment faster than those with the finer zeolite initial material (< 0.1 mm). The release rate of the substrates is roughly correlated to the total amount of ions released. Larger concentrations of ions were consistently found in the substrates that contain the coarser zeolite initial material. The conductivity measurements show that the lowest concentrations of ions were released from the pure apatite and both zeoponics with the zeolite : alginite ratio of 1:5. The highest amount of released ions was observed for zeoponic with the coarser zeolite and alginite in a ratio of 5:1 (Fig. 2).

Chemical analyses of the solutions support the results of the conductivity measurements. The largest amount of the released ions was found in the solutions in contact with the Klinofert fertilizer and the Pula alginite (Tab. 2). The difference between zeoponics with coarser and finer zeolite fractions was clearly established after 32 days. Among the zeoponic substrates, the largest number of cations was released from the one with coarser zeolite and alginite in a ratio of 5:1 (Tab. 2, Fig. 3).

The largest amount of ammonium was released from the Klinofert fertilizer. Both NH_4- and K-saturated zeolite fractions released a twice smaller NH_4 concentration (Tab. 2). The absolute concentration of NH_4 in the aqueous phase increased with the increase of the zeolite fractions in the prepared substrates (Fig. 3).

The largest amount of potassium was also released from the Klinofert fertilizer. In addition to the fertilizer, the zeolites and zeoponic substrates also released a significant amount of K. The amount of K released for the substrate composed of the coarser zeolite and alginite in a ratio of 5:1 is comparable to that released by the Klinofert fertilizer. The absolute concentration of K in the aqueous phase increased with the increase of the zeolite fraction in the substrates (Tab. 2, Fig. 3).

The largest amount of phosphate was released from the Klinofert fertilizer and the Pinciná alginite. Both pure alginites released more phosphate than pure apatite. On the other hand, substrates with apatite provided more phosphate than the substrates with alginite. The substrates with the finer zeolite released more phosphate than those with the coarser zeolite (Tab. 2). The relative concentration of phosphate in the solution increased with the increasing zeolite:apatite or zeolite:alginite ratios (Tab. 3). The greatest amount of phosphorus per 1 g of an additional component was released from apatite in a zeoponic with an apatite : zeolite ratio of 1:20. This trend indicates the ability of the zeolites to control of the apatite dissolution (Lai & Eberl, 1986; Allen et al., 1993; Ming & Allen, 1999). Beiersdorfer et al. (2003) noticed that P concentrations initially increased with increasing the zeolite : apatite ratio until the solution P reached a maximum value. A further increase of the zeolite : apatite ratio led to a decline in solution P concentration.

The largest amounts of Ca^{2+} and Mg^{2+} were released from the Pula alginite. This material released 25x more Ca^{2+} than the Pinciná alginite and pure apatite and 30x more Mg^{2+} than

Tab. 3. Phosphorus concentrations in solution after 32 days of interaction between substrates and water in a closed system. Values are in mg per 1 g of additive (*-apatite, **-alginite) to zeoponic substrates.

substrate		< 0.1 mm	< 4 mm
zeolite		0.07	0
zeolite : apatite 1:1		0.06*	0.05*
zeolite : apatite 5:1		0.35*	0.32*
zeolite : apatite 20:1		0.98*	0.82*
zeolite : alginite 1:5		0**	0.02**
zeolite : alginite 1:1		0.07**	0.07**
zeolite : alginite 5:1		0.09**	0.18**
apatite	0.05*		
alginite	0.14**		

