



Synthesis, Development and Applications of Glass Fertilizers on Khariff Paddy

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Abstract

Glasses in the phosphate system acting as slow release fertilizer were synthesized by melt- quenching technique. A new glass-material was prepared, which can be used as slowly soluble fertilizer for different type of plants. *Glasses were melted at the temperature (800 – 950°C) with a soaking period of 1hr. which was earlier reported to be melted not below 1000°C. Leaching study of these glasses with a maximum time period of 300 hrs were conducted under Soxhlet distillation condition with distilled water. A Fourier transform infrared (FTIR) spectrum was recorded in the 400-4000 cm⁻¹ range, revealed optical phonons specification for the phosphate matrix. FTIR studies show absorptions at 760, 879, 920, 1087, 1110, ~ 2193-2870, and ~3440-3500 cm⁻¹. ⁵⁷Fe Mossbauer spectroscopy studies were presented. Mössbauer studies were done in order to analyze their structure. Amorphous nature of glass was confirmed by XRD. The morphology of glass materials was analyzed by Scanning Electron Microscopy. SEM of some selected glasses was presented. X-ray Fluorescence (XRF) technique is used for elemental analysis and chemical analysis. The effect of different modifier ions like Na⁺, Fe³⁺, Mg²⁺, Ca²⁺, and K⁺ in the basic phosphate networks on melting's and time of melting has been found to be evident. The model structure of glasses has been considered taking the role of some glass formers/ modifiers which ultimately has an effect on the chemical durability of these glasses. For GF (glass fertilizer) minimum solubility was measured for the sample containing Iron Oxide (Fe₂O₃) and maximum solubility for base sample and from GF (glass fertilizer) maximum solubility appeared for the sample with molybdenum oxide. The results of the experiments reported here demonstrate that is possible to adjust the release of phosphate from the fertilizer to phosphate demand of the plant. Weight losses were followed with respect to cumulative time period of leaching. For some glass fertilizer samples, the leach rates as calculated from BET surface area measurements. They were in the range 6.3 x10⁻³ to 2.3 x10⁻³ g.m⁻².hr⁻¹ at 90°C. The pH determination ranging from 4.80 up to 7.50 of the leachate solution at ambient temperature under varying time intervals shows interesting and regular variations. The results are in conformity with the change of equilibrium pH under varying leaching time reported by other authors. The leaching study of such glasses under Soxhlet condition shows Ca²⁺, Mg²⁺ and K⁺ to be a candidate as modifier towards leach resistance. The findings have been corroborated in terms of ionic size, ionic radii and hence ionic potential of the modifier ions incorporated into the glass structure. Application of glass fertilizers was done on khariff paddy.*

Keywords: Phosphate glass; Leaching; Glass Fertilizers; Soaking period; Ionic potential; SEM; FTIR; Mössbauer; XRD; BET surface area

Introduction

The chemical composition of various essential minerals and elements meant for the regular as well as hastened growth and nutrition of all plants is termed as fertilizer. Using of fertilizers in agriculture can be very useful for food production, but on the other side it may be harmful for environment. Hence only necessary amount of fertilizers can be used for successful vegetation. It means that we must use fertilizers, which are dissolved quickly as is nutrient requirement of plants. In this case it is not a contamination hazard for environment. All the fertilizers have been categorized into several types depending on their constituents, strength and various other features (organic, inorganic, macronutrients, micronutrients, eco-friendly, controlled release glassy fertilizers etc.) [1-3]. Pure phosphate glass (vitreous P_2O_5), is highly hygroscopic and is not appropriate for application. The properties of this glass can be improved by addition of different network modifier – alkali and alkaline earth oxides. In that way, the multi component phosphate-based glasses or glass-ceramics having many specific properties that can be obtained. As such, these materials can find wide technological application [4,5]. As reported earlier the phosphate glasses of various compositions possess bioactivity and can be used as bio or eco-materials. Calcium phosphate glasses and glass ceramics for the bone implants in surgery and dentistry are well known biomaterials [6,7]. Recently, because of gradual solubility the attention was paid to the phosphate based glasses which can be used as new ecologically safe fertilizers [8,9]. The fact is that conventional technologies for land cultivation based on application of traditional mineral fertilizers are responsible for pollution of environment.

