

ASSESSMENT OF SOIL CONTAMINATION ON THE AREA OF 'CUMERIO-COPPER'

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The main activity of 'Cumerio copper' Sa is pyro-metallurgical processing of sulfide copper concentrate. The nature of carried out many decades (about 50 years) intensive production activity is related to contamination of the lands and the soils. Prospecting of the status and stage of soil contamination on the territory of the ground is completed by field exploration of the territory and laboratory tests. The sampling is done by hand drilling equipment 'geological cane' on depths: 0–0,05 m; 0,05–0,1 m; 0,1–0,2 m; 0,2–0,4 (0,6) m. The samples are analyzed to determine total sulphur and its forms (sulphide and sulphate), active soil acidity, content of heavy metals and metalloids (Cu, Pb, Zn, As, Cd). The analyses are carried out according ISO methods. The results show that the production activity on pyro-metallurgical processing of sulfide type copper concentrates impact strongly on: soil genesis integrity disturbing; degradation processes – increased acidity of near surface soil layers (0–5 cm); the soils are contaminated mainly by heavy metals and metalloids – Cu, Pb, Zn, As and Cd (total and mobile states); higher concentrations of total sulphur content in the near surface layers (0–5 cm).

Key words: soil contamination, heavy metals, acidification.

Ключови думи: замърсяване на почвите, тежки метали, киселяване.

Introduction

The main activity of 'Cumerio copper' Sa is pyro-metallurgical reprocess of sulfide copper concentrate. The nature of carried out many decades (about 50 years) intensive production activity ('Cumerio copper' SA) is related to contamination of the lands and the soils (1). It is by: contamination of the soils by heavy metals and metalloids, degradation, related to changes of pH (acidity) and mechanical disturbing – of the surface soil horizons or soil genesis.

The aim of this investigation was analysis and assessment of status and stage of soil contamination on the territory of the ground 'Air divide workshop' - 'Cumerio copper' SA and 'AIR LIQUID' SA Pirdop town.

The objects of this investigation were lands and soils on the territory of the 'Air divide workshop' – 'Cumerio copper' and 'AIR LIQUID' SA.

Methodology

Prospecting of the status and stage of soil contamination on the territory

of the ground 'Air divide workshop' is completed by: field exploration of the territory of the 'Air divide workshop and laboratory tests by license laboratories.

Six soil bore holes are done to determine environmental soil condition on covered by buildings and equipment areas (PB1–PB6). The dense and location of the borehole network is determinate in relation to cover all building and equipment free area in the prospected territory. The sampling places are located in western, southwestern, southern (2 samples), southeastern and northeastern areas of the workshop territory (see scheme number 1). Every sampling point is formed as average of 3–4 single samplings. The total depth of the hand drilling equipment is 11.3 m.

The sampling is done by hand drilling equipment 'geological cane'. It is core type, and done on following depths: 0–0.05 m; 0.05–0.01 m; 0.01–0.02 m; 0.02–0.04 (0.06) m. Six shallow boreholes are done (PB1–PB6). Average soil samples (24 numbers – P1–P24) are taken. The sampling is according BDS (Bulgarian State Standard) 17.4,5,01-85 and Instruction number RD-00-11/1994.

The samples are analyzed to determine total sulphur and its forms (sulphide and sulphate), active soil acidity, content of heavy metals and metalloids (Cu, Pb, Zn, As, Cd).

The analyses are carried out according following methods:

- Sample preparation – ISO number 11466;

- Total sulphur and its forms (sulphide and sulphate) – ICPOES after

acid leaching;

- Active acidity (pHH₂O) – BSS ISO 10390;

- Total and mobile forms of heavy metals – ISO 11466, BSS ISO 11885.

Out coming chemical analyses results of the samples are compared to the requirements of the Bulgarian normative acts (Regulation number 3/2008). The aim of this comparison is to assess stage of contamination on prospected grounds.

