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Nadežda Ćalić, Ljubiša Andrić,
Igor Miljanović, Ivana Simović

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ECO-MATERIALS FOR SOIL REMEDIATION BASED ON POLYPHOSPHATE GLASSES

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Abstract: In this paper the results of examination of the dissolution process of the polyphosphate glass $45P_2O_5{\cdot}25K_2O{\cdot}15CaO{\cdot}10MgO{\cdot}3SiO_2{\cdot}ZnO{\cdot}MnO$ [mol%] in 2% citric acid at temperatures of 15, 20 and 30 ºC were presented. The dissolution experiments were performed on glass powder grain size of 0.1-0.3 mm and 0.3-0.65 mm. The mass loss of glass, normalized concentration of PO_4^{3+} and K^+ ions and the conductivity of solution (χ) as a function of leaching time was determined. It was revealed that for short reaction times, the changes of normalized mass loss (f_m) are linear with time and the rates of glass dissolution under given conditions are highest. By increasing the dissolution time the dissolution rate of glass decreased. The initial release rates r_0 (PO_4^{3-}) = 3.550 [g/m^{2}h] and r_0 (K^+) = 2.133 [g/m^{2}h] at t = 30^{0}C were calculated for glass powder sample 0.3-0.65mm. 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. The results of the dissolution experiments indicated that this glass can be used as an eco- fertilizer in soil remediation

Keywords: : *soil remediation, eco- fertilizer, polyphosphate glass, citric acid , dissolution.*

INTRODUCTION

In modern production of vegetables and flowers seedlings the substrates improved with different types of ingredients are used. Often, these materials were not analyzed sufficiently and subsequently the problems in production of plants appeared (Verhagen 1996). Therefore, it is important to study the effects of these materials on plants, soil and water sources. Discovering of new alternative substrates and their components is very important for production of plant in greenhouses. The application of these substrates can effect on decrease of the production costs and can enable the supply of the safe food (Bayer *et al.* 2007]. Application of appropriate eco-materials in modern agricultural production is an imperative rather than a new modern trend (Samadi, 2011).

The phosphate glasses as one of new possible components of substrates can be considered. The comprehensive studies have shown that the glasses because of their amorphous structure revealed the properties which make them capable to participate in the biological processes of living organisms (Waclawska et al ,2009).

Regarding to the mineral fertilizers the dissolution of glass is a complex process which depends on several factors: glass compsition, pH solution, temperature, time of reaction, etc (Karapetyan G et al, 2004). 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. The activity of these glasses in plant nourishing can be determined by glass dissolution in a citric acid which simulates the activity of organic compounds located around plant root for extraction of the useful components from the soil (Tosic et al, 2010, Nikolic et al.,2011).

In this paper the results of examination of the dissolution process of the polyphosphate glass $45P_2O_5{\cdot}25K_2O{\cdot}15CaO{\cdot}10MgO{\cdot}3SiO_2{\cdot}ZnO{\cdot}MnO$ [mol%] in 2% citric acid were presented.

EXPERIMENTAL

The appropriate glass batch composition was prepared from reagent grade raw materials $(NH_4)_2HPO_4$, K_2CO_3, $CaCO_3$, SiO_2, MgO, ZnO and

MnO_2 in open porcelain crucible. The melting was performed in an electric furnace Carbolite BLF 17/3 at T = 1230 °C during t = 1 h. The glass was obtained by quenching the melt on a steel plate. Powder X-ray diffraction (XRD) analysis confirmed the quenched melts to be vitreous.

The chemical composition was determined by spectrophotometer (AAS – PERKIN ELMER 703, PHILIPS UV/VIS 8610 spectrophotometer) and gravimetric methods.

Leach tests were conducted with 2% citric acid. The glass grains size 0.1-0.3 mm and 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=15,20 and 30 ºC) and kept for the fixed time (0.5 - 480 h). The solution from a volumetric flask was filtered and afterwards χ (conductivity of solution) and the content of the present elements were determined. The rest of glass grains was dried at T=100 ºC to constant mass of sample and then the mass of dissolved glass was calculated.

