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Investigation and restoration of land disturbed by industrial activity

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Abstract

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Research was conducted on the territory of the workshop for the production of sulfuric acid, which is located on the industrial site of "NEOHIM" JSC, Dimitrovgrad.

The site area was found to be characterized by heavy metal content exceeding the upper threshold requirements of the Dutch Soil and Groundwater Standard List for copper.

Measures are foreseen to overcome the unfavorable characteristics of the soils, which include the following:

– site clearance;
– liming of the site;
– filling the cleared areas with geological materials from the "Novi Rudnitsi" region, which are characterized by a sandy-clay mechanical composition, a neutral reaction to the environment and a low supply of the main nutritional elements for plants – nitrogen, phosphorus and potassium;
– spreading a layer of humus materials with a thickness of 40 cm;
– weeding, which will be done by sowing grass mixtures.

Keywords: geological material; disturbed land; surface mining; biological regeneration; land reclamation

Introduction

The production of raw materials for the chemical and processing industries is related to continuous modernization and optimization of the production process. This implies the liquidation of facilities and industrial sites that have fallen out of use. At the same time, the freed areas, as a rule, are characterized by complete disturbance, contamination and partial destruction of the soil cover. It is necessary to undertake specific actions to establish the degree of disturbance and pollution, followed by the development of a system of measures to restore the productive potential of the surface soil layer on the territory of the site (Banov et al., 2009a).

The purpose of the present development is to establish the current state of the surface soil layer on the territory of the former workshop for the production of sulfuric acid, located on the industrial site of „NEOHIM" JSC, Dimitrovgrad.

Characteristics of the Research Object

The workshop for the production of sulfuric acid, the territory of which is the subject of the present study, is located on the industrial site of "NEOHIM" JSC – about 3 km east of the city of Dimitrovgrad (Chuldzhiyan et al., 1995).

The site for the production of sulfuric acid occupies an area of 11.1 ha, on which 36 units are located such as buildings, flyovers and other facilities that are foreseen. On the site there are railway lines, concrete roads, overhead and underground pipelines, overhead and underground electric wires. All underground power lines in the area of the site are not operational and are disconnected from the power supply. The underground pipelines in the area of the site such as: technological pipelines, fire protection and drinking water pipelines, etc. are at a depth greater than 1.50 m, are not operational and are excluded from the respective operational branches.

In terms of climate, the area of the site belongs to the transitional continental climatic sub-region of the European continental climatic region – climatic region of Eastern Central Bulgaria (Climatic guide for the Republic of Bulgaria, 1983). It is characterized by mild winters and warm summers (Table 1).

Winter is relatively mild, with frequent warming. The lowest temperature is in the month of January. Spring comes relatively early and summer is hot.

The annual distribution of precipitation is distinguished by two maxima and two minima characteristic of the transitional continental climate subregion – May (68 mm) and October (62 mm); March (37 mm) and September (36 mm). The average annual rainfall varies between 606 and 668 mm (Table 1). The distribution of average rainfall amounts by season is as follows: spring – 158 mm; summer – 148 mm; autumn – 150 mm; winter – 150 mm;

Precipitation conditions are of a continental type – with a maximum in June and July, but the transitional nature of the climate is expressed in the significant winter precipitation.

Geologically, the area of the site is made up of Eocene (Priabon) and Pliocene marine and lacustrine deposits and of Quaternary alluvial and deluvial sediments. On the surface, the Priabonian limestones are widely exposed, participating in the construction of several shallow fold structures, of which the Black Sea anticline and the Dimitrovgrad syncline are more important. Limestones and marls make up the entire chain of elevations, which in the studied area outline the southern edge of the Marishka valley.

Hydrogeological, the groundwater is karst type (in the limestones of the Priabon) and porous (in the sand and gravel layers of the Pliocene and in the alluvial deposits of the rivers Maritsa, Merichlerska, Omurovska, Mechka, etc.). The direction of movement of the groundwater is mainly north and northeast. The main hydrological unit is the Maritsa River.

A field study was carried out to establish the soil diversity in the area of the site. Based on the field determination, it was found that the soil differences in the area of the site are as follows:

- Vertisols (Pellic);
- Rendzic Leptosols;
- Fluvisols;

Materials and Methods

Samples were collected from the area of the site to determine the degree of soil contamination from the activity of the sulfuric acid workshop. The samples were taken with a hand probe at a depth of 0 – 30 cm and 30 – 60 cm. The collected samples were analyzed in the laboratory of the Institute of Soil Science, Agrotechnology and Plant Protection „Nikola Poushkarov“, Sofia, regarding the following indicators:

- reaction of the environment (pH in water) – potentiometrically (Arinushkina, 1962);
- content of heavy metals – accounting of ACC – ISO 114 66: 1995.

The obtained analytical results are reflected in Table 2.

