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Leachability of zinc ions from ternary phosphate glasses

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With a view to using glasses as a source of zinc, which is one of the micronutrients required by plants, a systematic study on leachability of zinc ions from ternary phosphate glasses having molar composition $60ZnO \cdot 5X \cdot 35P_2O_5$ (where $X = Li_2O$, Na_2O, K_2O, CaO, B_2O_3 and SiO_2) was carried out. Leaching of zinc ions has been studied as a function of pH and the results show that leaching increases with increasing pH of the solutions. The concentration of zinc ions in the leachate decreases with increasing bond strength between non-bridging oxygen ions and the cations in glasses. The leaching of zinc ions increases with increase in leaching time and decreases with increase in particle size of glasses. P_2O_5 was also leached along with zinc ions. The leaching characteristics of P_2O_5 from the glasses are also reported. © *2003 Kluwer Academic Publishers*

1. Introduction

It is well known that 13 elements—nitrogen, phosphorus, potassium, calcium, magnesium, sulphur, chlorine, boron, copper, iron, manganese, zinc and molybdenum are essential for the growth of plants. The first six are required in comparatively large amounts and hence are called ‘major’ or macronutrients. But the elements such as zinc, manganese, boron, copper, molybdenum, iron and chorine are required in very small amounts and are known as ‘minor’ elements or micronutrients. These nutrients are taken up by the plants as anions or cations from the soil or the water in which they grow.

One of the most troublesome and widespread problems of agriculture in India is that of zinc deficiency, caused either by bright sunlight to heavy soils or to sandy soils containing peat, slightly acid or neutral soils, or by the soil micro-organisms competing with the plants for their existence [1, 2]. The action of zinc towards plants is similar to that of vitamins in a human body and is essential for the proper physiological functioning of the plants. Even where soil contains sufficient amounts of zinc element nevertheless a deficiency of zinc can occur in plant growing in that soil due to chemical and physiological processes, which render it unavailable to the plants or make it inactive in the physiological functioning within the plants. Deficiency of zinc causes disease to the plants and affects the yield and quality, both adversely.

Various ways have been suggested to overcome the deficiency of micronutrients. Controlled release of ions from phosphate glass has become the subject of various studies [3, 4] because of the ability of phosphate glass to gradually release the constituents in aqueous solution. Regarding the application of these glasses, various areas have been identified such as bioceramics [5], herbicides, fungicides [6] and slow release of plants nutrients in agriculture containing micronutrients [7–12]. Leaching characteristic of glasses containing macro nutrient elements has been studied [13] using blast furnace slag.

The release of zinc ions depends upon the soil conditions and the particle size of the glass. For controlled release of zinc ions suitable for various soil conditions (Most Indian soil have pH values in the range of 5 to 9) different control agents have been introduced in binary zinc phosphate glasses. Glasses having molar composition $60ZnO \cdot 5X \cdot 35P_2O_5$ (where $X = Li_2O$, Na_2O, K_2O, CaO, B_2O_3, and SiO_2) were chosen because they have low melting points and also because they have phosphorus as one of the constituents which is a macronutrient element also. In this system P_2O_5 acts as glass network former and also as a carrier for zinc ions. In the present investigation the leachability of zinc ions from ternary phosphate glasses has been studied using various control agent. The study is expected to provide sufficient information for agricultural applications suitable for different soil conditions in India which may be helpful in increasing the yield of paddy, wheat etc. which are needed for the large population suffering from food deficiencies.

2. Experimental methods

2.1. Preparation of glasses

Analytical and reagent grade chemicals were used to prepare ternary phosphate glasses. Zinc was introduced as Analytical reagent grade ZnO and acid washed Indian quartz was used for introducing SiO_2 in the glass. Glass batches of 100 g were melted in alumina crucibles of 100 ml capacity in an electric furnace at 900 ± 5°C. They were melted for two hours. The melts were quenched by pouring the glasses into cold water. The glass was dried and ground in a mortar so that

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the glass powder passed through a 500 μm sieve but was retained by a 300 μm sieve. These were graded as −500 + 355, −355 + 300 and −300 μm particles sizes. These were washed separately with acetone, dried at 110°C and stored in a desiccator.

2.2. Determination of leachability

The buffer solutions from 5.5 to 8.5 pH were prepared by taking 2.5% v/v glacial acetic acid in water and by adding concentrated ammonia solution until the desired pH value was reached. The pH of the solution was measured using a digital pH meter (Type DPH-500). 0.2 g each of the glasses were taken in one litre-Erlenmeyer flasks and shaken with 250 ml of ammonia–acetate buffer solution of different pH from 5.5 to 8.5 for different time periods at a constant temperature of 20 ± 2°C. Three samples were taken at a time and an average was taken for locating each point on the curves.

Since the micronutrients are used in the small quantities in the field, higher volumes (250 ml) were taken to minimize the error and also to be more applicable to actual use. After the desired time period between 2 to 24 hours, the content was filtered through Whatman 41 filter paper.

2.3. Determination of zinc [14]

20 ml of leachate was taken in a 250 ml conical flask. pH of the solution was adjusted to a value of 5.3 by dropwise addition of NH_4OH (1:1) and 20 ml buffer solution of pH 5.3. The solution was then titrated with standard ethylene diamine tetra acetic acid (EDTA) solution using xylenol orange as indicator.

