



Gold, Silver and Iron in Iron Oxy-hydroxide Precipitate Formed in Process of Acid Mine Drainage

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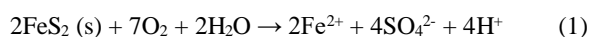
Silver

Abstract

Oxidation of sulfide-containing ores is the main cause of Acid Mine Drainage (AMD), which is an environmental problem associated with both the abandoned and active mines. Iron-bearing sulfide minerals can be oxidized and form mine waters with high sulfate content, low pH, high electrical conductivity, high redox potential, and high concentrations of iron, aluminum, and other heavy metals. In the process of AMD, precipitation of poorly crystalized oxy-hydroxides of iron with a large active surface can occur. On the surface of iron oxy-hydroxide, the precipitated particulate matter, anions, and cations (metals) could be adsorbed. Mine waters can contain a certain amount of precious metals that can also be adsorbed onto an iron particulate matter surface, which is investigated in this research work. In this work, the samples of iron oxy-hydroxide particulate matter at abandoned gold mine waste in Bakovići (Central Bosnia and Herzegovina) are used. Several parameters including pH, water content, particle size distribution, sulfate content, electrical conductivity, redox potential, and amounts of gold, silver, and iron are measured on the selected mine waste samples. The results obtained indicate that significant amounts of gold (average: 6.8 mg/kg) and silver (average: 7.13 mg/kg) are present in the iron precipitate. Adsorption of precious metals onto the iron oxy-hydroxide surface is strongly pH-dependent. At a very low pH value, desorption of precious metals is favorite. Thus, precious metals are only partially adsorbed onto the iron oxy-hydroxide surface.

1. Introduction

Mining of minerals that contain sulfide ions is associated with acid mine drainage (AMD), which is one of the most important environmental issues dealing with mining and mine wastes [1]. AMD is produced when a sulfide-bearing material is exposed to air and water, which occurs usually in iron sulfide–aggregated rocks. One of the better-known minerals that produce AMD is pyrite (FeS₂). Pyrite is a sulfide mineral that, if exposed to air and water, produces high concentrations of H⁺, sulfate anions, and iron ions (Equation 1) [2, 3].



Releases of AMD have a low pH, high electrical conductivity, and high metal and sulfate contents [4]. One of the characteristics of AMD is high concentration of iron in mine waters. Iron is present in two oxidation states, as the Fe²⁺ and Fe³⁺ ions. Iron enters the solution as Fe²⁺ ions. These ions can be oxidized to Fe³⁺ ions, and this is controlled by the pH of mine water, the amount of dissolved oxygen, and the presence of iron-oxidizing bacteria. The precipitation of secondary minerals is common for the AMD environments. The iron precipitates commonly occur as colorful bright reddish–yellow to brown solids [5-7]. The

precipitates of iron consist of a variety of amorphous, poorly crystalline, and crystalline Fe^{3+} hydroxides, oxy-hydroxides, and oxy-hydroxide sulfate minerals [8]. The precipitation of solids is accompanied by a decrease of elements and their compounds, resulting in lower total dissolved solids. The surface of iron hydroxides can adsorb metal ions. Their surfaces are generally amphoteric, i.e. the surface is pH-dependent. The sorption of anions is favored at a low pH value, while the sorption of cations is favored at a high pH value [9]. At the zero net charge, both anions and cations are adsorbed. In the case of iron hydroxides, the zero net charge lies between the pH values of 6 and 10 [10]. On the surface of iron oxy-hydroxides, metal cations could be adsorbed, for instance, cations of copper, lead, and cadmium [11]. Since cations of metals can be adsorbed onto oxy-hydroxides of iron that are precipitated in the AMD process, it is theoretically possible for the precious metals to be adsorbed as well, for example, cations of gold or silver. The precious metals like gold and silver (especially gold) are well-known as not reactive metals (they occur in the elemental state in nature) because they could behave differently regarding adsorption on oxy-hydroxides of iron formed in AMD. On the other hand, the extraction procedures that are applied at a mine area are never 100% efficient, and waste materials from metal mining such as mineral tailings often contain significant amounts of potentially valuable metals [12]. The subject area for this investigation is the abandoned gold mine of Bakovići in central Bosnia and Herzegovina, which is the biggest gold deposit in the country [13]. In this mine, gold- and silver-bearing pyrite and siderite is mined, and it is possible for AMD to occur. Trace metals (including gold and silver) move between the dissolved and particulate phases. Adsorption is the term that is used to describe the removal of ions from solution and their adherence to the surface solids [14]. The attachment of the solutes onto the particulate matter (iron oxy-hydroxides) does not represent a permanent bond, and the adsorption is based on the electrostatic attraction between the solid phases and solutes (metals). The kind of metal adsorbed is a function of several parameters, i.e. a) solution pH, b) presence of complexing ligands, and c) metal concentration. While the precipitate may remove ions from solution, it may also release adsorbed metals if the medium is later acidified. As a result of a higher acidification (lower pH), certain metals could be desorbed from the particulate matter formed in AMD (oxy-hydroxides of iron) and be

partially present in the water part of the precipitate. According to all facts regarding AMD and the possible presence of precious metals arise the aim of this research work: characterization of adsorption of precious metals (gold and silver) on the surface of the iron oxy-hydroxide precipitate formed during the AMD process with special emphasis on the pH value.

