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Дигитални репозиторијум Рударско-геолошког факултета Универзитета у Београду

[ДР РГФ]

Geochemistry of neutral mine drainage at sulfide deposits – example of the „Grot“ Pb-Zn mine, South-Eastern Serbia | Snežana Kretić, Jana Štrbački, Nebojša Atanacković | Journal of the Serbian Chemical Society | 2024 | |

10.2298/jsc230811013k

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J. Serb. Chem. Soc. 89 (3) 429–440 (2024)
JSCS–5730

Geochemistry of neutral mine drainage at sulfide deposits – Example of the „Grot“ Pb–Zn mine, south–eastern Serbia

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(Received 11 August, revised 21 October 2023, accepted 19 February 2024)

Abstract: This study examines the chemistry of mine waters of the “Grot” Pb–Zn mine and identifies the hydrogeochemical factors that influence the formation of mine waters chemical composition. Eleven mine water samples were collected at six locations across the area of Kriva Feja in order to determine their chemical composition. Data analysis revealed that the waters belong to the HCO_3^- – SO_4^{2-} – Ca^{2+} and SO_4^{2-} – Ca^{2+} water types, with neutral pH values. The concentrations of metals in these waters (zinc, lead, barium, copper, chromium) are generally low, and most of the samples meet drinking water quality criteria (USEPA standards). Modelling using the PHREEQC software indicates that the dominant processes in the formation of the chemical composition of these waters are the dissolution of carbonate minerals and the oxidation of sulphide minerals. Carbonate minerals have a scarcer occurrence compared to sulphide minerals, such as galena, sphalerite and pyrite, which are dominantly distributed. The low intensity of sulphide mineral oxidation is interpreted to result from a rapid water exchange and reduced contact time between the water and the rock. The occurrence of this process is localized only in the ore body zone. This study highlights the importance of kinetics (in terms of the chemical reaction rate) as the main factor influencing the oxidation of sulphide minerals and, subsequently the quality of mine waters.

Keywords: groundwater; acid mine drainage; hydrogeochemical factors; metals; PHREEQC modelling; saturation index.

INTRODUCTION

Negative environmental effects occur when surface water or groundwater comes into contact with primary and secondary minerals from the ore deposit under oxidizing conditions.¹ The deposits containing sulphide minerals tend to generate acid mine drainage (AMD) during the oxidation process of these minerals (*e.g.*, pyrite, marcasite, and pyrrhotite).^{2–4} The acid mine drainage refers to

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<https://doi.org/10.2298/JSC230811013K>

water with low pH values (between 3.5 and 5), high sulphate concentrations, and elevated metal concentrations.^{4,5} The oxidation of sulphide minerals, primarily pyrite, depends on physicochemical conditions, the type of oxidant (O_2 or Fe^{3+}), its concentration, activity, and the presence of microorganisms.^{6–8} According to Lottermoser, several types of pyrite oxidation can be distinguished, including: abiotic oxidation by oxygen, biotic oxidation by oxygen, abiotic oxidation by oxygen and iron and biotic oxidation by oxygen and iron.³ The formation of acid mine drainage is strongly influenced by the reaction rate (kinetics) and its duration.⁹ The rate of biotic oxidation is always higher than abiotic, and pyrite oxidation in the presence of Fe^{3+} can be 2–3 times faster than in the presence of O_2 as the oxidant.⁵ Depending on the geological environment in which groundwater circulates (*i.e.*, the type of ore and host rocks), acid mine drainage may not always form. Unlike pyrite, the oxidation of other sulphide minerals such as galena, sphalerite or arsenopyrite in the presence of oxygen does not directly produce acid mine drainage.^{10–12} This is due to their lower reactivity, resulting from greater crystal structure stability, low concentrations of released iron and the formation of poorly soluble minerals.¹³ The absence of sulphide mineral oxidation, in addition to kinetics, can also result from the presence of minerals that neutralize the acidity of mine drainage (carbonates, silicates, and hydroxides).^{2,3} The neutralization process occurs under the same conditions as the sulphide mineral oxidation process and is independent of the oxygen concentration in the water.³ Neutral mine drainage (NMD) will form in some sulphide deposits due to the previously mentioned processes. Neutral mine drainage refers to waters with a neutral pH value (between 6.5 and 7) and high metal concentrations (most commonly lead, zinc, copper and cadmium).³ In these waters, sulphates and bicarbonates are the main anions, and calcium, magnesium and sodium content is elevated compared to acid mine drainage.³ The occurrence of neutral pH and lower metal concentrations in some mine waters can be attributed to kinetic factors, *i.e.*, the slow dissolution and oxidation of sulphide minerals compared to rapid water exchange in mine waters.² Additionally, the surfaces of sulphide minerals can be covered with insoluble oxides or carbonates, which limits the oxidation.² Instances of neutral mine drainage have been found in Pb–Zn deposits throughout the United Kingdom and Italy.^{14–17} These examples are characterized by neutral pH and increased concentrations of trace components such as lead, zinc, copper, arsenic and cadmium (depending on the specific locality where the mine waters are formed). The studies considering these occurrences as the most common reason for the formation of neutral mine drainage cite the neutralization process in the presence of carbonate minerals.^{14–17}

