Bulgarian Journal of Agricultural Science, 26 (No 1) 2020, 192–197

Reclamation of heaps and industrial sites built in the region of Madjarovo mine (Bulgaria)

Martin Banov, Venera Tsolova[*] and Ivaylo Kirilov

Agricultural Academy, "N. Pushkarov" Institute of Soil Science, Agrotechnologies and Plant Protection, 1336 Sofia, Bulgaria
[*]*Corresponding author:* venera_tsolova@abv.bg

Abstract

Banov, M., Tsolova, V. & Kirilov, I. (2020). Reclamation of heaps and industrial sites built in the region of Madjarovo mine (Bulgaria). *Bulg. J. Agric. Sci., 26 (1)*, 192–197

The Madjarovo open pit for lead-zinc ore extraction is located in the land of Madjarovo city, Kardzhali District. The reclamation of technogenic territories build as a result of mining is legally carried out in two stages – (mine-) technical and biological reclamation. This article presents an option for technical and biological remediation of heaps and industrial sites built in the region of Madjarovo mine, based on the results of their pedogenic and agro-eco-chemical studies and good practices in the field of reclamation. The results show that in order to achieve an optimal restoration of natural landscape, a number of activities have to be carried out in these territories. In general, they are:

• Clearing the disturbed territories from constructional and other wastes and leveling.
• Amelioration to reduce the redistribution of metals-pollutants in environment.
• A topsoil formation by pilling of geological materials with appropriate physicochemical characteristics for complete alignment and improvement of anthropogenic territories.
• Grassing with suitable vegetation.

Keywords: mining; pollution; reclamation; amelioration; suitability

Introduction

Functioning of "Madjarovo" mine (including constructional, transport and operational activities) resulted in building of heaps and industrial sites that render the following negative impacts on environmental components:

– the natural relief and landscape are disturbed and transformed into industrial;

– soils and soil diversity is destroyed even when pre-existing humus and productive soil layers are seized up and deposited;

– biodiversity is also destroyed simultaneously with soils, mainly in forest territories;

– soils, water, air and vegetation are mechanically polluted by dust emissions from the mine;

– soils, water and vegetation are chemically polluted with heavy metals by their dissolution and transport through the water flow.

Similar problems have been identified in many mining areas in Bulgaria, indicating that major industrial and logistic activities, both, individually and together, contribute to a radical change of the environmental setting (Tsolova & Banov, 2017). It is often thought that identical problems enable identical solutions, but this would lead to new environmental problems if the specific nature of disturbed territory is not taken into account. For this reason, this article aims to propose an option for technical and biological reclamation of heaps and industrial sites built in the region of Madjarovo mine, based on the results of their pedogenic and agro-eco-chemical studies and good practices in the field of reclamation.

Materials and Methods

Soil survey

Literary data were used to identify the soil diversity in studied region (Soil Map of Bulgaria at M 1: 400000, 1968). The field study complies with FAO principles (2006) and specifics of studied sites, and includes two sampling methods:

– the standard BDS ISO 18400-205(2019) is applied in natural soils;

– in heaps and industrial sites (also called disturbed terrains) samples were taken at a depth of 0-20 cm according to a specially prepared scheme, shown in Table 1. Each sample was formed according to Bulletin № 27 (MA, 1994) as a mixture of 10 (ten) single samples. The geological materials suitable for reclamation (surface layer formation) of heaps and industrial sites have also been sampled to a depth of 20 cm in accordance with the same method (Table 1).

Laboratory assays

• Total organic carbon was determined by modified dichromate oxidation method of Kononova – Belchikova (Filcheva & Tsadilas, 2002). Humus content is calculated by multiplication of organic carbon content with the coefficient 1.724;

• The content of trace elements was determined after sample mineralization with aqua regia (ISO 11466:1995) via AAC (ISO 11047: 1998) on a Perkin-Elmer 2100;

• Total nitrogen content was quantified by modified Kjeldahl method (BDS ISO 11261:2002); content of mineral nitrogen (available forms) – by Bremner and Keeney procedure (1965).