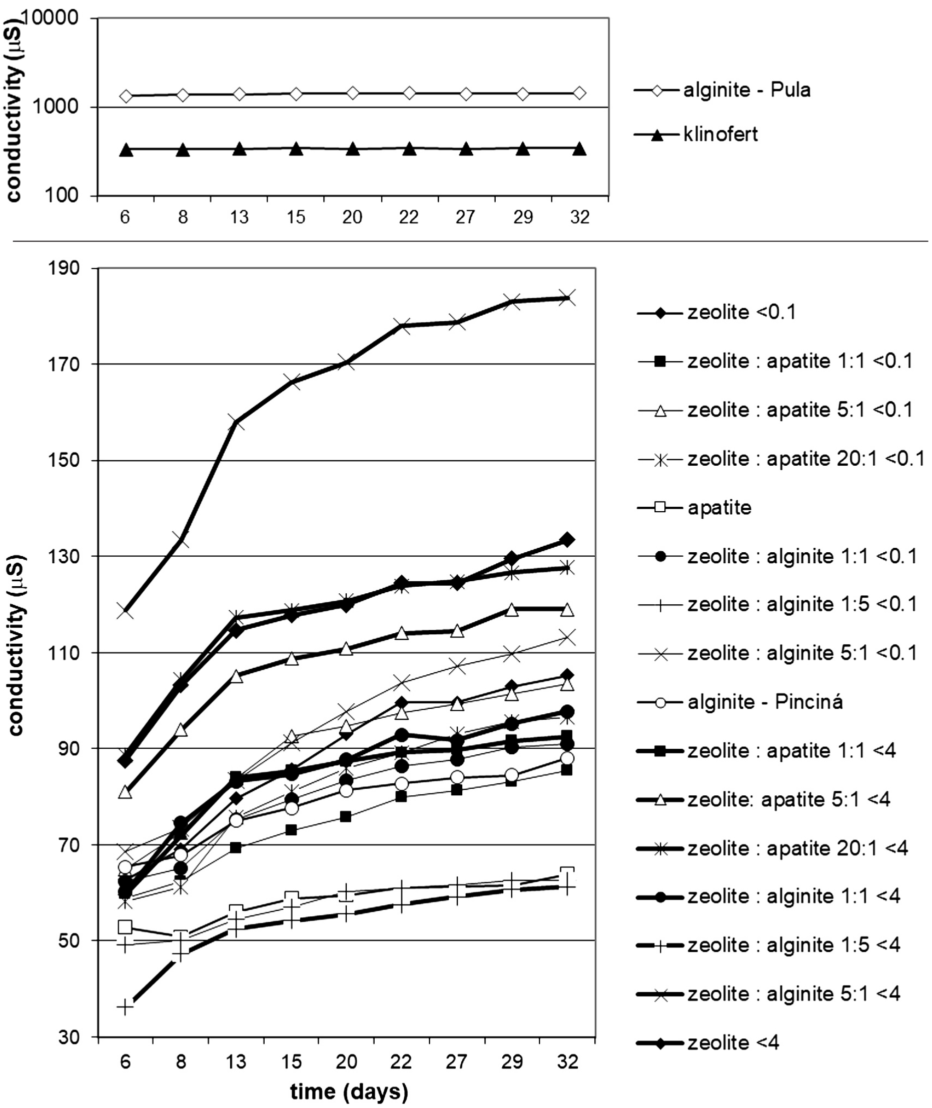

Fig. 2. The conductivity in solutions after immersing substrates to water in a closed system in dependence on time.

