Static Tests to Assess Acid Mine Drainage Potential of Copper Sulphide Flotation Tailings

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AGENDA

❖ INTRODUCTION AND OBJECTIVE.

❖ METHODOLOGY.

❖ RESULTS AND DISCUSSION.

❖ CONCLUSION.

INTRODUCTION AND OBJECTIVE

- ❖ **Copper is important metal** in the construction, appliance and energy industries.
- ❖ Main Cu-bearing minerals aiming the production of copper metal are chalcopyrite (**CuFeS$_2$**), bornite (**Cu$_5$FeS$_4$**), chalcocite (**Cu$_2$S**), enargite (**Cu$_3$AsS$_4$**), and covellite (**CuS**).
- ❖ Most copper sulphides mines generate a large amount of tailing after its concentration (flotation), with **mass recovery varying only from 2% up 5% of total feed ore**.
- ❖ **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.
- ❖ It is worthwhile to mention that **the storage of copper tailings** in dams **also represents a threat to the surrounding environment**.
- ❖ **Copper flotation tailings contain** a significant amount of **non-copper sulphides minerals and a low amount of copper sulphides minerals** that 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**.

Figure 1. Roman Portal with Acid Rock Drainage – Spain
INAP, The international Network for Acid Prevention (2014)

The objective of this study was to evaluate the acid mine drainage (AMD) potential of different copper flotation tailings using **static acid drainage tests.**
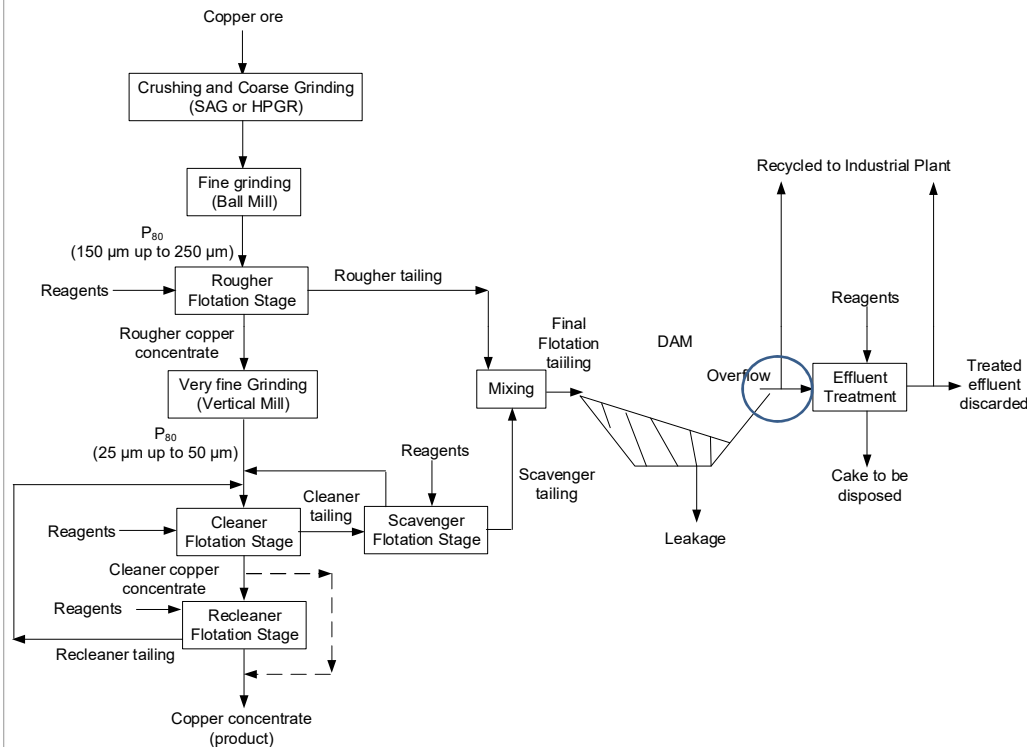
INTRODUCTION

Figure 2. Typical block diagram of copper flotation process route

❖ Copper ore is crushed and ground to P_{80} between 150 and 250 µm to achieve the required liberation for the rougher flotation stage. In this step, it is expected to achieve the highest copper recovery.

❖ The rougher concentrate is submitted to regrind (P_{80} between 25 and 50 µm), followed by cleaner/recleaner flotation stage aiming to achieve the Cu grade desired.

❖ The cleaner tailing feeds the scavenger flotation stage. The rougher and scavenger tailings will form the final tailing that will be sent to the DAM.

