Global Journal of Science Frontier Research: B
Chemistry
Volume 14 Issue 4 Version 1.0 Year 2014
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

A Review on Controlled Release Advanced Glassy Fertilizer

By G. Hazra & T Das
Kalna College The University of Burdwan, India

Abstract- Large scale applications of fertilizer nitrogen (N) have also shown deleterious effects on groundwater quality, especially its nitrate content, which is harmful to health. Furthermore, gaseous losses of N as NH_3 and NO_x resulting from N fertilization have adverse effects on the environment. Therefore, the goal of all agriculture has to be to "increase food-grain production with the minimum and efficient use of chemical fertilizers". This calls for a sincere effort on the part of agricultural scientists including extension workers to increase the efficiency of fertilizers applied in the farm fields. Glass fertilizers are new type of advanced and controlled released fertilizer and made of glass matrixes with macro elements (K, P, Mg, S, Ca) most useful for plants and also incorporated with microelements (B, Fe, Mo, Cu, Zn, Mn) which are important to the growth and development of corps or plants. The quantity of the microelements incorporated in the glass as oxide in the range 1-5%. The use of glass fertilizers offers lot of advantages: due to low or controlled solubility it avoid underground water pollution; the soil pH can be regulate by the pH of the glass matrix; do not release acid anions (Cl-, SO2-) which are harmful for plants so there is no risk of soil burning when they are incorrectly dosed; in a single type of fertilizer can be embedded almost all useful elements for plants; the controlled rate of solubility in water can be adjust easily by changing the composition of glass matrix.

Keywords: *glass fertilizer; controlled release; plant nutrients; phosphate glass; advanced fertilizer; vitreous fertilizer; eco-friendly fertilizer.*

GJSFR-B Classification : *FOR Code: 050304*

AREVIEWONCONTROLLEDRELEASEADVANCEDGLASSYFERTILIZER

Strictly as per the compliance and regulations of :

A Review on Controlled Release Advanced Glassy Fertilizer

G. Hazra [α] & T. Das [σ]

Abstract- Large scale applications of fertilizer nitrogen (N) have also shown deleterious effects on groundwater quality, especially its nitrate content, which is harmful to health. Furthermore, gaseous losses of N as NH_3 and NO_x resulting from N fertilization have adverse effects on the environment. Therefore, the goal of all agriculture has to be to "increase food-grain production with the minimum and efficient use of chemical fertilizers". This calls for a sincere effort on the part of agricultural scientists including extension workers to increase the efficiency of fertilizers applied in the farm fields. Glass fertilizers are new type of advanced and controlled released fertilizer and made of glass matrixes with macro elements (K, P, Mg, S, Ca) most useful for plants and also incorporated with microelements (B, Fe, Mo, Cu, Zn, Mn) which are important to the growth and development of corps or plants. The quantity of the microelements incorporated in the glass as oxide in the range 1-5%. The use of glass fertilizers offers lot of advantages: due to low or controlled solubility it avoid underground water pollution; the soil pH can be regulate by the pH of the glass matrix; do not release acid anions (Cl-, SO2-) which are harmful for plants so there is no risk of soil burning when they are incorrectly dosed; in a single type of fertilizer can be embedded almost all useful elements for plants; the controlled rate of solubility in water can be adjust easily by changing the composition of glass matrix.

Keywords: glass fertilizer; controlled release; plant nutrients; phosphate glass; advanced fertilizer; vitreous fertilizer; eco-friendly fertilizer.

I. Introduction

The worldwide per capita land base for agricultural production has declined dramatically over the past few decades and is expected to continue to decrease. For example, it's estimated that by the year 2025 the land in production per person will be 56 percent less than it was in 1965. The world population in 25 years is expected to be about 8 billion…2 billion more than the current 6 billion so the world average arable land per capita (ha) gradually decreases in every year which is shown in Fig.1. This trend will require that crop yields per unit of land continue to increase. The revolution which has resulted in a phenomenal increase in crop output per unit of land and has so remarkably scaled down the dimensions of the food crisis, has its roots in two main sources – the evolution of innumerable new varieties of crops with high yield potentials and the ready availability of fertilizers which form the life line for the meeting their increased nutritional demands i.e. these yield increases will in turn require greater nutrient inputs. The essential plant nutrients and their forms and typical concentration in plants is given in the Table-1. The effect of pH on nutrient availability is shown in Table-2.

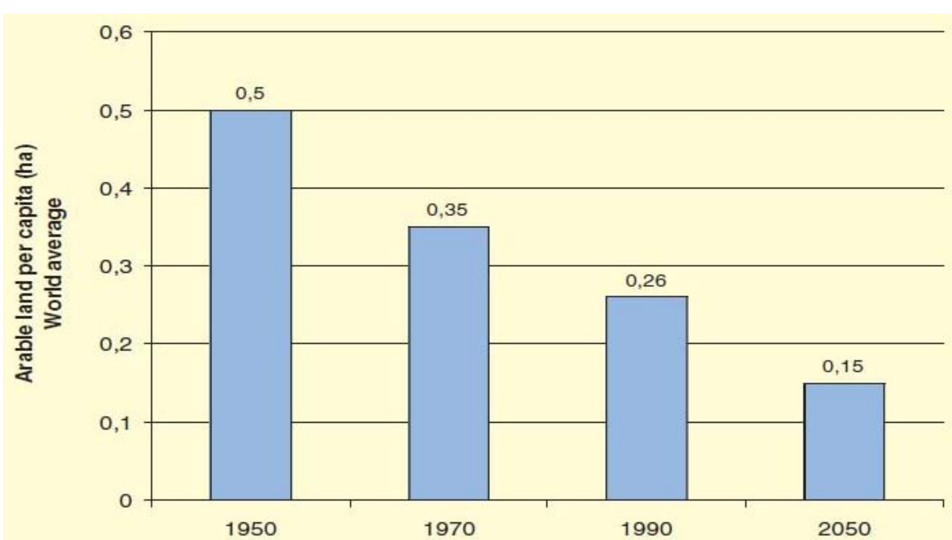

Figure 1 : Globally, arable land per capita is diminishing as population increases: while arable land remains constant, improved yield is required to meet the growing world food demand; [From: Phosphate Newsletter 23 (2005)]

Author α : Department of Chemistry, Kalna College, Kalna, Burdwan, India. e-mail: hazragoutam1980@rediffmail.com
Author σ : Department of Chemistry, The University of Burdwan, Burdwan, India.

Concomitant with frequent addition of high doses of fertilizers, is the magnification of the environmental hazards the soil and water. Accumulation of anions like Cl^- and SO_4^-, soil salinisation and acidification, leaching of NH_4^+, NO_3^-, etc., and subsequent contamination of ground water are some of the damages caused by long term fertilizer application. It's also reasonable to assume that the impact of agriculture on the environment will be increasingly scrutinized since the public's influence over production is growing [1].