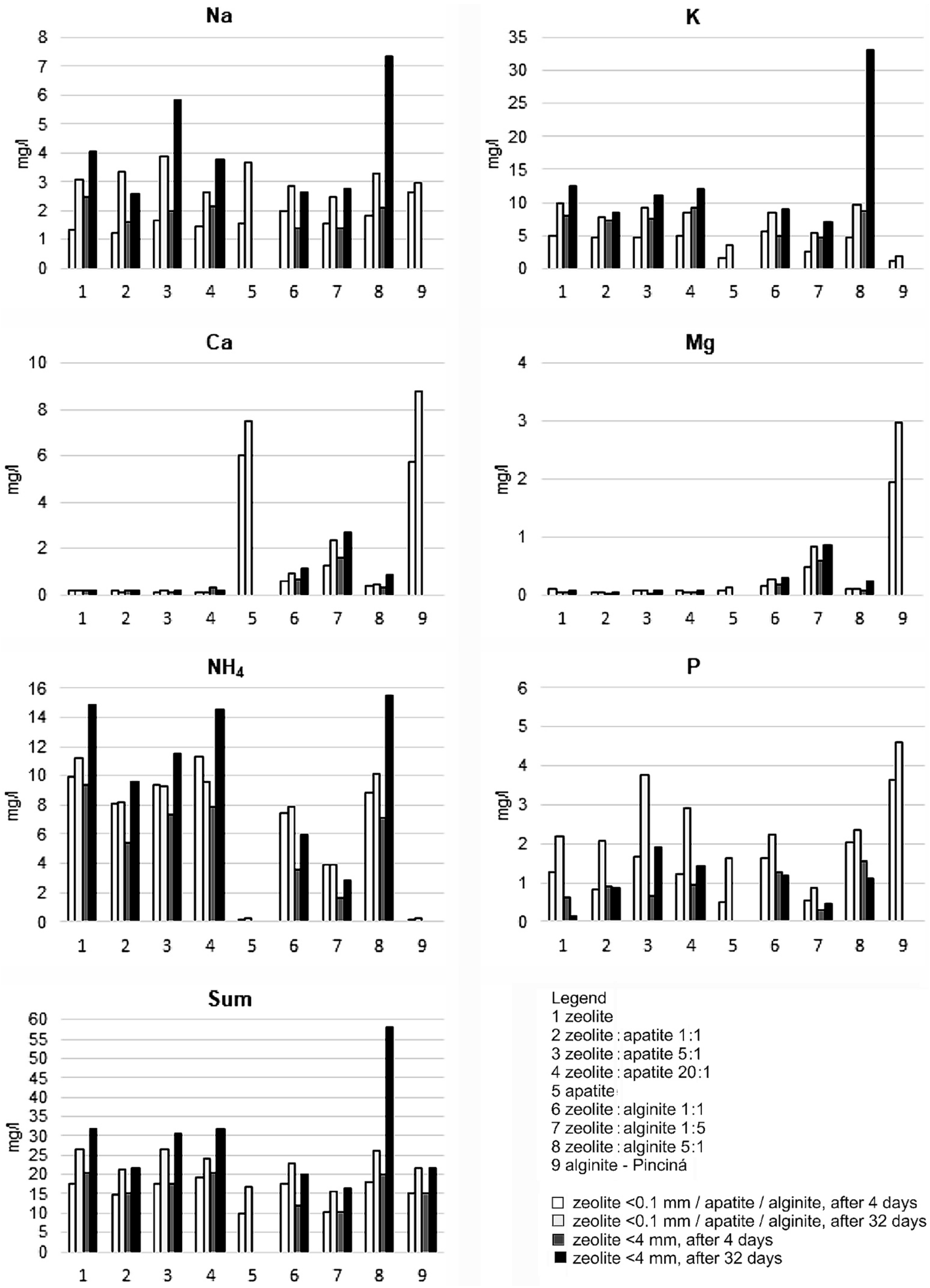

Fig. 3. Comparison of the chemical composition of solutions after 4- and 32-day interaction of zeoponic substrates with water in a closed system. (SUM – presents the sum of six measured elements)

the Pinciná alginite. In contrast, all substrates released only low concentrations of Ca^{2+} and Mg^{2+}. Only the solutions in contact with the substrates with a higher alginite fraction had higher concentrations of Ca^{2+} and Mg^{2+} (Tab. 2, Fig. 3). The largest amount of Na^{2+} was released from the substrate with a zeolite : alginite ratio of 5:1 (Tab. 2, Fig. 3).

Exchange of cations between the solid and aqueous phase – open system

The repetitive exchange of water in the simulated open system caused a decrease in pH (Fig. 4). The smallest pH variation was noticed for suspensions with the substrate with a zeolite : alginite ratio of 1:1 (from 7.75 to 7.24). The highest pH (8.59) was measured in the solution with a substrate in zeolite : alginite ratio of 5:1. The largest drop of pH (from 7.69 to 5.83) was recorded for the suspension with a zeolite : alginite ratio of 1:5 (Fig. 4). This pH drop is due to the largest fraction of alginite in the substrate. The alginite from Pinciná contains a relatively high number of sulphates (Vass et al., 1997). When alginite is the dominant component in the substrates, zeolites are no longer capable of maintaining a circumneutral pH of the suspension. More significant decrease in pH at substrate zeolite : alginite 1:5 caused an increase in conductivity in the last week of the experiment (Fig. 4–6).