The objectives of this study are to identify factors that could influence the formation of neutral mine drainage, determine the mineral phases being dissolved, and identify the dominant hydrogeochemical processes that affect the rel-

ease of trace elements into water. Such an approach could contribute to the adaptation of the mineral resource exploitation methods to reduce the negative impact on the environment and water resources.

EXPERIMENTAL

Study area

Details related to study area are given in Supplementary material to this paper.

Sampling and chemical analysis

Mine water samples were collected at eleven locations during the year's low flow period (September–November). During that period, 16 mine water samples were collected, while 11 samples were further considered in the study. The considered samples were taken at various locations across the exploitation field at discharge points from the adits before the sedimentation ponds, while the samples taken at locations after the ponds were omitted due to the possibility of the removal of certain components from the water. Mine water sampling was performed according to ISO 5667-1:2006, ISO 5667-3:2012 and ISO 5667-10:1992 standards at the adits discharge points.¹⁸⁻²⁰ Sampling and chemical analyses were carried out by the Institute of Public Health Vranje.

The determination of the pH was performed potentiometrically according to the ISO 10523:2008 standard.²¹ The water mineralization was determined by the analytical procedure as the dry residue at 103–105 °C using the US EPA 160.3 method.²² Main cation composition (Na⁺, K⁺, Mg²⁺, Ca²⁺) together with metals (zinc, lead, manganese, barium, copper, chromium) were determined by the induced coupled plasma with the atomic emission spectrometry ICP-AES (according to ISO 11885:2007 standard).²³ The content of arsenic in mine waters was determined by the atomic absorption spectrophotometry using the hydride technique (ISO 11969:1996).²⁴ The content of ammonium, nitrate, and nitrite ions was determined by spectrophotometric methods (ISO 7150-1:1984, ISO 7890-3:1988, ISO 6777:1984).²⁵⁻²⁷ The content of sulphate ions was determined by the turbidimetric method (SRPS H.G8.115:1984), while the chloride content was determined volumetrically according to the ISO 9297:1989 standard.^{29,29} Bicarbonate ions in water were determined by titration, in accordance with ISO 9963-1:1994.³⁰ The content of dissolved oxygen was determined by the volumetric method (ISO 5813:1983), while hydrogen sulfide was determined spectrophotometrically (SZZZ, 1990).^{31,32}

Analysis and calculations

The degree of saturation of groundwater in relation to a certain mineral can be determined by comparing the product of ionic activity (*IAP*) of a real water sample and the solubility product of that mineral (*K_{sp}*), according to:³³

$$SI = \log \frac{IAP}{K_{sp}} \quad (1)$$

where *SI* is the saturation index.