2.4. Determination of P_2O_5

After the titration of zinc amount of standard Lanthanum chloride solution was added with constant swirling. The Lanthanum phosphate was precipitated out quantitatively. The contents of the flask were heated at 60°C to 70°C and excess Lanthanum chloride was back titrated with standard EDTA solution at pH 5.3 using Xylenol orange indicator. A blank titration of the added Lathanum solution was made with the same EDTA solution to obtain Lanthanum, equivalent of EDTA. The amount of P_2O_5 was obtained from the difference of the two titre values.

3. Results

3.1. Effect of control agents on the leachability of ZnO and P_2O_5

The effect of cations on the leachability of ZnO from ternary phosphate glasses in the buffer solutions of 5.5, 7.0, 8.0 and 8.5 pH are presented in Figs 1–3. These figures show that the concentration of ZnO increases in the order Si < B < Ca < Li < Na < K with increase in pH. The leachability of P_2O_5 also increased in the same order as above which are shown in Fig. 4. Thus in Figs 1–4 solid lines show how the relationship between percent ZnO/P_2O_5 leached from ternary phosphate glasses with shaking time at different pH values.

3.2. Effect of pH of the leaching solution

The leachabilities of ZnO and P_2O_5 are reported at four different values of pH 5.5, 7.0, 8.0 and 8.5 and the results are summarized in Figs 1–4. These figures shows the leachabilities of ZnO and P_2O_5 are increased with increase in pH of the buffer solution.

3.3. Effect of shaking time on the leachability

The glass samples were shaken with buffer solutions of different pH for various time periods from 2 to 24 hours at a constant temperature of 20 ± 2°C. The results are

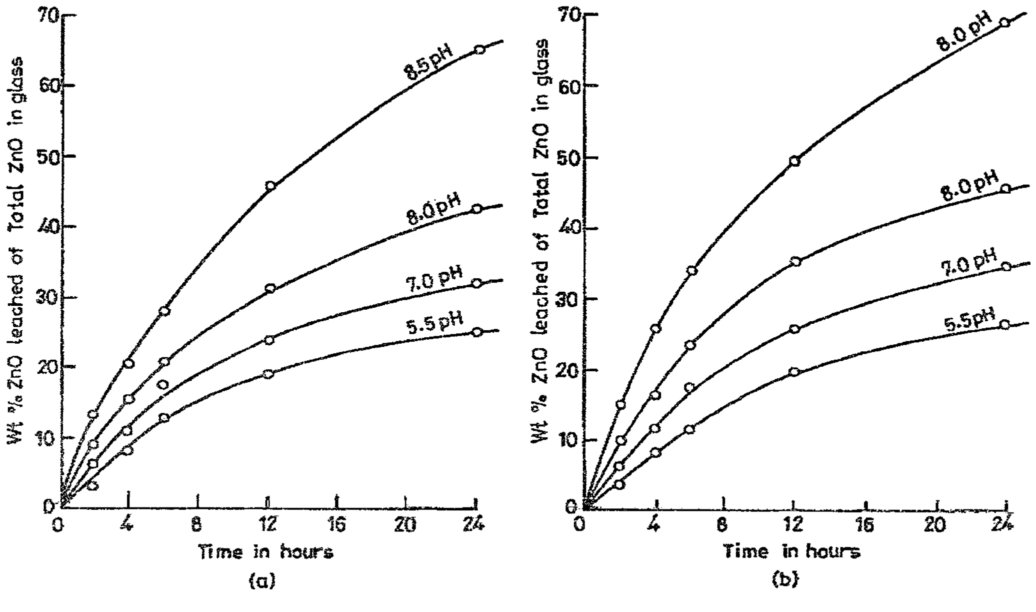


Figure 1 Effect of shaking time on the leachability of ZnO from ternary phosphate glass for different pH values at 20 ± 2°C (particle size −500 + 355 μm): (a) $60ZnO \cdot 5Li_2O \cdot 35P_2O_5$ and (b) $60ZnO \cdot 5Na_2O \cdot 35P_2O_5$.