The rate and the total amount of ions released from the substrates are a function of the zeolite : alginite ratio (Figs. 5 and 6). The largest variations and largest differences among individual substrates were observed in the initial stages of the experiment.

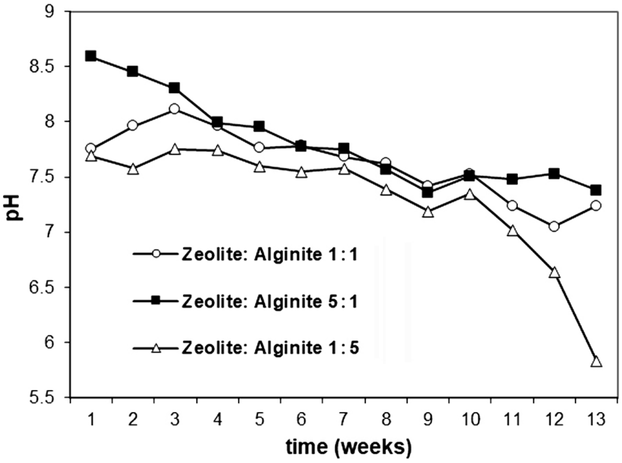

Fig. 4. Trends of pH measuring in simulated open water system with alginite zeoponics.

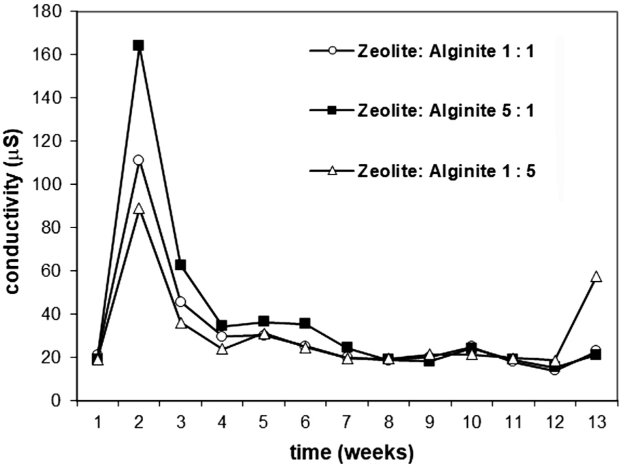

Fig. 5. Trends of measured conductivity in simulated open-water systems with alginite zeoponics.

Tab. 4. Production of grass on the prepared substrates. (zeol. – zeolite, alg. – alginite, ap. – apatite)

