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Application of Steel-Smelting Slags as Material for Reclamation of Degraded Lands

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ABSTRACT
Presently, the highest level of waste generation is characterized by ferrous metallurgy enterprises, the large-tonnage wastes of which are slags of various industries. Taking into account the negative impact of slags on the environment, the limited opportunities for expanding dump volumes, as well as the depletion of sources of raw mineral raw materials, the aim of research was to develop an alternative method for the utilization of steel-smelting slags of the mining and metallurgical complex. Tthe steel smelting slag of the Novolipetsk metallurgical plant and the sewage sludge of the city water treatment station in Lipetsk were selected as the materials for the study. In the laboratory, the chemical composition of the waste was determined by means of a complex of modern analytical methods, including atomic emission spectrometry with inductively coupled plasma, X-ray fluorescence spectrometry, and atomic absorption spectrometry with electrothermal atomization. The results of the analysis enabled to assess the possibility of sharing waste as a soil additive to improve the quality of the soil. Then, under laboratory conditions, the grass mixture was grown on model soil samples with a soil additive consisting of the investigated waste with a different mass ratio. On the basis of the obtained data on seed germination, the growth of the aerial part of the biomass, the height of the leaves, and also the content of the accumulated metals in the plants, a formulation of an organomineral additive was proposed for poor soils of disturbed lands.

Keywords: mining and metallurgical enterprises, steelmaking slag, sewage sludge, organomineral additive, recultivant, growing of grass

INTRODUCTION

The quality of human habitat is influenced by several factors, including the ones caused by human activities. Waste generation is one of the negative consequences of human life. Today in Russia, about 80 million tons of wastes are stored in dumps and tailing dumps. The enterprises of ferrous metallurgy are characterized by the highest level of waste generation, the annual output of slags at these plants is more than 95 million tons, whereof 79 million tons are blast furnace slag, steel smelting, foundry and ferroalloy productions [Shapovalov et al., 2013]. The area of land occupied by slag heaps in Russia is more than 1 million hectares, with an annual fee for waste disposal reaching tens of millions rubles.

Operation of waste disposal sites leads to environmental degradation and, as a consequence, an increase in the morbidity level. The main reason for the atmospheric air quality decrease is sweeping-away of waste fine fraction from the surface of dumps. This subsequently leads to the contamination of soils and vegetation cover of adjacent territories. Accumulation of pollutants takes place in the upper layer of the soil, which significantly affects the vital activity of plants and biodiversity in the area influenced by the enterprises of the metallurgical industry. Infiltration of atmospheric precipitation and surface runoff through the body of slag dump promotes leaching of pollutants from waste, including heavy metals, which, entering the soil, underground and surface waters, form polluted area and pollution streams. In order to reduce the negative impact of slag dumps on the environment in the iron and steel enterprises recycling system have successfully been implemented. At modern metallurgical plants, blast furnace slags are practically not stored in dumps, but are used as technogenic raw materials in various industries. However, the application of steel smelters in the cement industry and road construction, without special processing, is limited due to the inconstancy of the chemical and mineral compositions, as well as the lack of stability of the emerging structure. As a result, only 20-30% of the total steelmaking slag generated in the Russian Federation is recycled annually [Yaroshenko, 2011].

The development of alternative ways of recycling and processing steelmaking slags has become the goal of research. These methods are aimed at reducing the technogenic load on the environment.

The steel-smelting slag of the Novolipetsk Metallurgical Combine was the subject of research. Annually, the enterprise consumes about 14 million tons of iron ore. One of the main environmental problems of the company is the storage of steelmaking slag in a total area of 16 hectares, while the capacity of slag disposal is about 2 million tons. In this regard, the main tasks of the conducted research were studying the composition and properties of steelmaking slag, as well as reducing its negative impact on the environment by using waste as a product for the reclamation of disturbed lands.

MATERIALS AND METHODS

Insufficient use of metallurgical slag leads not only to the incomplete profit, but also to a rise in the price of the main metallurgical products, due to the high costs of transportation of slags and the maintenance of huge dumps. At present, there are many promising methods for processing steelmaking slags, including obtaining staflux for the sinter production, the production of crushed slag stone for road and industrial construction, the use of waste as fertilizer. [Bobrova et al., 2015, Kogan & Shakhparonova, 2017]. However, all of them still remain unexplored or unclaimed for a number of reasons. Thus, the use of steel-smelting slags in agriculture is limited primarily because of the presence of toxic elements such as As, Pb, Cd, Co, Cr, etc., which can be washed out of the slag and cause the death of plants and soil contamination. In this connection, a series of experimental studies was carried out at the Laboratory of the Mining University devoted to a comprehensive analysis of the chemical composition of the steel smelting slag of the Novolipetsk Metallurgical Combine and the cultivation of grass mixtures on model soil samples with a mineral additive in the form of the studied slag. The primary task was to determine the chemical composition of the material using such modern analytical methods as X-ray fluorescence spectrometry and atomic absorption spectrometry with ETA. The results of the determination of the macrocomponent composition of the sample are shown in Table 1.

