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MINING AND ENVIRONMENTAL PROTECTION**

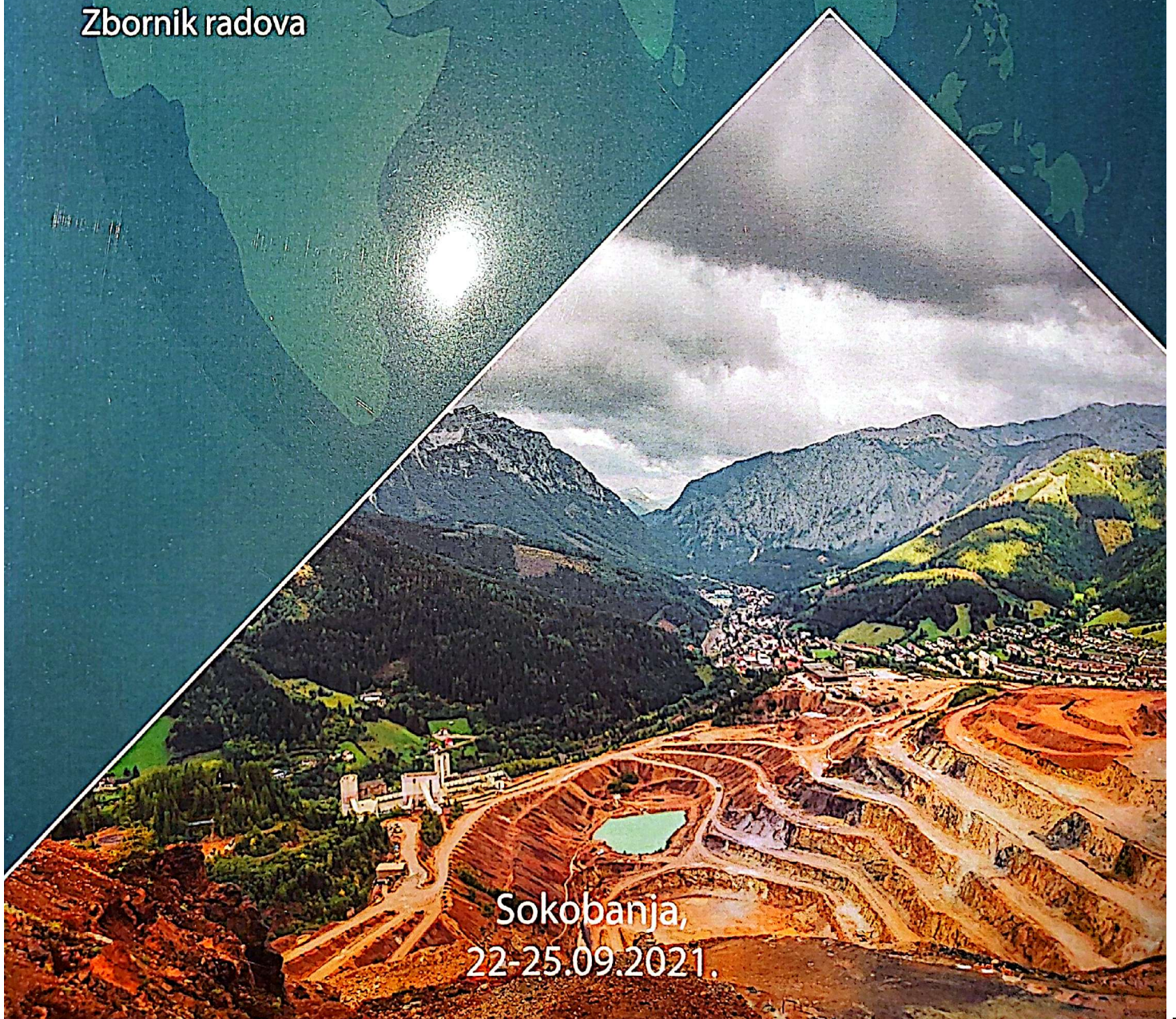


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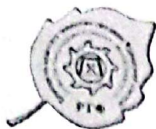
PROCEEDINGS