2. Materials and methods

2.1. Area under investigation

The biggest gold deposit in Bosnia and Herzegovina is located in Bakovići near Fojnica (46°56'N, 17°56'E), central Bosnia and Herzegovina (Figure 1). The first exploration works started at the site in 1880. The sampled ore contained 8 to 15 g/t Au. In 1894, the systematic exploration started until 1918. In 1934, the mining activities were reactivated. In the first phase of reactivated mining, it favoured the mining of gold-bearing limonite ore because it did not make difficulties in the extraction using the method of cyanization. The limonite was crushed, pulverized, mixed with the lime in containers of 40 L in volume, and afterwards the gold was extracted with NaCN. The extraction coefficient raised to 82 % (mainly between 75% to 77%). In the period from 1936 to 1937, 19.386 t of limonite with 13.9 g/t of Au was mined, as well as 3.700 t of limonite from older wastes, which contained 21.15 g/t Au. After excavation of gold-bearing limonite, it started with excavation of pyrite that contained gold. A total of 4000 t of gold bearing pyrite was mined, with 13,5 g/t of Au. The total ore production in Bakovići mine in a period from 1895 to 1938 (without data for 1908, 1909, and 1918) was 2240 kg of gold and 7475 kg of silver. In some places, pyrite is almost the only mineral, while in the others, it is a subordinate mineral. Quartz and siderite are very common, and they make 20% to 50 wt% of the ore, with very variable proportions but quartz is more abundant than siderite [13]. Apart from pyrite, quartz and siderite are the dominant minerals, whereas tetrahedrite, galena, stibnite, arsenopyrite, barite, and gypsum are the accessories. Iron oxy-hydroxides are the predominant secondary minerals. Mining was active until the Second World War. Now, the gold mine in Bakovići is abandoned.

As a sampling medium, an iron oxy-hydroxide precipitate formed in AMD and brought by mine waters. Investigation of mine waters in the vicinity of the abandoned gold mine site shows typical chemical characteristics of AMD [15]

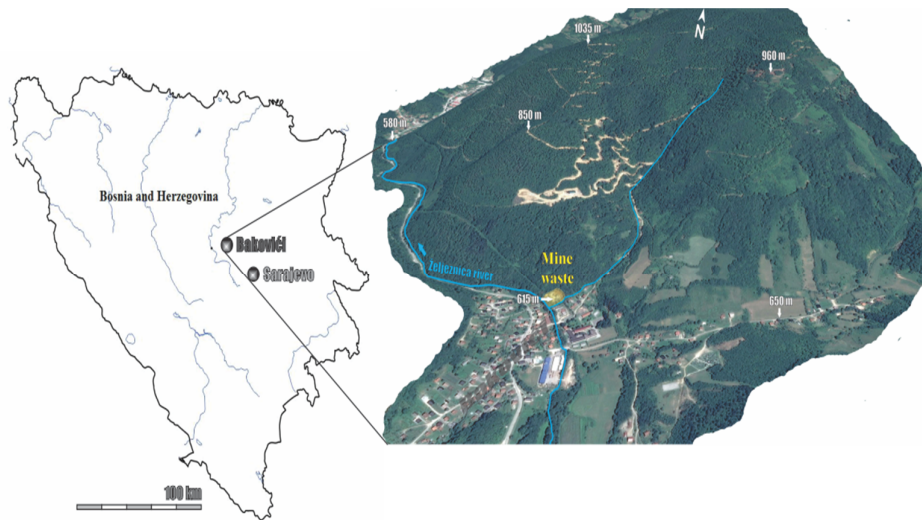


Figure 1. Bakovići location in Bosnia and Herzegovina, with Morphological view of mine area.

2.1.1. Hydrogeological characteristics of terrain

In a hydrogeological view, the observed terrain is built of metamorphic and magmatic rocks that are mostly watertight. The general feature of these rocks is prismatic, crevice, and cavernous porosity. In areas of intense cracks, there is a possibility that surface waters are infiltrated into mining operations, especially those at deeper depths. Metamorphic (various types of shingles) and magmatic rocks (marialites) belong to a group of hydrogeological conductors, which do not contain significant amounts of groundwater. Given the morphology of the terrain and the types of porosity present, infiltrated water moves to lower levels and drains through old mining operations.

2.1.2. Mine wastes of abandoned gold mine “Bakovići”

Mine wastes that were left behind after the mining of gold and silver in Bakovići (1938), according to their genesis, are associated with anthropogenic embankments or scattered reservoirs.

Five mine wastes have been detected in the terrain, four of which are located in the slopes of Mount Ključ, while one of the mine wastes is located near River Željeznica, close to the village of Bakovići. Mine wastes located in the slope of Mount Ključ hill have a thickness of about 3-4 m. The mine waste on the right bank of the River Željeznica has a considerably greater thickness, ranging from 8 to 12 m. This mine waste was the object under investigation in this work. Location of the site is not covered by trees; it is accessible and close to the residential buildings of the Bakovići settlement. In the northern part of the mine waste, there is one source of mining water. On the main export shaft, the ore was processed after excavation.

2.2. Sampling

The mine waste used in this research work is composed of economically not profitable side rock. It is located in front of the main export shaft and has an area of about 700 m² and a very heterogeneous appearance. The reddish-brown parts of therein were formed by depositing particles that were created in the AMD process and by rinsing of the mine. This area was in a significant part of the time covered by the water that was coming down the hill where excavations were made. The second part is in gray color, and it is mainly made of quartz and muscovite. The investigation was conducted on the reddish-brown part of mine waste. This part of mine waste was formed in a long period of time by rinsing of mine and precipitation of iron oxy-hydroxide particulate matter formed in AMD.