The obtained *SI* value can indicate oversaturation or undersaturation of the water sample with respect to a given mineral, with the possibility of precipitation (*SI* > 0) or dissolution (*SI* < 0) of the specific mineral.³³

Saturation indices for specific mineral phases and the dissolved forms of inorganic substances in water were calculated using PHREEQC software (interactive version 3.7.3-15968).³⁴ This software is widely used in geochemical and mine water research for these types of cal-

culations.^{15,35-37} When calculating *SI* for carbonate minerals, the MINTEQ database was used, as it covers a wide range of inorganic parameters (metals) and organic compounds.³⁸ The LLNL database was used for the calculation of *SI* for sulphur-bearing minerals because it has the most extensive dataset, making it more suitable for such calculations.^{33,34} For example, it includes the reaction of pyrite with water.³⁴

Excel workbook was used to determine statistical parameters (minimum, maximum, median) to determine the variations of certain parameters in mine waters. Also, this program was used for the graphical presentation of chemical parameters in the form of Box-Plot diagrams.

RESULTS AND DISCUSSION

Hydrochemistry of neutral mine drainage of the „Grot“ Pb–Zn mine

According to their physical properties, the examined mine waters are colourless and odourless. These waters belong to the category of cold waters. The water temperature ranges from 7.1 to 14.5 °C, depending on the air temperature. The mineralization (*TDS*) ranges from 163 to 719 mg L⁻¹ (Tables I and S-I of the Supplementary material). These waters can be classified as low-mineralized, except for one sample with *TDS* > 500 mg L⁻¹.

TABLE I. Physical–chemical parameters and concentrations of macrocomponents in mine water samples from the exploration area

Parameter	Unit	Min	Median	Max	<i>N</i>	Criteria ¹⁸
<i>t</i>	°C	7.1	9.5	14.5	11	–
<i>TDS</i>	mg L ⁻¹	163	353	719	11	–
<i>EC</i>	μS cm ⁻¹	180	431	632	11	<3000
pH	–	7.04	7.5	7.6	11	6-9
Dissolved O ₂	mg L ⁻¹	5.4	9.3	10.9	11	>0.4
Dissolved H ₂ S		0.006	0.048	0.351	11	≤1.0
Ca ²⁺		25.6	40.4	56.8	6	–
Mg ²⁺		1.2	3.65	4.2	6	–
Na ⁺		3.5	4.64	6.6	6	–
K ⁺		1	1	1.1	6	–
HCO ₃ ⁻		61	88.45	91.5	6	–
SO ₄ ²⁻		37.4	93.2	177.7	11	<300
Cl ⁻		4	6	18	11	<250
NO ₃ ⁻		0.83	1.7	12.09	11	<15
NO ₂ ⁻		0.005	0.041	0.333	11	–
NH ₄ ⁺		0.033	0.54	1.5	11	<1.5

The pH value of analysed waters ranges from 7.04 to 7.6, classifying them as neutral. According to the USEPA standards (2018), the pH of drinking water should be within the range of 6.5 to 8.5, which is met in all samples.³⁹

The most dominant cation is Ca²⁺, with 25.6 to 56.8 mg L⁻¹ concentrations. Concentrations of Mg²⁺ range from 1.2 to 4.2 mg L⁻¹. The second most abundant cation in these waters is Na⁺, with concentrations ranging from 3.5 to 6.6

mg L⁻¹. K⁺ concentrations do not vary significantly in analysed samples (1 to 1.1 mg L⁻¹), having the lowest abundance among all cations in these waters.

The dominant anions in mine waters are bicarbonates and sulphates. HCO₃⁻ in mine waters occur in the range of 61 to 91.5 mg L⁻¹. SO₄²⁻ concentrations in these waters vary from 37.4 to 177.7 mg L⁻¹. Chlorides in these waters occur at low concentrations (4 to 18 mg L⁻¹). The content of NH₄⁺, NO₂⁻ and NO₃⁻ in the water is also low.

Concentrations of dissolved oxygen (O₂) range from 5.4 to 10.9 mg L⁻¹, while the concentrations of dissolved hydrogen sulphide (H₂S) are relatively low (from 0.006 to 0.351 mg L⁻¹).