substrate	subs.:sand	zeolite fraction (mm)	growth of grass (cm)			
			after 28 days	after next 46 days	after next 39 days	in total
1 zeol. : alg. 1:1	1:1	< 0.1	6.5	10	12	28.5
2 zeol. : alg. 5:1	1:1	< 0.1	7	9.5	8.25	24.75
3 zeol. : alg. 1:5	1:1	< 0.1	8	10.5	15	33.5
4 zeol. : alg. 1:1	4:1	< 0.1	4.5	9.5	12.5	26.5
5 zeol. : alg. 5:1	4:1	< 0.1	5.5	10	12	27.5
6 zeol. : alg. 1:5	4:1	< 0.1	8.5	8.75	15	32.25
7 zeol. : alg. 1:1	1:4	< 0.1	8.5	9.25	8.25	26
8 zeol. : alg. 5:1	1:4	< 0.1	8.5	9	6	23.5
9 zeol. : alg. 1:5	1:4	< 0.1	8	9	11.5	28.5
10 zeol. : ap. 1:1	1:1	< 0.1	7.5	5.5	14.5	27.5
11 zeol. : ap. 5:1	1:1	< 0.1	7.5	9.5	11.5	28.5
12 zeol. : ap. 20:1	1:1	< 0.1	8	6	6.75	20.75
13 zeol. : ap. 1:1	4:1	< 0.1	5.5	10	8.25	23.75
14 zeol. : ap. 5:1	4:1	< 0.1	5	10.5	10.5	26
15 zeol. : ap. 20:1	4:1	< 0.1	5	10	8.25	23.25
16 zeol. : ap. 1:1	1:4	< 0.1	7.5	10.5	11.5	29.5
17 zeol. : ap. 5:1	1:4	< 0.1	8.5	8.5	5.5	22.5
18 zeol. : ap. 20:1	1:4	< 0.1	8.5	8.5	9.5	26.5
19 zeolite	1:1	< 0.1	6	9	7.75	22.75
20 zeolite	1:4	< 0.1	8.5	7.5	6	22
21 zeolite	4:1	< 0.1	7.5	7.75	6.5	21.75
25 sand			7.1	5	3.5	15.6
26 klinofert : sand			9.5	10	6.25	25.75
27 zeol. : alg. 1:1	1:1	< 4	10.5	21	19.9	51.4
28 zeol. : alg. 5:1	1:1	< 4	10.5	20	20.25	50.75
29 zeol. : alg. 1:5	1:1	< 4	11	17	20.25	48.25
30 zeol. : alg. 1:1	4:1	< 4	9	17	14.25	40.25
31 zeol. : alg. 5:1	4:1	< 4	9	14.5	16.5	40
32 zeol. : alg. 1:5	4:1	< 4	12	16.5	16.9	45.4
33 zeol. : alg. 1:1	1:4	< 4	11	21.5	20.6	53.1
34 zeol. : alg. 5:1	1:4	< 4	10	22.5	20.25	52.75
35 zeol. : alg. 1:5	1:4	< 4	10.5	22.5	16.13	49.13
36 zeol. : ap. 1:1	1:1	< 4	9.5	20.5	0	30
37 zeol. : ap. 5:1	1:1	< 4	9.5	16.5	13.5	39.5
38 zeol. : ap. 20:1	1:1	< 4	8.75	16	18.75	43.5
39 zeol. : ap. 1:1	4:1	< 4	9.5	16	15	40.5
40 zeol. : ap. 5:1	4:1	< 4	9	16	18	43
41 zeol. : ap. 20:1	4:1	< 4	9.5	17	15.4	41.9
42 zeol. : ap. 1:1	1:4	< 4	9.5	21.5	18.4	49.4
43 zeol. : ap. 5:1	1:4	< 4	9.75	21.5	22.5	53.75
44 zeol. : ap. 20:1	1:4	< 4	10.5	21.5	19.13	51.13
45 zeolite	1:1	< 4	8.5	10	6.75	25.25
46 zeolite	4:1	< 4	9	7.5	6.75	23.25
47 zeolite	1:4	< 4	8	16.5	7.9	32.4
49 alg. Pinciná	1:1		7.5	6.5	5.25	19.25
50 alg. Pinciná	4:1		7	6.5	6	19.5
51 alg. Pinciná	1:4		7.5	5.5	5.6	18.6
52 alg. Pula	1:1		10	13	7.5	30.5
53 alg. Pula	4:1		10.5	10	9.4	29.9
54 alg. Pula	1:4		7.75	7	7.13	21.88

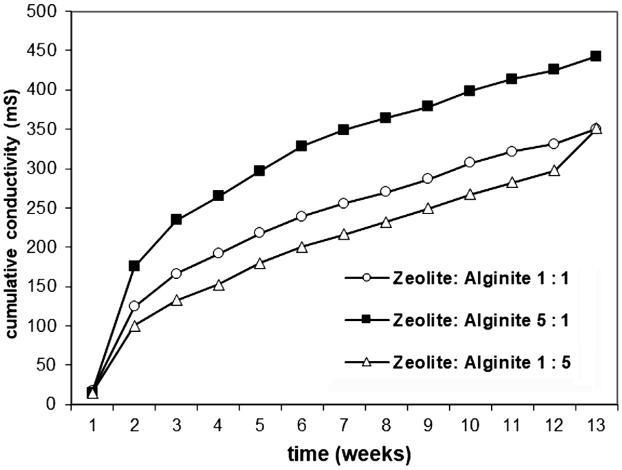

Fig. 6. Cumulative curves of measured conductivity in simulated open-water system with alginite zeoponics.

