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Role of low solubility glasses as a source of plant nutrients- A review paper based on ‘ an effort to protect fertility of land(soil) against chemical fertilizer effects’

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INTRODUCTION

It is known to all of us that our motherland has been sicked because of over and over use of chemical fertilizers, insecticides and pesticides. Initially in decades of 50 when we started the use of chemical fertilizer but our Indian crops did not accept these chemical fertilizers but after few years, hybrid varieties of crops were developed in which 80% chemical fertilizers were being used. Because of this, it has been observed by researchers that our soil is facing deficiencies of one or more micronutrients**[1&2].** Our soil may be considered healthy only when there must be a balance of all micronutrient elements.

Our fruits, flowers, vegetables and crops are continuously degrading and they are also losing their taste due to climatic pollution, deficiency of micronutrients and over use of chemical fertilizers to enhance the production. By the effect of these agricultural chemicals, many diseases like- cancer, heart attack, blood pressure, Tuberculosis, paralysis and many skin diseases are become most common in human beings. If we really love our motherland, environment and body (health), we have to take some preventive measures to regain natural smell and taste in our fruits, flowers, vegetables and crops.

Although researchers and technologists are experienced about the pollution of soil, ground water contamination and non-fertility of soil/ land all around the world. Some efforts have been made in India and in other countries also towards the development of glass frits containing plant nutrients but the efforts have not yet yield a viable technology.

Without a full complement of these vital plants nutrients, we can not truly experience the full flavour of fresh vegetables, the over powering of fragrance of roses and the true essence aromatics of culinary kitchen herbs.

Finally glasses can offer an excellent opportunity because of its composition and solubility, the use of such products that will supply sufficient amounts of plant nutrients having a desired ionic mix over a long duration i.e. sustained release of the nutrients and every constituents of the glass should be used for the growth of the plants.

How are glasses used as fertilizers

It is well known that for better productivity of crops there is balance need water, mineral elements, carbon di oxide and solar light. Besides all these, plants require seventeen elements for completing their life cycle. Elements required in relatively in large quantities (like-N ,P,& K) are known as major plant nutrients where as those needed in smaller amounts are known as micronutrients. Boron, copper, iron, manganese, molybdenum, nickel, zinc, cobalt and chlorine are needed by the plants in micro-quantities. These nutrients are taken up by the plants as cations or anions from the soil or water in which they grow.

The function of each of the nutrient is very specific and cannot be met by any other nutrient. The action of micronutrients towards plants is similar to that of vitamins in human body. They are essential for the proper physiological functioning of plants and their deficiency causes many diseases that may lead to the death of the plant/ plant parts.

The requirements of different nutrients, however, changes with age of the plants. Further the rate of nutrient intake also varies at different periods during their life cycle. This implies that the plant nutrients should be available over the whole of their life cycle.

Advantages of glasses as plant nutrients over chemical fertilizers

A significant fraction of the conventional fertilizer applied to the soil is lost into the ground water along with percolating water because they are almost fully water soluble. These losses are excessive in sandy soils in comparison to that in clay soils. This not only causes loss of fertilizer nutrient applied but also pollutes both the soil and ground water. Secondly, the excess use of chemical fertilizers and their fast action due to good solubility in water are making our land/soil non-fertile. More and more use of chemical fertilizer for the improvement of production is the need of hour from the point of view of commercialization. Substitution of chemical fertilizer by slowly soluble glass enriched with plant nutrients that can fulfill the objective. Use of such glasses will be fulfilled our need over chemical fertilizers as follows-

(1)The solubility of glasses in water should be relatively small to prevent a quick release of nutrient elements. As a result glass nutrients will work more than one or two years in the agriculture fields.

(2)The glass nutrients are always non-toxic in nature even in high enough concentrations to all living beings.

(3)The glass nutrients are always economical over chemical fertilizers.