The main reason for this is the near total dependence on the use of water soluble salts as macro- and micro-nutrient fertilizers. The high solubility of fertilizers is not only the factor for the leaching and contamination of ground water but is also, for same reason, an economically wasteful proportion. Thus quite often, even up to 80% of urea added to soil, may be lost by leaching and volatilisation and only a small fraction micronutrients that are used as foliar sprays, is available for plants.

Glass fertilizers are new type of advanced and controlled released fertilizer and made of glass matrixes with macro elements (K, P, Mg, S, Ca) most useful for plants and also incorporated with microelements (B, Fe, Mo, Cu, Zn, Mn) which are important to the growth and development of corps or plants. The quantity of the microelements incorporated in the glass as oxide in the range 1-5%. The use of glass fertilizers offers lot of advantages: due to low or controlled solubility it avoid underground water pollution; the soil pH can be regulate by the pH of the glass matrix; do not release acid anions (Cl-, SO2-) which are harmful for plants so there is no risk of soil burning when they are incorrectly dosed; in a single type of fertilizer can be embedded almost all useful elements for plants; the controlled rate of solubility in water can be adjust easily by changing the composition of glass matrix. With the growing need for efficient utilisation of resources, such glass fertilizers (CRF) are most deplorable and call for a radical changes in the inorganic fertilizers.

Table 1: Essential plant nutrients, forms taken up and their typical concentration in plants [2]

Nutrient(symbol)	Essentiality established by	Forms absorbed	Typical concentration in plant dry matter
	Macronutrients		
Nitrogen (N)	De Saussure (1804)	NH_4+, NO_3^-	1.5%
Phosphorus (P, P2O5)	Sprengel (1839)	$H_2PO_4^-$, HPO_4^{2-}	0.1–0.4%
Potassium (K, K2O)	Sprengel (1839)	K^+	1–5%
Sulphur (S)	Salm-Horstmann (1851)	SO_4^{2-}	0.1–0.4%
Calcium (Ca)	Sprengel (1839)	Ca^{2+}	0.2–1.0%
Magnesium (Mg)	Sprengel (1839)	Mg^{2+}	0.1–0.4%
	Micronutrients		
Boron (B)	Warington (1923)	H_3BO_3, $H_2BO_3^-$	6–60 μg/g (ppm)
Iron (Fe)	Gris (1943)	Fe^{2+}	50–250.μg/g (ppm)
Manganese (Mn)	McHargue (1922)	Mn^{2+}	20–500.μg/g (ppm)
Copper (Cu)	Sommer, Lipman (1931)	Cu^+, Cu^{2+}	5–20.μg/g (ppm)
Zinc (Zn)	Sommer, Lipman (1931)	Zn^{2+}	21–150.μg/g (ppm)
Molybdenum (Mo)	Arnon& Stout (1939)	MoO_4^{2-}	below 1.μg/g (ppm)
Chlorine (Cl)	Broyer et al., (1954)	Cl^-	0.2–2 percent

Table 2 : Effect of pH on nutrient availability [2]

Nutrient availability	Very low pH (lessthan 5.0)	Low pH (5.0–5.5) Optimum pH	Optimum pH(5.6–6.2)	High pH (6.5–7.0)
Soluble—available to plant roots		Manganese, iron,	Copper and zinc	Boron
Insoluble—not available to plant root	Magnesium, calcium	Molybdenum, Calcium, Magnesium, sulfur		Phosphorous, iron,manganese, copper, zinc, boron
Highly soluble—toxic levels	Ammonium, manganese, iron,copper, zinc, boron			

II. Different Kind of Controlled Release Fertilizers

Only compounds from which plant roots can extract ions by exchange reactions, and compounds which undergo hydrolysis and solubilisation at optimum rate to fulfil the requirements of the plants, are suitable as fertilizers. The controlled release fertilizers must be, therefore, either 'slow-releasing' or must contain nutrients in exchange sites. Slow-releasing or controlled-releasing fertilizers are the latest concept in fertilizer technology. A real controlled-releasing fertilizer can only be formulated at the molecular level. In recent use there have different types of slow or controlled release fertilizers [3] some of them are as follow:

- Sulphur Coated Urea (SCU)
- Sulphur Coated Compound Fertilizer
- Resin Coated Fertilizer
- Urea formaldehyde
- Urea and Nitrification inhibitors
- Tower Melt Spraying Granulation Compound Fertilizer
- Urea Melt Spraying Granulation Compound Fertilizer
- Chemically Modified Biomass Coating Urea for Controlled Released
- Bulk Blend Fertilizer and
- Glass fertilizer

a) *Glass Fertilizers*

Projected growth of population approximately 1% a year over the next 20 years will take the world population from its current level of 6 billion to 7.5 billion by 2020. Due to economic growth as people become wealthier, they consume more and higher-quality food; the International Food Policy Research Institute (IFPRI) forecasts a 40% increase in demand for grain by 2020.The arable land is scarce in many parts of the world and under pressure from urbanization and industrial uses; accordingly, there is continual pressure to increase the productivity of available land resources. Without increases in productivity, more land will have to be brought under cultivation, with potentially severe adverse impact on the environment. The projected food grain production in relation to nutrient (N-P_2O_5-K_2O) consumption, removal and gap are clear from the Fig.2. The innovations provide new benefits and new opportunities in crop production, e.g. precision agriculture, use of environment friendly glassy fertilizers…etc.[4].Phosphate nutrient is part of the fertilizer package that remains the driving force for the growth of crop yields and crop production that is necessary to meet the global food demand

Glass is an amorphous (non-crystalline) solid material. Most of the glasses are typically brittle, optically transparent, as a substance, plays an essential role in science and industry. The chemical, physical, and in particular optical properties make them suitable for applications such as flat glass, container glass, optics and optoelectronics material, laboratory equipment, thermal insulator (glass wool), reinforcement materials (glass-reinforced plastic, glass fiber reinforced concrete), glass art (art glass, studio glass) and recently as glass fertilizers for plants nutrients (macro & micro).

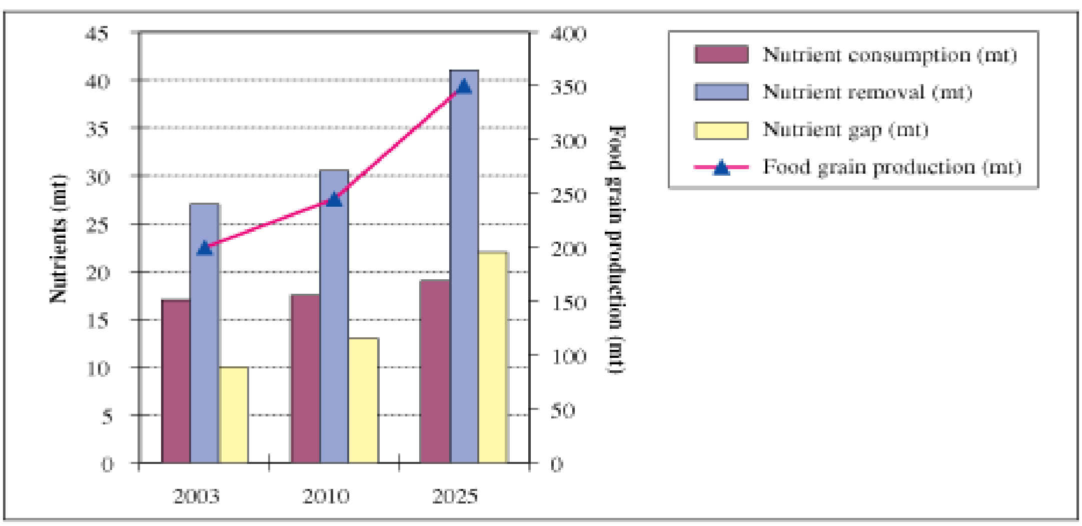

Figure 2 : Projected food grain production in relation to nutrient (N-P_2O_5-K_2O) consumption, removal and gap [5].

