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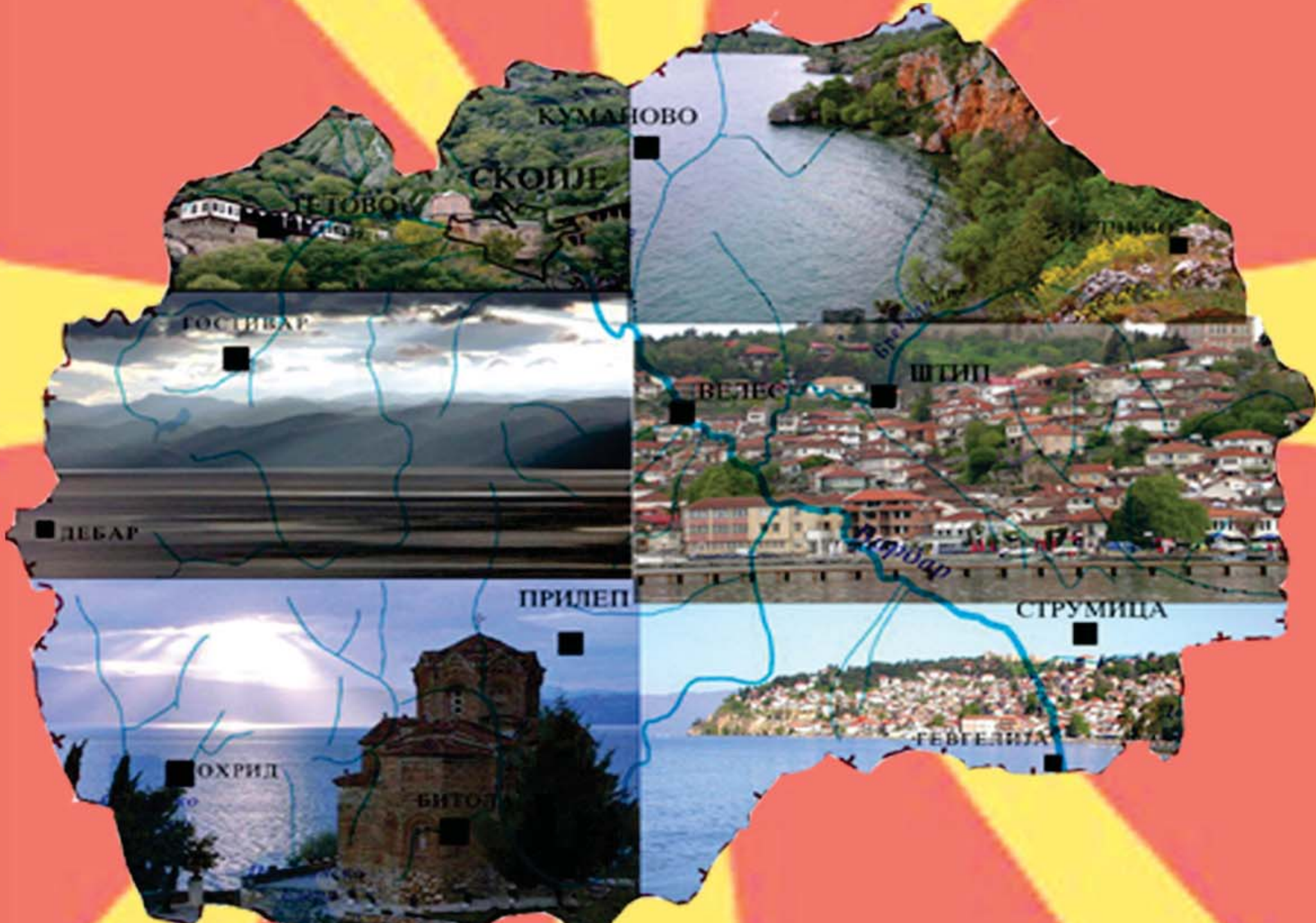
МАКЕДОНСКО ГЕОЛОШКО ДРУШТВО

ВТОР КОНГРЕС
на
Геолозите на Република Македонија

ЗБОРНИК НА ТРУДОВИ



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ПРЕДГОВОР

Геолошката наука на територијата на Република Македонија има долга традиција, а е поврзана пред се со рударската активност. Познати се локалитети каде се најдени монети од бакарната и бронзената доба. Сочувани се траги на експлоатација на злато од речниот нанос на Коњска Река-Гевгелиско и на други места, од времето на Александар Македонски. Во источна Македонија рударењето било интензивно за римско време.

