

Static tests to assess acid mine drainage potential of copper sulfide flotation tailings

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Abstract

Most copper flotation tailings contain a significant amount of sulfide minerals that can generate effluent resulting from the oxidation of sulfides when they are exposed to oxygen and water. This study aimed to characterize and evaluate the acid drainage potential of five different copper flotation tailings, named samples I, II, III, IV, and V. Sample I was taken from an industrial operation, while Samples II, III, IV, and V were produced in pilot plant tests. All samples were characterized and submitted to static acid drainage tests, such as paste pH, Net Acid Generation (NAG) pH, and Modified Acid-Base Accounting (MABA). The sulfur as sulfide/total sulfur mass ratios varies from 0.40 up to 0.89 showing the presence of a high amount of minerals rich in pyrite and alunite, being higher than 13 wt% of pyrite in samples IV and V and around 19 wt% of alunite in sample III. Samples I and II presented a high number of alkaline elements, totalizing more than 8 wt% of $K_2O+CaO+MgO$, while samples III, IV, and V show the lowest amount of these elements (<4 wt%). Only samples III, IV, and V show Paste pH results lower than 5.0, indicating superficial oxidation on their surfaces and/or the presence of water-soluble acidity minerals. Due to the high pyrite content in samples III and IV, it was not possible to measure their NAG pH due to the high heat released with the addition of hydrogen peroxide. The low NAG pH obtained with sample III (5.30) was due to its high pyrite content (0.30 wt%) in comparison with the results obtained with sample I (NAG pH of 8.15 and 0.10 wt% of pyrite), and sample II (NAG pH of 8.18 and 0.10 wt% of pyrite). The MABA results show that samples III, IV and V presented acid drainage potential due to the neutralization potential (NP)/acidity potential (AP) ratio being lower than 1. On the other hand, samples I and II presented NP/AP ratio higher than 4, not showing potential to generate acid drainage. Due to these results, it is recommended to carry out acid drainage kinetic tests with samples III, IV, and V to determine the long-term weathering rates, evaluate lag time to acid generation and provide reaction rates for geochemical modeling.

Keywords: Static tests; Acid drainage; Copper; Flotation; Tailings.

1 Introduction

Copper is essential to economic and technological development, so substantial growth in its applications has continued in the 21st century, driven by the rapid industrialization of China and other emerging markets [1].

However, most copper mines generate a large amount of tailing after concentration of mined ore [2-8]. For sulfide copper ores, tailings are obtained from the flotation process and account for ~98% of the ore fed to the concentrator [1]. It is estimated that the total quantity of mine tailings is about 45 billion tons, accounting for more than 80% of the total amount of industrial solid wastes in China [9-11].

As a solution to this problem, the copper tailings have been either piled up or stored in dams, which requires complex structures and huge investment, as well as cost-effective maintenance and environmental fees [9]. It is worthwhile to mention that the storage of copper tailings in dams also represents a threat to the surrounding environment [12].

Recently, many methods have been developed and applied to prevent possible acid drainage pollution such as opening drainage channels around the mine site and limestone filling applications [13], passive and active treatment

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methods [14-16], modeling with clay-geomembrane for ensuring impermeability [17].

Sulfide mineral oxidation, mainly pyrite (FeS_2) and pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$), are the main cause of acid drainage generation. Sulfide oxidation occurs whenever the water in the presence of oxygen percolates through sulfide minerals, acquiring high acidity and high concentrations of metal ions, such as Fe^{2+} and/or Fe^{3+} , and sulphates in the solutions [18-20].

As most sulfide copper flotation tailings contain a significant amount of non-copper sulfide minerals and a low amount of copper sulfide minerals, they can generate effluent resulting from the oxidation of sulfides when they are exposed to oxygen and water. Low mine water pH will occur if the rate of acid generation due to sulfide oxidation is more than acid consumption by neutralizing minerals [21].

In addition to the acidity produced, the consequent solubilization and mobilization of metals at low pH, such as Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn, can lead to contamination of aquatic and soil environments. In 1989, it was estimated that 19,300 km of streams and rivers, and 72,000 ha of lakes and reservoirs worldwide had been seriously damaged by mine effluents [22]. Acid drainage is one of the most problematic environmental issues facing the mining and minerals industry.

By predicting mine-waste drainage quality before the inception of mining, planning for mineral-resource development and mine-waste management can be made to minimize adverse environmental impacts throughout the lifetime of the working mine, and after mine closure [21,23,24]. The most widely used tests to quantify acid drainage potential are static tests and kinetic tests. The goal is to use static and kinetic tests in conjunction with other relevant data to assist in developing strategies for the environmentally sound management of mine wastes [25].

This study aimed to characterize and evaluate the acid drainage potential of different copper flotation tailings. The copper flotation tailings, named as samples I, II, III, IV, and V, presented different chemical compositions, size distributions, and mineral assemblages. All samples were submitted to static acid drainage tests, being the following: Paste pH, NAG pH (Net Acid Generation), and MABA (Modified Acid-Base Accounting). The combination of these results allowed us to classify the flotation tailings according to their potentially acid-forming (PAF) or non-acid forming (NAF) as well as to identify the samples that require kinetics testing to predict their long-term impacts in the environment.

