Assessment of heavy metal pollution from mine waters

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Abstract – **Acid mine waters (AMW) or Acid mine drainage (AMD) are the result of oxidation processes in sulfide minerals and represent a serious environmental threat. This study presents a methodology for taking, preparing and analyzing samples to determine the concentrations of heavy metals (Fe, Mn, Cu, Zn, Cd, Ni, Co) and to study the pH of the samples. Results from 5 samples are presented and an analysis and assessment of their impact on water and the environment is performed.**

Keywords – **acid mine waters, heavy metals, monitoring, water analysis.**

I. Introduction

Mining plays a crucial role in the economic development of several countries, including Bulgaria. Although mineral extraction offers economic advantages, it significantly harms the natural environment. A major issue from mining is the emission of acidic mine waters. These waters, also known as acid mine drainage, contain acids and heavy metals that can contaminate surface and groundwater sources, damage ecosystems, and pose a threat to human health. [1-3]

The main characteristics describing this type of water are a very acidic environment, due to the formation of sulfur, the presence of heavy metals in it, high electrical conductivity, and substantial toxicity. Some of the main characteristics of acidic mine waters are given in Table 1.

Table 1. Main characteristics of acid mine waters [4].

Parameter	Typical value
pH	2-5
SO_4^{2-}	>1000 mg/L
Fe	10-10000mg/L
Mn	1-100mg/L
Al	5-500mg/L
Zn, Cd, Cu	Up to 100mg/L depending of the ore

In Bulgaria, a well-known example is the region around the Pernik mine and the Erma River area. There, elevated concentrations of metals and acidity have been observed in nearby surface waters. Another notable examples of acid mine drainage are the waters near the Madzharovo ore field, the Curilo uranium deposit, the Grantcharnitsa deposit, and the Elatsite mine area [5-7]. A global example is the Rio Tinto mine in Spain, where mine waters have turned a river blood red and completely destroyed biological life in the area [8, 9].

II. Mining in Bulgaria

The development of mining in Bulgaria has a long history and is of strategic importance for our economy. The first steps in mining date back to the Thracians, who mined gold and silver thousands of years ago. During the Middle Ages and the Ottoman period, metal mining was a significant source of livelihood in certain regions.

This sector makes a significant contribution to the national economy, providing a substantial share of the gross domestic product (about 4–5%) and employment, especially in industrially less developed regions. Bulgaria has rich deposits of non-ferrous and precious metals (copper, gold, lead, zinc), coal (lignite and brown), as well as non-metallic minerals (limestone, kaolin, gypsum) [10, 11].

The primary mines located within the country's territory are presented in Table 2.

Table 2. Main mines in Bulgaria

Type	Main regions
Brown Coal	Pernik and Bobov dol
Lignite coal	Maritsa basin
Cu	mainly in the Panagyurishte region
Gold	Chelopech, Krumovgrad
Pb-Zn	Rhodopes (Madan, Rudozem, Lucky).

The location of the leading mining in Bulgaria is shown in Figure 1.

Fig. 1 Main mine in Bulgaria [12]

The modern development of the mining industry is characterized by the influx of foreign investment, a high degree of mechanization, and an increasing focus on environmental standards. However, the industry faces

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serious challenges related to the sustainable management of natural resources, public discontent, and commitments under the EU Green Deal, including a gradual abandonment of coal power [13, 14].

The aim of this article is to assess the presence of heavy metals in samples collected near one of the mines in Bulgaria.

III. Methodology of the Experiment

The samples used in the study were collected from a river affected by mining, located in Bulgaria. The samples were taken at a coal mine located on the territory of Bulgaria. Sampling was conducted at various points along the river, with two locations close to the mine drainage flow and the other three along the river (Fig. 2).

The samples were taken in the following way: three of the samples (1,2 and 5) were taken at a distance of 500 m from the mine, and the remaining 2 were taken 1 km from the exit mine. The river in both sections, as can be seen in Fig. 2, has a calm character with low speeds. This gives us reason to believe that the place for selecting samples is well chosen, since there is no fast-flowing water that can wash away heavy metals.

