Advanced Controlled Release Glass Fertilizer: An Inner view

[1]Biswajit Mandal, [2]Tanmoy Das, and [3*]Goutam Hazra
[1]Research Fellow, Department of Chemistry, The University of Burdwan, Burdwan-713104, W.B., India, Email: [2]Assistant professor, Department of Chemistry, The University of Burdwan, Burdwan-713104, W.B., India,
[3]Assistant Professor, Department of Chemistry, Kalna College, Kalna-713409, W.B., India,

Abstract: The present work designated as “Advanced Controlled Release Glass Fertilizer” was taken up to study the optimum operating conditions at laboratory scale. The objective of this study was to preparation and characterization of glass fertilizer. Fertilizer may cause serious problems in the environment, so the environment protection is very urgent in the world. For the production of food we can use fertilizers in agriculture, but on the other side it may be very dangerous for environment. Therefore, only necessary amount of fertilizers can be used for successful vegetation. It means that we must use fertilizers, which dissolved quickly as is nutrients requirements of plants. In this situation, it is not a contamination hazard for environment. The aim of this study was development of such fertilizers where glass fertilizers are new type of advanced and controlled released fertilizer. When we use fertilizer in the agricultural field nitrogen (N) have also shown noxious effects on groundwater, specially its nitrate content, which is injurious to health. In addition to this, gaseous such as ammonia (NH_3) and NO_x losses from N fertilization have adverse effects on the field of agriculture and the environment. Therefore, the aim of all agriculture has to be to “increase food-grain production with the minimum and efficient use of chemical fertilizers”. Glass fertilizers (vitreous fertilizer) are new type of advanced and controlled released fertilizer and made of glass matrix with low and controlled solubility in water (made of macro elements K, P, Mg, S, Ca most useful for plants) and also incorporated with micro-nutrients or trace elements containing B, Fe, Mo, Cu, Zn, Mn which are important to the growth and development of corps or plants. The quantity of the microelements(B, Fe, Mo, Cu, Zn, Mn) embodied in the glass as oxide in the range 1-5%.Here slow or Controlled Release Fertilizers (CRF) including Glass Fertilizer were described with their nutrients release mechanism. Disadvantages of different common commercially available fertilizers and advantages of organic fertilizer and controlled release fertilizers including Glass Fertilizer over common inorganic fertilizers properly explained here. There are numerous crops and plants which have different growing habits and Nutrients requirements. For usage of glass fertilizer, physical and dissolution properties were investigated according to variation of the SIO_2 and K_2O contents in silicate glasses. The application of vitreous fertilizer to rice plants indicated that the growth and quantity were similar to those used in chemical fertilizer. The glass fertilizer have several advantages: due to low or controlled solubility it does not contaminate the water system under the ground ;the soil pH can be regulated by the pH of the glass matrix; do not release acid anions such as Cl^-, SO^{2-} 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. When the glass fertilizer spread in the soil, it offers the nutrients as much as the plant needed for months to year, and those advantages will cause the greater possibility for the application of glass fertilizer.

Keywords: Glass fertilizer, Controlled release, Plant nutrients, Phosphate glass, Leaching, advanced Controlled Release Fertilizer, Vitreous fertilizer, Eco-friendly fertilizer.

1. INTRODUCTION:

In 2030 world population will increase about 11% with respect to nowadays and the need of water will then be a 40% higher. This situation will create a great problem: It will be lacking of food and water. In 2030 the world crop surface will increase only 7% respect to nowadays and there will be necessary to increase the use of fertilizers and irrigation water. This situation will also create a new problem: It will be an increase of soil and water pollution. So the world average cultivable land per capita gradually decreases in every year. This trend will require that crop production per unit of land continue to increases. The revolution which has resulted in a phenomenal increases in crop output per land and remarkably down the dimensions of food crisis; has its roots in two main sources –the evolution of innumerable new varieties of crop 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 yields increases will in turn require greater nutrient inputs.

Using of high doses of fertilizers is the magnification of the environmental hazards the soil and water. There occur soil salinization 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 due to accretion of anions like Cl- and SO_4^{2-} 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.

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, remain in the soil during the entire period of plant development, and do not pollute the phreatic water [2-5]. 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 [6,7], do not contain toxic compounds and do not release insoluble residues.

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 20-25 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. 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.

Glass fertilizers (GF) are a new type of advanced and-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. In general, conventional glasses are made from oxide network formers such as SiO_2, B_2O_3 and P_2O_5, oxide glass modifiers such as Na_2OandK_2O, glass stabilizers such as CaO and Al_2O_3, and other oxide additives such as Fe_2O_3, ZnO and MnO [8]. Among these oxides that contribute to the structure and composition of a glass, P_2O_5 and K_2O are considered macronutrients, whereas Fe_2O_3, P_2O_5 and K_2O are considered macronutrients, whereas Fe_2O_3,ZnO, MnO and other oxides are micronutrients for plant growth. These oxide elements are commonly the sub-products of the different compounds (nitrates, carbonates, etc.) normally included in conventional fertilizers. Keeping this in mind, a GF can then be formulated with P_2O_5 as glass former, K_2O as glass modifier, CaO, Al_2O_3, etc., as glass stabilizers, and other additives such as ZnO and MnO.

The aim of project was to develop a new GF conveniently formulated for application in tomato crops. First, different glass compositions, with adequate amounts of micro and macro components, were obtained and their P_2O_5 and K_2O release was determined for an extended period of time at a laboratory scale. The most appropriate GF composition was applied to a tomato crop of1 ha, and it was then tested and compared with another crop of similar area in which the most appropriate conventional NPK fertilizer was applied instead.

2. WHAT IS GLASS?

Glass is an amorphous and vitreous material. It is a product of fusion of inorganic compounds which has been cooled down from the liquid to solid state without the stage of crystallization. Glasses usually have a former (like Silica, P_2O_5, and B_2O_3) and many others. It also contains modifiers like CaO, Mgo, Y_2O_3 etc. whose function is to change the melting point abruptly lower. Additionally glass also contains an intermediate Al_2O_3.

2.1. THEORY OF GLASS:

Glass is one of the most ancient and useful materials known and used for people. Before people learned to make glasses, they had found naturally formed glasses like obsidian, fulgurites, and tektites and used these as arrow heads, knives and primitive jewellery [9]. The origin of first synthetic glass is lost in antiquity and legend. However, according to archaeologists' glass formation was discovered in ancient Egypt and Mesopotamia as far back as 3500 BC [10]. By the 15th century, the use of glass in architecture was well established. In the next two centuries, Europe was a Centre of glass related activity. By the end of the 17th century, glass making was industrialized in England. There, at the end of the 17th century, Ravenscroft invented lead glass: a combination of silica with potash and lead oxide. The development of lead glass allowed the construction of long range telescopes in the 18th century and nowadays still widely used due to its radiation shielding properties. Development of glass sheets with uniform thickness and very flat surface by float glass process (invented in 1959 by Pilkington Brothers) revolutionized architecture industry. Flat panel display glasses for television and computer screens are also produced by this process. Thus, this age-old material plays a key role in numerous applications like electronics [11], photonics [12], biomedicine [13], radioactive waste storage and many others, along with classical ones like windows, architecture, lenses, containers etc. Glass which was earlier considered mainly an optical, dielectric or passivating material can now be used to make active devices like switches, memories, sensors, solar cells, catalysts etc. [14]. These widespread uses reflect an ever increasing role of glass in our modern technical society and industry.