2 Methodology

2.1 Sample characterization

The procedures used to prepare and characterize the samples are shown in Figure 1. The characterization of samples comprises chemical analyses and modal mineralogy.

All samples were dried at 60°C until constant weight, cooled at room temperature ($\sim 20^\circ\text{C}$), screened to <1 mm to prevent the presence of lumps, and sub-samples were split for chemical analyses, particle size distribution, mineralogy, and static tests (paste pH, NAG and MABA). The samples for chemical analyses and static tests were pulverized to 100% <75 μm . The size distributions were carried out using pulps with 30% of solids. The analytical procedures are listed in Table 1 for solutions and in Table 2 for solid samples. Mineralogical characterization was determined using Quantitative Evaluation of Materials by Scanning Electron Microscopy (QEMSCAN). Mineral data were correlated with chemical analyses. These analyzes generated information such as mineral composition and element department for each sample. The size distribution followed conventional sieving for particles bigger than 45 μm and hydrocyclone loop for particles smaller than 45 μm .

2.2 Acid drainage static tests procedures

The following acid drainage static tests were carried out with five copper flotation tailings: NAG pH, MABA, and paste pH. The paste pH determines the potential short-term

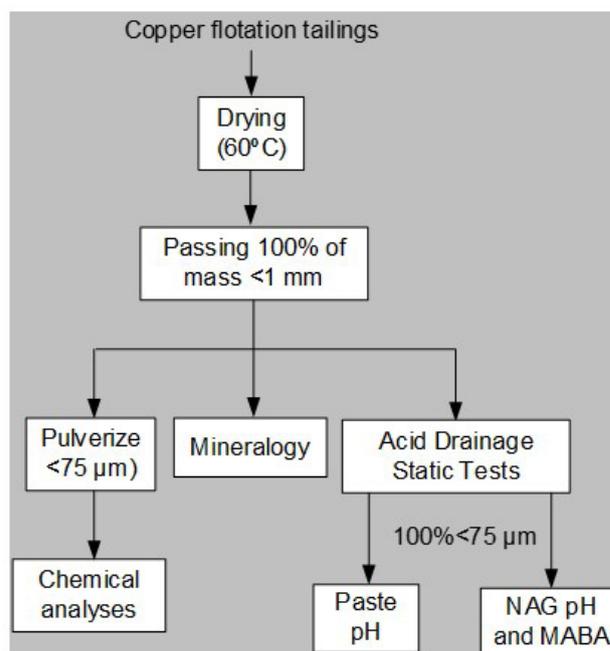


Figure 1. Block diagram for sample preparation and characterization.

Table 1. Analytical procedures for chemical analyses for solutions

Element	Analytical methodology
Metals	USEPA Method 3005A (1992) [26].
Anions	USEPA Method 300.0 (1993) and USEPA Method 300.1 (1997) [27].
Alkalinity	SMWW, 23 rd Edition - Method 2320 (2020) [28].
Acidity	SMWW, 23 rd Edition - Method 2310 (2018) [29].

Table 2. Analytical procedures for chemical analyses for solids samples

Element	Analytical methodology
Ca, Mg, Al, Fe, Mn, P and Si	Calcination at 600°C, fusion with Na ₂ CO ₃ and Na ₂ B ₄ O ₇ and reading ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry) from Agilent model 5110.
Sulfide	Leaching with calcium carbonate, direct combustion and reading in Infra-red from LECO model 844.
Cu, As	Total solubilization with aqua regia and reading in ICP-OES.
S	Direct combustion and reading in Infra-red from LECO model 844.
K	Solubilization in HCl + HF and reading ICP-OES.
Fluorine	Fusion with KNO ₃ and KOH, dissolution in water and reading in a selective ion electrode.
Chlorine	Fusion with KNO ₃ and KOH, dissolution in water and titration with AgNO ₃ solution.

effect of superficial and soluble salts on water quality and the stored acidity, the NAG pH measures the acid generation when the sulfides minerals are oxidized by hydrogen peroxide, and the MABA test establishes the overall acid-generating capability of material through a simultaneous reaction of acid-generating and acid-neutralizing components. The NAG pH assesses the maximum acidity potential, as all sulfides are assumed to be available for acid generation immediately.

2.2.1 NAG pH test

A mixture of 250 mL of 15% m/v H₂O₂ solution with 2.5 g dry copper flotation tailings 100% < 0.075 mm is prepared. It is boiled and stirred for 2 hours, followed by cooling, stirring, and measuring the NAG pH. According to Price [30], NAG pH < 4.5, likely acid mine drainage (AMD) potential or the sample is classified as PAF (Potentially Acid Forming), and if NAG pH > 4.5 no AMD potential or the sample is classified as NAF (Non-Acid Forming). If NAG pH > 4.5, the test is finished, if not, the pulp is neutralized with NaOH solution 0.10 mol.L⁻¹ until pH of 4.5 and pH of 7.0. The procedure of the NAG pH test is presented in Figure 2a.