Based on the dominant anions and cations, the analysed mine waters can be classified into two hydrochemical groups: HCO₃⁻-SO₄²⁻-Ca²⁺ and SO₄²⁻-Ca²⁺ waters (Fig. 1). The first group consists of mine waters that are not in direct contact with the rocks from the ore body (water that is pumped out before it reaches the active mining zone) and waters from sites where mining is currently not taking place. The second group consists of mine waters that are in direct contact with the rocks from the deposit, specifically the waters from the VI, VIII and IX horizons.

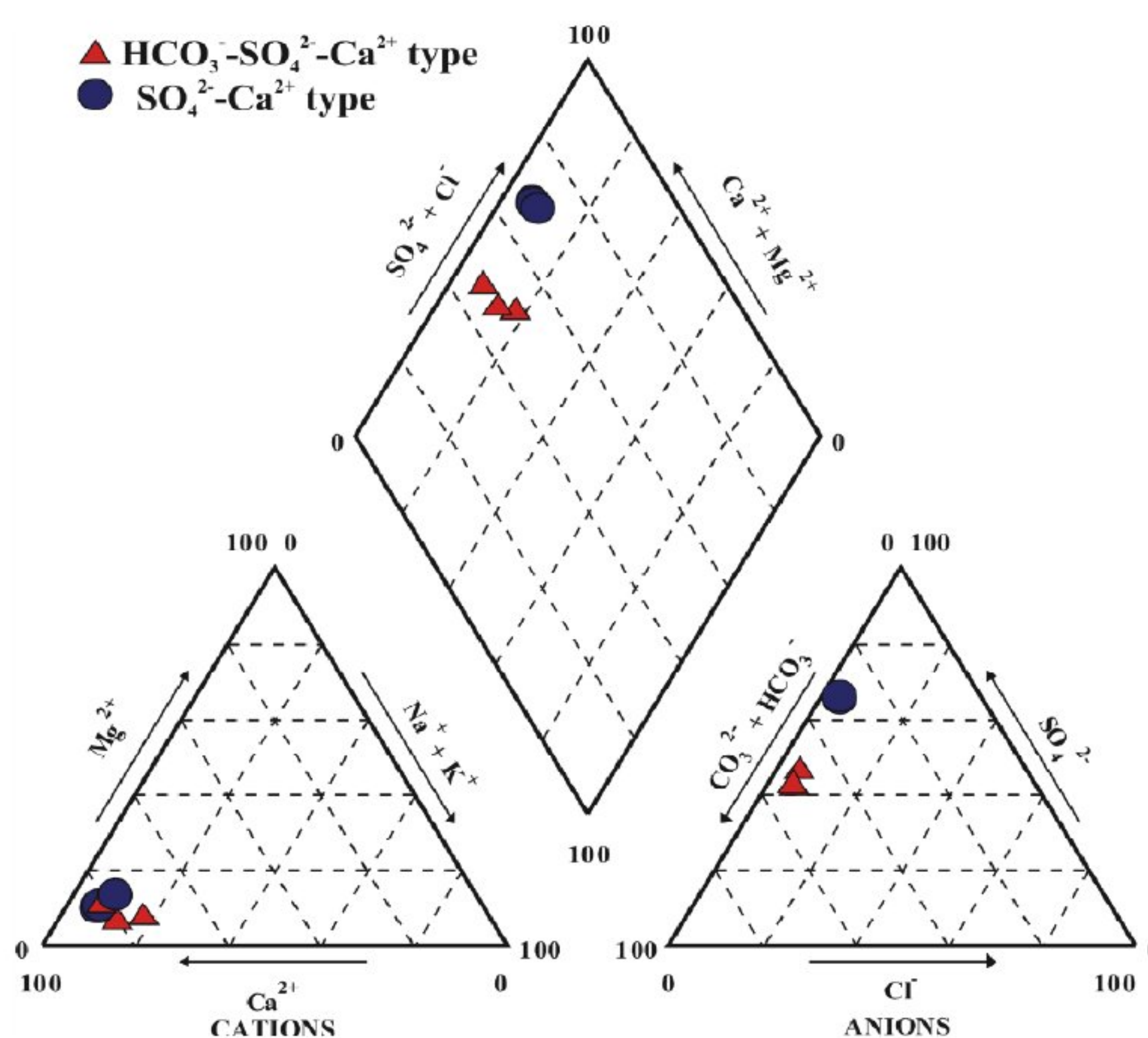


Fig. 1. Piper diagram of mine waters collected from six different locations within the exploration area.

