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ARTICLE

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GLASS FERTILIZER - A HISTORICAL OVERVIEW

GOURANGA SAHA[1] AND TANMOY DAS[2*]

India lives in villages and not in Towns" – as uttered by M.K. Gandhi. Farmers are the backbone of our Society———- their interest should be the prime area where Govt. should focus.

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^-, SO_4^{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. Though the technology is well-established one in international level, the R & D and application of the same in Indian context is poor. It was shown that after the application of the glass fertilizer, the growth and production of the khariff paddy was better than the normal application of the conventional fertilizers. Mössbauer spectrum of one glass fertilizer containing 5 weight percent Fe_2O_3 showed a doublet signifying the presence of nitroprusside (doublet) in comparison to ferrocyanide (Singlet)[1]

Introduction

Now the world wide population increases gradually the world average 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. so remarkably scaled down the dimensions of the food crisis 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. For large production of crops 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

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Arable land per capita World average

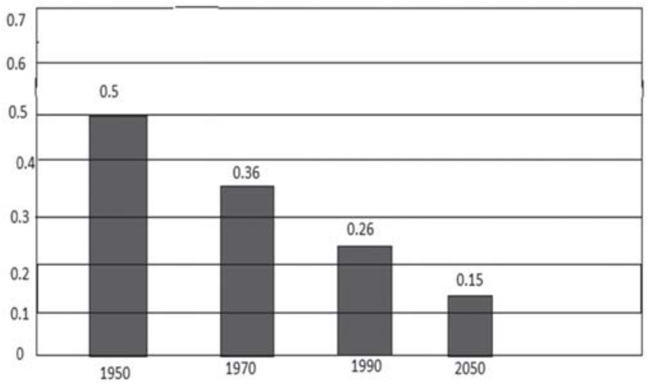

Fig. 1 : Globally, arable land per capita is diminishing as population increases: while arable land remains constant, improved yield is required to meet the growing world food demand; [From: Phosphate Newsletter 23(2005)]

micronutrients that are used as foliar sprays, is available. So controlled released glass fertilizer used.

In the perspective of agriculture in India it is the paddy which is being cultivated and produced in terms of the fertility of the land. More specifically it is the 'Khariff' which is being cultivated by approximately 89.33 million farmers. The word 'fertilizer' comes from 'fertile'. The greater the fertility the better the soil in terms of requirement of external fertilizer.

As fertilizers are applied to all the crops production and controlled released glass fertilizer and its application is our projected theme therefore front area Agriculture being on the first priority.

In the perspective of agriculture in India it is the paddy which is being cultivated and produced in terms of the fertility of the land. More specifically it is the 'Khariff' which is being cultivated by approximately 89.33 million farmers. The word 'fertilizer' comes from 'fertile'. The greater the fertility the better the soil in terms of requirement of external fertilizer. The projected production amount to 20- 25 million tonnes by 2024 -2025.

As far as the nature of the soil is concerned it is the "clay soil" which occurs naturally in our land but it is not fertile enough. Again the above soil has the limitation of producing Khariff paddy only. The drawback of the particular soil is that it can produce the grain one in a season so also with the application. It is in this context that application of nutrients (N,P,K, Mg, Fe, Zn, Ca, B etc.) in the form of fertilizer. Additionally right from the seeding up to the final product it requires sufficient supply of water. In our country only 20-25 % of the agricultural land comes under preview of irrigated water the rest being compensated through artificial means like pumps requiring liquid fuel.

In view of this perspective the proposed glass fertilizer will act as a dual nature both in terms of the conventional fertilizer so far available in the market as well the requirement of excess water. In a country like us which is basically summer base climatically the rainy season exist only for a limited 2.5-3.0 months in a year. The total time of whole period of whole of the process right from the seeding to final grain formation requires and other activity ranges maximum up to six months a year. The rest of the year the farmer of our country becomes jobless and compelled to do other alternative activities in private sector for their day to day earning. Thus this becomes a problem of unemployment for the fellow farmer, which naturally becomes a headache of both as state as well as central government in involving the poor farmers in engaging them into employments. This is a common phenomenon in our country of this helpless farmers leading to suicide. In the proposed development of glass fertilizer with its slow diffusion of above nutrients of crop root with less but controlled leaching rate(which can be manipulated through R&D work), the soil being discussed will remain fertilized minimum three years in a single application thus minimizing the waste of costly so far available fertilizers. As well as the inherent mechanism of absorption of the corresponding nutrients through costly (irrigated/ applied pump) irrespective of the nature of costly ground water particularly in drought-prone area.

Activities and outputs details

- To formulate new slow releasing glass fertilizers in laboratory containing macro and micronutrients suitable for rice.
- To study the rate of solubility/ release of nutrients from newly developed 'glass fertilizers' under laboratory condition.
- To study the efficacy of newly developed ''glass fertilizers" to Khariff rice under green house and field conditions