❖ The DAM overflow effluent could be recycled to industrial plant or treated to generate the treated effluent that could be disposed or also recycled to industrial plant.
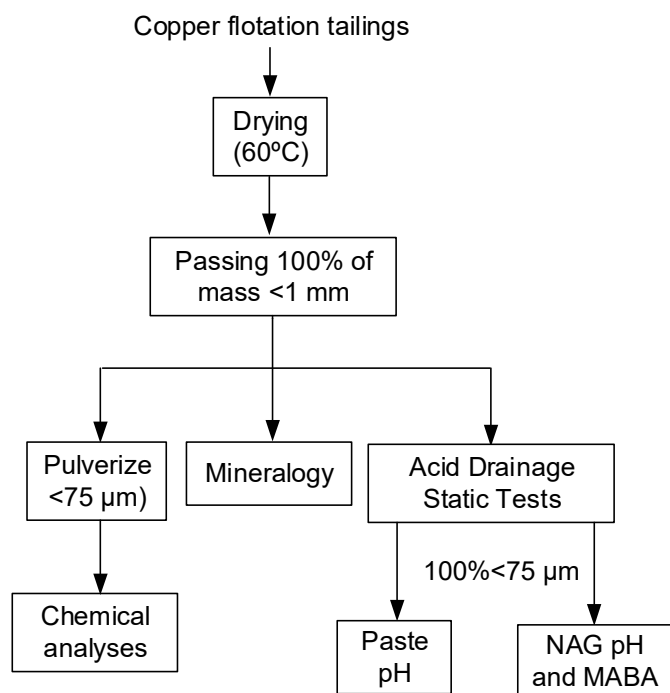
METHODOLOGY

Copper flotation tailings

↓

Drying (60ºC)

↓

Passing 100% of mass <1 mm

- Pulverize <75 μm)
  - ↓ Chemical analyses
- Mineralogy
- Acid Drainage Static Tests

  100%<75 μm
  - Paste pH
  - NAG pH and MABA

Figure 3. Block diagram for sample preparation and characterization

Table 1. Analytical procedures for assays for solids samples

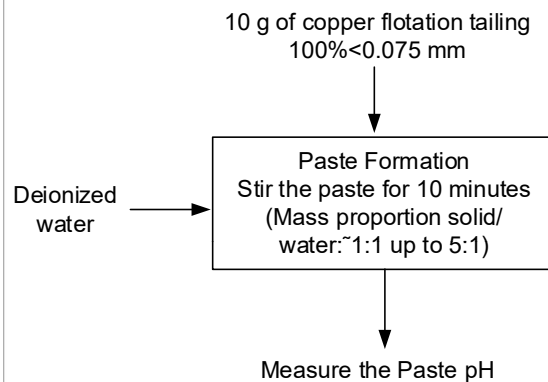| Element	Analytical methodology
Ca, Mg, Al, Fe, Mn, P and Si	Calcination 600°C, fusion $Na_2CO_3/Na_2B_4O_7$, reading ICP-OES
S sulphide	Leaching calcium carbonate, direct combustion, reading infra-red
Cu, As	Total solubilization with aqua regia and reading ICP-OES.
S	Direct combustion and reading Infra-red from LECO.
K	Solubilization in HCl + HF and reading ICP-OES.
Fluorine	Fusion KNO_3/KOH, dissolution water and reading selective ion electrode.
Chlorine	Fusion KNO_3/KOH, dissolution in water and titration with $AgNO_3$ solution.

