University of Belgrade
Technical Faculty in Bor

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and Industry of Serbia

XV International Mineral Processing & Recycling Conference

IMPRC
INTERNATIONAL MINERAL PROCESSING & RECYCLING CONFERENCE

Proceedings

Editors:
Jovica Sokolović
Milan Trumić

17-19 May 2023 | Belgrade SERBIA

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BOR DISCRICT RIVERS WATERCOURSES CONTAMINATION BY Cu AND Ni IONS

R. Marković[1#], V. Gardić[1], R. Kovačević[1], Z. Stevanović[1], A. Isvoran[2], V. Marjanović[1], A. Petrović[1]

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ABSTRACT – The influence of the acid mine drainage and metallurgical wastewater on Cu and Ni ions concentration on the Bor district rivers watercourses is tested in the period from September 2020 to September 2021. Four sampling campaigns are realized in this period. Sampling points are selected in relation to the impact on Bor River, Krivelj River, Bela River, Timok River and Danube River. The presence of Cu and Ni ions in metallurgical wastewater has the dominant influence on the presence of Cu and Ni ions in the Bor district river watercourses.

Keywords: Wastewater, Acid Mine Drainage, Metallurgical, Cu, Ni.

INTRODUCTION

The need for minerals and metals necessary for global development makes mining one of the most important branches of the economy. The development of mining and related industries of production leads to significant economic growth and the benefit of countries on the one hand and on the other hand to the generation of different type of wastes. Mining operations have a huge local impact on the environment and population and the common challenge of all human society is to reduce the pollution and environmental damages produced by different processes. Even if the mining activities are stopped, the accumulated waste continuously pollutes and conduct to environmental damages and health effects. In the Bor Discrict, copper mineralization is mostly porphyry type of deposits containing mainly sulphur minerals associated with pyrites that are one of the sulphuric acid generators in contact with the atmosphere. Generally, the pH drops to values below 4, which causes dissolving of the metal ions [1,2]. Also, mining wastes generated during the copper ore treatment could be divided in the next types: tailings generated during flotation processes containing a variety of metallic and non-metallic minerals, spent ores consisting of the material remaining in either dump or heap leach piles when leaching ceases, acid rain resulting from the combination of rain and SO_2 causing damage to crops, trees and buildings for many miles downwind. Furthermore, the disposal of an enormous volume of tailings dumps poses a serious risk to the surrounding environment through air pollution due to air-dried out tailings,

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erosion of the tailings with the potential of valuable land degradation, and leaching of soluble inorganic potentially toxic chemical species (Cu, Ni, Pb, Zn, Cd, and Cr) occurring in a variety of minerals present in the solid wastes [3].

During the metallurgical activities, harmful and dangerous materials also are generated.

In the area of the influence of mining and metallurgy activities the wastewater are discharged into the local watercourses through the Bor and Timok rivers as a tributaries of Danube River [3].

In order to find measures and solutions for the reduction, remediation and elimination of Cu and Ni ions, it is necessary to have a true picture of the consequences of more than a century of continuous mining and metallurgical activities in the Bor District. The influence of the type of wastewater on the Cu and Ni ions concentration in the rivers downstream was analyzing in a period from September 2020 to September 2021 on fifteen sampling points that are selected in relation to the impact on Bor River, Krivelj River, Bela River, Timok River and Danube River as a target river.

EXPERIMENTAL

In this paper, aiming to assess the risk of mining activities in the vicinity of the Bor copper mine from Serbia which pollutes the surface water of Bor and Krivelj rivers with Cu and Ni ions, physico-chemical analysis of the collected samples were performed. Sampling was performed quarterly in the period September 2020 to September 2021, of the Bor River (W5), as well as from locations upstream and downstream of the Bor River (marked W1-W4, W6-W10). The sampling points that are selected for the Cu and Ni ions concentration monitoring are: W1 - Robule accumulation (AMD); W2 - Robule accumulation 1 (AMD); W3 - AMD from flotation tailing dam RTH; W4 - Metallurgical wastewater; W5 - Bor River; W6 - Krivelj River; W7 - Bela River after the confluence of Bor and Krivelj rivers; W8 - Ravna River; W9 - Bela River after flows of Ravna River; W10 - Bela River before of confluence with Timok River; W11 - Timok River before of confluence with Bela River; W12 - Timok River after confluence with Bela River (near the village Rajac); W13 - Timok River (near the village Mokranje); W14 - Timok River (near the village Bukovce); W15 - Danube River (near the village Radujevac). After confluence of Bor and Krivelj rivers downstream from the village of Slatina arises the Bela River. Ravna River which is outline of the copper mining activities inflows in Bela River, and Bela River inflows in Timok River which flows in Danube River. Bor and Krivelj rivers are polluted by the acid mine drainage originating from the active copper mining activities or from delayed mine overburden and flotation tailings. Krivelj River is polluted with the wastewater originating from the active mines (Bor pit, Veliki Krivelj, Cerovo, tailing dam in operation), as well as with the wastewater from the waste dump and flotation tailings which are not in operation during the long period (field 2 of the large flotation tailings Veliki Krivelj) [4]. The pollution of the Bor River is a consequence of the untreated municipal wastewater, metallurgical wastewater from copper metallurgical plant, wastewater from the mine tailings dump of the old Bor mine and Bor flotation tailing, as well as, from the old flotation tailings in Bor.

