

Glassy Environmentally Friendly Fertilizers of Prolonged Action

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Abstract

New R&D international project aimed at elaboration of novel materials and technology to restore territories damaged by intensive industrial exploitation has been presented. The project is based on results of development and application of glassy ecologically friendly fertilizers in agriculture and results of experiments on restoration of soil polluted by petroleum. It is proposed to elaborate a mineral fertilizer made from porous phosphate glass granules saturated by bacteria strains. The fertilizer is intended for restoration of territories of former coal quarries and mines.

INTRODUCTION

This paper is a short presentation of a new international R&D project aimed principally at creating novel material and technology to restore territories damaged by intensive industrial exploitation.

Industrial impacts to the environment may cause partial or total changes in the conditions of natural agrobiosystems that entail huge damages to the environment. Thus, the problem of restoration of damaged ecosystems is of special importance.

It is a fact that the coal production much decreased in European Union because it needed governmental subsidies to be competitive in the world market. Hard coal production in Europe is expected to fall down more than 2 times during two decades. This necessitates the restoration of the territories of former coal quarries and mines.

Unfortunately, conventional technologies for land cultivation have a series of basic disadvantages connected with the use of applied fertilizers that have polycrystalline structure and cannot be used to solve the ecological problems. In particular, these types of fertilizers are quickly washed out and weathered that leads to environmental pollution including surface and underground water areas. Besides, the composition of these fertilizers does not guarantee appropriate plant nutrition because the soil erosion exceeds the rate of biochemical accumulation of humus¹.

For these reasons, we put forward the idea to combine the knowledge on structure, composition, and properties of phosphate glasses accumulated in S.I. Vavilov State Optical Institute with technology of manufacturing and application of glassy environmentally friendly fertilizer AVA™ commercially produced by JSC AGROVIT and the experimental results on soil restoration by means of glassy granules saturated with bacteria strains.

The main goals of the proposed investigation are as follows:

- Design of novel glassy materials and technology for production of environmentally friendly glass fertilizers of prolonged action. The fertilizers will conform to bacteria strains stimulating soil restoration.
- Elaboration of novel technology of biological and microbiological restoration of agrobiocenosis on the territories of former coal quarries and mines, and selection of optimum plant associations.

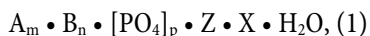
EXPERIMENTAL RESULTS AND DISCUSSION

To avoid the above-mentioned disadvantages of polycrystalline mineral fertilizers, we elaborated an essentially new type of combined glassy granular fertilizers of prolonged action².

The fertilizers are characterized by a whole set of controlled parameters and advantages unattainable in traditional land tenure:

- Variable rate of output of necessary nutritious substances in a water-soluble phase depending on humidity, temperature, season, amount of precipitation and soils type.
- Increased duration of the fertilizer action in a soil up to several years.
- Increased (not less than 90 %) ratio of utilizing useful substances by plants.
- Usage of the fertilizer as an active carrier of immobilized active micro flora for microbiological and biological restoration of damaged agrobiological systems.

The general formula of bioactive phosphate glasses is shown in Eq.1:



Where:

A_m is the single valence cations of the First Group;

B_n is the two valence cations of the Second Group;

Z is the doping microelements (Zn, Mn, Fe, Cu, Co, Ni, Mo, V, Se, Ag);

X is the dopants (SiO_2 , B_2O_3 , Al_2O_3 , V_2O_5 , SO_3 , SeO_3) to vary dissolution kinetics.

The base composition of AVA glass fertilizer adapted to soil, climatic, and agricultural conditions of North Western Russia is shown in Table 1. The AVA glass fertilizer constitutes glass granules of 3-5 mm diameter with fire polished surfaces.

The principal difference of AVA fertilizer from conventional polycrystalline mineral fertilizer lies in the mechanism of its solution in soil water and its uptake by plants as illustrated in figure 1.

As one can see from the figure 1 showing the model developed by Prof. G.Karapetyan et al., various layers of a glassy granule are being dissolved under the influence of different chemical and physical chemical processes including ion exchange, hydrolytic destruction of polyanion network, electrolytic dissociation of diffusive zone followed by growth of biomass and nutrient solution in it³.