i. *Glass ingredients*

Quartz sand (silica) and P_2O_5 are the main raw material in commercial glass production. While fused quartz (primarily composed of SiO_2) is used for some special glass applications but pure silica or quartz are not very common used due to its high glass transition temperature of over 2300°C. Normally, other substances are added to simplify processing i.e. to minimise the melting temperature. One of them is sodium carbonate (Na_2CO_3), which lowers the glass transition to about 1500°C. However, calcium oxide (CaO), generally obtained from limestone, magnesium oxide (MgO) and aluminium oxide (Al_2O_3) are added to provide for a better chemical durability [6]. The resulting glass contains about 70% - 74% silica by weight is called a soda-lime glass. Soda-lime glasses are comparatively more water soluble and account for about 90% of manufactured glass. The oxide components added into a glass batch may be sub-divided as (1) glass formers, (2) intermediates and modifiers. These are grouped on the basis of functions that they performed with in the glass.

Glass formers and network formers include oxides such as SiO_2, B_2O_3, GeO_2, P_2O_5, V_2O_5 and As_2O_3 which are indispensible in the formation of glass since they form the basis of the random three dimensional networks of glasses. For the glasses which are used as fertilizers for plants nutrients P_2O_5 or phosphate salts of alkali metals or alkaline earth metals are used as glass former which have low melting point as well as serve as phosphate nutrients for the plants nutrients.

Intermediates include Al_2O_3, Sb_2O_3, ZrO_2, TiO_2, PbO, BeO and ZnO. These oxides are added in high proportions for linking up with the basic glass network to retain structural continuity [7].Modifiers include MgO, Li_2O, BaO, CaO, SrO, Na_2O and K_2O. These oxides are added to modify the properties of glass. The other additions in glass are the fluxes which lower the fusion temperature of the glass batch and render the molten glass workable at reasonable temperature. But, fluxes may reduce the resistance of glass to chemical attack render it water- soluble or make it subject to partial or complete devitrification, or what is called crystallisation, upon cooling. Devitrified glass is un desirable since the crystallineareas are externally weak and brittle. Stabilizers are therefore added to the glass batch to overcome these problems. Most common glass has other ingredients added to change its properties. The common silicate glass network structure and glass network with modifiers is shown in Fig.3.

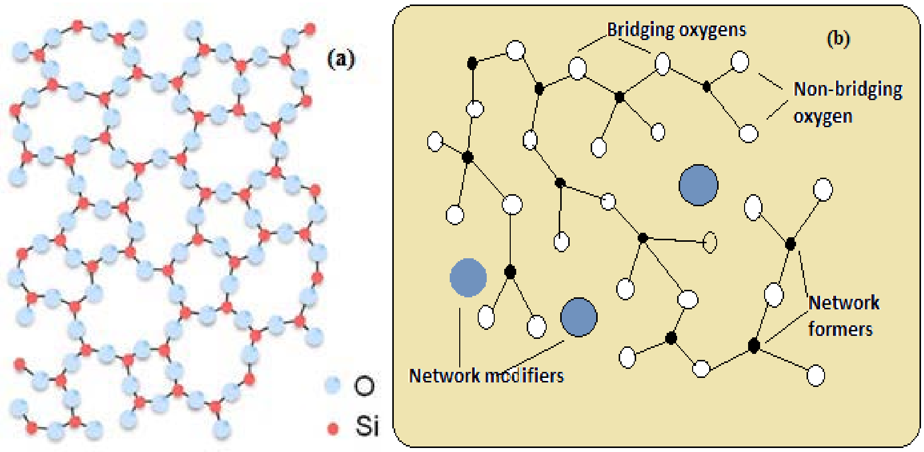

Figure 3 : (a) Silicate network structure, (b) Glass network with modifier

The interesting characteristic of phosphates which are used as former for glass fertilizers makes them so suitable for the production of polymeric fertilizers is that the ortho-phosphate ion, i.e., PO_4^{3-} , polymerises on hating with formation of linear chains of P-O-P bonds, In final stages of condensation, branches chain polymers may also be formed [8]. Thus, in a metaphosphate containing linear phosphate chain the negativity charged oxygen atoms may be neutralised by K^+, Mg^{2+}, Ca^{2+} or NH_4^+ ions (corps nutrients). Since these ions are held in exchangeable positions on an anionic polymer chain, they possess the dual property of being almost insoluble in water but being readily solubilised by complexants and by cation exchange. Moreover, slow hydrolysis of the P-O-P group occurs [9] causing solubilisation of the cations. It is noteworthy that polyphosphates of all the macro- and micro- nutrient ions may be prepared; additionally, their solubility can be varied to desire to levels by controlling the degree of polymerisation of chain. The model Network structure of the glass fertilizers with different corps nutrients is drawn in Fig.4.

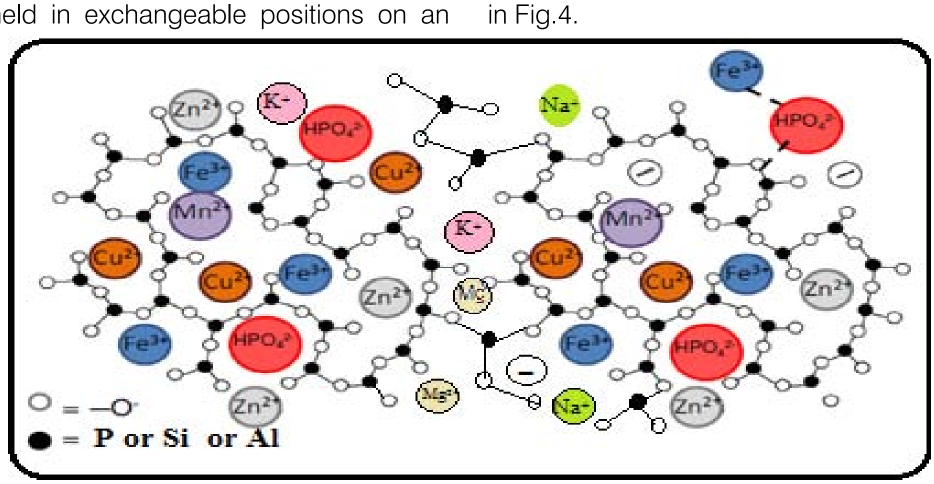

Figure 4 : Network structure of the glass fertilizers with different corps nutrients

ii. *Composition of different glass fertilizers with various types of nutrients*

The composition of different glass fertilizers with various types of nutrients for different corps is presented in the following tables (Table-3a to Table-3e).

