

# Porous Slow Release Silicate-Phosphate Glasses Synthesized by Polymer-Derived Ceramics Method Appropriate for Plants Nourishment

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**Abstract:** As an alternative to conventional fertilizers, e.g. NPK (the Nitrogen-Phosphorous-Potassium-containing chemical fertilizers) which release their nutrients in a short time glass fertilizers are ideal as they release macro- and micronutrients for crops and plant nourishment more gradually. Also, despite conventional ones, they have no ground-water pollution. In the present study, glass fertilizers were synthesized via polymer-derived ceramics (PDC) method. Despite the melt-casting procedure, PDC needs lower temperatures in heat treatment. The precursors consist of poly-siloxane and active fillers. Thus, thanks to gaseous release during heat treatment of the present active fillers, i.e.  $\text{Ca}(\text{OH})_2$ ,  $\text{MgCO}_3$ , and  $\text{Al}(\text{OH})_3$ , a porous microstructure can be generated. In order to manipulate the pore size and specific surface area, fractions of calcined active fillers were used. The experiments showed that upon the increase of non-calcined active fillers, the specific surface area and the amount of porosity were increased due to more gaseous release during heat treatment. Thus, affected by microstructure, the release rate of macro and micro-elements was higher in the sample containing non-calcined active fillers, in comparison to other samples. Additionally, the porous samples were able to be loaded by extra nutrients containing Nitrogen, like  $\text{KNO}_3$ .

**Keywords:** Glass fertilizer, Polymer-derive ceramics, Slow release, Active fillers.

## 1. INTRODUCTION

Conventional chemical fertilizers like NPK fertilizer (the Nitrogen-Phosphorous-Potassium containing chemical fertilizer), has been proved to affect negatively on the environment. They either are washed out by irrigation, due to their high solubility in water, and subsequently flow into groundwater or release into the air in the form of gaseous compounds such as  $\text{NH}_3$ [1]. It has been reported that over 50% of nitrogen and 30% of phosphorous in the rivers originate from chemical fertilizers. As a result, not only conventional fertilizers cannot contribute to the nourishment of agricultural products properly, but also they are harmful to ecosystems for long periods [2]. On the other hand, the demand for food production has been increased continuously, thus, the need for high quality and efficient cultivation is indispensable. However, the substitution of conventional fertilizers by novel fertilizer resources or other new routes seems inevitable. To provide essential nutrients for plant growth, the fertilizer substances should contain a series of macro-and micro-elements [3].

Glass fertilizers are amorphous rigid materials comprising macro- and micro-elements that are vital for the growth of plants. The necessary macro-elements (needed in high quantity) are K, P, N, Mg, S, and Ca and the micro-elements (needed in low quantity) are usually B, Fe, Zn, and Cu[3], which should be incorporated into the glass structure homogeneously [4,5]. Glass fertilizers are slowly dissolved in aqueous solutions and able to remain into the soil for long periods; thereby, the probability of groundwater pollution can be diminished [6]. Moreover, despite NPK, glass fertilizers do not release  $\text{SO}_4^-$  and  $\text{Cl}^-$  which are detrimental to ecosystems or do not make the problem of soil acidification and salinization[7].

The leaching of glass fertilizers in contact with water includes the diffusion of small proton ions ( $\text{H}^+$ ) into the glass network and ion exchange with other ions, e.g.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cu}^{2+}$ . As a result, the glass structure becomes more chemically unstable and leads to the leaching of some network formers like  $\text{P}^{5+}$ . While some ions like  $\text{Si}^{4+}$  may not dissolve in soil easily and this phenomenon increases the amount of sand in the soil after fertilization by

this type of material [8, 9, 10]. Also, the solubility of glass fertilizers can be accelerated in slightly acidic media as a result of citric acid released from plant roots, so that, the plant can itself adjust the dissolution process rate and gain the nutrients better [11].

In the conventional melt-casting method to produce glass fertilizers, the raw materials must react at high temperatures (1300-1400 °C) to form a homogeneous melt [12]. Whereas in polymer-derived ceramics (PDC) method the amorphous materials are obtained at temperatures below 800 °C. In this process, soft and shapeable poly-siloxane is first mixed with several active fillers to afford appropriate composition. Then, the mixture is heated in the air up to the pyrolysis temperature of the polymer. At this stage, which is called Ceramization, the polymeric chains turn into amorphous structures and some gases, e.g. CO<sub>2</sub>, CO, H<sub>2</sub>, etc. [13]. The produced gases generate an interconnected porous microstructure the pressure of which determines the size and fraction of the porosities [14].

According to the requirement of crops and plants, the ratio of macro-elements should be adjusted. In NPK fertilizers, For instance, the P<sub>2</sub>O<sub>5</sub>/K<sub>2</sub>O ratio is about 0.5 to 1; Thus, this one should be taken into account in the formulation of glass fertilizers [15]. By the increase in the amount of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, the rate of glass dissolution decreases, and vice versa. Moreover, some elements, like zinc, iron, copper, manganese, etc., which are micro-elements, can be supplied by leaching from the glass matrix [9, 12, 16].

In this work, in addition to the fabrication of glass fertilizer by the PDC method, the generation of porous microstructures has been assessed, especially based upon the effect of active fillers. Also, the rate of release was evaluated based upon the microstructure of obtained samples.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Starting Materials

The chemical composition of the used glass fertilizer was SiO<sub>2</sub> 32.63; P<sub>2</sub>O<sub>5</sub> 31.57; K<sub>2</sub>O 22.10; CaO 4.21; MgO 3.15; Al<sub>2</sub>O<sub>3</sub> 5.26; ZnO 0.26; CuO 0.26; and Fe<sub>2</sub>O<sub>3</sub> 0.52 (%wt). To provide SiO<sub>2</sub>, a commercial-grade poly-siloxane,

RTV silicone resin was used. This material was accompanied by a corresponding liquid organic hardener. The SiO<sub>2</sub> yield of this silicone resin was determined by about 56.6 wt%, after heat treatment at 700 °C in the air atmosphere for 3 hours. Other raw materials (active fillers) were K<sub>2</sub>HPO<sub>4</sub> (Merck-CAS 7758-11-4), Al(OH)<sub>3</sub> (Merck-CAS 21645-51-2), Ca(OH)<sub>2</sub> (Merck-CAS 1305-62-0), MgCO<sub>3</sub> (Merck-CAS 12125-28-9), ZnO (Merck-CAS 1314-13-2), CuO (Merck-CAS 1317-38-0), and Fe<sub>2</sub>O<sub>3</sub> (Sigma Aldrich-310050).

