6th BALKAN CONFERENCE
ON
MINERAL PROCESSING

PROCEEDINGS

September 18-21 1995 Ohrid
Republic of Macedonia

Organizers:

VI Balkan Conference

on

MINERAL PROCESSING

Editors

Prof. Dr. Boris Krstev, M.Sc, D.Sc
Blagoj Golomeov, M.Sc

Organized by:

Faculty of Mining and Geology, Stip

Commitee for Mineral Processing of the Republic of Macedonia

In Cooperation with:

Faculty of Mining and Geology, Belgrade, Yugoslavia
I. T. U. Mining Faculty, Istanbul, Turkey
University of Baia Mare, Baia Mare, Romania
University of Mining and Geology, Sofia, Bulgaria
Faculty of Geology and Mining, Tirana, Albania
University of Ljubljana, Ljubljana,Slovenia

Ohrid, Macedonia, 18 - 21.09.1995

Main Sponsor:

Mining and Metallurgical Copper Company
"BUCIM" Radovis

Sponsors:

Faculty of Mining and Geology, Stip
Ministry of Science in Government of the Republic of Macedonia
Open Society Institute - Skopje
Rudproekt - Consulting & Engineering Services, Skopje
Mining Institute, Mineral Processing Department, Skopje
REK "Bitola", Bitola
Opalit Mine, Cesinovo
"Sasa" Mine, M. Kamenica
HEK "Jugohrom", Jegunovce
"Fenimak", Skopje
"Sileks" Mine, Kratovo
"Zletovo" Smelter, T. Veles
"Zletovo" Mine, Probistip
"Toranica" Mine, Kriva Palanka
"Niko Petrol", Stip
"Zletovo - Sasa" D.O.O., Skopje
"Goldmak", Radovis

INTERNATIONAL SCIENTIFIC COMMITTEE

Prof. Dr. Kirjak Kovachev, Bulgaria (President)
Prof. Dr. Mijalce Nikolovski, Macedonia
Prof. Dr. Dusan Salatic, Yugoslavia
Prof. Dr. Paraschiev Ilie, Romania
Prof. Dr. Guven Onal, Turkey
Prof. Dr. Mirko Perisic, Slovenia
Prof. Dr. Kimet Fetahu, Albania

ORGANIZING AND EXECUTIVE COMMITTEE

Prof. Dr. Mijalce Nikolovski, Chairman
Prof. Dr. Boris Krstev, Vice Chairman
Boris Fidancev, Vice Chairman
Mr. Blagoj Golomeov, Executive Secretary
Mr. Mirjana Golomeova, Secretary
Vangel Karagunov, Interpreter

MEMBERS

Prof. Dr. Blazo Boev
Prof. Dr. Vanco Cifliganec
Prof. Gjorgji Orovcanov
Mr. Risto Grozdanov
Mr. Klime Arsov
Zivko Gocev
Spase Iliev
Dragan Spasovski
Petre Runcev
Stevko Bosevski
Blagoj Petrov
Stanko Vladimirov
Trajce Jovanovski
Mile Mitovski

КОНЦЕНТРАЦИЈА НА ТЕШКИ МЕТАЛИ ВО ВОДИТЕ НА КИСЕЛИЧКА РЕКА И ТЕЧЕНИЕТО НА ЗЛЕТОВСКА РЕКА

CONCENTRATION OF HEAVY METALS IN THE WATERS OF THE RIVER KISELICKA AND THE REACH OF THE RIVER ZLETOVSKA

S. LEPITKOVA[*] & B. BOEV[*]

Introduction

The survey district (Fig. 1) is situated near the towns of Probistip and Zletovo and from geologic aspect it belongs to the Kratovo-Zletovo volcanic area which contains various mineralization styles and lead-zinc deposits. The abundant lead and zinc occurrences in the whole geochemical district resulted in increased concentration of these elements in individual geochemical environments such as soil, water and so on. Fortunately, the concentrations are within the allowed limits and the environment is not polluted by these elements.