Први геолошки податоци на научна основа за територијата на Македонија се јавуваат во првата половина на XIX век, а првите печатени геолошки трудови за нашите простори се среќаваат кај А.Буе (1828-1870) и Виксенел (1842). Од крајот на XIX век па се до денес во зависност од интензитетот на истражувањата напишани се голем број на трудови од сите области на геологијата.

Активностите на стручните лица од областа на геологијата се изведуваат преку Македонското Геолошко Друштво кое е формирано во 1952 година.

Во 2008 година се одржа Првиот Конгрес на Геолозите на Република Македонија од кој излезе зборник со преку 50 научни трудови од кои добар дел беа подготвени од меѓународни тимови.

Во периодот помеѓу 2008 и 2012 година во нашата земја се изведоа голем број на активности во сите полиња на геологијата. Особено важни да се споменат се интензивните истражувања на метални и неметални минерални суровини, регионалните, геохемиските и инженерско-геолошките, итн.

Вториот Конгрес на Геолозите на Република Македонија претставува сублимат на научните сознанија базирани на споменатите геолошки истражувања и испитувања кои се одвиваа на територијата на нашата земја во периодот од 2008-2012 година. Исто така, на конгресот е презентирана и дел од работата на колеги геолози од соседните земји, така да и овој пат со задоволство може да констатираме дека конгресот има меѓународен карактер.

PREFACE

Geological science on the territory of Republic of Macedonia has long tradition, and is mainly connected to the mining activities. There are numerous localities where coins from copper and bronze age are found. Traces from exploitation of gold in the river Konjska-Gevgelija and other places are known, in the time of Alexander the Great. In eastern Macedonia the mining was very intensive during the Roman period.

First scientific geological data for the territory of Macedonia are found in the first half of XIX century, and the first printed papers for our region are found at A.Bue (1828-1870) and Viksenel (1842). From the end of XIX century until today, depending on the intensity of the investigations numerous publications are presented in all fields of geology.

The activities of geological scientists are performed in the frame of the Macedonian Geological Society which is formed in 1952.

In 2008 the First Congress of Geologists of Macedonia was held. Proceedings with over 50 papers were published. Numerous papers were prepared by international teams.

In the period between 2008 and 2012 investigations in all fields of geology were performed. Especially important to mention are the investigations of metallic and non-metallic mineral resources, regional, geochemical, engineering-geological, etc.

The Second Congress of Geologists of Republic Macedonia presents sublimate of scientific knowledge based on the mentioned geological investigations which were conducted in the period 2008-2012. Also, the congress presents part of the work of colleagues from neighboring countries, so with great pleasure we can once again confirm its international character.

Претседател
на организационен одбор

President
of organizing committee

Проф. д-р Милорад Јовановски

СОДРЖИНА

CONTENTS

PHYSICOCHEMICAL CHARACTERISTICS OF MINE WATERS AT ABANDONED MINING SITES IN SERBIA

Veselin Dragišić[1], Nebojša Atanacković[1], Vladimir Živanović[1], Gordana Milentijević[2]

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Abstract

Both exploration and mining of mineral resources in Serbia have been quite extensive. Over the past several years, investigations of the physicochemical characteristics of mine waters were undertaken at several tens of abandoned mining sites across Serbia, featuring different types of ore deposits.
Hydrochemical investigation revealed distinct variations in the chemical compositions of the mine waters. Based on the results reported in this paper, mine waters originating from gold and magnesite deposits exhibit chemical compositions identical to that of the groundwater in the extended area. Contrary to these, mine waters which trace to abandoned copper, molybdenum and polymetallic deposits feature elevated total dissolved solids (TDS) and low pH levels. With regard to their chemical composition, these are sulfate waters with elevated heavy metal concentrations. Mine waters originating from abandoned stone coal mining sites exhibit chemical properties which are similar to those of mine waters from polymetallic deposits.

Analyses of the dependency between pH levels and the chemical compositions of mine water samples revealed a high correlation between the pH index and the concentrations of sulfates and metals.