Table 2. Analytical procedures for assays for liquors

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

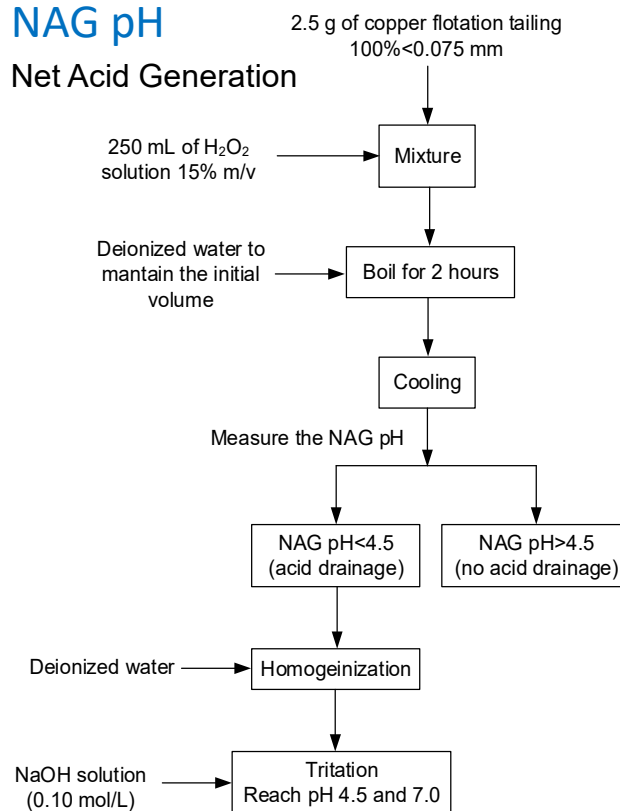❖ Mineralogical: QEMSCAN. Mineral data were correlated with chemical assays.
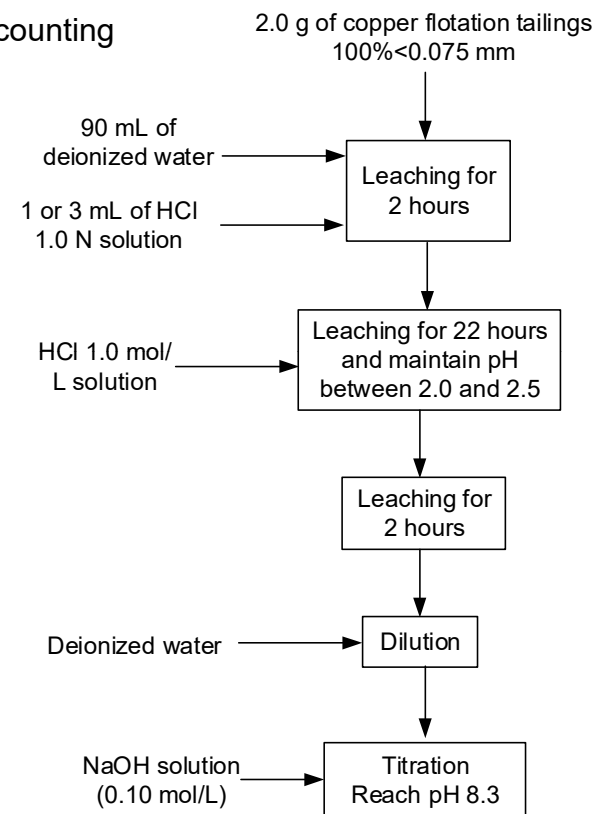
METHODOLOGY

Paste pH

10 g of copper flotation tailing 100%<0.075 mm

Deionized water →

Paste Formation
Stir the paste for 10 minutes
(Mass proportion solid/
water:~1:1 up to 5:1)

↓

Measure the Paste pH

NAG pH

Net Acid Generation

2.5 g of copper flotation tailing 100%<0.075 mm

250 mL of H_2O_2 solution 15% m/v →

Mixture

↓

Deionized water to mantain the initial volume →

Boil for 2 hours

↓

Cooling

↓

Measure the NAG pH

NAG pH<4.5 (acid drainage) | NAG pH>4.5 (no acid drainage)

Deionized water →

Homogeinization

↓

NaOH solution (0.10 mol/L) →

Tritation
Reach pH 4.5 and 7.0

MABA

Modified Acid-Base Accounting

2.0 g of copper flotation tailings 100%<0.075 mm

90 mL of deionized water →

1 or 3 mL of HCl 1.0 N solution →

Leaching for 2 hours

↓

HCl 1.0 mol/L solution →

Leaching for 22 hours and maintain pH between 2.0 and 2.5

↓

Leaching for 2 hours

↓

Deionized water →

Dilution

↓

NaOH solution (0.10 mol/L) →

Titration
Reach pH 8.3

RESULTS AND DISCUSSION

Samples

Five flotation copper tailings identified as Samples I, II, III, IV and V, being:

- ❖ **Sample I** is from an **industrial operation** in Brazil, **Samples II, III, IV and V** are from **pilot plant tests**.

- ❖ Samples I and II are final flotation tailings from two different copper sulphide ores which the main Cu-bearing mineral is chalcopyrite ($CuFeS_2$).

- ❖ Samples III, IV and V are flotation tailings from a different copper sulphide ore which the main Cu-bearing minerals are covellite (CuS) and enargite (Cu_3AsS_4). 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).

