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Review Article *Natural Resource Management*

Evaluation of the Possibility of Using Industry Mineral Waste in Agriculture, Russia

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Abstract

The main conditions for the application of waste are the excess concentration of elements that the soil needs, and environmental safety. The protective properties of soils are important to consider when applying unconventional fertilizers. The possibility of using mining waste, coal enrichment and thermoelectric stations wastes, chemical wastes, ferrous and non-ferrous metallurgy wastes for growing plants was examined. Studies on the use of agronomic ores to improve soil fertility started in Russia a long time ago. Currently, scientists are conducting research on nanosuspensions of agrominerals: brown coal, glauconite, sapropel and phosphate, and its application in particular for pre-sowing treatment of seed. Experience of application in agriculture of combustible shale ash and brown coal, sulfate wastes has been accumulated. Phosphogypsum can be used as a chemical ameliorant, as it contains up to 94% $CaSO_4$, and as a calcium-phosphorus-sulfur fertilizer. The use of waste from ferrous and non-ferrous metallurgy in agriculture is the most difficult, but of particular interest. We focus on the possibility of using waste from the secondary processing of copper smelting slag for the cultivation of some agricultural plants. The addition of 5% waste from the secondary processing of dump copper-smelting slag to the soil had a stimulating effect on the investigated plants: germination, development and growth increased. Research is important for understanding the transformation of biogeochemical cycles in the conditions of technogenesis and ensuring sustainable development.

Keywords: Mineral waste, unconventional fertilizers, sustainable development, ameliorants, Russia

1. Introduction

Waste mining and processing industries occupy huge areas around the world (Tripathy, 2009; Mensah et al., 2015). In particular, for the Ural region (Russia), about 25% of the territory is estimated as crisis due to pollution caused by dumps. Rational use of mineral waste is necessary to ensure the environmental safety of large industrial centers. Areas of research to solve this problem are diverse and, above all, are aimed at the recovery of industrial waste or their recycling (Makhnev and Zavyalova, 2012). Studies assessing the possibility of using mineral industrial waste as fertilizer and ameliorants in agriculture are of particular interest.

The main condition for the use of mineral waste in agriculture is an excess of components in which the soil needs (Gagarina and Abakumov, 2003). Criteria for the suitability of the use of industrial waste in the cultivation of agricultural plants were developed: waste should not

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contain associated impurities and elements that lead to soil pollution; the possibility of recycling waste with the goal of the most complete extraction of the main mass of accompanying elements is excluded; recycling is not possible in other directions with great economic effects. The use of mineral waste as fertilizer is excluded if the concentration of toxic elements significantly exceeds the approved maximum permissible concentrations for soil, the value of background or clarke content (Kapelkina, 1993).

The protective properties of soils or the possibility of their self-purification are important to consider when using unconventional fertilizers (Golov and Timofeeva, 2005). It is known that the buffer properties of soils depend on the content of humic acids, fine particles, oxides of iron and aluminum, carbonates and the acidity (Ilyin and Syso, 2001). Humic acids are the main binding component for soil pollutants. They can form such strong bonds that toxicants, such as dioxin or copper, are not absorbed by plants and are not washed away by sediments from the soil. A significant factor that increases the absorption capacity of humic acids is the reaction of the soil (pH): in neutral and alkaline reactions it is much higher than in acidic. Therefore, liming of soils or systematic application of alkaline fertilizers will increase potential absorption capacity and the environmental sustainability of soils. Another effective mechanism of soil self-purification is iron-manganese nodules, which accumulate in large quantities in periodically overmoistened soils. Iron-manganese nodules can firmly bind and remove such heavy metals as lead, nickel, chromium, cadmium from the biogeochemical cycle for a long time (Golov and Timofeeva, 2005).

When using mineral fertilizers from industrial waste, short-term effects due to easily bioavailable metal forms from waste and long-term effects due to the dynamics of metal speciation or other biogeochemical processes in the soil-plant system after the application of waste should be considered (Cornelis, 2008).

2. Agronomic Ores

Studies on the use of natural mineral formations to improve soil fertility started in Russia a long time ago. The classification of rocks according to their degree of suitability for agriculture was developed (Gorbunov et al., 1971). However, the practical application of agronomic ores (a term introduced by the Soviet scientist Ya.M. Samoilov in 1921) is still extremely limited. Mass application of agronomic ores is hampered by the lack of developed methods, proven environmental safety and economic benefits compared with mineral fertilizers. According to Saprykin (1984), ameliorants can be rocks of sedimentary or magmatic origin, which, when introduced in large doses (100-500 m^3/ha), improve the structure and water-physical properties of soils. Magmatic rocks-ameliorant include intrusive and volcanogenic rocks, while sedimentary rocks include various carbonate, clay, sandy formations, combustible and carbonaceous shales, brown and black coals. Separate rocks-ameliorant breeds are also promising as fertilizers (Gagarina and Abakumov, 2003).