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PROCEEDINGS

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Prof. dr Ivica Ristović

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THE EFFECT OF COMPOSITION ON CHEMICAL DURABILITY OF PHOSPHATE GLASS FERTILIZERS

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Abstract: Phosphate glassy fertilizers are the new type of advanced and controlled released fertilizer, whose glassy matrixes consist of macroelements (K, P, Mg, Ca) most useful for plants and microelements (Fe, Cu, Zn, Mn) which are important to the growth and development of plants. The flexibility of glasses enables the variation of their composition and properties over a wide range. The dissolution behavior of glasses from the $P_2O_5-SiO_2-K_2O-CaO$ -MgO system doped with various microelements in bidistilled water and the 2% aqueous solution of citric acid under static conditions was studied. The leaching tests were performed with glass powder samples (0.3–0.65 mm) at T=37 °C for periods up to 480 h. The samples mass loss, the changes of pH, as well as the concentration of elements in solution were determined.

Keywords: phosphate glass, dissolution, controlled released fertilizer

1. INTRODUCTION

The process of healthy food production is very important in Europe as well as in a large part of the world. Ideas like "Sustainable agriculture" and "Ecological agriculture" are very important topics for the governments of most developed countries, for which the health of the nation is important [1,2]. In intensive agricultural production, artificial fertilizers are used to provide the necessary amounts of nutrients for different crops. On the other hand, "new technologies" used in agriculture are focused on reducing the use of chemicals that have a negative impact on the environment and the use of new materials to obtain products of superior biological quality [3,4].

Production technology of controlled release fertilizers, which includes glassy fertilizers, has been developing for a long time. The main advantages of glassy fertilizers against conventional fertilizers are: they increase the grade of assimilation by plants, do not release insoluble compounds in soil, remain in the soil during the entire period of plant development, and do not pollute the phreatic water [5,6].

Glass matrixes based fertilizer consist of macronutrients (K, P, Mg, Ca) most useful for plants and also incorporated with micronutrients (B, Fe, Mo, Cu, Zn, Mn) which are important to the growth and development of crops or plants. The flexibility of glasses enables the variation of their composition and properties over a wide range. There are two-fold advantages to incorporate the ingredients into a glass fertilizer: (a) glass can accommodate almost all the elements of the periodic table and (b) the leach resistance of the glass which may vary is very high. 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 [7-11].

Glassy fertilizers developed at the Center of Inorganic Technology, ITNMS, are phosphate glasses demonstrating the ability to accept in their composition the presence of several elements indispensable in the biological processes of the growth of plants. Mechanism of chemical reactivity of phosphate glasses in two different solutions is the subject of the present study.

2. EXPERIMENTAL

2.1 Glass synthesis

Two glass batches were prepared from reagent grade raw materials $(\text{NH}_4)_2\text{HPO}_4$, K_2CO_3 , CaCO_3 , SiO_2 , MgO , ZnO , CuO , Fe_2O_3 and MnO_2 . To minimize the foaming of the melts, the crucible was slowly heated up to $T = 190^\circ\text{C}$ and then maintained for 3 h to release the gases, such as water vapor and NH_3 . The melting was performed in an electric furnace Carbolite BLF 17/3 at $T = 1230^\circ\text{C}$ for one hour in 200 ml open unglazed ceramic crucible. The glasses (PFG1 and PFG2) were obtained by quenching the melts on a steel plate.

2.2 Dissolution experiment

Dissolution experiments were conducted in two solvents:

- bidistilled water ($\text{pH} = 6.93$ at $T = 25^\circ\text{C}$) and
- 2wt% aqueous solution of citric acid ($\text{pH} = 2.31$ at $T = 25^\circ\text{C}$),

under static conditions. The experiments were conducted in bidistilled water are supposed to model surface conditions of grain dissolution in moist soil. The chemical activity of glasses was estimated based on their solubility in 2 wt% citric acid solution, which is an indicator of assimilateness of fertilizer components by plants [7].