Role and chemistry of glasses as a plant nutrients

The chemistry of glasses as plant nutrients can be explained by considering the following factors **[3]**

[a] The structure of glass

[b]The ion exchange properties of glass

[c]The glass/solution interface and kinetics of hydrolysis

Considering the structure of glass when it will come in contact with water and soil, initially, dissolution of glass will start by leaching (via ion exchange) of some weak bonded species from the glass net-work **[4 & 5].**

Further, the mono valent cations are more easily diffused because of their mobility in comparison to doubly charged (divalent cations) and triply charged (trivalent cations) which are tightly bound with the glass net-work. In the similar way divalent cations and trivalent cations may also migrate out from the glass net-work which results slow leaching of glass nutrients. It may be due to the fact that increase in charge on cations decrease its mobility. Finally tetravalent cations will be leached out from the glass net-work **[6& 7].**

In the dissolution mechanism of glass net-work, it is important to outline the types of chemical reactions that may take place between glass net-work and water.

The release of micronutrients and other constituents of glass net-work in water may be due the following hydrolysis reactions **[8]**

$$\equiv Si - OR + H_2O = \equiv Si - OH + R^+ + OH^-$$

$$\equiv Si - O - Si\equiv + OH^- = \equiv Si - OH + \equiv Si - O^-$$

The non bridging oxygen formed in above reaction interact with further molecules of water producing a hydroxyl ion which is free to repeat chemical reaction over again.

$$\equiv Si - O^- + H_2O = \equiv Si - OH + OH^-$$

Several other hydrolysis reactions to understand dissolution mechanism of glass net-work has been suggested by researchers **[3,9 &10]** regarding the leaching behavior of mono valent, divalent, trivalent and tetravalent cations

With mono valent cations

$$ZnO.R_2OP_2O_5 + 2NH_4OH + 3H_2O = (NH_4)_2ZnO_2 + 2ROH + 2H_3PO_4$$

Where R is Li ,Na or K

With divalent cations

$$ZnO.RO.P_2O_5 + 2NH_4OH + 3H_2O = (NH_4)_2ZnO_2 + 2R(OH)_2 + 2H_3PO_4$$

Where R is Ca or Mg

With trivalent cations

$$ZnO.R_2O_3P_2O_5 + 2NH_4OH + 3H_2O = (NH_4)_2ZnO_2 + 2R(OH)_3 + 2H_3PO_4$$

Where R is B or trivalent cations

With tetravalent cations

$$ZnO.RO_2P_2O_5 + 2NH_4OH + 3H_2O = (NH_4)_2ZnO_2 + 2R(OH)_4 + 2H_3PO_4$$

Where R is Si or tetravalent cations

In the hydrolysis reaction, coulumbic force/bond strength with mono valent cations is the lowest. It increases when the mono valent cation is replaced by a divalent , trivalent and tetravalent cation. It is greater with a tetravalent cation **[11 &12].** Thus, release of these nutrients from glasses can graded as

Monovalent cation > Divalent cation> Trivalent cation > Tetravalent cation

In addition to this regarding the hydrolysis reaction and mechanism of glasses, initially weak bonds of the glass net-work are broken which may further lead to the ultimate destruction of completely glass net-work with the slow leaching of constituents. This rate of hydrolysis is characteristic of the particular cations present in the glass net-work and the water and soil conditions employed. The following may be main factors/ aspects influencing the rate of hydrolysis and leachability from the glass net-work.

(i)The nature and size of the cation present in glass net-work

The bond between cation and non- bridging oxygen changes with the nature and size of cation. As the columbic force between non-bridging oxygen and cation increases, the bond strength is expected to increase resulting in a greater chemical barrier **[13]** and ultimately the quantity of a particular micronutrient in the leachate decreases as the bond strength between non-bridging oxygen and cation increases.

(ii)The oxidation of the micronutrient ions

With increasing ionic radii of alkali ions or with increasing concentration of alkali ions in the same series of glasses, redox equilibria shifts more towards the oxidized state **[14,15 &16].** The leach ability of glasses increases with increasing the oxidized state of the micronutrient ions. Thus the leach ability of micronutrient ion increases with the higher valence states of micronutrient ion by replacing Li^+ by Na^+ and Na^+ by K^+ ions. When K^+ ions were replaced by Ca^{2+} or B^{3+} or Si^{4+} ions, micronutrient ion showed a reduced state in the sequence Ca <B <Si and the leachability of micronutrient ions decrease in the order Ca <B <Si.