The chemical composition of various essential minerals and elements meant for the regular as well as hastened growth and nutrition of all plants is termed as fertilizer. The use of fertilizers in agriculture can be very useful for food production, but on the other hand, it may be harmful to the environment. Hence the only necessary amount of fertilizers can be used for successful vegetation. It means that we must use fertilizers, which are dissolved quickly as the nutrient requirement of plants. In this case, it is not a contamination hazard for the environment. All the fertilizers have been categorized into several types depending on their constituents, strength, and various other features (organic, inorganic, macronutrients, micronutrients, eco-friendly, controlled release glassy fertilizers, etc.)[2-4]. Pure phosphate glass (vitreous P_2O_5) is highly hygroscopic and is not appropriate for the application. The properties of this glass can be improved by the addition of different network modifiers - alkali and alkaline earth oxides. In that way, the multi-component phosphate-based glasses or glass-ceramics having many specific properties can be obtained. As such, these materials can find wide technological applications[5,6]. Recently, because of gradual solubility, the attention was paid to the phosphate based glasses, which can be used as new ecologically safe fertilizers[7,8]. The fact is that conventional technologies for land cultivation based on the application of traditional mineral fertilizers are responsible for the pollution of the environment. The main advantage of glasses is the possibility to manipulate their chemical compositions by the addition of new elements in different quantities. Therefore, the kinetics and mechanism of the dissolution process can be tailored as needed[9]. In the case of plant nutrition, it is important that the release rates of glass components are equal to the absorption rates of plants or microorganisms[10]. In this way, the possible damaging effects of accumulation or deficiency of elements can be avoided. In this context, a glass fertilizer can take a dual role. In addition, as the leach resistance of glass is very high, i.e., when applied to a soil, the fertilizer is released very slowly, satisfying the optimum level of requirement with no misuse. It has been found that when such fertilizer is applied on tree-like mango remains 20-25 years at the root and it grows and gives fruits with a single charge of fertilizer[11]. There are two-fold advantages to incorporate the ingredients into a glass fertilizer: a) a glass can accommodate almost all the elements of the periodic table (secular matrix) and b) the leach resistance of glass which may vary is very high, i.e., it is not washed out easily in water. Glass fertilizer slowly distributed into the root of the plant /crops is distributed thus into fruits of the crops and in due course, it flourishes. The excess of the amount of glassy fertilizer remains in the soil and help for the next two batches of the crops[11]. Glass fertilizers (GF) are a new type of advanced and controlled release fertilizer made from glass matrices containing the most useful macro elements (N, 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[11,12]. The main advantages of a new type of fertilizers against conventional fertilizers are increased grade of assimilation by plants, do not release insoluble compounds in soil, and remain in the soil during the entire period of plant development and do not pollute the phreatic water[13-16]. 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 many useful microelements[17]; do not contain toxic compounds; and do not release insoluble residues[18].

An Approach of Glass, Fertilizer and Glass Fertilizer

Definition of Glass: A glass is defined in ASTM[19] 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 (amorphous) solid material obtained by a melt-quenching process. Most of the glasses are typically brittle, as a substance, plays an essential role in science and industry. The most familiar, and historically the oldest, types of glass are "silicate glasses". 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 plant nutrients (macro & micro). 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.

A Brief Approach of Fertilizer and Glass Fertilizer

The common silicate glass network structure and glass network with modifiers is shown in Fig.2. and Fig.3. respectively

Phase Separation in Glasses: Borosilicate glasses in certain composition regions as given in the figures below tend to separate into a silica-rich phase, and a borate-rich phase upon heat treatment. In common industrial glass composition regions, the silica-rich phase is continuous, while the borate-rich phase is either continuous given a sufficiently high borate concentration, or at low borate concentrations the borate-rich phase may be incorporated in the form of small droplets into the major silica-rich phase. Figure. 4 shows the glass structure for the case

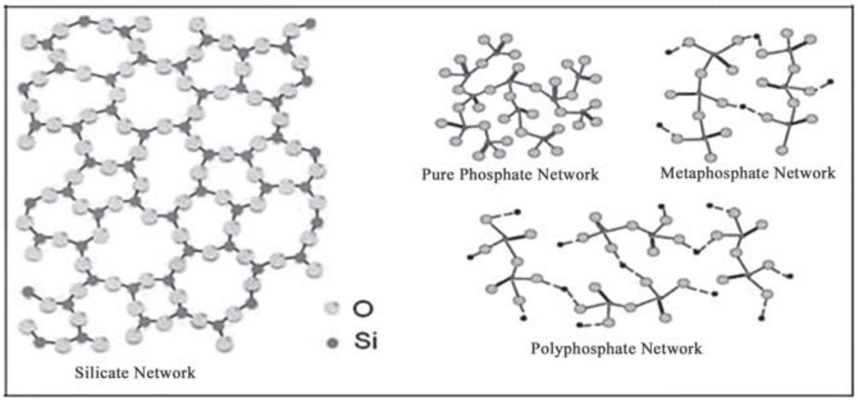

Fig. 2 : SiO_2 network and Phosphate network.

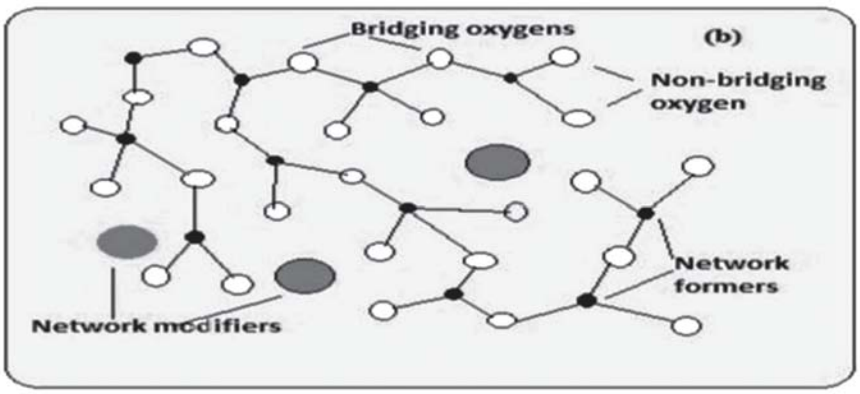

Fig. 3 : Glass network structure with modifier.