The experiments were performed with glass powders particle size 0.3–0.65 mm. The glass powders were prepared by crushing the bulk glass in an agate mortar and sieving it to an appropriate grain size. Samples of the glasses powders (1 g) were weighed and transferred into 50 ml volumetric flasks and then one of the two solvents was added. The closed flasks were placed in a water bath. The dissolution experiments were performed at 37°C for different times in the range of 0.5 to 480 h. After completion of the experiment, the flask content was filtered and the pH and the concentration of ions were determined in the obtained solutions. Also, the mass loss of the glass samples was determined.

2.3 Characterization of the glasses

Powder X-ray diffraction (XRD) analysis was realized using a Philips PW-1710 automated diffractometer with a Cu K_α radiation tube operating at 40 kV and 32 mA.

The chemical composition of the glasses and the concentration of the ions in solutions after glasses dissolution, were determined using a Perkin Elmer 703 atomic absorption spectrometer and a Philips UV/VIS 8610 spectrophotometer.

The specific surface area of these powders was determined by the Laser Particle Sizer Fritsch Analysette 22.

A Consort C830P pH meter was used for the pH measurements in solutions, after the glass powder dissolution experiments in bidistilled water and 2wt% aqueous solution of citric acid. The measurements were conducted at $T = 25^\circ\text{C}$.

3. RESULTS

Powder X-ray diffraction (XRD) analysis confirmed the quenched melts to be vitreous. The results of the chemical analysis of the glasses, PGF1 and PGF2, are given in Table 1.

Table 1. Chemical composition of glasses

Oxides (wt%)	P ₂ O ₅	SiO ₂	K ₂ O	CaO	MgO	Microelements			
						ZnO	MnO	CuO	Fe ₂ O ₃
Glass	65	2	22	7	3	0,5	0,5		
PGF1	60	2	22	7	3	0,5	0,5	2	3
PGF2									

The results of the chemical composition analysis shown in Table 1, show that the glass PGF1 belongs to the group of polyphosphate glasses and that the glass PGF2 belongs to the group ultraphosphate glasses. The binary compositions of the glasses are: PGF1=0,515MeO·0,486NFO and PGF2=0,391MeO·0,609NFO (Me are ion modifiers, NF are network former ions). In polyphosphate glasses, PGF1, the fractions of Q¹ and Q² tetrahedra are y(Q¹) = 0,062, y(Q²) = 0,938 and the average tetrahedron chain length is L_{av} = 32,3. The fraction of Q² and Q³ tetrahedra are y(Q²) = 0,642, y(Q³) = 0,358 in PGF2 glass [12]. Molecular mass of glasses are: M(PGF1)=103,9 gmol⁻¹ and M(PGF2)=115,71 gmol⁻¹.

From measured data from mass release during dissolution as well as the concentration of ion present in solutions after dissolution, calculate the normalized mass loss and normalized ion concentrations in solution according to equation (1):

$$f_i = \frac{c_i \cdot V}{\delta_i \cdot S} \quad (1)$$

where c_i is the mass concentration of leached species in time t, δ_i is the mass fraction of species i in the glass, S is the glass surface in contact with a solution and V is the solution volume [12,13].

The dependence of normalized mass release on dissolution time in bidistilled water and 2wt% aqueous solution of citric acid for both glasses is represented in Fig.1.