As shown in Table 1, the main component of slag is calcium. A phase analysis by X-ray powder diffractometry was carried out to establish the shape of calcium in the waste. The results of the diffractometric analysis showed that the calcium in the sample is mainly portlandite ($CaO·H_2O$), calcite ($CaCO_3$), sperrit ($2Ca_2SiO_4·CaCO_3$), calcium aluminate ($5CaO·3Al_2O_3$), calcium silicate (Ca_2SiO_4). It is known that lime and calcite contribute to the nutrition of plants, reduce the acidity of the soil, loosen it, contributing to the retention of moisture, stimulate the vital activity of useful microorganisms [Stepanova & Shamaraeva, 2012]. Some of the lime is strongly bound in silicate compounds, which hinders its rapid washing, observed with conventional calcareous fertilizers, thereby increasing the absorption capacity of the soil and prolonging the operation of the mineral additive. In addition, calcium silicates have practically the same neutralizing effect as oxide and calcium carbonate. In significant amounts, magnesium in the form of brucite ($Mg(OH)_2$) and periclase (MgO) is detected in the waste, the lack of which is caused by diseases in plants. The elements useful for plants such as iron, silicon and aluminum also entered the macrocomponent composition of the slag. In particular, silica is well absorbed by plants and increases the strength of stems.

Further on the high-tech equipment, the micro-component composition of the steel-smelting slag was determined. The results are shown in Table 2.

Table 1. Chemical composition of steel-smelting slag (Novolipetsk Metallurgical Combine)

Element	Ca	Fe	Mg	Si	Al	Mn	C
Content, %	30.4	18.4	3.4	6.8	1.3	1.2	1.1

Table 2. Microcomponent chemical composition of the steel-smelting slag (Novolipetsk Metallurgical Combine)

Element	Units	Content
Ti	%	0.2
V	%	0.1
S	%	0.1
Cu	mg/kg	71
Zn	mg/kg	640
Pb	mg/kg	120
Cr (III)	mg/kg	38
Cd	mg/kg	5.9
Ni	mg/kg	0.2
Hg	mg/kg	0.1
As	mg/kg	<0.05

The results presented in Table 2 indicate that most of the impurity elements are represented by heavy metals. In terms of significance, heavy metals for plants can be divided into two groups:

- necessary for the life of plants in small concentrations (Co, Cr, Cu, Fe, Mn, Mo, Ni, Zn), become toxic only with a significant increase in their content in soil and plants;
- not participating in the metabolism of plants (Cd, Hg, Pb, V) and toxic even at very low concentrations.

The role of the necessary heavy metals in the vital activity of plants is extremely high. Metals-microelements stimulate growth, synthesis of proteins, fats and carbohydrates, participate in metabolic processes, bind to biologically active substances (hormones, vitamins, proteins), increase the plant immunity and chlorophyll content, as well as stabilize green pigments during aging of chloroplasts [Baisetova & Sartaeva, 2014, Titov & Laidinen, 2007]. That causes the use of a number of heavy metals as microfertilizers. For this reason, it was decided to develop a preparation for the reclamation of disturbed lands under laboratory conditions. As part of the preparation for reclamation, steel smelting slag of the Novolipetsk Metallurgical Combine was used. It was decided to grow the mixture on model soil samples. The production of a highly effective complex additive in the soil involves the use of both mineral and organic components. As a source of organic substances in the experiment, the sewage sludge of the urban aeration station was used. It is assumed that a mixture of sediment and slag will create an organomineral additive that can be used as fertilizers for planting forestry crops along roads, in seed plots of forest and ornamental crops, for reclamation of disturbed lands and slopes of highways and solid waste dumps. As a control sample, the soil of the Lipetsk region was used, which refers to gray forest soils. Before planting the mixture, the annual permissible doses of slag and sludge were determined, which can be introduced into the soil taking into account its properties and actual contamination.

The permissible dose of metals in soil, taking into account its properties and the actual pollution in terms of dry matter, g / ha, was calculated by means of the following formula

$$\mathrm{D}_{ad} = (0{,}8 \cdot \mathrm{MPC} - \mathrm{F}) \cdot \mathrm{M} \tag{1}$$

where: 0.8 – the correction factor that reduces regulatory entry of heavy metals into soil by 20%;
MPC – maximum permissible concentration of metals in soil, g/t;
F – the metal content in soil, g/t;
M – the soil arable layer mass in terms of dry matter, t/ha (3000 t/ha).