Sampling is realized by a hand tools, according to the sampling methods: SRPS EN ISO 5667-1; SRPS EN ISO 5667-3; SRPS ISO 5667-4; SRPS ISO 5667-6 [4].

Atomic emission spectrometer with inductively coupled plasma (ICPAES), model Spectro Arcos was used for determination the Cu and Ni ions concertation. The method of calibration curve was used. All reagents used for the Reagents of high purity grade chemicals were used for analyses. The certified reference material (CRM) and blank samples were used for quality control of chemical analysis. Measurement of the sample pH values was conducted in the field by the pH meter, model Dostmann.

RESULTS AND DISCUSSION

Results for pH values as so as the values of Cu and Ni ions concentration obtained during the measurement campaigns are discussed in this paper. Measured pH values for the water sampling points are presented in Figure 1. From Figure 1 it can be seen that the lowest pH value is registered for the sample point W4 (metallurgical wastewater) during each sampling campaign. The pH values that are in the range from 1.87 to 5.61 are lower than the allowable pH values regarding to Serbian legislation (range from 6.5 to 8.5) [5,6,7]. pH values for the sampling points W6 and W11 – W15 are in accordance with Serbian legislation.

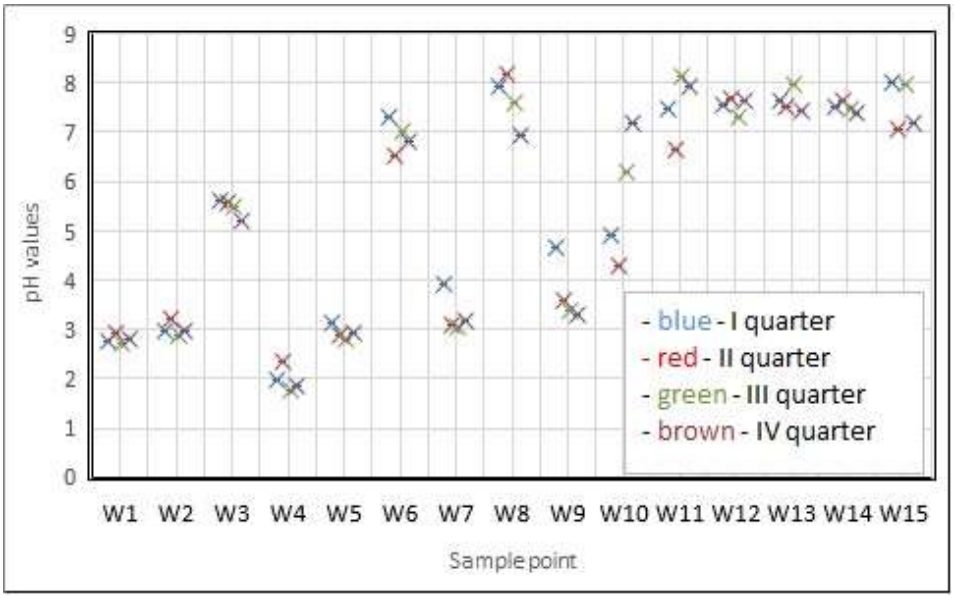

Figure 1 pH value

The pH values for the similar sample points, except for W10 - Bela River before of confluence with Timok River, were the similar for realized sampling campaigns.

The values of the Cu and Ni ions concentration in the water samples from the selected sample points are presented in Figure 2.

Cu ions maximal concentration is measured for the sampling point W4 - Metallurgical wastewater for all sampling campaigns. Having in mind that W4 – metallurgical wastewater inflows in Bor River (W5), concentration of Cu ions is also high in those samples. Cu ions are also present in AMD samples (W1, W2 and W3). Bela River (W7), a

river formed by the joining of W5 – Bor River and W6 – Krivelj River has the lower values for the Cu ions concentration. The presence of the Cu ions in the other sampling points is consequence of the inflows of W4 – metallurgical wastewater and AMD from the sampling points W1 - Robule accumulation, W2 Robule accumulation 1 and W3 - AMD from flotation tailing dam RTH. Concentration of Cu ions in metallurgical wastewater is about 300 times higher that maximal allowed concentration (MAC) according to the Serbian legislation for the IV class waters (Cu = 1 mg/l) and concentration of Cu ions in the AMD waters is maximal about 65 times higher than MAC. Similar flow rate of those wastewater confirmed that the Cu ions concentration from the metallurgical wastewater has the significant influence on the rivers downstream of the sampling points. Values for Cu concentration in W6 – Krivelj River, W8 - Ravna River and W11- Timok River upstream of the copper mining activities, are the lower than MAC value. After confluence of Bela River with Timok River, concentration of Cu ions has the lower values than MAC value for III water class of 0.5 mg/l.