Table 3a : Oxide composition of some vitreous fertilizer used in field crops[10].

Code	P_2O_5mol%	MgOmol%	K_2O mol%	B_2O_3mol%	Fe_2O3mol%	ZnOmol%
AG2	41.84	22.45	35.71	-	-	-
AG2.1	32.08	16.98	26.42	24.52	-	-
AG2.2	40	21.05	32.63	-	6.32	-
AG2.3	38	20	32	-	-	10

Table 3b : Oxide composition of some Van Dien FMP fertilizer

P_2O_5 (%)	MgO (%)	Ca0 (%)	SiO_2 (%)	Microquantities
a15 - 18	≥15	≥28	≥ 24	Fe, B, Mn, Z Zn, Co, Cu,Mo

Table 3c : Oxide composition of some nitrate sulphate phosphate glass fertilizer used in field crops

Sample No.	Chemical composition (wt.%)					
	P_2O_5	KNO_3	$NaNO_3$	$KHSO_4$	Admixture	Temp.(350º-400º)C
1	61.5	28.5	10.0	-	-	Fused
2	45·3	36·5	18·2	-	-	Fused
3	45·3	27·4	27·3	-	-	Fused
4	29·2	27·5	9·6	33·8	-	Fused
5	36.5	28.5	9.9	25.0	-	Fused
6	45·0	28·8	10·0	16·2	-	Fused
7	49·0	28·7	10·0	12·4	-	Fused
8	56·7	28·5	9·9	4·9	-	Fused
9	44·8	28·8	3·6	17·5	5·3	Fused
10	42·3	27·2	3·4	16·5	10·5	Fused

Types of admixtures: $Mg(NO_3)_2$, $Zn(NO_3)_2$, $Cu(NO_3)_2$, $Fe(NO_3)_3$, B_2O_3, NH_4VO_3, $NH_4Mo_2O_7$

Table 3d : Oxide composition of glasses for spring and autumn crops, in weight % [11]

Oxide→ ↓Sample	P2O5	MgO	K2O	B2O3	Fe2O3	ZnO	MoO2	Total
AG2	58.76	8.74	32.5	-	-	-	-	100
AG2.1	47.96	7.13	26.52	18.39	-	-	-	100
AG2.2	53.42	7.94	29.54	-	9.1	-	-	100
AG2.3	54.05	8.04	29.9	-	-	8.01	-	100
AG2.4	53.18	7.92	29.41	-	-	-	9.5	100

Table 3e : Oxide composition of glasses for wine-grape, in weight % [11]

Oxide→ ↓Sample	P_2O_5	MgO	K_2O	CaO	B_2O_3	Fe_2O_3	ZnO	MoO_2	MnO_2	Total
AG3	43.47	18.48	32.61	5.44						100
AG3.1	39.64	16.85	29.74	4.96	8.81					100
AG3.2	40.57	17.25	30.43	5.08		6.67				100
AG3.3	42.41	18.03	31.82	5.31			2.43			100
AG3.4	42.15	17.91	31.61	5.27					3.06	100
AG3.5	42.21	17.94	31.66	5.28				2.91		100

iii. *Structure and some properties of some glassy fertilizers*

In theFig.5 the different types of magnesium phosphate and their network-structure is shown which is formed in the magnesium containing phosphate glass fertilizers. The Typical structure of a new slow-releasing iron fertilizer is shown in the Fig.6.

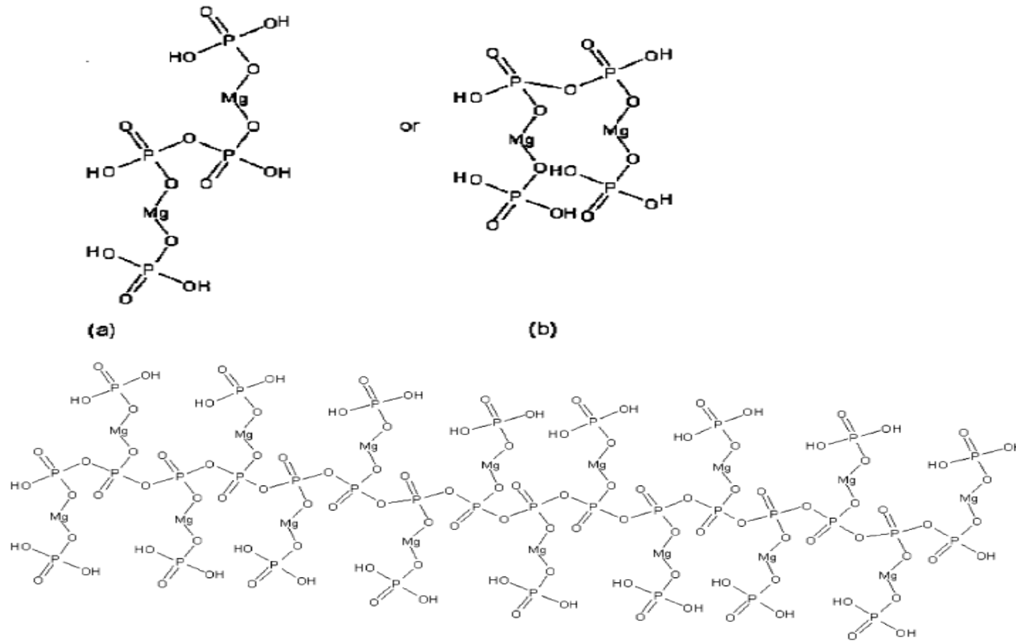

Figure 5 : Polymerization steps showing metal tetraphosphate dimer of less-stable (b) and more-stable (a) forms, plus the stable form of a multidimensional polymer (brickwall-like structure). Magnesium is shown as an example of a metal [12]