2.1.2. Glass definition and properties, glass-forming oxides (former, modifiers, intermediates)

A glass is defined in ASTM [15] as an inorganic product of fusion, which has been cooled to rigid condition without crystallization‘. According to this definition, a glass is a non-crystalline solid material obtained by a melt-quenching process. Glass is also defined as an amorphous/non-crystalline solid completely lacking in long-range periodicity and exhibit glass transition behavior [16]. The terms amorphous and non-crystalline are synonymous. The glass transition is a phenomenon in which a solid amorphous phase shows an abrupt change in the derivative thermodynamic properties from solid like to liquid like values with change of temperature [16]. Nowadays, non-crystalline materials that can‘t be distinguished from melt-quenched glasses of the same composition are obtainable by using various other techniques such as chemical vapour deposition, sol-gel process, etc. Therefore, most glass scientists regard the term glass' as covering all non-crystalline solids that show a glass transition' regardless of the preparation method. Glass is also defined as a configurationally frozen liquid which exhibits glass transition behaviour [17]. From a thermodynamic point of view, the glassy' state is a meta-stable state and unlike crystalline state it is not unique. The glassy' state depends upon the thermal history of the melt and represents a local minimum in the free energy. Given adequate time,

2.1.3. Properties and Theory of Glass

Glass is an amorphous (non-crystalline) solid material. Glasses are typically brittle, and often optically transparent. The most familiar type of glass, used for centuries in windows and drinking vessels, is soda-lime glass, made of about 75% silica (SiO_2) plus Na_2O, CaO, and several minor additives. Often, the term glass is used in a restricted sense to refer to this specific use.

Glass ingredients: Glass formers and/ or 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 as shown in the Fig.1 and Fig.2.

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.

Modifiers include MgO, Li_2O, BaO, CaO, SrO, Na_2O and K_2O. These oxides are added to modify the properties of glass.

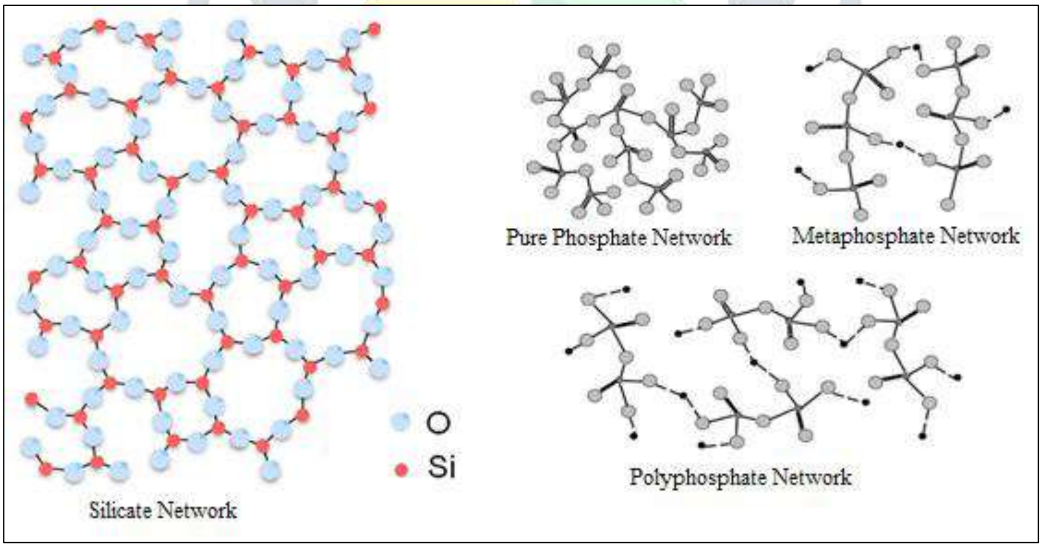


Figure 1: SiO_2 network and Phosphate network.

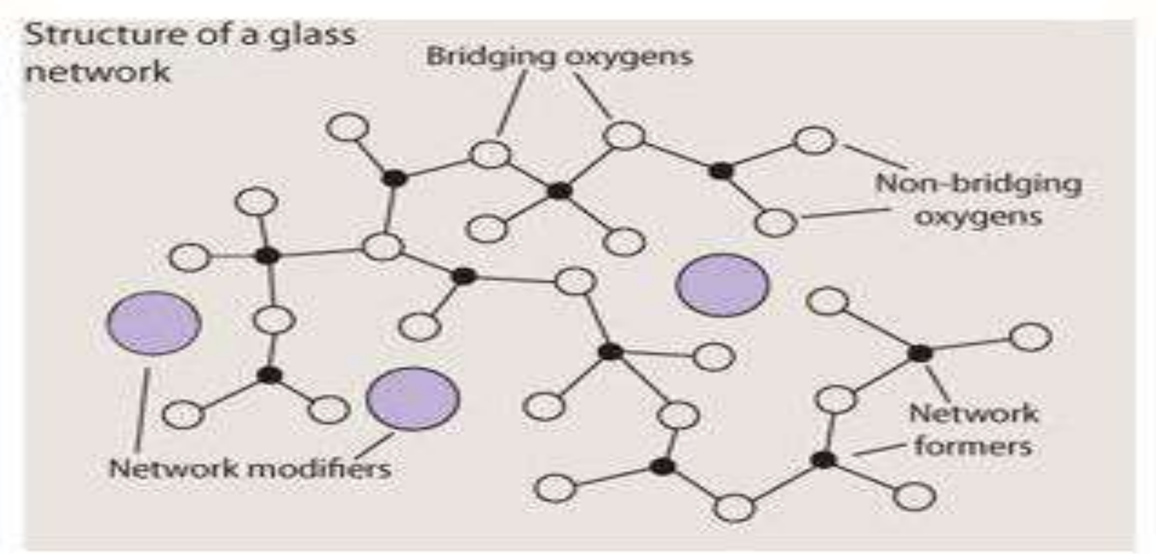


Figure 2: Glass network structure with modifier

3. WHAT IS A FERTILIZER?

The chemical composition of various essential minerals and elements meant for the regular as well as hastened growth and nourishment of all plants is termed as fertilizer. As these fertilizers have been used invariably to promote and enhance the productivity of commercial crops, therefore they are called agricultural fertilizers. Fertilizers enhance the richness of the soil and nourish it with required nutrients. By enriching the soil, fertilizers also increases the productivity of the crops. Fertilizers are the nutrient filled sources which nourish the plants with essential nutrients and soil acts as a medium between the crops and the fertilizers(Bokhtiar et al. ,2005).A substance(Such as manure or a special chemical) that is added to soil to help the growth of plants(Merriam-Webster.html,2016).