Technological processes used in flotation plants dump waste waters in special waste dumps. Waste waters flow into rivers or tributaries without being cleaned .

Our investigations covered river waters which flow close to waste dumps in order to discover whether certain elements, first of all those which belong to the group of heavy metals, can be found and to determine the distribution pattern.

Methods

Methods of work included several stages:

- Initial sampling: Sampling depends upon the possible infuence of waters on the soil with the course of time time. For example spacial variations in lakes is a consequence of the stratification of the cold and warm water. In rivers it is a result of the influence of the water from tributaries and water of the river itself which do not mix several kilometers in length. Samples were taken avoiding taking grounds. Vessels and conservation reagents were clean and a bathometer was used.
- Filtering: Natural waters always contain hard waste substances which increase the content of dissolved elements. The sample was filtered by a 0.45 micron membrane filter on the spot and the amount of water that passed through the filter was regarded as solution.
- Collecting: The best way to preserve the relations of the cations of the composition of the chemical elements in waters are vessels of white polyethylene or polypropylen cloth. A short period of time in boronsilicate glass was allowed. In such case there is always a risk of forming an envelop of boron alkali element between the vessel and the water. Vessels

[*]Faculty of Mining and Geology, Stip

were prepared for additional use after keeping it in 1 % triton solution for 24 hours and rinsing it by 1:20 deluted nitric acid.

- ◊ Stabilization: Samples were preserved by a 1% mineral acid solution. It is common to add 1 to 2 ml pure nitric acid into 1 litre water sample. This step lowers the ion chemosorption and prevents the hydrolysis process. In some cases preservation by nitric acid is necessary (when analysis is carried out by hydride generator). Samples were kept on temperature from 0 to 4 C and the best thing is the samples to be frozen. Special attention was paid to possible chemical effects when introducing the stabilazers.
- ◊ Analytical methods: Collected materials or water samples were analized by atomic absobtion spectrophotometry and method of inductive joint plasma was applied.

Results and Discussion

Water samples of the Zletovo, Koritnica, Globica, Strmos, Buciste, Ziganci and Ularci sites were analysed. The results obtained are shown in Table 1:

Table 1: Heavy metal content in water given in mg/l

Measure site	Pb	Zn	Fe	Mn	Cd
Zletovo	0.041	0.054	0.357	0.056	0.004
Koritnica	0.131	2.071	3.660	87.36	0.018
Globica	0.081	0.176	0.383	0.066	0.009
Kiselica	0.952	0.026	1.191	76.45	0.029
Strmos	0.171	2.445	1.999	89.97	0.026
Buciste	0.429	0.577	1.417	9.73	0.017
Ziganci	0.119	0.159	0.225	0.197	0.019
Ularci	0.078	0.095	0.214	0.196	0.013

Zletovo measure site was taken as a standard for relative pure water in the district. If we compare the results obtained with those related to the allowed concentrations of heavy metals in individual waters in Table 2. we will come to the conclusion that: the concentration of heavy metals under consideration in the Zletovo measure site is within the allowed limits for first category of waters. This means that they are relatively clean drinking waters, although they pass through an environment which is polluted by heavy metals. It can also be inferred that solubility of lead, zinc, manganese, cadmium which are present in rocks is relatively low.

Table 2: Heavy metal concentration in individual categories of waters mg/l

	1 and 2 category	3 and 4 category
Pg	0.05	0.1
Zn	0.2	1.0
Cd	0.005	0.01
Fe	0.3	1.0

The concentration of all mentioned heavy metals in the Koritnica measure site is far over the allowed. So those waters which belong to the fourth category should not be used as drinking waters. The concentration of heavy metals in that measure site is high because of he high pullution caused by the waste waters from the Dobrevo mine pits. The waste waters flow into the River Zletovska and take in concentrations of heavy metals.This is especially evident in the Globnica measure site which is located near the River letovska below the mouth of the River Koritnica. The concentration of heavy metals under consideration in this measure site is larger than that in the Zletovo measure site. The water belongs to the second category and as such it can be used as drinking water.

