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Principal studies on phosphate glasses for fertilizers

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Abstract

Compared to traditional phosphate fertilizers which are usually produced by dissolution of phosphate rock with acids, this functional fertiliser is a fusion product of basic substances used for manufacturing glass and pure phosphates. The particular advantage: variation of major compounds, duration and temperature in the smeltering and cooling process yields materials with solubility features that differ widely.

The results of the experiments reported here demonstrate that via glass composition the solubility rate of phosphate and silica-phosphate glasses can be effectively controlled. By adding silica the dissolution rate of these glasses can be varied at fixed relations of nutrients in the glasses. At the same time, these additions allow increasing pH of glass solutions and keeping their neutral reaction. Viscosity and crystallization ability of the glasses allow their easy granulation. The glasses could be adapted to a nearly complete solubility in 2 % citric acid within only a couple of days to up to four years. Thus it is possible to adjust the release of phosphate from the fertilizer to phosphate demand of the plant.

Keywords: glass, fertilizer, phosphorus

Zusammenfassung

Grundlegende Untersuchungen zur Eignung von Phosphatgläsern für die Herstellung von Düngemitteln

Im Gegensatz zu herkömmlichen Phosphordüngern, die üblicherweise durch Lösen von phosphorhaltigen Gesteinen in Säuren hergestellt werden, wird dieser Dünger aus den klassischen Grundstoffen der Glasherstellung unter Zusatz reiner Phosphate erschmolzen. Der besondere Vorteil: durch Variation von Ausgangstoffen sowie von Dauer und Temperatur im Schmelz- und Auskühlungsprozess lassen sich Materialien mit über weite Bereiche definierbaren Lösungseigenschaften fertigen. Durch Veränderung der Glaszusammensetzung können Lösungszeiten in 2 %iger Zitronensäure von wenigen Tagen bis zu vier Jahren eingestellt und so die Versorgung aus dem Dünger optimal an den Phosphorbedarf der Pflanze angepasst werden.

Schlüsselwörter: Glas, Düngemittel, Phosphor

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1 Introduction

The possibility to use phosphate glasses as fertilizers is being considered at least since the year 1945 [1, 2, 3]. The general background to use glassy phosphates in agriculture is based on their slow dissolution unlike one of crystalline phosphate fertilizers, which, after dissolution of the fertilizer in soils are rapidly immobilized through chemical precipitation and re-crystallization processes [4]. The idea is that a slow and controlled dissolution of phosphate glasses provides phosphorus and other nutrients more adjusted to plant uptake and also for several years. Dissolution rate and variety, and amounts of nutrients are parameters for optimization in the glassmaking process. The flexibility of glasses enables the variation of their composition and properties over a wide range. Fine-tuning of the composition of glasses is designed in such way that temperature dependent glass dissolution rates match plant growth and nutrient uptake rates. In some cases it is also desirable to have neutral or about neutral reaction of the soil solution when a glass-fertilizer dissolves. Generally, this can be also controlled through the composition of glass fertilizers. Thus, to evaluate the applicability of glass-fertilizers it is necessary to have reliable data on the relationship between composition and solubility of glasses, techniques to govern the acidity of the glass-fertilizer - water solution and methods to control the glass solubility if the nutrient composition (e.g. contents of K, Ca, and Mg [4] [5]) is fixed. Other advantages of glass fertilizers are the possibility to dope the glass with microelements for special plant nutritional requirements or for improving the granulation process.

The objective of this paper is to present a systematic study of phosphate glasses from the viewpoint of their suitability as fertilizers that includes their synthesis, characterization and solubility.
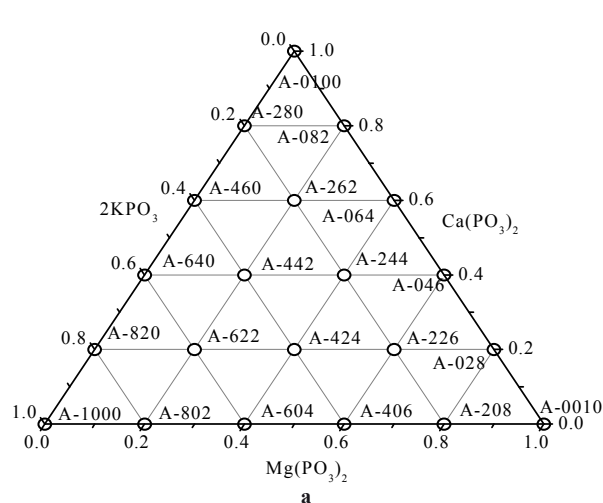
2 Materials and methods

2.1 Glass composition, synthesis, characterization and processing

Three types of glasses were synthesized and studied in the reported research project. Set A : phosphate glasses systematically varying in their composition in order to obtain information about the relationship between glass composition and the dissolution rate of the glass; Set B: phosphate glasses providing reasonable dissolution rate and neutral reaction of the solutions used in glass dissolution; Set C: silica-phosphate glasses allowing additional control of solution acidity and dissolution rate by adding silica. In addition, the most prospective glass was doped with microelements considered as essential for plant growth.