Based on the results obtained from laboratory analysis, all water samples have met the prescribed criteria for wastewater (Table S-I).⁴⁰ A part of the mine water is used for the water supply of the Kriva Feja settlement and the mining complex,⁴¹ indicating that some of the water samples also meet the criteria for drinking water.

Microelements in mine waters

According to the laboratory testing results, the concentrations of metals (zinc, barium, chromium, copper) in the mine waters are generally low (Table S-I and Fig. 2).⁴⁴ These results are not specific to sulphide deposit mine waters, which typically have low pH values and high metal concentrations, defined as the acid mine drainage (AMD).

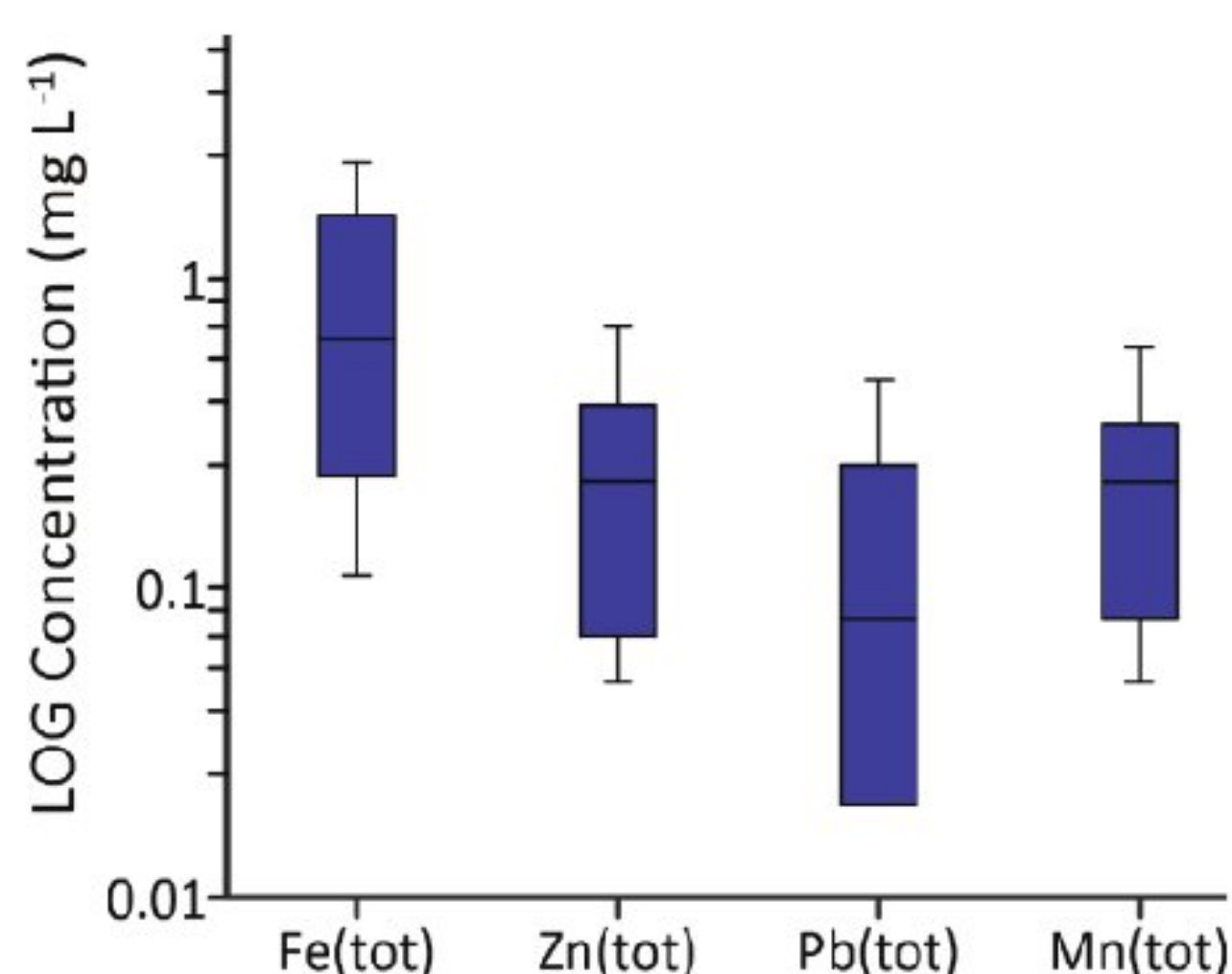


Fig. 2. Metal content in mine waters of the „Grot“ Pb–Zn mine in mg L⁻¹.

The iron concentrations in the tested waters range from 0.11 to 2.37 mg L⁻¹. The elevated concentrations of iron can be the indicator of the presence of oxidation of sulphide minerals.² Zinc concentrations in these waters are low (ranging from 0.05 to 0.7 mg L⁻¹), while lead concentrations vary from 0.02 to 0.47 mg L⁻¹. The concentrations of barium in the waters from this area are below 0.05 mg L⁻¹. Chromium and copper are present in trace amounts in these waters, with concentrations below 0.02 mg L⁻¹ for chromium and below 0.03 mg L⁻¹ for copper.

Manganese concentrations in mine waters range from 0.05 to 0.6 mg L⁻¹, while arsenic concentrations are below 0.05 mg L⁻¹.

Speciation modelling and saturation indices

The most of trace elements and many major elements in surface water and in groundwater exist in the form of complexes rather than free ions.⁴² The presence of certain metals in water can indicate the reactions such as dissolution and precipitation of mineral phases.⁵

According to the modelling results in PHREEQC software, a list of the most prevalent ionic species in mine waters is provided (Table II). Me²⁺ and MeSO₄