RESULTS AND DISCUSSION

By using the mass loss experimentally determined (Δm) and the specific surface areas of glass powders S, 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 15, 20 and 30 °C are shown. Fitting the experimental results yields the curve in Figure 1 that corresponds to equation [1]:

(Helebrant et al., 1989):

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

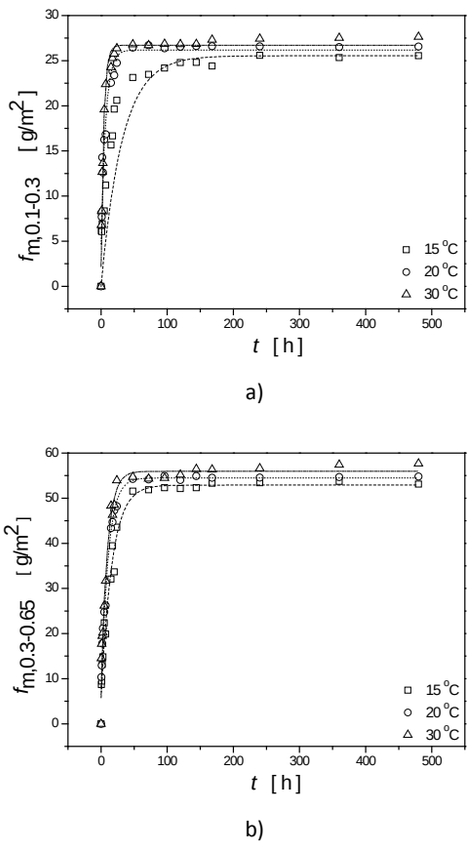
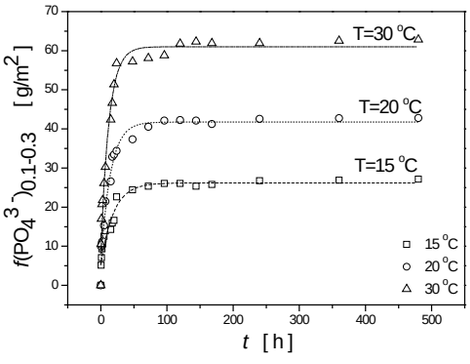


Figure 1, The time dependence of f_m for glass powder sample particle size a)0.1-0.3 mm b) 0.3–0.65 mm at different temperatures

At the beginning for short times, the changes of f_m are linear with time and the rates of glass dissolution under given conditions are highest. This linear area is followed by an intermediate area where the changes f_m becomes slower with increasing time and the dissolution rate of the glass decreases. For longer times the changes of f_m are very small. (Tosic et al.,2013).

In Figure 2 and 3, the time dependence of $f[PO_4^{3-}]$ and $f[K^+]$ for powder samples at temperatures 15, 20 and 30 °C are shown.



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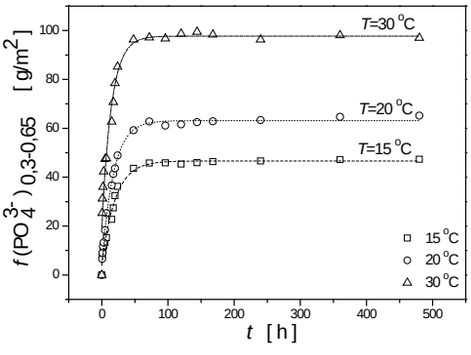

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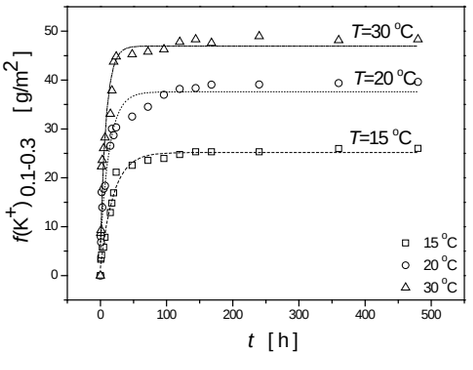
Figure 2, The time dependence of f [PO_4^{3-}] *for glass powder sample particle size a)0.1-0.3 mm b) 0.3–0.65 mm at different temperatures*



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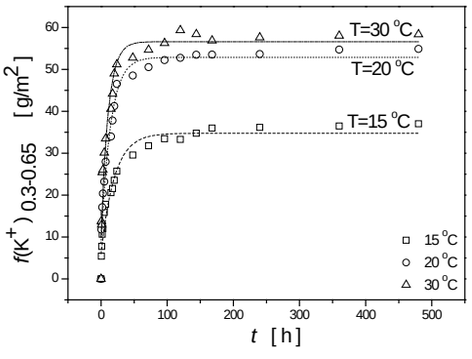