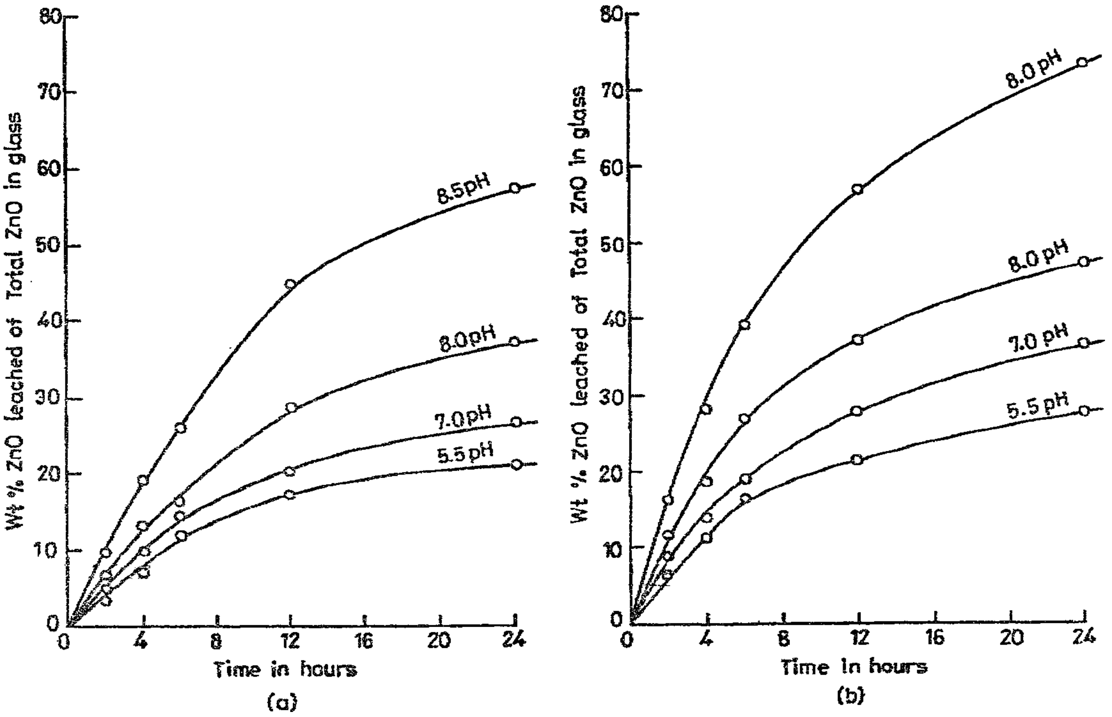


Figure 2 Effect of shaking time on the leachability of ZnO from ternary phosphate glass for different pH values at 20 ± 2°C (particle size −500 + 355 μm): (a) $60ZnO \cdot 5CaO \cdot 35P_2O_5$ and (b) $60ZnO \cdot 5K_2O \cdot 35P_2O_5$.

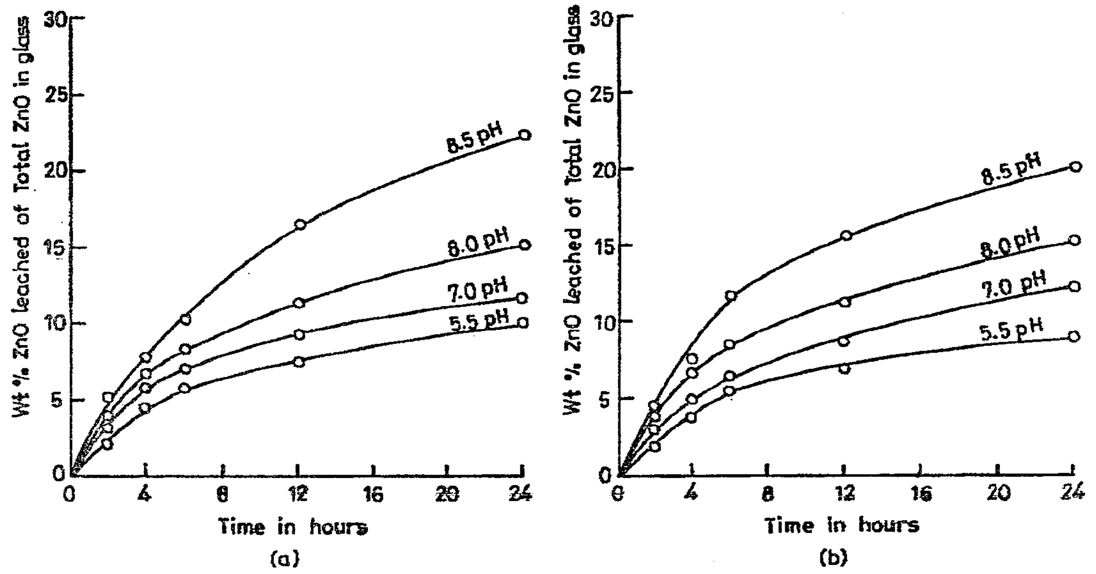


Figure 3 Effect of shaking time on the leachability of ZnO from ternary phosphate glass for different pH values at 20 ± 2°C (particle size −500 + 355 μm): (a) $60ZnO \cdot 5B_2O_3 \cdot 35P_2O_5$ and (b) $60ZnO \cdot 5SiO_2 \cdot 35P_2O_5$.

shown in Figs 1–4. These figures show that the leachabilities of ZnO and P_2O_5 increase with increase in shaking time. It was observed that fast leaching takes place in the beginning and becomes slower with prolonged shaking time.

3.4. Effect of particle size

In present experiment it was found that the concentrations of ZnO and P_2O_5 leached in the solution decrease with increasing particle size of the glass powder (Table I).