Key words: *mine waters, abandoned mines, hydrochemistry*

INTRODUCTION

Mine waters were sampled from 2009 to 2011 at abandoned mines in several tens of ore-bearing deposits. Specifically, physicochemical characteristics were analyzed of mine water samples from deposits of metallic and polymetallic mineral resources (Cu, Fe-Ni, Pb-Zn, Sb, Mo, Au), radioactive elements (U), non-metals (Mg, F) and stone coal. The chemical composition of mine water is generally a result of several factors, the most important being the geological makeup of the deposits, the mineral composition of the ore and the surrounding rocks, the hydrogeological characteristics of the rock masses, and the mining technology applied. Mine waters which circulate at a mining site come into contact with primary and secondary minerals in oxidation conditions, whereby the minerals become dissolved.

The oxidation of pyrite (FeS_2) and other sulfides plays a dominant role in the formation of the chemical composition of mine waters, during which hydrogen ions are released and cause the pH level to decrease and the concentrations of certain elements in the mine water to increase, such as those of sulfates, heavy metals (Fe, Cu, Pb, Zn, Cd, Co, Cr, Ni, Hg), metalloids (As, Sb) and other elements (Al, Mn, Si, B, Li) (Lottermoser B., 2007). In parallel, the activity of certain microorganisms, primarily *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*, accelerate processes which lead to the deterioration of mine water quality. Depending on the pH/Eh conditions at the site and the composition of the mine waters, certain secondary minerals are deposited on the mine walls as sediment or film, whose composition is dominated by iron oxides and hydroxides which give them a characteristic reddish-orange color. Similar processes take place in stone coal deposits. However, in certain other deposits the hydrolytic reaction is the main process of disassociation of the ore and surrounding minerals, and the resulting mine water does not differ significantly from naturally occurring groundwater (Dragišić V., 2012).

The objective of the research reported in this paper was to identify, on a regional scale, the physicochemical characteristics of mine waters originating from abandoned mining sites associated with different ore deposits within the represented metallogenetic units. The outcomes of this effort constitute the basis for further, detailed investigations of certain mine water occurrences from the environmental perspective, and for analysis of geochemical and hydrochemical processes which govern the chemical composition of the mine waters.

SAMPLING AND CHEMICAL ANALYSES

Mine water was sampled for chemical analyses at the points of discharge from adits and from pools at the lowest levels of opencast mines. The investigations encompassed ore-bearing sites in eastern, western and southern Serbia, as well as in Kosovo and Metohija (Figure 1). Measurements of pH, conductivity (μS/cm) and temperature (ºC) were conducted in-situ, using a Mi805 unit with an MA851D/1 parametric probe. Chemical analyses of the mine water samples were performed at Hemolab in Belgrade. Water samples were stored and transported in 1.5 l and 0.5 l polyethylene (PET) bottles. Samples in smaller bottles were acidified with 10-20 drops of a 50% HNO_3 solution to prevent the sedimentation of metals from the water. Among the basic physical quantities, T, pH and Ep were determined in-situ, while dry residue (at 180ºC), total hardness and $KMnO_4$ consumption were analyzed in the laboratory.