• Total content of phosphorous – by Urumova procedure (1974); available content – method of Ivanov (1984);

• Soil samples were pre-treated according to BDS ISO 11464 (2012) standard;

• pH was measured in 2.5:1 water soil suspension (1 part soil and 2.5 parts deionized water) according to FAO protocol (2006).

• Particle size distribution – method of Kachinski (1958) was applied simultaneously with ISO 11277 (2009). This method differs from ISO standard mostly in sample pre-treatment (with NaOH) and sieve mesh sizes. The following sizes of major fractions are recognized by Kachinski: Sand – this fraction involves particles with 1.00-0.05 mm equivalent spherical diameter; Silt fraction – from 0.05 to 0.001 mm equivalent diameter; and Clay < 0.001 mm.

Pollution assessment

In order to estimate the degree of contamination of reclaimed sites the integrated indicator, sum of pollution index (PI*sum*) is used (Gong et al., 2008) simultaneously with the precaution values for heavy metals contents in soils (Ordinance № 3, 2008). It presents (eq. 1) the sum of pollution indices of all the individual elements named single pollution index (PI):

$$\mathrm{PI}sum = \sum_{i}^{m}\mathrm{PI}, \tag{1}$$

where m is the count of heavy metals;

i – each metal determined.

Single pollution indexes (eq. 2):

$$PI = \frac{Cn}{Bn}, \tag{2}$$

Table 1. Sampling scheme in heaps and industrial sites from the region of Madjarovo mine

Sample	Sample depth, cm	Location
1	0 – 20	Disturbed terrain below a gas station adjacent to a reclaimed plot
2	0 – 20	Disturbed terrain beneath a gas station bordering reclaimed plot
3	0 – 20	Disturbed terrain over a metal waste warehouse
4	0 – 20	Disturbed terrain over a metal waste warehouse
5	0 – 20	Heap under the emergency deposit of enrichment factory (EF), horizon 170, core 3
6	0 – 20	Heap under the emergency deposit of EF, horizon 170, core 3
7	0 – 20	Heap J 52, horizon 190, section “Momina Skala”
8	0 – 20	Heap J 52, horizon 190, section “Momina Skala”
9	0 – 20	Heap J 52, horizon240, section “Momina Skala”
10	0 – 20	Heap J 52, horizon240, section “Momina Skala”
11	0 – 20	Heap J 52, horizon290, section “Momina Skala”
12	0 – 20	Heap J 52, horizon 290, section “Momina Skala”
13	0 – 20	Heap J 52, horizon 340, section “Momina Skala”
14	0 – 20	Heap J 52, horizon 340, section “Momina Skala”
15	0 – 20	Heap J 55, horizon 190, section “Momina Skala”
16	0 – 20	Heap J 55, horizon 190, section “Momina Skala”

where *Cn* is heavy metal content in soil; *Bn*, background concentration of heavy metal (n) according to Ordinance № 3 (1996).

PI*sum* values are estimated on the following scale (Gong et al., 2008; Inengite et al. 2015):

PI*sum* < m, low degree of contamination; m ≤ PI*sum* < 2m, moderate degree of contamination; 2m ≤ PI*sum* < 4m, considerable degree of contamination; and PI*sum* > 4m, very high degree of contamination.

Results and Discussion

Pedogenic and agro-chemical characteristics of natural soils in the region of Madjarovo mine