The annual dose of applying metal to the soil in terms of dry matter for 10 years, t / ha, was determined with the formula:

$$\mathrm{D}_{\mathrm{av}} = \frac{\mathrm{D}_{\mathrm{ad}}}{\mathrm{T} \cdot \mathrm{C}} \tag{2}$$

where: T – the maximum total period of fertilizer application for the same site, years (10 years);
C – the concentration of the metal in the additive, g/t.

Table 3 shows that the maximum permissible concentration of metals in the soil will not be exceeded for all the components under study if the

Table 3. Calculation of the permissible doses of heavy metals, arsenic and the average annual dose of slag and sewage sludge to soil

Element	Admissible doses, kg/ha	Annual dose, t/ha	
		Sewage sludge	Slag
Cd	2.0	152.3	33.6
Cu	158.2	98.9	222.8
As	11.9	438.9	11850.0
Ni	93.0	794.9	46500.0
Hg	4.4	740.0	4440.0
Pb	153.0	327.6	127.5
Zn	262.0	49.2	40.9
Cr (III)	13.4	27.2	35.5

following amounts of sediment and slag are added to the soil in terms of dry matter: 27.2 and 33.6 t/ha, respectively. These values are determined on the basis of the maximum permissible amounts of chromium (III) and cadmium, which may appear in the soil sample after the incorporation of additives.

On the basis of the calculated data, the following types of soil additives were prepared:

- "Type 1" – steelmaking slag;
- "Type 2" – sewage sludge of the urban aeration station;
- "Type 3" – sewage sludge of the urban aeration station + steelmaking slag (1 : 3);
- "Type 4" – sewage sludge of the urban aeration station + steelmaking slag (1 : 1);
- "Type 5" – sewage sludge of the city aeration station + steelmaking slag (3 : 1).

The masses of additives introduced into the soil were determined based on the area where the fertilizer was applied, as well as the moisture values of the steelmaking slag and the sewage sludge. Table 4 presents the estimated doses of sewage sludge from the water treatment plant and steelmaking slag for laboratory research.

In order to prepare the soil additive, the steelsmelting slag was crushed to a size of 0–5 mm. The homogenization of the steelmaking slag and sewage sludge was carried out by mixing. The resulting mixture was applied to the depth of the arable layer (15–20 cm), after which sowing of the lawn grass mixture (60 kg/ha), represented by English bluegrass (perennial tare), was carried out.

English bluegrass is well-adapted to the conditions of a humid temperate climate and refers to the plants of the winter medium-ripening type of development. The main advantage of this herb is its ability to form dense herbage a month after sowing. Particular attention in the process of cultivation was paid to the observance of optimal microclimatic conditions: illumination, temperature and humidity. One of the important factors affecting the growth of plants is the temperature that regulates the activity of enzymes. The optimal temperatures for plant growth are in the range from +18 to +30°C. Illuminance, necessary for photosynthesis in plants, is 600–2000 lux. Sufficient illumination triggers the process of photosynthesis in plants, through which they produce organic compounds from inorganic ones. Humidity also affects the growth and development of plants. Low air humidity increases transpiration and evaporation of water from the substrate. The lower the humidity of the air, the greater the evaporation of water by leaves and soil, and more irrigation is required. On average, the humidity level for normal plant growth should be 60–90% [Zimina & Kukushkin, 2014]. Table 5 presents

Table 4. Estimated doses of sedimentation of sewage sludge and steelmaking slag

Additive type	Fertilized area, cm^2	The annual dose taking into account humidity, g/cm^2	
		sewage sludge	steelmaking slag
1	152	-	57 165
2		71 715	-
3		21 686	41 980
4		40 604	26 201
5		56 950	12 250

Table 5. Microclimate characteristics of laboratory room

Characteristic	Units	Condition
Air temperature	°C	20
Air humidity	%	88
Illumination	lux	770

the microclimatic characteristics of the room in which the grass mixture was grown.