Set A (21 glasses) included metaphosphate compositions only, which are displayed as a triangle (Figure 1) and formalized as $x2KPO_3 \cdot yCa(PO_3)_2 \cdot zMg(PO_3)_2$, where $x + y + z = 1$ with x, y, and z running through values 0, 0.2, 0.4, 0.6, 0.8, and 1, or $(xK_2O + yCaO + zMgO) \cdot P_2O_5$, which is the same. These glasses were designated as Axyz, where x, y, z are x, y, z multiplied by 10. To anticipate a little, the dissolution rate of these glasses varied within 4 orders while the acidity (pH) of the aqueous solutions used in dissolution experiments did not depend on glass composition and tended to value 2.9 to within $\pm$ 0.1. This value was supposed to be due to a fixed content of phosphorus in the glasses which, when dissolving, provided the solvent with the same quantity of phosphorus-based acids. Therefore, one could expect a decrease in phosphorus content (a shift of glass compositions from meta- to pyrophosphates) to result in an increase in the solvent pH, up to the neutral reaction (pH ~7). To check this possibility, glasses with decreasing content of phosphorus (set B) were synthesized

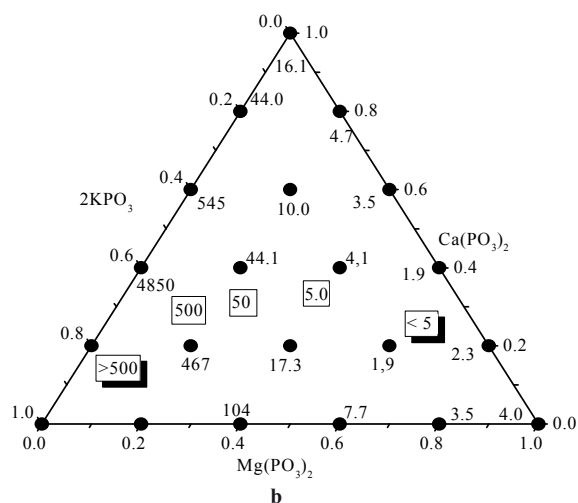Figure 1:

Compositions of the melted metaphosphate glasses of set A (left) and their dissolution rate constants in m/s $\times 10^{11}$ at 35 ºC and pH = 2.9 (right)

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(4 glasses). The nutrient content in the glasses of set B were chosen in such a way to provide 2-year dissolution of a 5-mm glass granule under the following climatic conditions: mean annual temperature equal to 10 ºC and its variation amplitude equal to 15 ºC. The compositions of these glasses can be formalized as $(xK_2O + yCaO + zMgO) \bullet P_2O_5$ with $x + y + z > 1$ (namely; $x + y + z = 1.33, 1.5, 1.71,$ and 2), $x = y + z$, and $2\,y = z$ (for glass B-1, $2\,z = y$).

Adding small amounts of silica to metaphosphate glasses decreases the relative phosphorus content and shifts glass compositions to pyrophosphate types. This may also change the acidity of a soil solution when such a glass dissolves. A higher content of silica can move glass composition out of the miscibility region and induce formation of two-phase glasses (Figure 8). These two-phase glass can contain either drops of other glass or crystallites as the second phase can influence relevant glass properties, too. Thus, spiking glasses with silica could be an additional way to control glass solubility without varying the relationship between basic components of glasses, that is, P, K, Mg and Ca. Glasses of set B (except glass B-1) were selected for silica spiking, and these new silica-doped phosphate glasses were designated as glasses of set C. Compositions of glasses of sets B and C are presented in Table 1.

Table 1:

Compositions of glasses of sets B and C

Glass code	Mol %					Note
	P_2O_5	K_2O	CaO	MgO	SiO_2	
			Set B			
B-1	33.33	33.3	11.1	22.2	0	
B-2	36.84	31.6	21.1	10.5	0	
B-3	40.00	30.0	20.0	10.0	0	
B-4	42.86	28.6	19.0	9.5	0	
			Set C			
C-1	39.4	29.6	19.7	9.9	1.5	
C-2	38.8	29.1	19.4	9.7	2.9	
C-3	38.1	28.6	19.0	9.5	4.8	Opalescent
C-4	37.7	28.3	18.9	9.4	5.7	Opalescent
C-5	36.7	27.5	18.3	9.2	8.3	Opalescent
C-6	41.7	27.8	18.5	9.3	2.8	
C-7	40.5	27.0	18.0	9.0	5.4	Opalescent
C-8	39.5	26.3	17.5	8.8	7.9	Opalescent
C-9	35.7	30.6	20.4	10.2	3.1	Opalescent
C-10	34.7	29.7	19.8	9.9	5.9	Opalescent

In accordance with the performed research, glass B-3 appeared to be the most promising one (due to its dissolution rate, solubility, and neutrality of solution reaction), and it

was chosen for doping with microelements. Two syntheses with this glass differing in total content of microelements were performed:the first glass was named B-3M1 and the second one B-3M2. Microelements were added in glass B-3 over 100 wt %, and their composition is presented in Table 2.

Table 2:

Compositions of microelement-doped glasses

	CuO	MnO_2	MoO_3	Fe_2O_3	ZnO	CoO	S	B_2O_3
B-3M1	0.61	0.61	0.61	0.61	0.61	0	0	0
B-3M2	0.025	0.051	0.024	0.012	0.024	0.026	0.025	1.44