Fig. 2 Study sampling

Clean polypropylene containers were used, previously rinsed with distilled water (Fig. 3). After collection, 2 mL of concentrated HNO_3 was added to each sample to maintain pH < 2. The samples were stored in refrigerated conditions (4 ± 1°C) until analysis. Filtration was performed in the laboratory by vacuum filtration through 0.45 µm membrane filters (nitrocellulose or polytetrafluoroethylene, PTFE). This step aims to separate the soluble forms of the metals from the insoluble fractions.

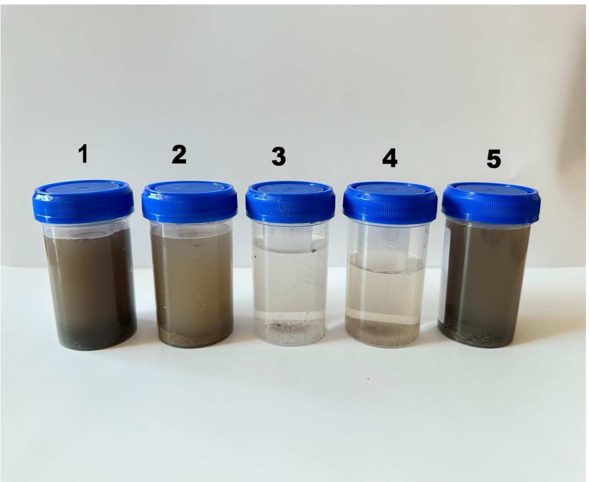

Fig. 3 Samples for analysis

Samples with visibly high turbidity or color were pre-diluted (1:5 to 1:50) with deionized water with conductivity < 0.05 µS/cm to avoid oversaturation of the instrument.
A PerkinElmer 2280 atomic absorption spectrophotometer was used to determine heavy metals in the samples.

The values of pH is measured with a device Milwaukee-MW101-Soil.

IV. Experimental Results

Based on the experimental studies conducted, the following results were obtained regarding the presence of heavy metals in the collected samples. All the results are presented at fig. 4-11.