Results

Soil disturbance

The territory of the 'Air divide workshop' is 28.825 dka. The natural soils are partly scraped up / fill up by coarse aggregate, cover with asphalt and concrete, in ground building because relief features (terrain slope on S, SW). The soils on the 'Air divide workshop' are of disturbed or totally destroyed surface soil layer by building activities and vertical planning according normative acts in Bulgaria. The little open areas, projected as 'area of greenery' are 6.772 dka. They are built up by filled up soils and terrestrial masses preserved in the Plant building.

Morphology

The morphological profile of the soils is characterized by token samples. They show distinct features of anthropogenic origin. These features are observed on entire ground area. The soils are poured into compressed masses of felt

and gravel. They are mixed with sandy fraction on same places. The poured in soil materials are of small thickness (about 30–35 cm). They are built up probably by Delluvial Fluvisols and /or Hromic Luvisols soils (widely developed in the region).

Active soil acidity ($\text{pH}_{\text{H}_2\text{O}}$)

The not disturbed soils in the region of 'Cumerio copper' SA are characterized by strongly acidic pH (4.1–4.6 for Delluvial soil) and (4.6–4.8 for Hromic Luvisols) reaction in water. Carbonates have not been detected in the soil profile.

Out coming analytical data of active soil acidity on the territory of the

workshop show acidic results only in shallow soil layers (0–5; 5–10 cm) – fig. 1. These results probably are related to: 1). Past melioration, carried out to decrease soil acidity; 2). Processes of degradation of the soil, affecting only shallow layers; 3). Alkaline to strongly alkaline reaction in depth. It is related to presence of strongly congest gravel layer of carbonate origin.

Heavy metals and metalloids

The results from carried out prospecting and investigations of heavy metals and metalloids content in filled up soils on the territory of the 'Air divide workshop' – 'Cumerio copper' are presented in Table 1. The heavy metals and metalloids

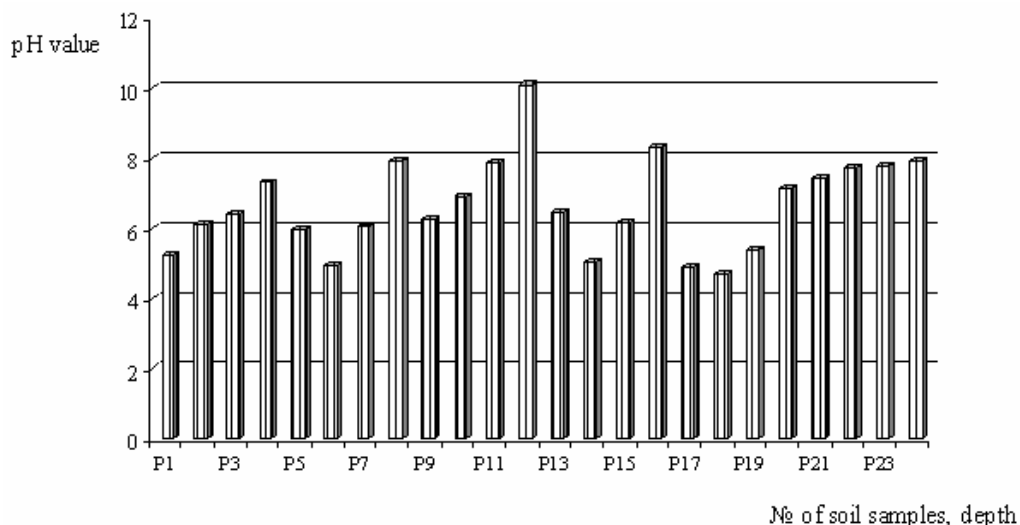


Fig. 1. Changes of pH values of the soil sin 'Air divide workshop' – 'Cumerio Copper'
Фиг. 1. Промяна в стойностите на pH в почви от цех „Сгъстен въздух“ – „Кумерио Мед“