Currently, scientists of Tatarstan are conducting research on the creation of fertilizers based on nanoscale agrominerals: brown coal, glauconite, sapropel and phosphate (Yapparov et al., 2016; Sharonova et al., 2018; Sukhanova et al., 2018). The use of natural fertilizers of agrominerals for pre-sowing treatment of seed in the form of makro- and nanosuspensions directly in the growth zone provided cultures with the necessary nutrients at the initial stage of crop development and improve grain quality in the future. Nanostructured suspensions provided the best indicators of the qualitative assessment of grain compared with the treatment of macro suspensions. Small particles of agromineral (20-30 nm) in water suspensions freely penetrated into the plant organisms without damaging the structure, and stimulated biochemical processes in cultures (Sukhanova et al., 2018).

Studies on the development of technology for the production of alkaline magnesium ameliorant from mining waste (olivine-containing and serpentine-containing) exist. The effectiveness of this ameliorant was tested to restore woody vegetation, which defoliated due to an imbalance in the absorption of nutrients (Manakova, 2005).

3. Coal Enrichment and Thermoelectric Stations Wastes

Effective complex fertilizers (“Donbass”) were obtained by processing rocks of mine waste heaps of the Donbass coal basin. As a result of the gravitational separation of some coal, it is possible to separate high-ash fractions (waste rock), in which the content of a number of trace elements (Ag, As, Cd, Mn, Mo, Ni, Pb, etc.) is 1.3–14 times higher than in the original coals (Panishev et al., 2015).

Experience of application in agriculture of combustible shale ash (Rebane and Epika, 1982; Turbas, 1992) and brown coal (Rudoy, 1983) has been accumulated. The coals of different deposits and, accordingly, the ashes formed by burning them differ significantly in content and ratio of the main elements. They contain oxides of such elements as silicon, aluminum, calcium, iron, magnesium, sodium, potassium, rare earth metals, whose content is less than 0.1% (Panishev et al., 2015). The ash of brown coal is not inferior to lime in neutralizing ability, it also acts as a catalyst for biochemical processes, accelerates the decomposition of plant residues and the intensity of nitrification, contributes to the synthesis of new compounds, including humic acids. The possibilities of using ash and slag from thermal power stations in the agricultural production are not limited to land reclamation. Research is underway on the use of waste for cleaning ponds and the cultivation of nutrient mass for food to fish.

4. Chemical Industry Waste

Sulfate wastes from the chemical industry are used as complex fertilizers: borogypsum (Golov and Timofeeva, 2005) and phosphogypsum is especially widely used (Belyuchenko, 2014; Akanova et al., 2018).

Phosphogypsum is a by-product of phosphoric acid production. It can be used as a chemical ameliorant, as it contains up to 94% $CaSO_4$, and as a calcium-phosphorus-sulfur fertilizer. Oxides Fe_2O_3, FeO, MgO, TiO_2, MnO_2, Cr_2O_3, CuO, SiO_2, BaO_2 are included in the composition of phosphogypsum in addition to the main macroelements. These compounds have a positive effect not only on the preservation of soil fertility, but also on the productivity and quality of plants (Angelov et al, 2000).

Akanova and her colleagues (Akanova et al., 2018) presented the results of the efficiency of neutralized phosphogypsum in rain fed agriculture of Krasnodar region on corn and sunflower crops grown on leached chernozem. The increase in crop yields depended on doses of phosphogypsum in combination with mineral fertilizers. Neutralized phosphogypsum has a prolonged effect, its effective action does not fade in the fourth year after introduction.

The possibility of using dihydrate phosphogypsum obtained by mechanical crushing and chemical processing of natural Kovdor apatites of the Kola Peninsula in the formation of complex composts was investigated (Belyuchenko, 2014). Phosphogypsum improves the physical properties of the soil, which leads to the preservation of organic matter and nitrogen, an increase soils moisture and aggregation.

5. Ferrous and Non-ferrous Metallurgy Wastes

Methods for the production of mineral fertilizers and ameliorants from ferrous metallurgy waste are known (Dovgopol, 1980; Ermolaev, 2005), patents are registered. Waste of steel-smelting productions, in the form of slag flour, is used for a liming of acid soils. The technical conditions for the use of slag flour regulate the content (CaO+MgO) - not less than 43%, humidity - 2%, maximum grain size - not more than 2mm, the amount of fraction passing through a sieve 0.5mm - 90%, through a sieve 0.25mm 70% (Lotosh, 2002). Sludges of mining and processing plants for the enrichment of iron ores can be used as microfertilizers.