The most widespread soil type among natural soils in the region was studied, since new terrains should have identical soil characteristics with surrounding soils according to existing normative documents in the country (Ordinance № 26, 1996; Law for soils, 1998). Studied Leached cinnamon forest soils, shallow, heavily eroded, light to heavy sandy-clay were formed on Pliocene and Old Quaternary carbonate and non-carbonate materials under the influence of dry rare forests and shrubs, and active erosion processes. They have a humus horizon of cinnamon color, with very hard consistence and lumpy structure. This horizon, 12 to 16 cm thick, abruptly transits in to a solid rock. Among particle size fractions dominated the medium and fine sand (up to 50.8%). It has medium to high (11.95-20.3 g/kg) organic carbon content (according to the scales introduced by Ordinance № 4, 2009) and very low to high total nitrogen content (0.96-2.28 g/kg). Carbon to nitrogen ratio indicates a medium to high enrichment of humus with nitrogen (C:N 9-12) and that may ensure good N flow. In terms of total phosphorus, soils are well supplied (2380-3900 mg/kg). Carbonates have not been established. The soil reaction (determined by FAO method, 2006) is strong to medium acidic (pH_{KCl} 4.4-4.7). According to the WRB (2014), these soils are: Someriumbric Leptosols (Siltic, Nechic) or Someriumbric Leptosols (Loamic).

Main factors that determine the pedogenesis of studied soils are climate, soil-forming materials and vegetation. The most characteristic feature of climate is a mild humid winter with relatively rare snowfall (due to its proximity to the Aegean Sea) and warm dry summers. The sum of winter rainfall is maximum and in the driest month, August, precipitation is 20 mm/m^2 on average. The ratio of winter and summer rainfall is typical of the Mediterranean climate region, although the studied area belongs to the Continental Mediterranean Climate Region and the South-Bulgarian Climate Sub-Region (Sabev & Stanev, 1963; Velev, 1990).

Soil forming materials are volcanic rocks from the andesite-basalt series of volcanic eruptions of the Madjarovo volcano (Sarov et al., 2008). The rocks have a basic to medium acid composition (shoshonite – latite), but medium acid prevails, and increased sodium and potassium content in places where hydrothermal change is actively developed. In most cases, content of K_2O is higher than Na_2O (Sarov et al., 2008). According to Marchev et al. (1994), these are hybrid rocks (mingled hybrids), formed by mixing a relatively primitive “basic” magma with latite. This explains the alternation of stripes with different composition and petrographic features in the rocks.

Predominant plant species in the past and now as well, are of the southern type of deciduous vegetation. Particularly typical are the communities of hornbeam, maple, oak and beech with a single undergrowth of hawthorn. Rare grassy vegetation is also observed.

Pedogenic and agro-eco-chemical characteristics of heaps and industrial sites in the region of Madjarovo mine

The analytical data obtained (Table 2 and Figure 1) testify for a strong influence of the Madjarovo mine production activity on chemical features of studied objects. Lead, zinc and copper are major trace elements in heaps and industrial sites (Figure 1) and quantitatively significantly exceed the

Table 2. Agrochemical parameters of heaps and industrial sites in the region of Madjarovo mine and their major descriptive statistics

Sample	Sample depth, cm	pH	$\sum NH_4+NO_3$ mg/kg	P_2O_5 mg/100 g
1	0 – 20	6.4	2.9	5.4
2	0 – 20	5.4	4.5	3.6
3	0 – 20	2.8	2.2	2.2
4	0 – 20	2.8	4.1	1.3
5	0 – 20	3.8	3.5	4.8
6	0 – 20	3.9	5.3	2.2
7	0 – 20	4.1	2.2	3.5
8	0 – 20	3.9	3.5	2.7
9	0 – 20	3.9	3.2	4.1
10	0 – 20	4.2	2.8	3.2
11	0 – 20	2.8	5.2	2.8
12	0 – 20	3.2	3.6	2.9
13	0 – 20	4.3	2.3	3.1
14	0 – 20	4.0	2.4	4.0
15	0 – 20	4.6	4.2	2.7
16	0 – 20	4.5	3.3	3.6
Mean		*4.0*	*3.5*	*3.3*
Max		*6.4*	*5.3*	*5.4*
Min		*2.8*	*2.2*	*1.3*
CL for mean (95.0%)		*0.5*	*0.5*	*0.5*