Note: Number of soil sample, contains carried out soil drillings on depth: PB1: P1 (0–5); P2 (5–10); P3 (10–20); P4 (20–40); PB2: P5 (0–5); P6 (5–10); P7 (10–20); P8 (20–45); PB3: P9 (0–5); P10 (5–10); P11 (10–20); P12 (20–45/60); PB4: P13 (0–5); P14 (5–10); P15 (10–20); P16 (20–50); PB5: P17 (0–5); P18 (5–10); P19 (10–20); P20 (20–45); PB6: P21 (0–5); P22 (5–10); P23 (10–20) and P24 (20–60). PB – prospecting borehole

Table 1
Таблица 1

Heavy metals content and pH in soil samples – 'Air divide workshop' – 'Cumerio corper' SA, mg/kg
Съдържание на тежки метали и рН в почвени проби – „Цех за разделяне на въздуха”
– „КУМЕРИО МЕД” АД, mg/kg

Borehole number номер на сондаж	Sample number № проба	Depth, дълбо- чина, cm	pH H2O	Heavy metal and metalloids content, mg/kg съдържание на тежки метали и металоиди, mg/kg									
				Cu	CuMAC CuMDK	Pb	PbMAC PbMDK	Zn	ZnMAC ZnMDK	As	AsMAC AsMDK	Cd	CdMAC CdMDK
PB1	P1	0-5	5.23	10781	500	257	500	270	600	45	40	6	10
	P2	5-10	6.13	1313	500	51	500	126	600	12	40	2	10
	P3	10-20	6.44	1125	500	46	500	114	600	10	40	1	10
	P4	20-40	7.31	600	500	63	500	155	600	7	40	1	10
PB2	P5	0-5	5.96	41731	500	705	500	765	600	50	40	12	10
	P6	5-10	4.95	2253	500	65	500	185	600	12	40	4	10
	P7	10-20	6.06	1060	500	46	500	166	600	7	40	2	10
	P8	20-45	7.92	929	500	46	500	160	600	15	40	1	10
PB3	P9	0-5	6.28	27522	500	530	500	574	600	39	40	12	10
	P10	5-10	6.91	1269	500	39	500	150	600	6	40	4	10
	P11	10-20	7.78	762	500	38	500	130	600	5	40	2	10
	P12	20-45/60	10.12	516	500	40	500	150	600	9	40	1	10

PB4	P13	0-5	6.47	28620	500	456	500	661	600	49	40	11	10
	P14	5-10	5.04	1363	500	47	500	154	600	9	40	2	10
	P15	10-20	6.21	802	500	52	500	140	600	7	40	1	10
	P16	20-50	8.29	533	500	43	500	135	600	9	40	1	10
PB5	P17	0-5	4.90	8600	500	146	500	355	600	14	40	5	10
	P18	5-10	4.69	1654	500	50	500	140	600	7	40	2	10
	P19	1-20	5.37	1511	500	42	500	118	600	8	40	1	10
	P20	20-45	7.14	980	500	55	500	145	600	6	40	1	10
PB6	P21	0-5	7.46	7140	500	137	500	308	600	8	40	7	10
	P22	5-10	7.72	1189	500	47	500	140	600	6	40	1	10
	P23	10-20	7.78	815	500	46	500	133	600	6	40	1	10
	P24	20-60	7.91	328	500	43	500	115	600	7	40	<1	10

contamination stage of the soils is determine according Bulgarian State normative acts – Regulation number 3/2008. According Regulation number 3 related to limit of maximum allowable concentrations (MAC) of heavy metals and toxic elements in the soil (Regulation number 3/2008):

Copper – (Cu) content in the soils vary in large limits (328–41738 mg/kg). It exceeds many times MAC (in all prospected depths). Tendencies of accumulation of maximum concentrations of this element in near surface layer (0–5 cm) are well expressed. Copper concentration decreased in depth. The highest Cu concentrations (3–4 times higher then rest of core drillings) is detected in the surface layer of the soils located southern of the workshop in front of the fence (PB2, PB3 and PB4).