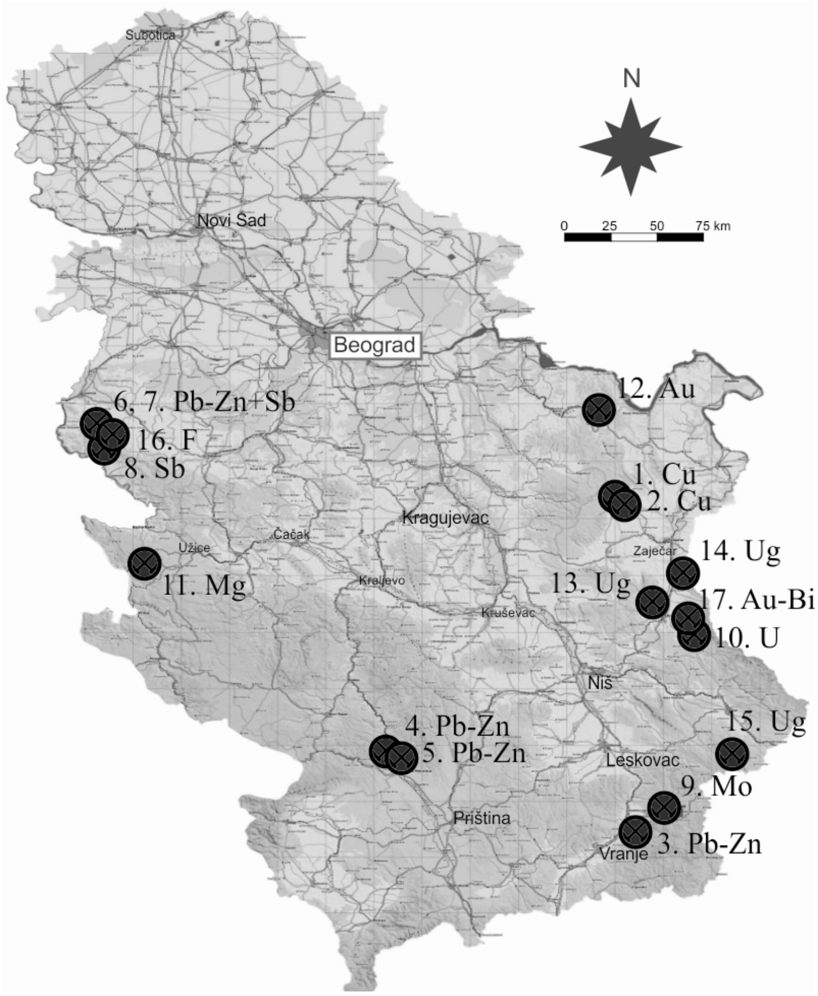

Figure 1. Sampling location

With regard to macrocomponents, the analyses included the main cations and anions (Na^+, Ca^{2+}, Mg^{2+}, K^+, CO_3^{2-} HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-). The microcomponents analyzed were non-metals (NH_4^+, NO_2^-, P, SiO_2) and metals and metalloids (Fe tot., Mn tot., Cr tot., Zn, Cu, Pb, Cd, Ni, As). The concentrations of P, Cr, Cd and Pb were below the limits of detection and, as such, were not included in the study.

Table 1. *Results of chemical analysis of mine waters*

Item	Ore deposits	Mining site	pH	Ep	Dry residue	Ca	Mg	Na	K	HCO_3	Cl	SO_4	SiO_2	Fe	Mn	Zn	Cu	As
1	Cu-As	Gornja Lipa opencast mine	1.95	8200	7200	300.2	78.4	9.4	12.1	<0.5	-	4950	-	1650	19.94	16	51.5	1.3
2	Cu-Mo	Cerova tailing site	3.3	>4000	3500	287	1430	14.8	1.8	<0.1	22	13600	80.2	15.8	45	52.1	1120	0.0002
3	Pb-Zn	Pište adit	6.4	210	170	31.2	7.5	2.6	1.3	114	5.2	18	19.3	6.2	1.45	5.6	0.005	0.1
4	Pb-Zn	Žuta Prlina	6.9	1538	1660	40	141.5	-	-	183	8	298.2	-	10.4	6	10	0.01	0.0054
5	Pb-Zn	Koporić	7.4	418	266	25.6	88.8	-	-	195.2	8	124.8	-	3.1	0.56	0.11	0.03	<0.002
6	Pb-Zn + Sb	Bobija opencast mine	2.5	>4000	5800	371	141	3.5	0.8	<0.5	2	3900	65	780	11.3	142	30	2.8
7	Pb-Zn + Sb	Bobija adit	6.0	1500	1300	316	37	2.1	1.3	104	6.8	850	12.8	11.3	1.6	38.7	0.004	0.022
8	Sb	Stolice adit	6.8	1200	810	210	50.5	11.2	2.8	410	7	400	7.5	1.1	0.35	0.002	0.001	0.012
9	Mo	Mačkatica adit	7.5	880	790	164.7	22.6	12.5	2.4	156	7.2	402	31.5	42.2	3.3	0.002	0.05	0.0003
10	U	Gabrovnica adit	6.7	603	420	100.6	17.2	18.3	2.1	427	7	16	26.7	0.07	0.34	0.006	0.002	0.0004
11	Mg	Liska	8.3	420	260	8.2	57.1	0.5	0.2	280.3	3.5	<1	25.1	0.01	0.003	0.002	0.001	0.001
12	Au	Sveta Barbara	7.0	350	270	70.1	12.8	4.1	3	213.5	5.2	40	3.2	0.01	0.004	0.002	0.001	0.002
13	Stone coal	Dobra Sreća	6.9	>3000	2420	347	187.1	150	5.5	880	12.4	1200	32.2	4.76	0.53	0.004	0.001	0.0008
14	Stone coal	Sveti Đorđe	6.7	1800	1540	232	142	40.5	14.4	732	12.8	680	16.5	6.1	0.12	0.002	<0.001	0.0004
15	Stone coal	Kozarnik	6.45	810	540	126.2	30.4	1.7	2.1	210.2	5.8	260	7.2	6.7	0.4	0.002	0.002	0.008
16	F	Krupanj	6.9	1520	1250	342	30.6	6.4	1.3	384	17.8	650	14.8	3.22	0.77	0.14	0.002	0.005
17	Au-Bi	Aljin Do	7	510	390	61.2	42.5	9	0.6	308.1	12.4	70	-	0.002	0.003	0.002	0.00075	0.5