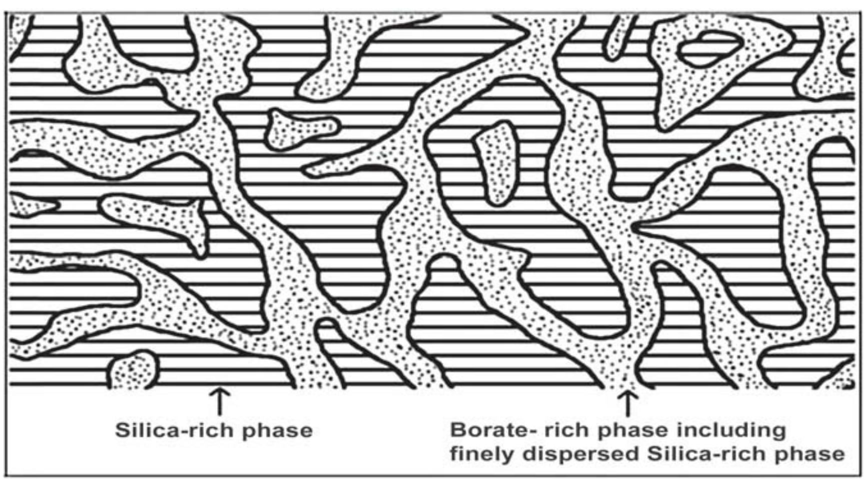

Fig. 4 : Interconnected structure of phase - separated borosilicate glass.

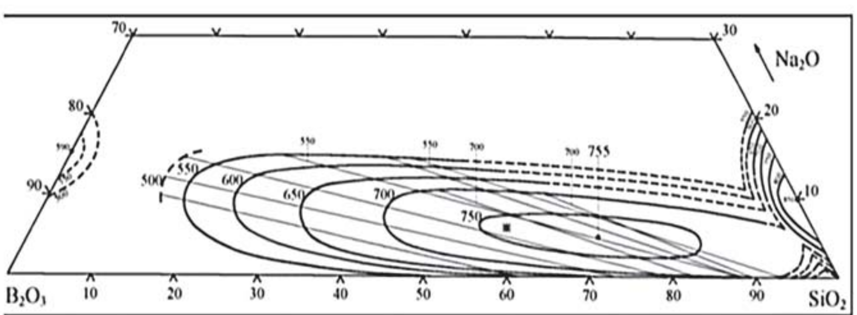

Fig. 5 : Critical temperatures in the ternary system SiO2-B2O3-Na2O below which phase separation occurs.

that both, the silica-rich and borate-rich phases are continuous (interconnected) three-dimensionally throughout the whole sample.

Often the borate-rich phase does contain finely dispersed droplets of the silica-rich phase due to the secondary phase separation effect [20] during cooling of the specimen. Figure 5 displays the critical temperatures in the ternary system SiO_2-B_2O_3-Na_2O below which phase separation occurs. All concentrations in Fig .5 are in wt% and temperatures in ºC. Fig 6. also shows the tie-lines at selected temperatures. The tie-lines give the chemical composition of the immiscible phases. The photo micrograph of the corresponding glass is shown as shown in the SEM Fig-7.

Glass Transition (Tg) Phenomenon: When a liquid is cooled either crystallization may take place at the freezing point (or melting point 'T_m'), or else the liquid will become supercooled liquid for temperature below T_m. This supercooled liquid becomes more viscous with decreasing temperature, and ultimately attains the viscosity (dPas) characteristic of a solid.

Although glass has atomic arrangement akin to liquid state, in terms of all other properties such as rigidity etc., glass is unequivocally a solid. This phenomenon can be understood readily by monitoring the changes in enthalpy/volume as a function of temperature (Figure 8). The crystallization process is manifested by an abrupt change in extensive thermodynamic variables like enthalpy 'H' or volume 'V' at Tm, whereas glass formation is characterized by a gradual change in slope. The temperature range over which the change of slope occurs is called the 'glass - transformation range'[21,22]. As the transition of liquid to the glassy state is continuous, the T_g cannot be uniquely defined. However, for convenience the Tg is expressed as 'fictive' temperature 'T_f', the temperature obtained by intersection of the extrapolated liquid and glass curves (Figure 9). It depends on the rate of cooling of the super cooled liquid. The slower the rate of cooling, the larger is the region in which the liquid may retain super cooled state, implying lower T_f or T_g, as shown in Figure 9. Thus, the 'T'_g' of a glass is not an intrinsic property but depends on its thermal history[22]. Dependence of T_g on the cooling rate q is given as:

$$q = q_0 e^{-1/C\left(1/T_g - 1/T_M\right)}$$

where T_g and T_M are glass transition and melting temperature respectively and c and qo are constants. The experimentally measured value of T_g is not unique. The value of T_g depends on the time scale of the experiment used to observe it.

