SURFACE AND UNDERGROUND WATERS' POLLUTION IN PROCESSING OF Pb-Zn MINE 'SASA' M. KAMENICA, R. MACEDONIA

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ABSTRACT
Natural waters (surface and underground) are the main source which provides the necessary quantity of drinking water as well as water for various industrial and agricultural needs. The discharge of the infected waters into the natural recipients can lead to environmental pollution and disrupt the ecological balance in the water ecosystem.
The pollution as a consequence of the mining activities comprises the pollution of acid mining waters, hard metals, chemical reagents from the process of production, suspended materials and detached and overflow of waters in the hydro-refuse dumps.
The most serious problem from an ecological aspect, connected to the flotation slag, is the discharge of the infected waters in the surface underground flow.
The long-term discharge of the infected waters into the waters of the river Kamenicka, a great part of the vegetal and animal forms will be destroyed and their place will be replaced with those plants and animals that have a greater level of resistance.
The figures presented in this paper are from the latest research concerning the presence of hard and toxic metals from the samples of the river Kamenicka.
Key words: *Kamenicka river, mining waters, hard metals, underground and surface waters, pollution, hydro-refuse dumps, mine Sasa.*

1.0 INTRODUCTION

Waste material which are contained in the tailing of the hydro dump Sasa though the Kamenicka River in the hydroaccumulation Kalimanci. Water of the hydroaccumulation Kalimanci is used for irrigation, and part of it flow into Bregalnica River. Waste waters of the Kamenicka River, hydroaccumulation Kalimanci and the Bregalnica River contaminate land (sediments and soil), and also the underground waters accumulation in the wells which are located on the flow of the Bregalnica River.

The tailing which is disposed in the hydro-dump Sasa is waste derived from the process of selective flotation concentration in which concentration of the lead and zinc minerals are concentrated. The composition of the waste minerals is directly connected with the type and quantity of the flotation reagents, sharacteristics of the processed ore, process of enrichment and also pH value of the pulp. The liquid phase of the flotation tailing is composed of highly mineralized waste water with increased concentrations of sulphates, heavy metals, phenols and other toxic materials.

According to the geographical position of the investigated terrain and the direction of the waste waters, there is possibility of contamination of the underground waters.

Preliminary investigation results of this type can be found in the publication from (Mircovski, Spasovski at al. 2004, [1]; Spasovski at al. 2007, [2]; Spasovski, Doneva, 2007, [3][4]), Spasovski, Mitev, 2009 [5].

2.0 Geological and hydro-geological characteristics of terrain

The moving of the waste waters underground depends of the hydro-geological characteristics of the terrain, which will be further present more detailed. On the investigated terrain are Quaternary alluvial sediment of the Kamenicka River and Neogene sediments in the vicinity of Kamenica and on the left side of the Bregalnica River in the vicinity Kocani.

Alluvial sediments of the Kamenicka River consist of sand, gravel, and on some places sandy clays. This composition of the alluvial sediments made it possible accumulation of significant quantities of waste water with possibility of contamination if the sediments and soils. Neogene sediments in the vicinity of Kamenica and on the left side of the Bregalnica River in the vicinity of Kocani are made of marly clays and Quaternary alluvial sediments presented by clays, sandy clays, sands and gravels.

There are open type wells on the investigated terrain with free level in which the level of underground water is near the surface. Good filtration coefficient and direct hydraulic connection with the Kamenicka River shows the possibility of contamination of the underground waters, sediments and soils with the waste from the hydro-dump of the Sasa mine.

2.1 Materials and methods

Preliminary field investigations were carried out in order to obtain essential data in the terrain. It included data on the Kamenicka River water courses slected as possible station for sample collection.

Samples from water flows and spring were collected in order to obtain data no the most critical points in terms of heavy metal contamination and how to direct future sampling and analyses.