represent the two dominant ionic species for calcium and magnesium, while trivalent iron is most commonly present as $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_3$. Metals such as lead and copper are predominantly present as free ions and MeCO_3 ionic pair, while manganese is most commonly found as free ions or MnSO_4 ionic pair. Both types of mine waters have a similar distribution of ionic species. Only minor differences in the distribution of ionic species of zinc are observed. In both types of water, zinc predominantly occurs as free ions. Additionally, the presence of the MeCO_3 ionic pair is noticeable in the HCO_3^- - SO_4^{2-} - Ca^{2+} water type, while the MeSO_4 ionic pair is more dominant in the SO_4^{2-} - Ca^{2+} water type.

TABLE II. The distribution of ionic species in mine waters (presented in terms of median molalities and the median percentage distribution of ionic species relative to the total molality of metals)

Species	HCO_3^- - SO_4^{2-} - Ca^{2+}	SO_4^{2-} - Ca^{2+}	HCO_3^- - SO_4^{2-} - Ca^{2+}	SO_4^{2-} - Ca^{2+}
	Molality, mol/kg		%	
Calcium				
Ca^{2+}	6.10×10^{-4}	1.16×10^{-3}	94.85	87.94
CaSO_4	2.94×10^{-5}	1.52×10^{-4}	4.60	11.38
Iron				
$\text{Fe}(\text{OH})_2^+$	3.19×10^{-6}	2.06×10^{-6}	68.46	76.85
$\text{Fe}(\text{OH})_3$	1.11×10^{-6}	4.97×10^{-7}	23.48	18.60
Magnesium				
Mg^{2+}	5.87×10^{-5}	1.53×10^{-4}	95.12	88.83
MgSO_4	2.51×10^{-6}	1.75×10^{-5}	4.06	10.15
Sodium				
Na^+	2.03×10^{-4}	2.00×10^{-4}	99.83	99.51
Lead				
PbCO_3	8.30×10^{-8}	8.07×10^{-8}	85.95	83.61
Pb^{2+}	7.89×10^{-9}	1.07×10^{-8}	6.64	7.00
PbHCO_3^+	3.34×10^{-9}	9.38×10^{-9}	3.30	3.71
Zinc				
Zn^{2+}	8.49×10^{-7}	9.85×10^{-7}	77.28	67.26
ZnCO_3	1.01×10^{-7}	1.37×10^{-7}	11.57	9.94
ZnHCO_3^+	5.47×10^{-8}	8.39×10^{-8}	5.10	5.86
ZnSO_4	4.78×10^{-8}	2.08×10^{-7}	4.46	14.15
Manganese				
Mn^{2+}	8.71×10^{-7}	1.38×10^{-6}	95.11	89.09
MnSO_4	3.52×10^{-8}	1.40×10^{-7}	3.87	9.61
Copper				
$\text{Cu}(\text{OH})_2$	2.84×10^{-7}	2.99×10^{-7}	60.16	63.25
CuCO_3	9.01×10^{-8}	1.02×10^{-7}	19.09	21.56
$\text{Cu}(\text{HS})_3^-$	6.66×10^{-8}	3.96×10^{-8}	14.10	8.38