### 2.2. Preparation of Samples

In the present work different porous glass structures were manufactured using different fractions of preheated and not-preheated active fillers. Through this strategy, three kinds of samples were made according to Fig1. It should be noted that the first group was 'non-calcined' samples, such that, active fillers were all used without preheating and calcination. On the other hand, the second group was 'calcined' samples, in which the active fillers had been entirely preheated at 900 °C and ground to reach below 37 μm in particle size, by fast-mil (Sanat Ceram-1276). Finally, the third group was the 'partially-calcined' sample, which had half of its active fillers proportion, calcined at 900 °C, and the rest was non-calcined.

The samples were heated at the air atmosphere until 500 °C and kept at this temperature for 30 minutes and heated again to 700 °C with another 30 minutes soaking time at 700 °C before cooling to room temperature. The heating rate was 5 °C/min.

To supply Nitrogen, a starch-based gelation system containing potassium nitrate (KNO<sub>3</sub>) was prepared which 'non-calcined' samples were dipped in this suspension (the ratio of water:starch: KNO<sub>3</sub> was equal to 1:3:5). Furthermore, another heat treatment has been done at 350 °C for 30 min.

### 2.3. Characterization

To study the release behavior of glass materials, the leaching test was carried out in periods of 5, 15, 25, and 35 days. In this test, 1 g of each sample was inserted into vials containing 5 cc of deionized water. Every piece of glass was just studied for only a time. At the end of every period, 1 cc of the corresponding solution was used for analysis by inductively coupling plasma

instrument (ICP, Varian ICP-OES 730-ES, Palo Alto, U.S). X-ray diffraction analysis (XRD, Panalytical-2009, Cambridge, U.K.) employing Cu K $\alpha$  radiation (0.15418 nm) was carried out to evaluate the phase analysis after heat treatment. Field emission scanning electron microscope (FE-SEM, TeScan Mira III, Brno, Czech Republic) and transmission electron microscopy (TEM, Philips CM-200) were used to study the microstructure of samples. Furthermore, simultaneous thermal analysis (STA, TA instrument, Germany) was used to evaluate thermal behavior. Also to measure the specific surface area, Nitrogen adsorption (BET, BELSORP mini-II) was used for bulk samples.

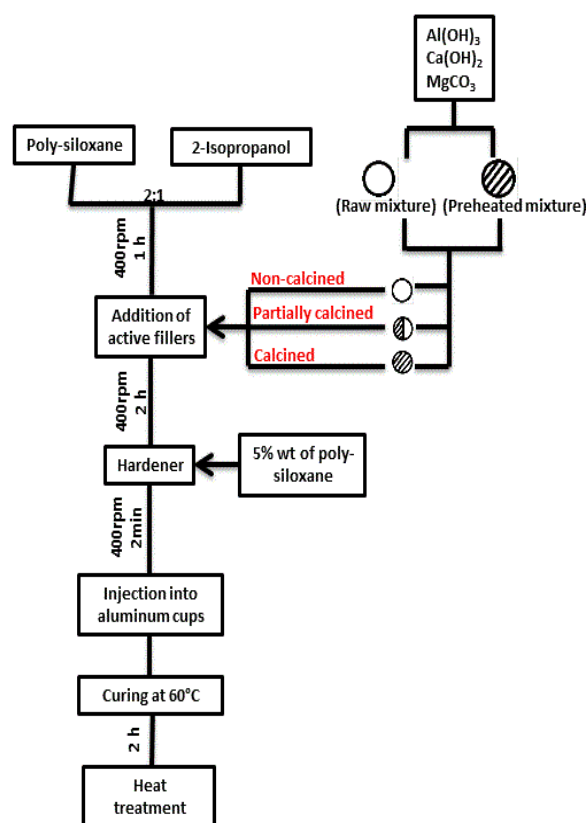


Fig. 1. the preparation processing of samples.

### 3. RESULTS AND DISCUSSION

#### 3.1. The Effect of Phase Separation

Fig 2 shows the XRD pattern of the 'calcined' sample after pyrolysis at 700 °C without any sharp peak indicating amorphous structure. Despite the absence of sharp peaks, it shows two broad peaks. The first one located at about 28° can be attributed to an amorphous separated silicate phase and the second one at 42° can be

related to an amorphous separated phosphate phase [8, 16]. The main reason for phase separation is the different roles of SiO<sub>4</sub> and PO<sub>4</sub> tetrahedral as net-formers [17].

The occurrence of such a phase separation can produce a low water dissolution resistant phase which is P and K rich, releasing significant macro-elements. However, the amorphous separated silicate phase remains in the soil, such that, the analysis of soil after fertilizing by this type of material has shown an increase in the amount of sand, at least 8% [9, 18].