Water samples werw collected below the flotation tailing pond whosw drainage waters flow into the Kamenicka River (fig. 1).The aim was to determine the effect that the mining activites and tailing pond have on the distribution of heavy and toxic metals in waters.

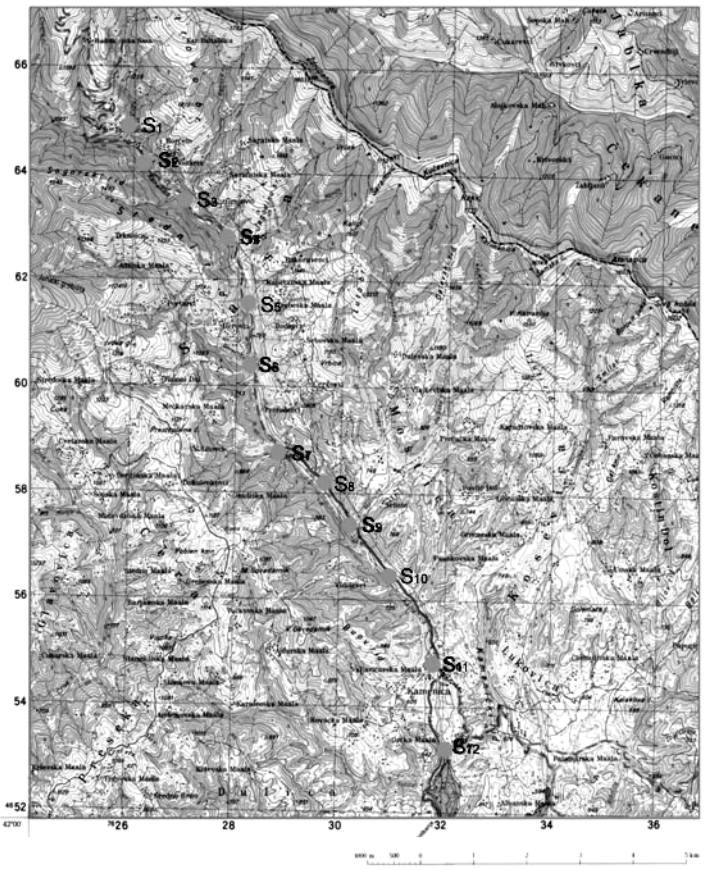

Fig.1. Topographic map with the sampling points

Water sampling was done with plastic syringe from the middle part of the water flow. The 50 ml of water from the syringe was transferred into a plastic vessel. It is of note when the water is transferred from the ssyringe to the vessel it is filtred through a paper filter the openings 45 µm. Acidizing with 0.4 ml of 50% nitric acid is done before closing the vessel. This is done to avoid settling of metals on the wall and bottom of the vessel.
The samples werw taken to laboratory for hemical analysis for heavy metal determination with AES-ICP.

3.0 Results and discussion

The results obtained from flowing water samples are given in Table 1, with comparison between maximum allowable (MAC) concentracion of heavy and toxic metals for III – IV classes.
Data shown in Table 1 make it possible to define the amount of heavy metals in the Kamenicka River water and its tributaries and the reasons for their occurrence.
Based on the data presented in Table 1, certain constants can be given concerning the presence of particular hard metals in the waters of the Kamenicka River in a distance between the hydroacumulation Kalimanci, as well as an opinion for the reasons which can contribute for the increased contents of particular metals.