The main advantage of glasses is that sample composition can be manipulated by varying the concentration of the macro and micro nutrients. Therefore, the kinetics and mechanism of the dissolution process can be tailored as needed [10]. In the case of plant nutrition, it is important that the release rates of glass components are equal to the absorption rates of plants or microorganisms [11]. In this way, the possible damaging effects of accumulation or deficiency of elements can be avoided.

It is in this context one glass fertilizer can take a dual role. In addition as the leach resistant of glass is very high i.e. when applied to a soil the fertilizer will be released very slowly satisfying the optimum level of requirement and no misuse there. It has been found that when such a fertilizer is applied on tree like mango remain 2025 years at the root and it will grow and give fruits with a single charge of fertilizer. 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 (secular matrix) (b) the leach resistance of glass which may vary is very high i.e., it does

not dissolve easily in water. Glass fertilizer slowly distributed into the root of the plant/ crops and is distributed thus into fruits of the crops and in the due course it will be flourished. The excess of the amount of glassy fertilizer will remain in the soil and help for the next two batches of the crops [12]. Glass fertilizers (GF) are a new type of advanced and controlled-release fertilizer made from glass matrixes containing the most useful microelements (K, P, Mg, S, Ca) for plants, and also incorporate some microelements (B, Fe, Mo, Cu, Zn, Mn) required for the correct growth and development of crops or plants [1,12,13].

The main advantages of new type of fertilizers against conventional fertilizers are increased grade of assimilation by plants, do not release insoluble compounds in soil, and remain in the soil during the entire period of plant development and do not pollute the phreatic water [14-17]. At the same time, these fertilizers have special peculiarities: controlled solubility in the time for many vegetable cycles, possibility to incorporate in the vitreous matrix of many useful microelements [18] do not contain toxic compounds and do not release insoluble residues [19].

The use of glass fertilizers offers a lot of advantages as a result of: (a) Low or controlled solubility it avoid underground water pollution; the soil pH can be regulated by the pH of the glass matrix (b) None release acid anions (Cl^- , SO_4^{2-}) which are harmful for plants so there is no risk of soil burning when they are incorrectly dosed.

The glass composition was adjusted by addition of the microelements in a form of oxides Zn^{2+} , Mn^{2+} , Fe^{3+} and Cu^{2+} . The Object of this work is related to the leaching study of the different glass fertilizers with different compositions under soxhlet distillation conditions. The aim of this work is to study the Leaching of the Different glass Fertilizers with Different compositions under Soxhlet Distillation Conditions. Leaching study of these glasses up to 300 hr. was conducted under Soxhlet distillation condition with steam distilled water. The variation of physical and chemical properties were taken into account with the changes in ionic charges and ionic radii and hence ionic potentials of different modifier ions, the source of which are the respective modifier oxides, viz. MgO, CaO, Fe_2O_3 , ZnO and MoO_3 for different glass systems.

Materials and Methods

Materials

The glass sample ID, GF contains the major compounds necessary for crops and sample contain the same base oxides together with micro-elements oxides necessary for plant growth, 5 wt. % for iron (Fe), 5 wt. % for Zinc (Zn), 5 wt. % for molybdenum(Mo) and 10 wt. % for boron(B) respectively

over 100 %. Table 1 presents the oxide composition of GF in weight%. The glass ID, GF5 contains four microelements together such as 15 wt.% of boron, 10 wt.% of iron, 8 wt.% of zinc and 6 wt.% of molybdenum respectively.

The glass batches used in the present work were prepared from the ingredients like Ammonium dihydrogenorthophosphate $[(\text{NH}_4)_2\text{H}_2\text{PO}_4]$, AR grade, HI Media laboratory, Mumbai), Magnesium oxide (MgO, AR grade, Merck Life Science Private Ltd. Mumbai), Potassium dihydrogen phosphate (KH_2PO_4) , AR grade, Merck Life science Private Ltd, Mumbai) and Calcium oxide (CaO, AR grade, Merck Life science Private Ltd. Kolkata) have been used as raw materials for macro-elements. Borax $(\text{Na}_2\text{B}_4\text{O}_7)$, AR grade, RANKEM, New Delhi) ferric oxide (Fe_2O_3) , AR grade, Merck Life science Private Ltd. Mumbai) Zinc oxide (ZnO, AR grade, Merck Life Science Private Ltd, Kolkata) and molybdenum trioxide (MoO_3) , AR grade, E. Merck, Germany) were added in order to supply the microelements. Five glass compositions were prepared using the following precursor

which has been shown in Table 1.