Results and Discussion

It is necessary to emphasize that the materials making up the object of the study are extremely diverse, both in terms of their areal distribution and in depth of the analyzed profiles. Layers of soil or geological materials, construction waste are observed, and in places (profiles No. 7 and No. 8) the presence of pyrite slag from the surface at a depth of up to 60 cm is found.

The analytical results obtained show a wide variation in the medium reaction values (pH in water). The indicator varies in the range from 2.9 to 7.4, with values from 3.5 to 5.4 prevailing – about 65% of all analyzed samples.

The content of heavy metals was evaluated according to the requirements of the Dutch list of standards for soils and groundwater (Table 3).

Table 1. Climatic characteristics of the studied area

	Months												Annual average
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	
Air temperature, °C	0.1	2.8	6.4	12.0	17.4	21.2	23.8	23.6	19.3	13.2	8.1	2.8	12.6
Rainfall amount, mm	54	40	37	53	68	64	45	39	36	62	52	57	606
	63	47	50	57	67	69	40	37	34	61	67	75	668
Wind speed, m/s	2.2	2.3	2.3	2.4	2.0	1.8	1.9	1.7	1.5	1.6	1.7	2.2	2.0

Table 2. Heavy metal content in samples from the sulfuric acid plant area, mg/kg

№ profile	Sample №	Depth of the sample. cm	pH	Cu	Pb	Ni	Zn
1	1	0 – 40	4.8	123.6	152.4	24.5	149
	2	40 – 60	7.2	89.1	95.6	15.7	287
	3	60 – 80	7.0	56.3	72.8	19.5	115
2	4	30 – 50	3.5	427.2	673.2	31.4	471
	5	50 – 80	5.7	172.5	184.3	17.5	285
3	6	50 – 80	3.5	271.0	342.1	31.3	274
		80 – 100	5.2	95.6	172.4	26.5	163
4	8	60 – 80	4.1	332.0	215.3	47.1	310
	9	80 – 100	6.6	110.4	183.5	35.6	186
5	10	0 – 40	4.3	353.7	167.2	34.4	512
	11	40 – 60	5.9	238.0	215.9	18.2	318
	12	60 – 80	5.7	142.5	93.5	21.7	256
6	12	60 – 80	3.5	384.1	392.5	37.2	308
	13	80 – 100	4.2	163.7	152.8	17.4	142
7	14	60 – 80	4.9	250.8	517.3	28.3	273
	15	80 – 100	5.4	148.3	243.7	15.8	129
8	16	60 – 80	2.9	458.1	485.1	31.6	325
	17	80 – 100	4.8	187.3	197.3	19.2	182
9	18	0 – 40	3.2	327.5	248.5	42.7	412
	19	40 – 60	5.7	152.6	192.6	28.5	264
10	20	0 – 40	4.8	311.4	315.1	36.2	327
	21	40 – 60	4.0	175.8	215.0	27.3	208
	22	60 – 80	5.3	152.6	115.4	21.5	247
Pyrite slag	23		3.3				

A lower threshold is called the limit value of heavy metal content, below which the soil is considered uncontaminated, and above which measures are prescribed to control and monitor the degree of contamination.

An upper threshold is called the limit value of heavy metal content above which soil restoration measures are prescribed.

Table 3. Dutch list of content standards of heavy metals in soils

Metals	Lower threshold, mg/kg (ppm)	Upper threshold, mg/kg (ppm)
1. Arsenic	29.0	55.0
2. Barium	200.0	625.0
3. Cadmium	0.8	12.0
4. Chromium	100.0	380.0
5. Cobalt	20.0	240.0
6. Copper	36.0	190.0
7. Mercury	0.3	10.0
8. Lead	85.0	530.0
9. Molybdenum	10.0	200.0
10. Nickel	35.0	210.0
11. Zinc	140.0	720.0

The results presented in Table 4 testify to an excess of the upper threshold in the content of heavy metals in relation to Cu from 1.3 to 2.4 times, which applies to 45% of the examined samples. Regarding Pb, only one of the investigated samples was found to exceed the upper threshold. The nickel and zinc content indicates that the materials are not contaminated with these elements. The results obtained, apart from those for copper, vary between the upper and lower thresholds.

No strict regularity is established regarding the amount of heavy metals in the analyzed sample, its location and the depth of collection.

The interpretation of the obtained results requires the seizure of the contaminated soil masses. The resulting volumes will be filled with geological materials from the „New Mines“ area. Geological materials are characterized by a sandy-clay mechanical composition. In terms of pH, the values of the indicator change in the range from 7.1 to 7.5 – neutral reaction of the environment (Table 5).

The content of the elements phosphorus and potassium in the geological materials is low (Table 5).

The presence of nitrogen in the studied materials defines them as poorly stocked with this nutrient (Table 5).