As the time progressed, the number of ions released from the various substrates converged to an equal value (Fig. 5). The same phenomenon can be read also from the cumulative curves whose slope is equal at the end of the experiment (Fig. 6).

Plant growth experiment

The amount of available nutrients in the soil environment is not the only important factor for healthy plant growth; the other significant factors include pH and aeration of soils, humidity and temperature, size of the root system, and light (Ivanič et al., 1984; Blume et al., 2016). For our experiments, all factors except for the available nutrients were kept constant. Therefore, the variation in the chemical and mineral composition of the substrates and their ability to release nutrients imposed the greatest influence on plant growth.

The biomass of the cultivated grass is linearly related to the length of the grass stalks, with only a few exceptions (Shiwa, 2004). Because of the linear dependence, the results are presented here only in terms of stalk length. The most important factor for plant growth appears to be the zeolite fraction size in the prepared substrates. The coarser zeolite fraction supported higher grass production because it provided conditions for better aeration of the soil (Tab. 4, Fig. 7) and more nutrients (Tab. 2, Fig. 3). Figure 7 shows that the substrates which support the greatest grass production are those in which zeolite, alginite, or apatite are mixed with a larger amount of sand. The grass production is enhanced, although the increased volume of sand as an inert component has decreased the total amount of the released nutrients to the system. In this case, the lesser amount of nutrients stimulates higher plant production. An explanation for this observation is that the substrates with a predominance of nutrients carrier overload the system with nutrients and actually have a detrimental effect on plant growth.

Although the length of the grass stalks is similar for the substrates with either apatite or alginite, the quality of plants is different. The differences were conspicuous after the simulated dry period especially. The grass on the alginite-bearing substrates was dark green with wide blades. On the other hand, the apatite-bearing substrates produced thin grass with light green to yellow colour. The difference is caused by several reasons. The finer grain size of the apatite concentrate, compared to the grain size of alginite, worsens the aeration of the artificial soil. Apatite is not able to retain a larger amount of water, but alginite is. Vass et al. (1997) found that a kilogram of the alginite from Pinciná can absorb and retain about 1 l of water. Simultaneously, the apatite-bearing substrates released smaller amounts of Ca^{2+} and Mg^{2+} (Tab. 2, Fig. 3). Both elements are important for normal plant growth, and their deficiency can cause the yellowing of the grass blades.

A shortage of Ca^{2+} is detrimental to the ontogenesis of the root system (Ivanič et al., 1984). Pure alginite and apatite released approximately the same amount of calcium (Tab. 2). A considerable reduction of released Ca^{2+} was detected after mixing the apatite with zeolite. In this case, the exchange capacity of zeolite removes this specific nutrient (Ca^{2+}) from the solution (Tab.5); Ca^{2+} replaced K^+ and NH_4^+ at the exchangeable sites in zeolites. Therefore, zeolites remove Ca^{2+} from the solution, but this removal forces additional K^+ and NH_4^+ into the solution (Lai & Eberl, 1986, Allen et al. 1993, Ming & Allen, 1999). A reduction of the released Ca^{2+} was also observed after mixing the alginite with zeolite but not so markedly. In this case, the amount of dissolved Ca^{2+} is suppressed by a relatively high amount of Mg^{2+} released from the alginite (Tab. 2, Fig. 3). The aqueous Ca^{2+} enhances the amount of the ammonium released from zeolite. As a result, the K^+ and NH_4^+ concentrations are comparable for substrates which release considerable Ca^{2+}. When we include no Ca-bearing component in the substrates, K^+ always dominated over NH_4^+ in the aqueous phase (Fig. 1). Our results point to a delicate interplay among the individual solid components and the aqueous phase. Zeolite from Nižný Hrabovec exchanges and releases ions in a different fashion in