TABLE I Effect of particle size on the leachability of ZnO and P_2O_5 at different pH (temperature: 20 ± 2°C, shaking time: 4 hours, volume of leaching solution: 250 ml). Glass composition: $60ZnO \cdot 5K_2O \cdot 35P_2O_5$

	ZnO (wt%) leached at pH values				P_2O_5 (wt%) leached at pH values			
Particle size	5.50	7.00	8.00	8.50	5.50	7.00	8.00	8.50
−500 + 355 μm	11.32	13.68	18.50	28.10	9.50	12.00	15.10	18.20
−355 + 300 μm	14.20	18.40	23.50	36.55	12.10	15.50	18.50	22.60
Passing 300 μm	16.40	21.60	27.16	40.90	15.20	19.10	23.80	27.70

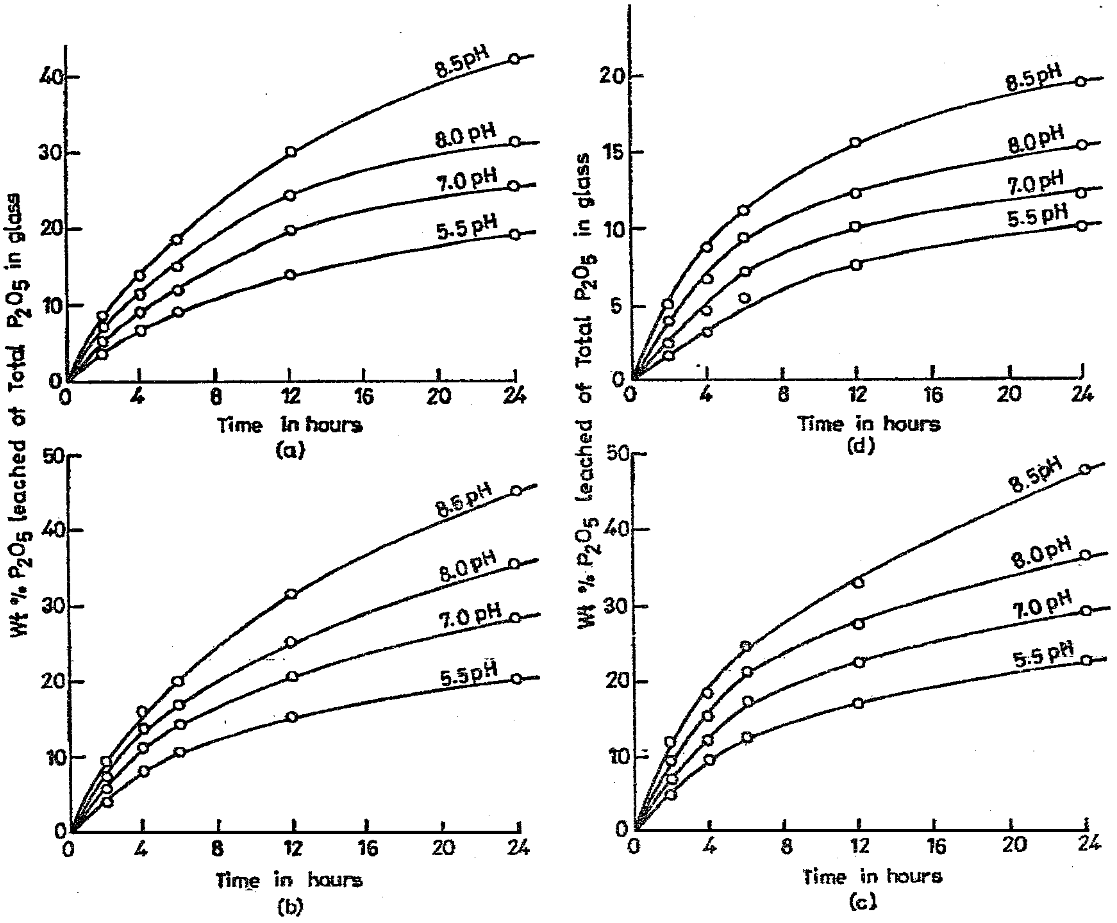


Figure 4 Effect of shaking time on the leachability of ZnO from ternary phosphate glass for different pH values at 20 ± 2°C (particle size $-500+355$ μm): (a) $60ZnO \cdot 5Li_2O \cdot 35P_2O_5$, (b) $60ZnO \cdot 5Na_2O \cdot 35P_2O_5$, (c) $60ZnO \cdot 5K_2O \cdot 35P_2O_5$, and (d) $60ZnO \cdot 5SiO_2 \cdot 35P_2O_5$.

3.5. Effect of volume of leaching solution

It was found that the quantity of ZnO and P_2O_5 leached increases with increasing the volume of the buffer solution used in the experiment as shown in Table II.

3.6. Effect of temperature

It was found that the amount of ZnO and P_2O_5 leached increase with increasing temperature of the buffer solution used in the experiment as shown in Table III.

4. Discussion

The results shown in Figs 1–4 can be explained by considering the following three factors:

(i) The structure of phosphate glass,
(ii) The ion exchange properties of the glass, and
(iii) The glass/solution interface and kinetics of phosphate hydrolysis.