#### 3.2. The Effect of Active Fillers on Microstructure

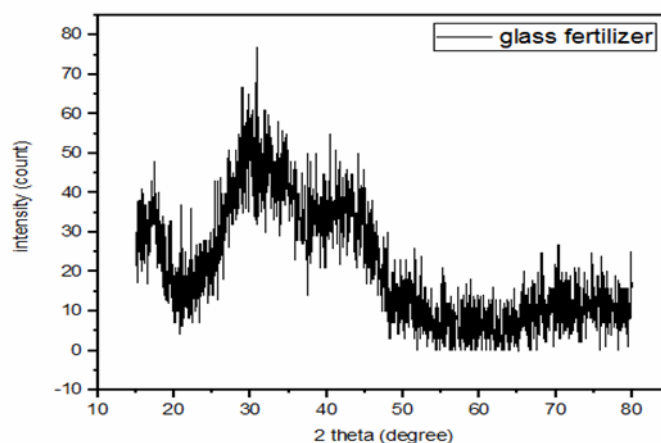
As it was noted, the silica constituent of the glass was provided by poly-siloxane, but the other ones have been supplied by active fillers. These active fillers were used in the form of calcined or non-calcined, or both of them. Non-calcined active fillers exhibit loss of weight while heat treatment producing high interconnected porosities [19, 20]. Thermal analysis was used to evaluate the reactions (Fig 3). According to Fig 3(a), the siloxane pyrolysis exothermic peak is located at about 510 °C, whose sharpness indicates the rapid occurrence of pyrolysis. For the 'non-calcined' sample, there is an endothermic peak at about 610 °C, which indicates the decomposition of active fillers, i.e., Ca(OH)<sub>2</sub>, Mg CO<sub>3</sub>, and Al(OH)<sub>3</sub>. In comparison to the 'non-calcined' sample, the intensity of this peak at the 'partially-calcined' sample has been reduced by about 4.5 μV, whereas, this peak has vanished at the 'calcined' sample.

According to Fig3(b), the weight loss which is attributed to siloxane pyrolysis at about 500-550 °C, has been occurred for each sample. Whereas, the weight loss which is from non-calcined active fillers has been taken place at about 600 °C. Furthermore, this weight loss is different for each sample; the weight loss for the 'non-calcined' sample is 5% in this section, while this one is about 3% for the 'partially-calcined' sample, and it is evident that no weight loss has occurred for the 'calcined' sample in this section.

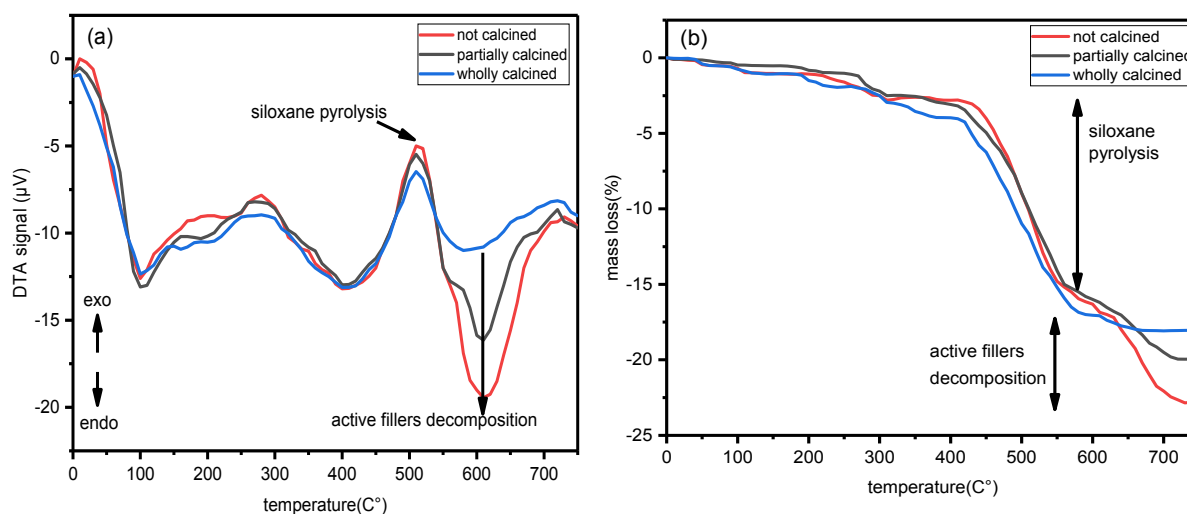
According to Fig 4, the visual features of 'calcined'(a), 'partially-calcined'(b), and 'non-calcined'(c) samples were different in roughness and pore size. According to Fig 5, the role of active fillers to form macro-porosities has been evaluated

by TEM. By the usage of calcined active fillers, no macro-porosity was evident; however, a network of micro/meso-porosities was obvious. It seems the formation of such a network is thanks to the pyrolysis of poly-siloxane at 500-550 °C, forming nano-canals to exhaust produced gases of organic moieties (Fig 5(a)). According to Fig 5(b), in

presence of non-calcined active fillers, the production and propagation of porosities in number and size have been intensified. Thus, macro-porosities were evident among interconnected canals of meso/micro-porosities, due to the effect of gas release by non-calcined active fillers while heat treatment (about 610 °C).



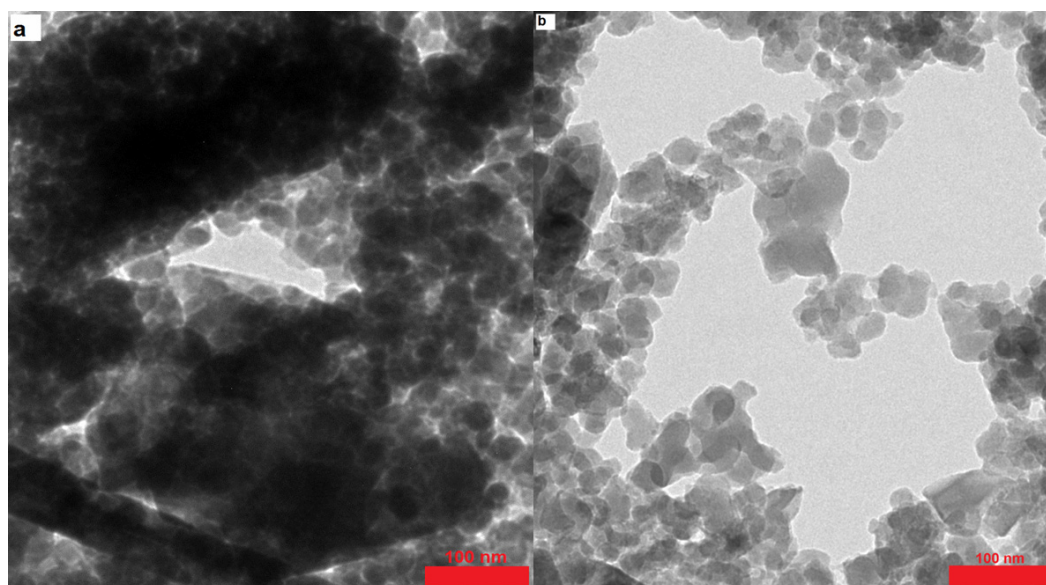
**Fig. 2.** XRD pattern of pyrolyzed sample



**Fig. 3.** (a) DTA of 'calcined', 'partially-calcined', and 'non-calcined' samples and (b) TG of 'calcined', 'partially-calcined', and 'non-calcined' samples.



