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## USEFULNESS OF NITROGEN-ENRICHED GLASSY FERTILISER IN PLANTS FERTILISATION

### PRZYDATNOŚĆ SZKŁA NAWOZOWEGO WZBOGACONEGO W AZOT DO NAWOŻENIA ROŚLIN

**Abstract:** The aim of the present study was to assess the possibility of using composite type of fertiliser, containing glassy fertiliser as a source of P, K, Ca and Mg, as well as ammonium sulphate providing nitrogen, in horticulture. Potassium water glass was used as a binder.

The study evaluated moreover the influence of composition and granulation of fertiliser composites (two granulations: 1.5 mm and 5 mm) on their solubility in laboratory conditions, and therefore on the components release. The usefulness of composites in the cultivation of celeriac was also estimated on the basis of the analysis of substrate and plant material, as well as biometric parameters. The achieved composites were characterised by the limited usefulness in plants cultivation, as ammonium sulphate dissolved too fast.

**Keywords:** glassy fertilisers, nitrogen, solubility, usefulness

Glassy fertilisers are mineral fertilisers providing a plant with basic nutrients, such as phosphorus, potassium, calcium and magnesium, as well as with microelements (Cu, Fe, Mn, Zn, B, Co). The internal structure of glass is similar to the structure of silicate minerals, and has a form of a network composed of silicon, phosphorus and oxygen atoms. In the free spaces of this network other components are contained in their biologically active form. The structure of glass does not contain  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and other anions usually hardly tolerated by plants. Glassy fertilisers are produced by melting (in 1300–1400 °C) the mixture of such materials as: apatite, phosphorite, serpentine marble, potash (anhydrous potassium carbonate), and oxides incorporating appropriate microelements. The glassy mass obtained this way is cooled and then crushed. Due to vitrification and appropriate chemical composition, glasses are difficult to dissolve in water, which counteracts the occurrence of losses by preventing nutrients leaching from the soil. They do not contaminate the groundwaters, which makes them ecologically

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safe. On the other hand, they dissolve in the solutions of organic compounds produced in the soil by the root system of plants. Through the roots, the plants are able to absorb the nutrients in the amounts needed for their growth without the risk of overdosage. The mechanism of releasing the components of glassy fertilisers resembles natural processes of erosion. In the soil environment, the crystallization of secondary minerals, such as calcium and potassium silicates, takes place on the surface of glass. They gradually decompose, and the cations contained in them are released. The cycle of these changes depends on the environmental conditions (pH, concentration of nutritive components, temperature, soil biological activity) [1, 2].

The aim of fertilisation is to create optimal conditions for nourishing the plants, and thus satisfying their demand for all nutrients. Nitrogen is one of the most important elements to the plants, therefore its use in fertilisation is essential. Treated as a slow release fertiliser, the glassy fertiliser tested so far did not contain nitrogen, as to introduce it into the structure of glass required a complicated technological process to be applied. Therefore, a new type of fertiliser had to be developed. The fertiliser had a form of a composite which was supposed to provide the plants with nitrogen.

The aim of the study was to assess the usefulness of nitrogen-enriched glassy fertiliser in plants fertilisation. The experiments included the analysis of the influence of the composite fertilisers' composition and granulations on their solubility in solutions and in the soil, as well as on the nutritional status of celeriac plants.

## Material and methods

In the Department of Advanced Ceramics, AGH – University of Science and Technology composite fertilisers were prepared in different weight ratios and with constant amount of potassium waterglass (metasilicate of  $K_2SiO_3$  composition) used as a binder. In horticulture potassium silicate can be used as a soluble source of potassium and silicon. The fertilisers were a mixture of glassy fertiliser (39.3 % of  $SiO_2$ , 15 % of  $P_2O_5$ , 10 % of  $K_2O$ , 22 % of  $MgO$ , 14.4 % of  $CaO$ ) granulated to 0.1 mm and ammonium sulphate serving as a source of nitrogen (Table 1).

Table 1

Composition of composite fertilisers under study

Composite fertiliser	Glassy fertiliser [g]	Ammonium sulphate [g]	Potassium waterglass [cm <sup>3</sup> ]
1	75	25	8
2	50	50	8
3	25	75	8

The acquired mass was sieved into two granulations: 1.5 mm and 5 mm. Fertiliser pellets were dried in temperature of 100 °C for 60 minutes. The material obtained in this way was used in further studies that were conducted in three steps.

### Evaluation of composite fertilisers' solubility in solutions

1 g of composite fertiliser was shaken out of 100 cm<sup>3</sup> of extractor by a rotary mixer for 30 minutes. As extractors, distilled water and solutions used for determining the content of mineral elements in substrates and in fertilisers, i.e. the solution of acetic acid of 0.03 mol · dm<sup>-3</sup> as an extractor that is commonly used in horticultural cultivation [3], the solution of citric acid of 2 % applied in determining the content of phosphorus in phosphoric fertilisers, were used [4].