Sampling of the material that was reddish-brown was carried out with a 100 cm long stainless-steel sampler. Probe sampling was carried out in two directions, stretching from the main export shaft to the River Željeznica every 10 m (Figure 2). The sampling lines were located at an angle of about 60°. In this way, a total of 6 probed samples (A, B, C, D, E, and F) were taken. In the first direction, there were a total of 4 probed samples (A, B, C, D), and there were two probed samples (E, F) in the other direction.

The sampling probe was immersed in various places at different maximal depths (the sampling depths were different for the individual sampling positions and ranged from 20 cm in the case of the probed sample F to 100 cm in the case of the probed sample A).

The difference in the sampling depths depended on the thickness of the iron oxy-hydroxide precipitate that was physically possible to probe. After the

sampling, 10 cm long sub-samples were taken (Table 1).



Photo: J. Jurković J.

Figure 2. Sampling positions.

Table 1. Sub-samples.

Sample	Depth (cm)	Sample	Depth (cm)	Sample	Depth (cm)
A ₁	0–10	C ₁	0–10	E ₁	0–10
A ₂	10–20	C ₂	10–20	E ₂	10–20
A ₃	20–30	C ₃	20–30	E ₃	20–30
A ₄	30–40	C ₄	30–40	E ₄	30–40
A ₅	40–50	C ₅	40–50	E ₅	40–50
A ₆	50–60	C ₆	50–60		
A ₇	60–70	C ₇	60–70	F ₁	0–10
A ₈	70–80			F ₂	10–20
A ₉	80–90	D ₁	0–10		
A ₁₀	90–100	D ₂	10–20		
		D ₃	20–30		
B ₁	0–10	D ₄	30–40		
B ₂	10–20	D ₅	40–50		
B ₃	20–30				
B ₄	30–40				

2.3. Sample preparation

A standardized method for digestion with *aqua regia* was used (ISO 11466: 1995). Approximately 3 g of dried and homogenized sample was weighted with precision of ± 0.0001 g. The sample was transferred into a round bottom volumetric flask, followed by an addition of 28 mL of *aqua regia* (HCl: HNO₃ – 3:1) (21 mL of concentrated HCl and 7 mL of concentrated HNO₃), and allowed to stand for 16 h. It was then heated under a reflux for 2 h. The obtained mixture was filtered on a quantitative filter paper and transferred to a 100 mL volumetric flask. Deionized water was used for making up the volume. This method does not extract the total amount of metals because *aqua regia* does not dissolve the metals in weakly soluble compounds such as sulfides or silicates.

2.4. Mineral characterization

An XRD analysis was carried out on a powder sample, with the analysis of the red-brown specimen using a 24-h long method (AXS Bruker D 5005), and using CuK α radiation at 293 K. Finely ground samples were placed on a Si single-crystal holder and measured in the range of $10^\circ < 2\theta < 70^\circ$. The diffraction data was analysed using the EVA program and the PDF Datafile.

2.5. Particulate matter Distribution

A particulate matter distribution was measured by sieving the sample through the following pore dimensions: 2 mm, 1 mm, 500 μ m, 355 μ m, 250 μ m, 180 μ m, 125 μ m, 63 μ m.

2.6. AMD parameter analysis methods

2.6.1. Moisture content determination

The moisture content was determined using the gravimetric method by drying the samples in an oven at 105 °C to a constant mass. The moisture was determined immediately after the samples were brought to the laboratory in three replications on a sample mass of 2 to 4 g.

2.6.2. pH value determination

The pH value was measured using a pH-meter (Mettler Toledo MP 220) with the ion-selective hydrogen electrode. The instrument was calibrated with buffers having pH values of 4.21 and 7.00. The sample was prepared with deionized water in a ratio of 1:5 (sample: deionized water) according to ISO 10390: 2005.

2.6.3. Electrical conductivity Determination

The electrical conductivity measurement was performed using a conductivity meter (Mettler Toledo MC 126), which was calibrated with known electrical conductivity standards, according to the EPA 9050 A method.

2.6.4. Redox potential determination

The measurement was performed with a redox potential measuring device (HANNA HI 98201). The instrument was calibrated with solutions of known redox potential. The redox potential was measured according to the APHA method.

2.6.5. Soluble sulfate content determination

Sulfates were extracted from the samples with deionized water at a 1:5 ratio. The resulting suspension was agitated at 180 rpm per minute for 2 h. The sulfate content was determined by ionic chromatography using the sulfate ion standards. The instrument used for ion chromatography was Varian Pro Star (Dionex conductivity detector, CD 20).

2.7. Metal content analysis method

Pseudo-total amounts of iron, gold, and silver were measured by the ICP-MS technique. The ICP-MS measurements were performed using the standard reference material (SRM 1640-a) on the ICP-MS Perkin Elmer ELAN DRC-e instrument. An external standard method was used to measure the metal concentration. Rhodium was used as an internal standard in this technique.

2.8. Statistical evaluation

The results of this research work were statistically evaluated using the SPSS 20.0 statistical program (SPSS Inc., Chicago, IL, USA) through the following analysis:

- Descriptive statistics (mean, maximum, and minimum values);
- Correlation is used to measure similarity between two groups of results. Description of correlation coefficients measuring the strength of connection between two variables is as follows: 0.0-0.19, very weak connection; 0.2-0.39, weak connection; 0.40-0.59, moderate connection; 0.60-0.79, strong connection; 0.80-1.0, very strong connection. Correlation can be uphill (the coefficient of correlation (r) is positive) or downhill (the coefficient of correlation (r) is negative).

