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CHEMICAL TECHNOLOGY:
SCIENCE, ECONOMY AND PRODUCTION

ЗБІРНИК НАУКОВИХ ПРАЦЬ

VI Міжнародної науково-практичної конференції

ХІМІЧНА ТЕХНОЛОГІЯ:
НАУКА, ЕКОНОМІКА ТА ВИРОБНИЦТВО

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Збірник наукових праць VI Міжнародної науково-практичної конференції «Хімічна технологія: наука, економіка та виробництво», м. Шостка, 23 - 25 листопада 2022 року. – Суми : Сумський державний університет, 2022. – 267 с.
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Збірник містить наукові праці учасників VI Міжнародної науково-практичної конференції «Хімічна технологія: наука, економіка та виробництво», що складаються з узагальнених матеріалів науково-дослідних робіт науковців різних галузей виробництв та наукових закладів України.

У збірнику висвітлюються актуальні питання спеціальної хімічної технології і виробництва боєприпасів, утилізації відходів виробництв різних галузей, енергозбереження, моделювання технологічних процесів, соціально-економічні аспекти виробництва та природокористування в умовах війни.

Збірник корисний робітникам хімічної промисловості, науковим співробітникам, аспірантам і студентам спеціальностей хіміко-технологічного та соціально-економічного профілів, фахівцям інформаційних технологій виробництва.

Наукові праці учасників конференції подаються в авторській редакції.

ECOLOGICAL PROPERTIES OF PHOSPHOGYPSUM AND ITS PRODUCTS: BIOGEOSYSTEM TECHNIQUE FOR MANAGEMENT

Y.Y. Chernysh[1], V.S. Chubur[1], N. Haneklaus[3,4], H. Roubik[2]
[1] Sumy State University, Sumy, Ukraine
[2] Czech University of Life Sciences Prague, Prague, Czech Republic
[3]Universität für Weiterbildung Krems, Krems an der Donau, Austria
[4]Technische Universität Bergakademie Freiberg, Freiberg, Germany
e.chernish@ssu.edu.ua

Introduction. In dried form, phosphogypsum is a fine powder, which becomes loose and prone to lump formation, and in the case of long-term storage in a fixed layer, it becomes caked. Hundreds of millions of tons of industrial waste phosphogypsum are available in five regions of Ukraine: Sumy, Kharkiv, Dnepropetrovsk, Rivne, and Cherkassy. Up to 10 million tons of phosphogypsum are produced annually. Certain problems are associated with the use of phosphogypsum, which are becoming increasingly important for reasons presented in Fig. 1.