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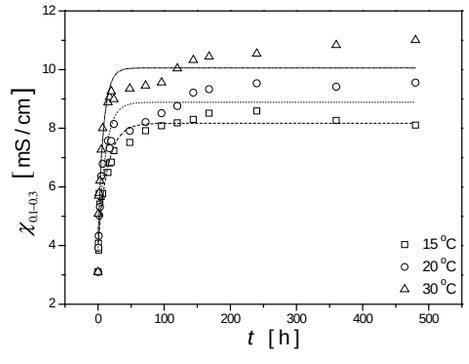
Figure 3, The time dependence of f [K^+] *for glass powder sample particle size a)0.1-0.3 mm b) 0.3–0.65 mm at different temperatures*

In Fig. 4, the dependences of χ on dissolution time at different temperatures for glass powder samples are shown.



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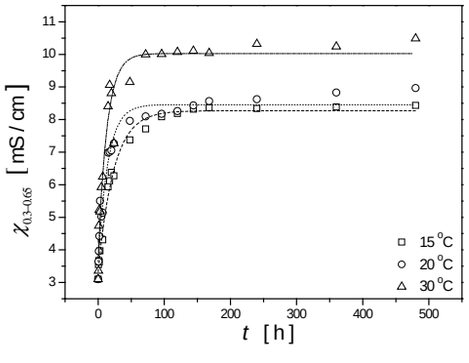


b)

Figure 4, The time dependence of χ for glass powder sample particle size a)0.1-0.3 mm b) 0.3–0.65 mm at different temperatures

The specific surface areas of these samples were found to be 0.0367 and 0.0178 m^2/g, respectively.The initial dissolution rate was calculated as the slope between zero and 20 h data point at experimental temperatures. The results are summarized in Table 1. and Table 2.

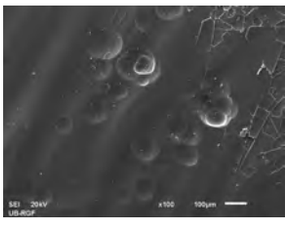
Table 1, Initial release rates r_0 and time constants τ for glass sample 0.1-0.3 mm

0.1-0.3 mm	T [°C]		
	15	20	30
$\tau(m)$ [h]	31.874	6.915	4.091
r_0 (m) [g/m^{2}h]	0.858	1.031	1.098
$\tau(PO_4^{3})$ [h]	19.054	14.368	12.165
r_0 (PO_4^{3-}) [g/m^{2}h]	0.943	1.434	2.366
τ (K^+)	19.699	13.794	8.787
r_0 (K^+) [g/m^{2}h]	0.880	1.262	1.868

Table 2, Initial release rates r_0 and time constants τ for glass sample 0.3-0.65mm

0.3-0.65 mm	T [°C]		
	15	20	30
$\tau(m)$ [h]	16.480	10.609	9.504
r_0 (m) [g/m^{2}h]	1.815	2.009	2.248
$\tau(PO_4^{3})$ [h]	20.401	17.417	14.392
r_0 (PO_4^{3-}) [g/m^{2}h]	1.510	2.037	3.550
τ (K^+)	20.004	14.288	10.622
r_0 (K^+) [g/m^{2}h]	1.071	1.939	2.133

The present results showed that a relative slow-release glass was selected. In Fig.5, the SEM micrographs of the surface of glass particles immersed in acid solution are shown. (Delahaye F. et al,1998).



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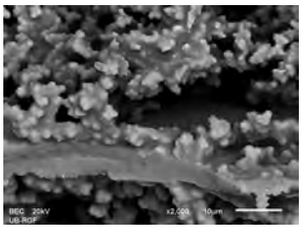

b)

Figure 5. SEM micrograph of the surfece of glass sample:surface of sample immersed in 2% citric acid at a)30 °C for 0.5 h and b) 30 °C for 96 h

CONCLUSION

The dissolution of $45P_2O_5{\cdot}25K_2O{\cdot}15CaO{\cdot}10MgO{\cdot}3SiO_2{\cdot}ZnO{\cdot}MnO$ [mol%] glass powders particle size 0.1-0.3 and 0.3-0.65 mm in acid solution at T = 15, 20 and 30 °C was studied. The results showed that the initial dissolution mass loss is linear with time. For longer reaction times the dissolution rate decreases. The grain size of glass does not affect markedly on dissolution rate. The values of dissolution rates indicated that this phosphate glass can be used as an eco-material in soil remediation.

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