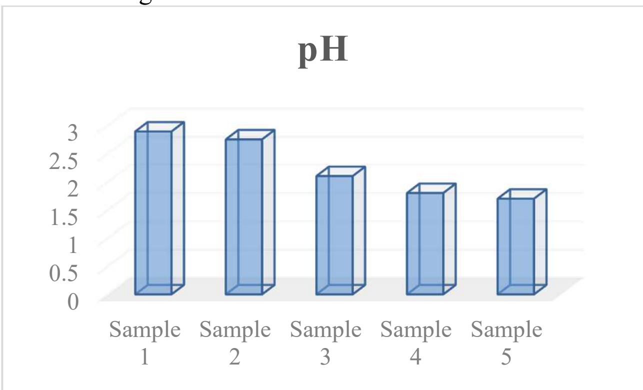

Fig. 4 pH values

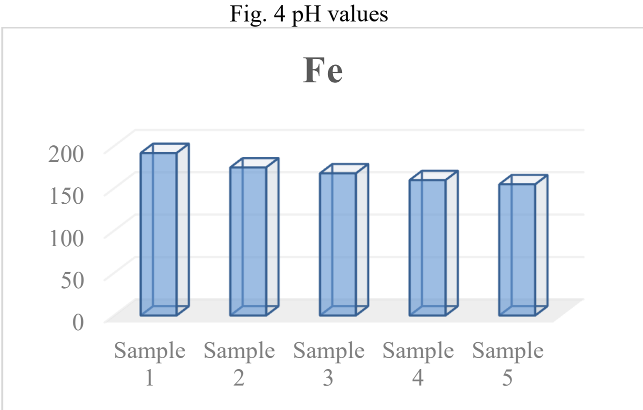

Fig. 5 Concentration of Fe,mg/dm^3

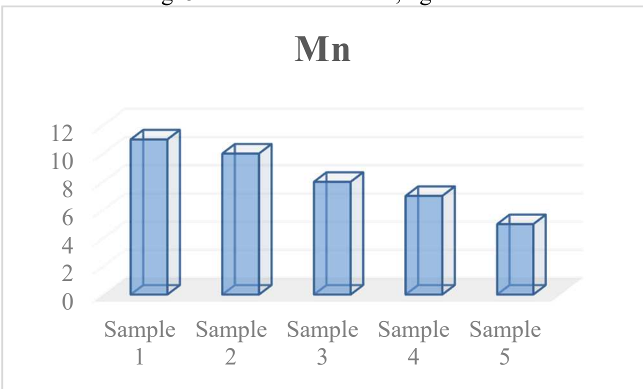

Fig. 6 Concentration of Mn, mg/dm^3

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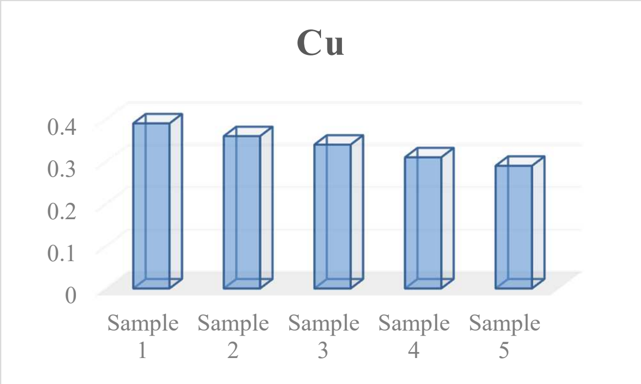