(iii)The pH of the solution [water + soil]

As the pH of the [water + soil] increases the hydroxyl ions which are aggressive in nature than H^+ brake the bonds of glass net-work and cause the increase in the concentration of micronutrients in the leachate **[17,18&19].**

(iv)The time of the leaching constituents

The quantity of the micronutrients leached increases with increase in the leaching time**[20]** and rate of leaching of constitutuents depends on the conditions employed

(v)The atmospheric temperature at which leaching of constituents occur

Leaching of micronutrients from the glass frits increases with increase in temperature because ions gain the available higher activation energy at enhanced temperature **[3].**

(vi)The particle size of the powder of the micronutrients/glass frits

The concentrations of micronutrients leached decrease with increasing particle size of the glass powder because of the fact that surface area is an important factor related to the leachability of ions and amount of various constituents leached from the glass net-work under the certain conditions are proportional to the surface area exposed**[3].** With decreasing the particle size of glass powder, the specific surface area increases and hence increase in leach ability of ions from the glass net-work.

Agricultural aspect of plant nutrients

It is necessary to understand specific nature of basic plant nutrients which play an important role in the physiological functioning of plants. The role and function of each micronutrient, whose deficiency impact and its remedial measures with respect to chemical fertilizers and glass nutrients may be definitely a part of studied. The following is the step-wise study of each macro and micro nutrient element from agricultural point of view.

The macronutrients Nitrogen, Phosphorous and potassium wash out of the soil over time requiring soil enrichment with chemical fertilizer to restore the balance and help plants attain their best growth potential. Different plants have different preferences regarding optimum levels of these nutrients particularly in regards to Nitrogen. For example, too much Nitrogen will stunt tomato production while Spinach and Broccoli feed heavily on this nutrient and require higher level to grow well.

Calcium, Magnesium and Sulphur are rarely low enough to cause concern but if the soil is missing these key ingredients, they can also be added as soil amendments. The micronutrients are required in such minute amounts for the plant growth and function. The lacking of trace elements may be particularly a problem. The best way to ensure a good supply of these plant nutrients is to feed our soil.

Nitrogen

Plants need more nitrogen than the other micronutrients. Nitrogen is responsible for the rapid growth of plants, seed and fruits production. Sufficient nitrogen gives a strong green colour to plants. Its deficiency can cause leaf yellowing (especially towards the bottom of plant) as well as slow or stunted growth.

Nitrogen builds proteins and the chlorophyll molecule and transfer energy within plant cells. Legumes possess nitrogen fixing bacteria which capture atmospheric nitrogen and make it available to plants root. Plants lacking nitrogen generally recover well on application of nitrogen fertilizers.

Potassium

Potassium increases resistance to diseases in drought conditions and produces plumps, firm seed and fruits. Plants need it for photosynthesis making plant enzymes and regulating water use. A lack of potassium results in yellow leaf edges, small, unevenly ripe fruits and grains and low yield. Potassium is supplied to plants by soil minerals, organic materials and fertilizers.

Calcium

Plants have rigid cell walls which give strength and structure to hold the plant up as it grows. Calcium is important in forming cell walls, cell membranes and regulating the flow of materials through the membranes. Lack of calcium causes mishappen or distorted new leaves and new shoots may die. Calcium is supplied to the plant roots on application of fertilizers like- gypsum, calcium nitrate and super phosphate.

Magnesium

Magnesium forms the central part of the chlorophyll molecule, essential for photosynthesis (which is making sugar from carbon di oxide and water in the presence of light) and growth. Plants need it oil and fat production. Formation of DNA, RNA, Sugar and starch and phosphate transport throughout plant tissues.

Sign of magnesium deficiency are leaves that have green veins with yellow areas between the veins. Leaves eventually turn red and spots of dying leaf tissue. Too much rain can wash magnesium from the soil. Supplement with foliar sprays or magnesium containing fertilizers (dolomitic limestone).

Phosphorous

Of tremendous importance of plant growth, phosphorous stimulates blooming, induces good bud set and seed formation and enhances cold hardiness. Inside the plant, phosphorous is essential for energy transfer, protein building and all the vital metabolic processes that occur in plants. Some sign of phosphorous deficiency are thick, leathery dark colour green leaves, leaves that have purplish-red edges or tips and poor flowering production. Di ammonium phosphate is supplied for its fulfilment.