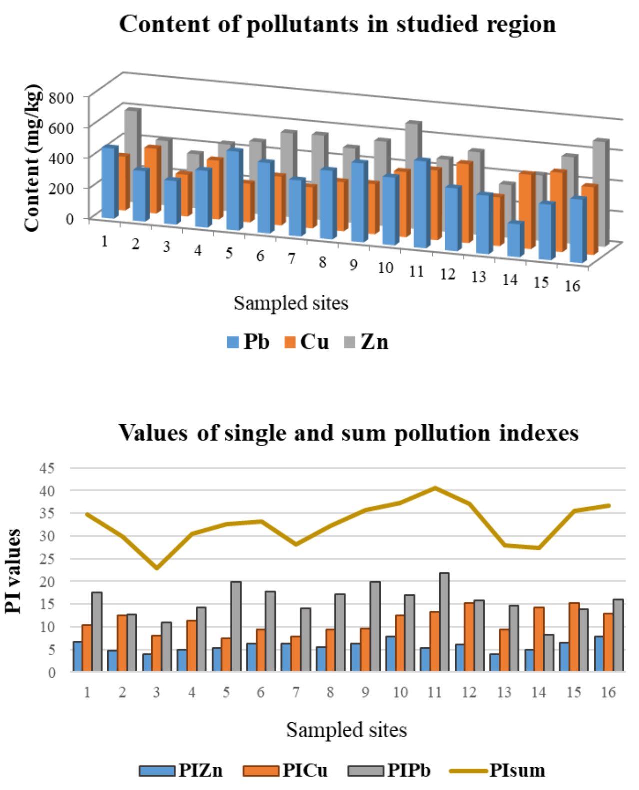

Fig. 1. Lead, copper and zinc contamination levels in heaps and industrial sites in the region of Madjarovo mine

maximum precaution values for heavy metals in soils (Ordinance № 3, 2008). Amount of Pb and Cu also exceeds the inventory concentrations which are considered very dangerous. The sum of pollution index also significantly exceeds the maximum value 12, and thus confirms very high toxicity of studied heaps and industrial sites (Figure 1). The reaction of medium, pH, varies from slightly acidic to strongly acidic and accelerates the mobility of trace elements and major nutrients (Table 2). An additional adverse circumstance is the low content of fine earth fraction in the samples, where the skeletal content ranges from 91.4 to 74.3%.

The established toxicity of studied plots requires the implementation of specific reclamation and engineering measures to prevent contamination. Field study showed that no collection of humus horizon of natural soils was carried out prior to the construction of man-made land (heaps and industrial sites). Therefore, we need of other materials with appropriate chemical and physical properties to form a surface layer of destroyed territories.

Pedogenic and agro-chemical characteristics of geological materials meant for reclamation

Geological materials that can be used for technical construction of surface horizon of disturbed and contaminated terrains are characterized with specific red-brown color. The coloring is probably due to the various iron minerals and their secondary weathering products, which give the characteristic color and properties of natural soils. These materials have pronounced adsorption properties in acidic media and can increase the effect of intended reclamation. Studied geological materials (reclamation substrate) are non-toxic but contain minimal amounts of nutrients, including organic carbon and must be also reclaimed to provide a good environment for vegetation growth. They are also slightly suitable physical media with sandy-clay texture (loamy sand, WRB classification).

Reclamation design

In order to achieve an optimal restoration of disturbed territories and natural landscape as well, a number of activities have to be carried out (Environment Protection Act, 2002; Law for soils, 1998; Law for preservation of the agricultural lands, 1996; Regulations for Implementation of the LPAL, 1997; Ordinance № 26, 1996). In general, they are:

• Clearing the disturbed territories from constructional and other wastes and leveling.

• Amelioration to reduce the redistribution of metals-pollutants in environment.

• A topsoil formation by pilling of geological materials with appropriate physicochemical characteristics for complete alignment and improvement of anthropogenic territories.

• Grassing with suitable vegetation.

Technical reclamation includes:

• Cleaning and leveling of the total area – 39.3 da, including horizontal part – 17.8 da and slopes – 21.5.