Glass batches of different compositions are synthesized from respective oxide in acetone medium and mixed repeatedly after taking them in an agate mortar and pestle. They are next dried and taken in a high quality alumina crucible and fired in muffle furnace fitted with programmer. In this melting operation the temperature of melting and time of melting were the key factor to be monitored. The melting duration was between four to six hours. The important point to mention here is that in the present work we could melt the glass at much lower temperature (700-950°C) with a soaking period of 30 min -1 hr. which were earlier reported to be melted not below 1000°C. The temperature and time of melting was varied. Table 2 shows the melting and time for different glasses. The prepared glass was ground to powder and was subjected to Soxhlet distillation taking the powder in a net.

Glass ID	Composition (Wt. %)								
	$(\text{NH}_4)_2\text{H}_2\text{PO}_4$	MgO	KH_2PO_4	CaO	$\text{Na}_2\text{B}_4\text{O}_7$	Fe_2O_3	ZnO	MoO_3	Total
GF1	40	16	29	5	10	-	-	-	100
GF2	40	20	30	5	-	5	-	-	100
GF3	40	20	30	5	-	-	5	-	100
GF4	40	20	30	5	-	-	-	5	100
GF5	40	12	-	-	15	10	8	6	100

Table 1: Composition of different glasses (wt. %).

Glass ID	M.P.(±2°C)	Soaking period (Minutes)
GF1	900	60
GF2	950	60
GF3	900	60
GF4	900	60
GF5	900	60

Table 2: Melting point (°C) and time of Soaking period for different glass compositions.

pH Study

For the pH determination of the leachate solution, the bulk glass was powdered to 0.3 – 0.425 mm size. The pH of the liquid was determined by a pH meter (Sartorius digital pH meter, Model- PB11). Then 1.0 gm. of each sample glass was vapor distilled in Soxhlet apparatus with a round bottom flask (500 ml. capacity) fitted with a condenser [20]. The distillation was carried out for varying period of time up to a maximum of 300 hr. The heating was done in a heating

mantle. The arrangement is shown in Such measurements of pH were carried out at regular intervals of 24 hr, 48 hr, 72 hr, 96 hr, 120 hr, 144 hr, 168 hr, 192 hr, 216 hr, 240 hr, 264 hr, 288 hr, and 300 hr. respectively. For phosphate glasses, the leachate extract after each operation of leaching for varying time intervals was subjected to pH measurement. Fig. 1 shows the pH change with respect to time.

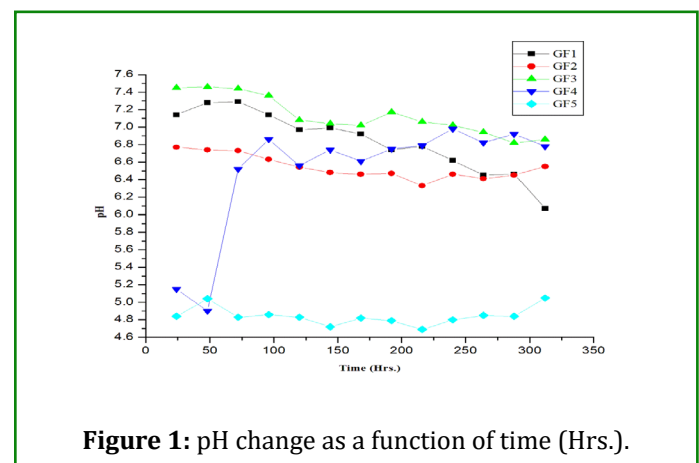


Figure 1: pH change as a function of time (Hrs.).