4. TYPES OF FERTILIZERS:

Fertilizers are composition of one or various chemical compounds or nutrients therefore depending on the constituent compounds and nutrients release mechanism, the agricultural fertilizers have been categorized into following categories:

a) Organic agricultural fertilizer

Organic fertilizers are those fertilizers which are manufactured using organic substances which are bio-degradable, i.e. Organic fertilizers are naturally occurring fertilizers and nutrient enhancers of the soil (Bokhtiar et al., 2005). Therefore every substance that occurs naturally and is easily bio-degradable is organic and if this organic material enhances the richness of the soil, it is termed as organic fertilizer. These organic substances are further decomposed and broken into smaller and soluble particles by numerous microorganisms. After being turned into soluble and simpler compounds, these fertilizers are taken in by the roots. Manure, slurry, worm castings, peat, seaweed, sewage, and guano are the naturally occurring Green manure and compost, blood meal, bone meal and seaweed extracts, etc. are manufactured organic fertilizers. Crops are also grown to add nutrients to the soil. Today what each farmer is looking forward to be proper solution to agriculture problem without compromising on the yield. Today the use of fertilizers is one of the greatest innovations of the agricultural revolution.

b) Inorganic agricultural fertilizer:

Those fertilizers which are constituted by inorganic chemical substances are referred to as inorganic agricultural fertilizers, i.e., granular triple superphosphate, potassium chloride, urea, anhydrous ammonia, etc. These fertilizers are usually non-biodegradable. And these are further divided into various categories based on their constituents and methods of preparations. These fertilizers are also called artificial or synthesized fertilizers as they are manufactured in the factories using latest technologies. The artificial manufacturing processes render these fertilizers a rough touch and propel them to be sturdy and highly per-formative.

c) Advantages of chemical inorganic fertilizer:

1. Readily available: as the most common form used, it is found everywhere.

2. Formula variety: it is easy for chemical companies to vary the elements to produce blends for different seasons and for specific plants.

3. Fast acting. Usually see results within 1-2 weeks if the formula used is appropriate for the season.

4. Inexpensive: typically, except for the better quality blends that have controlled release pellets.

5. Ease of application: using fertilizer spreaders. Rates and settings are usually calculated and displayed on bag.

6. Multiple forms: available in pellets, granules, liquid, tablets, spikes and slow-release, to suit every preference.

7. They are quite high in nutrient content; only relatively small amounts are required for crop growth (Madani et. al., 2011; Chen, 2006).

4.1) Macronutrients Fertilizers:

The concentration of each fertilizer in the dry base determines their strength and also their constituent elements. There are six main and most prominent elements which play a vital role in the growth of the plants. Nitrogen, phosphorus, and potassium are primary macro-nutrients. These macro-nutrients are very essential for the proper and anti retarding growth of any plant and further these nutrients enhance the yields by great differences. Calcium, magnesium, and sulphur come under the category of secondary macro-nutrients. Although all these nutrients are required by the plants in almost similar quantities however their availability marks the difference.

4.2) Micronutrients Fertilizers:

Plants also need certain nutrients in little but essential quantities and absence of these elements might hamper the growth in an effective manner. The plant growth can be retarded and can show a lasting impact on the yields as well. However, the micro-nutrient fertilizers are meant to serve the lessened but necessary needs of the plants and therefore these fertilizers are aimed at providing little portions of nutrients like iron, manganese, boron, copper, molybdenum, nickel, chlorine and zinc. The concentrations in which these elements are needed range vividly from 5-100 ppm. The essential plant nutrients (macro and micro), their forms taken up and their typical concentration in plants are shown in the Table 1 and effect of pH plant nutrient availability has been shown in Table 2.

Table-1: Essential Plant Nutrients, Forms taken up and Their Typical Concentration in Plants [18]

Nutrient (symbol)	Essentiality by	Established forms absorbed	Typical concentration in plant dry matter
		Macronutrients	
Nitrogen (N)	De Saussure (1804)	NH_4+, NO_3^-	1.5%
Phosphorus (P, P_2O_5)	Sprengel (1839)	$H_2PO_4^-$, HPO_4^{2-}	0.1–0.4%
Potassium (K, K_2O)	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)	Zn2+	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 [18]

Nutrient availability	**Very low pH (less than 5.0)**	**Low pH (5.0–5.5)**	**Optimum pH pH(5.6–6.2)**	**High pH (6.5–7.0) pH(5.6–6.2)**
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	--	--	--

5) WHAT IS CONTROLLED RELEASE FERTILIZER:

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. The compounds from which plants roots can extract ions by exchange reactions, and compounds which undergo hydrolysis and solubilization at optimum rate to fulfill the requirements of the plants, are suitable as fertilizers. 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 [8] some of them are as follow:

- Sulphur Coated Compound Fertilizer
- Sulphur Coated Urea (SCU)
- Resin Coated Fertilizer
- Urea formaldehyde
- Urea and Nitrification inhibitors
- Chemically Modified Biomass Coating Urea for Controlled Released
- Glass fertilizer

6) WHAT IS GLASS FERTILIZER?

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).

Glass fertilizer are new type of advanced and controlled released fertilizer and made of glass matrixes with macro nutrients (K, P, Mg, S, Ca) most useful for plants and also incorporated with micro-nutrient (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^- , SO^{2-}) which are malignant for plants so there is no risk of soil burning when they are incorrectly dosed; in a single type of fertilizer can be adorned 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 utilization of resources, such glass fertilizers (CRF) are most deplorable and call for a radical changes in the inorganic fertilizers.

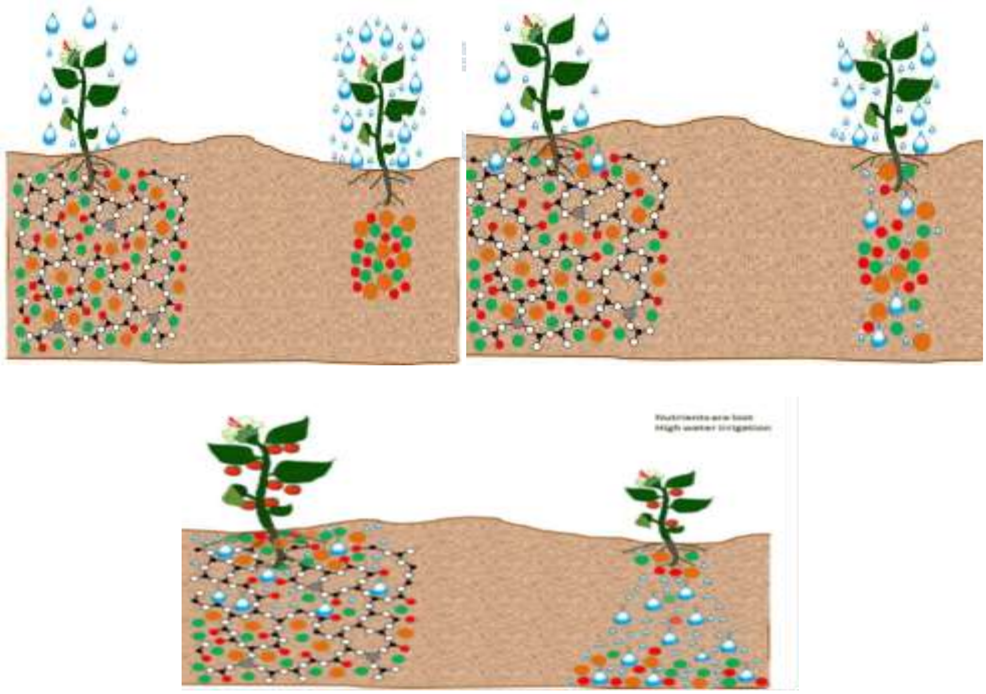
7) SYNTHESIS OF GLASS FERTILIZER (GF):