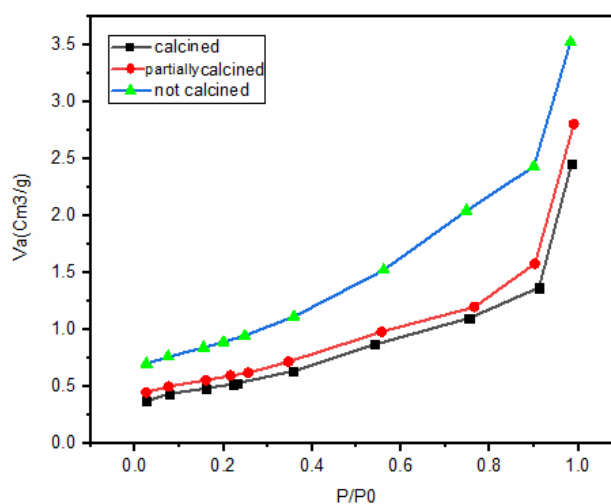
**Fig. 4.** (a) 'calcined' sample, (b) 'partially-calcined' sample, and (c) 'non-calcined' samples.



**Fig. 5.** TEM micrograph of (a) 'calcined' and (b) 'non-calcined' samples.

According to Fig 6, N<sub>2</sub> adsorption plots for 'calcined', 'partially-calcined', and 'not-calcined' bulk samples are different which have been interpreted via BET analysis (table 1). The results are in accordance with TEM (Fig 5), such that by an increase in the proportion of not calcined active fillers, free surface, saturation volume, and void volume have been increased.

The nature of active fillers is effective on microstructure, especially pore size, pore shape, and pores distribution. Albeit, there are other factors effective on microstructure, e.g. heating rate, the complexity of siloxane chains, the particle size of active fillers, etc. [13, 14], which have not been evaluated in the current investigation.



**Fig. 6.** the N<sub>2</sub> adsorption plots of 'calcined', 'partially-calcined', and 'non-calcined' samples.

**Table 1.** The results of BET analysis for 'calcined', 'partially-calcined', and 'non-calcined' samples

Sample	Free surface (m <sup>2</sup> /g)	Saturation volume at p/p0~1 (cm <sup>3</sup> /g)	Void volume per unit (cm <sup>3</sup> /g)×10 <sup>-3</sup>
calcined	1.7845	2.4568	3.8006
partially-calcined	2.0494	2.8054	4.3399
'non-calcined	3.1159	3.5235	5.4508