For the normal development of plants, the maintenance of soil processes and the level of soil fertility, the moisture content in the soil and the level of its acidity play an important role. When there is a lack of moisture, the turgor pressure of the cells decreases, their elasticity is lost, the dynamics of biochemical processes decreases, the absorption of carbon dioxide through the stomata decreases, and the inhibitor substances accumulate in the biomass. With an excess of moisture, the oxygen metabolism is disturbed in plants and in the soil-accumulated compounds, which leads to a decrease in the bioproductivity of the soil, as a result of the death of plants [Bayshanova & Kedelbaev, 2016]. In order to maintain the optimum moisture of the model samples, watering was done 1–2 times a week. The volume of added water corresponded to the norm of precipitation in the territory of the Lipetsk region in the warm period of the year. In view of the significant effect of soil acidity on the growth and development of plants, the soil acidity of the model samples was checked during the vegetative period of the grass mixture.

As a result, the main indicators of the experiment were:

- evaluation of seed germination;
- estimation of the increment in the aerial part of the biomass;
- assessment of the content of accumulated metals in grown plants.

RESULTS

Several features may be indicative of ongoing processes in plants growth. These include an increase in mass of plants and parts thereof, the number of cells, linear dimensions (length, height, thickness, and diameter). Separately, each of these signs does not always reliably indicate the presence of growth processes in plants, so a complete representation can be obtained by simultaneously taking into account several indicators. On the fourth day after sowing of the lawn grass mixture, seed germination was observed, while the laboratory seed germination in the control sample was 81%, germination in the remaining samples was 2–6% higher (Table 6), which was due to the introduction of additional substances into the soil.

After the rising of the grass mixture, the height of the leaves was maintained at 10 cm, while the aerial part of the biomass was weighed after each cutting. After 20 weeks, at the end of the growing season, the laboratory experiment was stopped. The value of the aerial part of the biomass is shown in Table 7.

The data shown indicate a decrease in the aerial part of the biomass of the grown grass mixture by 7.5% in the model sample with the addition of “type 1” relative to the control sample (soil) and the likely presence of a factor of plant oppression. A positive effect was observed when the sediment and slag were added together to the soil, based on the observed increase in the aerial part of the bio-

Table 6. Bluegrass seed germination in laboratory conditions

Sample	Seed germination, %
Soil (control sample)	81
Soil + additives «Type 1»	83
Soil + additives «Type 2»	85
Soil + additives «Type 3»	87
Soil + additives «Type 4»	87
Soil + additives «Type 5»	87

Table 7. Value of grass mixture aerial part obtained during the vegetation period

Value of the aerial part of the biomass, g/m^2					
Soil (control sample)	Soil + additives «Type 1»	Soil + additives «Type 2»	Soil + additives «Type 3»	Soil + additives «Type 4»	Soil + additives «Type 5»
825.9	763.6	877.0	858.4	987.1	1075.7

mass by 3.9–30.2%, relative to the control sample. During the experiment, the height of the leaves was measured weekly before the cutoff of the aerial biomass. It should be noted that the growth rate of the plants of the grass mixture planted on model samples was practically the same in all cases with minor deviations. The greatest increase was in the plants planted in model samples with the addition of organomineral additives. The introduction of additional substances into the soil only with slag led to the withering of the plants; thus, during the experiment, the smallest proportion of the aerial part of the biomass and the minimal growth of the plant leaves relative to the control sample were recorded in these model samples.

Comparing the obtained data of plant growth, it can be concluded that the deviations from a control reference sample (soil) exceeding 20% were not observed in any of the studied models, indicating that there is no toxic effect of the mineral and toxic additives used on the development of lawn grass mixtures. In addition, it is worth noting that during the growing season, diseases such as chlorosis and necrosis in plants were not observed. Throughout the vegetative period of the plants, the soil acidity of the model samples was monitored. The essence of the method was the extraction of exchangeable cations, nitrates and mobile sulfur from the soil with a solution of potassium chloride with a concentration of 1 mol / dm^3 (1 N) and potentiometric determination of the pH [GOST Soils, 1985]. The results showed that when applying both mineral and organic additives to the soil by the end of the growing season, the pH of the salt extract increased by 1 to 2 units of pH, relative to the reference. The greatest change in soil pH was observed in a model soil sample with the addition of slag, which probably leads to the inhibition of plants. However, in the remaining model samples, there was no apparent difference in plant growth and biomass increment relative to the control sample, which is due to the additional application of organic substances. Since the blue grass used in the studies refers to the plants with a high resistance to changes in soil pH values, in order to study the effect of soil acidity on the germination of plants in more detail, addition was also made to plant meadow fescue, also part of lawn grass mixtures, but more sensitive to increased acidity environment. As a result, the germination of plants in the soil with additives decreased with respect to the control reference sample. Consequently, while choosing the planned grass seed for recultivation, it is necessary to take into account its resistance to changes in the acidity of the medium. At the final stage, studies related to the determination of the content of accumulated metals in grown plants were carried out. This stage has become key since while using industrial waste and municipal services as fertilizers of agricultural soils, it is necessary to carry out systematic monitoring of soil pollution and plant production with heavy metals. At the end of the growing season, the aerial part of the grass cover was cut and dried to an air-dry state in a well-ventilated room. Afterwards, the plant samples were crushed and mineralized by the dry ashing method. In order to determine the accumulated metals in plants, their acid extraction from the mineralized part was carried out. Metals in the ash solutions of plant samples were determined by means of an atomic-emission spectrometer with inductively coupled plasma. The results of the determination of the accumulated metals in plant leaves of the mixture are shown in Table 8.