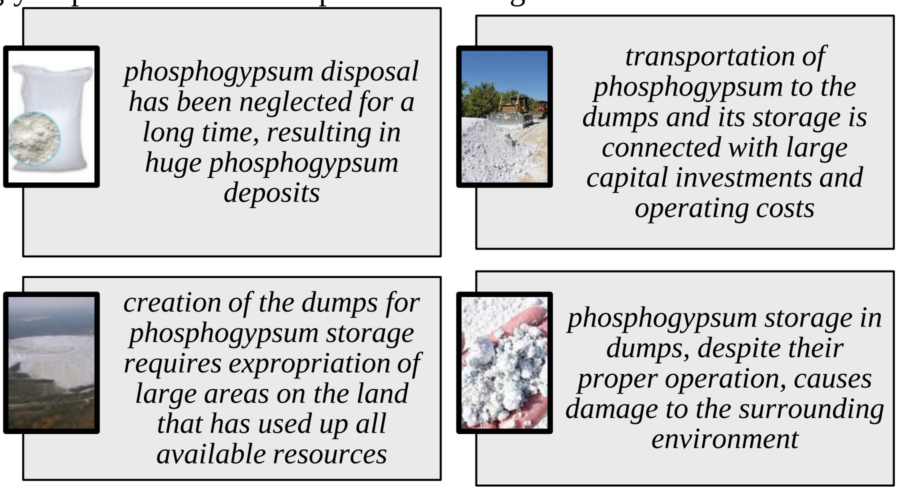

Fig.1 Challenges in the sphere of phosphogypsum management

The main source of environmental pollution in the areas of mineral fertilizer production (in Ukraine, these are Armyansk, Sumy, and Rivne) is phosphogypsum. The sulfuric acid method of opening the apatite concentrate produces 4,3-5,8 tons of phosphogypsum per 1 ton of H_3PO_4, depending on the raw materials and the adopted technology. At dry storage of phosphogypsum (without preliminary neutralization), about 10 g of fluorine per 1 ton of phosphogypsum is released into the gas phase, and approximately 10% of fluorine is washed out by atmospheric precipitation. Phosphogypsum should be stored in specially equipped storages isolated from water bodies. Phosphogypsum has to be neutralized with lime milk before it is placed in the storage facility [1].

Monitoring of active phosphogypsum dumps. The active dump site is located behind the Tokari village in the Sumy region at a distance of 800 (direct measurements) - 1 300 m (along the road) from the residential area and continues to receive new loads of dihydrate phosphogypsum produced by the enterprise "Sumykhimprom". Since 1972 the dumps of phosphogypsum have been organized around the city of Sumy, and today they amount to approximately 15 million tons of waste. The area of the dump is 492 m^2, with a sanitary protection zone of 637 m^2, and the perimeter of the active dump is about 1,900 m.

A significant factor affecting the chemical elements in the soil is the presence of acidic water-soluble and, therefore, mobile fulvic acids, which cause the processes of intense washout from the soil profile of many trace elements - Fe, Mn, Zn, Cd, Pb, Sr, V, including the heavy metals. The content of radioactive elements, rare earth elements, cadmium, and other heavy metals is directly dependent on their content in phosphate raw materials. Thus, phosphates of magmatic origin (Kola and South African apatites) contain more rare earth elements than phosphates of sedimentary origin (Morocco, Florida, Senegal, etc.) and less cadmium. Fractional composition of phosphogypsum produced by the enterprise "Sumykhimprom" is presented in Table 1.

Table 1. Fractional composition of phosphogypsum produced by enterprise "Sumykhimprom" (according to data from [1])

Sieve	Partial residue, gr.	Partial residue, %	Total residue, %
2.5	0	0	0
1.25	2	0.2	0.2
0.63	58	5.8	6.0
0.315	92	9.2	15.2
0.16	88	8.8	24.0
Passed the sieve 0.16	760	76	-

On a microscopic level, the main mass is represented by finely crystalline aggregates, which have sizes from 0.025 to 0.4 mm, with the size of individual crystals of about 0.003-0.005 mm.

To assess the properties of phosphogypsum as a substrate for plant growth and to find out whether phosphogypsum has no negative impact on plants, the areas where phosphogypsum is stored for an extended period were examined. Fig. 2 shows deposits maps of "Sumykhimprom" enterprise.

Fig. 2 Satellite images of the phosphogypsum dump in years monitored with Google Earth Pro

The waste material goes to the sludge collector, lowering the amount of fluid, dries up and is disposed into the dumps. During prolonged storage, the surface is caked, and a thin crust is formed on the surface, possibly inhibiting seeds' germination and sprouting formation. In some places, shallow cracks grow up to 10% of their area. In deep and wide cracks (about 30 cm deep and approximately 100 cm wide), patches of algae of yellowish green, yellow-brown, and sometimes black colour were observed. An example of plant settlement in surface sags was monitored for coltsfoot. The projective coverage of Coltsfoot in such areas reached 60% with the formation of clumps up to 10 m in size. In existing large cracks, rather large coltsfoot plants are often found, forming clumps of 2 m2 in area with a height of 35 cm.

Therefore, it should be noted that the genesis of phosphogypsum significantly affects the possibilities of its use and the ecological impact on the components of the environment. In addition to calcium, phosphogypsum also contains phosphorus (1-1.4%), sulfur (up to 38%), silicon (0.26%) and zinc (0.03%) necessary for the full development of plants, as shown in Fig. 3.