Tab. 5. Comparison of calcium concentration in water solutions with apatite or alginite zeoponics. 1 – how many mg/l of Ca^{2+} would be released if the zeolite ion exchange did not work, according to the concentrations of Ca^{2+} from pure apatite or alginite from tab. 2, 2 – how many mg/l Ca^{2+} was released.

	after 4 days		after 32 days	
	1	2	1	2
zeolite < 0.01 mm				
zeolite : apatite 1:1	3.08	0.15	3.38	0.15
zeolite : apatite 5:1	1.13	0.11	1.39	0.20
zeolite : apatite 20:1	0.44	0.10	0.51	0.15
zeolite : alginite 1:1	2.95	0.62	4.47	0.91
zeolite : alginite 1:5	4.80	1.30	7.34	2.32
zeolite : alginite 5:1	1.09	0.36	1.6	0.43
zeolite < 4 mm				
zeolite : apatite 1:1	3.07	0.16	3.84	0.18
zeolite : apatite 5:1	1.12	0.10	1.39	0.16
zeolite : apatite 20:1	0.42	0.30	0.52	0.20
zeolite : alginite 1:1	2.94	0.64	4.48	1.12
zeolite : alginite 1:5	4.79	1.60	7.35	2.70
zeolite : alginite 5:1	1.08	0.29	1.61	0.84