Based on the calculated *SI* values, the analysed waters are undersaturated ($SI < 0$) with the respect to minerals such as calcite, aragonite, cerussite, smithsonite, rhodochrosite, siderite and pyrolusite (Table III). The origin of Ca^{2+} and HCO_3^- in these waters could be linked to the dissolution of calcite and aragonite. The median *SI* values for calcite and aragonite are -0.80 and -0.95 , respectively. Both minerals have similar saturation index values, implying that they can be dissolved relatively equally in the investigated area.

TABLE III. Saturation Index (*SI*) values for selected minerals; $N = 6$

Mineral	<i>SI</i> min	<i>SI</i> median	<i>SI</i> max
Aragonite	-1.20	-0.95	-0.66
Calcite	-1.05	-0.80	-0.51
Cerussite	-1.10	-1.00	-0.64
Smithsonite	-2.90	-2.41	-1.54
Rhodochrosite	-1.97	-1.79	-1.10
Siderite	-3.91	-3.6	-2.81
Barite	0.16	0.44	0.68
Galena	-4.37	-3.84	-2.82
Sphalerite	-6.81	-6.06	-5.17
Pyrite	-19.55	-19.24	-18.63

The *SI* values for minerals such as cerussite, smithsonite and rhodochrosite range from -1 to -2.9 . The presence of Pb^{2+} in these waters can be attributed to the dissolution of cerussite. Since cerussite has a lower solubility product, this process occurs with lower intensity compared to the dissolution of calcium carbonates, resulting in lower concentrations of Pb^{2+} in the water.

The origin of Zn^{2+} and Mn^{2+} in mine waters may be associated with the dissolution of smithsonite and rhodochrosite. The occurrence of iron ions in these waters can be linked to the dissolution of siderite.

On the other hand, the saturation index values for mineral phases galena, sphalerite, pyrite, covellite and chalcopyrite are very low, indicating that the waters from this research area are undersaturated concerning the given minerals. The median *SI* value for the mineral phase pyrite is -19.24 , while for galena it is around -3.84 , and for sphalerite it is around -6.06 . Although sulphides minerals dominate over carbonate minerals in the investigated area, it can be assumed that the oxidation process of sulphides minerals occurs to a low extent.

The origin of SO_4^{2-} may be from the oxidation processes of pyrite, galena and sphalerite. This process is specific to the ore deposit zone. Therefore, the origin of lead, zinc, manganese and iron can be twofold, as these metals can originate from sulphide minerals (such as galena, sphalerite, pyrite, *etc.*) and carbonate minerals. Most probably, the dissolution of carbonate minerals also takes place during the oxidation process of sulphide minerals. Additionally, the origin of barium may be from galena and sphalerite, where this metal is concentrated.⁴³ The

saturation index values for barite in these waters are slightly positive (median *SI* 0.44), indicating the precipitation of secondary barium sulphate, due to the presence of an abundance of sulphate ions.