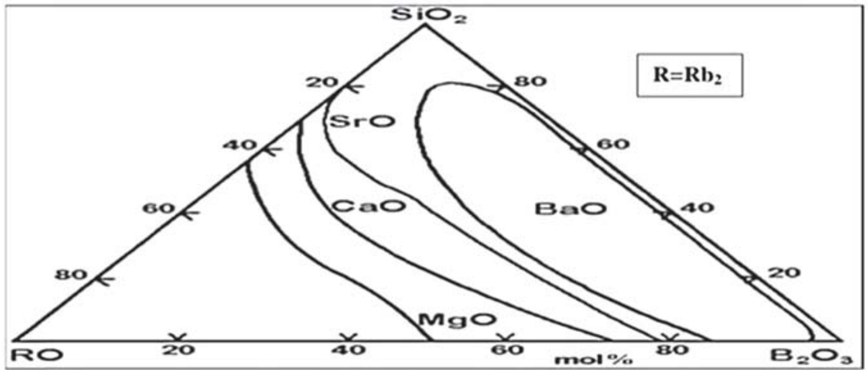

Fig. 6 : Stable phase separation in the systems SiO_2-B_2O_3-Rb_2O_2, mol%

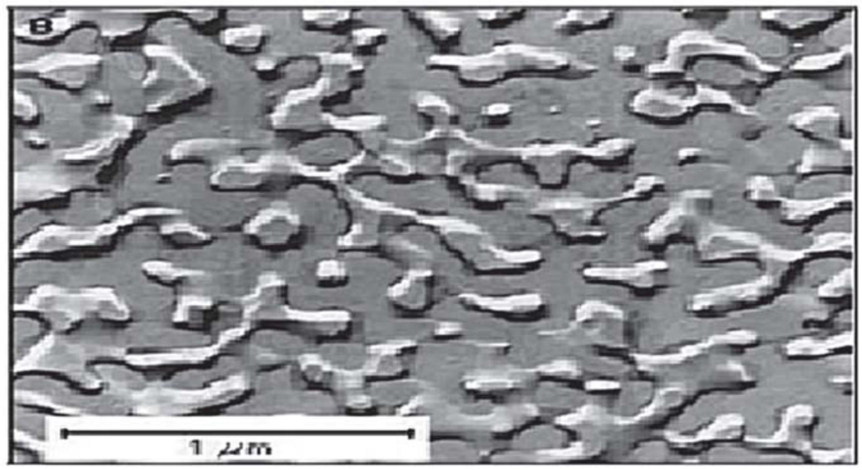

Fig. 7 : SEM micrograph of phase separation occurring in glass.

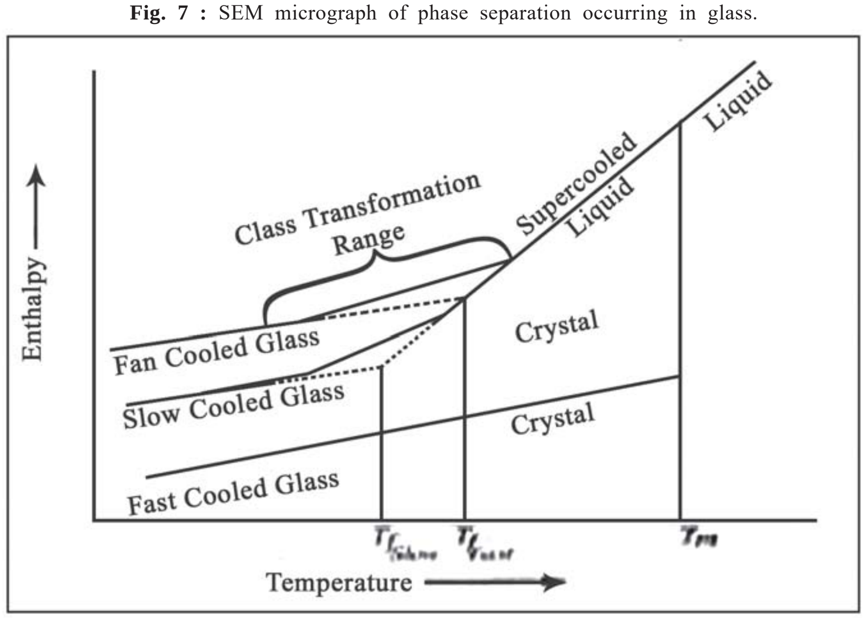

Fig. 8 : Variation in enthalpy or volume of a glass forming melt with the temperature.

Structural Theories and Observations of Glass Formation

Glasses have been broadly classified into two different ways. Glasses based on silicate, phosphate, borate, borosilicate etc., networks belong to the first category; whereas optical glasses, sealing glasses, laser glasses etc., correspond to the second category. Brief description regarding the different structural aspects and properties of some of the oxide glasses is presented in the following section.

Sillicate Glass

In silicate glass composed of SiO_2 only and it have three dimensional network structure with intermediate ionic / covalent bonds shown in Fig -9

In silicate glass alkali oxides such as Li_2O, Na_2O and MgO are often added to SiO_2 as fluxes to lower the melt viscosity and glass transition temperature. This allows alkali silicate glasses to be processed at lower temperatures than SiO_2. Each alkali ion added to the glass leads to the breaking of an Si-O-Si bonds to create a non-bridging oxygen (NBO) which the charge compensating alkali ion is then associated with. Normally oxygen atoms in the silicate network link two silicate tetrahedra, NBOs are only

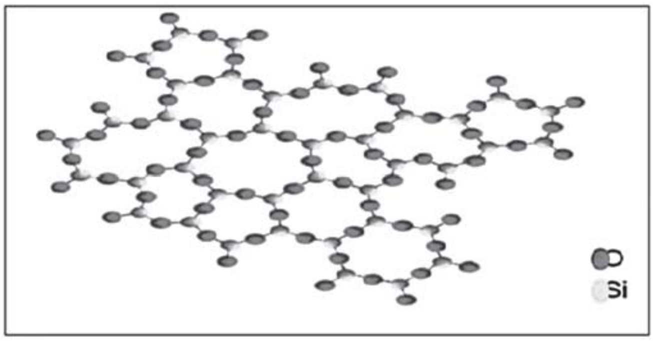

Fig. 9 : Simple structure of silicate glass.

associated with a single tetrahedron. The effect of the alkali additions on the glass structure is therefore to cause depolymerisation of the glass network. The depolymerisation process can be thought of as an acid-base reaction that, for a monovalent alkali oxide (M_2O), proceeds as follows. Fig-10 Unlike alkali metal oxides certain other metal oxides like PbO, ZnO etc have been found to behave both as network former as well as network modifier depending on their concentration.