Lead – Pb content in the soils vary from 38 to 705 mg/kg. Only two samples (PB2, PB3) from near surface layer (0–5 cm) have Pb concentrations (1.06 to 1.41 times) MAC. The lead content data show relatively constant values in depth. These concentrations are below MAC. All concentrations are below intervention.

Zinc – Zn content in the

soils vary from 114 to 765 mg/kg. Zinc concentrations over MAC are detected only at depth of 5 cm (samples from prospecting boreholes PB2 and PB4). The MAC exceed is from 1.12 to 1.3 times. All concentrations are below intervention.

Arsenic – Measured As content in the soils vary from 5 to 50 mg/kg. The values over LAC are detected in near surface layer (0–5 cm) in samples from prospecting boreholes – PB1, PB2 and PB4. The MAC exceed is from 1.12 to 1.25 times. All concentrations are below intervention.

Cadmium – Measured Cd content in the soils vary from 1 to 12 mg/kg. The

accumulation of Cd in PB2, PB3 and PB4 is in depth 0–5 cm (concentrations over MAC). The Cadmium show similar behavior as Zn in this cens. All concentrations are below intervention.

Series of analyses to determine following components are carried out in relation to detected high acidity in near surface soil layers and high levels of copper content (over the interventional levels).

Sulphur state

The results of carried out analyzes of part of the soil samples aiming determine of sulphur state are presented in Table 2.

Table 2
Таблица 2

Content of total, sulphide and sulphate sulphur in soil samples – ‘Air divide workshop’ – ‘Cumerio copper’ SA, %

**Съдържание на обща, сулфидна и сулфатна сяра в почвени проби
от територията на „Цех за разделяне на въздуха“ – „КУМЕРИО МЕД“ АД, %**

Borehole number Номер на сондаж	Sample number № проба	Depth, дълбочина, cm	S total, S обща, %	S sulphide, S сулфидна, %	S sulphate, S сулфатна, %	pH _{H2O}
PB2	P5	0–5	3.21	0.175	3.035	5.96
	P6	5–10	0.078	0.047	0.031	4.95
	P7	10–20	0.08	0.035	0.049	6.06
	P8	20–45	0.276	0.023	0.253	7.92
PB3	P9	0–5	2.615	0.163	2.452	6.28
	P10	5–10	0.063	0.025	0.038	6.91
	P11	10–20	0.061	0.028	0.033	7.88

The receiver results of total, Sulphide and sulphate sulphur in soil samples show:

The total sulphur content varies from 0.061 to 3.21 %. Higher concentrations

over normally admissible values from soil samples in Bulgaria (2 %) are detected only in the near surface layers (0–5 cm), respectively 3.21 % and 2.62 %.

The sulfate (oxidized) state of the

sulphur prevails in the composition of the total one.

Lower content of total, sulphate and sulphide state of the sulphur is

characteristic for deeper soil layers.

The contamination potential of the soils as a function of total sulphur content is illustrated in Table 3.

Table 3
Таблица 3

Contamination potential of the soils as a function of total sulphur content
Потенциал на замърсяване, като функция от съдържанието на обща сяра

% S in soil % обща сяра в почвата	Contamination potential потенциал на замърсяване
< 0.5	no/ няма
0.5–2.0	average/среден
2.0–5.0	large/ голям
> 5.0	very large/много голям

Comparison of the data presented in this table show that aerosol contamination of the soil affect in higher degree shallow layers of the prospected soils.