3. Results and discussion

3.1. Studied sample geochemical characterization

3.1.21. XRD analysis

Figure 3 shows the diffractogram of the mine waste sample. The results of X-ray diffraction show that in the sample, there are several different oxy-hydroxides of iron, and none of them is in a significantly higher concentration. Only one secondary mineral was found in a higher concentration than the others—goethite.

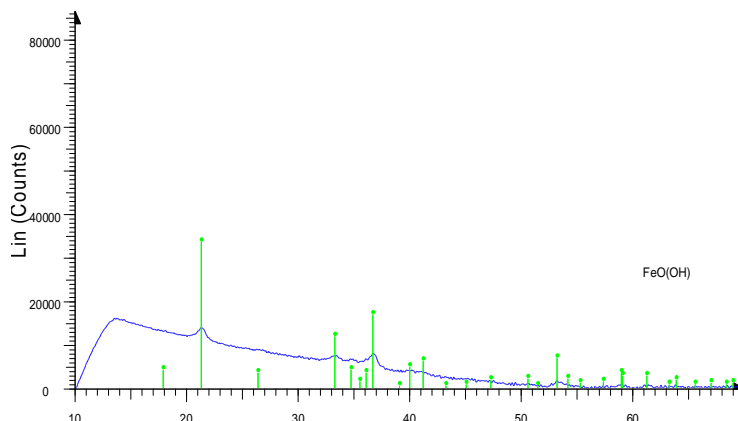


Figure 3. Diffractogram of iron oxy-hydroxide sample

3.1.2. Characterization of AMD process

3.1.2.1. Determination of moisture content

The results of moisture content determination are shown in Figure 4. From the value presented below, one can see the general trend of moisture content.

3.1.2.2. pH determination

The pH measurement results are shown in Figure 5. pH value in the mine waste samples is very low- it is a very acidic medium.

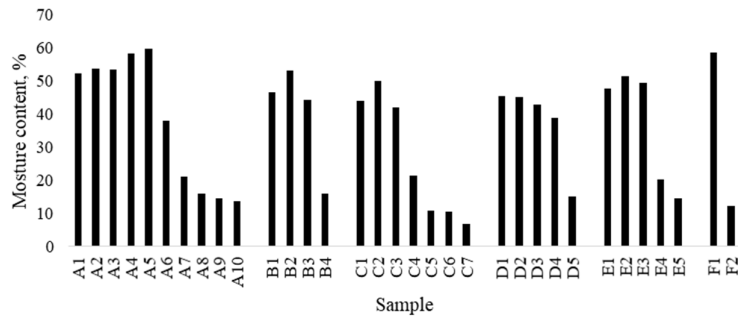


Figure 4. Diagram of moisture content in mine waste samples.

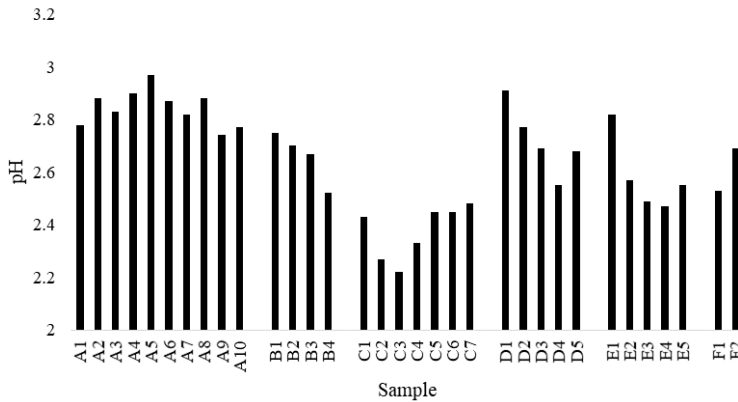


Figure 6. Diagram of pH value in mine waste samples.

3.1.2.3. Electrical conductivity determination

Electrical conductivity of the samples is shown in Figure 6. The electrical conductivity of waste samples shows high and uneven values.

3.1.2.4. Redox potential determination

The results of redox potential measurements are shown in Figure 7. Redox potential shows fairly uniform values. All values are within the oxidation area (the "+" sign).

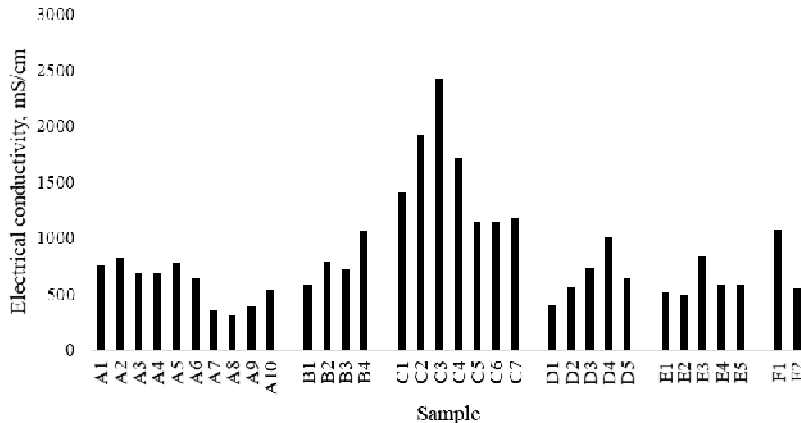


Figure 6. Diagram of electrical conductivity in mine waste samples.