Several GF compositions (Table 3) were prepared through a conventional glass melting process with different $SiO_2/Al_2O_3/CaO$ concentrations (in wt.%). In all cases the K_2O/P_2O_5 ratio (wt.%) was maintained at 0.65. The corresponding raw materials (silica sand, calcium carbonate, potassium carbonate, phosphorus oxide and potassium feldspar) were mixed for 2 h and then melted at 1300 ∘C for 2 h using mullite crucibles. To avoid phosphorus dissolution each GF was fritted in a metal plate, then crushed and sieved to the required grain size and stored in a desiccator until use. Grain sizes (2–3 mm), similar to conventional NPK fertilizers, were selected in order to facilitate the further application to crops using industrial agricultural machinery. In the selected GF for fertilization of the tomato crop, the corresponding micronutrients were added at the following concentrations (wt.%): S, 0.5; Mg, 1.5; Mn, 1.4; Fe, 0.6; Zn, 0.2; B, 1.5. These micronutrients were incorporated directly as oxides during the melting stage of the GF [19].

Table-3: Chemical composition of (wt %) of the GF used

Series	Chemical composition of (wt.%) of the GF used			
GF1	SiO_2	CaO	Al_2O_3	$P_2O_5.K_2O$
GF1/6S	6.5	0	0	0.65
GF1/20S	19.8			
GF1/30S	27.1			
GF1/40S	29.5			
GF1/50S	49.2			
GF1/60S	56.0			
GF2	29.5	0	0	0.65
GF2/0Ca		1.6		
GF2/1.6Ca		2.5		
GF2/2.5Ca		5.1		
GF2/5.1				
GF3	29.5		0	0.65
GF3/0Al			1.1	
GF3/1.1Al			1.1	
GF3/7.7Al			7.7	
GF3/10Al			10.2	

8) HOW THE NEW GLASS FERTILIZER WORKS, A PICTURE HAS BEEN SHOWN IN FIGURE:



New Glass Fertilizers contain Macro and Micro Nutrients. Nutrient release is controlled by the chemical glass composition. After Nutrient release new pores are formed inside the glass particles where irrigation water is absorbed to be used by the plants as shown in the above figure [20].

9) 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 2300ºC. Normally, other substances are added to simplify processing i.e. to minimize the melting temperature. One of them is sodium carbonate (Na_2CO_3), which lowers the glass transition to about 1500ºC. 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 [21]. 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 [22]. 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 crystallization, upon cooling. Devitrified glass is un desirable since the crystalline areas 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.

10) MECHANISM OF PHOSPHATE GLASS:

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-} , polymerizes on hating with formation of linear chains of P-O-P bonds, In final stages of condensation, branches chain polymers may also be formed [23]. Thus, in a meta-phosphate containing linear phosphate chain the negativity charged oxygen atoms may be neutralized 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 solubilized by complexants and by cation exchange. Moreover, slow hydrolysis of the P-O-P group occurs [24] 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 polymerization of chain. The model Network structure of the glass fertilizers with different corps nutrients is drawn in Fig.3.

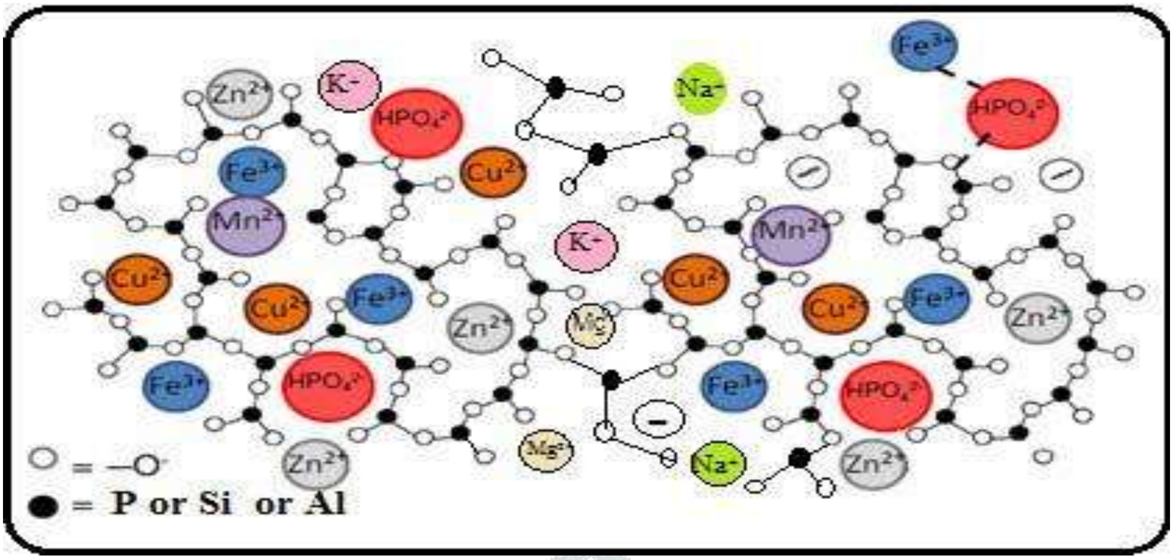


Figure 3: Network structure of the glass fertilizers with different crops nutrients [35].

11) DIFFERENT PROCESS OF MAKING GLASS FERTILIZER:

EXAMPLE 1. The glass was made by thoroughly mixing 55.8 g. of ammonium dihydrogen orthophosphate, 12.6 g of potasiumSulphate, 33.4 g of gypsum , 26.8 g of potassium carbonate and 15.2 g of aluminium Sulphate and heating the mixture at 1000° C. for 30 minutes and then by quenching the melt. The glass so obtained was checked for its solubility rate by treating 1.0gm of glass powder of size 0.6 to 1.0 mm with 50 ml of distilled water for 24 hrs. The solution is then filtered. The undissolved glass was weighed after drying the residue to the constant weight. Solubility of glass is 5.7%. The glass given in Example 1 is found suitable for food crops. There is 20-30% increase in grain yield in the case of wheat with reduced application of 30-40% K20. 70-80% CaO & 60-70% SO3 [25].

EXAMPLE 2. The glass was prepared by thoroughly mixing 34.8 g potassium Sulphate, 34.3 g of gypsum, 18.0 g of alminium sulfate and 46.0 g ammonium dihydrogenortho phosphate and heating the mixture at 850° C. for 40 minutes and then raising the temperature to 950° C. and kept for 10 minutes and then quenching the melt. The glass so obtained was checked for its solubility by treating 1.0 gm of glasspowder of size 0.6 to 1.0 mm with 50 ml of distilled water for 24 hrs. The solution is then filtered. The undissolved glass was weighed after drying the residue to the constant weight. Solubility of glass is 2.8% [25].

EXAMPLE 3. The glass was made by thoroughly mixing 26.3 g potassium disulphate. 35.6 g gypsum, 24.2 g ammonium dihydrogenorthloplhosplhate, 28.0 g potassium hydrogen phosphate and 11.7 g aluminium Sulfate and heating the mixture at 950° C. for 20 minutes followed by heating to 1050° C. for another 15 minutes and then by quenching the melt. The glass so obtained was checked for its solubility by treating 1.0gm of glass powder of size 0.6 to 1.0 mm with 50 ml of distilled water for 24 hrs. The solution is then filtered. The undissolved glass was weighed after drying the residue to the constant weight. Solubility of glass is 5.0% [25].