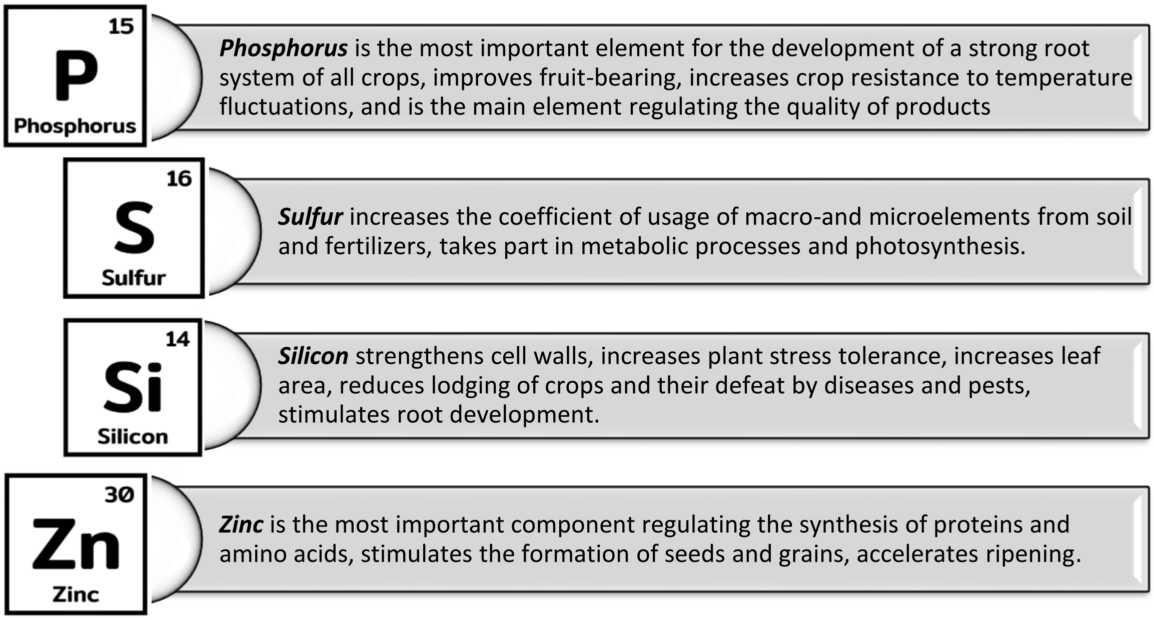

Fig. 3 Beneficial elements in the composition of phosphogypsum

In general, phosphogypsum does not suppress plant growth. During storage, wet phosphogypsum can be covered with algae, while dry phosphogypsum overgrowths with higher plants. All plants appearing on the storage maps are introduced from the surrounding phytocenoses, as the slopes of the dumps were never deliberately sown or planted.

Biogeosystem technique for phosphogypsum management. Fig. 4 shows the directions of the application of neutralized phosphogypsum to achieve a positive ecological effect. Improving technical solutions and technologies for the utilization of phosphogypsum in soil is required to solve the problem of developing environment-like technologies (the concept of bionics). Soil degradation is occurring and it is necessary to search for fundamentally new possibilities for soil management, which is a critical problem in the world today. It is important to synthesize the necessary compounds directly within the soil and manage the material composition of the soil solution. However, in addition to recognizing the relevance of the soil design problem, design tools are also needed.