The analysis of plants, grown using organic and mineral additives, revealed deviations in the content of copper, nickel and zinc, relative to the control soil sample. Thus, the use of steel melting slag as a soil for remediation leads to an increase in the copper content in plants by a factor of 2, nickel by a factor of 1.1, zinc by 1.3 times, with respect to the control sample. As a result of using the sewage sludge of the aeration station for recla-

Table 8. Metal content in the leaves

Sample	Metal content in plant leaves, mg/kg					
	Cd	Cu	As	Ni	Pb	Zn
Soil (control sample)	< 0.5	18.2	<0.05	<3.5	<5.0	26.4
Soil + soil additives Type 1	< 0.5	38.0	<0.05	4.0	<5.0	35.2
Soil + soil additives Type 2	< 0.5	23.3	<0.05	<3.5	<5.0	27.0
Soil + soil additives Type 3	< 0.5	34.5	<0.05	<3.5	<5.0	33.5
Soil + soil additives Type 4	< 0.5	31.0	<0.05	<3.5	<5.0	30.1
Soil + soil additives Type 5	< 0.5	29.5	<0.05	<3.5	<5.0	29.4
Permissible concentration in soil	1.0	66.0	5.0	40.0	65.0	110.0

mation, copper increases by 1.3 times, the content of nickel and zinc remains at the level of the reference sample. While using an organomineral additive with various weight ratios of sediment and slag as a soil for remediation, a minimal increase in the metal content is observed. Due to the fact that the model samples are planned to be used as fertilizers, a comparison of the content of accumulated metals in plants was carried out with the maximum permissible concentrations of metals in the soil. Despite the fact that the metal content in the grown plants on model samples with different additives is higher than the values in the control sample, the maximum permissible concentrations for these elements in the soil were not exceeded. Comparing the obtained data on the germination of plant seeds, the growth of the aerial part of the biomass, the height of the leaves, and also the content of the accumulated metals, it can be concluded that the most favorable conditions for the development of plants are the use as a soil for remediation of an organomineral mixture with a mass ratio of sewage sludge from a city aeration station and steelmaking slag 3: 1. The results of the conducted experiments open the prospect of using steelmaking slag in conjunction with the sewage sludge of urban aeration stations as an organomineral additive to the soil.

CONCLUSION

The carried out laboratory investigations allowed to work out in detail the issue of utilization of wastes represented by steel-smelting slag and sediment from municipal wastewater treatment, as well as to offer an actual solution to the existing problem of utilization of the investigated wastes, consisting in:

- application of steel smelting slag of the Novolipetsk metallurgical plant as a mineral component of the reclaimed land due to the high calcium content (30.4%) represented by portlandite ($CaO \cdot H_2O$), calcite ($CaCO_3$), sperrit ($2Ca_2SiO_4 \cdot CaCO_3$), calcium aluminate ($5CaO \cdot 3Al_2O_3$), calcium silicate (Ca_2SiO_4);
- application of sediment after the treatment of municipal wastewater as an organic constituent of the soil additive;
- development of a recipe for the preparation of a highly effective organomineral additive (reclamation agent) using steelmaking slag and urban sewage sludge in a weight ratio of 1 : 3;
- minimization of heavy metals (Cu, Ni, Zn, Cr(III)) influence on the environment, due to their participation in the metabolism of plants and favorable influence on the cultivated grass mixtures with the application of admissible doses;
- development of a methodology for researching soil additives under laboratory conditions, which includes assessing the germination of seeds, the increase in the aerial part of the biomass, and the content of accumulated metals in the grown plants, and also takes into account the effect of climatic parameters;
- an annual reduction in the volumes of dumps of steel-smelting slags by 3–5% and prevention of storage of newly generated waste.

In general, the introduction of the proposed method for joint utilization of slag from steelmaking and sludge after the treatment of urban wastewater leads to a significant decrease in their impact on the components of the environment, the cost of remediation works in the zone of mining and metallurgical complexes, and also allows taking a colossal step towards zero waste production.

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