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PROCEEDINGS

XXIII International Conference
Ecological Truth

Editors
Radoje V. Pantovic
Zoran S. Marković

EcoIst '15

Hotel "PUTNIK", Kopaonik, SERBIA
17-20 June 2015

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TECHNICAL FACULTY BOR

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THE INFLUENCE OF GLASS COMPOSITION ON THE DISSOLUTION RATE

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ABSTRACT

In this paper the results of investigation of the polyphosphate glasses dissolution in acid solution at temperatures of 20, 30 and 37 °C were presented. The dissolution process in citric acid is complex and can be explained by hydration reaction and hydrolysis, leading to the disruption of phosphate chains which form the structure of glass. Mechanism of chemical reactivity of polyphosphate glasses, acting as slow release fertilizers in soil solutions was presented. The results of the dissolution experiments indicated that this glass can be used as an eco- fertilizer in soil remediation.

Key words: polyphosphate glass, fertilizer, dissolution.

INTRODUCTION

Modern civilization creates increasingly great amounts of waste and toxic substances formed in the production processes and communal management or in agriculture. The national economies are responsible for serious disturbances in the natural environment since, according to statistical data over 50% of the content of nitrogen, 50% of organic compounds and 30% of phosphorus in rivers have their source in the contaminations caused by substances eroded from the soil [1,2].

The last decades have brought a considerable progress in the field of the synthesis of new glasses for various, often unconventional applications.

The glassy fertilizers are phosphate glasses demonstrating the ability to accept in their composition the presence of a number of elements indispensable in the biological processes of the growth of plants and ability of their selective release in the soil environment in a form available for the plants. Regarding to the mineral fertilizers the dissolution of glass is a complex process which depends on several factors: glass composition, pH solution, temperature, time of reaction, etc. This process takes place in several stages and this enables that the overall time of the process can be regulated by favoring or suppressing some of these phases [3].

Earlier studies have shown that biological activity of silicate–phosphate glasses modified by addition of macroelements in the form of Mg and Ca is connected with change in the type of domains which are formed in the structure of glasses depending on the mutual proportions between the components forming their structure [4]. The presence of increasing amount of modifier in the form of Mg^{2+} cations results in the formation of domains showing the structure corresponding to that of silicates and leads to the increase in solubility of glasses. However the increase in Ca^{2+} cations content results in the formation of domains exhibiting the structure similar to that of orthophosphates which are characterized by lower solubility [5].

Iron plays an important role as a microelement that is necessary in the growth process of plants. Silicate–phosphate glasses with iron addition find application as slow release fertilizers.The FTIR results obtained indicate that the increasing amount of Fe_2O_3 and P_2O_5 in the structure of silicate–phosphate glasses causes formation of domains, whose structure changes from that corresponding to silicates to the one characteristic for phosphates [6].

EXPERIMENTAL

Two appropriate glasses batches was prepared from reagent grade raw materials $(NH_4)_2HPO_4$, K_2CO_3, $CaCO_3$, SiO_2, MgO, ZnO, Fe_2O_3 and MnO_2 in an open crucible. To minimize foaming of the melts, the crucible was slowly heated up to T=190 °C and then maintained for 3 h in order to release the gases, such as water vapor and NH_3. The melting was performed in an electric furnace Carbolite BLF 17/3 at T=1230 °C for 1 h in 200 ml open Pt/Rh crucible. The glasses was obtained by quenching the melt on a steel plate. Powder X-ray diffraction (XRD) analysis confirmed the quenched melts to be vitreous.

Characterization of the glasses

The chemical composition was determined by gravimetric and spectroscopic methods, i.e., by AAS using a PERKIN ELMER 703 instrument and UV/VIS spectroscopy using a PHILIPS 8610 spectrophotometer.

Powder X-ray diffraction (XRD) analysis was realized using a Philips PW-1710 automated diffractometer with a Cu Kα radiation tube operating at 40 kV and 32 mA. Data were collected from 5 to 70° 2θ, with a step size of 0.02° and a counting time of 1 s per step.

Leach test

Leach tests were conducted with 2% Citric acid (pH=2.31 and χ=3.103 μS/cm) which simulates the activity of organic compounds located around plant root for extraction of the useful components from soil. The glass grains size 0.3-0.65 mm was used for experiments. The samples were prepared by crushing the bulk glass in an agate mortar and then sieving it to appropriate grain size. The specific surface area of these powders was determined by Laser particlesizer Fritsch Analysette 22. After washing in distilled water and drying, 1 g of glass sample was placed into volumetric flask of 50 ml and then 2% citric acid is added. The closed flask was placed in a water bath with the determined temperature (T=20, 30 and 37 °C) and kept for the fixed time (0.5 - 720 h).

