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ASSESSMENT OF THE POTENTIAL FOR ACID DRAINAGE GENERATION FROM MINING WASTE CONTAINING SULFIDE MINERALS USING THE SRPS EN 15875:2013 METHOD

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Abstract

Mining waste containing sulfide minerals is a potential source of acid drainage waters (Acid Rock Drainage – ARD), which can contribute to the mobilization of metals and other potentially harmful elements and pose a long-term risk to the environment. This study examines the potential for acid drainage generation from a sample of flotation tailings produced during the concentration of polymetallic lead-zinc sulfide ore. The ARD potential was assessed using the static method in accordance with the SRPS EN 15875:2013 standard by determining the acid potential (AP), neutralization potential (NP), neutralization potential ratio (NPR), and net neutralization potential (NNP). XRD analysis indicated the presence of approximately 4% pyrite, while the total and sulfur derived from sulfide minerals - sulfide sulfur contents were 2.20% and 1.95%, respectively. Based on the total and sulfide sulfur contents, NPR values of 0.13 and 0.15 and NNP values of −59.50 and −51.69 kg $CaCO_3$/t, respectively, were obtained. These results indicate a pronounced potential of the examined tailings for acid drainage generation.

Keywords: *mining waste; flotation tailings; pyrite; acid drainage water; ARD potential; SRPS EN 15875:2013.*

1. INTRODUCTION

Significant amounts of mining waste are generated during geological exploration, exploitation, preparation, and processing of mineral raw materials. Mining waste may include overburden, tailings, flotation tailings, and other waste materials that may contain heavy metals and other potentially harmful elements.

Flotation tailings generated during the processing of non-ferrous ores, such as copper, zinc, and nickel ores, may contain varying amounts of sulfide minerals, including pyrite and other sulfides. When exposed to oxygen and water, these minerals undergo oxidation and dissolution processes, which may result in the formation of sulfate ions and the release of acidity. The resulting acidity can contribute to increased mobilization of metals and other elements present in mining waste. If the neutralization capacity of the material is insufficient to neutralize the generated acidity, acid drainage

(Acid Rock Drainage – ARD) may develop, representing one of the significant long-term environmental risks associated with the disposal and management of sulfide-containing mining waste. Various static and kinetic test methods can be applied to assess this potential [1, 2].

Assessment of the acid generation potential is an important step in the characterization and appropriate management of sulfide-containing mining waste. The SRPS EN 15875:2013 method defines a static procedure for determining the Acid Potential (AP) and Neutralization Potential (NP) of sulfide waste, based on which its potential for acid drainage generation can be assessed. The results obtained can provide a basis for further evaluation of the long-term behavior of mining waste [4].

A particularly important parameter is the pyrite content, as its oxidation can represent a significant source of acidity. The extent of oxidation and the amount of acidity generated depend, among other factors, on the sulfide content, the mineralogical form of the sulfides, the availability of oxygen and water, and the presence of minerals capable of neutralizing acidity, such as carbonates. Therefore, determination of the total sulfur or pyrite content alone is not sufficient for the final assessment of ARD potential; rather, the relationship between the acid generation potential and the neutralization potential should also be considered.

1.1. SRPS EN 15875 standard method for testing ARD potential

The SRPS EN 15875:2013 method, "Waste characterization – Static tests for the determination of the acid and neutralization potential of waste containing sulfides", is used to assess the potential of sulfide-containing waste to generate acid drainage [5]. The standard defines procedures for determining the acid potential (AP) and neutralization potential (NP), based on which the net neutralization potential (NNP) and neutralization potential ratio (NPR) are calculated.

Testing according to SRPS EN 15875:2013 includes the determination of total and sulfur derived from sulfide minerals - sulfide sulfur contents, calculation of AP, determination of carbonate content, determination of NP, and calculation of NNP and NPR. The acid potential represents the maximum potential acidity that can be generated by the oxidation of sulfides. Its calculation is based on the assumption that the total sulfur originates from pyrite and that complete oxidation of pyrite results in the release of the corresponding amount of acidity.