All glasses were synthesized at 1200 - 1300 ºC by melting an appropriate 150-g batch in silica glass crucibles for 1 h with 10 minutes stirring. The initial reagents were KPO_3, $Ca(PO_3)_2$, $Mg(PO_3)_2$, and a fine powder of the prefabricated glass $K_2O \bullet 3SiO_2$. The melts were poured out into a carbon mould, and each resultant glass was annealed for 2 h at a temperature corresponding to the glass viscosity equal to $10^{12 \pm 0.5}$ Pa • s, for studied glasses these temperatures lay between 350 ºC and 550 ºC depending on glass composition. Only 3 glasses of set C were not opalescent, i.e. monophase ones. The last confirmed the expectations that spiking the basic phosphate glasses of set B (in particular, glasses B-3, B-4, and B-2) with SiO_2 shifted glass compositions to immiscibility region (in this particular case, to the region of liquid-liquid phase separation) when silica content exceeded ~1.5 mol. %.
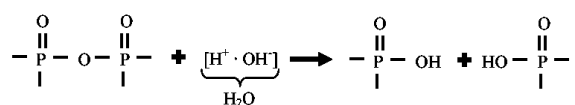
The majority of the synthesized glasses were studied by differential thermal analysis (DTA). In accordance with the DTA data, the studied glasses demonstrated one or two low-temperature exothermic peaks, corresponding to glass crystallization, followed by the same number of high-temperature endothermic peaks, corresponding to the melting of crystalline inclusions arising at lower temperatures. This study combined with the data on glass viscosity allowed determining temperature range, which could be used for glass granulation, i.e. where no crystallization occurred. In addition, the DTA curves were used for express determination of glass transition temperatures, which are necessary for glass annealing. The DTA studies were accompanied with the study of glass crystallization in the field of temperature gradient (polythermal analysis). This provided additional information on the type of glass crystallization (bulk or surface crystallization) and more exact temperature ranges where the glasses under study crystallized and, therefore, could not be granulated.

All opalescent glasses, the glass probes obtained after DTA and polythermal analyses were studied by X-ray powder diffractometry to get information on the crystal-

line phases precipitating in glasses after heat treatment or melting. For this purpose the glasses were either grinded to obtain a powder with given size of grains or cut, lapped and polished to obtain glass plates. In addition, several selected glasses were granulated.

2.2 Theoretical and Experimental studies on glass solubility

In the case of pure metaphosphate glasses or metaphosphate groups of glasses with lower phosphorus content, glass dissolution is supposed to develop though hydrolysis as follows:

$$-\overset{\overset{O}{\|}}{\underset{|}{P}}-O-\overset{\overset{O}{\|}}{\underset{|}{P}}- \ + \ \underbrace{[H^+ \cdot OH^-]}_{H_2O} \ \longrightarrow \ -\overset{\overset{O}{\|}}{\underset{|}{P}}-OH \ + \ HO-\overset{\overset{O}{\|}}{\underset{|}{P}}-$$

One can see that a pair of ions, that is, H^+ and OH^-, is involved in the process. Given the concentration of the pairs being unchangeable in the course of glass dissolution, the simplest model of glass dissolution kinetics appears to be a linear one, which implies a linear increase of the thickness of the dissolved layer d in time that is, $d(t) = kt$, where k is the dissolution rate constant and t is the dissolution time. Surely, the rate constant of glass dissolution depends on the acidity of the solution, i.e. on pH of the solvent. Glass dissolution being an activation process, the rate constant can be formally presented as $k(T) = k_0 exp(-Q/T)$, where k_0 is the constant parametrically dependent on the solvent pH and Q is the activation enthalpy of glass dissolution (in °K). Both Q and k_0 can be found from the kinetic curves describing a decrease of the glass sample weight, W, in time. As glass dissolution takes place at the surface of the glass sample only, the shape of kinetic curves $W(t)$ profoundly depends on the sample geometry, and it is evidently that plate-shaped samples are the most suitable for studying dissolution kinetics. It is because the total sample surface during its dissolution remains practically unchangeable, and, therefore, dissolution curves $W(t)$ correspond to a linear function and rate constants can be found just from the slopes of these linear curves $W(t)$. In this study, the samples were plates with sizes $a = 0.02$ m, $b = 0.03$ m, and $c = 0.001$ m so that upon full dissolution their total surface decreases only by ~4 %. In accordance with the suggested model of glass dissolution and allowing for $c \ll a$, $c \ll b$, and $2d \le c$, the dissolution kinetics can be described by equation $W(t) = \rho V(t) = \rho\{ab[c -2d(t)]\}$, where ρ is the glass density, V is the sample volume. After substituting $d(t)$, a, b, and c and corresponding reductions, the kinetics equation can be written as $W(T,t) = W_0 -0.0012 \rho k(T)t$, where W_0 is the initial weight of the sample. For each glass the dissolution rate constant k at fixed temperature and solvent pH can be found from the slope of linear dependence $W(t)$. The values Q and k_0, in its turn, can be found from the temperature dependences of $ln[k(T)]$ plotted against $1/T$.

Activation parameters Q and k_0 found at a given pH can be used to evaluate the life-time of spherical glass granules in the solvent (soil solution) with this pH and under condition of arbitrarily changing temperature. In the present study the pH of the soil solution is considered to be equal to ~3, and temperature evolution during a year is characterized by a sine curve oscillating around 10 °C with the oscillation amplitude equal to 15 °C. In this simulation, except the temperature dependence of k, the fact that glasses cannot dissolve below 0 °C (as the soil solution is frozen) is allowed for. In the life-time simulations, spherical shape of glass granules is taken into consideration via the corresponding modification of the kinetics equation that is $W(t) = \rho V(t) = 4/3 \cdot \pi\rho[R - d(t)]^3$ (or $W(t)^{1/3} = W_0^{1/3} - (4/3 \cdot \pi\rho)^{1/3}kt$), where R is the initial granule radius. The criteria of glass selection are their life times lying within 2 - 4 years and technological glass properties meeting all the requirements to glass granulation. The latter implies, in particular, the absence of glass crystallization at the temperature range where glass viscosity allows glass granulation.