2.2.2 MABA test

The acidity potential (AP) was calculated using the S as sulfide content and the neutralization potential (NP) was determined by leaching 2.5 g of copper flotation tailings, 100% < 0.075 mm, with 250 mL of 1.0 mol.L⁻¹ HCl solution for 24 hours. The pH was maintained between 2.0 up to 2.5 by the addition of 1.0 N HCl solution. The not reacted HCl is measured by the addition of 0.10 mol.L⁻¹ NaOH solution. With the values of AP and NP was possible the predict the acid-base balances for samples. According to Price [30], for neutralization potential ratio: NP/AP < 1, likely acid mine drainage (AMD) potential or sample classified as PAF; NP/AP between 1 up to 4, possibly AMD potential or in an uncertain region and NP/AP > 4, no AMD or sample classified as NAF. The procedure of the MABA test is presented in Figure 2b.

2.2.3 Paste pH test

A mixture of deionized water and dry copper flotation tailings was prepared in a 1:5 up to 1:1 mass ratio, such as

2 ml up to 10 ml of deionized water and 10 g of dry copper flotation tailings 100% < 0.075 mm. The paste is stirred with a spatula as required to saturate (no puddling of water or dry appearance of solid) and carefully placed the pH electrode to measure of paste pH. Although this test cannot predict long-term conditions, it is very quick, inexpensive, easy to perform in the field and laboratory. It can be useful monitoring tests for operational mine waste management. According to Price [30], if the paste pH is lower than 5, the sample is classified with acidity potential or NAF, but if the paste pH is higher than 7, it is classified as neutral or PAF. The procedure of the paste pH test is presented in Figure 2c.

3 Results and discussion

3.1 Sample characterization

Flotation tailings from three different sulfide copper ores were assessed. The Sample I was taken from an industrial operation, while Samples II, III, IV and V were generated in pilot plant tests.

Samples I and II are flotation tailings from two different copper sulfide ores which the main Cu-bearing mineral being chalcopyrite (CuFeS₂). These final tailings are a mixture of 90 wt% of rougher and 10 wt% of scavenger tailings. Samples III, IV, and V are from different copper sulfide ore which the main Cu-bearing minerals are covellite (CuS) and enargite (Cu₃AsS₄). Sample III is the rougher tailing, Sample IV is the scavenger tailing, and Sample V the final tailing (70 wt% of sample III and 30 wt% of sample IV). The processing of the ore generates two flotation tailings with distinct characteristics since the rougher tailing is characterized by low sulfides content and the scavenger tailing is composed of more than 40% of pyrite. The block flow diagram shown in Figure 3 represents the general flowsheet from which the tailings were produced.

The copper ore is crushed and ground to P₈₀ between 150 and 250 µm to achieve the required liberation for the rougher flotation stage. The rougher concentrate is submitted to regrind (P₈₀ between 25 and 50 µm), followed by the cleaner flotation stage (cleaner and/or recleaner, depending on the ore). Cleaner tailings feed the scavenger flotation stage. The rougher and scavenger tailings will form the final tailings that will be sent to the tailings dam.