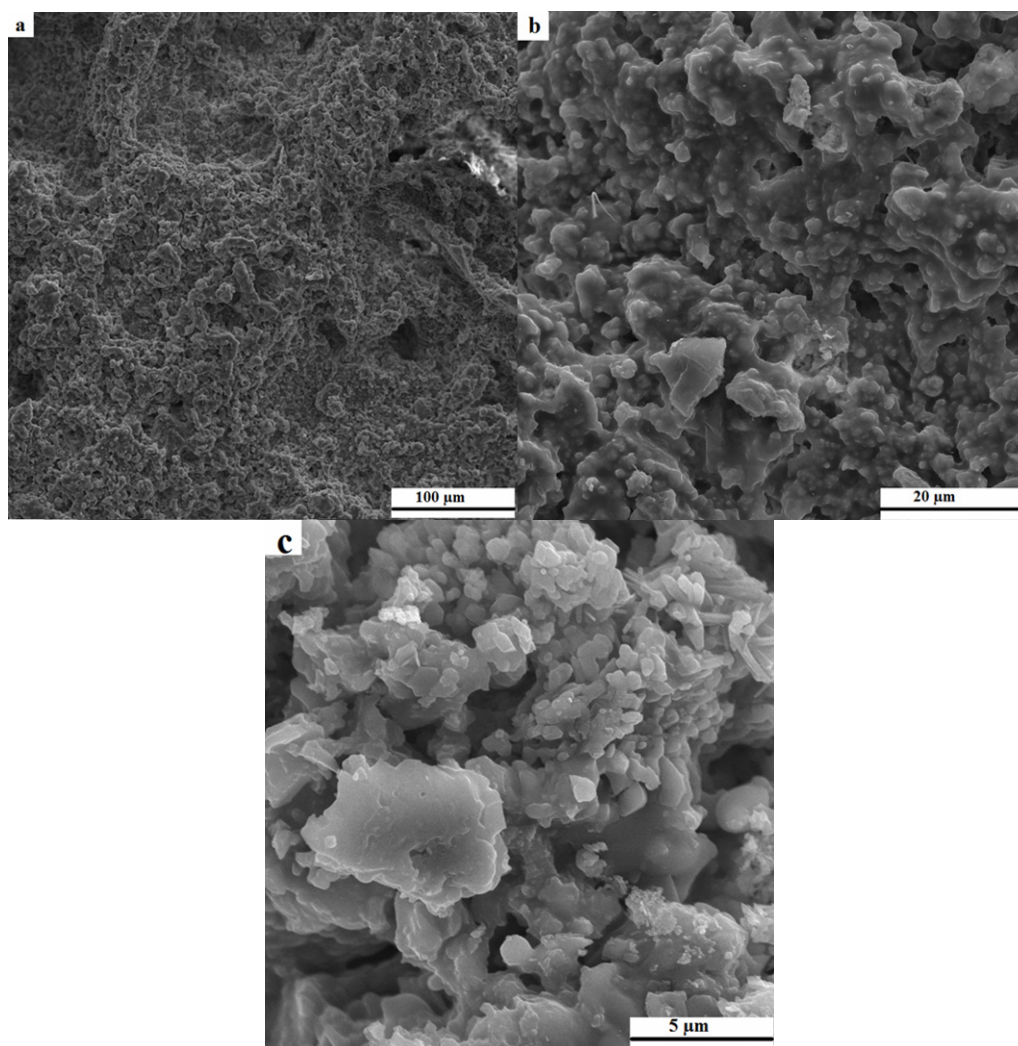


The microstructure of the 'calcined' sample has been shown in Fig 7, with a limited number of macro porosities (Fig 7(a)), due to the usage of calcined active fillers. Even, the number of small porosities was restricted (Fig 7(b) and Fig 7(c)). Although, based upon TEM micrograph (Fig 5(a)), 'calcined' sample contained a network of micro-porosities which cannot be seen via FE-SEM. Nevertheless, a 'calcined' sample cannot be categorized as a macro/mesoporous material.

The microstructure of the 'partially-calcined' sample has been shown in Fig 8. Some macro-porosities were obvious seldom (Fig 8(a)), which were interconnected (Fig 8(b)), such that, macro-porosities were surrounded by small ones. These

interconnected porosities have been distributed all over the texture, forming a mesoporous material (Fig8(c)). Thus in accordance with BET analysis(Fig 6), the more interconnectivity of porosities in the 'partially-calcined' sample has introduced more free surfaces, in comparison to the 'calcined' sample.

'non-calcined' sample was completely porous (Fig 9). Despite 'calcined' and 'partially-calcined' samples, there were many large porosities in the microstructure of the ' non-calcined' samples, which have been produced as a result of the release of gases (Fig 9(a) and Fig 9(b))[19, 20]. Although, there were still many interconnected meso-porosities, making a macro/mesoporous material(Fig 9(c)).



**Fig. 7.** FE-SEM micrograph of 'calcined' sample at magnitude (a) 498 $\times$ , (b) 3k $\times$  , and(c) 10k $\times$

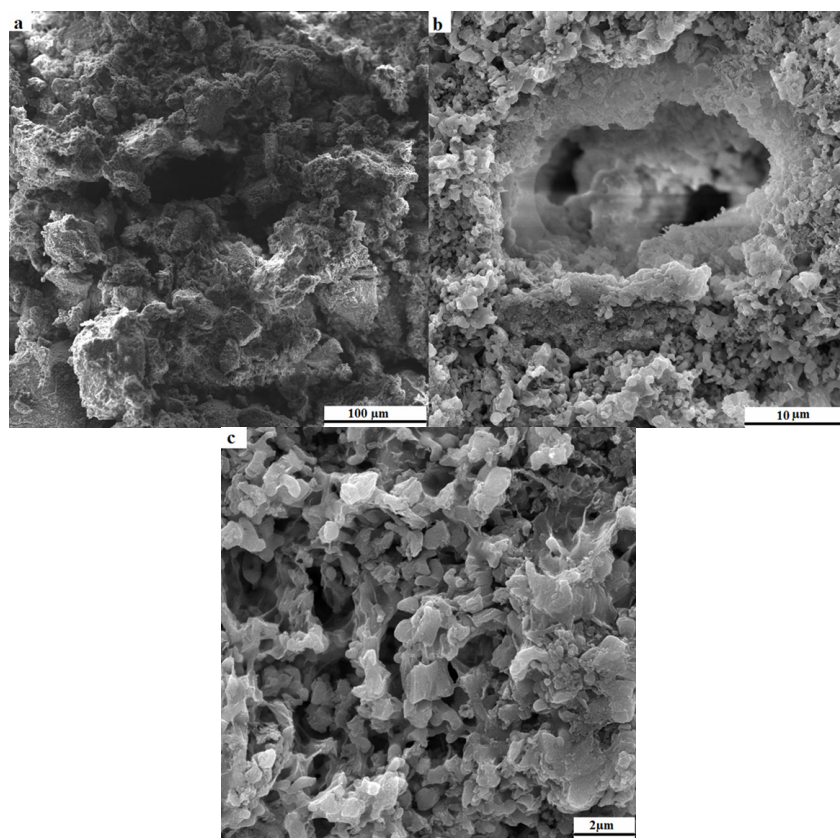


Fig. 8. FE-SEM micrograph of 'partially-calcined' sample at magnitude (a) 500 $\times$ , (b) 5k $\times$ , and (C) 15k $\times$