Table 1. *Contents of heavy metals in flowing waters in the surrounding of the Sasa Mine (mg/l).*

Sample	**Pb**	**Zn**	**Cd**	**Fe**	**Mn**	**Cu**
S_1	1,13	0,030	0,016	0,059	0,059	0,01
S_2	1,041	16,751	0,123	0,120	8,740	1,270
S_3	0,305	9,210	0,059	0,063	2,325	0,381
S_4	6,00	12,034	0,094	0,103	3,370	0,121
S_5	12,44	13,780	0,051	0,021	2,320	0,01
S_6	0,034	1,701	0,083	0,034	0,694	0,01
S_7	0,109	1,687	0,025	0,060	14,720	0,051
S_8	0,030	0,746	0,009	0,076	0,823	0,054
S_9	0,058	0,491	0,020	0,405	0,305	0,017
S_{10}	0,156	0,379	0,022	0,539	0,211	0,052
S_{11}	0,051	0,238	0,027	0,133	0,330	0,017
S_{12}	0,049	0,053	0,030	0,090	0,079	0,017
Standard	**0,03**	**0,20**	**0,01**	**1,000**	**1,000**	**0,05**

The data for the concentration of zinc (Table 1) indicate its increased presence in most of the samples which were analyzed. The greatest concentrations of zinc are found in the sample S_2, which are 16.751 mg/l. The increased concentrations of zinc are also found in the samples: S_4, S_5, S_6, S_7, S_8, S_9 and S_{10}. In the remaining samples the concentration of zinc is present in amounts less than the standard ones. Generally, it can be concluded that the entire research area is contaminated with zinc. The increased concentrations of zinc are a result of the active working of the Mine for lead and zinc Sasa.
The increased concentration of lead are noticed in the samples S_5 (12,44 mg/l), S_4 (6,00 mg/l), S_1 (1,13 mg/l), S_2 (1,041 mg/l), S_{10} (0,156 mg/l), S_7 (0,109 mg/l), S_3 (0,305 mg/l), S_{11} (0,051 mg/l), S_9 (0,058 mg/l) and S_{12} (0,049 mg/l). It is obvious that increased concentrations of lead are found in most of the samples, but the great sample concentrations of lead are found in those samples where increased concentrations of zinc were also found, which confirms the statement of the great influence of the hydro-waste dump and the active working of the Mines Sasa for the pollution of the environment with these metals.

In all the samples cadmium is found in extremely larger concentrations compared to maximum allowed concentration. The great sample concentrations of cadmium are noticed in the samples S_2 (0,123 mg/l) S_3 (0,059 mg/l), S_4 (0,094 mg/l), S_5 (0,051 mg/l) and S_6 (0,083 mg/l). This behavior of the cadmium is due to its geochemical characteristics (easily soluble, low mobility). The increased concentrations of cadmium follow the parts which are contaminated with zinc because it geochemically follows the minerals in the zinc.

The increased concentrations of copper are found in most of the samples, but the great sample concentrations of copper found in the samples S_2 (1,270 mg/l), S_4 (0,121 mg/l) and S_3 (0,381 mg/l), while in the remaining samples the concentrations of copper are close or less than in maximum allowed concentration. The presence of the copper in the waters of river Kamenicka is a result of the occurrence of chalkopyrite in an association with the minerals of the lead and zinc.

Iron is present in concentrations lower than maximum allowed concentration and is not a significant contaminant of the drainage system of the river Kamenicka.

Attention should be paid for the high concentrations of the manganese in the samples: S_7 (14,720 mg/l), S_2 (8,740 mg/l) and S_4 (3,370 mg/l). The reason for the occurrence of the manganese in high concentrations in the waters of the river Kamenicka is a permanent hydro-waste dump in the direct environment of the river Kamenicka as a presence of the waste waters from the Mines Sasa.

Conclusion

Based on the results obtained from the analyses of the samples collected along the Kamenicka River it can be inferred that the drainge area is higly contaminated.

The increased concentracions of heavy metals are a consequence of the geological composition of the terrain, anthropologic activites such as early mining and stockpiling of waste material, the use of fertilizers in agriculture as well as the physical and chemical character of the water solutes.

It can be said in the end that the largest distribution and resulting contamination with heavy metals were found in the drainge stream leaving the mine and flowing into the Kamenicka. From ecological point of view this entails the need of rehabilitation of the area in oder to prevent flora and fauna intoxication in the water medium an the surrounding and prevent the negative effect on the health of the population.

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