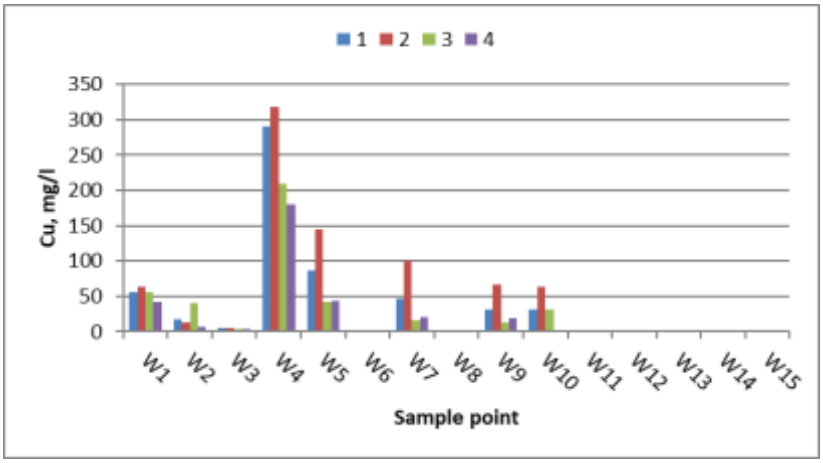

Figure 2 Cu ions concentration for different sampling quarters

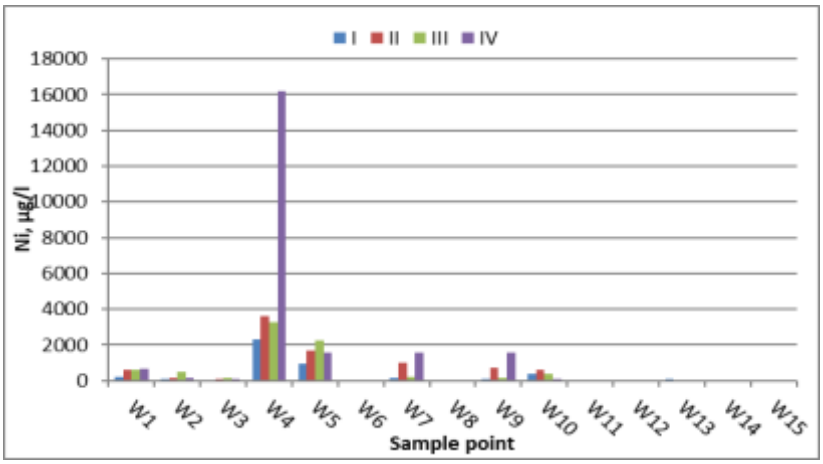

Figure 3 Ni ions concentration for different sampling quarters

Maximal value of Ni ions concentration is registered in the sample W4 - Metallurgical wastewater and this value is about 470 times higher than MAC value (Ni = 34 µg/l). Regarding the maximal concentration of Ni ions in AMD wastewater (sample W1), obtained value is about 20 times higher than MAC value for IV water class [7]. Based on the data presented in Figure 3, increased Ni ions concentration in W5 - Bor River, W7, W9 and W10 – Bela River on a different sampling points regarding to the confluence with the other rivers downstream of Bor River is consequence of the Ni ions content in metallurgical wastewater and AMD. Also, as in the case of the wastewater type influence on Cu ions concentration in the in the Bor district rivers watercourses, metallurgical wastewater has the significant influence on the value of Ni ions concentration in the rivers. After confluence of Bela River with Timok River the Ni ions concentration is reduced, but only in W15 – Danube River concentration is for realized sampling campaigns was lower than MAC value for II surface water class according to Serbian legislative.

CONCLUSION

Obtained results for Cu and Ni ions concentration in AMD and metallurgical wastewater sampling points are confirmed that values are higher than MAC values according to the Serbian legislation. Concentration of Cu ions in metallurgical wastewater is about 300 times higher than the MAC value and Ni ions concentration is higher about 470 times than the MAC. Value for Cu and Ni ions concentration in the AMD wastewater is higher for about 65 times and 20 times, respectively. Also, pH value of metallurgical wastewater sample is much lower than the pH of AMD samples. Results are confirmed that the high concentration of Cu and Ni ions in metallurgical wastewater has the main impact on Cu and Ni content in the Bor district rivers watercourses.

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