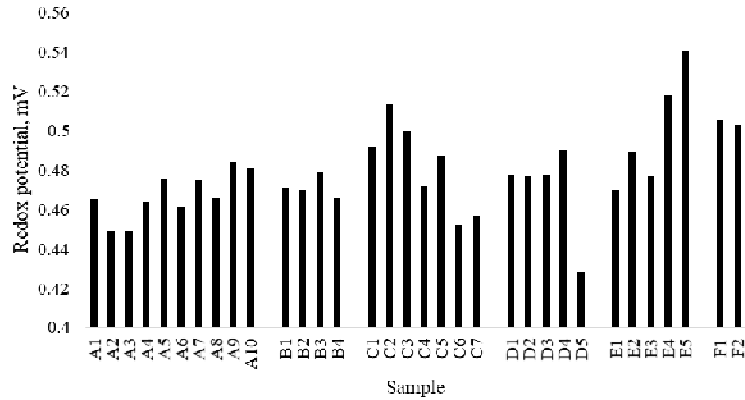


Figure 7. Diagram of redox potential in mine waste samples.

3.1.2.5. Sulfate content determination

Concentrations of sulfate in investigated samples are shown in the Figure 8. Sulfate concentrations in most cases decrease with depth.

3.1.3. Metal content determination

The results of gold, silver, and iron content measurements are shown below.

3.1.3.1. Gold content determination

The investigated mine waste contained significant amounts of gold (average value, 6.18 mg/kg). In most cases, the concentration of gold first increased and then decreased with depth. The results of gold concentrations are shown in Figure 9.

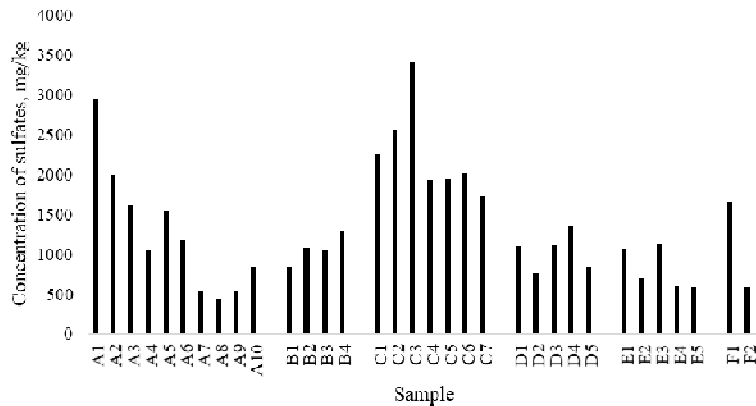


Figure 8. Diagram of sulfate concentration in mine waste samples

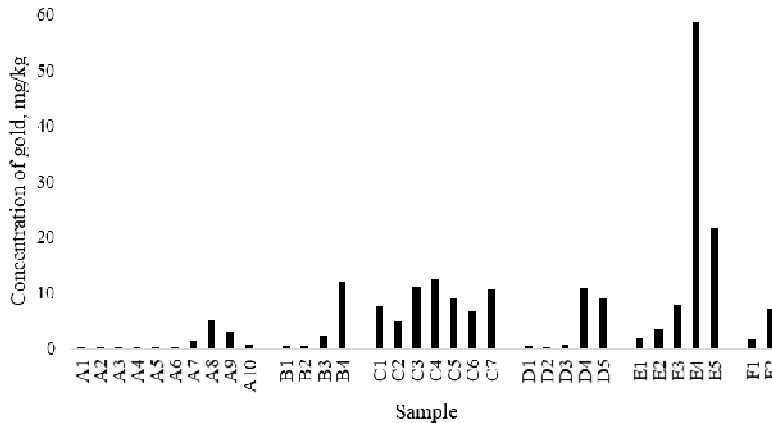


Figure 9. Diagram of gold content in mine waste.

3.1.3.2. Silver content determination

The samples of mine waste contained silver in significant concentrations (average value, 7.13 mg/kg). From the obtained results for silver, it can be seen that the silver content for most sampling positions at first decreased with depth and then increased. On Figure 10, the results of amounts of silver are shown.

3.1.3.3. Iron content determination

Iron is an element observed to have the highest concentration of all the analyzed elements. Such a result was expected because mostly iron ore (pyrite, siderite) containing gold and silver was deposited in the mine. Concentrations of iron are shown in the Figure 11.

In Table II, results of following parameters are shown: moisture content, pH value, electrical conductivity, redox potential, sulfate content, and content of gold, silver, and iron.