EXAMPLE 4. Another way of making the glass was by melting a homogeneous mixture of 18.1 g of calcium carbonate, 55.4 g of potassium disulphate, 46.5 g of ammonium dihydrogen orthophosphate and 11.6 g of aluminium sulfate at 1000° C. for 30 minutes and then by quenching the melt. The glass so obtained was checked for its solubility by treating 1.0gm of glass powder of size 0.6 to 1.0 mm with 50 ml of distilled water for 24 hrs. The solution is then filtered. The undis solved glass was weighed after drying the residue to the constant weight. Solubility of glass is 15.0% [25].

EXAMPLE 5. Another way of making the glass was by melting a homogeneous mixture of 31.8 g of gypsum, 46.8 g of potassium disulphate, 34.2 g of ammonium dihydrogen orthophosphate and 10.3 g of aluminium sulfate at 950° C. for 30 minutes and then by quenching the melt. The glass so obtained was checked for its solubility rate by treating 1.0 gm of glass powder of size 0.6 to 1.0 mm with 50 ml of distilled water for 24 hrs. The solution is then filtered. The undissolved glass was weighed after drying the residue to the constant weight. Solubility of glass is 53.0% [25].

12) LEACHING PROPERTIES OF GLASS:

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.4.

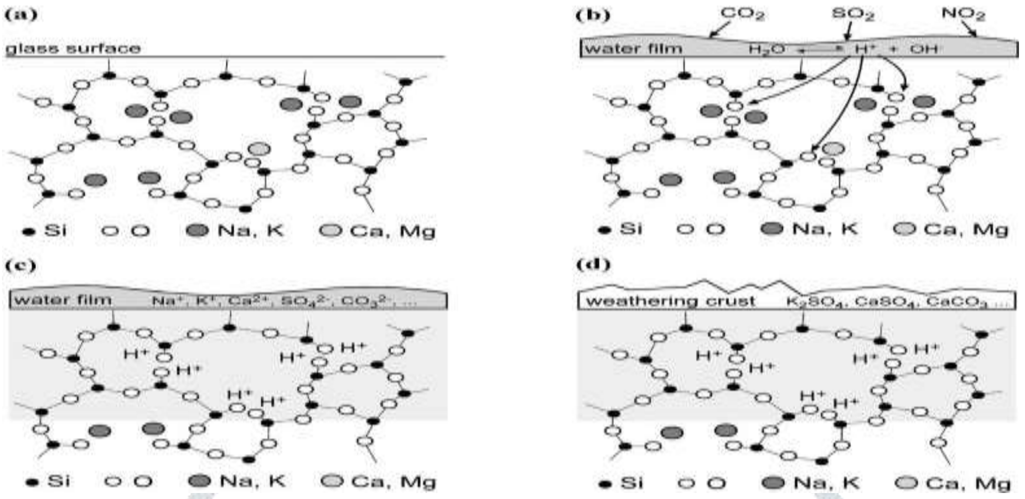


Figure 4: (a) Glass weathering process starting from a clean surface, (b) a formation of a water film, (c) a leached layer containing Hydrogen,(d) crystalline weathering products on the glass surface.

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.4. 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 [26].

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

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.

$$\ln\frac{C_s - C_o}{C_s - C} = \frac{k'At}{Vb} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. (2)$$

For pure solvent C_o = 0, therefore,

$$C = C_s(1 - e^{\frac{-k'At}{Vb}}) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots (3)$$

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 T_g and T_s [27].

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 [28].

13) SIGNIFICANCE OF LEACHING OF GLASS FERTILIZER:

The selection of the most ideal composition of GF for fertilizing tomato crops has been carried out by analyzing the leaching behavior of P_2O_5 and K_2O under laboratory conditions for all studied fertilizers. The dissolution kinetics of the different ions allows us to determine the availability of the different nutrients in the crop. Thus we have calculated the lixiviation kinetics of each element by fitting percent P_2O_5 and K_2O leached in glasses where the SiO_2 concentration was varied from 6.5% to 56% (Fig. 1). We have fitted the curves to the general lixiviation kinetics equation: $Q = kta1$ (1) where Q is the amount of ions released at time t, and k and α are the reaction constant and exponent, respectively. This equation is valid for the determination of the leaching kinetics of alkaline ions from a solution at constant pH [29]. In general, for non-saturated solutions $\alpha = 1$;[30] however, Douglas and co-workers[31–33] considered that the value of α should be close to 0.5 for short periods of time and ambient temperatures, but the value of α approaches unity in the case of long leaching times and high temperature. Leaching studies carried out by El-Shami et al. [34] demonstrated that α could reach values as low as 0.35 for leaching period's below4 h but then increase to 1. As shown in Fig. 1, both components are released quite fast and the maximum amount of P_2O_5 and K_2O released is a function of the SiO_2 content. In NPK fertilizer the maximum release takes place within the first3 days, a similar behavior that it is observed for GFwith only 6.5% SiO_2. No significant increase either in the K_2O or P_2O_5 amount was detected from the first 72 h to the end of the experiment (35 days). With high SiO_2 concentrations, a continuous and slight increase in the amount of oxides released was detected despite the rapid release that occurs during the first 3 days. This can be better observed in the differential plots (Fig. 2), where for GF containing30–56% SiO_2 a low concentration of P_2O_5 and K_2O was released at leaching periods of 10–15 days. In order to determine the effect of CaO on the release of the main components of GF, the GF2 series were analyzed. GF2 contained a fixed amount of 30% SiO2, and the amount of CaO was varied from0 to 5%.Leaching of P_2O_5 and K_2O as a function of irrigation for glass fertilizer of different concentration SIO_2 has been shown in respectively Fig.5 and Fig.6.