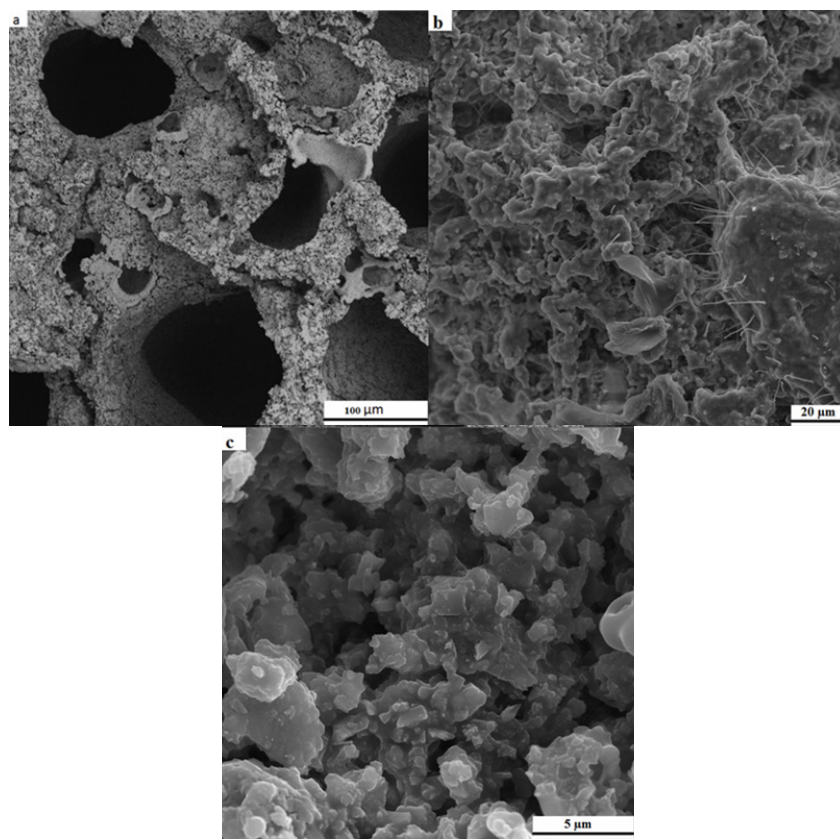
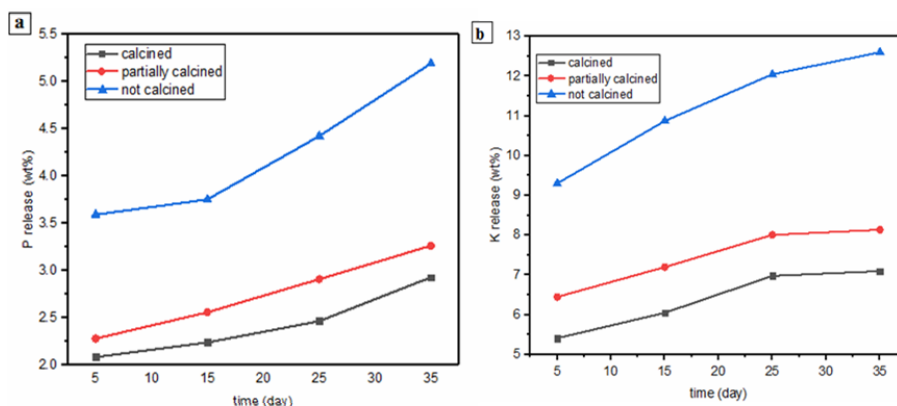


Fig. 9. FE-SEM micrograph of 'non-calcined' sample, at (a) 500 $\times$ , (b) 1.37k $\times$ , and (c) 3k $\times$

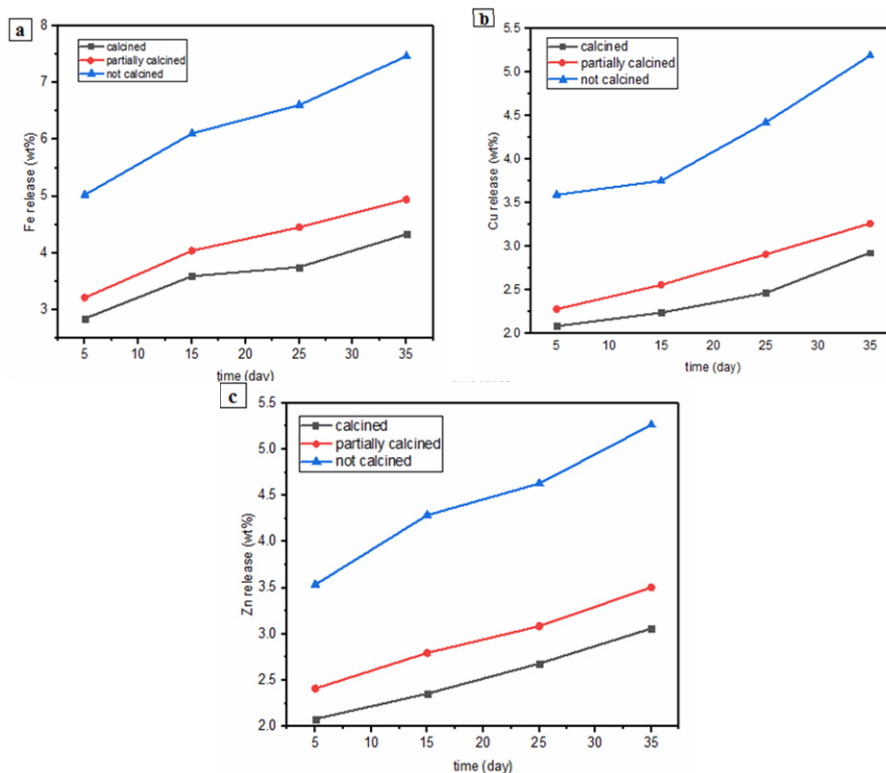
### 3.3. The Slow-Release Behavior

The rate of nutrient release is the main difference between glass fertilizers with conventional chemical ones, such as, NPK fertilizers which release above 80% of phosphorous (P) and potassium (K), just after 5 days. Furthermore, this substance is lost entirely after 25 days [3]. According to Fig 10, for obtained samples, the release rates of P and K have been controlled. The 'calcined' sample has shown lower than 3 and 6% release of P and K, respectively. These contents have been just 4 and 7% for P and K, respectively, after 35 days. In 'non-calcined' sample, more than 7 and 12% release of P and K have been observed

after 35 days. This difference is because of the higher free surface (Fig 6), such that, the free surface of the 'non-calcined' sample was almost 75% greater in comparison to the 'calcined' sample. The release of micro-elements, e.g. Fe, Cu, and Zn, from fertilizers and adsorption of them by crops and plants, is essential for the growth process. For instance, there is a minimum need for Fe in the leaf or fruit of orange trees which is about 50-250 ppm. The lack of Fe in this plant makes a special disease, called Fe chlorosis, in which the feature and the taste of the fruits change, unfavorably [3, 21]. Thus, the release of Fe from glass fertilizers has been evaluated (Fig 11).