2.3 K-technique (kinetics of glass dissolution)

To find values Q and k_0, dissolution kinetics of glasses is studied in an aqua solution of citric acid with fixed pH (equal to 2.9 ± 0.1) at 3 temperatures, namely; 35, 50, and 65 °C. Temperature variations do not exceed $\pm$ 1 °C. Preliminary weighted samples are immersed in the solvent with stirring for a certain time long enough to obtain a weight loss essentially exceeding the accuracy of the used balance ($\pm$ 0.0005 g). Between weightings the samples are dried by warm air. This procedure is repeated several times to obtain perceptible changes in the sample weights. The volume of the solvent is 2 liters, and the number of the samples in a single experiment is 10 so that the total samples' volume and the volume of the solvent are in the ratio of 3 to 1000. In the experiments performed at different temperatures the solvent pH, which depends on temperature is maintained the same and equal to 2.9 ± 0.1 by varying concentration of citric acid. Glass dissolutions are performed with permanent monitoring of pH.

To characterize and evaluate the influence of glass composition on the solvent pH and glass solubility, two additional techniques have been used. They are called "Express" (E-technique) and "Long-term" (L-technique).

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2.4 E-technique

A 2-g probe of the glass powder (grain size equal to ~300 μm) is dissolved in 50 ml of distilled water (solvent) whilst stirring in a beaker made of silica glass. The solvent pH is measured during the glass dissolution (in every minute during the first 10 minutes, and then, every 10 minutes during 1 hour). The solvent pH is measured with a standard pH-meter. E-technique allows an express evaluation of the solvent pH varying in the course of the glass dissolution. At the same time, given the total open surface of the powder being rather large (~160 cm^2) and the volume of the solvent used being small, E-technique is supposed to model surface conditions of grain dissolution in moist soil.

2.5 L-technique

A rough-grinded and weighted glass sample 25×15×8 mm^3 (about 5 ÷ 8 g) is dissolved in 30 ml of distilled water (solvent) without stirring in a closed glass beaker. The beaker with the sample is kept in a desiccator at 35 ºC for a long time (up to ~200 h). Periodically, the beaker is weighted with and without the glass sample, the solvent pH is measured at room temperature, and the sample is weighted after drying at 35 ºC up to the moment when its weight ceases changing. Concentration of the dissolution products, C [g/l], passing into the solvent is calculated from the weight loss of the sample and with allowance for the loss of the solvent volume due to evaporation. In distinction from E-technique, L-technique in a certain sense is considered to model real processes in soil, where the circulation of soil solution in the vicinity of a fertilizer grain is rather slow and the volume of soil solution directly involved in dissolving a single grain is small. Note, that the initial weight of the glass samples used (3 cm^3) is only 10 times lower than the solvent volume (30 ml).

2.6 EU-technique

Finally, the most promising glasses have been characterized by a standard EU technique used for the certification of glassy fertilizers [6]. The main parameter to be determined is the amount of phosphorus passing into the solvent under standard conditions that are: gradation of glass powder - 160 μm, dissolution time - 30 min and temperature - 20 ºC, weight ratio of the glass probe and the solvent - 1:100, stirring - 40 round of the stirrer per minute, and solvent composition - 2 % (or 10 %) aqua solution of citric acid. In addition, it appeared to be reasonable and important to perform experiments on direct dissolution of granulated glasses (EUbis-technique). This study has been performed in accordance with the same EC regularities,

with the only difference being in that the glass granules (~6 mm in diameter) are used instead of the glass powders. The experiments performed consisted in the following. Glass granules were dissolved at 20 ºC in an aqua solution of 2 mol. % citric acid stirred by shovel-like stirrer rotating 40 rounds per minute, with the ratio of the weights of the glass granules and solution being 1:100. The value to be characterized was the amount of phosphorus released to the solvent in full glass dissolution. In parallel, the amount of phosphorus released to the solvent per time unit has been monitored as well that allows evaluating the granule life-time in soil.

3 Results

3.1 Glasses of set Axyz (metaphosphate glass-fertilizers)

Glasses of set Axyz were treated as the basis and starting point in the development of glass-fertilizers. All these glasses had metaphosphate composition while the relative compositions of the nutrient components (Ca, K, and Mg) varied within the full available ranges that is from 0 to 1. Thus a study of these glasses by K-technique could give valuable information about the influence of these components on the glass dissolution rate, which could be used in predicting behavior and optimizing compositions of the final glassy fertilizers. An example of glass dissolution kinetics at 50 ºC by K-technique is presented in Figure 2a, and the dissolution rate constants (at 35 ºC) of all the glasses of set Axyz are presented in Figure 1b. From Figure 2a one can see that all the kinetic curves are almost linear. Small deviations from linear dependences were found to be caused by the weak drift of pH during the dissolution process. The dissolution kinetic curves obtained at different temperatures were processed to find the dependence of k on temperature for each glass. Plotting these dependences in the coordinates ln$k$ - 1/T (see Figure 2b) allowed calculating values of Q and k_0. It was found that for all glasses their dissolution activation enthalpies were equal to the same values (Q = 8600 ºK) to within 12 %, that is, for all glasses the slope of linear dependences ln$k$ = f(1/T) was the same. At the same time, the values of k_0 differed by several orders (see Table 3).