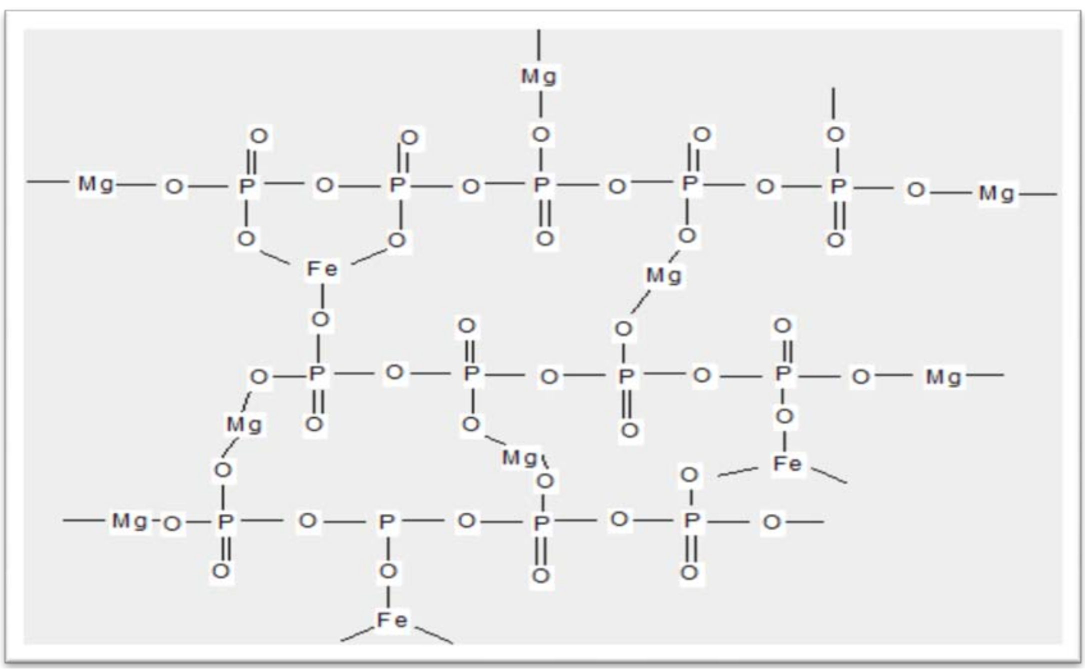

Figure 6 : Typical structure of a new slow-releasing iron fertilizer
(From: Chem. Eng. Journal, 2009)

The FTIR spectra and Raman spectra of various types of glass fertilizers with different compositions, shown in the Table-3d and Table-3e are shown in the Fig.7 and Fig.8 respectively.

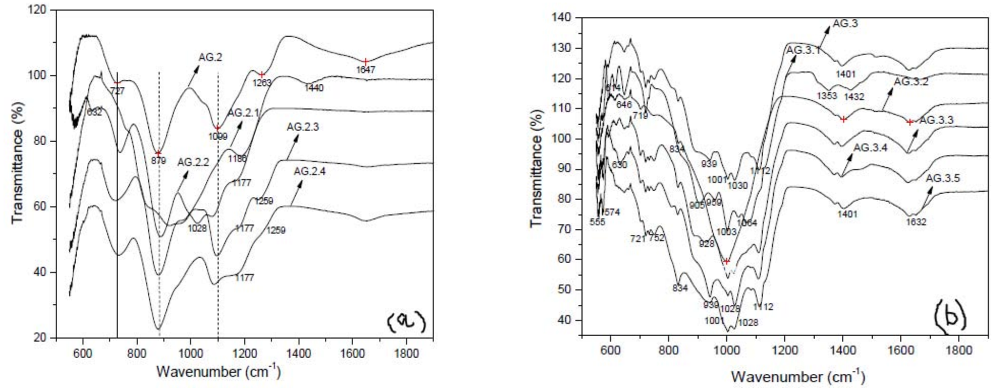

Figure 7 : Transmission FTIR spectra for potassium magnesium-phosphate glass samples, (a) AG2 type (Table-3d) and (b) AG3 type (Table-3e) [11].

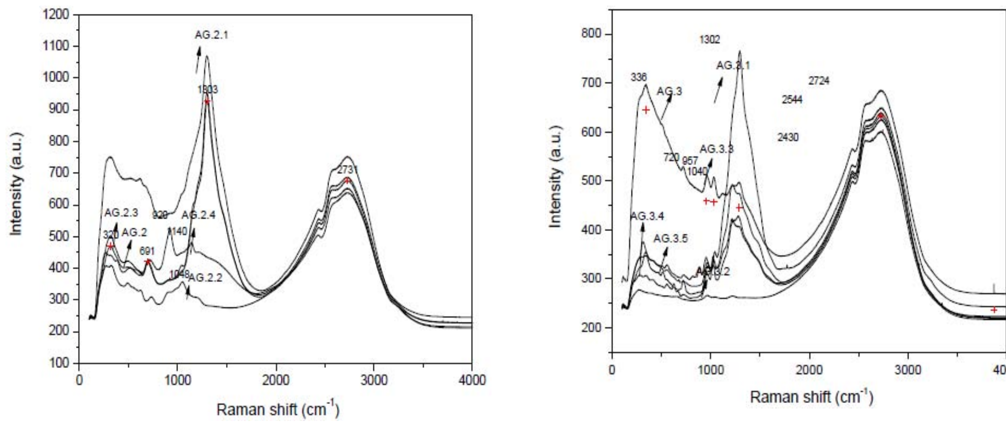

Figure 8 : Raman spectra of the glass samples from AG2 series (Table-3d) and AG3 series, (Tablle-3e) recorded in the 100-4000 cm-1 domain [11].

III. Functional Activity (With Structures)

The schematic binding procedure of 'glass fertilizers nutrients' with the soil component and plant's root showing its' network structure is presented in the Fig.9.

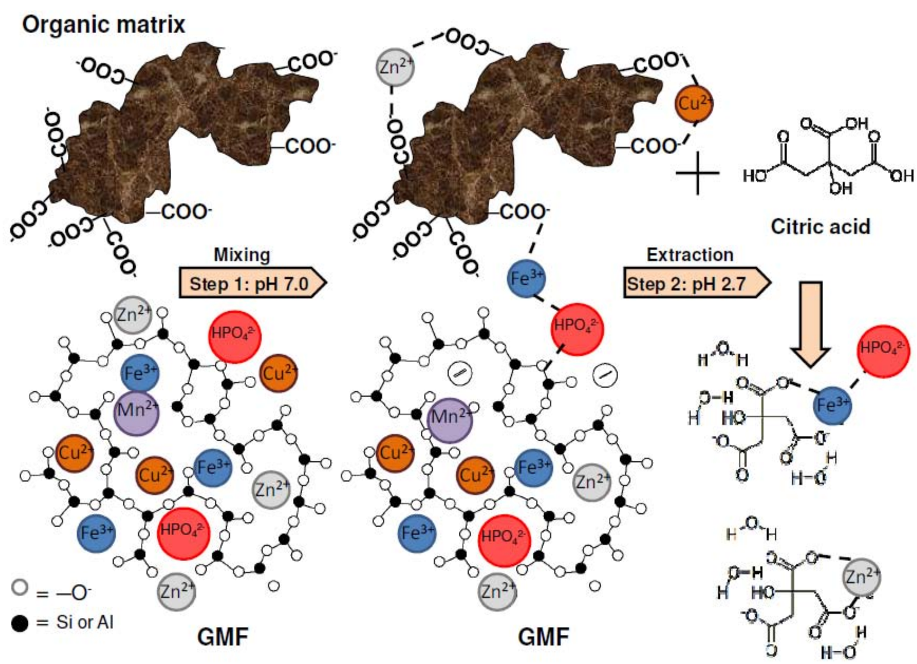

Figure 9 : Schematic binding procedure of glass fertilizers' nutrients with soil showing its' network structure [13].