The neutralization potential is determined by reacting the sample with hydrochloric acid, followed by determination of the amount of acid consumed by back-titration with sodium hydroxide. In the procedure, the pH of the suspension is initially adjusted by adding hydrochloric acid and, after a defined reaction period, back-titration is performed to pH 8.3.

AP and NP can be expressed as $CaCO_3$ equivalents, most commonly in kg $CaCO_3$/t of waste, which enables direct comparison of the acid and neutralization potentials of the material.

NPR values < 1 indicate insufficient neutralization capacity relative to the potentially generated acidity and indicate a potential for acid drainage generation. Conversely, NPR values > 1 indicate that the neutralization capacity exceeds the potentially generated acidity. However, the ratio between the acid potential (AP) and neutralization potential (NP) does not, by itself, provide a completely reliable indication of the actual behavior of the material under natural conditions.

The reaction rates of minerals contributing to acidity generation and those possessing neutralizing properties may differ significantly. Their reactivity and availability can be influenced by mineralogy, crystal structure, specific surface area, and other physicochemical factors. Therefore, a certain range of NPR values can be considered a zone of uncertainty in which the potential for ARD generation cannot be reliably assessed based on NPR values alone.

Although NPR is one of the basic indicators used to assess the potential of mining waste for acid drainage generation, NNP can provide additional information for the interpretation of test results. NNP represents the difference between the neutralization potential (NP) and the acid potential (AP) and enables assessment of the balance between the potential acidity and the neutralization capacity of the material.

Based on the criteria applied in this study, the ARD potential of mining waste can be assessed by considering NNP and NPR values simultaneously:

- If NNP < −20 kg $CaCO_3$/t and NPR < 1, the material can be classified as having a high potential for acid drainage generation. If there are indications that the sulfides present are non-reactive or only weakly reactive, additional tests should be performed to obtain a more reliable assessment.
- If $-20 \leq NNP \leq +20$ kg $CaCO_3$/t and $1 \leq NPR \leq 3$, the material falls within the zone of uncertainty, and additional investigations are required for a more reliable assessment of its ARD potential.
- If NNP > +20 kg $CaCO_3$/t and NPR > 3, the results of the static test indicate that the material has sufficient neutralization capacity relative to its potential acidity and is considered to have a low potential for acid drainage generation [6].

2. MATERIALS AND METHODS

Demineralized water, hydrochloric acid (HCl), p.a., at a concentration of 1 mol/L, and sodium hydroxide (NaOH), p.a., at a concentration of 0.1 mol/L were used in the experiment. The laboratory equipment included an analytical balance, 250 mL containers made of inert material, a magnetic stirrer, crushing equipment, a pH meter, pipettes, and sieves.

The laboratory sample was prepared by crushing and homogenization, ensuring that at least 95% of the sample mass had a particle size smaller than 0.125 mm. After determining the dry residue content and calculating the required sample mass, the test was performed according to the procedure defined by the SRPS EN 15875:2013 standard [5].

The ARD potential was assessed using a sample of flotation tailings generated during the flotation concentration of polymetallic lead-zinc sulfide ore. According to the XRD analysis, quartz, alkali feldspar, mica, kaolinite, and pyrite were identified in the examined sample. The estimated pyrite content was approximately 4%. Table 1 presents the identified minerals, their chemical formulas, and their estimated contents.

Table 1. *Names and assessment of mineral content in the sample*

No.	Name of mineral	Content assessment (%)
1.	Quartz	56
2.	Alkali feldspar	31
3.	Mica	4
4.	Kaolinite	5
5.	Pyrite	4

The total sulfur content was determined using the high-temperature combustion method according to ISO 15178 and was 2.20%, while the sulfide sulfur content was 1.95%. The carbonate carbon content was determined using the dry combustion method according to EN 13137:2001, Method A, and was 0.65%. The obtained results were evaluated and calculated in accordance with the SRPS EN 15875:2013 standard. The test results are presented in Table 2.