For all glasses the activation parameters that were determined were used to evaluate life-times of spherical glass granules, the granules being 5 mm in diameter and other conditions being the same as indicated in section Theoretical and Experimental. In accordance with the above-mentioned criteria (also indicated in section Theoretical and Experimental), two glasses, namely A424 and A262, were selected for granulation. Results of the simulation of dissolution of granules made from these glasses are presented in
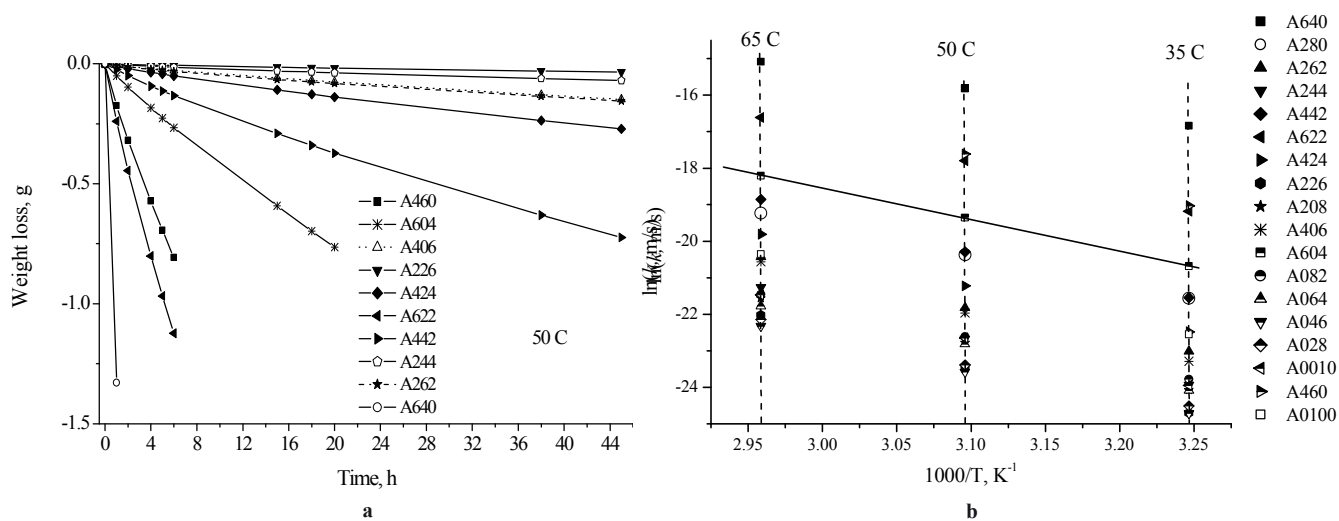
Figure 2:

Kinetics of glass dissolution at 50 C (a) and temperature dependences of dissolution rate constant (b)

Table 3:

Pre-exponent factor k_0 of dissolution rate constant of glasses of set A

Glass	A0100	A460	A0010	A028	A046	A064	A082	A604	A406	A208
$\ln(k_0, m/s)$	5.32	9.02	3.98	3.25	3.05	3.82	4.02	7.28	4.67	3.85
Glass	A226	A424	A622	A442	A244	A262	A280	A640*	A820	A802
$\ln(k_0, m/s)$	3.20	5.41	8.84	6.34	3.96	4.82	6.27	10.81	-	-

* Due to the fast dissolution, the accuracy of determining activation parameters of this glass was rather low.
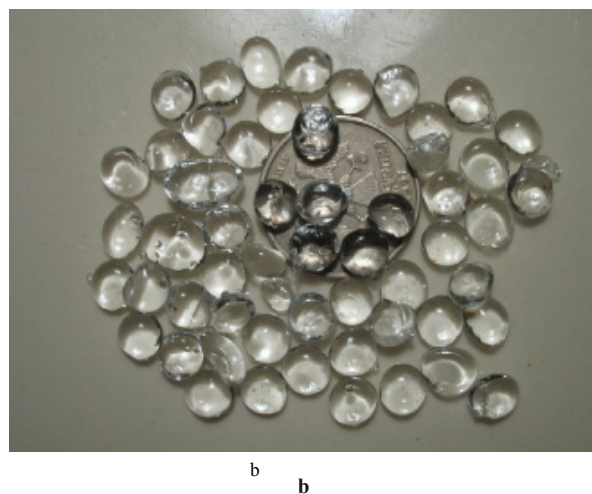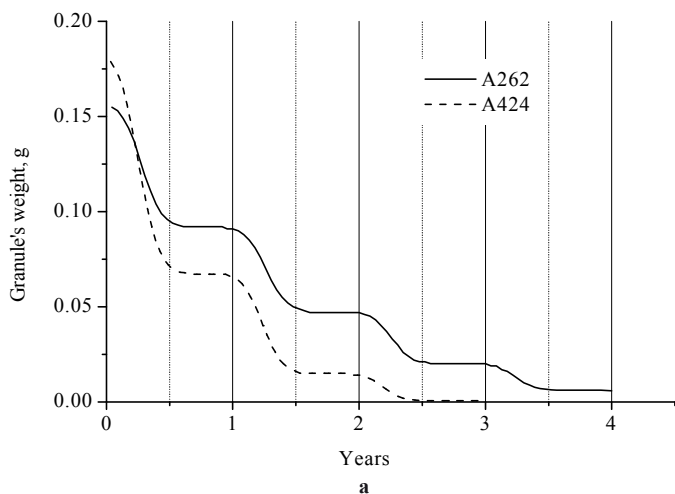
Figure 3:

Evolution of 5-mm granule life in soil with pH = 2.9 and at temperature oscillating during a year with amplitude equal to 15 ºC around its average value equal to 10 ºC (a) and granules of glass A262 (b)

Figure 3 together with a photograph of the produced granules. This simulation gives evidence that the glasses of set A could be used as fertilizers with prolonged action after performing necessary agricultural experiments.