• Amelioration with 850 kg/da calcareous materials. This norm is calculated by the method of Ganev (1990) as an average value. Materials might originate from natural (in raw form or purified) and industrial sources. They must contain a sufficiently high amount of neutralizing substance (over 70% CaO or $Ca(OH)_2$) to achieve the required ameliorative effect at low financial cost. Calcareous materials must also be finely ground and enough dry to be evenly distributed by depth and do not contain heavy metals in toxic concentrations or other impurities harmful to humans and plants. Lime materials from the area of Dimitrovgrad city would reduce the costs of reclamation.

• Pilling of geological materials to form a surface layer 30 cm thick.

Design of biological reclamation activities:

• Manure addition in norm 6 t/da.

• Grassing and fertilization.

Herbaceous species: white clover (*Trifolium repens*), red clover (*Trifolium pretense*), red fescue (*Festuca rubra*), meadow fescue (*Festuca pratensis* Huds.) and birdsfoot (*Lotus corniculatus*) are preferable for reclamation. They are resistant to dry climatic conditions in the region and not very pretentious to soil environment (Tsolova & Krasteva, 2008; Tsolova et al., 2012). They are not very competitive and may grow together. The grassing mixture, with the sowing rate in total 12 kg/da, will be form as follows: white clover – 3 kg/da, red clover – 3 kg/da, red fescue – 3 kg/da, meadow fescue – 2 kg/da and birdsfoot – 1 kg/da.

Fertilization will be carried out with ammonium nitrate – 25 kg/da and superphosphate – 31 kg/da.

These activities should be performed in the following technological order:

– application of phosphorus fertilizer (superphosphate);

– surface tillage by disc till 10 cm;

– sowing the grass mixture – in early spring /March – April/;

– post-seeding rolling;

– application of N fertilizer – twice, in April and early June, to make nitrogen absorption more complete.

Conclusion

Functioning of Madjarovo mine (including logistic and operational activities) resulted in building of heaps and industrial sites that have negative impacts on the environment related to destruction of natural relief, disturbance of soil and biodiversity, pollution of soils, water, air and vegetation in the mine area, formation of industrial landscape.

In order to overcome the identified adverse effects, several major activities is envisaged: clearing and leveling the surface; amelioration (reclamation) by lime materials; topsoil formation by pilling of geological materials with appropriate physicochemical characteristics for complete alignment and improvement of anthropogenic territories; fertilization and manuring; grassing with suitable vegetation.

References

BDS ISO 11261 (2002). Soil quality – Determination of total nitrogen – Modified Kjeldahl method.

BDS ISO 11464 (2012). Soil Quality – Pretreatment of Samples for Physico-chemical Analysis.

BDS ISO 18400-205 (2019). Soil quality – Sampling – Part 205: Guidance on the procedure for investigation of natural, near-natural and cultivated sites (ISO 18400-205:2018).

Bremner, J. M. & Keeney, D. R. (1965). Steam distillation method for determination of ammonium, nitrate and nitrite. *Annal. Chim. Acta, 32,* 485-495.

Environment Protection Act. (2002). DV item 91 (last amended, DV item 98, 28.11.2014). (Bg)

FAO (2006). Guidelines for soil description. Fourth edition. Food and agriculture organization of the United Nations, Rome, 97 p.

Filcheva, E. & Tsadilas, C. (2002). Influence of clinoptilolite and compost on soil properties. *Communications of Soil Science and Plant Analysis, 33, 3-4,*595-607.

Ganev, S. (1990). Modern Soil Chemistry. *Science and Art*, Sofia, 371 (Bg).

Gong, Q., Deng, J., Xiang, Y., Wang, Q. & Yang, L. (2008). Calculating pollution indices by heavy metals in ecological geochemistry assessment and a case study in parks of Beijing. *Journal of China University of Geosciences, 19(3),* 230–241. https://doi.org/10.1016/S1002-0705(08)60042-4.