There is an enormous increase in concentration of heavy metals in the water of the River Kiselica. This small river flows close to the waste dumps of the Zletovo lead and zinc mines and all waste waters from the flotation processes flow into it. It is certain that insufficiently purified waste waters from the flotation plants pollute the river most. The water of this river belongs to the fourth category and is not used as drinking water.

The concentration of heavy metals in the Strmos measure site is also high because the site is located near the waste waters of the flotation plant. The water belongs to the fourth category and is not used as drinking water.

The Buciste measure site is located near the River Zletovska below the empty of the River Kiselicka into River Zletovska. Although the waters of the two rivers mix, the concentration of heavy metals is stll very high. The waters belong to the fourth category and are not used for drinking. If we compare the water of the River Zletovska in the Buciste site to the water in the Zletovo measure sites which are several kilometers far from each other we can find out that the water of the River Zletovska in the Buciste measure site is polluted by heavy metals which come from the waste waters of the Zletovo flotation plant.

In the Ziganci measure site which is several kilometers from the Buciste site along the River Zletovska course large concentrations of several heavy metals (lead, manganese, cadmium) can still be found. Based on these data it can be inferred that concentrations of heavy metals are still very high (over the allowed) and the polluted waters belong to the third category. As such they are not used as drinking water.

In the Ularci measure site which is located near the mouth of the River Zletovska into the Bregalnica only the concentration of cadmium is over the allowed. The water belongs to the fourth category. All other elements are within the allowed limits.

Conclusion

Based on the results of the investigations carried out it can be concluded that the influence of the waste waters from the Zletovo mines flotation plants on the waters of the River Kiselicla and the River Zletovska is high and they pollute the two flows. It can be concluded that there are increased concentrations of heavy metals in the waters along the whole river course. The lead and zinc mines in Probistip must take steps in purifying the waste waters which come out of the flotation plants in order to prevent the pollution of the River Zletovska and the ecosystem in the district.

The Pollution of the environment (the ecosystem) by the mining industry in the Republic of Macedonia

This paper deals with the manner of pollution by the Zletovo, Sasa and Toranica Pb-Zn mines which use underground method of mining, the Buchim Cu and Au mine as well as FENI Fe-Ni mine in which surface method of mining is applied. The paper also deals with

the disrupt of the natural environment by the surface mining operations in nonmetallic raw matarial excavation with special account of the Suvodol. Brik, Oslomej and Drimkol collieries. Besides the analysis of air and soil contamination, spacial emphasis will be placed on ground and underground water contamination which are of vital interst in the area. We should also bear in mind that the area of East Macedonia (the Ovce Pole) is the most arid part in Europe
(with annual precipitaion beneath 400 mm) which is an additional problem in the renewal of the hydro system. In this manner the contamination of the environment becomes more complex. The analysis carried out in the aforementioned mining industry will help categorize the regions and contaminators. An attempt will be made to urge each contaminator find most efficient and most economical methods in eliminating the contamination effect or its minimizing without disturbing the exploitation process in the mining of mineral resources in the mines under consideration.

References

1. A. Velickov, V. Ristova, I. Trajkov, i dr. 1990: Teskite metali olovo, kadmium, cink vo pocvata i zemjodelskite kolturi na podracjeto na Titov Veles, 3-Naucen sobir, Zastita na zivotnata sredina Titov Veles, 1993

2. S. Danova. T. Kojundzieva.: Sanitary chemical characteristics of heavy metals in Stara Zagora district

3. M. Nikolovski, 1991:Sostojba vo zastita od zagaduvanje na okolinata i procistuvanje na otpadnite vodi pri prerabotka na mineralnite surovini vo R. Makedonija IV Kolokvium za Podgotovka na mineralni surovini Belgrad, 1991