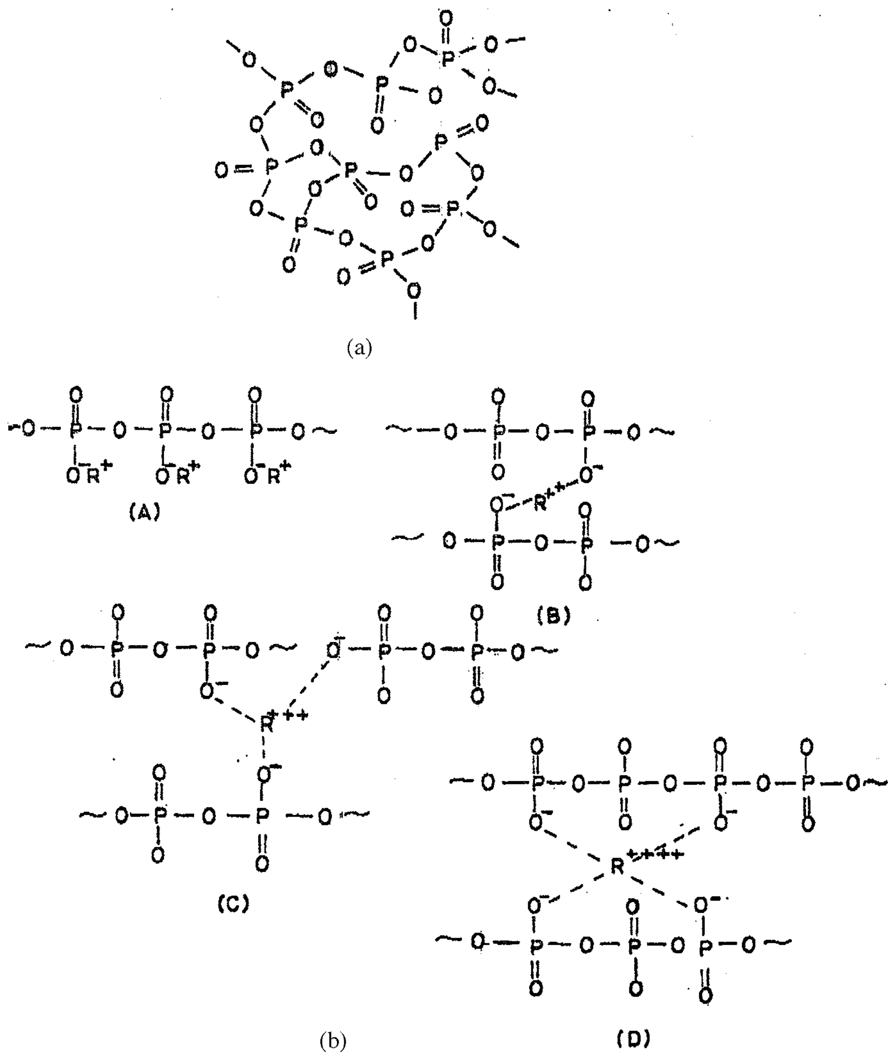
The basic structural unit of phosphate glass is the PO_4^{3-} group, which can be attached to a maximum

TABLE II Effect of volume of leaching solution on the leachability of ZnO and P_2O_5 at different pH (temperature: 20 ± 2°C, shaking time: 4 hours, Particle size: $-500+355$ μm). Glass composition: 60ZnO, $5K_2O \cdot 35P_2O_5$

Volume of leaching solution	ZnO (wt%) leached at pH values				P_2O_5 (wt%) leached at pH values			
	5.50	7.00	8.00	8.50	5.50	7.00	8.00	8.50
150 ml	10.05	11.80	17.30	26.70	9.10	11.15	13.50	16.40
250 ml	11.32	13.68	18.50	28.10	9.50	12.00	15.10	18.20
400 ml	13.84	15.96	23.10	34.20	10.90	13.50	18.20	23.00

TABLE III Effect of temperature on the leachability of ZnO and P_2O_5 at different pH (shaking time: 4 hours, particle size: $-500+355$ μm, volume of leaching solution: 250 ml). Glass composition: $60ZnO \cdot 5K_2O \cdot 35P_2O_5$

	ZnO (wt%) leached at pH values				P_2O_5 (wt%) leached at pH values			
Temperature	5.50	7.00	8.00	8.50	5.50	7.00	8.00	8.50
20°C	11.32	13.68	18.50	28.10	9.50	12.00	15.10	18.20
25°C	12.10	14.80	20.75	33.40	10.00	13.50	16.80	20.40
35°C	13.90	16.85	24.10	43.75	12.12	15.40	21.25	25.80



(a)

(b)

Figure 5 (a) Structure of P_2O_5 glass. (b) Metal chelate type structure with: (A) monovalent cations, (B) divalent cations, (C) trivalent cations and (D) tetravalent cations.

of three neighbouring groups as in P_2O_5 because one of the oxygen atoms in each tetrachedron has to be linked through a double bond (Fig. 5). The number of cross-links in the polymer is defined as the number of PO_4 groups attached to three others through bridging oxygen. The addition of modifying cations to the glass results in the cleavage of P—O—P linkages and the creation of non-bridging oxygen in the glass. The cross link density [15] for such glasses, ranging from pure P_2O_5 to those containing 50 mol% P_2O_5, is given by:

$$Z = (2Y - 1)/Y$$

Where Z the cross link density and Y is the mole fraction of P_2O_5. The cross link density of pure anhydrous phosphate glass decreases when the mole percent of P_2O_5 decreases from 100 to 50%. Pure P_2O_5 glass, as reported in the literature [15], has the maximum cross link density i.e., oxygen ions are bridged between PO_4^{3-} units. As P_2O_5 contents decrease or concentration of control agent in the glass increases, the number of non-bridging oxygen increases.