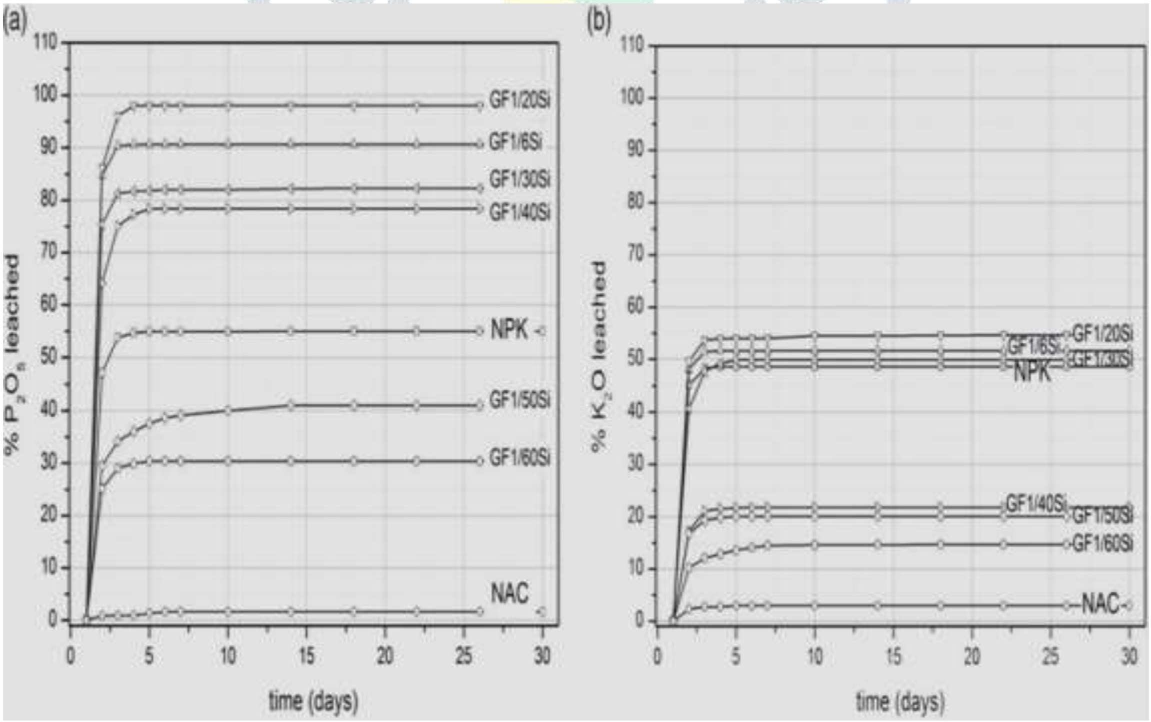


Figure 5: Leaching of P_2O_5 (a) and K_2O (b) as a function of irrigation days for GF of different SiO_2concentrations [19].

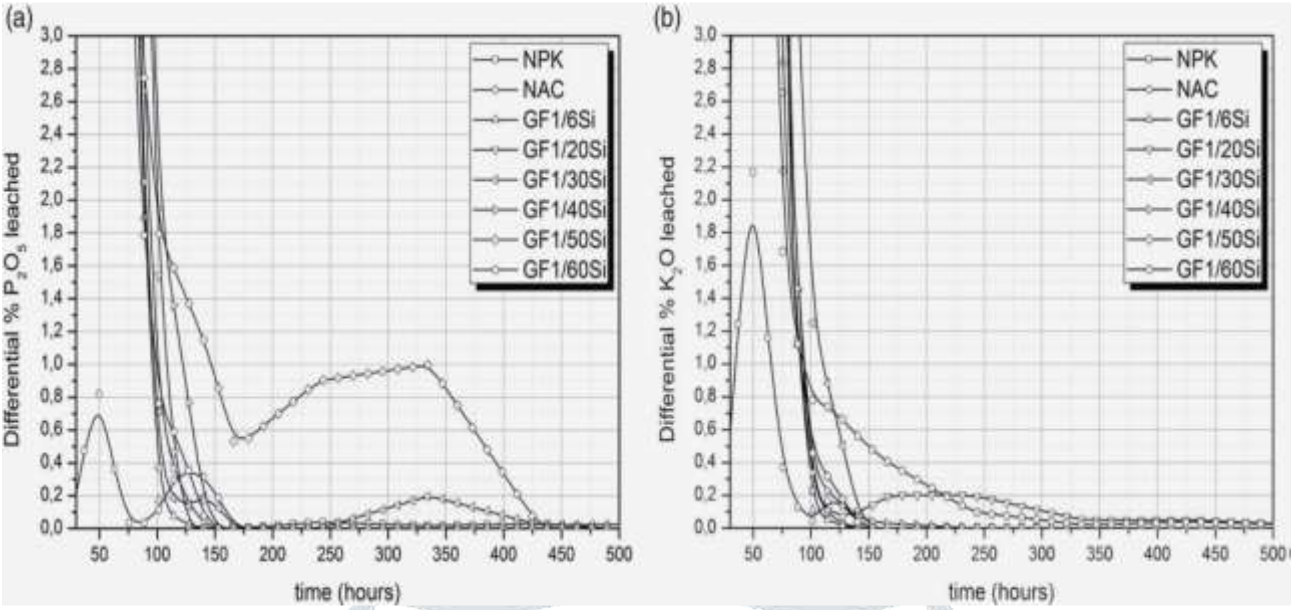


Figure 6: Differential leaching of P_2O_5 (a) and K_2O (b) as a function of irrigation hours for GF of different SiO_2 concentrations [19].

14) MECHANISM OF BINDING (FUNTIONAL ACTIVITY):

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.7.

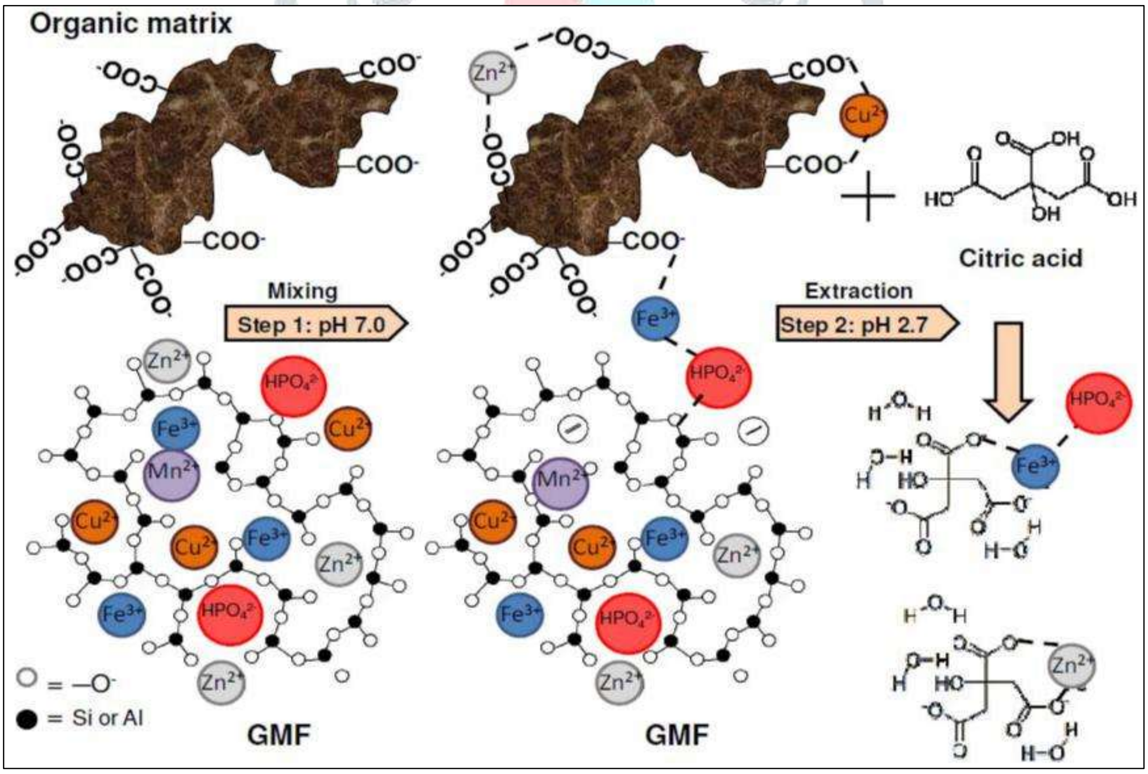


Figure 4: Schematic binding procedure of glass fertilizers' nutrients with soil showing its' network structure [35].