Fig. 7 Concentration of Cu, mg/dm^3

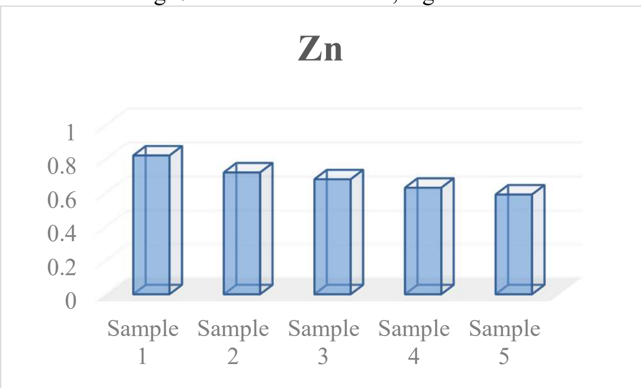

Fig. 8 Concentration of Zn, mg/dm^3

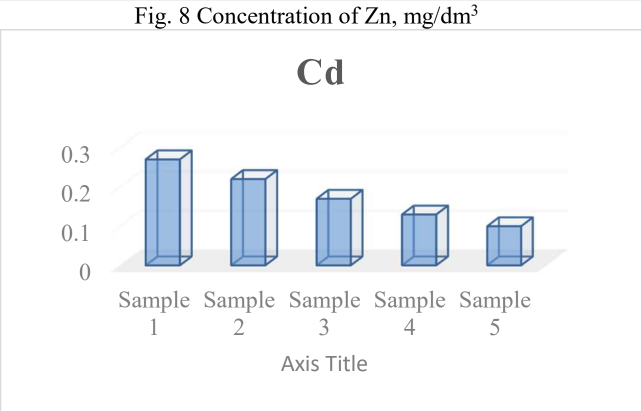

Fig. 9 Concentration of Cd, mg/dm^3

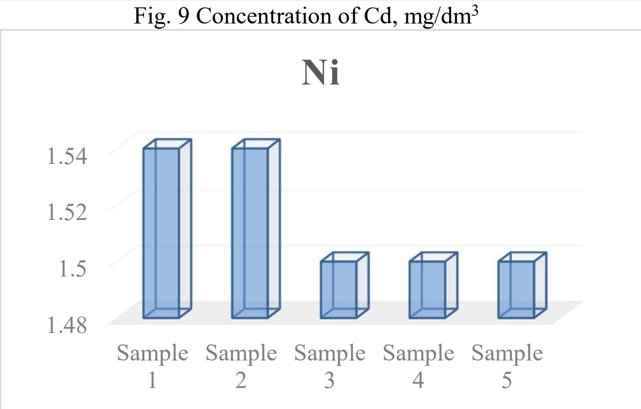

Fig. 10 Concentration of Ni, mg/dm^3

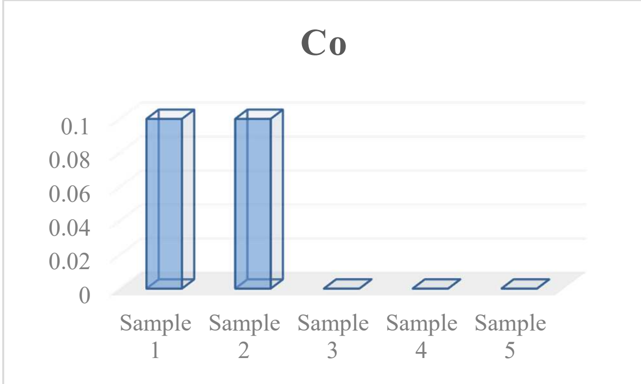

Fig. 11 Concentration of Co, mg/dm^3

A detailed and in-depth analysis of the processed results is given in section 5.

V. Discussion

The emission limits according to the legislation of the Republic of Bulgaria and water management in the studied area must be within the limits of the permissible concentrations for heavy metals in surface waters (fresh waters, including fish habitats), set out in Annex No. 1 of Regulation No. H-4/2012 (Regulation on the characterization and classification of surface waters).[13]

From the samples examined and the results obtained, it can be said that in all samples, increased values of heavy metals were observed above those that are permissible in [13].

The results obtained for the studied heavy metals, as well as the acidity of the soil, can be summarized as follows: When studying contaminated waters, it is important to consider the effects on living organisms caused by exposure to high levels of heavy metals, specifically the metals studied in the present work: Fe, Mn, Cu, Zn, Cd, Ni, and Co.

Iron is a vital trace element crucial for key physiological processes like oxygen transportation and antioxidant protection [14]. However, excessive iron intake can be detrimental. It can generate free radicals that induce oxidative stress, damaging lipids, proteins, and DNA, thereby increasing cancer risk [15]. Too much iron can also harm the nervous system, blood, lungs, liver, kidneys, and other organs, potentially leading to degenerative diseases similar to Parkinson's or Alzheimer's [14]. Furthermore, high iron levels in water can promote eutrophication, adversely affecting aquatic ecosystems and water quality [15].

Manganese (Mn) is an essential trace element required for various physiological functions, serving as a cofactor in multiple enzymatic reactions in both humans and animals [16, 17]. While Mn deficiency is rare due to its widespread availability in soil, the lithosphere, and dietary sources, excessive exposure can be toxic. Chronic low-level exposure has been linked to Parkinsonian symptoms [18]. Moreover, elevated manganese concentrations in drinking water have been negatively associated with neurodevelopment, behavioral outcomes, and academic performance in children [19].

Copper (Cu) is an essential micronutrient involved in numerous physiological processes; however, elevated concentrations can disrupt cellular function, cause oxidative damage, and lead to organismal toxicity or death [20].

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Sensitive species are damaged at lower concentrations, while more tolerant organisms are increasingly affected as contamination levels rise. Sublethal copper exposure can cause tissue harm, hindered growth and development, and biochemical changes like altered enzyme activity and blood chemistry. In aquatic environments, copper toxicity diminishes photosynthetic efficiency in submerged plants, leading to declines in biomass and habitat cover. Furthermore, elevated copper levels have been linked to reduced male fertility and increased risk of genetic disorders [21].