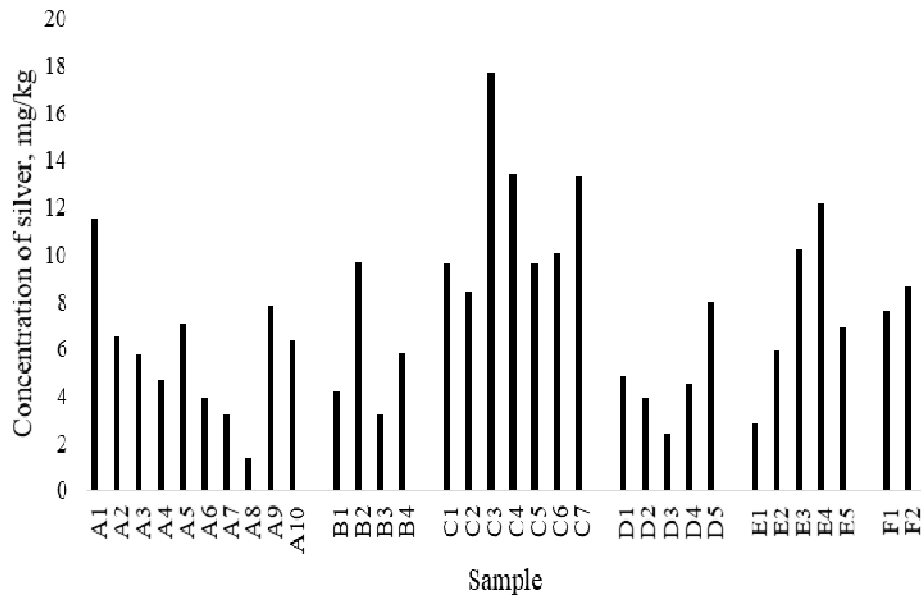


Figure 10. Diagram of silver content in mine waste.

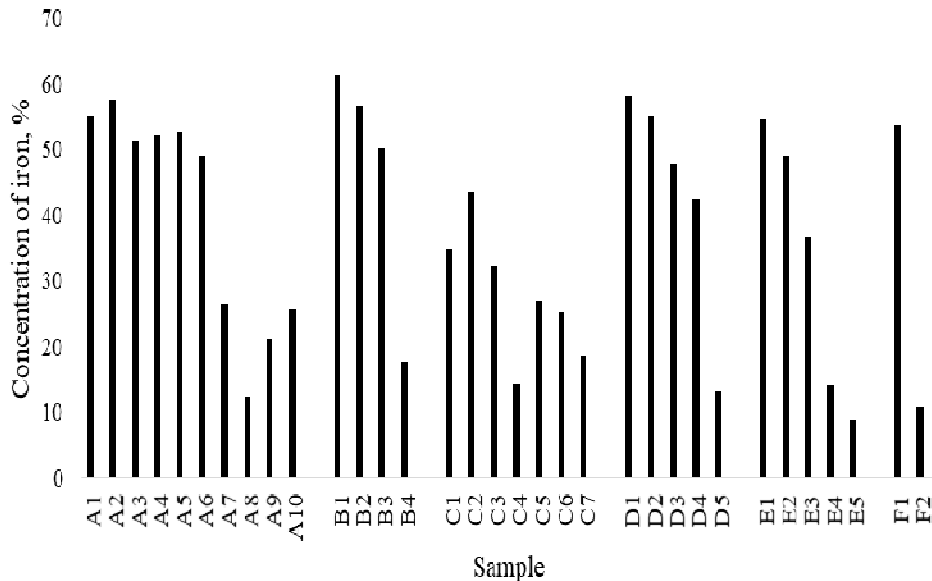


Figure 11. Diagram of iron content in mine waste.

Table II. Chemical characterization of samples.

Sample	Moisture (%)	pH	EC (mS/cm)	Redox potential (V)	SO ₄ ²⁻ (mg/kg)	Au (mg/kg)	Ag (mg/kg)	Fe (%)
A ₁	52.22	2.78	758	0.465	2945.51	0.33	11.52	55.02
A ₂	53.62	2.88	819	0.449	1999.51	0.17	6.49	57.52
A ₃	53.25	2.83	685	0.449	1621.73	0.03	5.77	51.39
A ₄	58.24	2.9	679	0.464	1057.99	0.07	4.67	52.23
A ₅	59.58	2.97	777	0.476	1546.82	0.1	7.05	52.58
A ₆	37.84	2.87	631	0.461	1178.66	0.16	3.93	48.95
A ₇	21.14	2.82	359	0.475	528.68	1.39	3.18	26.41
A ₈	15.77	2.88	309	0.466	427.36	5.00	1.34	12.42
A ₉	14.48	2.74	392	0.484	529.99	2.96	7.84	21.14
A ₁₀	13.64	2.77	539	0.481	831.58	0.76	6.37	25.56
B ₁	46.51	2.75	582	0.471	838.31	0.36	4.19	61.18
B ₂	53.07	2.7	791	0.47	1084.08	0.39	9.67	56.54
B ₃	44.18	2.67	717	0.479	1039.93	2.29	3.195	50.29
B ₄	15.97	2.52	1068	0.466	1286.67	11.88	5.83	17.65
C ₁	43.85	2.43	1401	0.492	2252.52	7.65	9.63	34.84
C ₂	49.94	2.27	1919	0.513	2553.39	4.81	8.37	43.63
C ₃	41.8	2.22	2420	0.5	3401.73	11.04	17.65	32.19
C ₄	21.27	2.33	1718	0.472	1933.92	12.31	13.37	14.49
C ₅	10.72	2.45	1136	0.487	1951.73	8.9	9.59	26.89
C ₆	10.45	2.45	1142	0.452	2008.72	6.59	10.05	25.25
C ₇	6.77	2.48	1175	0.457	1716.15	10.68	13.28	18.70
D ₁	45.26	2.91	401	0.478	1101.69	0.37	4.85	58.09
D ₂	45.12	2.77	561	0.477	764.6	0.19	3.92	55.03
D ₃	42.77	2.69	723	0.478	1114.45	0.58	2.425	47.75
D ₄	38.78	2.55	1013	0.49	1362.98	10.86	4.52	42.25
D ₅	15.17	2.68	648	0.428	848.83	8.78	7.95	13.04
E ₁	47.71	2.82	517	0.47	1062.73	1.89	2.86	54.53
E ₂	51.27	2.57	493	0.489	688.5	3.56	5.92	48.88
E ₃	49.35	2.49	838	0.477	1125.99	7.78	10.21	36.77
E ₄	20.21	2.47	586	0.518	605.53	58.71	12.18	14.17
E ₅	14.38	2.55	583	0.541	591.77	21.53	6.91	8.97
F ₁	58.44	2.53	1074	0.505	1668.76	1.56	7.6	53.78
F ₂	12.07	2.69	557	0.503	576.52	7.26	8.615	10.87