IV. Leaching Studies

a) Destruction of Glass Surfaces

Just like metal rusts, glass is undergoes to a corrosion process caused by reactions between the glass surface and gases in the atmosphere or different (chemical) solutions which come in contact. Glass is hydrophilic i.e. it attracts and holds moisture. All glass has a molecular layer of moisture on the surface as shown in the Fig.10.

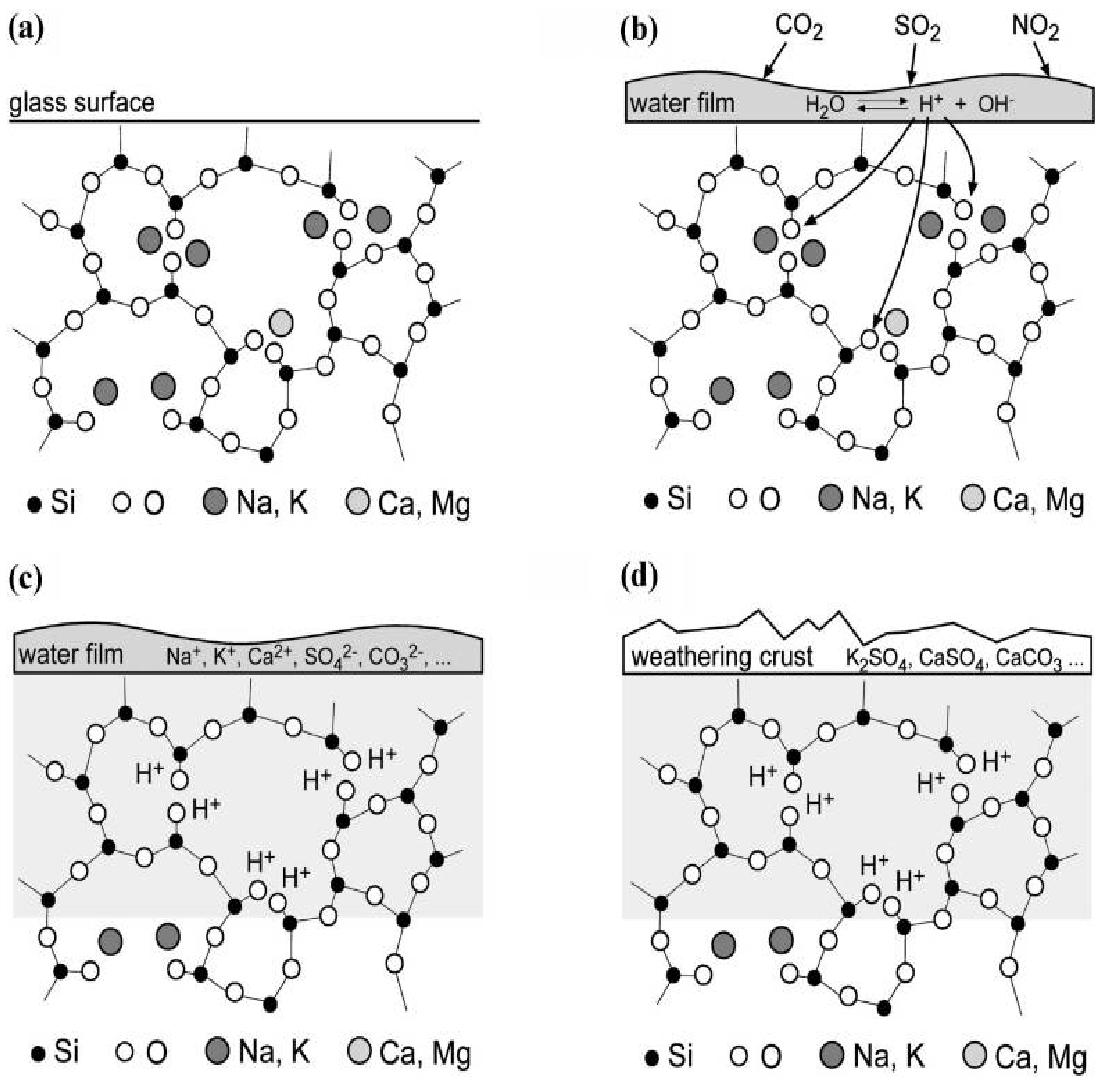

Figure 10 : (a) Glass weathering process starting from a clean surface, (b) a formation of a water film, (c) a leached layer containingHydrogen,(d) crystalline weathering products on the glass surface.

When this layer increases because of humidity or rainfall, it participates greatly to the destruction of the surface of the glass which is shown in Fig.10. There are two distinct stages to the corrosion process, occurring together or separately. One of them is aqueous corrosion, caused by moisture and is referred to as ion exchange or alkali extraction (leaching). An ion exchange occurs between alkali ions (K^+,Na^+) from the glass and hydrogen ions from the corrosion solution. The remaining components of the glass are not altered, but the effective surface area in contact with the solution is increased. This increase in surface area leads to extraction or leaching of the metal ions as nutrients from the glass fertilizers. As former (SiO_2 / P_2O_5) concentration in the glass goes down, surface area increases through dissolution of the glass surface. The pH of the solution in contact with the glass surfaces will greatly affect the corrosion process. The rapid increase in pH will cause a rapid breakdown of the glass surface. There are two types of aqueous corrosion, static and dynamic. Static aqueous corrosion is caused by an entrapment of moisture on the surface of the glass. In dynamic aqueous corrosion, the corrosion solution is replenished due to condensation run-off. In the mass transfer controlled leaching process, the fluids are always in motion e.g. batch processes with continuous mixing thus means that the fluid flows in a turbulent state past a solid surface, however, because the fluid velocity is zero at the surface of the particles, there must be a film of fluid adjacent to the surface. Using the idea that a thin film is responsible for the resistance of transfer, one can write the equation for mass transfer as [14].

$$\frac{dM}{dt} = \frac{k' A(C_s - C)}{b} \quad (1)$$

Where,

A is the area of solid -liquid interface,

b is the effective thickness of the liquid film surrounding the particles,

C is the concentration of the solute in the solution bulk at time t,

C_S is the concentration of the saturated solution in contact with the particles.

M is the mass of solute transferred in time t, and

k' is the diffusion coefficient.

$$ln\frac{C_S - C_o}{C_S - C} = \frac{k' A}{Vb} t \quad (2)$$

For pure solvent $C_o = 0$, therefore

$$C = C_S(1 - e^{\frac{k' A}{Vb} t}) \quad (3)$$

To made the suitable glass fertilizer, physical, chemical and dissolution properties were investigated according to variation of the composition in both phosphate and silicate glass systems. Among them phosphate system is more suitable one because phosphate component act as a former as well as macronutrient for the glass fertilizers and plant respectively. In glass forming region, K_2O-CaO-SiO_2-P_2O_5 and K_2O-MgO-SiO_2-P_2O_5 glass systems were used as most of the glass fertilizers. The glass transition temperature (Tg) and softening temperature (Ts) were gradually shifted to the higher temperature range according to increase of SiO_2 contents. The K_2O and Na_2O contents, which could cause the structure change from network structure to polymeric chain structure, have direct proportion with the thermal expansion coefficient and inverse proportion with Tg and Ts[15].