Table 2. *Results of static testing of mining waste according to the SRPS EN15875 method*

Parameter	Unit	Sample
Dry residue of the laboratory sample (w_{dr})	g	2.00
Volume of added demineralized water	ml	90
pH at t = 0 before acid addition	-	6.32
pH after t=22 h before acid addition	-	3.25
pH after t=22 h after acid addition	-	2.01
Total volume of added HClHCl (V_A)	ml	3.35
pH at t = 24 h after water addition	-	2.15
Volume of NaOH used for titration (V_B)	ml	29.80
Sulfur content (total sulfur- w_S	(%)	2.20
Sulfide sulfur content	(%)	1.95
Carbonate rating expressed as carbon content (total carbon), CO_3-C	(%)	0.65
Calculation based on total sulfur content and NP determined from HCl consumption		
AP	H^+ mol/kg	**1.38**
AP	($CaCO_3$) kg/t	68.75
NP	H^+ mol/kg	**0.19**
NP	($CaCO_3$) kg/t	54.17
NPR	H^+ mol/kg	**0.13**
NNP	H^+ mol/kg	-1.19
NNP	($CaCO_3$) kg/t	**-59.50**
Calculation based on sulfide sulfur content and NP determined from HCl consumption		
AP	H^+ mol/kg	**1.22**
AP	($CaCO_3$) kg/t	60.94
NP	H^+ mol/kg	**0.19**
NP	($CaCO_3$) kg/t	54.17
NPR	H^+ mol/kg	**0.15**
NNP	H^+ mol/kg	-1.03
NNP	($CaCO_3$) kg/t	**-51.69**

3. RESULTS AND DISCUSSION

The results of the static test showed an unfavorable relationship between the acid and neutralization potentials of the tested flotation tailings. Based on the total sulfur content, an AP of 68.75 kg $CaCO_3$/t, an NP of 54.17 kg $CaCO_3$/t, an NPR of 0.13, and an NNP of −59.50 kg $CaCO_3$/t were calculated. The calculation based on the sulfide sulfur content yielded an AP of 60.94 kg $CaCO_3$/t, an NP of 54.17 kg $CaCO_3$/t, an NPR of 0.15, and an NNP of −51.69 kg $CaCO_3$/t.

The obtained values of NPR < 1 and NNP < −20 kg $CaCO_3$/t indicate that the neutralization capacity of the tested tailings is insufficient to neutralize the potentially generated acidity. According to the criteria applied in this study, the examined material can be classified, based on the static test results, as having a pronounced potential for acid drainage generation (ARD). These results are consistent with the identified presence of pyrite, whose oxidation represents a potential source of acidity.

It is particularly important that the final assessment of the potential for acid drainage generation should not be based solely on the NPR value, but should consider AP, NP, and NNP together with the mineralogical composition and the reactivity of the sulfide and neutralizing minerals present.

Based on the results of the static test according to SRPS EN 15875:2013, presented in Table 2, the examined flotation tailings sample shows a pronounced potential for acid drainage generation, resulting from the unfavorable balance between acid and neutralization potentials.

4. CONCLUSION

The obtained results indicate a potential long-term risk of acid drainage generation and the consequent mobilization of metals and other potentially harmful elements from the mining waste.

The results of the study confirm the importance of assessing ARD potential as part of the characterization of sulfide-containing mining waste and indicate the need for appropriate management measures aimed at preventing or reducing contact between the waste, water, and oxygen, thereby limiting potential impacts on surface water, groundwater, and soil.

When a significant acid generation potential is identified, the potential for the mobilization of metals and other potentially harmful substances should also be assessed. The results of static and kinetic tests, together with the chemical composition and leaching test results, can provide a basis for assessing long-term environmental risks and selecting appropriate measures for the management of such mining waste.

The time required for the onset of acid drainage generation can vary significantly and depends on the mineralogical composition of the waste, the content and reactivity of sulfide minerals, the presence of neutralizing minerals, and hydrological and climatic conditions.

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