15) COMPOSITION OF THE DIFFERENT GLASS FERTILIZERS:

The composition of different glass fertilizers with various kinds of nutrients for different crops is presented in the following Table 4(a-d).

Table- 4a: Oxide composition of some vitreous fertilizer used in field crops [36]

Glass Code	**P_2O_5 Mol. %**	**MgO Mol. %**	**K_2O mol%**	**B_2O_3 Mol. %**	**Fe_2O3 Mol. %**	**ZnO Mol. %**
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-4b: Oxide composition of glasses for spring and autumn crops, in weight % [37]

Oxide→ ↓Sample	**P_2O_5**	**MgO**	**K_2O**	**B_2O_3**	**Fe_2O_3**	**ZnO**	**MoO_2**	**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-4c: Oxide composition of glasses for wine-grape, in weight % [37]

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

Table-4d: Raw materials composition for vitreous fertilizers oriented to spring and autumn crops [36]

Sample code	Raw materials[g]						
	$K_3PO_4H_2O$	P_2O_5	$MgCO_3$	B_2O_3	Fe_2O_3	ZnO	$(NH4)_6Mo_7O_{24}$
AG2	778	424.4	182.8				
AG2.1	778	424.4	182.8	225.4			
AG2.2	661.3	360.7	155.38		85.07		
AG2.3	661.3	360.7	155.38			74.06	
AG2.4	661.3	360.7	155.38				103.08

16) SPECTROSCOPIC STUDIES OF GLASS FERTILIZERS:

The FTIR spectra and Raman spectra of various types of glass fertilizers with different compositions, shown in the Table-c and Table-d are shown in the Fig.5 and Fig.6 respectively.

FTIR: 670-800 cm^{-1}: P-O-P Symmetrical Stretching.
980-1050 cm-^{1}:PO3^{2-} symmetric Stretching.
1100-1170 cm-^{1}:PO2 Symmetrical Stretching.

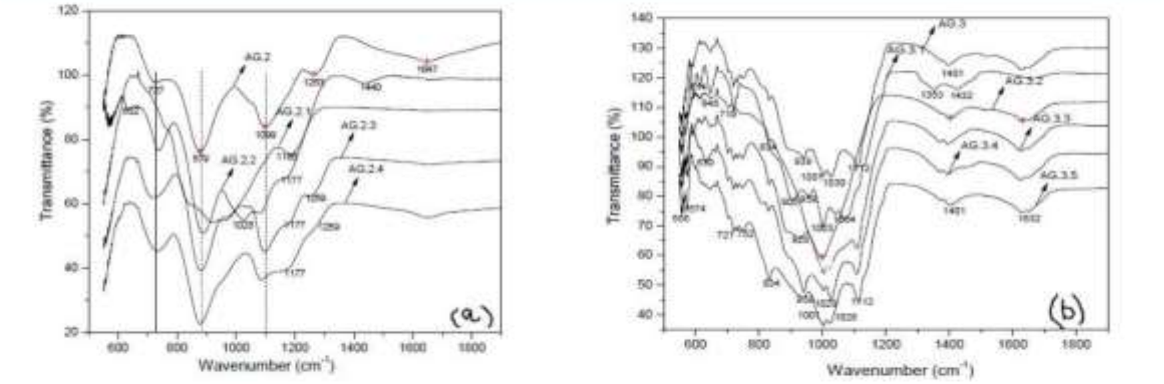


Figure-5: Transmission FTIR spectra for potassium magnesium-phosphate glass samples, (a) AG2 type (Table-c) and (b) AG3 type (Table-d) [38].

Raman spectra:

1180 cm-1: Symmetric Stretching of PO2
1270 cm-1: Asymmetric Stretching of PO2
695-750 cm-1: Symmetric Stretching of P-O-P linkage.

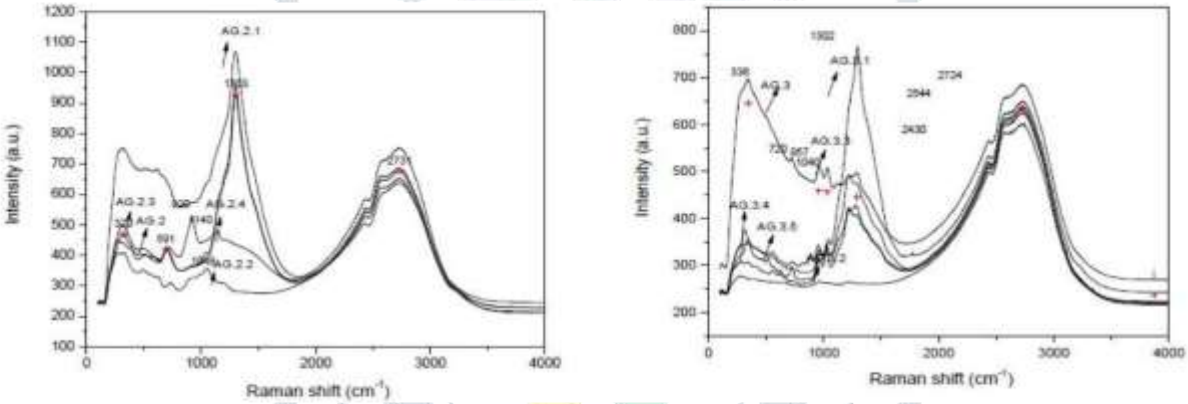


Figure-6: Raman spectra of the glass samples from AG2 series (Table-c) and AG3 series, (Table-3) recorded in the 100-4000 cm-1 domain [38].

17) STRUCTURE AND SOME CHARACTERISTICS PROPERTIES OF GLASS FERTILIZER:

The different types of magnesium phosphate and their network- structure are shown in Fig.7 and Fig.8 which is formed in the magnesium containing phosphate glass fertilizers.