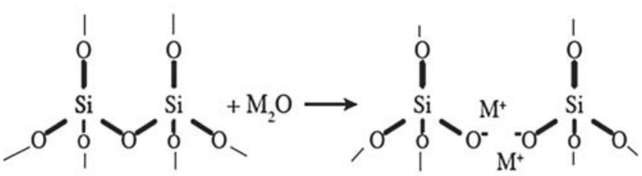

Fig. 10 : SiO_2 reacting with Alkali Oxide.

Introduction of Phosphate Glass

Phosphate glass has been researched for over one hundred and fifty years [23], Phosphate glass is the most familiar polymorph comprises molecule of P_4O_{10}. Fig-11 The other polymorph atoms are polymeric, but in each case the phosphorus atoms ,one of which forms a terminal P=O bonds.

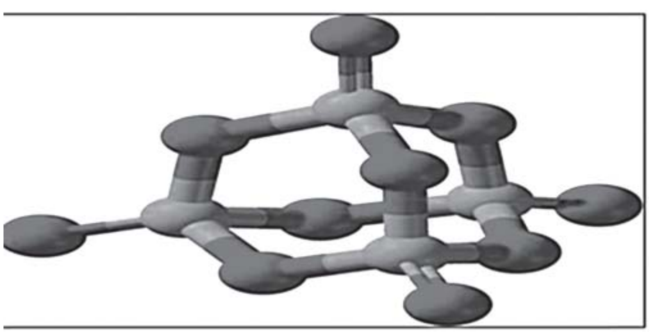

Fig. 11 : Structure of P_2O_5 (P_4O_{10})

Phosphate Glass Structure

Phosphate glasses are inorganic polymers based upon the tetrahedral phosphate anion, Figure 12, which results from the formation of sp^3 hybrid orbitals by the phosphorus outer electrons ($3s^23p^3$). The fifth electron is promoted to the 3d orbital where strong ð-bonding molecular orbitals are formed with oxygen 2p electrons, with charges balanced by polymerization or the presence of metallic ions. Fig-13

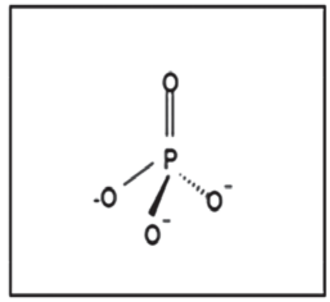

Fig. 12 : Structrue of the tetrahedral phosphate anion (charges are balanced by either polymerisation or metal cations).

Polyphosphate anions linked via oxygen bridges which may be branched or linear or a combination of the two The tetrahedral are classified using the Q_i -terminology originally devised for silicon glasses [24] but has been applied to phosphates [25], where i represents the number of bridging oxygens per tetrahedron, figure-14

Borate and Borosilicate Glasses

Pure Borate glasses are difficult to prepare under normal conditions without any moisture content. Water free Borate glasses are prepared by Poch [26] by melting ortho- boric acid for several hours at a pressure of 1 mm of Hg. Various structural studies carried out on pure borate glasses revealed that the structure of the glass agree well with the model proposed by Krogh-Moe [27]. According to this model B_2O_3 glasses mainly contain boroxol rings. The classic work of Krogh-Moe indicated the possible presence of 5 different types of borate species in the glass structure (Figure 15). Glass formation of B_2O_3 with various metal oxides has been extensively studied by various authors [28, 29] and they have pointed out that some anomalous behaviour exists for these glasses. For example, in Na_2O-B_2O_3 system two separate regions of glass formation exists in the range of composition 28.5 to 33.5 mol% of B_2O_3 and 62 to 100 mol% of B_2O_3.

Borosilicate glasses, as their name suggests, contain both silicon and boron as network formers and represent the first generation waste form for the immobilisation of high and intermediate level nuclear waste, with plants operating throughout the world [30]. In addition to lowering the processing temperature, the addition of boron (at levels below 15 wt. %) to silicate glasses has a number positive benefits: thermal expansion coefficient is reduced and chemical durability and resistance to mechanical abrasion are also improved [30]. Silicon in oxide glasses is invariably coordinated by four oxygen atoms. By comparison, boron exhibits a variable coordination state and can exist either as BO_3 triangles or BO_4 tetrahedra. The addition of alkali atoms to vitreous B_2O_3, rather than leading to the formation of NBOs (as described for silicate glasses) instead initially causes the conversion of BO_3 to BO_4 [31-33]. This increases the polymerisation of the boron network and leads to a minimum being observed in the thermal expansion coefficient at around 16 mol. % Na_2O (this is the opposite of what happens when modifiers are added to vitreous silica). This behaviour is normally referred to as the 'boron-anomaly'. The number of fully polymerised BO_4 tetrahedra increases up to a maximum value as a function of alkali concentration, further alkali additions then lead to formation of NBOs in the borate network Fig -16

What are Fertilizers , Types of Agricultural Fertilizers and Why Are They Necessary?

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.

The agricultural fertilizers have been categorized into following categories-

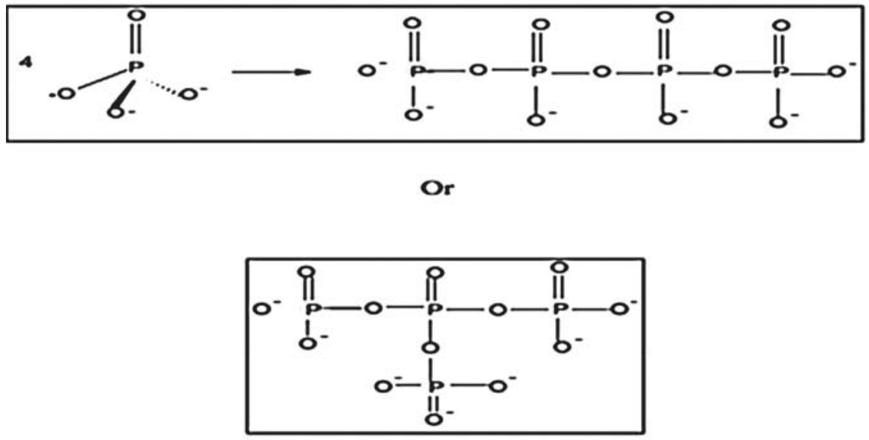

Fig. 13 : Polymerisation of the phosphate anion gives rise to various polyphosphate anions linked via oxygen bridges which may be branched or linear or a combination of the two.