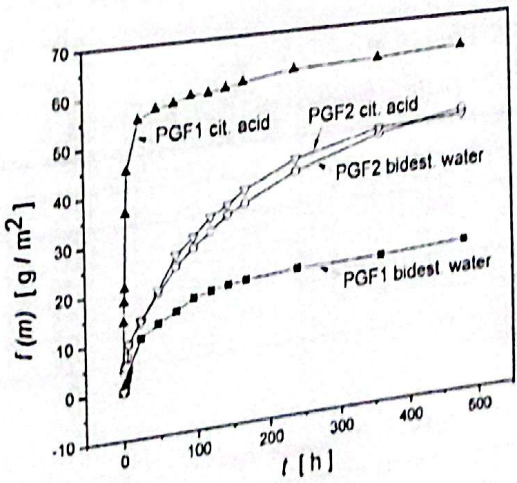
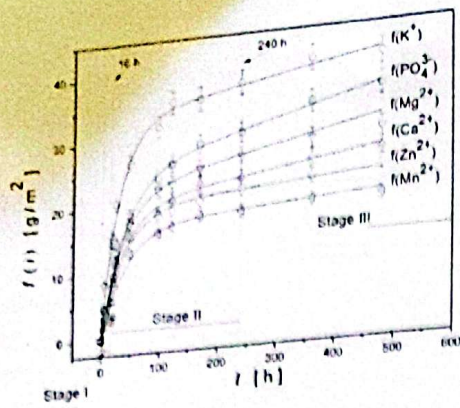
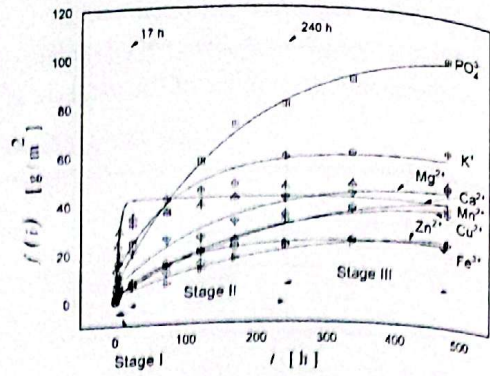


Figure 1. Dependence of normalized mass release on dissolution time in bidistilled water and 2wt% aqueous solution of citric acid for PGF1 and PGF2 glasses.

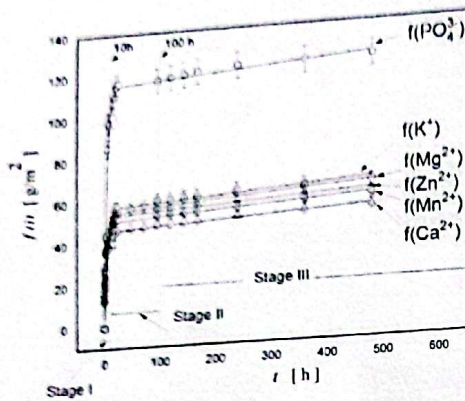
Fig.2. represents the dependence of normalized ions concentration on dissolution time for both glasses in bidistilled water and 2wt% aqueous solution of citric acid.



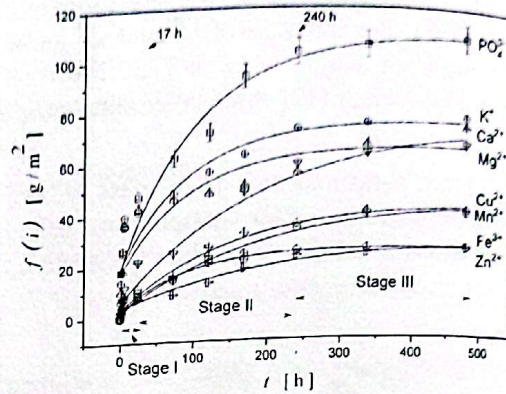
a)



b)



c)



d)

Figure 2. Time dependence of $f(i)$ for: a) PGF1 bidistilled water; b) PGF2 bidistilled water; c) PGF1 citric acid; d) PGF2 citric acid.

Using the experimentally determined dependencies of normalized mass release and normalized ion concentrations (Fig. 2) on dissolution time, initial ions release rates ($r_{0,i}$) and the ions dissolution rates in final stage ($r_{h,i}$) were calculated from the slopes of the linear parts of the curves (Stage I and Stage III) for both glasses. The results are represented in Table 2 and 3.