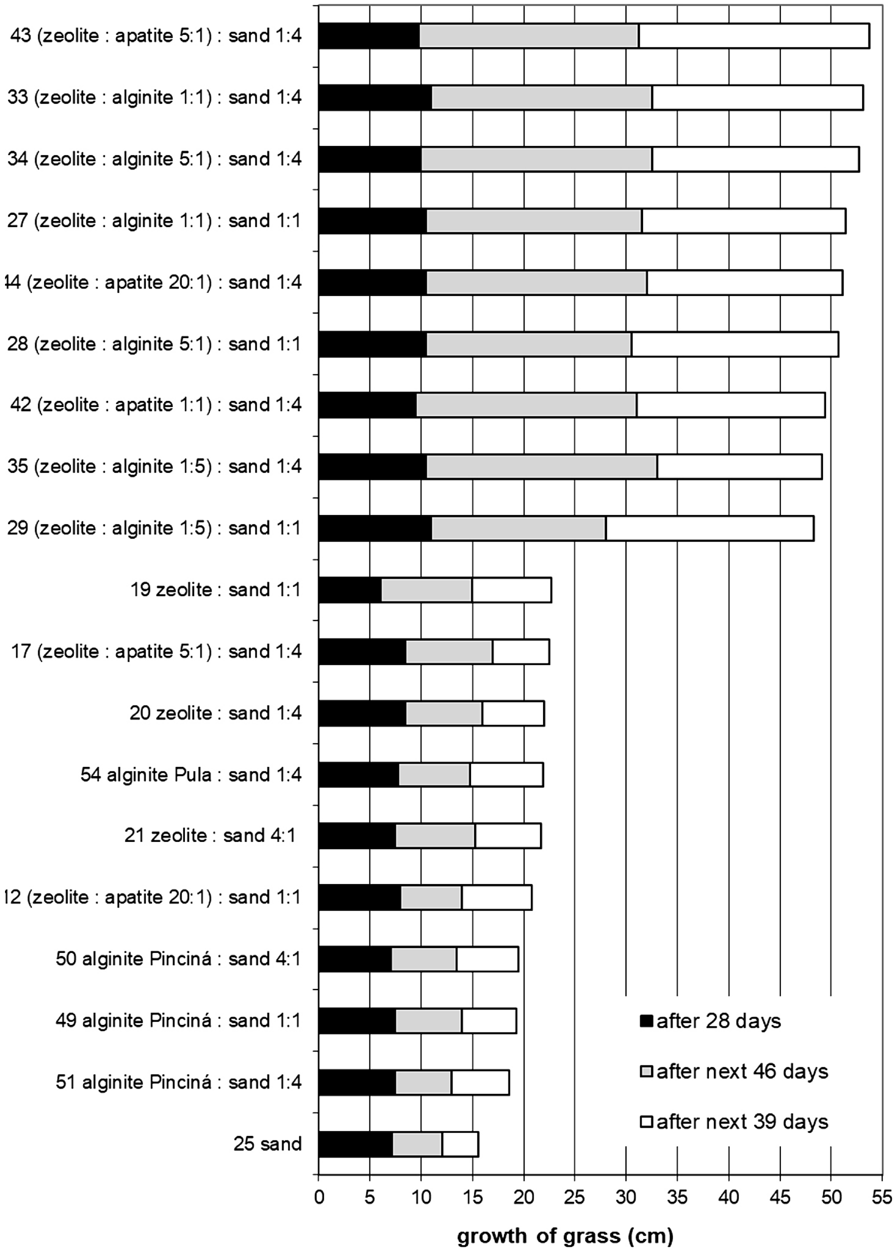

Fig. 7. Review of grass production. Selection of substrates with the longest and shortest blades. Zeolite fraction used in substrates number: 43, 33, 34, 27, 44, 28, 42, 35, 29 - <4 mm and in substrates number: 19, 17, 20, 54, 21, 12, 50, 49, 51, 25 - <0.1 mm.

the various binary and multiphase mixtures (Fig. 1, 3, Tab. 2).

Grass production on the alginite-quartz sand substrates is only half of that on the zeoponic substrates (Tab. 4, Fig. 7). The growth inhibition is caused by the K^+ and partly Na^+ deficiency in the alginite-quartz substrates (Tab. 2). Therefore, the combination of alginite with zeolite provides better conditions for the plant growth.

The changes in grass production were noticed during the grass growth on the sand with the Klinofert fertilizer. The grass belonged to the best after the first cut. Klinofert immediately provided a sufficient amount of nutrients (Tab. 2, Fig. 2). The size and quality decreased after the next cuts (Tab. 4). In the sandy substrates, the nutrients were quickly washed away to an underlying bowl. The sandy nature of these substrates strongly suppresses the upward and sideward capillary flow and depletes the pool of nutrients available to the plants (Kendle, 2001).

5. CONCLUSIONS

We have studied the ion-exchange capacity of NH_4- and K-saturated zeolites from Nižný Hrabovec. The zeolites, either pure or in a mixture with other components (apatite, alginite), release nutrients essential for plants into the aqueous phase and therefore are suitable as a component of zeoponic substrates.

In a mixture of NH_4- and K-saturated zeolites, the amount of NH_4^+ released is a more complicated function of the K-saturated zeolite fraction. Pure NH_4-zeolite released almost negligible NH_4^+. The mixtures of NH_4- and K- zeolites in ratios of 1:1 and 1:4 released the highest amount of NH_4^+ because of exchange reactions. The amount of NH_4^+ released from the NH_4-zeolite increased in the multi-component systems where Ca^{2+} is present.

A mixture of NH_4- and K- zeolite and apatite concentrate can provide the essential nutrients (N, P, K, Ca) and release them slowly, in agreement with previously published works about the zeoponic substrates.

The alginite Pinciná is a good substitute for apatite in the zeoponic substrates. Substrates with alginite provided better conditions for grass growth than those with apatite because of better aeration and a greater amount of available macro- and micronutrients. Our results show that a mixture of alginite from Pinciná and zeolite from Nižný Hrabovec is a fitting zeoponic substrate for cultivating garden turf, potted plants, or a simple soil conditioner.

The size fraction of the substrates influences plant growth. The coarser fraction (< 4 mm) allows for better aeration of the soil, more intergranular space for fluid migration, and consequently, also a greater amount of released nutrients. On the other hand, an overabundance of nutrients can affect plant production negatively. Every plant has a special set of requirements, which should be considered when applying the zeoponic substrates to the crops.

We determined that the best substrates for grass growth are the zeoponic substrates with the coarser zeolite fraction from Nižný

Hrabovec and alginite from Pinciná (in a ratio of 1:1 and 5:1). For the optimal nutrient release and balance, these substrates should then be mixed with sand in a ratio of 1:4 and 1:1. If such substrates are to be used commercially, an additional information about the long-term nutrient release, the production cost, and the cost effectivity in comparison with other marketed products will be needed.

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