Chemical assays

Table 3. Chemical assays of five copper sulphide 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 sulphide (wt%)	**0.07**	**0.09**	**0.08**	**23.57**	**7.87**
K_2O total (wt%)	2.18	0.94	3.37	2.25	3.00
Al_2O_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_2O_3 total (wt%)	15.77	29.02	0.98	29.01	9.57
MgO total (%)	**4.56**	**4.50**	**<0.25**	**<0.25**	**<0.25**
MnO total (wt%)	<0.07	0.52	<0.07	<0.07	<0.07
P_2O_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	445
As total (mg/kg)	<4	10	10	146	65
U total (mg/kg)	2	55	0	0	1
S sulphide/ S total mass ratio	**0.80**	**0.40**	**0.02**	**0.89**	**0.76**
K_2O+CaO+MgO (wt%)	14.32	8.18	<3.71	<2.59	<3.34

RESULTS AND DISCUSSION

Mineralogy
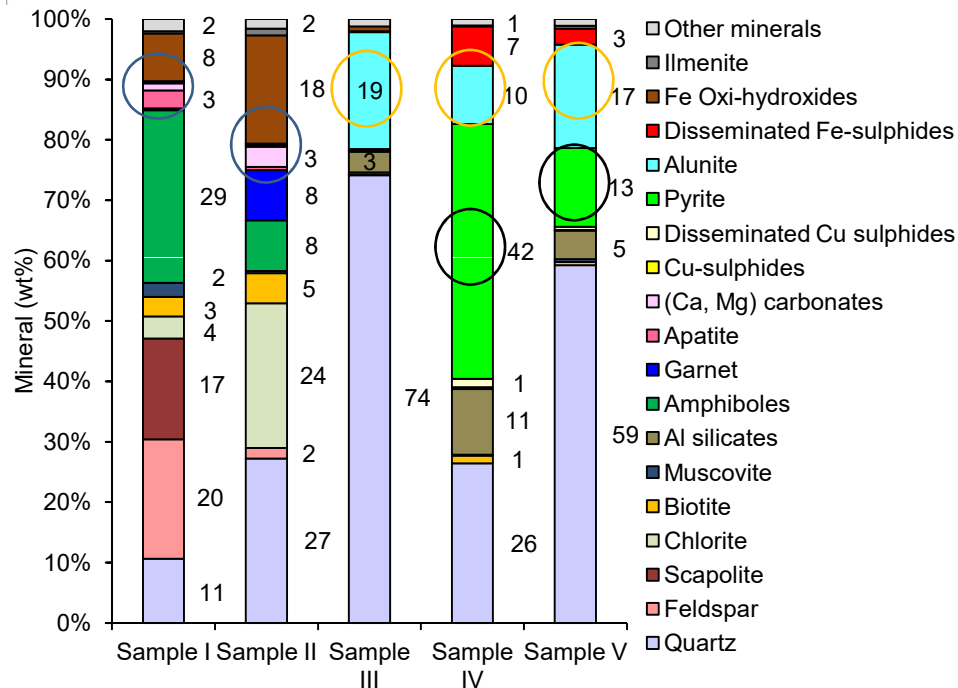
* Samples I and II present the most complex mineral assemblage, both have many Fe-Al silicates and Fe oxi-hydroxides.

* The main minerals in sample I are amphiboles (29 wt%), feldspar (20 wt%), scapolite (17 wt%), quartz (11 wt%), and Fe oxi-hydroxides (8 wt%), totalizing 84 wt% of the total mass.

* Sample II has quartz (27 wt%), chlorite (24 wt%), Fe oxi-hydroxides (18 wt%), amphiboles (8 wt%), and garnet (8 wt%), which correspond to 86 wt% of the total mass.

* Basically, sample III is composed of quartz (74 wt%) and alunite (19 wt%), representing 93 wt% of the total mass.

* Sample IV contains pyrite (42 wt%), quartz (27 wt%), aluminum silicates (11 wt%), alunite (106 wt%), and disseminated Fe-sulphides (7 wt%), which together are 96 wt% of the total mass.

* The main minerals in sample V are quartz (59 wt%), pyrite (13 wt%), and alunite (17 wt%), composing 89 wt% of the total mass.

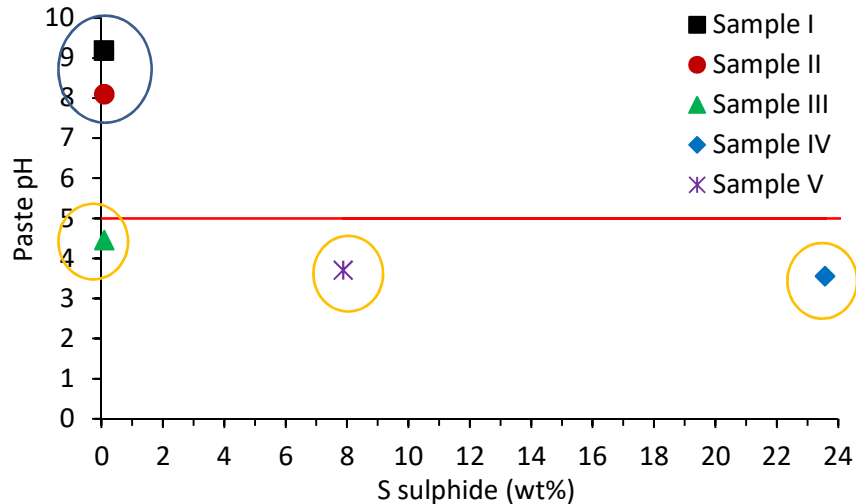* No pyrite in Samples I and II, only 0.3 wt% of pyrite in Sample III.