Table 1: Base Composition of AVA™ Glass Fertilizer

Oxides (weight %)

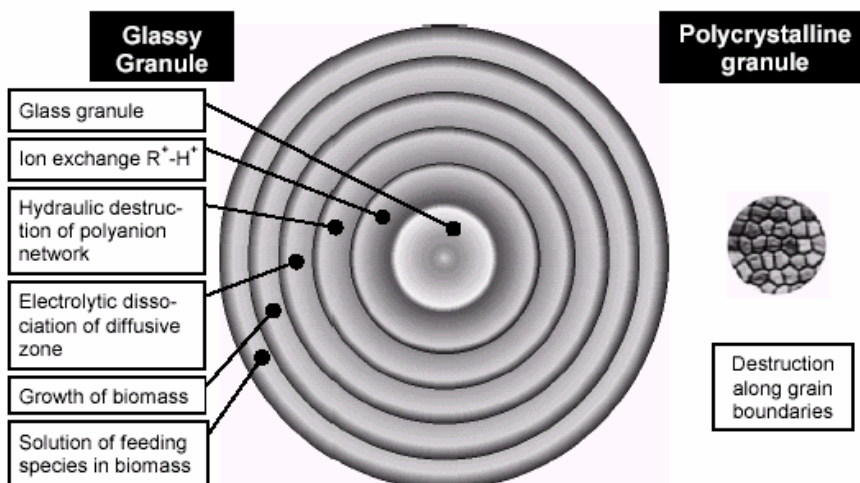
P ₂ O ₅	K ₂ O	CaO	MgO	SiO ₂	B ₂ O ₃	Fe ₂ O ₃
57.5	20	12.5	5.5	2.0	1.5	1.0

Elements (weight %)

O	P	K	Ca	Mg	Si	B	Fe
47.5	31.4	13.7	4.4	1.2	0.5	0.3	1.0

Content of useful components (weight %) (without oxygen)

P	K	Ca	Mg	Si	B	Fe
59.8	26.2	8.4	2.2	0.9	0.6	1.9

**Figure 1: Glassy granular fertilizer**

Hence, special physical-chemical properties of the granules ensure their very low dissolution in the soil surface with subsequent release of chemical species for plant nutrition. On the contrary, a polycrystalline granule built from crystalline grains is dissolved along grain boundaries. The main advantages of these glass granules will be analyzed below.

Firstly, they contain only species needed for plants nutrition as shown in Table 1. Their compositions may be easily modified for any plant, soil, and climatic conditions. As field tests demonstrated, the fertilizer increased the crop capacity from 10 to 50% being applied in soil one time every 3 years. It should be emphasized that it does not contain any nitrogen.

It is a fact that the problem of excessive presence of nitrogen in the form of nitrates and nitrites is declared as an important problem for modern food production saturated with lot of nitrogen from conventional mineral fertilizers. Its consumption by people with food and its increased concentration in soil and natural water is a separate serious problem.

Experiments showed that replacement of nitrogen containing crystalline fertilizers by nitrogen free glassy fertilizers led to the reduction of harmful influence of nitrates and nitrites onto the environment while plants managed to receive the needed amount of nitrogen because AVA glassy fertilizers stimulated vital activity of soil micro organisms bonding nitrogen from air into forms suitable for plants nutrition.

The second advantage of glassy granular fertilizer is its variable kinetics of dissolution strongly depending on temperature that is confirmed by figure 2 showing the weight loss kinetics of a granule at day-and-night variation of temperature typical for North Western Russia in July.