For the application of environment friendly glass-fertilizer, K_2O-CaO-P_2O_5 glasses were chooses and the dissolution properties of these glasses were investigated using pH meter and ICP analyzer by H.K. Lee et al in 2005.[Hoi Kwan Lee et al., 2005, Materials Science Forum, 486-487, 407].The results shown that pH values depended on the glass compositions, and the ICP analysis confirmed that the dissolution rate was inversely proportional to the change of the K_2O/P_2O_5 ratio, which was a main factor in controlling chemical durability of the glass fertilizer, and which could be controlled by mother glass matrix composition. Therefore, the phosphate glasses are expected to provide the slow-releasing nutrient fertilizers that are easy to produce, environmentally safe, and widely applicable [16].

Pure vitreous P_2O_5 consists in a continuous random network (polymeric structure) of quasi-tetrahedral PO_4 units wherein phosphorous is four coordinated and only three of the oxygen atoms of each unit bridge to neighbouring units, while the forth is doubly bonded to the central phosphorous atom. The presence of the modifier like alkali and alkaline earth species decreases the number of bridging oxygens (P-O-P bridge) in PO_4 units, while its negative charge increases. Two PO_4tetrahedra sharing an oxygen, that can be represented as $(PO_3)^{2-}$ –O–$(PO_3)^{2-}$, form the $(P_2O_7)^{4-}$ pyrophosphate anions. Both in the melt and during the quenching process will occur an equilibrium between the pyrophosphate anions and their products as follows [17] $(PO_3)^{2-}$ –O– $(PO_3)^{2-}$ ↔ $(PO_4)^{2-}$ + –O–(PO_2). The dissolution resistance has to be also related to the presence of Na2O in the glass matrix, having in view that the alkali ions diminish the network consistency [18].

The initial stages of the aqueous reactions always results in the leeching of alkali and alkaline earth species from the surface of the glass to create a P2O5-rich surface layer. It is generally believed that in the initial stages of the leaching reaction, the contact of liquid water or vapour water with the glass surface leads to an exchange of alkali and alkaline earth ions in the glass with hydrogenated ions in the aqueous environment. (i.e. ion exchange or interdiffusionmechanism).

Another mechanism proposed is based on the diffusion of molecular water into the glass and its chemisorption at the non-bridging oxygen sites where alkali and alkaline earth species reside in the glass [19].

b) Advantages of Glassy Fertilizers

- Each element (former and modifier) in glass fertilizer has an effect to give a very high increase in the fertility of the soil and they are not water-soluble yet easily soluble in weak acidic content in the soil or generated by plant roots. Solubility of each substance in 2 %citric acid is same as shown in the Table 4.

Table 4 : Solubility of some oxides in the 2 % citric acid.

P_2O_5 :	98 – 99%
CaO, MgO :	over 98%
SiO_2:	over 95%
Fe_2O_3 :	approx. 90%

If the glass fertilizers are water-soluble, then P_2O_5 shall combine with minerals (i.e. iron, aluminium) presence in the soil to form precipitants which are hardly absorbed by plants thereby reducing considerably the effect to increase the fertility of the soil. The residual of the common fertilizer shall dissolve in water and is washed out after few hours of its application. Glass fertilizer does not have that weak point, thus it is not washed out easily, not disintegrated in the soil and can supply the nutrients for a long time with effect of increasing fertility of the soil.

- The glass fertilizer can neutralize toxic acids and can bind the heavy metals in the soil and from other fertilizers. The effect of glass fertilizer is characterized by acidity, within pH 8.0 – pH8.5.
- Controlled release glass fertilizer is very convenient for use and can be preserved for a long time because it absorb less moisture, does not disintegrate even in damp weather or (below 500°C).
- Glass fertilizer does not contain toxics substances, since it does not have an acidic sulphate or chloricradical, glass fertilizer does not cause acidity to the soil, toxic gas or hydro sulphuric acid that can destroy plant roots on rice-fields [20]. Normally, the soil is poor in phosphate (P2O5), therefore, P_2O_5 is necessarily to be added. P2O5 is the important constituents of plant root cells which assist the roots in growing strongly thus further improving the yield. The glass fertilizer is not easily water-soluble, it lies within the soil and continues providing necessary nutrients for the plants on the other hands common fertilizers are easily soluble in water, for example, super phosphate, and ammoniac sulphate can have immediate effects but are easily held by aluminium in the soil thus rapidly washed out. Plant roots still continue to dissolve P_2O_5 via immediate contact with glass fertilizer in the soil. This effect is very important to the type of soil originating from volcano ashes, wild soil and exhausted fields poor in P_2O_5 [20].
- The glass fertilizer not only helps increase the fertility of the soil, suitable for many kinds of plant but also help prevent lack of magnesium and some other nutrients in the soil that support the plants' growth [3]. Mg is very necessary for creating Chlorophyll in plant leaves, the main constituent of the plants. Mg plays an essential role in the production of protein and fat in plants. Mg improves the effect of phosphate, helping plants absorb the nutrients lying inside the soil and also participate in transporting P_2O_5 that has been absorbed in the tree-trunk. Fused Magnesium Phosphate (FMP) fertilizer i.e. one kind of glass fertilizer can be seen as the most suitable one in tropical and subtropical zones poor in P_2O_5. In such zones, many kinds of nutrient of plants are in the process of washing out; this situation can be improved by using controlled released glass fertilizer continuously, on the other hand it assists the soil in maintaining the nutrients in an efficient manner [11,20].
- Unlike classical common fertilizers, which are used only 35-40% by plants, glass fertilizers are totally absorbed, which protects the soil from pollution. On the other side, glass fertilizers used quantities was at least two times smaller than in the case of classical ones, which implies decreasing of production costs and very significant reduction of pollution. At the same time, the soil pressing grade is significantly reduced. The use of vitreous fertilizers showed it efficiency, together with the classical ones, but also at using them without the classical ones [11,21].

V. Conclusion

Since the inception of Green Revolution there has been a race for increasing food grain (mainly cereals) production using chemical fertilizers in India. However, cereal production in the country increased only five fold, while fertilizer consumption increased 322 times during the 1950–51 to 2007–08 period, implying a very low fertilizer use efficiency [22]. The Controlled Release Fertilizers delivers up to 10 weeks of healthy plant growth and colour, so you can make fewer applications in a season. Less product breakage means less quick release, less surge growth and longer residual feeding. Fewer products are lost to leaching and volatilization, reducing environmental impact. Slow release fertilisers are less nitrogen "lock-off" that means we get the nitrogen we're paying for in the expected time frame. The CRF can trace elements that can be fitted into slightly soluble glasses for slow release in soil. The experiments have shown a 25-50% increase in the crop production with use of these micro nutrient glass fertilizers and the benefits can be seen for over 20 years of each addition. Micro Nutrient Glass Fertilizers release micronutrient trace chemicals in soil for balanced plant growth, over a 10-20 year period, and are not easily washed away [3,20].