3.2 Glasses of set B (glass-fertilizers out of metaphosphates)

The result of characterization of glasses of set B by E-technique, with distilled water used as a solvent, is presented
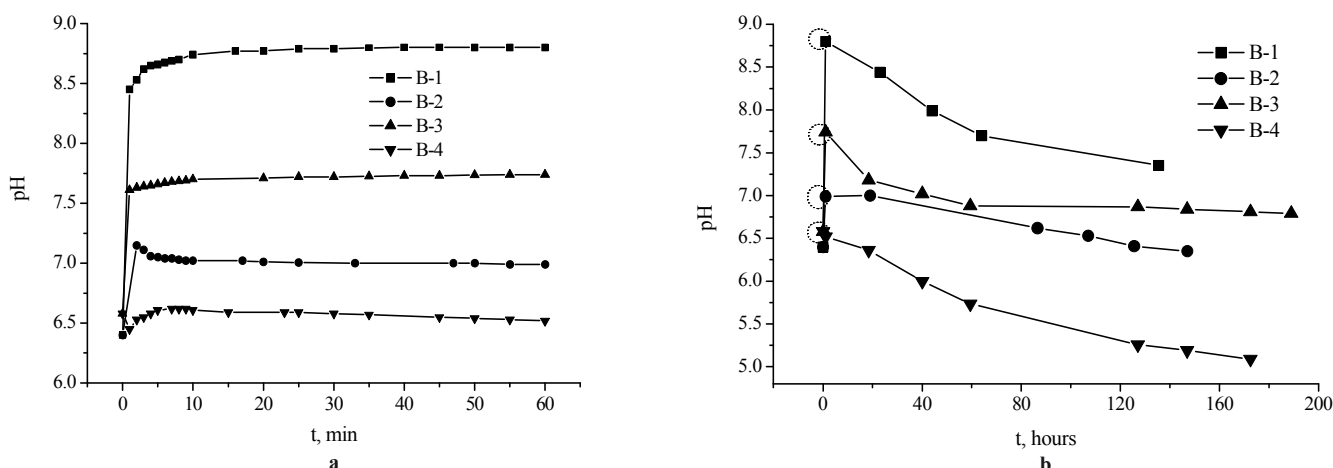
Figure 4:

Kinetics of the solvent pH in the progress of dissolution of glasses B-1, B-2, B-3, and B-4. a) E-technique, b) L-technique

in Figure 4a. One can see a jump of the solvent pH in the very beginning of the dissolution process, which is followed by saturation. Depending on the glass, the saturation was achieved at a solvent pH between 5.5 and 8.5. The pH value increased with a rise in the sum $x + y + z$ (= 1.33, 1.5, 1.71, and 2) that is a shift of glass composition from metaphosphates to orthophosphates led to an increase in the solvent pH. A weak drift of the solvent pH down to lower values was observed, if L-technique is used (Figure 4b). In addition, it was found that the resultant solvents were slightly opalescent due to a part of the dissolution products forming insoluble sediment.

Being presented as a function pH(C) (see Figure 5), these dependences behave like ones typical for buffer solutions, that is, the solvent pH weakly depends on C. It should be noted that such behavior of the solvent pH is rather useful, as fertilizers made from these glasses are capable of providing a stable pH of soil. Thus the modification of glass composition allowed effective governing pH of their water solution, and pH close to one of neutral media was obtained.
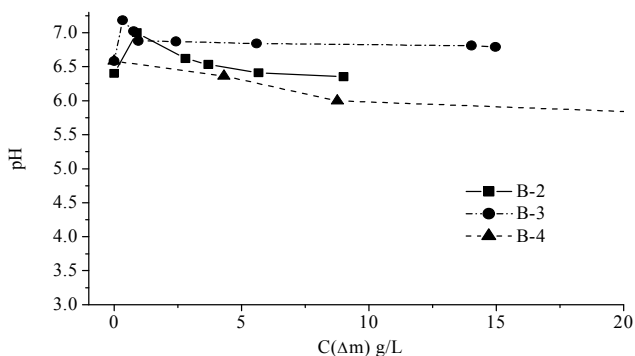
Dissolution rate of these glasses was evaluated by K-technique. In Figure 6 there is an example illustrating that the dissolution rate of phosphate glass decreases with a rise in the sum $x + y + z$.
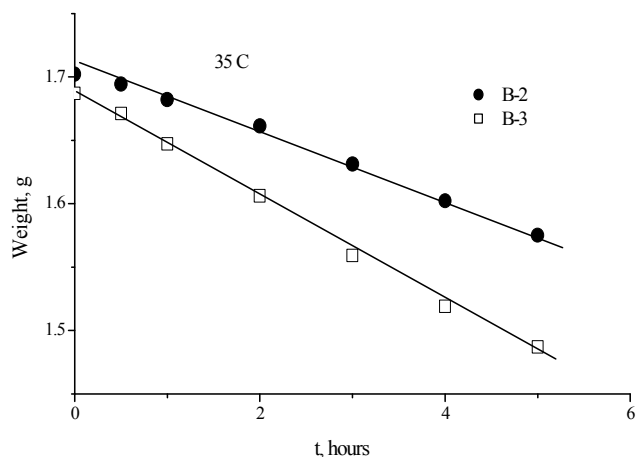

Figure 6:

Dissolution kinetics of glass B-3 compared to glass B-2 with decreased phosphorus content

3.3 Glasses of set C (silica-phosphate glass-fertilizers)

The silica-doped glasses of set C presented in Table 1 can be classified as follows. Glasses C-1, C-2, C-3, C-4, and C-5 are glass B-3 doped with 1.5, 3, 5, 6, and 9 mol. % of silica over 100 mol. %, glasses C-9 and C-10 are glass B-2 doped with 3 and 6 mol. % of silica over 100 mol. %, and glasses C-6, C-7, and C-8 are glass B-4 doped with 3, 6, and 9 mol. % of silica over 100 mol. %, respectively. Most of the glasses with a silica content exceeding 6 mol. % were opalescent (see notes in Table 1) , and it was found that in case of a higher P_2O_5 content, the higher silica content did not result in opalescent glasses. X-ray diffraction