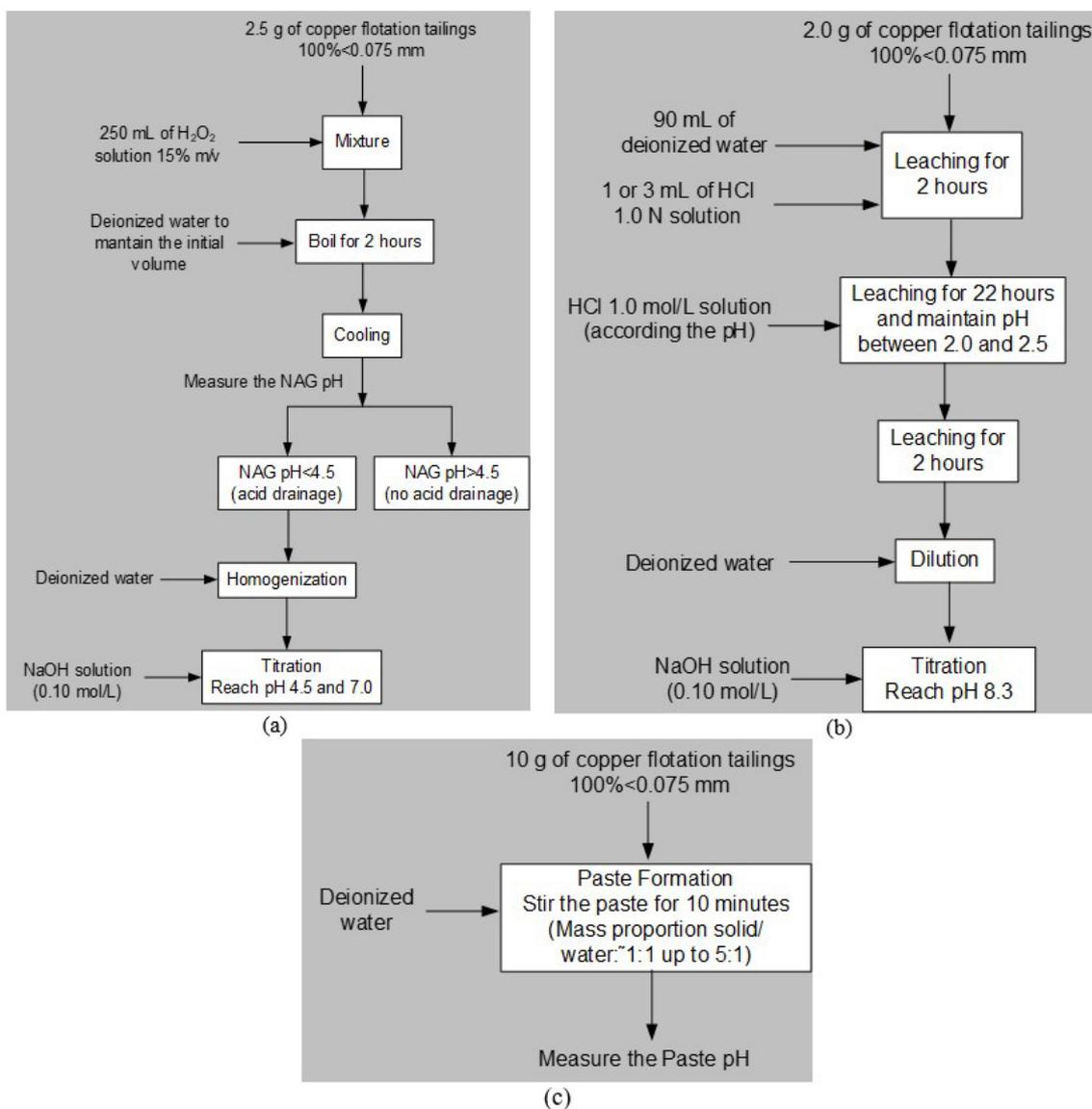


Figure 2. Block diagram of the static acid drainage tests procedures: (a) NAG pH, (b) MABA test and (c) paste pH.

The DAM overflow effluent can be recycled to industrial operation or treated to generate the treated effluent to be either disposed or recycled.

3.1.1 Chemical analyses

The chemical composition of five copper sulfide flotation tailings is listed in Table 3. Sample IV presents the highest copper content (~0.51 wt%) and sample II with the lowest potassium oxide (0.47 wt%) and the highest uranium content (55 mg/kg). The samples IV and V show the highest sulfur (>10.30 wt%) and arsenic content (>65 mg/kg). Sample I had the lowest aluminum oxide (1.71 wt%) and the highest calcium oxide (7.58 wt%) content, as well as the highest chloride content (6042 mg/kg). The highest fluoride (>1000 mg/kg) and magnesium oxide (~4.50 wt%)

content were checked in samples I and II, while the highest silicon oxide (>62 wt%) content was in samples III and V.

More than 75% of sulfur is from sulfides in samples I, III, and IV, which a S as sulfide/total S mass ratio above 0.75. Sample II and Sample III present 40% and 47% of total sulfur from sulfides, respectively. The highest iron oxide content (>29 wt%) is in samples II and IV. The high arsenic content in samples IV and V indicate the presence of enargite, as it is known that this mineral is found in trace amounts in this specific ore. Most of the arsenic in sample V, a mixture of 70 wt% sample III and 30 wt% of sample IV, was due to the addition of sample IV in its composition.

Sample I presented the highest P_2O_5 (1.81 wt%), and $K_2O+CaO+MgO$ content (13.23 wt%), showing a high potential to neutralize acidity due to the alkaline character of K_2O , CaO , and MgO .