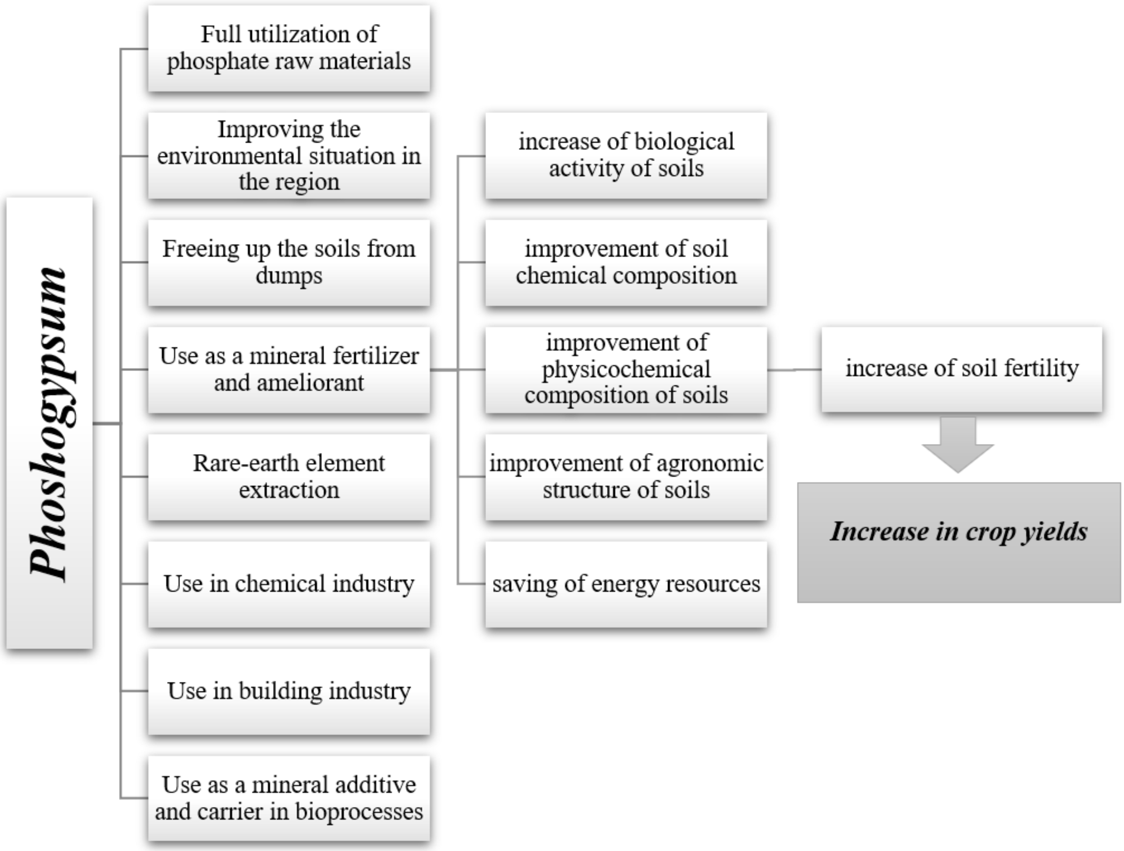

Fig. 4 Scope of phosphogypsum application

By preventing excessive soil humidity, the unproductive geochemical runoff of material from the soil can be drastically reduced, and the negative consequences of the hydromorphic soil regime, including the destruction of organic matter and the reduction of sulfates to sulfides, can be eliminated. Regulation of soil moisture within a favorable range for plants also strengthens the effect of the geochemical barrier, the "soil-rhizosphere", since the solubility of compounds harmful to trophic chains is thereby controlled. Moreover, associated and complex ions are formed in soil solution, and the possibility of strengthening the action of geochemical barriers based on this has been shown in the example of Pb, Cd and Sr [2].

It should also be noted that instead of washing saline soils with Na + and -, these ions should be selectively extracted from the soil without affecting the other macro-element ions. All that is a major part of the scientific and technical field called biogeosystems engineering. These are technical solutions and technologies that have no direct analogues in nature to manage the biogeochemical cycle of substances in the gaseous, liquid, and solid phases. Biogeosystem engineering focuses on the environmentally safe recycling of substances in soils, the increase of resources and food, and on consistent solutions to production and environmental problems of the noosphere in a unified technological cycle following the principle of naturalness. The priority task is to ensure the quality of the environment for a healthy habitat. In addition, it is necessary to consider the issue of the neutralization of phosphogypsum. Back in the day, the problem of keeping phosphogypsum in stock for its disposal solved the problem in a way that caused less environmental damage than sludge collectors. However, for the reclamation of saline soils, phosphogypsum should not be neutralized because the residual acids contained in it increase the solubility of calcium compounds in the soil, contributing to the process of replacing sodium with calcium in the soil. For this reason, the supply of phosphogypsum to consumers in reusable containers that could be used for soil application seems to be a rational solution. The mixing of phosphogypsum with ash from power plants appears promising for optimizing the utilization of by-products [3]. The lower the the quality of coal, the higher the CaO content in the the ash, and the higher the pH, the neutralization of the phosphogypsum. At the same time, recycling in the soil of both materials is achievable.