**Fig. 10.** the release percentage of (a) P, and (b) K, as a function of immersion time.



**Fig. 11.** the release percentage of (a) Fe, (b) Cu, and (c) Zn, as a function of immersion time.



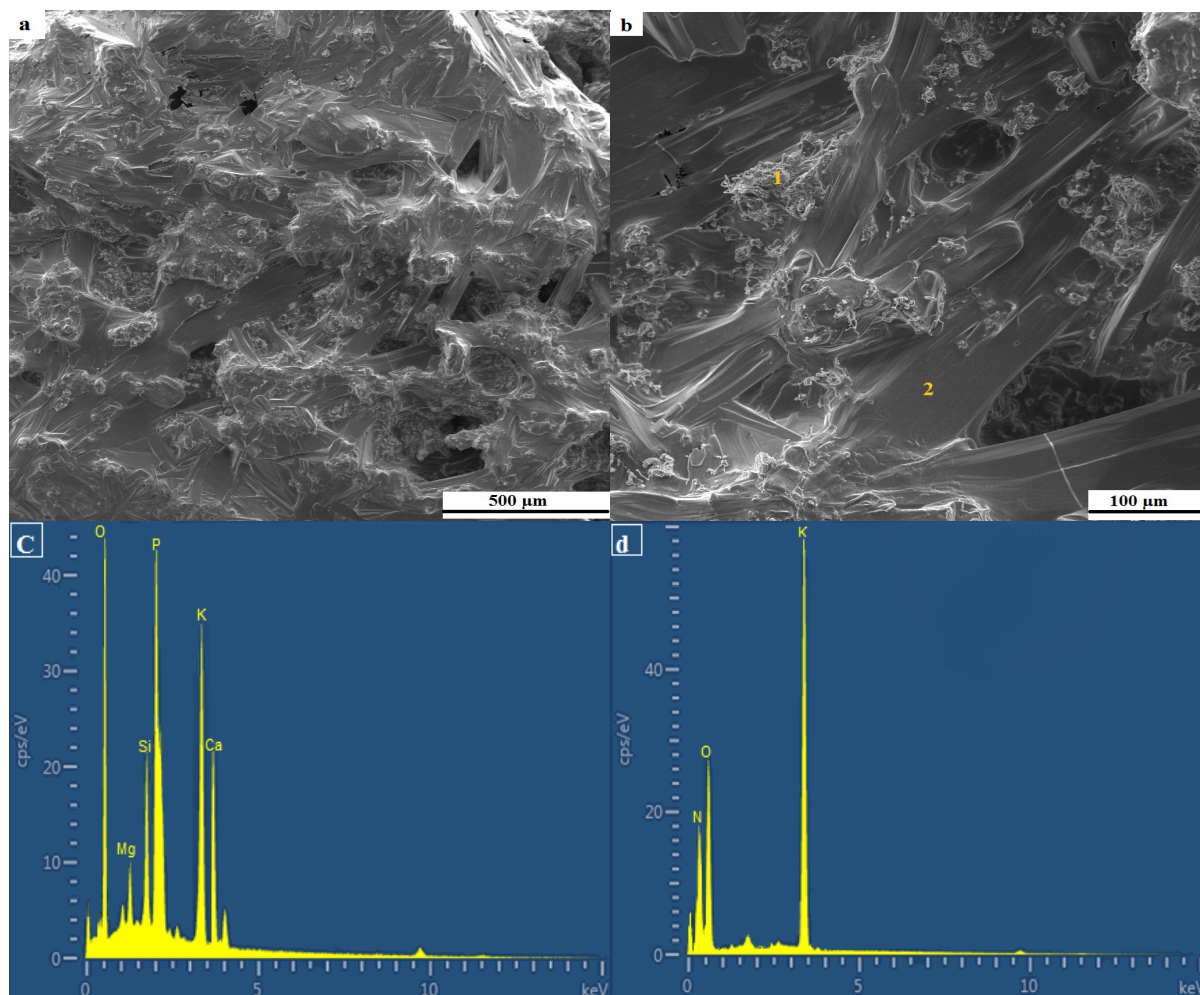
After 35 days, about 5, 4, and 7% of Fe has been released from 'calcined', 'partially-calcined', and 'non-calcined' samples, respectively (equal to 151.6, 173.1, and 261.4 ppm, respectively) (Fig 10(a)). Furthermore, the release of Zn and Cu have been evaluated (Fig 11(b) and Fig 11(c)).

### 3.4. Loading of Potassium Nitrate

A significant macro-element for plant nourishment is nitrogen (N). It is difficult to add this element to a slow-release glass composition; however, thanks to porous interconnected microstructure, it is possible to load desirable substances, like nitrogen-containing materials. A substance that has been reported as a source of nitrogen for crops and plants is potassium nitrate ( $\text{KNO}_3$ ) [22, 23].

According to Fig 12,  $\text{KNO}_3$  has been loaded in porosities of 'non-calcined' sample via a starch-based gelation system to stabilize particles of  $\text{KNO}_3$ . After loading, a second heat treatment at  $350^\circ\text{C}$  was carried out and the particles of  $\text{KNO}_3$  have been aggregated.

The porous structure which has surrounded the aggregates is the glass skeleton containing macro/micro-elements, except N (Fig 12(c)), whereas the aggregated particles have N and K (Fig 12(d)). The aggregation of  $\text{KNO}_3$  particles reduces the free surfaces which are essential for leaching, so it can reduce the rate of  $\text{KNO}_3$  leaching. Furthermore, these aggregates are surrounded by glassy walls of porosities, thus, it can limit the accessibility of water to the  $\text{KNO}_3$  particles.



**Fig. 12.** FE-SEM micrograph of  $\text{KNO}_3$  loaded sample ('non-calcined' sample) after second heat treatment at  $350^\circ\text{C}$ , at magnitude (a)  $58\times$  and (b)  $250\times$ , and EDS spectrums of (c) porous glass structure and (d) aggregated  $\text{KNO}_3$ .