3.2. Results and discussion

The samples of AMD precipitate from this research work are composed of various oxy-hydroxides of iron. The mixture of iron oxy-hydroxides is poor in crystallization, and it is difficult to see some other secondary mineral than goethite. Goethite is one of the oxy-hydroxides of iron that is the most stable form of Fe (III). Goethite also precipitates from AMD (especially at lower redox conditions and sulfate content) [16].

The first parameter that was measured in the samples was moisture content. The maximum value of the moisture content in the waste samples was measured from the probed sample A in the sub-sample A₅ (59.58%). The probe position A is closest to the main export shaft. In the vicinity of the main export shaft mine water is discharged. The minimum moisture content was measured from the probed sample C, in the C₇ sub-sample (6.77%). The results of the determination of moisture show lower values in the upper layers in most cases (because of evaporation). The moisture content grew in deeper layers, and then towards the end of the probed sample, it decreased again. The moisture content values show a very strong correlation with the iron value (r = +0,893). This

very strong correlation with the iron content can be explained by the fact that water has a high affinity for iron oxy-hydroxides precipitated in the AMD process of [17].

The maximum pH value was measured in the probed sample A, the sub-sample A₅ (2.97), and the minimum pH value was measured in the probed sample C, the C₃ sub-sample (2.22). The pH values are fairly uniform and show very strong negative correlation with conductivity (r = -0.791), strong negative correlation with silver content (r = -0.682), moderate negative correlation with sulfate content (r = -0.480), and gold content (r = -0.458). A strong negative correlation with electrical conductivity means that the higher conductivity is, the lower pH will be. This result is expected since a higher concentration of H⁺ ions increases the conductivity and, at the same time, lowers the pH value. A strong negative correlation with an amount of silver and a moderate negative correlation with a sulfate content shows that silver is rather soluble in waste and associated with sulfur compounds.

The electrical conductivity of the waste samples shows high and uneven values. The highest electrical conductivity was measured in the probed

sample C, and the highest value was found in the C₃ sub-sample (2420 mS/cm). The probed sample C is located at a distance 30 m from the main export shaft. The minimal electrical conductivity was measured in the probed sample A and in the sub-sample A₈ (309 mS/cm). The electrical conductivity shows a very strong negative correlation with the pH value ($r = -0.791$), a very strong correlation with the sulfate content ($r = +0.823$), and a strong correlation with the silver content ($r = +0.682$). The correlation of electrical conductivity and pH value is explained in Section 3.2.2. A very strong positive correlation between the sulfate content and electrical conductivity can be explained by the fact that the higher concentration of sulfate is (higher amounts of ions), the higher electrical conductivity will be [18].

The highest value for the redox potential was measured at the probed sample E, in the E₅ sub-sample (+ 0.541 V). The minimum redox potential was measured in the probed sample D, the D₅ sub-sample (+ 0.428). The redox potential shows a moderate negative correlation with the pH value ($r = -0.435$). This correlation means that a lower pH gives a higher redox potential (more oxidative value). This can be explained by the fact that the ions in this research work that contribute most to the pH value (amounts of H⁺, and amounts of SO₄²⁻-consequently H⁺ ion) cannot be oxidized more and exist in their highest oxidized form in solution. The highest values for the sulfate content were measured in the case of the probed sample C, in the C₃ sub-sample (3401.7 ppm). The sampling position C is 30 m away from the main export shaft. The minimum content of sulfate was measured in the probed sample A, in the sub-sample A₈ (427.4 ppm). The lowest sulfate average values were measured in the probed samples B and E. These two boreholes are located at the same distance from the main mineral export shaft. The sulfate content shows a very strong correlation with electrical conductivity ($r = +0.823$), a strong correlation with silver content ($r = +0.615$), and a moderate correlation with pH value ($r = -0.480$). A strong correlation with silver content can lead us to the conclusion that sulfate partially comes in compounds with silver.

From the results of electrical conductivity, pH value, and sulfate content, we can see that the lowest pH value, highest conductivity, and sulfate content are found in the probed sample C, in the sub-sample C₃. This sampling position is 20 m away from the main export shaft, and the subsoil C₃ is at a depth of 30-40 cm.