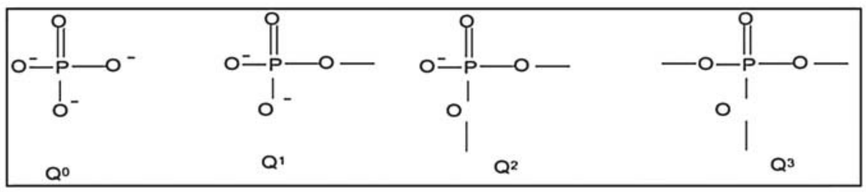

Fig. 14 : The foure types of Q1 species found in condensed phosphats, where I is the number of bridging oxygens with in a particular phosphate tetrahedron.

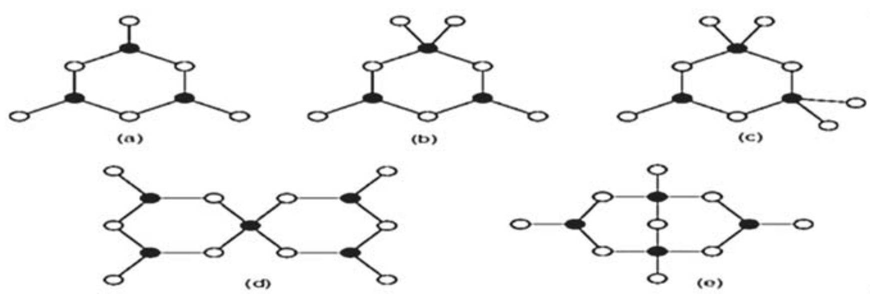

Fig. 15 : A selection of super structural units composing of boron (●) and bridging oxygens (0) a) boroxol ring B_3O_6 b) triborate B_3O_7 c) di-triborate B_3O_8 d) diborate, B_4O_9.

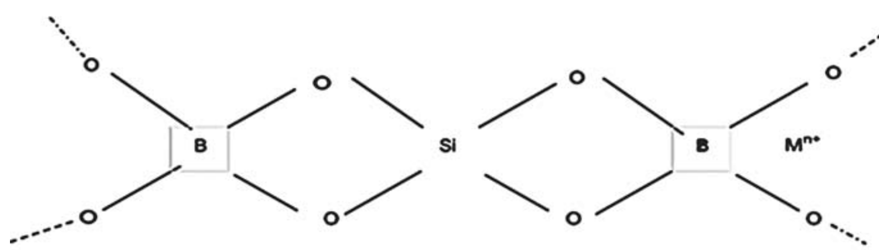

Fig. 16 : Borosilicate network

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.[34] . 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.

b) **Inorganic Agricultural Fertilizer:** Those fertilizers which are constituted by inorganic chemical substances that contain nutrient elements for the growth of crops 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 [35]. The inorganic fertilizers are of the following types:

Nitrogen Fertilizers: Nitrogen fertilizers contain nitrogen necessary for the development of crops. Nitrogen is the main constituent of chlorophyll that maintains a balance in the process of photosynthesis. It is also a part of amino acids in plants and constitutes protein. Nitrogen fertilizers improve the production and quality of agricultural products.

Phosphorus Fertilizer: The main nutrient in a phosphorus fertilizer is phosphorus. The efficiency of fertilizer depends upon effective phosphorus content, methods of fertilizing, properties of soil and crop strains. Phosphorus found in the protoplasm of the cell plays an important role in cell growth and proliferation. The phosphorus fertilizer is beneficial for the growth of roots of the plants crop strains. Phosphorus found in the protoplasm of the cell plays an important role in cell growth and proliferation. The phosphorus fertilizer is beneficial for the growth of roots of the plants.

Advantages of Chemical Inorganic Fertilizer

1. Readily available: as the most common form used, it is found everywhere and easy to transport, store, and apply.
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 results are shown 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 [36-37].
8. They are water-soluble and can easily dissolve in the soil. Hence, they are easily absorbed by the plants. They have a rapid effect on the crops. They increase the crop yield and provide enough food to feed the large population. They are predictable and reliable.

C) **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 [38.] 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 [39- 40].

d) **Micronutrient 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 56 impact on the yields as well [38, 40.] 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 [38, 39]. The concentrations in which these elements are needed range vividly from 5-100 ppm.

e) Various Types of Controlled Release Fertilizers

Only compounds from which plant roots can extractions 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[38-39, 41-43]. 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

Concept of Glass Fertilizer

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%.

Synthesis of Glass Fertilizer:

Glass Fertilizers can be synthesised from the ingredients like ammonium dihydrogen ortho phosphate , Magnesium oxide , Potassium di hydrogen phosphate (all AR/GR grade) as raw materials for macro elements and Borax , Ferric oxide , zinc oxide and molybdenum tri oxide in order to supply the microelements and mixing them vigorously followed by firing them at 750 ^{o}C for 30 mins under ambient condition in a Mufflefurnace after taking the batches in high alumina crucibles[44,45,46].

Advantages of the Controlled Release Glass Fertilizers

1) Decrease fertilizer application rate and save labour. Slow/controlled release fertilizer can produce the same yield with the rate 10-40% less than conventional fertilizer. Sometimes, only single application is required, which can reduce labour cost by 75%[39,47, 48].