Sulphur

Plants need sulphur to make vitamin A and oils including the compounds that give distinctive odours as garlic, onions, and mustard. Plants also need sulphur for the correct action of nitrogen in their growth. Sulphur helps in seed formation, root growth and development of cold tolerance. Its deficiency can create yellow leaves beginning at top of plants and working its way down the stem with stunted slow maturing growth. Potassium sulphate, ammonium sulphate and gypsum are supplied to renew the sulphur content.

Boron

Boron helps in the use of nutrients and regulates other nutrients. It aids production of sugar and carbohydrates. It is essential for seed and fruits development. Its sources are organic matters and borax solution as spray.

Copper

Copper is important for reproductive growth of plants. It aids in root metabolism and helps in the utilization of proteins. For its deficiency application of copper sulphate to the soil incorporation and in standing crops lime should be mixed and used as foliar spray.

Iron

Iron is essential for the formation of chlorophyll. Iron sulphate and iron chelates can supply for its fulfillment.

Maganese

It functions with enzymes system involved in breakdown of carbohydrates and nitrogen metabolism. Soil is the source of manganese**.**

Zinc

Zinc is essential for the transformation of carbohydrates. It regulates consumption of sugar. Zinc is the part of enzyme system which regulates growth of the plant. Its main sources are soil, zinc oxide, zinc sulphate and zinc chelates.

Molybdenum

Molybdenum helps in the use of nitrogen. Due to its deficiency plants remain stunted, older leaves show yellow spots, marginal tissues of leaves die and finally leaves curve inside. Sodium molybdate and ammonium molybdate is used for its fulfilments.

Chlorine

Tip portion of leaves wilt which later on, turn red coloured and wither away. Chlorine also aids in plant metabolism. Ammonium chloride may be used to overcome its deficiency problem.

Sodium

Leaves of the plants turn to almond colour and tissue start degrading. To overcome this deficiency problem application of foliar spray of sodium sulphate is beneficial.

Cobalt and Vanadium

No specific symptom is observed due to deficiency of these nutrients in plants but for overcoming the deficiency problem application of cobalt sulphate and foliar spray of vanadium tri chloride sufficient to meet respective requirements.

In addition to above it is also mandatory to understand the another important aspect during the development of glass frits. The micronutrients and their critical range which are absorbed or intake directly by the plants of crops in the form of cations or anions. This will help us to maintain a variation in composition of glass matrix for the proper utilization in our agriculture fields particularly for eastern U.P and some district of Bihar because as we are aware that each crop has its own unique requirement of these nutrients in its life cycle. Table 1 shows critical range of some micronutrients for different crops.

Micronutrients	Various Crops	Critical range(ppm)
Boron	Wheat/Barley/ Maize	0.1- 0.3
	Other Crops	0.1- 0.5
Copper	Wheat	2.0- 3.0
	Rice	3.0- 7.0
	Vegetables	8.0- 20.0
	Legumes	9.0- 18.0
Zinc	Wheat	1.0- 3.0
	Rice	3.0- 5.0
Maganese	wheat	10.0- 15.0
	Rice	10.0- 15.0
	Potato	7.0- 40.0
Iron	wheat/ Maize	0.5- 5.0
	Rice	0.5- 4.5
	Legumes	0.5- 5.0
Molybdenum	Maize	0.5- 1.3
	Rice	0.5- 1.6
	Wheat	0.5- 1.0
	Sugarcane	0.5- 1.5

CONCLUSIONS

In view of significant role of macro and micro nutrients in maintaining soil fertility and increasing food production to feed the growing population of India. In the present paper to fulfil all our above said need and its related aspects, we are preparing fertilizer compounds having a glass matrix. As we are aware that a fertilizer compounds having a glass matrix comprise among the forming oxides of the glass matrix P_2O_5 as partial and full replacement of silica, among the modifier oxides of the glass matrix K_2O as partial and full replacement of soda and one or more trace elements. This change of the K_2O / P_2O_5 ratio will effect to control the chemical durability and physical properties such as density and hardness. In this way plants will have specific nutrientional requirements that must be satisfied to achieve their optimum state of health and finally our productivity will be enhanced and better. Ultimately, glass frits may be good substitution of chemical fertilizers in cheaper way.

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