Zinc (Zn) is an essential micronutrient required by humans, animals, and plants for numerous physiological and biochemical functions. In humans, it plays critical roles in protein folding, DNA synthesis, growth hormone function, and male fertility. In plants, zinc is vital for chlorophyll production, protein synthesis, and overall development, making it fundamental to ecosystem health [22]. However, excessive zinc intake or environmental exposure can be harmful. In aquatic ecosystems, elevated Zn levels disrupt reproductive and developmental processes in fish, as well as impair physiological functions in plants, including photosynthesis, respiration, and nutrient uptake. In humans, excessive zinc may interfere with copper absorption, leading to gastrointestinal distress and, in severe cases, dysfunction in hematological, respiratory, cardiovascular, and neurological systems [23].

Cadmium (Cd) is a toxic heavy metal with no known physiological function in humans. Due to its widespread use in industrial processes, cadmium has become a significant environmental contaminant. Human exposure to contaminated water leads to bioaccumulation, particularly in the kidneys. Chronic exposure is associated with nephrotoxicity, skeletal damage due to disrupted bone metabolism, and an increased risk of osteoporosis and fractures. Cadmium is categorized as a Group 1 carcinogen with strong associations to lung and prostate cancers. It also plays a role in cardiovascular disease and reproductive issues. In the environment, cadmium harms plant growth and microbial communities, causing phytotoxicity and disrupting nutrient cycling, which ultimately affects ecosystem stability and function [24].

Nickel (Ni) is a common transition metal that is an essential micronutrient for many microorganisms and plants. However, at elevated concentrations, it exhibits significant toxicity. Human exposure may result in a range of adverse health effects, from allergic reactions such as contact dermatitis to more severe outcomes, including respiratory disorders, cardiovascular and renal diseases, and cancers of the lung and nasal cavity. The toxicological mechanisms involve oxidative stress, inflammation, and epigenetic modifications, all of which contribute to the development of carcinogenesis [25]. In animals, elevated nickel exposure has been associated with respiratory impairment, growth retardation, reproductive dysfunction, and organ toxicity [26]. Aquatic organisms are especially susceptible due to bioaccumulation and biomagnification, leading to broader ecological disruptions. Nickel contamination in soil and water can impair microbial activity, induce phytotoxicity, and negatively affect wildlife. Environmental factors such as pH, temperature, and the presence of other contaminants modulate nickel's toxicity and mobility [26].

Cobalt (Co) is an essential trace element required for human and animal metabolism, primarily due to its role in the synthesis of vitamin B12. While necessary in small amounts, elevated cobalt exposure can be detrimental to health. Toxic effects have been observed in the thyroid, cardiovascular, and hematopoietic systems. Cobalt is also associated with occupational health risks, including lung disease, allergic reactions, and potential tumor development. The International Agency for Research on Cancer (IARC) has classified cobalt as a Group 2A agent, indicating it is probably carcinogenic to humans [27].

One of the most serious environmental problems is the generation of acidic drainage waters flowing from various deposits, ore heaps and waste dumps. Due to their high acidity (extremely low pH), the generation of these waters leads to the disappearance of all flora and fauna in the water bodies into which they are discharged. The authors discuss the environmental and social impacts caused by mining, with a focus on the effects of water discharges related to mining in a previous study [28].

VI. Conclusion

This study examines the significant environmental impact of acid mine drainage (AMD) in regions of Bulgaria affected by mining activities. The collected water samples near a coal mine showed raised levels of heavy metals, including iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), cadmium (Cd), nickel (Ni), and cobalt (Co), along with low pH levels. These findings exceeded the regulatory limits set by Bulgarian legislation. Based on the already known effects of the heavy metals on living organisms, these findings confirm that acid mine drainage (AMD) has a harmful impact on water quality, aquatic ecosystems, and potentially human health.

Acknowledgment

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