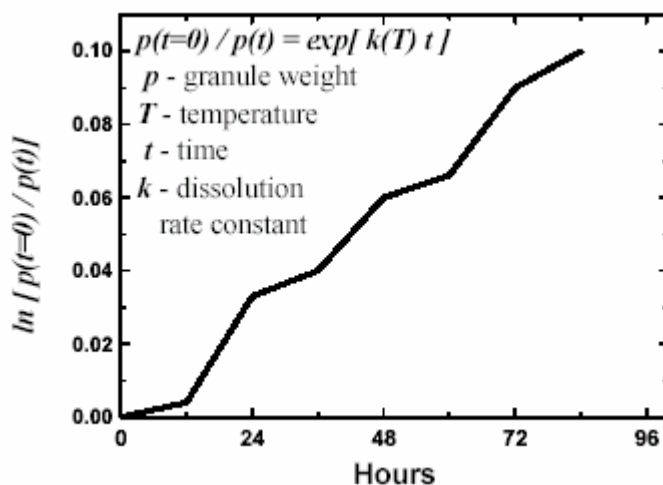


Figure 2: Influence of daily temperature variation on granule dissolution

Figure 3 shows influence of season temperature on dissolution rate constant that significantly increases in summer months when plants especially have high nutrient requirements.

Recently, we made the next step and modified the glassy fertilizer to solve ecological problem caused by petroleum pollution of soil and underground waters because of breaking down of petroleum tubes and other industrial catastrophes. Technology to manufacture foamed phosphate glasses of 0.8 g/cm^3 density and pores of $0.01 \div 2 \text{ mm}$ diameter was developed.

To eliminate thin petroleum layer on water surface before the pollutant and water are mixed and form emulsion, JSC AGROVIT developed a novel biopreparation named AVALON™.

It consists of an association of bacteria strains immobilized on a porous sorbent, that is foamed glassy granular fertilizer AVA. The foamed phosphate glass ensures optimum conditions for living of bacteria during a long time. Porous water soluble sorbent works as a carrier of bacteria on water surface and a source of their feeding simultaneously^{4,5}.