#### 4. CONCLUSION

Soil fertilizers based on inorganic glass materials have been successfully manufactured through the PDC method that was able to leave a slow-release porous structure behind, composing necessary constituents for plant growth, e.g. K, P, Fe, Cu, and Zn. Thanks to the gas release of some active fillers ( $\text{CaCO}_3$ ,  $\text{Mg(OH)}_2$ , and  $\text{Al(OH)}_3$ ), the porous structure could be generated in samples. The content of porosities and their connectivity was related to the fraction of calcined active fillers to non-calcined active fillers that were used in the batch. The microstructures were completely different, such that, there were just micro-porosities in the 'calcined' sample, but interconnected macro/meso-porosities were obvious in 'partially-calcined' and 'calcined' samples. The slow-release behavior of samples was related to their microstructure. The amount of release has been increased from 'calcined' sample to 'non-calcined' sample, such that, after 35 days, 'non-calcined' sample showed just 7 and 12% release of P and K, respectively which this amount is sufficient for plants nourishment. Moreover, Due to the macro/mesoporous structure of the 'non-calcined' sample, it was also capable of being loaded with other nutrients, like  $\text{KNO}_3$  which releases Nitrogen components.

#### REFERENCES

- Hazra, G., Das, T., "A review on controlled release advanced glassy fertilizer." *Global J. Sci. Front. Res.*, 2014, 14, 33-43.
- Waclawska, I., Szumera, M., "Reactivity of silicate-phosphate glasses in soil environment." *J. Alloys & Comp.*, 2009, 22, 246-253.
- Shand, C., "Plant Nutrition for Food Security; A Guide for Integrated Nutrient Management." *J. Experimental Agri.*, 2007, 43, 132-132.
- Lewis, M. H., *Glasses and glass-ceramics*, Chapter1, a new spectroscopic technique for structure, ed. 1<sup>st</sup>, Springer, Netherland, Amsterdam, 1989, 2-59.
- Rezvani, M., Yekta Eftekhari, B., Marghousian, V. K., "Mechanical and chemical properties of  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$  glass-ceramics in the presence of various nucleating agents." *Iranian J. Mat. Sci. Eng.*, 2008, 5, 15-21.
- Quamruzzaman, M., Rao, A. S., Reddy, K. S., Sherchan, D. P., Karki, K. B., Sherchan, D. P., Karki, K. B., Improving plant nutrient management for better farmer livelihoods, food security and environmental sustainability, Part IV, South Asian countries, Rome: Rap Pub., U.N., FAO, 2006, 13-72.
- Prasad, R., "Efficient fertilizer use: The key to food security and better environment." *J. Tropical agri.*, 2009, 47(1), 1-7.
- Sava, M., Sava, B. A., Boroica, L. U., Diaconu, A. D., Ursu, L., Elisa, M., "Efficiency of vitreous phosphato-potassium fertilizers on autumn crops." *J. Sci. Papers*, 2010, 53, 187-93.
- Tamayo, A., De la Torre, R., Ruiz, O., Lozano, P., Mazo, M. A., Rubio, J., "Application of a glass fertilizer in sustainable tomato plant crops." *J. Sci. of Food & Agri.*, 2018, 98:12, 4625-4633.
- Stoch, L., Waclawska, I., Ciecinska, M., "Thermochemistry of biologically active glasses." *J. Therm. Anal. & Calorim.*, 2001, 65(2), 341-350.
- Lityński, T., Jurkowska, H., Górlach, E. "Analiza chemiczno-rolnicza in Polish - Chemical-agricultural analysis" *Nawozów. Państwowe Wydawn.*, 1976, 2, 149-149.
- Shelby, J. E. *Introduction to glass science and technology*, Chapter4, Immiscibility/phase separation. Royal soc. of chem., 2<sup>nd</sup> ed., Cambridge, UK, 2005, 51-70.
- Colombo, P., Mera, G., Riedel, R., Soraru, G. D., "Polymer-derived ceramics: 40 years of research and innovation in advanced ceramics." *J. Am. Cer. Soc.*, 2010, 93 (7), 1805-1837.
- Elsayed, H., Rebesan, P., Crovace, M. C., Zanutto, E. D., Colombo, P., Bernardo, E., "Biosilicate® scaffolds produced by 3D-printing and direct foaming using preceramic polymers." *J. Am. Cer. Soc.*, 2019, 102 (3), 1010-1020.
- Powlson, D. S., Pruden, G., Johnston, A. E., Jenkinson, D. S., "The nitrogen cycle in the Broadbalk Wheat Experiment: recovery and losses of  $^{15}\text{N}$ -labelled fertilizer applied in spring and inputs of nitrogen from the atmosphere." *J. Agri. Sci.*, 1986, 107 (3), 591-609.

16. Paul, A. Chemistry of glasses, Chapter 6, Acid-Base concepts in glasses. 1<sup>st</sup> ed. Chapman & Hall, New York, US, 1982, 174-203.
17. Kreidl, N. J. Inorganic glass-forming systems, Chapter I, Glass-Forming Systems. 1<sup>st</sup> ed. Academic Press Inc., Glass Sci. & Tech., Cambridge, UK, 1983, 105-299.
18. Trenkel, M. E. Slow-and controlled-release and stabilized fertilizers: an option for enhancing nutrient use efficiency in agriculture, Chapter 2, Development and manufacture of slow- and controlled release fertilizers and nitrifications and urease inhibitors. 1<sup>st</sup> ed. IFA, Paris, France, 2010, 17-20.
19. Elsayed, H., Colombo, P., Bernardo, E., "Direct ink writing of wollastonite-diopside glass-ceramic scaffolds from a silicone resin and engineered fillers." J. Euro. Cer. Soc., 2017, 37 (13), 4187-4195.
20. Fiocco, L., Babakhanova, Z., Bernardo, E., "Facile obtainment of luminescent glass-ceramics by direct firing of a preceramic polymer and oxide fillers." J. Cer. Inter., 2016, 42 (6), 6770-6774.
21. Torrisi, B., Trinchera, A., Rea, E., Allegra, M., Rocuzzo, G., Intrigliolo, F., "Effects of organo-mineral glass-matrix based fertilizers on citrus Fe chlorosis." Euro. J. Agronomy, 2013, 44, 32-37.
22. Sartain, J. B., Hall, W. L., Littell, R. C., Hopwood, E. W., "Environmental impact of fertilizer on soil and water." ACS Symp. series, 2004, 872, 180-195.
23. Vitosh, M. L., "NPK Fertilizers." Michigan S. Uni. Ext. Bulletin. 1996, 896, 1-5.