Inengite,A. K., Abasi, C. Y. & Walter, C. (2015). Application of pollution indices for the assessment of heavy metal pollution in flood impacted soil. *International Research Journal of Pure & Applied Chemistry 8(3),* 175-189. DOI https://doi.org/10.9734/IRJPAC/2015/17859

ISO 11047 (1998). Soil Quality – Determination of Cd, Cr, Co, Cu, Pb, Mn, Ni and Zn in Aqua Regia Extracts of Soils – Flame and Electrothermal Atomic Absorption Spectrometric Methods.

ISO 11277 (2009). Soil quality – Determination of particle size distribution in mineral soil material – Method by sieving and sedimentation. 2nd edition.

ISO 11466 (1995). Soil Quality – Extraction of Trace Elements Soluble in Aqua Regia. Switzerland.

IUSS Working Group WRB (2014). World Reference Base for Soil Resources 2014. International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports № 106. FAO, Rome.

Ivanov, P. (1984). A new acetate-lactate method for determination of plant available phosphorus and potassium in soil. *Soil Science and Agrochemistry*, *4,* 88-98 (Bg).

Kachinski, N.A. (1958). Textural and Microaggregation Composition of Soils, Methods for Study It. Moscow (Ru).

Law for Preservation of Agricultural Lands (1996). DV item 35 (last amended and supplemented, DV item 83, October 9, 2018) (Bg).

Law for Soils (2007). DV item 89, 6 November 2007 (Bg).

Marchev, P., Raicheva, R. & Larson P. (1994). Magma mixing in a collisional setting: preliminary data from the tertiary volcanism in the Eastern Rhodope mountains, Bulgaria. *Reports of BAS, 47(3),* 63–66 (Bg).

Ministry of Agriculture (1994). Instruction for determining the type and extent of pollution of agricultural soils by settlements and the regime of their use. Information Bulletin № 27 (Bg).

Ordinance № 3 on Norms for Admissible Content of Harmful Substances in Soil (2008). DV item 71/12 August 2008 (Bg).

Ordinance № 4 of January 12, 2009 on Soil Monitoring. Ministry of Environment and Water. DV item 19/13 March 2009 (Bg).

Ordinance № 26 for Reclamation of Disturbed Terrains, Improvement of Poorly Productive Lands, Removal and Utilization of Humus Layer.(1996). DV item 89 (Bg).

Regulations for Implementation of the Law for Preservation of Agricultural Lands. (1996). DV item 84 (amended and supplemented item 100/97) (Bg).

Sabev, L. & Stanev, Sv. (1963). The Climatic Regions of Bulgaria and Their Climate. *Zemizdat*, Sofia, 180 (Bg).

Sarov, S., Yordanov, B., Georgiev, S., Valkov, V., Balkanska, E., Grozdev, V., Marinova, R. & Markov, N. (2008). Explanatory Note to the Geological Map of the Republic of Bulgaria M 1:50 000, map sheet K-35-88-B (Madjarovo). Ministry of Environment and Water and Bulgarian National Geological Survey. Unicorp Ltd., Sofia, 125 (Bg).

Soil map of Bulgaria in M 1: 400 000.Sofia, 1968 (Bg).

Tsolova, V. & Banov, M. (2017). Accumulation of microelements in technogenic ecosystems from the vicinity of the "Medet" opencast mine. *Bulg. J. Agric. Sci., 23 (6)*, 1011–1015.

Tsolova, V. & Krasteva, V. (2008). Relative evaluation of anthropogenic soils. *Soil Science, Agrochemistry and Ecology*, *1,* 18-25 (Bg).

Tsolova, V., Hristova, M., Krasteva, V. & Kolchakov, V. (2012). Relative evaluation of Technosols.III. Suitability for forage crops cultivation. *Soil Science, Agrochemistry and Ecology, XLVI (1)*, 42-50 (Bg).

Urumova, A. (1974). Method for decomposition of samples for determination of total nitrogen and total phosphorus in soil. *Soil Science and Agrochemistry*, *5* (Bg).

Velev, St. (1990). The climate of Bulgaria. *Narodna Prosveta*, Sofia (Bg).

Received: July, 22, 2019; *Accepted:* October, 15, 2019; *Published:* February, 29, 2020