After they have been sieved, the samples were analysed for the content of such mineral elements as NH<sub>4</sub>-N, NO<sub>3</sub>-N, P, K, Mg and Ca. Mineral nitrogen was determined with Bremner's micromethod (modified later by Starck), and other components by means of ICP AES method [3].

### Incubation of composite fertilisers

The experiments were conducted on a brown soil containing (in 1 dm<sup>3</sup>): 3.8 mg NH<sub>4</sub>-N, 6 mg NO<sub>3</sub>-N, 77.7 mg P, 196 mg K, 84.4 mg Mg and 954.2 mg Ca. The soil acidity was expressed as pH = 7.33, and the total concentration of the salt (described by it EC) was 0.116 mS · cm<sup>-1</sup>. Composite fertilisers granulated to 1.5 mm and 5 mm were introduced into the substrate. Constant temperature of 22–25 °C and constant humidity of 60–70 % of the substrate was maintained during incubation. In the 3<sup>rd</sup>, 5<sup>th</sup>, 7<sup>th</sup> and 9<sup>th</sup> day single composite granules were taken to analysis. The surface of the composite fertiliser was evaluated with the scanning electron microscope (SEM) equipped in an adapter to X-ray analysis conducted within the micro-area monitored with energy dispersive X-ray spectroscopy (EDS).

### Pot cultivation of celeriac plant

In the second half of May, 3 g · dm<sup>-3</sup> of composite fertilisers granulated to the diameter of 1.5 and 5 mm were added into the pots filled with a brown soil in which celeriac seedlings (*Apium graveolens* L. var. *rapaceum* (Mill.) Gaud.) were planted. Each of the seedlings had 3–5 leaves measuring around 10 cm in length. The reason of choosing celeriac as the study object was its great demand for nitrogen, phosphorus and potassium. Now the process assumes using half of the advisable dose of nitrogen before planting the seedling, and then applying the rest once or twice by top dressing [5]. The use of slow nitrogen release fertiliser could however limit the top dressing fertilisation. To grow optimally, celeriac plant needs to be cultivated in the substrate of pH = 6.5–7. The study conducted so far on the glassy fertiliser showed the increase in the substrate acidity, irrespective of using physiologically acidic fertilisers [6]. After 8 weeks of cultivation (bunch harvest [5]), biometric measurements were conducted: the number of leaves, the length of leaves and stalks and the mass of the aboveground parts were evaluated.

At the same time index parts (stalks) were taken to analysis for the nutritional status of plants. The mineral and total nitrogen, as well as other nutrients' content was

determined with common methods [3]. The analyses of the substrate for the content of basic mineral components were done twice, ie before and after cultivation.

## Results and discussion

The solubility of composite fertilisers was evaluated in laboratory conditions in the analysis of the number of mineral elements released (leached) from these fertilisers. The content of  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ , P, K, Mg and Ca was measured in the samples. (Table 2, Fig. 1).

Table 2

Release of nitrogen from composite fertilisers by different extractors as shown by the example of 1.5 mm fraction

Composite fertiliser	Extractor	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	$\text{N}_{\text{min.}}$	N introduced in $(\text{NH}_4)_2\text{SO}_4$
		[mg · 100 cm <sup>-3</sup> ]			
1	Water	22.4	2.10	24.50	53
	Citric acid	22.4	2.45	24.85	53
	Acetic acid	26.3	3.65	29.90	53
2	Water	65.8	3.15	68.95	106
	Citric acid	61.3	3.15	64.40	106
	Acetic acid	73.85	4.03	77.88	106
3	Water	114.8	2.80	117.60	159
	Citric acid	114.5	3.15	117.65	159
	Acetic acid	131.9	4.38	136.33	159

The solubility analysis of individual composite fertilisers showed that it was ammonium sulphate and potassium water glass releasing nitrogen and potassium into the solution which dissolved first. The amount of mineral nitrogen available in solutions after shaking increased in line with the increase of ammonium sulphate in composite fertiliser. Both in citric acid and in water the amounts of nitrogen leached were similar. Acetic acid turned out to be the strongest extractor for this element. Greater amounts of ammonium nitrogen in comparison with nitrate nitrogen were noted in the solutions. Potassium is a component both of a glassy fertiliser and a binder. While dissolving in the extractors used, this element entered into the solution faster and in greater amount than the elements coming from the structure of glassy fertiliser alone.

Composite fertilisers showed poor mechanical resistance; the granules disintegrated during shaking.