In the Sverdlovsk region (Ural, Russia) in the 70s, researches on the possibility of using industrial waste to increase the productivity of farmland were conducted. Ivanov (1981) assessed the efficiency of using liquid and solid wastes of the Verkhne-Pyshminsky factory to increase the yield of green mass of corn, pea-oat mixture and barley of "Luch" variety.

In the 90s in the Urals, studies to assess the feasibility of using waste from the secondary processing of copper smelting slag of the Sredneuralsk copper smelter ("SUMZ") for the cultivation of some agricultural plants were carried out (Vlasenko et al., 1996). In the article, this waste is named the iron-quartz product of slag flotation. For the experiment, the authors used sod-podzolic soil and evenly mixed with the iron-quartz product in different concentrations, mainly, 5, 15 and 30%, in some cases 50 and 100%. The control was the soil without additives. They were tested 8 types of plants: tomatoes (*Lycopersicon esculentum* Mill), cabbage (*Brassica oleracea* L.), salad broad-leaved (sowing) (*Lactuca saliva* L.), garden dill (*Anethum graveolens* L.), onion (*Allium cepa*), red fescue (*Festuca rubra* L.), *Bromopsis inermis* (Leyss.) Holub. and meadow bluegrass (*Roa pratensis* L.). The researchers found that a 5% increase in the soil of waste from the secondary processing of dump copper-smelting slag of "SUMZ" had a stimulating effect on the tested plant species: germination, development and growth increased (Vlasenko et al., 1996). Increasing the slag fraction to 15% also had a positive effect for all tested species, except cabbage and tomatoes. They had a decrease in plant height, root length and plant mass. The lower part of the leaves and the stem of tomatoes acquired a purple color. A higher concentration of iron-quartz product in the soil (30%) negatively influenced the development of most of the studied plants: tomatoes, dill, red fescue and meadow bluegrass. Slag concentrations of 50 and 100% inhibited the germination, growth and development of all tested crops. The content of heavy metals and sulfur was determined on an atomic adsorption spectrophotometer. The above-ground part of the onion, leaves and fruits of tomatoes grown at 5 and 15% concentration of waste from the secondary processing of copper smelting slag were analyzed. The analysis revealed a tendency to the accumulation of chemical elements in the plants leaves, especially in such elements as Fe, Ni, Cu, S. At the same time, it was revealed that tomato plants contain more metals in fruits than in leaves. However, the values of maximum permissible concentrations established for food products were not exceeded anywhere.

Currently, the environmental group of the Zavaritsky Institute of Geology and Geochemistry of Ural Branch of Russian Academy of Sciences conducts comprehensive studies on the waste of secondary processing of dump copper smelting slag of the Sredneuralsk copper smelter, and evaluates the prospects for their use (Leontyev and Ryabinin, 2005; Leontyev et al., 2006; Kotelnikova et al., 2014; Kotelnikova and Ryabinin, 2018).The technology of secondary processing of waste copper smelting slag includes crushing followed by the production of copper concentrate. Fine material (slag particle size ≤0.05 mm), the so-called "technical sand", accumulates as waste. It contains about 3.4% zinc, 0.4% copper, 0.4% lead, 35.0% iron (Kotelnikova and Ryabinin, 2018). One of the possible directions of the waste of secondary processing of dump copper smelting slag use is as a mineral fertilizer. Laboratory and field experiments on the cultivation of agricultural plants, lawn grasses and seedlings of the main wood species of the Urals are carried out to establish the environmental safety and effectiveness of the use of "technical sand" of "SUMZ". A geochemical assessment of the distribution of elements (before and after waste application) in the soil profile of sod-podzolic and gray forest soils is given (Leontyev and Ryabinin, 2005; Leontyev et al., 2006), studies on brown mountain forest soils have been initiated. Elemental analysis of soil and plant samples is carried out at the “Geoanalytic” Center for Collective Use of the Zavaritsky Institute of Geology and Geochemistry of Ural Branch of Russian Academy of Sciences. Research is important for understanding the transformation of biogeochemical cycles in the conditions of technogenesis and ensuring sustainable development.

6. Conclusion

The use of mineral waste of mining and processing enterprises in agriculture is possible and extremely important for solving the problems of utilizing industrial waste dumps. Agronomic ores, ash of combustible shale ash and brown coal, borogypsum and phosphogypsum, metallurgy waste can be used to improve soil properties and increase crop yields. The waste of secondary processing of dump copper smelting slag is promising for use as a mineral fertilizer for growing some agricultural plants, but further research is needed.

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