In one sample of mine waste, a significantly higher pseudo-total gold content (E₄) was found with a maximum value of 58.7 ppm. Maximum values of gold in 4 out of 6 wells (B, C, D, E) were measured in a sub-sample located at a depth of 30-40 cm. The minimum value of gold content was found in the probed sample A, in the sub-sample A₃ (0.03 ppm). The gold shows a moderate negative correlation with iron content ($r = -0.555$), redox potential ($r = +0.461$), and pH value ($r = -0.458$). It is significant that only gold, among all the investigated parameters, shows a positive weak connection to 2-mm granulometric fraction ($r = 0.365$). The largest fraction of samples enables most water flow. This finding is in correspondence with the results that show that gold is mostly found in water fraction of iron AMD precipitate. The finding that gold is in larger amounts in the water phase, and not adsorbed on iron particulate matter, is probably due to a very low pH value of samples. The low pH value favors desorption of gold from particulate matter and disables gold adsorption. In one sample (E₄), a significantly higher concentration of gold was found. At a very low pH value found in this investigation, gold could be in water solution present in the form of AuHS, which was described in [19].

The maximum value of the pseudo-total content of silver in the samples of mine waste was measured in the case of the probed sample C, in the C₃ sub-sample (17.6 ppm). The minimum value of the silver content was measured in the probed sample A, in the sub-sample A₈ (1.3 ppm). Silver showed a strong negative correlation with pH value ($r = -0.682$), and a strong positive correlation with electrical conductivity ($r = +0.682$) and sulfate content ($r = +0.615$).

The red-brown part of the mine waste composing mainly of iron oxy-hydroxide was formed by the processes of mine rinsing and acid mine drainage. In surface areas, the iron content was uniform in all the samples. In the samples from the probed sample A (closest to the main export shaft), the values of iron content were almost constant up to a depth of 60 cm. For the samples from the probed samples B, D, E, and F, the concentration of iron in one part suddenly decreased with depth, in most cases this was a depth of 30-40 cm (the value of iron content decreased to about 15%). The maximum value of iron content when extracted with aqua regia (pseudo-total quantity) was measured in the probed sample B, in the B₁ sub-sample. The minimum value of iron content was measured in the probed sample E, in the E₅ sub-sample. In the statistical analysis of the results, iron showed a very strong

correlation with the value of the moisture content ($r = +0.893$), and a moderate negative correlation with gold ($r = -0.555$). Correlations for iron are described in the section regarding moisture and gold content. Iron does not correlate with pH value, which is also shown in [20]

4. Conclusions

The AMD process in the investigated mine waste is still active, which is proved by a low pH, a high conductivity, a high sulfate, and a high iron content. In the precipitate of iron oxy-hydroxide formed during AMD, significant amounts of precious metals are present: gold (average value, 6.8 mg/kg) and silver (average value, 7.13 mg/kg). This finding is a proof for scavenging effect of precipitating iron in mine waters, which is the main surface process responsible for removing most heavy metals from mine waters, and the loading of the same metals in stream sediments. A negative correlation between the results for gold (silver) and iron was found, which indicated that gold and silver were only partially adsorbed on oxy-hydroxides of iron. Adsorption of gold and silver is disabled by the low pH of the mine waste since desorption of metals from iron oxy-hydroxides is favored at a low pH value [21].

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طلا، نقره و آهن در رسوبات هیدروکسید آهن تشکیل شده در فرآیند زهاب اسیدی معدن

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چکیده:

اکسید شدن ماده‌ی معدنی حاوی سولفید عامل اصلی زهاب اسیدی است (AMD)، که یک مسئله زیست محیطی مرتبط با معادن فعال و متروک است. مواد معدنی سولفیدی حاوی آهن می‌توانند اکسید شده و آب معدن را با محتوای سولفات زیاد، pH پایین، هدایت الکتریکی بالا، پتانسیل ردوکس زیاد و غلظت بالای آهن، آلومینیوم و سایر فلزات سنگین تشکیل دهند. در فرآیند AMD، رسوب گذاری اکسید-هیدروکسیدهای کریستالیزه ضعیف از آهن با یک سطح فعال بزرگ می‌تواند رخ دهد. بر روی سطح اکسید هیدروکسید آهن ذرات رسوب شده، آنیون‌ها و کاتیون‌ها (فلزات) می‌توانند جذب شوند. آب معدن می‌تواند حاوی مقدار مشخصی از فلزات گرانبها باشد که می‌تواند روی سطح ذرات آهن نیز جذب شود، که در این کار تحقیقاتی مورد بررسی قرار گرفته است. در این تحقیق از نمونه‌های ذرات اکسید هیدروکسید آهن در باطله‌های یک معدن طلا متروک در باکوویچی (بوسنی و هرزگوین مرکزی) استفاده شده است. پارامترهای متعددی از جمله pH، آب محتوی، توزیع اندازه ذرات، میزان سولفات، هدایت الکتریکی، پتانسیل ردوکس و مقادیر طلا، نقره و آهن بر روی نمونه‌های باطله‌های معدن اندازه گیری شد. نتایج به دست آمده حاکی از آن است که مقادیر قابل توجهی طلا (میانگین: 6/8 میلی گرم بر کیلوگرم) و نقره (میانگین: 7/13 میلی گرم بر کیلوگرم) در رسوب آهن وجود دارد. جذب فلزات گرانبها روی سطح اکسید هیدروکسید آهن به شدت وابسته به pH است. مقدار pH کم برای جذب سطحی بیشتر بسیار مناسب خواهد بود. بنابراین، فلزات گرانبها فقط تا حدی روی سطح اکسید هیدروکسید آهن جذب می‌شوند.

کلمات کلیدی: زهاب اسیدی معدن، معدن، باطله معدنی، رسوبات، آهن، طلا، نقره.