In the second stage of dissolving, leaching of such elements as P, K, Mg and Ca originating from the structure of glassy fertilizer occurred. The more glassy fertilisers were contained in the composite fertilisers, the more elements originating from the

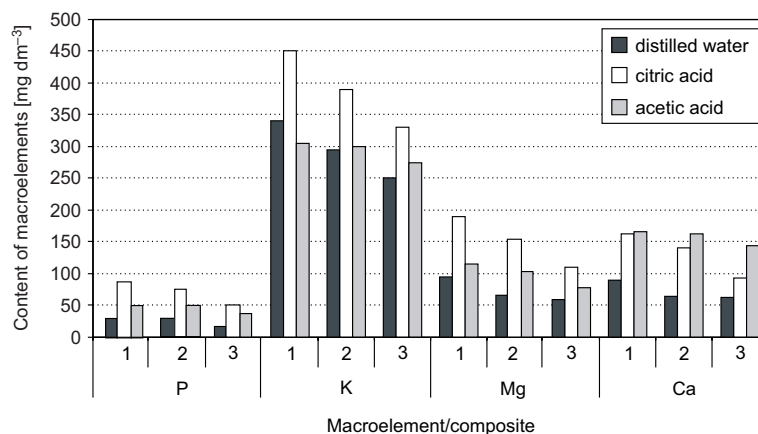


Fig. 1. Release of P, K, Ca and Mg from composite fertilisers by different extractors, as shown by the example of 1.5 mm fraction (1, 2, 3 – composite fertiliser)

structure of glass went into the solution. Citric acid turned out to be the strongest extractor for P, K and Mg, whereas the acetic acid for calcium (Fig. 1).

To assess the usefulness of composite fertilisers in horticulture, the processes of releasing nitrogen and the remaining mineral elements from the surface of glassy fertilisers during incubation in the soil were analysed. Dissolving of elements in the substrate went significantly slower than in the extraction solutions. However, after 3 days of composites incubation in the soil the presence of nitrogen was not detected. After 5 days, profuse occurrence of secondary calcium and magnesium phosphates were observed on the surface of glass. The size of composite granules had no effect on the occurrence of changes on the surface of glassy fertiliser. On the other hand, prolonged time of incubation caused dissolving of crystallised phosphates and gradual release of elements from them. After 9 days of soil environment's acting on the composite fertilisers, the total release of elements contained in the glassy fertiliser was noted, and the surface of the glassy fertiliser was enriched with silica.

Celeries intended to be sold in bunches are harvested when the plants have grown ca 10 leaves, which is between 6–8 weeks after planting of the seedlings [5]. Celeries collected after 8 weeks of cultivation had dispersed shape and weak leaf stalks. The parameters of leaves were similar (Table 3), although there was a tendency of observing higher values for the composites granulated to the smaller size. With the greatest content of ammonium sulphate introduced into the composite, the longest leaves and leaf stalks, as well as the aboveground parts were noticed, irrespective of the granulation.

Table 4 presents the results of determining the content of mineral nitrogen in the material under study. The sufficient level of  $\text{NO}_3\text{-N}$  in the largest celeriac leaf stalks is  $9000 \text{ mg} \cdot \text{kg}^{-1}$  [7]. It was only the plants fertilised with composite fertilisers of the smallest content of ammonium sulphate in which the amount of nitrates was similar to that value. In the rest of the object the concentration of  $\text{NO}_3\text{-N}$  exceeded that value very much.

Table 3

Selected parameters of the celeriac plant depending on the composition and granulation of the composite fertiliser

Composite fertiliser	Granulation [mm]	Average number of leaves/plant	Average length		Average mass of aboveground part [g]
			of leaf	of stalk	
			[cm]		
1	1.5	12.75	46.00	26.25	51.35
	5.0	12.25	46.00	25.50	49.84
2	1.5	12.50	46.25	26.25	55.02
	5.0	12.25	45.75	25.75	50.05
3	1.5	12.75	49.38	28.38	56.12
	5.0	12.75	47.50	27.00	55.46

Table 4

Average content of mineral N P, K, Ca and Mg in the celeriac leaf stalks

Composite fertiliser	Granulation [mm]	NH <sub>4</sub> -N	NO <sub>3</sub> -N	N <sub>min.</sub>	P	K	Mg	Ca
		[mg · kg <sup>-1</sup> ]			[%]			
1	1.5	2162.48	9204.84	11367.32	0.419	8.601	0.290	1.274
	5.0	2011.18	8377.83	10389.01	0.371	8.333	0.293	1.098
2	1.5	2495.45	19892.51	22387.96	0.339	7.732	0.240	1.063
	5.0	2438.74	18222.02	20660.76	0.344	8.024	0.227	0.931
3	1.5	6986.86	22320.97	29307.83	0.247	7.471	0.202	0.869
	5.0	3741.03	21942.06	25683.09	0.272	6.548	0.190	0.716

The contents of soluble forms of the remaining elements in the stalks of celeriac leaves are shown in Table 4. In the middle phase, the level of the element sufficient for PO<sub>4</sub>-P and K in celeriac stalks was 0.4 and 7 %, respectively [7]. The plants characterised by the optimal phosphorus content were only obtained when the ratio of glass to (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in the composite fertiliser was 3:1. On the other hand, the phosphorus content in the celeriac plants (excluding object 3 with granulation of 5 mm) exceeded the advisable value.