If a mixture of phosphate rock and olivine or serpentine (magnesium silicate) is fused in an electric furnace [11]. The molten product is quenched with water and used in a finely divided state as a fertilizer. The product, a calcium magnesium phosphate (CMP) glass, contains about 20% P_2O_5 and 15% MgO. Over 90% of the product is soluble in citric acid. The minerals are variable in compositions; iron, nickel, and sometimes manganese may substitute for magnesium.

The change of the K_2O/P_2O_5 ratio is the main key factor to control water solubility, physical properties such as density and hardness and chemical durability. In the abnormal glass properties such as fast dissolution in aqueous solution, it was presented that the glass can be a good candidate for agriculture fertilizer [15,23].

It can be concluded that the glass composition and structure can be designed in order to control the solubility in water and to obtain valuable vitreous fertilizer with special application in plant production.

Most important of all, water and soil pollution hazards are minimised and the economics of fertilizer use is significantly improved. All this can be achieved with just cheap and readily available raw materials and using processes that are both technical simple and fairly low energy consuming. It would appear that in the long run polyphosphates are indeed the answer to the problem of choosing the right fertilizers for the needs of the future [1].

A higher effectiveness of lead ions elimination from the examined chloride solutions in relation to cadmium ions has been observed [24]. The presence of citric acid solution simulating natural soils environment has an inhibiting effect on the process of bonding lead and cadmium into the form of insoluble phosphates.

For maximizing health and growth of crops, plants need to ingest certain elements, such as borax, cobalt, iron, manganese and nickel in trace quantities. Use of the common salts of these chemicals do not help very much, not only because excess quantities may actually be harmful, but these salts are usually soluble in water, and are washed away with the first rain, and so, are not only wasted, but contaminate the soil nearby with excess micronutrients. Micronutrient glass fertilizers, on the other hand, contain these micronutrients in the form of slightly soluble glassy granules, which cannot be washed away easily, and dissolve into the soil slowly, so that 200gms per sq. metre of micronutrient glass fertilizer provides the required nutrients over a period of 20-30 years, for the fertilized area before replenishments are required. So this is holistic approach to the environment.

VI. Acknowledgements

Discussion with Dr. J. Mukerji and Dr. A. S. Sanyal, retired Scientist, CGCRI, from time to time in sharing their expertise and valuable guidance is gratefully acknowledged.

References Références Referencias

1. Varadachari C. Phosphoric Acid, Phosphate and Fertilizers for the Future. Proc. Indian natn. Sci. Acad. B. 1992;58(2&3):119-126.
2. Roy RN, Finck A, Blair GJ, Tandon HLS. Plant nutrition for food security: A guide for integrated nutrient management. FAO FERTILIZER AND PLANT NUTRITION BULLETIN 16.
3. Trenkel M. E. Controlled-Release and Stabilized Fertilizers in Agriculture –, Published by the International Fertilizer Industry Association, Paris, December 1997.
4. Role of Fertilizer Industry in Meeting the Increasing Demand for Food. Phosphate Newsletter 23. (2005):23; www.imphos.org.
5. Improving plant nutrient management for better farmer livelihoods, food security and environmental sustainability (Page Number-2): FAO Corporate Document Repository http://www.fao.org/docrep/010/ag120e/AG120E09.htm#9.1.1.
6. Hazra G. Leaching Study of the some Lead-Iron Phosphate Simulated Nuclear Waste Glasses with Different Modifiers under Soxhlet Condition. IJAREAS. 2013;2(12):30-47.
7. Petitjean V, Fillet C, Boen R, Veyer C, Flament T. Development of Vitrification Process and Glass Formulation for Nuclear Waste Conditioning -WM'02 Conference, February-2002:24-28.
8. Van Wazer J.R. 1966 Phosphorous and its Compounds Vol. I (New York: Interscienc).
9. Ohashi S. Condensed Phosphates containing other oxo acid anions; in Topics in Phosphorous Chemistry. Vol. I. (ed. M Grayson and E J Griffith). New York: John Wiley. 1964: 189-240.
10. Sava B. A, Boroica L, Sava M, Elisa M, Vasiliu C.I, Nastase F, Nastase C, Medianu R. Potassium phosphate glasses used as agro-fertilizers with controlled solubility. Optoelectron. Adv. Mater.2011; 13(11-12):1534 – 1541.
11. Sava M, Sava BA, Boroica L, Diaconu A, Ursu L, Elisa M. Efficiency of Vitreous Phosphato-Potssium Fertilizers on Autumn Corps. Scientific Papers, UASVM Bucharest, Series A. 2010; Vol. LIII: 187-193.
12. Bhattacharya I, Bandyopadhyay S, Varadachari C, and Ghosh K. Development of a Novel Slow-Releasing Iron–Manganese Fertilizer Compound. Ind. Eng. Chem. Res. 2007; 46(9):2870–2876.
13. Trincheraet al.Organo-mineral fertilizers from glass-matrix and organic biomasses: a new way to release nutrients. A novel approach to fertilisation based on plant demand. J. Sci. Food Agric. 2011; 91(13) :2386-2393.
14. Geankoplis, Christie J., Transport Process and Unit operations, 3rd Ed., Prentice Hall, 1993.
15. Lee Y.S, Kang W.H. Structure and Dissolution Properties of Phosphate Glasses for Glass Fertilizer. Materials Science Forum. 2004; 449-452:737-740.
16. Lee HK et al. Preparation of K_2O-CaO-P_2O_5 Eco-Glass Fertilizers and Effect in Crops. Materials Science Forum.2005;407:486-487.
17. SimonandV, Mocuta H. Glass Formation and Dissolution Properties of Na_2O-CaO-P_2O_5Glassesin Simulated Body Fluids. Romanian Reports in Physics. 2004;56(3):424 – 429.
18. Tomozawa M, Li H. Effects of water in simulated borosilicate-based nuclear waste glasses on their properties. J. Non-Cryst. Solids. 1996; 195:188-198.
19. Smets BM, Lommen TPA. The Leaching of Sodium Aluminosilicate Glasses Studied by Secondary Ion Mass Spectrometry. Phys. Chem. Glasses.1982; 23: 83-87.
20. Presentation of Van Dien Fused Magnesium Phosphate Fertilizer Company http://www.vinachem.com.vn/TCTYHC/Gifadv/Van_Dien/TA.pdf
21. Cahill S, Osmond D, Weisz R and Heiniger R. Evaluation of alternative nitrogen fertilizers for corn and winter wheat production. Agron. J. 2010; 102: 1226-1326. DOI:10.2134/agronj2010.0095.

22. Prasad R. Efficient fertilizer use: The key to food security and better environment, Journal of Tropical Agriculture. 2009; 47 (1-2) : 1-17.
23. Cacaina D, Simon S. Calcium Influence on Dissolution rates of Potassium Phosphate Glasses. J. Optoelectron. Adv. Mater. 2003; 5(1):191 – 194.
24. Wac-Awska I., Szumera M., Smerek A., Sopel I. Interaction of Glassy Fertilizers and Toxic Elements. Ceramic Matetials. 2010; 62(4):572-576.