Leaching Study

For leaching studies about 1.0 g of glass powder (0.3-0.425 mm in size) samples were taken in nylon net, the dimension of which was such that the glass powder did not pass out through it. Next it was then steam distilled in borosilicate glass made Soxhlet apparatus with a round bottom flask (500 mL) fitted with a condenser [20,21]. The distillation was carried out for varying period of time up to a maximum of 300 hr. The heating was done in a heating mantle [22]. The arrangement is shown in a figure 2. The Weight loss after each run of leaching was measured by a four-decimal electronic balance (Sartorius) and was converted into % wt. loss. Fig.3 shows the % weight loss against time for different glasses. In order to find the leach rates, BET surface area of the glasses were determined under liquid nitrogen temperature and then leach rates were calculated from the total weight loss for the total cumulative leaching time [23].

The leach rates for GF1, GF3 and GF5 glasses after leaching were determined from BET surface area analysis from CSIR-CGCRI, Kolkata. The leach rate (LR) was measured according to the following relationship:

$$LR = \frac{W_i - W_f}{SA \times t}$$

Where W_i and W_f are the initial and final sample weights respectively, SA is the BET surface area of the sample and t is the time exposed to the leachant.

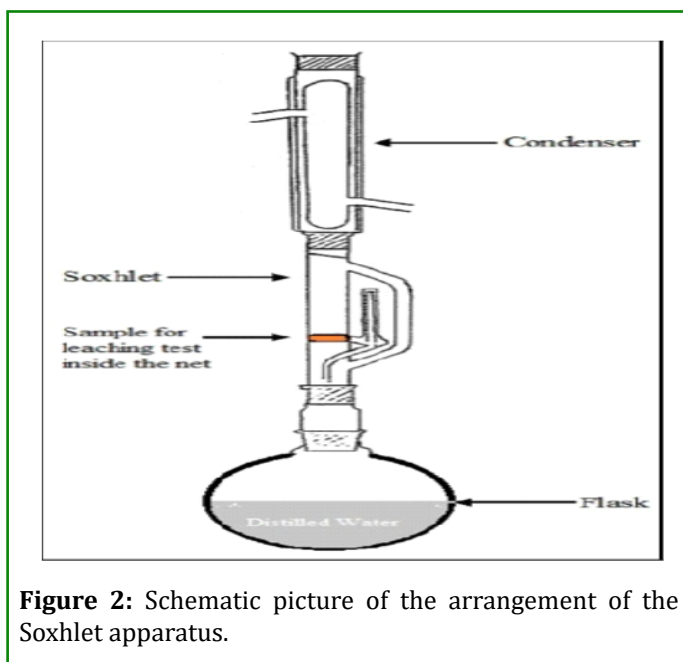


Figure 2: Schematic picture of the arrangement of the Soxhlet apparatus.

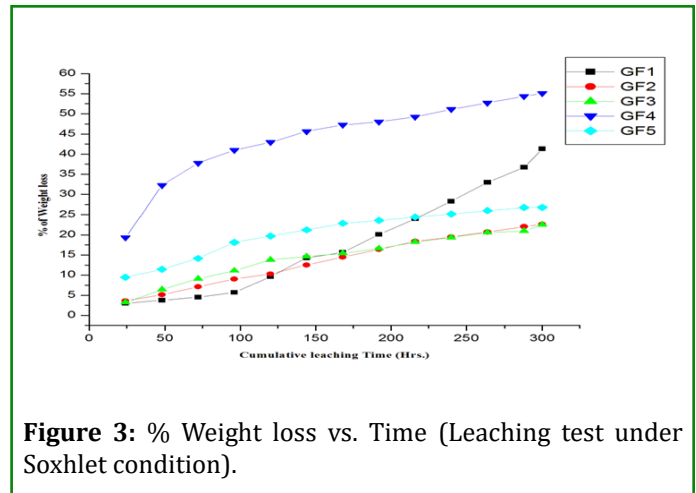


Figure 3: % Weight loss vs. Time (Leaching test under Soxhlet condition).