Table 2. Initial release rates ($r_{0,i}$) (Stage I)

Glass	$r_{0,i}$ [$\text{g m}^{-2} \text{h}^{-1}$]								
	$\Gamma_{0,m}$	$\Gamma_{0,\text{PO}_4^{3-}}$	$\Gamma_{0,K}$	$\Gamma_{0,Ca}$	$\Gamma_{0,Mg}$	$\Gamma_{0,Zn}$	$\Gamma_{0,Mn}$	$\Gamma_{0,Fe}$	$\Gamma_{0,Cu}$
PGF1b.w.*	0.44	0.44	0.82	0.32	0.34	0.17	0.17	-	-
PGF1 c.a.*	6.08	12.92	8.72	6.68	7.26	5.70	6.45	-	-
PGF2b.w.	1.53	2.86	3.30	5.34	1.80	0.85	0.93	0.78	1.19
PGF2 c.a.	1.83	7.71	7.52	6.88	2.06	1.62	1.05	0.89	1.41

*b.w.-bidistilled water, c.a.-citric acid

Table 3. The release rates $r_{h,i}$ in Stage III

Glass	$r_{h,i}$ [$\text{g m}^{-2} \text{h}^{-1}$]								
	$\Gamma_{Z,m}$	$\Gamma_{Z,\text{PO}_4^{3-}}$	$\Gamma_{Z,K}$	$\Gamma_{Z,Ca}$	$\Gamma_{Z,Mg}$	$\Gamma_{Z,Zn}$	$\Gamma_{Z,Mn}$	$\Gamma_{Z,Fe}$	$\Gamma_{Z,Cu}$
PGF1b.w.	0.436	0.0231	0.0116	0.0124	0.0106	0.0094	0.00423		
PGF1 c.a.	0.0118	0.0073	0.0052	0.0083	0.0115	0.0101	0.0137		
PGF2b.w.	0.037	0.093	0.020	0.015	0.027	0.012	0.021	0.012	0.022
PGF2 c.a.	0.021	0.024	0.020	0.073	0.032	0.011	0.028	0.0044	0.020

In acid solution, a rapid equilibrium may be set up between the phosphate and hydrogen ion (reaction (1)), the phosphate ion on the right-hand side may more readily accept the nucleophilic attack of the water molecule than the phosphate on the left-hand side. According to this, the hydrolysis process is much faster in acid medium than in a neutral medium [13-15].

The results of experiments in 2wt% aqueous solution of citric acid, showed that the time dependency of $f(PO_4^{3-})$ is similar to $f(Me)$, where Me are metal cations released by ion-exchange reactions in the glass. These results indicate a significant influence of ion exchange reactions on the hydrolysis of the polyphosphate chains of glass.

By comparing the values for normalized mass release in both solvents for PGF2, it can be seen that very similar values were obtained for all dissolution times (Fig.1). This result is not surprising. Among the phosphate glasses, ultraphosphates are the least durable due to the instability of the branching points (Q3). The preparation and handling of anhydrous ultraphosphate glasses are rather difficult because water adsorption occurs within a few minutes of exposure to air. Phosphoric acid is formed on the surface of ultraphosphate glass which is in contact with air due to the hydrolysis reaction. The presence of hydroxyl groups in ultraphosphate glasses accelerates the process of water absorption from the air [16]. From Fig.2b and 2d (PGF2) it can be seen that Stage I, for dissolution in both solutions, ends after 17 hours and Stage II after 240 h. For this examined glass and under such experimental conditions, it can be stated that the type of solvent does not affect the dissolution rate.

The pH of the solution for dissolution in bidistilled water (Fig.4), decreases in a short time and remains relatively constant, both for PGF1 and PGF2. For the complex compositions, each reaction influences the kinetics and mechanisms of the other reactions. Thus, the breakage of a P-O-P bond releases an H^+ ion, which leads to a further decrease in the pH of solution. It could be considered that the change in the solution pH from neutral to acid supports the reactions that occur in the hydrated layer. In this layer, the glass network is dissolved with the hydrolysis of the phosphate chains. At the beginning of the reaction, a rapid equilibrium between phosphate groups and hydrogen ions was achieved.