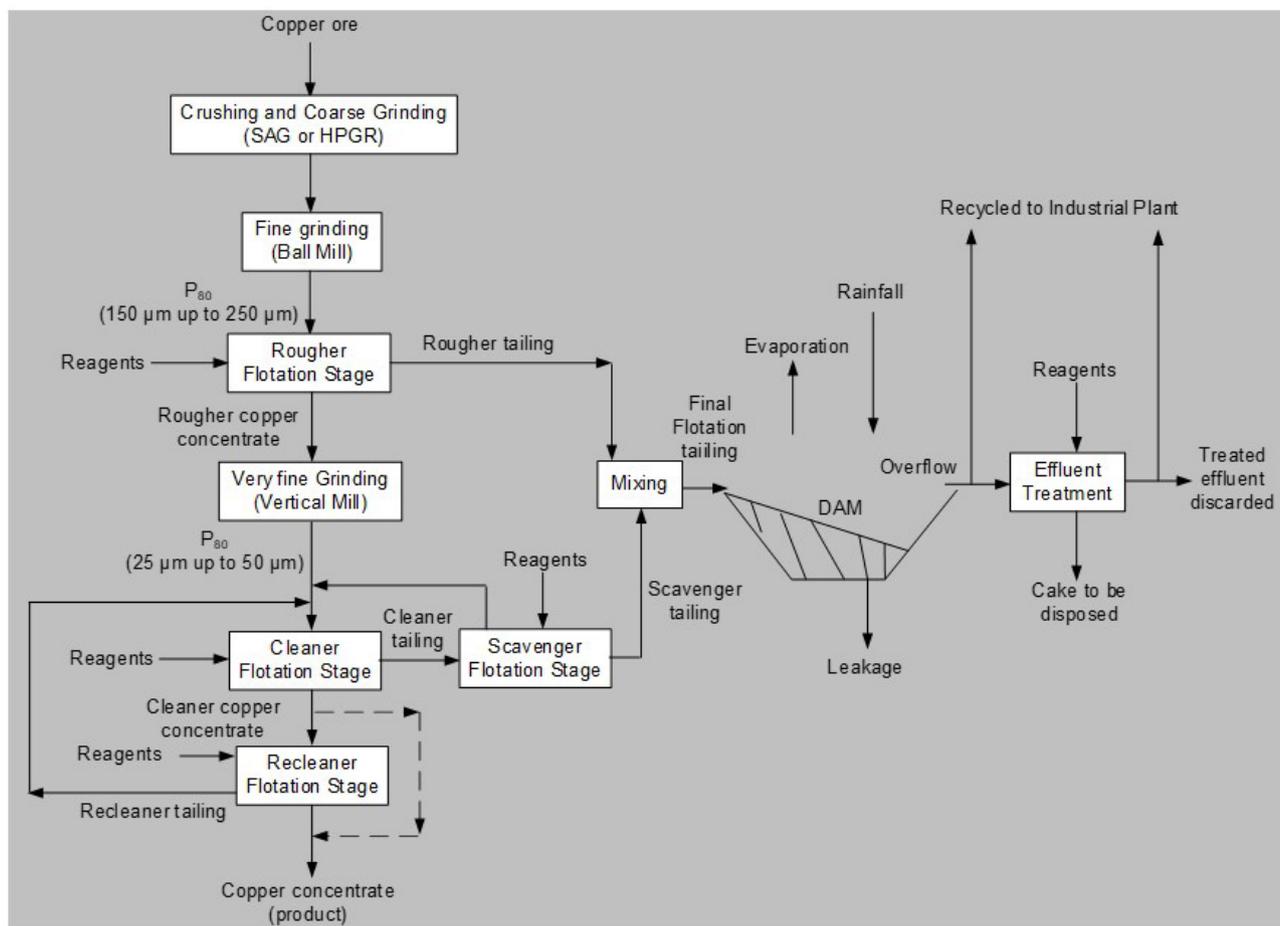


Figure 3. Block diagram of copper process routes that generate and storage the copper flotation tailings.

Table 3. Chemical analyses of five copper sulfide flotation tailings.

Element/ ID	Sample I	Sample II	Sample III	Sample IV	Sample V
Cu total (wt%)	0.06	0.18	0.05	0.51	0.19
S total (wt%)	0.09	0.22	3.79	26.40	10.30
S sulfide (wt%)	0.07	0.09	1.77	23.57	7.87
K ₂ O total (wt%)	1.09	0.47	1.68	1.13	1.50
Al ₂ O ₃ total (wt%)	1.71	8.00	9.45	7.53	8.79
CaO total (wt%)	7.58	2.74	0.10	<0.09	0.09
Fe ₂ O ₃ total (wt%)	15.77	29.02	0.98	29.01	9.57
MgO total (%)	4.56	4.50	<0.30	<0.30	<0.30
MnO total (wt%)	<0.07	0.52	<0.07	<0.07	<0.07
P ₂ O ₅ total (wt%)	1.81	0.44	0.12	0.13	<0.12
SiO ₂ total (wt%)	48.07	45.73	73.65	35.44	62.31
F total (mg/kg)	1080	1226	416	308	365
Cl total (mg/kg)	6042	685	434	596	1445
As total (mg/kg)	<4	10	10	146	65
U total (mg/kg)	2	55	0	0	1
S sulfide/ total S mass ratio	0.80	0.40	0.47	0.89	0.76
K ₂ O+CaO+MgO (wt%)	13.23	4.50	<2.00	<2.00	<2.00
Cu/S mass ratio	0.68	0.83	0.01	0.02	0.02

The high alkaline content indicates that sample I could be used as soil mineralizers. Samples III, IV, and V do not have the potential to neutralize acidity due to the

low (K₂O+CaO+MgO) content. According to Tanda et al. (2017) [31], minerals containing K, Ca and/or Mg in its compositions such as biotite (K(Mg,Fe)₃AlSi₃O₁₀(OH)₂),

chlorite $((Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6)$, calcite $(CaCO_3)$ and dolomite $(CaMg(CO_3)_2)$ consume acid, releasing metals to the solutions.

Sample II presents the highest Cu/S mass ratio (0.83) while samples III, IV, and V have the lowest Cu/S mass ratios (0.02). Sample II shows an intermediate Cu/S mass ratio (0.63). A low Cu/S mass ratio is an indication of high pyrite content (FeS_2) or any mineral containing sulphate in its composition.

3.1.2 Mineralogy

The mineralogy of copper sulfide flotation tailings is presented in Figure 4. Samples I and II present the most complex mineral assemblage, both have many Fe-Al silicates and Fe oxi-hydroxides. The main minerals in the sample I are amphiboles $(Fe,Mg,Ca)_7Si_8O_{22}(OH)_2$, feldspar $(K,Na)AlSi_3O_8$, scapolite $(Na,Ca)_4(Al_3Si_9O_{24})Cl$, quartz (SiO_2) , and Fe oxi-hydroxides, totalizing 85 wt% of the total mass. Sample II has quartz, chlorite $((Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2)$, Fe oxi-hydroxides, amphiboles, and garnet $(Fe,Mn,Mg)_3Al_2(SiO_4)_3$, which correspond also to 85 wt% of the total mass.

Sample III is composed of quartz and alunite $((K,Na,Ca_{0.5})Al_3(SO_4)_2(OH)_6)$, representing 93 wt% of the total mass. Sample IV contains pyrite or FeS_2 , quartz, aluminum silicates (Al_2SiO_5) , alunite, and disseminated Fe-sulfides, which together are 96 wt% of the total mass. The main minerals in sample V are quartz, pyrite, and alunite, composing 89 wt% of the total mass.