RESULTS AND DISCUSSION

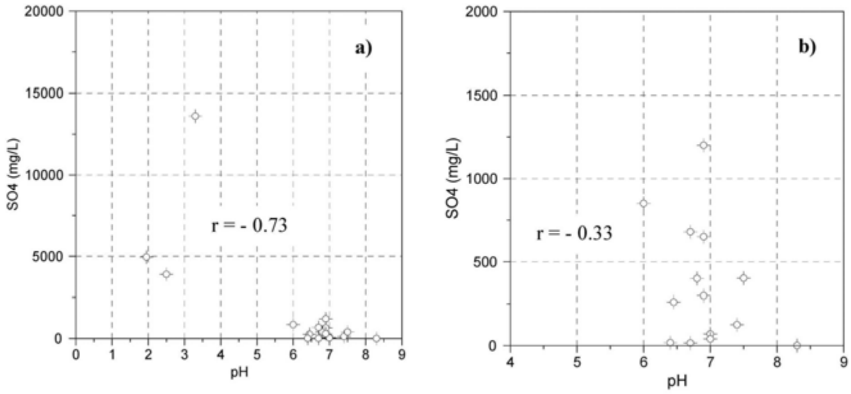

Figure 2. Concentrations of the SO_4^{2-} ion in relation to pH.

The results of hydrochemical analyses of mine water samples collected from abandoned mining sites (Table 1) revealed considerable differences in the chemical compositions, as a result of highly complex conditions leading to their formation. Some authors believe that the composition of mine water at each mining site is specific, due to the differences between the mineral deposits. This claim seems to be confirmed by the broad range of values of the parameters analyzed within the scope of this research. A pH index of 1.95 (Lipa opencast mine) was indicative of a highly acidic medium, while the mine water from the adit at Liska was found to be alkaline, with a pH index of 8.3. In addition to pH, the concentrations of SO_4^{2-} also varied (Figure 2). Figure 2 (a) shows that extremely high SO_4^{2-} concentrations were found in mine waters whose pH was very low. However, with the exception of the three extremely low pH values (Figure 2 (b), this correlation was much less pronounced in most of the analyzed samples. Mine waters from the Cerova copper mine and the Dobra Sreća stone coal mine exhibited elevated concentrations of the sulfate ion, while their pH levels between 6 and 8 were similar to those of most of the samples.

Conversely, when mine waters were grouped based on the dominant minerals in the compositions of the ore deposits, a certain correlation could be established. Cu deposits and polymetallic Pb-Zn deposits were found to be largely comprised of sulfide minerals. Compared to the Cu and Pb-Zn deposits, mine waters originating from the deposits of other minerals exhibited much lower chemical composition variations (Figure 3).

TDS values of most of the mine water samples associated with stone coal, Sb, Mo, U, F, Mg and Au deposits were found to be close to or less than 1000 mg/l, while the TDS range of the Cu and Pb-Zn deposits of the sulfide type was considerably broader (Figure 3 (a)). Similar to the concentrations of dissolved substances, pH levels associated with sulfide deposits varied to a large extent, while in mine waters from other analyzed deposits they were in the interval from 6.0 to 8.3, generally around 7 (Figure 3 (b)).