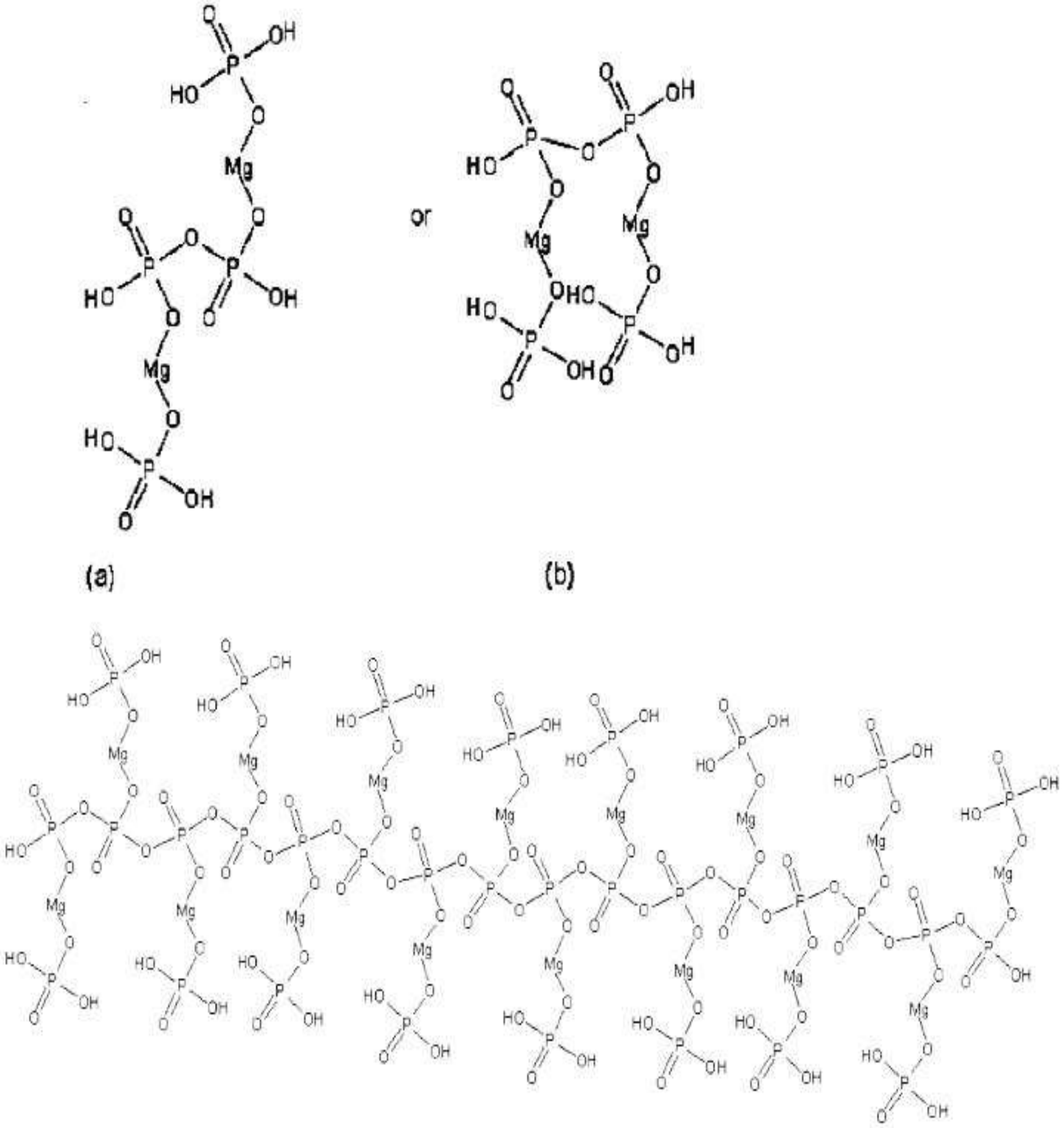


Figure-7: Polymerization steps showing metal tetra phosphate dimer of less-stable (b) and more-stable (a) forms, plus the stable form of a multidimensional polymer (brickwall-like structure). Magnesium is shown as an example of a metal [39].

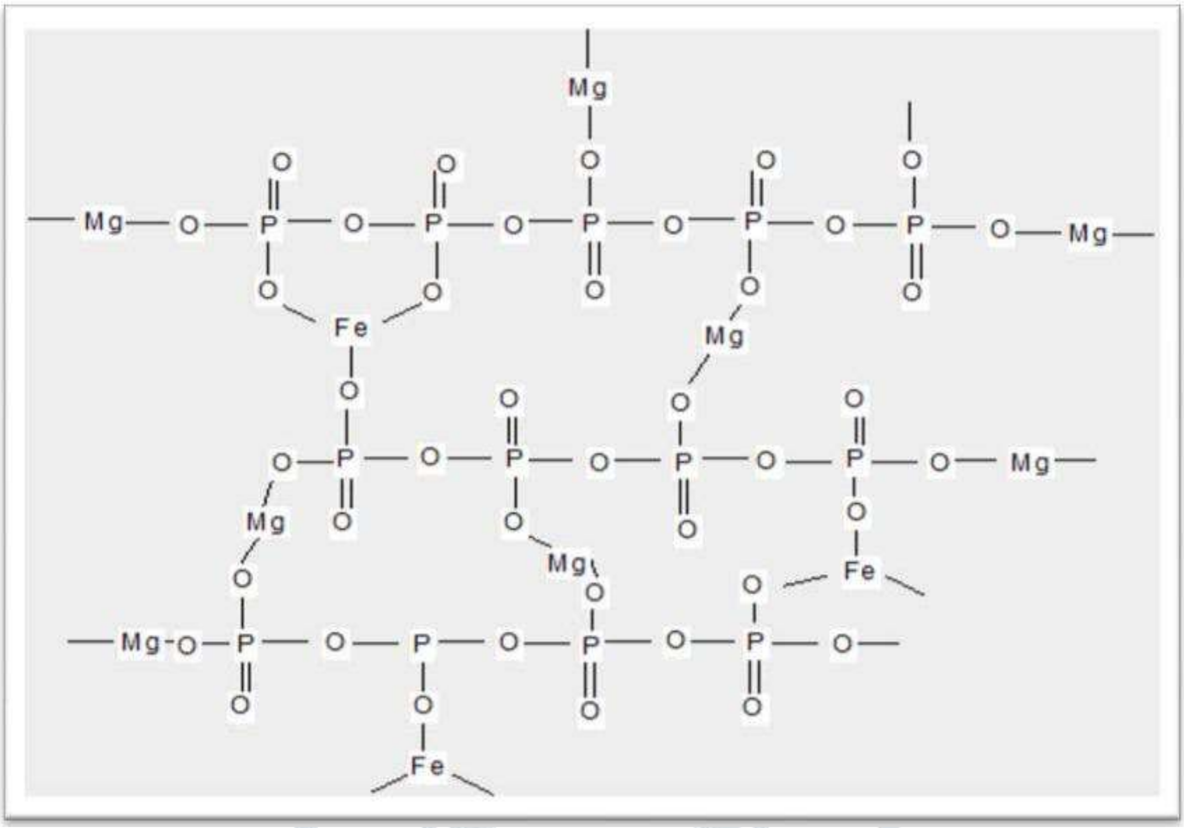


Figure-8: Typical structure of a new slow-releasing iron fertilizer *(From: Chem. Eng. Journal, 2009)*

18) FACILITIES OF GLASS FERTILIZERS:

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 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 [40 -42].

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 toxic 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[40].Normally, the soil is poor in phosphate(P_2O_5), therefore, P_2O_5 is necessarily to be added. P_2O_5 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 plants on the other hands common fertilizers are easily soluble in water, for example, super phosphate, and ammonium 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 unlike classical effect is very important to the type of soil originating from volcano ashes, wild soil and exhausted fields poor in P_2O_5 [40, 43-44].

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 plant's growth[8].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 absorbs 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 kind 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 [38, 40, 42, 45-46]

19) 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, cereals production in the country increased only five fold, while fertilizer consumption increased 322 times during the 1950-51 to 2007-08 periods, implying very low fertilizer use efficiency. 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 fertilizers 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.

If a mixture of phosphate rock and olivine or serpentine (magnesium silicate) is fused in an electric furnace. 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.

Most important of all, water and soil pollution hazards are minimized 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.

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. meter 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.

A higher effectiveness of lead ions elimination from the examined chloride solutions in relation to cadmium ions has been observed. 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.

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.

20) ACKNOWLEDGEMENT:

It is indeed, a great pleasure for me to express my heartfelt gratitude to Dr.J. Mukerji, Central Glass & Ceramic Research Institute, Jadavpur, Kolkata, for time to time in sharing their expertise and valuable suggestions.

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