3.2 Acid mine drainage static tests

3.2.1 Paste pH test

The amount of sample and deionized water used to form a paste and to measure the paste pH of five copper sulfide flotation tailings are present in Table 4, while the Figure 5 shows the relation between paste pH and sulfur as sulfide content. The pH of deionized water used in the tests was 6.48.

The lowest paste pH was obtained for samples III, IV, and V, which were 4.46, 3.56, and 3.71, lower than the deionized water (pH of 6.48). Based on these results, samples III, IV, and V could be classified as PAF (Potentially Acid Forming) or with a high potential to generate acidity solution, while Samples I and II would be classified as NAF (Non-Acid Forming).

The low paste pH seems to be due to the presence of alunite in their compositions, being 19.6 wt% in sample III, 9.6 wt% in sample IV, and 17.1 wt% in sample V. The low pyrite content in sample III shows that this mineral is not the main reason for the low paste pH.

Reactions 1 and 2 explain the low paste pH for Samples III, IV, and V. Alunite is easily solubilized by water, generating Al^{3+} ions, which hydrolyze forming H^+ ions, responsible for the low paste pH. It is observed that is formed more H^+ ions than OH^- ions for 1 mol of alunite solubilized.

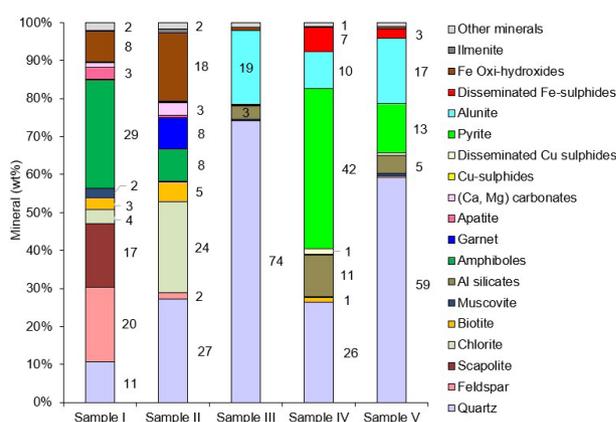
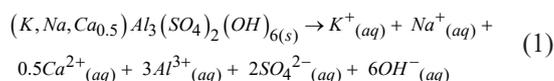


Figure 4. Mineralogy of copper sulfide flotation tailings.

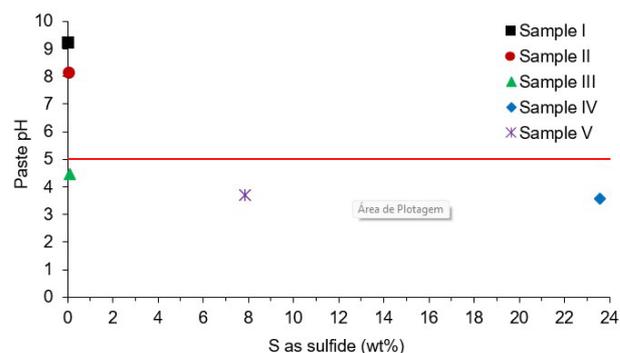
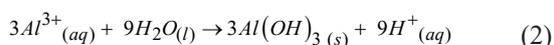


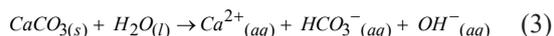
Figure 5. Paste pH versus S sulfide content for five copper sulfide flotation tailings.

Table 4. Paste pH of five copper sulfide flotation tailings

	Sample I	Sample II	Sample III	Sample IV	Sample V
Sample mass (g)	10.0037	10.0406	10.0271	10.0651	10.0250
Deionized water mass (g)	3.2933	3.2448	2.5087	2.4460	2.4244
Mass ratio (sample/deionized water)	3.0	3.1	4.0	4.1	4.1
Paste pH	9.19	8.10	4.46	3.56	3.71



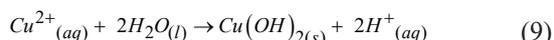
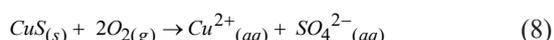
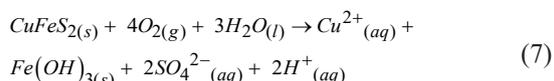
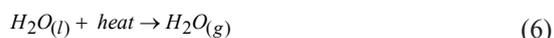
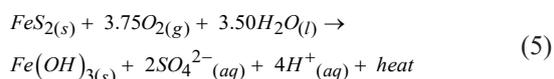
On the other hand, the paste pH was higher than the deionized water for samples I and II. It can be explained by the presence of calcium carbonates in their compositions, being 1.1 wt% in sample I and 4.7 wt% in sample II. The increase in pH can be explained by the formation of OH⁻ ions according to Reaction 3.



3.2.2 NAG pH test

The NAG pH obtained with five copper sulfide flotation tailings are present in Table 5.

The oxygen released from hydrogen peroxide oxidizes the pyrite according to Reactions 4 and 5. As reaction 5 is exothermic, water vapor is released (Reaction 6) causing the solution to overflow from the flask. Chalcopyrite and covellite can also be oxidized according to Reactions 7 to 8, respectively. The Cu²⁺ ions hydrolyze generating acidic solutions due to the presence of H⁺ ions (Reaction 9).