The tendency of diminishing the content of phosphorus, potassium, calcium and magnesium in the plant material, as well as the decrease in the amount of glassy fertiliser into the composite was observed. The lower content of elements was noted also when the granulation of the composites was greater.

To grow optimally, celeriac plant needs to be cultivated in the soils of pH = 6.5–7 [5]. When the share of glassy fertiliser in the composite was greatest (irrespective of granulation), the lower acidity and the lowest total content of salt in the substrate was observed (Table 5). What was also noticed was a clear acidifying activity of ammonium nitrate (physiologically acid fertiliser) [8]. The higher amount of ammonium sulphate was introduced into the composite, the lower was the acidity of the substrate. At the

same time, the total content of salt increased, as ammonium sulphate belongs to the group of fertilisers that have the greatest effect on the increase of the salt concentration in the substrate [8].

Celeriac is a plant of significant fertilisation needs. The soil used for cultivation must be rich in nutrients and humus. The optimal content of assimilable forms of nutrients amount to (in 1 dm<sup>3</sup>): 100–130 mg N, 60–80 mg P, 200–250 mg K, 60–80 mg Mg and 1000–1500 mg Ca [5].

Table 5

Content of mineral components, pH and EC in the soil, after the cultivation of celeriac plant

Composite fertiliser	Granulation [mm]	pH	EC [mS · cm <sup>-1</sup> ]	NH <sub>4</sub> -N	NO <sub>3</sub> -N	N <sub>min.</sub>	P	K	Mg	Ca
				[mg · dm <sup>-3</sup> ]						
1	1.5	6.99	0.49	42.0	14.0	56.0	204.1	137.9	290.7	1683.4
	5.0	7.17	0.54	24.5	17.5	42.0	183.8	119.6	288.0	1572.9
2	1.5	5.30	1.19	73.5	98.0	171.5	140.4	103.6	276.4	1533.4
	5.0	5.50	1.07	56.0	84.0	140.0	113.9	59.1	257.5	1470.4
3	1.5	5.25	1.32	94.5	115.5	210.0	111.2	55.7	235.7	1277.6
	5.0	4.95	1.33	112.0	168.0	280.0	92.9	49.9	231.2	1245.1

The greatest content of mineral nitrogen in the soil was observed in the objects with the highest value of ammonium sulphate in the composite fertiliser. The soil into which composites with glassy fertiliser and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in a ratio of 3:1 were introduced, the amount of nitrogen did not satisfy the needs of the celeriac plant. In the rest of the object the content of that element exceeded the advisable value. The increase in the amount of glassy fertiliser in the composite triggered the increase of its components in the soil. The amount of phosphorus and magnesium in the soil was high, whereas that of potassium was low. The concentration of calcium in the soil was within the range of standard values. The size of composite granules had little effect on the content of elements in the soil.

## Conclusions

1. The effects of using ammonium sulphate as a compound which introduced nitrogen to the composites were far from satisfactory.
2. Potassium water glass used as a binder did not slow down the dissolving of ammonium sulphate in the soil environment. Therefore the time of nitrogen release could not be prolonged.
3. It seems that the study on how to enrich the glassy fertiliser in nitrogen by using other sources of that element (eg urea), as well as other kind of a binder that would limit dissolving of the nitrogen-containing compound, needs to be continued.

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### PRZYDATNOŚĆ SZKŁA NAWOZOWEGO WZBOGACONEGO W AZOT DO NAWOŻENIA ROŚLIN

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**Abstrakt:** Celem badań była ocena możliwości wykorzystania w ogrodnictwie nawozu typu kompozytu nawozowego, zawierającego w swoim składzie nawóz szklisty jako źródło P, K, Ca i Mg, oraz siarczan amonu dostarczający azot. Jako lepsze zastosowano potasowe szkło wodne. Określano także wpływ składu i uziarnienia kompozytów nawozowych (dwie granulacje: 1,5 mm i 5 mm) na ich rozpuszczalność w warunkach laboratoryjnych, a tym samym uwalnianie składników. Oceniano również przydatność wytworzonych kompozytów w uprawie selera na podstawie analizy podłoża i materiału roślinnego, a także parametry biometryczne. Uzyskane kompozyty charakteryzowały się ograniczoną przydatnością do uprawy roślin, ponieważ zawarty w nim siarczan amonu zbyt szybko ulegał rozpuszczeniu.

**Słowa kluczowe:** szkła nawozowe, azot, rozpuszczalność, przydatność