Phosphate glasses are made up of long chain polymeric phosphate anions, which are connected to one another by ionic bonds to the modifying cations. For such a structure, it is observed that other cations can serve as ionic cross-links between the non-bridging oxygen of the two different chains. van-Wazer *et al.* [16] suggested that such a cross linkage could take the form of the metal chelate structure as shown in Fig. 5b. For phosphate glasses containing 50 mol% P_2O_5 or less the number of mean chain length is given by Stevels equation [17].

$$\tilde{n} = 2/\Psi - 1 \quad \text{where } \Psi = \sum nM/P$$

where $\tilde{n}$ = number of structural units in mean chain length, n = oxidation state of the cations in the glass, M = mole fraction of cations in the glass, P = mole fraction of phosphorus in the glass.

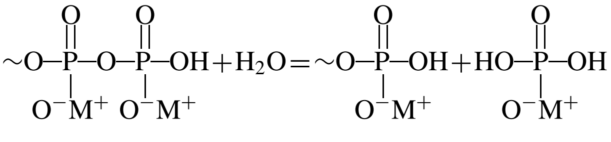
The value of mean chain length calculated for different glasses used in the present work are given in Table IV. It is evident that as the mean chain length decreases, the leachabilities of ZnO and P_2O_5 decreases.

In the determination of dissolution mechanisms, it is important to outline the types of reaction that may take place between water and phosphate glasses. The release of ZnO, P_2O_5 and others constituents from phosphate glasses in aqueous solution is due to the hydrolysis

TABLE IV Mean chain length and coulombic forces of ternary zinc phosphate glasses

S.No	Glass composition	Mean chain length	Coulombic force using paulings radius (bond strength)
1.	$60ZnO \cdot 5Li_2O \cdot 35P_2O_5$	0.326	0.250
2.	$60ZnO \cdot 5Na_2O \cdot 35P_2O_5$	0.326	0.181
3.	$60ZnO \cdot 5K_2O \cdot 35P_2O_5$	0.326	0.134
4.	$60ZnO \cdot 5CaO \cdot 35P_2O_5$	0.311	0.350
5.	$60ZnO \cdot 5B_2O_3 \cdot 35P_2O_5$	0.298	1.17
6.	$60ZnO \cdot 5SiO_2 \cdot 35P_2O_5$	0.286	1.22

reaction [18] as given below:



$$\sim O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-M^+}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-M^+}{|}}{P}}-OH + H_2O = \sim O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-M^+}{|}}{P}}-OH + HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-M^+}{|}}{P}}-OH$$

In the hydrolysis of phosphate glasses the P—O—P bonds are broken, which may lead to ultimate destruction of the polymeric phosphate network and may produce orthophosphate. The route and rate of hydrolysis are characteristic of the particular cation and the conditions employed. The seven main factors influencing the rate of hydrolysis of the polymeric phosphate network are discussed below.

4.1. Nature of cations present

The leachabilities of ZnO and P_2O_5 decrease with increasing coulombic force between non-bridging oxygen and cations. In ternary phosphate glasses of the present series having the molar compositions $60ZnO \cdot 5X \cdot 35P_2O_5$ (where $X = Li_2O$, Na_2O, K_2O, CaO, B_2O_3 and SiO_2) the following types of bonds are present

$$\geqslant P—O—P \leqslant \qquad (i)$$

$$\geqslant P—O^-Zn^{++}O^-—P \leqslant \qquad (ii)$$

$$(\geqslant P—O^-)_n R^{n+} \qquad (iii)$$

(where n is valence state of cation R)

Bonds of the type (i) & (ii) are common in all the glasses of the present series and their number also remains approximately constant. However, on replacement of one cation by another on a molar basis, the bond between cation and non-bridging oxygen ions presented in (iii) changes with the nature and size of the cation. As the coulombic force between the non-bridging oxygen and the cation increases, the bond strength is expected to increase resulting in a greater chemical barrier to ZnO and P_2O_5. The concentrations of ZnO and P_2O_5 leached out from different glasses were plotted against coulombic forces of the cations and the results are presented in Fig. 6. It can be observed that the quantities of ZnO and P_2O_5 in the leachate decrease as the bond strength between non-bridging oxygen and cations increases.