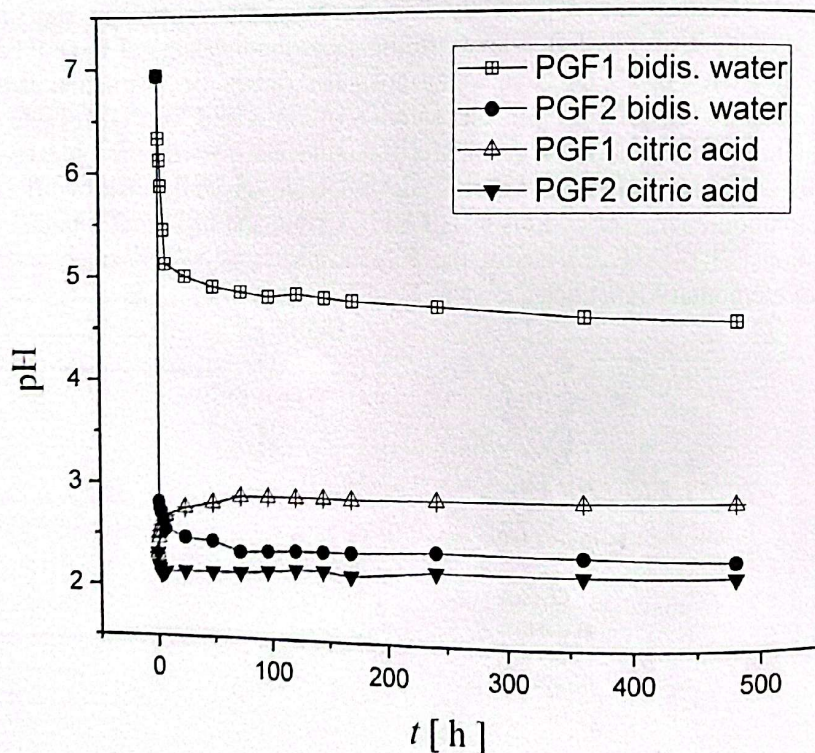


Figure 4. The time dependence of the solution pH

It may be seen in Figure 4, for dissolution of both glasses in 2 wt% aqueous solution of citric acid for that the pH increased and for relatively short times reached values that were unchanged at a given temperature. For longer times, the change of hydrogen ion concentration is diminishing due to reduced glass dissolution and pH tends to a constant value that corresponds to steady-state conditions at a given temperature.

As it can be seen from the dissolution experiments, ultraphosphate glass, PGF2, shows greater resistance in an acidic environment than PGF1 glass. This can be explained by the fact that iron phosphate glass is attributed to the presence of more hydration-resistant Fe-O-P bonds compared to P-O-P bonds available in other phosphate glasses [17].

3. CONCLUSION

The dissolution behavior of two phosphate glasses (65P2O5•1SiO2•22K2O•7CaO•3MgO•0.5ZnO•0.5MnO (PGF1) (wt %) and 60P2O5•1SiO2•22K2O•7CaO•3MgO•0.5ZnO•0.5MnO•3Fe2O3•2CuO (PGF2) (wt %) in bidistilled water and 2 wt% citric acid aqueous solution at the temperature of 37 °C for different time was investigated. All experiments were conducting in static conditions. The time dependence of the elements' concentration in solution, mass release and pH values were analyzed. It was shown that three different stages can be distinguished during glass dissolution in both bidistilled water and citric acid solution. The dissolution of these glasses can be successfully described with an ion exchange mechanism which takes place simultaneously with hydrolysis of the covalent bonds of the glasses networks. The chemical composition of investigated glasses have a huge impact on the complex dependence of the normalized leached masses of ions on time. In the case of dissolution experiments in bidistilled water, for both glasses, it was shown that pH values decreased in the initial stage of dissolution and then remained constant. The dependence of the pH value of 2 wt% aqueous citric acid solution on time, for both investigated glasses, showed that the pH value increased in the initial stage of dissolution and then remained constant.

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