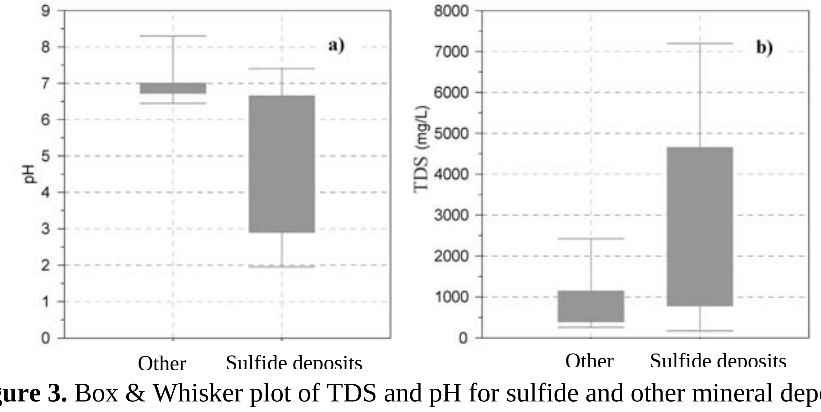

Figure 3. Box & Whisker plot of TDS and pH for sulfide and other mineral deposits.

The piper diagram (Figure 4) of the concentrations of the main cations and anions shows two distinct groups of mine waters. With regard to the main anions, the compositions of the mine water samples from

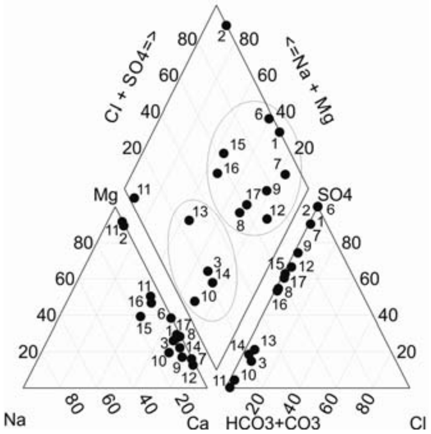

Figure 4. Piper diagram.

Cu, Pb-Zn, Mo, Sb, F and stone coal deposits were dominated by the sulfate ion, while the deposits of Au, U and Pb-Zn (adit at Pište) featured the highest concentration of the HCO_3^- ion. The cation compositions of all the samples were dominated by the Ca^{2+}, except the mine waters associated with the Liska magnesite mine and the Cerova opencast mine where magnesium concentrations of more than 80%eqv were recorded.

Low pH values of mine waters are generally a function of the geological characteristics and mineral composition of the pertinent rocks. Occurrences of acidic mine waters are attributed to rocks which do not contain carbonates. Deposits of metallic minerals genetically trace to magmatic intrusions, volcanic activity and the hydrothermal solutions associated with these processes. Acidic magmatic rocks which contain poorly soluble silicate minerals provide a favorable setting for the formation of mine waters with low pH values, while in basic and ultrabasic rocks made up of highly soluble silicate materials, alkaline waters are formed. (C.A.J. Appelo, 1996). Apart from carbonate minerals, pH levels increase when gibbsite – $Al(OH)_3$ is dissolved, whereby the concentrations of aluminium in the mine waters increase.

As minerals from the sulfide and oxide groups dissolve, the concentrations of metals in mine waters increase. This process primarily depends on the pH level of the mine waters (Wolkersdorfer C., 2008). The analyzed mine water samples featured elevated Fe and Mn concentrations.

Extreme concentrations of Fe were recorded in the samples collected from the Lipa copper mine, as well as the Bobija lead and zinc mine whose mine water samples also exhibited high zinc concentrations. Iron and zinc concentrations correlated with the pH index (Figure 5). As the pH level increased, the concentrations of these metals in the mine water samples declined. The samples from these two mines also featured elevated concentrations of Cu and As. The mineral composition of the respective deposits is dominated by pyrite, where the paragenesis exhibits other sulfides (galenite, sphalerite) as well. In the zone of the abandoned Lipa mine, in addition to pyrite, enargite (Cu_3AsS_4) also occurs as a primary mineral ore (Janković S., 1990), which is the source of arsenic in the mine waters. As the pH levels of the mine water samples decreased and the concentrations of metals (primarily Fe and Zn) increased, the concentration of arsenic rose (Fig 5).

Very high concentrations of microcomponents were found in the chemical composition of the mine waters tracing to the Cerova opencast mine, where the concentration of Mn was 45 mg/l, of Zn 52.1 mg/l and of Cu 1120 mg/l. The mineral composition of the fluorite deposits at Ravnaja, in addition to fluorite (CaF_2), features sphalerite, galenite and pyrite. The mineral association at this site has caused the mine waters from Ravnaja to correspond to those tracing to polymetallic deposits.