2) Reduce environmental pollution caused by fertilizer. To increase fertilizer use efficiency with slow/ controlled release technology equals to the increase in fertilizer production. The current urea production in China is approximately 20 million tonnes, if coated with sulphur; the nitrogen use efficiency can be improved by 20%[38-39, 41-42, 47, 49].

3) Each element contained in controlled release fertilizer has an effect to give a very high increase in the fertility of the soil; each nutrient of CRF is not water-soluble yet easily soluble in weak acidic content in the soil or generated by plant roots[38-39, 41-42, 48.]

4) The CRF neutralize toxic acids and toxic elements in the soil and from other fertilizers[50].

5) Glass fertilizer does not contain toxics substances, since it does not have an acidic sulphate or chloric radical, glass fertilizer does not cause acidity to the soil, toxic gas or hydro sulphuric that can destroy plant roots on rice-fields. 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 water-soluble, it lies within the soil and continues providing necessary nutrients for the plants, meanwhile, other kinds of fertilizer are easily soluble in water, for example, super phosphate, and ammoniac sulphate can have immediate effects but are easily held by aluminum 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 important to the type of soil

originating from volcano ashes, wild soil and fields poor in P_2O_5[47].

6) 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. Mg and Ca are much in the soil but due to long-term weathering in acidic alum soil, the alkali effect is void, this frequently occur in tropical and subtropical zones [39,47].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. Fussed magnesium phosphate fertilizer can be seen as the most suitable one in tropical and subtropical zones poor in P_2O_5[51].

7) Controlled release glass fertilizer is very convenient for use and can be preserved for a long time because it absorbs less moisture, does not disintegrate even in damp weather or (below 500ºC).

Network Structure of the Glass Fertilizers

The model network structure of the glass fertilizers with different crops nutrients is drawn in Fig.17

Properties and Structure of Some Glassy Fertilizers

The different types of magnesium phosphate and their network- structure is shown in the Fig. 18 which is formed in the magnesium containing phosphate glass fertilizers.

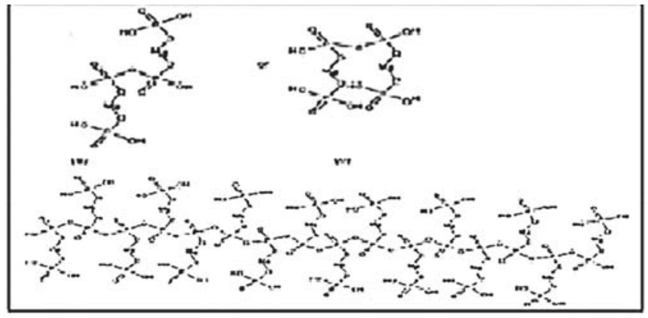

Fig. 18 : Polymerization steps showing metal tetra phosphate dimer of less stable (b) and more-stable (a) forms, plus the stable form of a multidimensional polymer (brickwall-like structure). Magnesium is shown as an example of a metal.

The Typical structure of a new slow-releasing iron fertilizer is shown in the Fig.19.

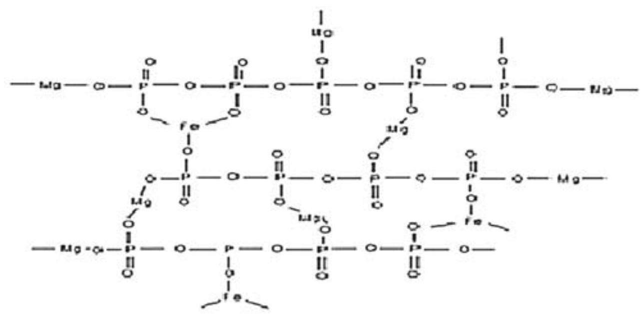

Fig. 19 : Typical structure of a new slow-releasing iron fertilizer (From: Chem. Eng. Journal, 2009).

Structures with Functional Activity

The schematic binding procedure of "glass fertilizers nutrients with the soil component and plant's root showing it's network structure is presented in the Fig.20

Leaching Studies of Glass

Glass is undergone to a corrosion process just like metal rust, 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.21. 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.21. 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

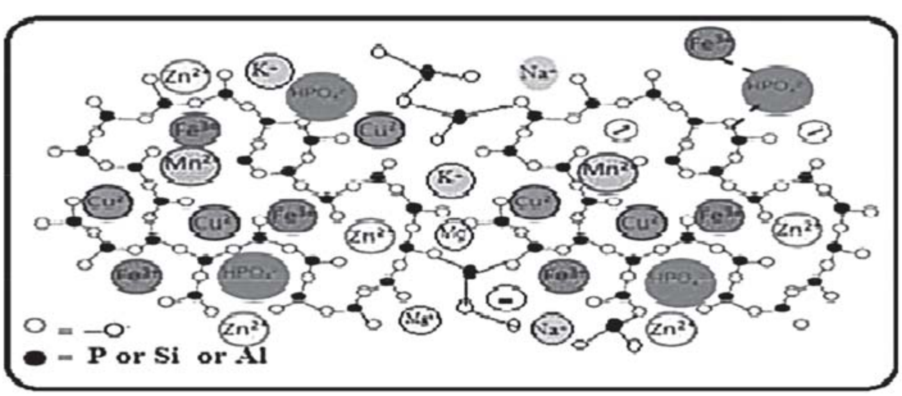

Fig. 17 : Network structure of the glass fertilizers with different corps nutrients.

to as ion exchange or alkali extraction (leaching). Anion 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. Fig.22