4.2. Effect of pH of the solution

The effect of pH on the leachability of ZnO and P_2O_5 from ternary phosphate glasses was studied and the results presented in Figs 1–4, show that the leachabilities of ZnO and P_2O_5 in the solutions increase with increasing pH of the solution. The buffer of pH 5.5, 7.0, 8.0 and 8.5 contain a constant (2.5% v/v) amount of acetate ions and H^+ ions but contain increasing amounts of ammonium ions and OH^- ions. These hydroxyl (OH^-) ions break the P—O—P bond increasingly fast as the pH of the solution increases and cause the increase in the

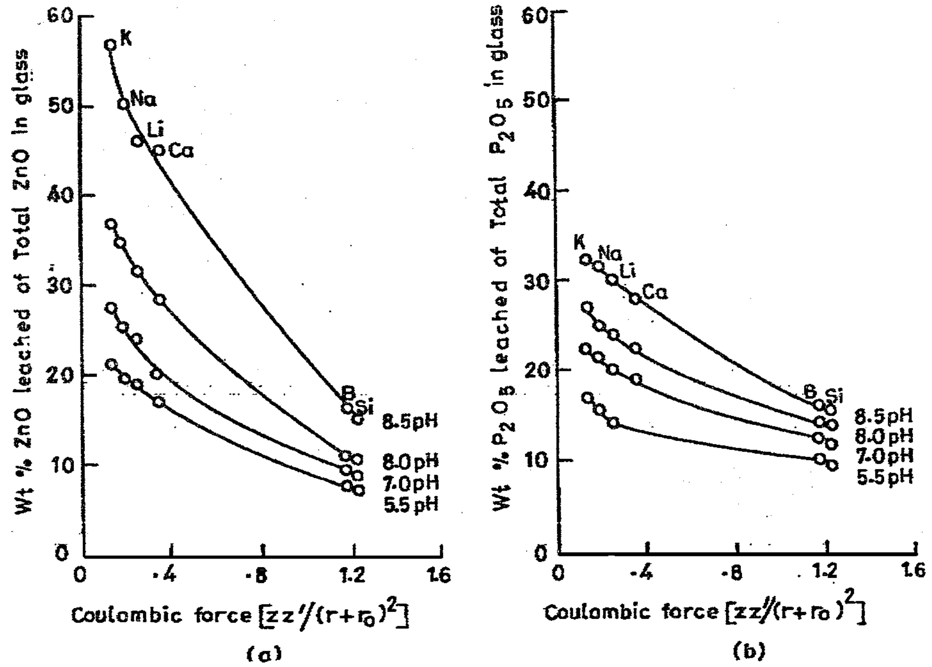


Figure 6 Effect of coulombic force on the leachability of ZnO and P_2O_5 from ternary phosphate glasses having molar composition $60ZnO \cdot 5X \cdot 35P_2O_5$ for different pH values at 20 ± 2°C (particle size: −500 + 355 μm (leaching time: 12 hours)): (a) ZnO and (b) P_2O_5.

concentration of ZnO and P_2O_5 in the leachate. Leaching of ZnO and P_2O_5 is controlled by the pH value and depends critically on the nature and concentration of the buffering base [7, 12, 19, 20].

In order to model the experimental data the zinc phosphate glasses have been treated as a two component system [17] (i) glass forming oxide (glass former) and (ii) metal oxide (glass modifier). Hydroxyl ions are more active in the buffer solutions and cause hydrolysis both of the network former and of the modifier. Several hydrolysis reaction, proposed with monovalent, divalent, trivalent and tetravalent cations acting as control agent, which can model the on going process are as follows:
With monovalent cations:

$$\mathrm{ZnO \cdot R_2O \cdot P_2O_5 + 2NH_4OH + 3H_2O}$$
$$\longrightarrow \mathrm{(NH_4)_2ZnO_2 + 2ROH + 2H_3PO_4}$$
$$\text{where R is Li, Na or K.}$$

With divalent cations:

$$\mathrm{ZnO \cdot RO.P_2O_5 + 2NH_4OH + 3H_2O}$$
$$\longrightarrow \mathrm{(NH_4)_2ZnO_2 + R(OH)_2 + 2H_3PO_4}$$
$$\text{where R is Ca or divalent cation.}$$

With trivalent cations:

$$\mathrm{ZnO \cdot R_2O_3 \cdot P_2O_5 + 2NH_4OH + 5H_2O}$$
$$\longrightarrow \mathrm{(NH_4)_2ZnO_2 + 2R(OH)_3 + 2H_3PO_4}$$
$$\text{where R is B or trivalent cation.}$$

With tetravalent cations:

$$\mathrm{ZnO \cdot RO_2 \cdot P_2O_5 + 2NH_4OH + 4H_2O}$$
$$\longrightarrow \mathrm{(NH_4)_2ZnO_2 + R(OH)_4 + 2H_3PO_4}$$
$$\text{where R is Si or tetravalent cation.}$$

It is evident from Table IV that coulombic forces/bond strength in ternary phosphate glasses with monovalent cations is the lowest. It increases when the monovalent cation is replaced by a divalent, trivalent or tetravalent cation. It is greatest with a tetravalent cation. Thus formation of R(OH) e.g., LiOH, NaOH or KOH is simplest and in glasses with monovalent cations as control agents release of ZnO and P_2O_5 is energetically favoured [21, 22]. Release of these nutrients from glasses containing divalent cations as control agent is slower than those containing monovalent cations. Formation of $R(OH)_3$ from glasses containing trivalent control agent is a slower process as compared to above two and the release of ZnO and P_2O_5 is slowed down. It is further slowed down with tetravalent control agents in the glasses.