The solution from a volumetric flask was filtered and afterwards pH and the content of the present elements were determined. The rest of glass grains was dried at T=100 °C to constant mass of sample and then the mass of dissolved glass was calculated.

The measurement of pH values was performed with the pH-meter Consort, model C830P previously calibrated with appropriate standards.

Test on plants

The study was performed during 2011 and 2012 in greenhouse (Faculty of Agriculture - Belgrade). The flower selected are: a) Marigold (*Tagetes patula L*), series "Bolero"- Pan American Seed, b) domestic species of pepper (*Capsicum annum* L) "*Župska rana"*.

The polyphosphate glass BA-2 powder particle size < 0.5 mm was added in dosage: 0,1,2,3 and 5 g/l substrate.

RESULTS AND DISCUSSION

The results of chemical analysis of glasses composition presented in Table 1.

Table 1. Chemical composition of glasses

Oxide [mas %]	P_2O_5	K_2O	CaO	MgO	SiO_2	ZnO	MnO	Fe_2O_3
BA-1	62.0	23.2	7.8	3.6	1.8	1.0	0.6	
BA-2	68.0	22.0	1.6	1.4	2.9	0.8	0.7	2.6

By using the mass loss experimentally determined (Δm) and the specific surface areas of glass powders S [m^2], the normalized mass release f_m [g/m^2] was calculated. In Figure 1, the time dependence of f_m for powder samples at temperatures 20, 30 and 37 °C are shown. Fitting the experimental results yields the curve in Figure 1 that corresponds to equation (1):

$$f_m(t) = \tau \cdot r_o \left[1 - \exp\left(-\frac{t}{\tau} \right) \right] \tag{1}$$

where r_o is the starting dissolution rate, τ is a time constant and t is the dissolution time [7].

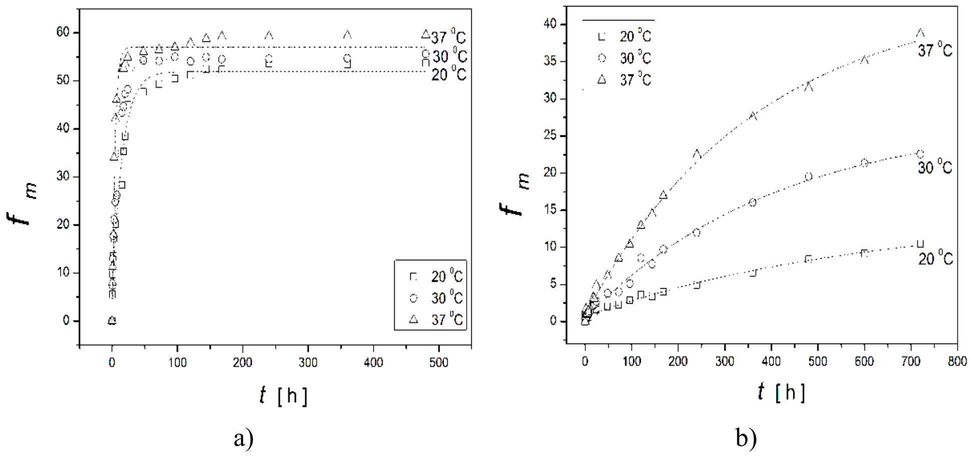


Figure 1. The time dependence of f_m for glass powder sample particle size 0.3–0.65 mm at different temperatures for a) BA-1 glass and b) BA-2 glass