Figure 5:

pH versus concentration L-technique data for B-2, B-3, B-4 glasses

analysis did not show any crystalline phases in opalescent glasses that argued in favor of liquid-liquid phase separation taking place in glass melting.
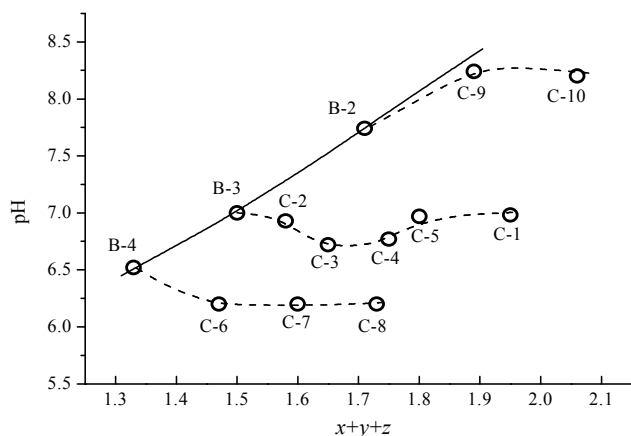

Figure 7:

pH (E-technique, 30 min) data for B-2, B-3, B-4 glasses with SiO_2 additives. The content of silica increases in lines B-4 → C-8, B-3 → C-1, and B-2 → C-10. Along the same lines the glass compositions are shifter in direction from metaphosphate to pyrophosphate.

The glasses of set C were characterized by E- and L- techniques with distilled water used as the solvent. It was found that the doping of glasses with SiO_2 changed the solvent acidity. The dependence of the solvent pH on silica content is depicted in Figure 7. In this figure, the pH values were measured 30 minutes after starting the process, and the dash-line separates the results obtained for transparent glasses (to the left from the line) from opalescent glasses (to the right from the line). It can be seen that first portions of silica, which did not result in opalescent glasses, lead to a decrease in the solvent acidity, while the next portions, yielding opalescent glasses, resulted in an increase in the solvent pH. Characterization of glasses by E- and L- techniques was also performed using 2- and 10-mol. % aqua solutions of citric acid. In general, qualitative results of this study do not differ from those obtained in case of the solvent being distilled water, and, therefore, they are not presented. The main difference was that sediments precipitating in the course of glass dissolution were reduced with a rise in citric acid concentration.

The influence of silica additives on the dissolution rate of glasses is illustrated by Figure 8, from which one can see that small additions of silica, which were incorporated by the glass without the formation of a second phase, decrease the dissolution rate. This dependence is plotted in relative units, for it is the same for all studied glasses in spite of their difference in the absolute value of the dissolution rates. This is an expected result because the introduction of SiO_2 in the glass composition formally moves it further from metaphosphates, and this should decrease

the dissolution rate. However, once the glass becomes a two-phase one, its dissolution rate increases. This can be explained only if in two-phase glasses the phase precipitating in glass synthesis incorporates the most part of silica and is insoluble.
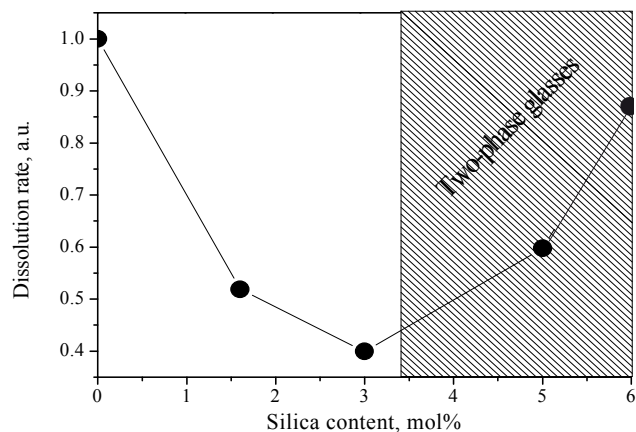

Figure 8:

Relative variation of glass dissolution rate versus silica content (set C)

3.4 Promising glass to be used as fertilizers

The studies have demonstrated the possibility of governing glass dissolution rate and pH of the solvent through varying glass composition (sets A and B, respectively) as well as the technique to control glass dissolution rate for a fixed relation of nutrient contents in the glass (set C). Performed glass syntheses proved the possibility of wide-scale production of such glasses, and the possibility of their granulation was verified, too. However there is one more item essential for a possible use of the developed family of glasses as fertilizers, and this is the correspondence of these glasses to the EC regulations for phosphate fertilizers. That is why the most promising glasses have been characterized in accordance with the corresponding EU regulations (EU-technique) [6]. The selected glasses were B-2, B-3, B-4 and B3-M2. As it can be seen from Figure 9a, all glasses released all phosphorus of dissolution in 2 % citric acid. Similar experiments performed with glass granules (EU-bis-technique) demonstrated also an effective transfer of glass phosphorus to the solvent (see Figure 9b).