The above reactions may be helpful to the agricultural scientist when selecting zinc micronutrient glass compositions, which can suit the soil of particular pH.

4.3. Effect of particle size

Surface area is an important factor in leachability of ions and the amount of various constituent leached from a glass under certain conditions are proportional to the surface area exposed. With decreasing the particle size of glass, the specific surface area increases, hence increase in leachability of ions from the glass. Thus the leachability of ZnO and P_2O_5 increases with decreasing the particle size of glass as given in Table I.

4.4. Effect of volume of leaching solution

As given in Table II the leachability of ZnO and P_2O_5 increases with increasing the volume of the buffer solution at each pH. The total quantity of Hydroxyl (OH^-) ions increases with increasing the volume of buffer solution which break the P—O—P bond more and more and cause to increase the amount of ZnO and P_2O_5 in the leachate.

4.5. Effect of leaching time

Phosphate glasses chosen in the present study dissolve in solution of different pH in the range of 5.5–8.5. The results presented in Figs (1–4) indicate that rapid leaching takes place in the beginning but that the rate decreases with increasing time.

The leachability of ZnO and P_2O_5 from ternary phosphate glasses as shown in Figs (1–4) can be explained by an empirical equation of the following form.

$$Q = a\sqrt{t} + bt$$

where t is leaching time and a and b are empirical constant. The equation shows that the quantity of ZnO leached increases with the square root of time for short leaching time and increases linearly with time for prolonged leaching.

4.6. Effect of temperature

The quantity of ZnO and P_2O_5 leached from a glass in a given period of time increases with increasing temperature as presented in Table III. The result fit in Arrhenius equation

$$S = B\exp(-E/RT)$$

where S is the rate of leaching, B is a constant, R the gas constant, T the absolute temperature and E the activation energy. Taking the logarithm of this becomes:

$$\log S = -E/2.303RT + \log B$$

On plotting log S with reciprocal of absolute temperature at different pH of molar glass composition $60\mathrm{ZnO \cdot 5K_2O \cdot 35P_2O_5}$ is shown in Fig. 7 and the value of activation energy are calculated from slopes of the curve. The value of activation energy are found to be (2.301, 2.51, 2.929 and 4.811) KJ/mol for ZnO and (2.092, 2.51, 3.556 and 3.766) KJ/mol for P_2O_5 at pH values 5.5, 7.0, 8.0 and 8.5 respectively.

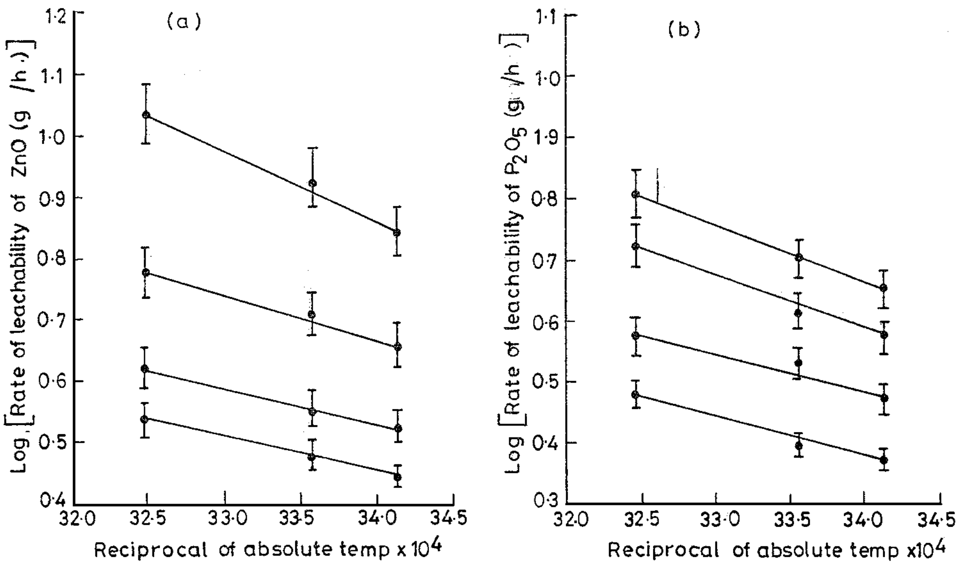


Figure 7 Variation of rate of leachability with reciprocal temperature at different pH (shaking time: 4 hours, particle size: $-500 + 355$ μm volume of leaching solution: 250 ml) of molar glass composition $60ZnO \cdot 5K_2O \cdot 35P_2O_5$: (a) ZnO and (b) P_2O_5.

4.7. Effect of shaking

The shaking which was utilized induced liquid flow relevant to the condition prevailing in the soil where the micronutrient is used for the growth of the plant. Agitation or vigorous stirring was not employed because of the deviation from the real problems of agriculture. However, leaching of ZnO and P_2O_5 are expected to increase at higher agitation level.

5. Conclusions

The results of the present work clearly indicate that leachability of ZnO and P_2O_5 from ternary $60ZnO \cdot 5X \cdot 35P_2O_5$ glasses can be controlled for agricultural use by incorporating different control agents suitable for different soil conditions. Application of this knowledge would increase the yield production of major crops and improve India's position in agriculture.

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