Table 4. Degrees of excess of the upper threshold in the content of heavy metals in samples from the area of the former sulfuric acid plant

Sample No	Depth of sample, cm	pH	Exceeding the upper threshold in times			
			Cu	Pb	Ni	Zn
1	0 – 40	4.8	–	–	–	–
2	40 – 60	7.2	–	–	–	–
3	60 – 80	7.0	–	–	–	–
4	30 – 60	3.5	2.2	1.3	–	–
5	60 – 80	5.7	–	–	–	–
6	50 – 80	3.5	1.4	–	–	–
7	80 – 100	5.2	–	–	–	–
8	60 – 80	4.1	1.7	–	–	–
9	80 – 100	6.6	–	–	–	–
10	0 – 40	4.3	1.9	–	–	–
11	40 – 60	5.9	1.3	–	–	–
12	60 – 80	5.7	–	–	–	–
13	60 – 80	3.5	2.0	–	–	–
14	80 – 100	4.2	–	–	–	–
15	60 – 80	4.9	1.3	–	–	–
16	80 – 100	5.4	–	–	–	–
17	60 – 80	2.9	2.4	–	–	–
18	80 – 100	4.8	–	–	–	–
19	0 – 40	3.2	1.7	–	–	–
20	40 – 60	5.7	–	–	–	–
21	0 – 40	4.8	1.6	–	–	–
22	40 – 60	4.0	–	–	–	–

The content of total C in the geological materials from "New Mines" varies from 3.17 to 6.55%, which is practically the result of the presence of coal impurities in the examined samples (Table 5).

The content of heavy metals in the studied materials shows that they do not contain concentrations exceeding the MPC (Table 6).

In conclusion, it can be said that the geological materials from the area of „Novi Rudnitsi" can serve as a substrate for filling the cleared sites on the territory of the former sulfuric acid workshop.

Before filling the cleared areas, it is recommended to perform liming of the terrain (Banov et al., 2009b), and the rate of liming is calculated according to the formula:

Table 5. Chemical characteristics of samples from the area of "Novi Rudnitsi"

№	Depth, cm	pH		P_2O_5	K_2O	NH_4-N	NO_3-N	Total C, %
		H_2O	KCl	mg/100 g soil		mg/kg soil		
1	Geological materials	7.1	6.1	7.2	-	5.94	7.34	4.72
2	Geological materials	7.3	6.5	8.3	-	6.12	8.52	6.55
3	Geological materials	7.5	6.2	6.5	-	7.45	8.76	4.35
4	Geological materials	7.5	7.2	7.6	-	6.57	7.84	3.17

Table 6. Content of heavy metals in samples from the area of "Novi Rudnitsi" mg/kg

Sample №	Pb	Cu	Ni	Mn	Fe	Zn
1. Geological materials	61.2	54.2	41.5	840	34200	145.0
2. Geological materials	55.4	45.7	34.2	720	26400	160.5
3. Geological materials	65.6	61.3	37.3	650	31500	157.0
4. Geological materials	60.7	57.2	44.6	810	29450	162.5

Norm = dose of CaO x 100/content of CaO in the material

According to the analytical data for the neutralization of the materials subject to liming, it is necessary to introduce 900 kg/da CaO. According to the above formula, with a content of 53% CaO in the calcareous materials, it is obtained:

Norm = 900 x 100/53 = 1700 kg/dka lime materials

According to our preliminary calculations, the liming rate is 1700 kg/da.

After liming and filling the cleared areas, it is proceeded to:

– spreading a layer of humus materials. The thickness of the layer is 40 cm. In this way, the necessary environment for the development of the root system of the grass species that will be used during the biological stage of reclamation will be provided.

– weeding, which will be done by sowing grass mixtures. When choosing the composition of the grass species, the specific soil-climatic and temperature conditions in the area of the site, the altitude, the type of terrain, etc. were taken into account. A preference is given to low-growing, long-lasting grasses that create a healthy and sustainable turf. The selection of species for grass mixtures is based on the aggressiveness and competitiveness of individual species according to the groups in which they fall:

– Group I – species with high competitive ability;

– II group – species with medium competitive ability;

– III group – species that are suppressed by the species of I and II groups.

In accordance with the above, the following types of grass are included in the composition of grass mixtures: sedge, red fescue and red clover.

Conclusion

As a result of the studies carried out, it was found that the area of the sulfuric acid plant is characterized by a content of heavy metals exceeding the upper threshold according to the requirements of the Dutch List of Standards for Soils and Groundwater with regard to copper. The nickel and zinc content indicates that the materials are not contaminated with these elements. No strict regularity is established regarding the amount of heavy metals in the analyzed sample, its location and the depth of collection.

Measures are foreseen to overcome the unfavorable characteristics of the soils, which include the following:

– clearing the site of the object;

– liming the field;

– filling the cleared areas with geological materials from the "Novi Rudnitsi" region, which are characterized by a sandy-clay mechanical composition, a neutral reaction to the environment and a low supply of the main nutritional elements for plants – nitrogen, phosphorus and potassium;

– spreading a layer of humus materials with a thickness of 40 cm;

– weeding, which will be done by sowing grass mixtures.

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