4 Discussion

The applicability of the used model of glass dissolution ensues from the parallelism of all dependences shown in Figure 2b. This gives evidence that all glasses had the same activation enthalpy of the dissolution process. This again indicates that glass dissolution functions by breaking bridging P-O-P bonds through hydrolysis. In such a
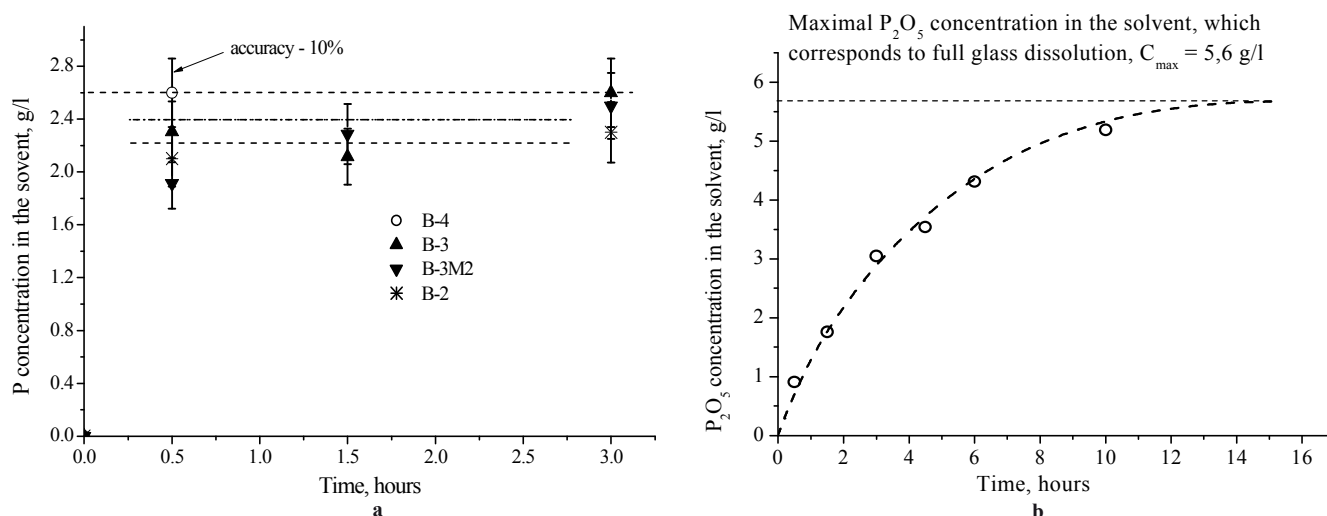
Figure 9:

Concentration of phosphorus in the solution of powdered glasses B-4, B-3, B-3M1 and B-2 in 2 mol. % citric acid versus duration of processing (a); horizontal lines corresponds to maximal possible concentration, i.e. to the situation when glass is fully dissolved, the experiments performed in accordance with regulations [4], and concentration of phosphorus in the solution of glass B-3M2 (b) measured in experiment on dissolution of 5 mm granules of this glass immersed in 2 mol % citric acid at 20 C.

case, it appears that the absolute value of the dissolution rate constant of a glass should depend on the weight of the kinetic unit participating in a single act of glass dissolution. One can expect the weight of such a unit to be proportional to the molar weight of the glass, and, therefore, there should be a correlation between the molar weight of the glass and k_0 which, in fact, is a product of the weight of the participating kinetic unit and some frequency factor. Figure 10 argues on favor of such a correlation. The used model of glass dissolution explains all correlations between glass composition and dissolution rate found in the presented research work. Indeed, an increase in the sum $x + y + z$ should decelerate glass dissolution because surface concentration of P-O-P bond decreases, while the relative concentration of heavier metals at a given value of the
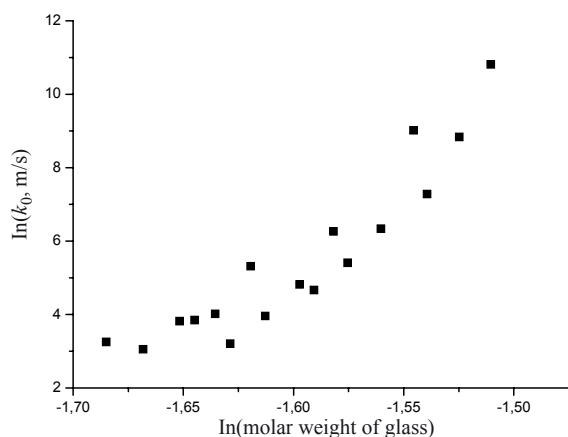
sum $x + y + z$ should accelerate glass dissolution because the weight of effective kinetic unit increases.

The jump in the very beginning stage of glass dissolution (see Figure 4) is supposed to be conditioned by the process called the electrolytic dissociation. This process is an ion exchange of metal ions contained in glass with hydrogen ions in the solvent. This ion exchange leads to the impoverishment of the solvent with hydrogen ions and, therefore, an increase in the solvent pH. Note that the height of this jump depends on the sum $x + y + z$ that also runs from the used model. Indeed, glasses with higher sum $x + y + z$ demonstrate higher jumps, and it is due to the increased amount of metal ions on the surface of glasses with higher sum $x + y + z$.

Dependences of the solvent pH on glass composition can be explained by the stoichiometry of phosphate glasses varying with a rise in the sum $x + y + z$. As was above-mentioned, a rise in the sum $x + y + z$ (in the line B2 => B3 => B4 => B1) transforms glass structure from metaphosphate to pyrophosphate ones. From the obtained data it can be concluded that a lower content of metaphosphate groupings is associated with a higher pH of the solvent after dissolution. This presumes that phosphate glasses dissolve through the hydrolysis of phosphate network in accordance with the used model (P-O-P + H_2O => 2P-OH), and phosphorus comes to the solvent due to the disruption of bridging oxygen bonds. In general, breaking bridging bounds by hydrolysis supplies the solvent with different forms of phosphate anionic groups based on PO4 tetrahedrons. The metal cations and hydrogen ions existing in the solvent compete to occupy these anionic groups in accordance with the corresponding dissociation con-

Figure 10:

Dependence of k_0 on molar weight of glasses of set A

stants. With dissociation constants of phosphate salts being lower as compared to ones of any form of phosphoric acid, the resultant pH of the solvent should depend on the total concentration of all metal cations (K^+, Ca^{2+}, Mg^{2+}). The higher concentration of metal ions in the solvent, the higher solvent pH. It is because a rise in the sum $x + y + z$ means an increase in total metal concentration in a glass and, in glass dissolution, disruption of one P-O-P bridging bond in the glass with higher content of metals leads to a higher content of these metals in the solvent per one phosphorus ion.

Acknowledgement

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