At the Jerma mining site, mine waters are discharged at a rate of 4-5 l/s from the abandoned adit at the Kozarnik stone coal mine, where iron concentration was found to be 6.7 mg/l. The point of discharge is covered with yellowish-red iron hydroxide film. In the catchment area of the Veliki Pek River, within the gold deposits at Blagojev Kamen, the abandoned adit of the Sveta Barabara mine discharges 4 l/s of low-TDS mine waters of the hydrocarbonate class, calcium group, where heavy metal concentrations equal natural background levels. On Mt. Stara Planina, at the Aljin Do site, there are gold deposits with high concentrations of bismuth. Here the abandoned Ilijin Grob mine discharges mine waters whose chemical composition is of the low-TDS HCO_3-Ca-Mg type, with low concentrations of metals and an elevated concentration of arsenic (0.5 mg/l).

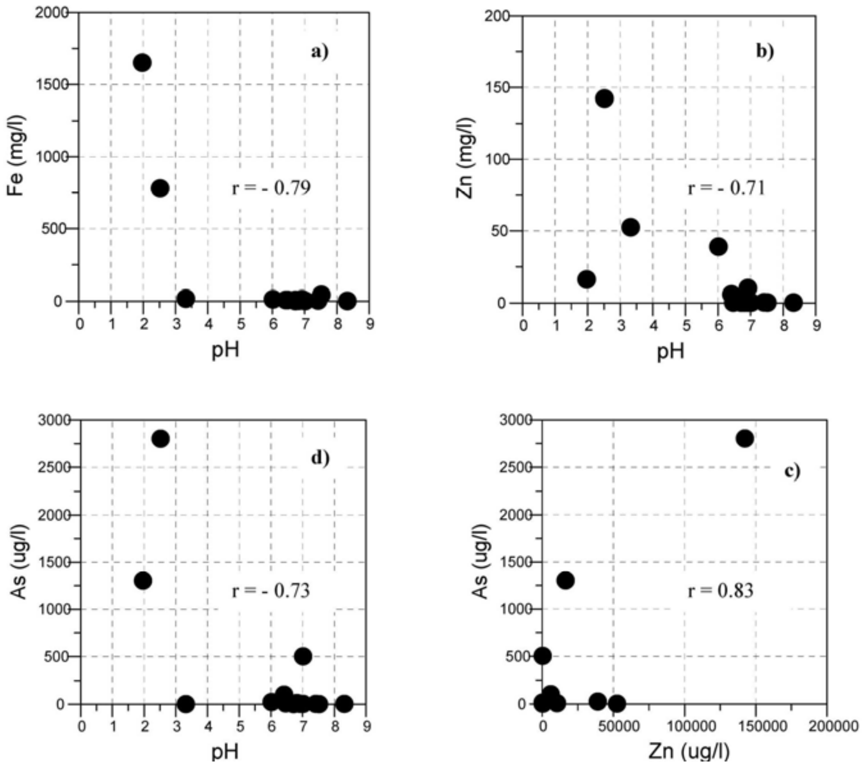

Figure 5. Correlation between pH levels and metal/metalloid concentrations in mine waters

CONCLUSION

Hydrochemical analysis of mine waters originating from abandoned mines in Cu, Pb-Zn, Sb, Mo, Mg, F, U , Au and stone coal deposits in Serbia revealed the following:

- Mine waters tracing to deposits of metallic minerals, whose composition is dominated by minerals from the sulfide group, exhibit pronounced TDS and pH variations. Based on their macrocomponent composition, these waters belong to the sulfate class, calcium group. They feature elevated concentrations of heavy metals and metalloids (Fe, Mn, Cu, Zn, As).
- Mine water samples collected from abandoned stone coal mines belong to the neutral group, based on their pH levels. Their compositions exhibit elevated concentrations of sulfates and iron.
- Mine waters discharged from abandoned mines in gold and magnesite deposits belong to low-TDS waters of the hydrocarbonate class, calcium and magnesium groups, with metal concentrations corresponding to natural background levels.
- Analyses of the correlation between pH levels and metal/metalloid concentrations showed that as the pH level of the mine water samples decreased, the concentrations of Fe, Zn and As increased.

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