All the minerals under consideration have been detected in the ore deposit, which is deposited in specific horizons within the schists.⁴³

The origin of the mine waters is mainly atmospheric, with significant amounts of rainfall occurring in this area throughout the year. The low intensity of sulphide mineral oxidation may be attributed to the rapid exchange of these waters. Since the process of pyrite oxidation is low, this process is probably not dominant in shaping the chemical composition of these waters. The low concentrations of metals in the water are another indication of the low intensity of this process. Additionally, the sulphide minerals' solubility products are much lower than those of carbonate minerals. Therefore, the dissolution of carbonate minerals occurs before the dissolution of the sulphide minerals.

CONCLUSIONS

According to the results of chemical analysis, the mine waters of the "Grot" Pb–Zn underground mine have a neutral pH value and low concentrations of the trace elements except for manganese and iron. The analysed mine waters are classified into two groups based on their chemical composition. These differences can be attributed to the fact that the first group of waters of the HCO_3^- – SO_4^{2-} – Ca^{2+} type drains before contacting the ore body zone. On the other hand, the second group of waters of the SO_4^{2-} – Ca^{2+} type is in the direct contact with the ore body. However, it does not exhibit characteristics of acid mine drainage, probably due to the short water retention in the system. Modelling in PHREEQC software and the analysis of the obtained saturation index values revealed the two dominant processes in shaping the chemical composition of these waters: the dissolution of carbonate minerals and the oxidation of sulphide minerals. The intensity of sulphide mineral oxidation is low and localized to the ore zone. The lack of the intense sulphide mineral oxidation, despite their high occurrence in the study area, is due to the kinetics of this process. The longer rock-water contact is required to initiate this process, while the mine waters in this area are rapidly exchanged and have a short contact with the rock. Therefore, it can be concluded that the kinetic factor plays a crucial role in forming neutral, good-quality mine waters. At the same time, the neutralization in the presence of carbonate minerals is not a significant factor.

Since the acid mine drainage is a global issue, adapting some similar methods of the mineral resource exploitation and mine dewatering, where applicable, could further slow down this process. Finally, this study suggests that the mine drainage systems for mineral resource deposits should minimize the water retention in the system, ensuring a short contact time between water and rock.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/12540>, or from the corresponding author on request.

Acknowledgements. This research was funded by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia. The authors are also grateful to the Geological Survey and the Environmental Protection Service of the Grot mine for their support.

ИЗВОД

ГЕОХЕМИЈА НЕУТРАЛНИХ РУДНИЧКИХ ВОДА СУЛФИНИХ ЛЕЖИШТА НА ПРИМЕРУ Pb–Zn ЛЕЖИШТА “ГРОТ”

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У овом раду проучаван је хемијски састав вода из рудника и издвојени су хидро-геохемијски фактори који утичу на његово формирање. Сакупљено је 11 узорака воде са 6 локација на подручју Криве Феје, како би се утврдио њихов хемијски састав. Анализом података утврђено је да су воде са овог подручја високог квалитета, HCO_3^- - SO_4^{2-} - Ca^{2+} и SO_4^{2-} - Ca^{2+} типа, са неутралном рН вредношћу. Концентрације метала у овим водама (цинка, олова, баријума, бакра и хрома) генерално су ниске и већина узорака вода испуњава критеријуме воде за пиће (US EPA стандарде). Моделирање помоћу PHREEQC софтвера указује на то да су доминантни процеси у формирању хемијског састава ових вода растварање карбонатних минерала и оксидација сулфидних минерала. Карбонатни минерали имају мању заступљеност у односу на сулфидне минерале (попут галенита, сфалерита и пирита), који су доминантни на подручју истраживања. Слаб интензитет оксидације сулфидних минерала последица је брзе замене воде и смањеног контакта воде са стеном. Процес оксидације сулфидних минерала је локалног карактера и везује се само за зону лежишта. Ова студија указује на значај кинетике (тј. брзине хемијске реакције), као једног од главних фактора у процесу оксидације сулфидних минерала.

(Примљено 11. августа, ревидирано 21. октобра 2023, прихваћено 19. фебруар 2024)

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