Results and Discussion

Table 2 shows the melting temperature and time of melting of different glass compositions obtained in the present work. In melting operation, the temperature and time of melting are the principal factors to be monitored. In the present work we could melt the glass at much lower temperature (750-950°C) with a soaking period of 30 min -1 hr. which were earlier reported to be melted not below 1000°C [24-26]. The effect of different modifier ions like K^+ , Na^+ , Mg^{+2} , Fe^{3+} and Ca^{+2} in the basic phosphate networks glass systems on the melting points and time of melting is quite evident.

In addition to this effect the different modifier ions (added as oxides) can also lower the melting temperature of a particular composition in the phosphate system [27,28]. Here the mechanism is that the modifier ion (M^{n+}) dissociates a Si-O (or B-O or P=O) bond of network and generates anionic O sites (O^-) and gets attached to such sites ionic ally. Additionally the variation in melting point among different compositions in the particular phosphate system (GF1 to GF5) can be explained due to different types of modifier oxides being added.

Results of pH Studies and Variation of pH

The plot of variation of pH against time (in hour) for different glass system are shown in figure 1. The curve for GF5 runs lowest. The slightly increasing trend in the pH values may be due to the mixed oxide of phosphate system. The observed pH values are in good agreement with the equilibrium pH values [29] of glass system having composition close to present work. The range of pH obtained in a phosphate glass with different modifier cation covers that of hours. If we consider that the following equilibrium is being operated in our aqueous system:

$H_2O \rightleftharpoons H^+ + OH^-$ the extent of which (i.e., the forward or the reverse direction) is influenced by the different modifier ions released during the leaching of the glass sample.

The ionic radii (\AA) of the different modifier ions in our case are as follows: K^+ (1.38), Na^+ (1.02), Fe^{3+} (0.69), Al^{3+} (0.50), Ca^{2+} (1.00), Zn^{2+} (0.74), Mg^{2+} (0.72) and Mo^{6+} (0.59). The corresponding ionic potential (Charge/radius) increases as K^+ (0.72) < Na^+ (0.98) < Ca^{2+} (2.00) < Zn^{2+} (2.70) < Mg^{2+} (2.77) < Fe^{3+} (4.69) < Al^{3+} (6.0) < Mo^{6+} (10.16).

Now the greater the ionic potential of M^{n+} , the more it will attract OH^- ions to form the corresponding hydroxides $M(OH)_n$, the dissociation of H_2O as above will be shifted to the forward direction releasing more number of H^+ in the medium. Thus the resulting solution will increasingly become acidic with decreasing the pH of the leachate solution [30,31]. This behavior is reflected in our observed data. Glass GF5 with MoO_3 shows lower pH value than GF3 with no MoO_3 in the composition.

The increased pH agrees with the results may be explained by the Na^+ and H^+ exchange corresponding to hydration of an outer layer of phosphate chains. This reaction left excess OH^- in solution, giving an initial pH increase, which was maintained. pH change will obviously depend upon the ion exchange and therefore glass composition. Phosphate ions (PO_4^{3-}) ions can bind with H^+ ions to form H_3PO_4 (phosphoric acid) whereas the cations would associate with OH^- ions (producing hydroxide). Therefore, due to the glass composition, more alkaline entities would be released leading to a pH increase. Note also that the pH of the solution remained neutral and therefore did not further influence dissolution rate.

The decreasing trend in the pH value from 24 hr. to 300 hr. in Fig.1 data can be explained in the light that with higher extent of leaching more modifier cations are released into the solution increasing the ionic potential leading to lowering of pH values.

Leaching Study and the Leaching Rate of the Glasses in Distilled Water Under Soxhlet Condition

Leaching operation of glasses was done under soxhlet distillation condition up to 300 hr. and it was observed that the total weight loss (or % weight loss) with respect to cumulative time (h) varies as: $GF4 > GF1 > GF5 > GF2 > GF3$ respectively [32]. The corresponding plot has been shown in Fig. 3. The leach rates (LR) for GF1, GF3 and GF5 glasses after leaching are determined from BET surface area analysis (liquid N_2 temperature). The BET surface area (SA) are as follows: $(SA)_{GF1} = 0.349 \text{ m}^2 \cdot \text{g}^{-1}$; $(SA)_{GF3} = 0.382 \text{ m}^2 \cdot \text{g}^{-1}$; $(SA)_{GF5} = 0.398 \text{ m}^2 \cdot \text{g}^{-1}$. The Leaching rate (LR) values at 72 hr. are as