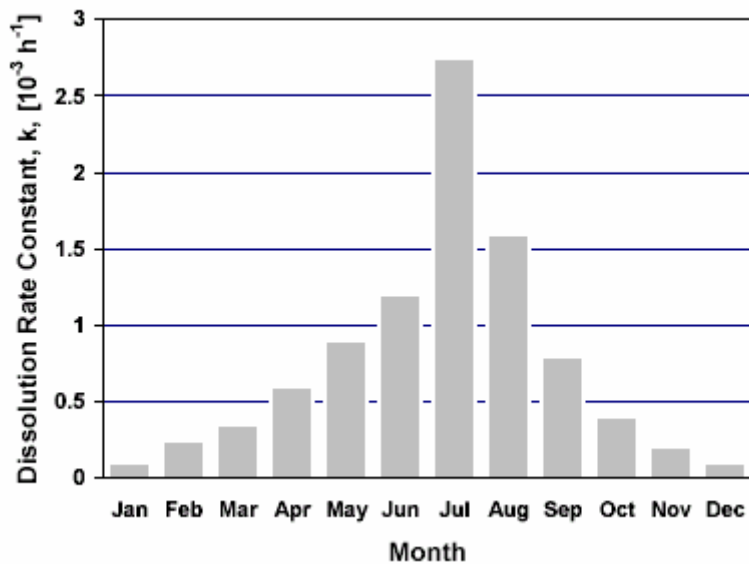


Figure 3: Influence of season temperature variation on granule dissolution

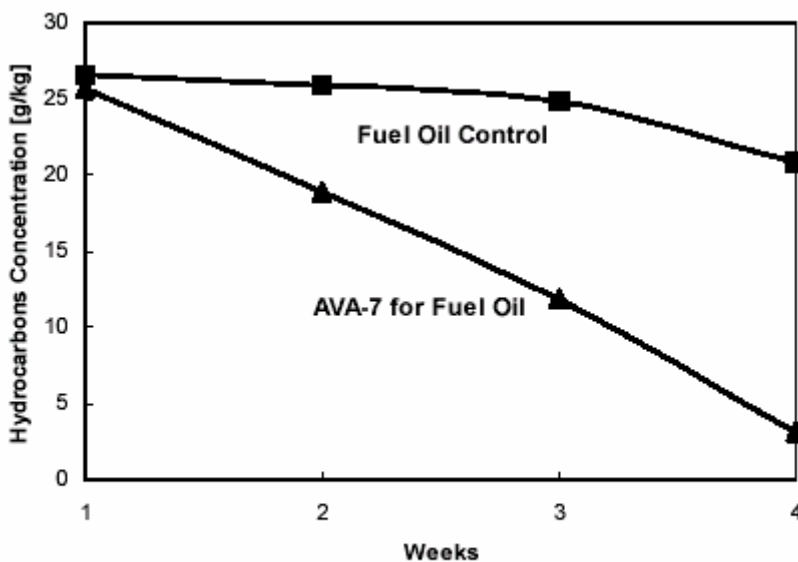


Figure 4: AVALON oil destruction

The permanent freshening of glass surface is an advantage of AVALON as compared to the well-known biopreparations based on the use of biologically passive bacteria carriers. *Serratia marcescens* PL-1, *Pseudomonas fluorescens* biovar II 10-1, *Acidovorax delafieldii* 3-1 were used in laboratory and field-testing^{6,7}.

Figure 4 shows the purification of water polluted by oil in the case of 2 modifications of phosphate glass sorbents compared with a very long process of natural purification.

PLANNED ACTIVITY

1. Study of relationships between composition, structure, and kinetics of dissolution of phosphate glasses in water by means of a set of structure sensitive spectral optical measurements. Formulation of the principles for choosing glasses with given dissolution kinetics.
2. Investigation of soils samples from damaged areas. Accumulation of analytical data about composition of soil micro flora and optimization of compositions of mineral glassy fertilizers on the basis of soil analysis.
3. Physical and physical chemical studies of micro inhomogeneous structure and kinetics of phase decomposition of phosphate glasses as function of their composition. Elaboration of procedure to form micro porous glass granules.
4. Optimization of compositions of porous glass granules for immobilizing microbiological strains. Selection of the best preparation forms, development of technology for their formation and application. Determination of the optimum assortment of species for biological restoration.
5. Development of combined biotechnology for soils restoration that includes usage of a set of glassy fertilizers and biopreparations on the basis of strains destroying xenobiotics, determination and application of specially selected plant associations, working out an assortment of the most labile kinds of plants for various kinds of pollution.

To achieve the Project goal, it is necessary

- to determine relationships between composition, structure, physical chemical properties, and biological activity of glass fertilizers,
- to design special bacteria strains for the territories to be restored,
- to develop the experimental industrial technology to synthesize new kinds of glass fertilizers – bacteria carriers – taking into account composition of soils under restoration, climatic peculiarities of the region, micro biological requirements, and plant growers' recommendations related to cultures ensuring fast land restoration,
- to carry out laboratory tests and field trials.

To investigate the problem comprehensively, it is planned to combine research efforts of physicists, chemists, and technologists working with S.I.Vavilov State Optical Institute and JSC AGROVIT with activity of biologists, microbiologists, and botanists working with All-Russia Institute for Plant Growing, Botanical Institute of Russian Academy of Science, All-Russia Institute for Plant Protection, etc.

EXPECTED RESULTS AND THEIR POSSIBLE APPLICATION

The performance of R&D Project under the financial support by the International Science and Technology Center will make it possible to achieve the following results:

Scientific results

Acquisition of data on the influence of composition and structure of porous glass fertilizers and bacteria strains on the processes of restoration of soil and plants on territories of former coal quarries and mines.

Technical results

- composition and structure of porous glass granules, bacteria strains, optimized for restoration of the territory chosen for experiments,
- new biopreparations for restoration of soils introduced in granules made from porous glass,
- new catalysts for permanent restoration of porous glass granules surface with bacteria strains,
- technology for manufacturing porous glass fertilizer with bacteria strains.

Commercial results

Novel product in high-tech market, that is the porous glass fertilizer saturated with bacteria strains and intended for restoration of soils and plants on territories of former coal quarries and mines.

CONCLUSION

The planned Project is based on our results related to the elaboration of granular glassy environmentally friendly fertilizers for agricultural application and experiments on restoration of soils by means of porous glass granules saturated with special bacteria strains.

The authors invite commercial and public institutions of EU countries, US, Japan, Korea, Norway to take part in the R&D Project “Glassy Environmentally Friendly Fertilizers of Prolonged Action” aimed at elaboration of new materials and technology for the restoration of soils damaged by intensive industrial activities and technical catastrophes.

Acknowledgement

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