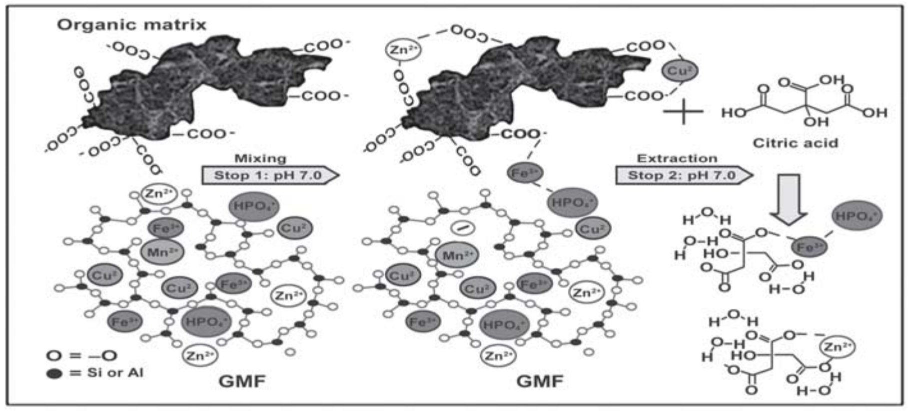

Fig. 20 : Schematic binding procedure of glass fertilizer nutrients with soil showing its network structure.

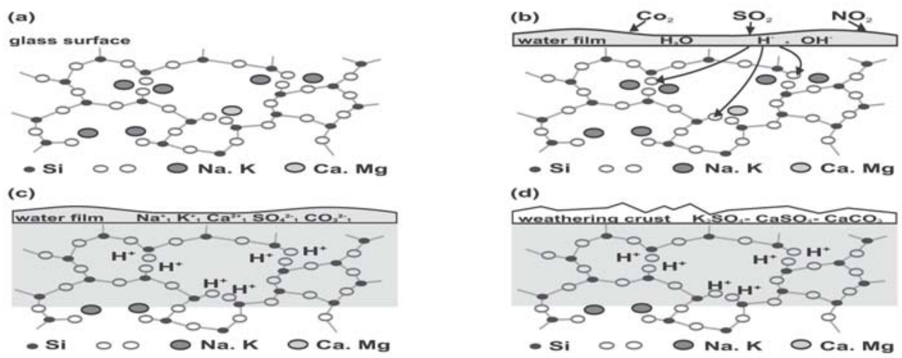

Fig. 21 : (a) Glass weathering process starting from a clean surface, (b) a formation of a water film, (c) a leached layer containing Hydrogen, (d) crystalline weathering products on the glass surface.

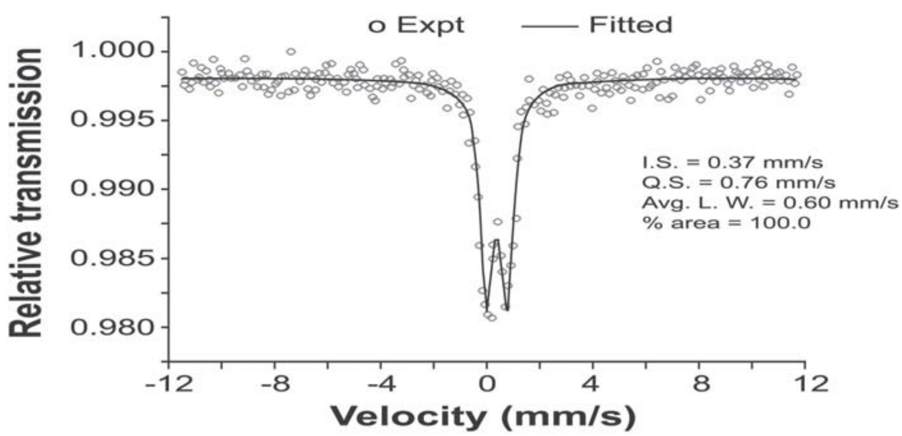

Fig. 22 : Mossbauer spectrum of one glass fertilizer containing 5 weight percent Fe_2O_3.

Application of Glass Fertilizer on the Paddy Field Through Pot Culture: application of glass fertilizers in pot culture experiment was also carried out to khariff rice during 2018- 2019 (Fig. 23). The study was carried out in collaboration with the Department of Soil Science and Agricultural Chemistry, Visva-Bharati, Sriniketan, West Bengal, India. The preliminarily study indicated a promising result of glass fertilizers.

Conclusion

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.24.

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. The Controlled Release Fertilizers delivers up to 10 weeks of healthy plant growth and colour, so one 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. 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 technically 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.

Fig. 23 : Photographs of pot experiment on paddy with a) and b) glass Fertilizer : c) conventional fertilizer and d) with out any type of fertilizer.

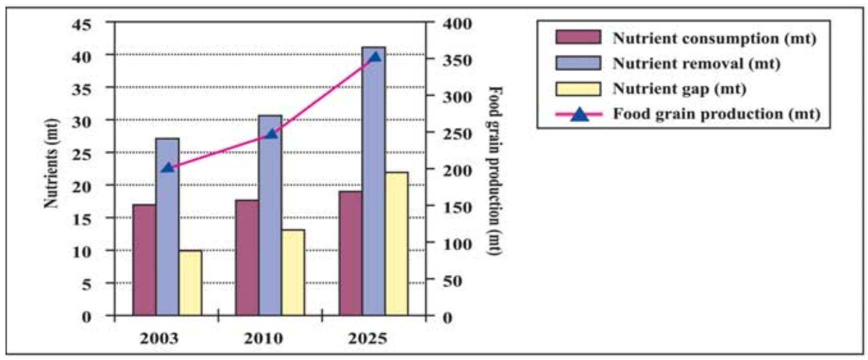

Fig. 24 : Projected food gain production in nutrient (N-P_2O_5-K_2O) consumption, removal and gap.

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