follows: $(LR)_{GF1} = 2.3 \times 10^{-3} \text{ g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$; $(LR)_{GF3} = 3.3 \times 10^{-4} \text{ g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$; $(LR)_{GF5} = 6.3 \times 10^{-3} \text{ g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. The leach rates decrease in the order: $GF5 > GF3 > GF1$. The LR values at 48 hr., 72 hr., 96 hr. and 120 hr. decreases in the same order: $GF5 > GF3 > GF1$. On the other side the LR values at 144 hr., 168 hr., 192 hr., and 216 hr. decreases in the same order: $GF5 > GF1 > GF3$. Again the LR values at 240 hr., 264 hr., 288 hr., and 300 hr. decreases in the same order: $GF1 > GF5 > GF3$. The LR values of glasses at different time interval are shown in the Table 4. Hence glass GF5 with MoO_3 have maximum LR values. These rates are 1000 times lower than those of other borosilicate systems [33-36] and thus glasses have much improved chemical durability. This is due to Fe_2O_3 content and structural role of Fe^{2+}/Fe^{3+} , which strengthens the cross bonding between the polyphosphate chains [37]. Per cent weight loss vs. cumulative time (hr.) studies show a distinct decrease in the % of wt. loss value with extended period of time of leaching signifying that the extent of leaching die down with time [38]. It is observed that the % weight loss decreases in the order: $GF4 > GF1 > GF5 > GF2 > GF3$ respectively.

Glass ID	Time interval (hr.)								
	24	48	72	96	120	144	168	192	216
GF1	4.6	2.8	2.3	2.2	2.9	3.6	3.4	3.8	4
GF3	4.4	4.4	3.3	3.8	3.8	3.4	3	2.8	2.7
GF5	12.6	7.6	6.3	6	5.2	4.4	4.3	3.9	3.6

Glass ID	Time Interval (hr.)			
	240	264	288	300
GF1	4.3	4.6	4.7	5
GF2	2.6	2.5	2.4	2.4
GF3	3.3	3.1	2.5	2.8

Table 3: Leaching rate of different glasses ($LR \times 10^{-3}$).

Application of Glass Fertilizer on the Paddy Field through Pot Culture

Application of glass fertilizers in pot culture experiment was also carried out to khariff paddy during 2018-2019. The study was carried out in collaboration with the Department of Soil Science and Agricultural Chemistry, Visva-Bharati, Sriniketan, West Bengal, India. The preliminarily study indicated a promising result of glass fertilizers.

Efficacy of Glass Fertilizers to Khariff Paddy

The studies on the efficacy of glass fertilizers will be carried out in successive crops and will be ascertained through yield, uptake, and quality of the product. A pot experiment was carried out with Kharif paddy in a typical lateritic soil (pH 6.2, Org. C 0.43 % and Sandy Loam texture) of Sriniketan,

Birbhum district of West Bengal. Soils after collection were air dried and processed through <2 mm sieve and 2 kg soils were taken in earthen pots, moistened and bring into puddled condition and a seedling of rice (Var.) of 16 days age were transplanted and water was added as and when required till maturity. Five types of glass fertilizers, prepared in laboratory, were used in 3 levels i.e. 50 ppm, 100 ppm and

150 ppm and are triplicated as per Completely Randomized Design (CRD) for pot experiment. The glass fertilizers were weighed in electrical balance as per levels i.e. 50, 100 and 150 ppm (i.e. mg/kg soil) and mixed with 2kg of soil. The grain yield and straw yield as the response of rice crop towards glass fertilizers were recorded after the harvest of rice and presented in Table 4.