Mobile state of heavy metals

The carried out soil analyzes results done to assess mobile state of heavy metals are presented in Fig. 2. The prove strong proportional relation between content of mobile copper and content of total copper in the soil and processes of increase of acidity. They are detected

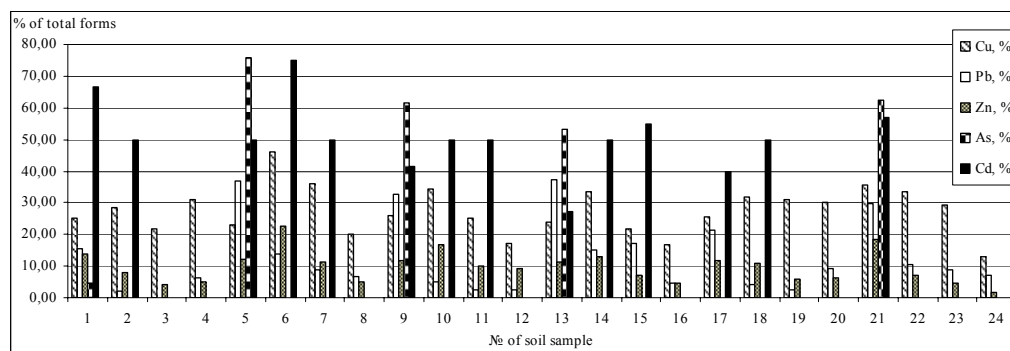


Fig. 2. Mobile state of heavy metals content (% of total presented states) in soil samples
Фиг. 2. Мобилни форми на тежки метали (% от общите количества) в почвени проби

Note: Soil samples, depths: PB1: 1 (0–5); 2 (5–10); 3 (10–20); 4 (20–40); PB2: 5 (0–5); 6 (5–10); 7 (10–20); 8 (20–45); PB3: 9 (0–5); 10 (5–10); 11 (10–20); 12 (20–45/60); PB4: 13 (0–5); 14 (5–10); 15 (10–20); 16 (20–50); PB5: 17 (0–5); 18 (5–10); 19 (10–20); 20 (20–45); PB6: 21 (0–5); 22 (5–10); 23 (10–20) and 24 (20–60). PB – prospecting borehole

in the near surface soil layers (0–5 cm; 5–10 cm).

Conclusion

1. The soils on the territory of 'Air divide workshop' - 'Cumerio copper' SA are strongly affected by long period of (about 50 years) production activities on pyro-metallurgical processing of sulfide type copper concentrates.

2. The production activity impact on soils located in the territory of the workshop is presented by: soil genesis integrity disturbing (dig out/pour in activities in workshop building – 22.053 dka, disturbed – build up, asphalted and

concreted areas 6.772 dka, formed by soil and terrestrial masses pour in), degradation processes – increased acidity of near surface soil layers (0–5 cm) – related to higher than standard content of total sulphur in near surface soil layers (0–5 cm). This is related to sulphate – oxidized sulphide sulphur and higher concentrations (over MAC) of heavy metals and metalloids – Cu, Pb, Zn, As, Cd (total and mobile states).

Referensis

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ОЦЕНКА НА ПОЧВЕНОТО ЗАМЪРСЯВАНЕ В РАЙОНА НА „КУМЕРИО-МЕД”

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Резюме

Основният предмет на дейността на „КУМЕРИО МЕД” АД е пирометалургично преработване на сулфидни медни концентрати. Естеството на провежданата многогодишна (около 50 години) и интензивна производствена дейност е свързано с увреждане на земите и почвите. Пробовземането е извършено с ръчна сонда „геоложки бастун”, ядково на дълбочини 0–0,05 m; 0,05–0,1 m; 0,1–0,2 m; 0,2–0,4 (0,6) m. **Пробите са анализирани** за определяне на обща сяра и нейните форми (сулфатна и сулфидна), активна почвена киселинност, съдържание на тежки метали и металоиди (Cu, Pb, Zn, As, Cd). **Анализите са** изпълнени по ISO методи. Резултатите показват, че пирометалургичното преработване на сулфидни медни концентрати въздейства силно върху: нарушаване на цялостния генезис на почвата; проява на деградационни процеси – вкисляване на повърхностните почвени пластове (0–5 cm); замърсяване на почвите с тежки метали и металоиди – Cu, Pb, Zn, As and Cd (общи и мобилни форми); високи концентрации на обща сяра в повърхностните почвени пластове (0–5 cm).