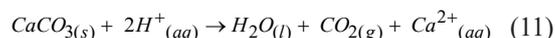
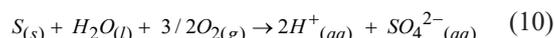


The lowest NAG pH was obtained with samples IV and V due to the high pyrite content in their compositions, which are 42.2 wt% and 13.0 wt% respectively. The respective liquors were tritiated with NaOH solution 0.10 mol/L showing free acidity of 320 kg H₂SO₄/tonne for Sample IV and 190 kg H₂SO₄/tonne for Sample V and acidity from hydrolysis of metals of 100 kg H₂SO₄/tonne for Sample IV and 30 kg H₂SO₄/tonne for Sample V. These values are expected due to the high pyrite and iron contents in sample IV.

The second lowest NAG pH was with sample III due to the presence of pyrite in its composition (0.3 wt%) in comparison with pyrite contents of Samples I and II (0.10 wt%, both) and also due to the lower (K₂O+CaO+MgO) content in Sample III. The pyrite was oxidized, generating H⁺ ions, and lowering the pH due to the lack of neutralizing minerals in Samples III. Based on these results, samples I, II, and III could be classified as NAF (NAG pH>4.50), while Samples III and IV would be classified as PAF (NAG pH<4.50).

3.2.3 MABA Test

The MABA results obtained with five copper sulfide flotation tailings are presented in Table 6. It is assumed that all S as sulfide content has been oxidized to sulfuric acid (H₂SO₄). It means that the acidity potential (AP) was calculated by multiplying the S sulfide content by 31.25 kg CaCO₃ per ton of sample, which value was obtained by dividing the molecular weight of calcium carbonate (100 g/mol) by the molecular weight of sulfur (32 g/mol). Reactions 10 and 11 show that 1 mol of calcium carbonate (CaCO₃) neutralizes two mols of H⁺ ions generated by the oxidation of 1 mol of sulfur (S).



The AP value is expressed as kg CaCO₃/t sample. For instance, a 0.07 wt% of sulfur as sulfide content means

Table 5. NAG pH of five copper sulfide flotation tailings

	Sample I	Sample II	Sample III	Sample IV	Sample V
NAG pH	8.15	8.18	5.30	1.96 (320 kg H ₂ SO ₄ /t sample until pH 4.5) (100 kg H ₂ SO ₄ /t sample from pH 4.5 to pH 7.0)	2.02 (190 kg H ₂ SO ₄ /t sample until pH 4.5) (30 kg H ₂ SO ₄ /t sample from pH 4.5 to pH 7.0)

Table 6. MABA results of five copper sulfide flotation tailings

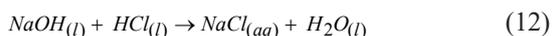
ID	Sample mass (g)	S as sulfide (wt%)	Additional volume of 1.0 mol/L HCl solution added (ml)	Volume of 0.10 mol/L NaOH solution consumed (ml)	AP (kg CaCO ₃ /t sample)	NP (kg CaCO ₃ /t sample)	NP/AP
Sample I	2,0041	0.07	4.00	21.57	2.19	45.98	19.88
Sample II	2,0014	0.09	5.00	25.97	2.81	60.03	22.17
Sample III	2,0071	1.77	2.00	6.20	55.31	34.37	0.62
Sample IV	2,0082	23.57	2.00	12.47	736.56	16.25	0.02
Sample V	2,0062	7.87	4.00	9.19	245.94	26.94	0.11

Table 7. Classification of samples for acid mine drainage potential

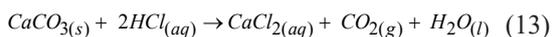
ID	Paste pH test	NAG pH test	MABA test	Final Classification (If at least one was classified as PAF, the final classification will be PAF)
	(If Paste pH <5.00, PAF)	(If NAG pH test <4.50, PAF)	(If NP/NA<1, PAF) (kg CaCO ₃ / t sample)	
Sample I	9.19 (NAF)	8.15 (NAF)	>4 (NAF)	NAF
Sample II	8.10 (NAF)	8.18 (NAF)	>4 (NAF)	NAF
Sample III	4.46 (PAF)	5.30 (NAF)	<1 (PAF)	PAF
Sample IV	3.56 (PAF)	1.96 (PAF)	<1 (PAF)	PAF
Sample V	3.71 (PAF)	2.02 (PAF)	<1 (PAF)	PAF

2.19 kg CaCO₃/t sample because 2.19=(0.07 wt% x 31.25). As expected, samples III (736 kg CaCO₃/t) and IV (246 kg CaCO₃/t) have the highest AP due to the highest sulfur as sulfides content.

With the volume of NaOH solution 0.10 mol.L⁻¹ consumed, it is calculated the amount of HCl added that was not consumed by the sample, according to Reaction 12. For example, sample I consumed 0.087 g of HCl, which means 0.182 g of HCl added (0.005 L x 1.0 mol/L x 36.45 g/mol) minus 0.095 g of HCl consumed (0.0261 L x 0.10 mol/L x 36.45 g/mol).