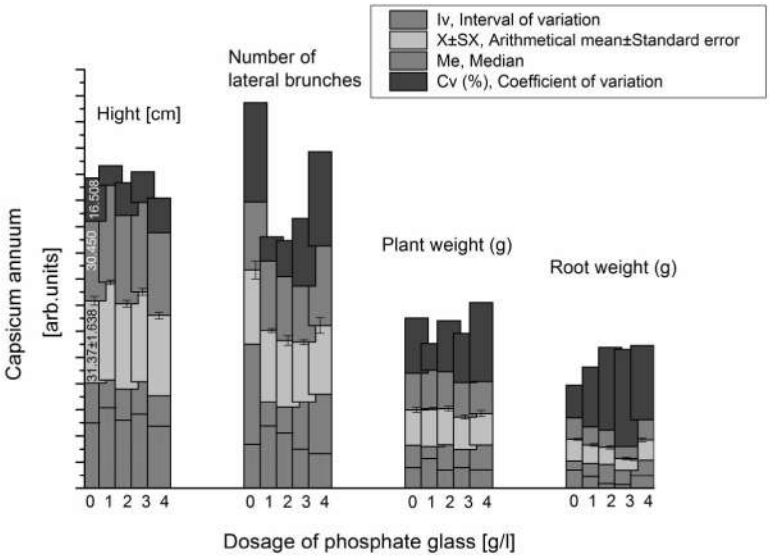
The initial dissolution rate was calculated as the slope between zero and 7 h data point at experimental temperatures, and then the time constants τ were determined using the equation (1).

Values of the dissolution rate constant k were calculated using the ratio $\tau = 1/k$. The results are summarized in Table 2.

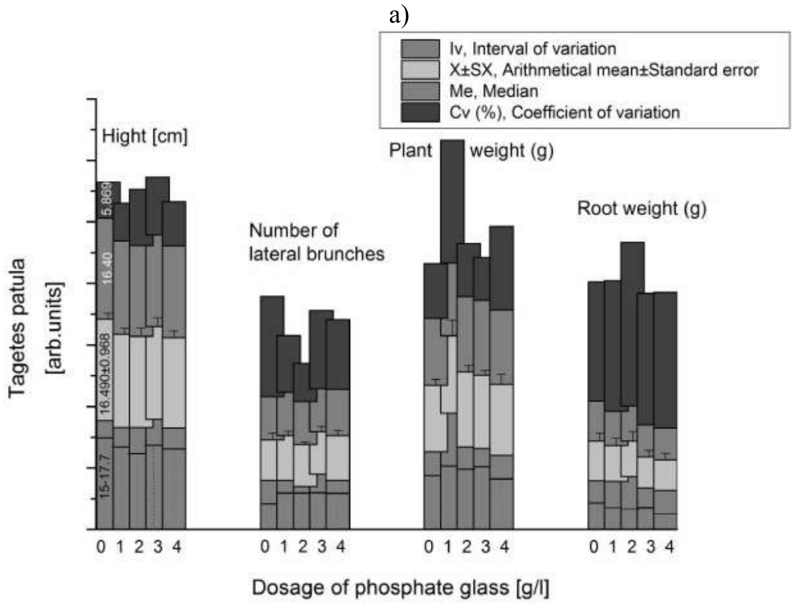
Table 2. Rates constants k and initial dissolution rates r_o

Glass	BA-1			BA-2		
T [°C]	20	30	37	20	30	37
k [h^{-1}]	0.064	0.096	0.245	0.0016	0.0024	0.0027
r_0 [g/ m^2 h]	3.672	3.745	6.592	0.089	0.135	0.195

From the obtained rate constants and starting rates it can be deduced that the dissolution rate for the glass BA-1 is approximately ten times greater than for the glass BA-2. This can be explained by higher presence of alkalies in the glass BA-1. Also, this is a confirmation of a fact that small changes of a glass composition can drastically change the dissolution rate of a glass, which is a way of obtaining appropriate fertilizers for plants.



a)



b)

Figure 3. The basic statistics indicators for the examined parameters of quality: a) pepper seedlings (Capsicum annuum L). b) marigold seedlings (Tagetes patula L) by the usage of various dosages glass

Based on parameters of development of plants examined it was determined that the glass dosage of 1 g/l is optimal. This dosage was affected significantly on increase of average height and the overground mass of the plants. In the case of pepper seedling an average overground mass determined is statistically significantly higher comparing the mass attained with glass dosage of 3 g/l. In relation to other additives for improvement of substrates (mineral fertilizers, wermicompost, etc) by addition of polyphosphate glass into substrate a better development of pepper seedlings was attained.

CONCLUSION

The results of the dissolution tests showed that this glass dissolved without back precipitation of the secondary corrosion products. The initial dissolution mass loss is linear with time. For longer reaction times the dissolution rate decreases.

The results of investigation indicated the positive effects of application of different dosage of polyphosphate glass in production of the marigold and pepper seedlings. The significant advantages can be reached: the contamination of agricultural soil is reduced and the total level of environmental protection increased.

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