Treatments	Grain weight (g/pot)	Straw weight (g/pot)
T1- GF1@50ppm	11.83	18.6
T2- GF2@50ppm	11.8	19.5
T3- GF3@50ppm	12.33	20.1
T4- GF4@50ppm	12.47	19.8
T5- GF5@50ppm	13.33	20.7
T6- GF1@100ppm	12.17	19.6
T7- GF2@100ppm	12.3	20.7
T8- GF3@100ppm	14.3	20.9
T9- GF4@100ppm	12.63	20.4
T10- GF5@100ppm	14.37	21.1
T11- GF1@150ppm	12.83	21.3
T12- GF2@150ppm	12.33	20.86
T13- GF3@150ppm	14.6	23.3
T14- GF4@150ppm	12.43	22
T15- GF5@150ppm	14.7	23.2
T16- Control	8.87	16.2
S.Em.	0.67	0.87
C.D. at 5%	2.25	3.5
C.V. (%)	12.34	12.34

Table 4: Effect of different glass fertilizers and their levels on grain and straw weight (g/pot) of Khariff paddy in a typical lateritic soil.

The effect of graded doses of different glass fertilizers on dry weight of rice straw are presented in Table 4. The results indicate that glass fertilizers and their levels (@ 50, 100 and 150 ppm) brought about significant increase in dry weight of rice straw over control [39]. At lower dose (@50ppm) of glass fertilizers, the highest straw yield (20.70 g/pot) was recorded in T5 i.e. GF5 containing essential plant nutrients viz. N, P, Mg, B, Fe and Zn and Mo followed by T3 (20.1 g/pot) i.e. GF3 (contains N, P, K, Mg, Ca and Zn), T4 (19.8 g/pot) i.e. GF4 (contains N, P, K, Mg, Ca and Mo), T2 (19.5 g/pot) i.e. GF2 (N, P, K, Ca, Mg and Fe) and T1 (18.6 g/pot) i.e. (N, P, K, Ca, Mg, Na and B) and which are at par among themselves. The

glass fertilizers at medium doses i.e. @ 100ppm are although registered higher straw yield than its lower dose i.e. @50 ppm but at par among themselves (T6, T7, T8, T9 and T10). The higher dose i.e., glass fertilizers @150ppm registered higher straw yield of rice over low (50ppm) and medium doses (100ppm) of fertilizers. The highest straw yield of rice was recorded with T15 (23.2 g/pot) followed by T13, T14, T11, and T12 and the least was recorded with control (no fertilizer). It is interesting to note that the straw yield of rice increased with increase in levels of glass fertilizers irrespective of compositions.



Figure 4: Photographs of pot experiment on paddy with: a) glass fertilizer GF3; b) glass fertilizer GF5; c) without any type of fertilizer; d) conventional fertilizer.

Conclusion

Chemical and physical properties of phosphate glasses depend on the glass composition. Calcium oxide (CaO) and magnesium oxide (MgO) are added to provide for a better chemical durability. By adding Fe_2O_3 it was possible to improve the chemical resistance and to decrease the crystallization rate. Thus improvement in chemical durability is due to Fe_2O_3 content and structural role of $\text{Fe}^{2+}/^{3+}$, which strengthens the cross bonding between the polyphosphate chains. Thus it may be concluded that a structural rearrangement occurs in the role of Fe in the glass structure from modifier to former. The structure of phosphate glasses consists of Fe-O-P-O chains with modifiers intercalating the structure, bounded to non-bridging oxygen atoms. Effect of modifier ions on melting temperature is evident in the present work and a much lower melt viscosity in the temperature range from 750°C to 950°C . Thus the role of modifier in both borosilicate and phosphate systems is very distinct in enhancing its leach resistance. The cumulative weight loss, i.e. leaching or leaching rate of the glasses depend on the addition of

modifier oxides into their compositions. It is shown that the glass with MoO_3 have maximum leach rate value. In general, addition of alkaline earth oxides increases the corrosion of phosphate glasses whereas addition of intermediate oxides decreases the corrosion of phosphate glasses.

Preliminary study on the efficacy of glass fertilizers prepared in laboratory to kharif paddy through pot experiment during 2018-2019 revealed that all the glass fertilizers under consideration are very much promising with regards to grain yield and total biomass production. Intensive efficacy studies with regards to uptake of nutrients by crops and soil status after harvest of crops of these glass fertilizers is required prior to acceptable by farmers as a viable option over conventional fertilizers and its production as commercial fertilizers.

It was shown that after the application of the glass fertilizer, the growth and production of the khariff paddy was good compared to that of normal application of the conventional fertilizers.

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