With the amount of HCl consumed, it is calculated the amount of calcium carbonate by Reaction 13. This value is divided by the amount of sample added to have the neutralization potential (NP) expressed in kg of CaCO₃ per ton of sample. For instance, 0.087 g of HCl consumed is equivalent to 0.120 g of CaCO₃ (0.120 = 0.087 x (100.05 g/mol / (2x36.45) g/mol)), which means a NP of 59.76 kg CaCO₃/t sample (59.73 = 0.120/2.001 x 1000).



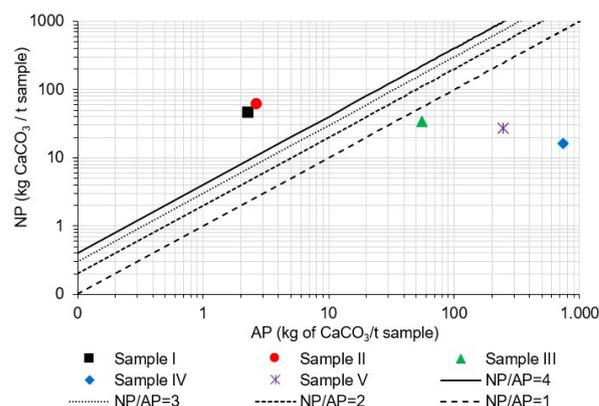
All AP and NP values are represented graphically in Figure 6, as well as the NP/AP mass ratios of 1, 2, 3, and 4.

According to the MABA tests results, only samples III, IV and V present acid mine drainage potential or can be classified as PAF since these two samples show NP/AP mass ratios lower than 1, while Samples I and II must be classified as NAF (NP/AP>4). The main reason for these low NP/AP mass ratios is the respective high AP, being approximately 55 kg CaCO₃/t for sample III, 736 kg CaCO₃/t for sample IV and 246 kg CaCO₃/t for sample V.

3.3 Sample acid drainage classification

The results of static acid drainage tests and classification of samples regarding the potential to generate or not acid solutions with metals dissolved are presented in Table 7. If at least in one criterion of static tests the sample is classified as PAF, it was maintained as final classification.

Samples III, IV, and V could be classified as PAF or with a high potential to generate acidity solutions, and

**Figure 6.** NP versus AP for five copper sulfide flotation tailings.

certainly with a high amount of metal dissolved, while Samples I and II could be classified as NAF. Due to these results, it is recommended to carry out acid drainage kinetic tests with samples III, IV and V to determine the long-term weathering rates, such as sulfide oxidation, dissolution of neutralizing minerals, trace metal release, under oxygenated conditions, to evaluate lag time to acid generation and to provide reaction rates for geochemical modeling. The kinetic test apparatus and procedures are based upon similar ‘humidity cell’ protocols [30-33].

4 Conclusion

The sulfur as “sulfide/total sulfur” mass ratios vary from 0.02 up to 0.89 showing the presence of a high amount of minerals rich in sulfides in samples IV and V, with more than 13 wt% of pyrite, and rich in sulphates in sample III, with 19 wt% of alunite. Samples I and II presented high amounts of alkaline elements, totalizing more than 8 wt% of K₂O+CaO+MgO, while samples III, IV, and V show the lowest amounts of them (<4 wt%). Sample IV was the finest and sample II was the coarsest with 80 wt% of particles (P₈₀) below 66 and 222 μm, respectively. The samples I, III, and V presented intermediate size distributions, with P₈₀ of 140, 176, and 147 μm, respectively.

Only samples III, IV, and V show paste pH results lower than 5.0, indicating superficial oxidation on their surfaces or the presence of water-soluble acidity minerals,

such as alunite. The high total sulfur content (>10 wt%) and high pyrite content in samples IV and V and the high alunite content in sample III are the main reasons for the respective low paste pH. Probably, pyrite was oxidized in contact with air and water and alunite was solubilized, both generating acidity solutions, decreasing the paste pH. Based on paste pH results, samples III, IV, and V were classified as PAF (Potentially Acid Forming) and Samples I and II were be classified as NAF (Non-Acid Forming).

Due to the high pyrite content in samples IV and V, it was not possible to measure the NAG pH of these samples. The low NAG pH obtained with sample III (value of 5.30), was due to its high alunite content. The high NAG pH for samples I (value of 8.15) and II (value of 8.18) were explained by the high $K_2O+CaO+MgO$ in their compositions. Based on NAG pH results, samples I, II, and III were classified as NAF, while Samples III and IV were classified as PAF.

According to the MABA tests results, only samples III, IV and V present acid drainage potential because these samples show NP (neutralization potential)/AP (acidity potential) mass ratios lower than 1. On the other hand, samples I and II present NP/AP higher than 4, not showing

potential to generate acid drainage. According to MABA results, only Samples III, IV and V were classified as PAF and Samples I and II as NAF.

Combining all static test results, only samples III, IV and V could have a final classification as PAF, showing a high potential to generate acidity solution, and certainly with a high amount of metal dissolved. The samples I and II could be a final classification as NAF.

Due to these results, it is recommended to carry out acid drainage kinetic tests with samples III, IV, and V to determine the long-term weathering rates, such as sulfide oxidation, dissolution of neutralizing minerals, trace metal release, under oxygenated conditions, to evaluate lag time to acid generation and to provide reaction rates for geochemical modeling.

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