Nowadays, the multistep multifactor expert-supported calculation procedure to obtain the pollution limit considering specific conditions and target groups of people, but not its specific value, is widespread [4].

Recent theory and practice are focused not on the observance of a particular value of the standardized indicator, but on the ranked-qualified examination of the situation in an ecosystem or natural-territorial complex. That allows to avoid the outdated practice of overly cautious rationing, when the norm was often lower than the clark, and to develop a weighted forward-looking approach to ensuring environmental protection. The U.S. Department of Agriculture (USDA) considers soil as a depository of pollutants and sets limits on their total, annual and cumulative accumulation for land users. Such a standard is assumed to stimulate the use of heavy metals from the soil as microfertilizers, i.e. the metals must constantly leave the soil to plants so that the geochemical cycle of the substance is preserved. Plants-phytomeliorants are chosen for reasons of more effective removal of heavy metals from the soil [5].

Cadmium (Cd) is considered a critical environmental pollutant. The limit of this bioavailable element is due to the specificity and diversity of its behaviour in different soil, hydrological conditions and trophic chains. The Cd limits are not prescribed in Regulation (EC) No. 2003/2003 of the European Parliament. For example, at the national level, when regulating Cd, CE members are guided by the opinion of the Scientific Committee on Toxicity, Ecotoxicity, and the Environment (CSTEE) that Cd content in fertilizer above 20 mg/kg leads to its accumulation in soil over a projection horizon within 100 years. However, in reality, the projection of Cd balance in European soils is negative.

The radioactivity of phosphate ores globally reaches 10000 Bq/kg, and the fertilizers made from them are 3800 Bq/kg [6]. The Environmental Protection Agency has banned the use of phosphogypsum with radioactivity greater than 370 Bq/kg in the United States since 1989 (Health and Ecosystem Protection, 2016). Disposal areas have radioactivity of up to 1,700 Bq/kg, so the bulk of phosphogypsum in the United States is stored in disposal areas (on closed private land with payment to land users), despite years of data from studies conducted in this country that demonstrate the harmlessness of phosphogypsum. Nevertheless, in the State of Florida, ways to reduce volumes of water-acid phosphogypsum are being developed - the rules on its use are being worked out. Important to note that in the EU, the radioactivity limit for non-nuclear materials is 30 times higher than the limit for nuclear materials.

The most radioactively pure apatite raw material is produced at the Siilinjärvi deposit (Finland), the apatite from the Kovdorskoye deposit is of practically the same high quality, and the raw material from the Khibinskoe deposit is slightly inferior. The radioactivity of raw materials is significantly higher in South Africa (Palfos) - 0.1 Bq/g, and Finland (Sokli) - 0.16 Bq/g. The maximum values are observed for the following deposits: Morocco (K-10) - 0.55 Bq/g, Senegal (Taiba) - 0.60 Bq/g, USA (Florida) - 1.0

Bq/g [7]. In this regard, for other promising deposits in the world based on the development of biogeosystem engineering, it is possible to propose fundamentally new technologies for the use of raw materials and for the processing of phosphogypsum [8, 9].

Conclusions. The issue of phosphogypsum utilization is worth reconsidering by improving the technical solutions and technologies of phosphogypsum disposal to use beneficial constituents of potential value in the life cycle. Regulation of the use of chemical waste needs to be revised, taking the maximum potential of the material, with environmentally friendly cycles closing in phosphogypsum biogeosystem management.

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