RESULTS AND DISCUSSION

Paste pH

Figure 6. Paste pH versus S sulphide grades for samples

Table 5. Paste pH of five copper sulphide flotation tailings

Parameter	Sample I	Sample II	Sample III	Sample IV	Sample V
Sample mass (g)	10.00	10.04	10.03	10.07	10.03
Deionized water mass (g)	3.29	3.25	2.51	2.45	2.42
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

❖ pH of deionized water of 6.48.

❖ The lowest paste pH was obtained for samples III, IV, and V, lower than the deionized water (pH=6.48).

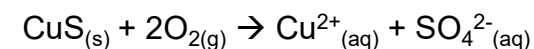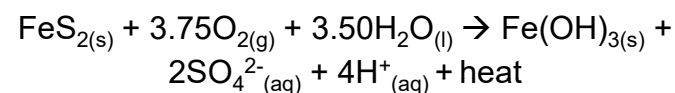❖ The low paste pH seems to be due to the presence of alunite in their compositions..

$$CaCO_{3(s)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + HCO_3^-_{(aq)} + OH^-_{(aq)}$$

$$KAl_3(SO_4)_2(OH)_6(s) \rightarrow K^+_{(aq)} + 2SO_4^{2-}_{(aq)} + \mathbf{3Al^{3+}_{(aq)}} + 6OH^-_{(aq)}$$

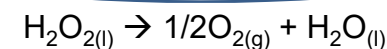$$3Al^{3+}_{(aq)} + 9H_2O_{(l)} \rightarrow 3Al(OH)_{3(s)} + \mathbf{9H^+_{(aq)}}$$
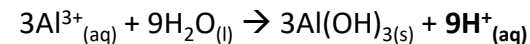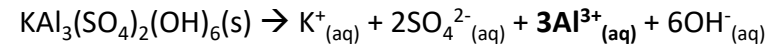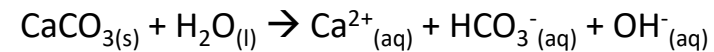
RESULTS AND DISCUSSION

NAG pH

❖ High pyrite content in samples IV and V. It was not possible to measure the NAG pH of these samples.

❖ The oxygen released from hydrogen peroxide oxidizes the pyrite. As the reaction is exothermic, heat and gas were released, causing the solution to overflow from the flask;

❖ Covellite can also be oxidized;

❖ Additionally, the absence of calcium carbonate in sample III does not allow the neutralization of its acidity with the addition of hydrogen peroxide.

Table 6. NAG pH of five copper sulphide flotation tailings

Parameter	Sample I	Sample II	Sample III	Sample IV	Sample V
NAG pH	8.15	8.18	5.30	Not possible to measure	Not possible to measure

$$H_2O_{2(l)} \rightarrow 1/2 O_{2(g)} + H_2O_{(l)}$$

$$FeS_{2(s)} + 3.75 O_{2(g)} + 3.50 H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 2SO_4^{2-}{}_{(aq)} + 4H^+{}_{(aq)} + heat$$

$$H_2O_{(l)} + heat \rightarrow H_2O_{(g)}$$

$$CuS_{(s)} + 2O_{2(g)} \rightarrow Cu^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

High formation of gases Samples IV and V

RESULTS AND DISCUSSION

MABA

Table 7. MABA results of five copper sulphide flotation tailings

ID	AP (Calculated) (kg CaCO$_3$/ t sample)	NP (Measured) (kg CaCO$_3$/t sample)
Sample I	2.31	59.76
Sample II	2.71	34.39
Sample III	2.50	16.26
Sample IV	736.43	26.95
Sample V	245.95	46.00

AP: $S_{(s)} + 3/2 O_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq))}$

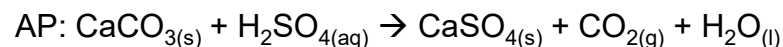AP: $CaCO_{3(s)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(s)} + CO_{2(g)} + H_2O_{(l)}$
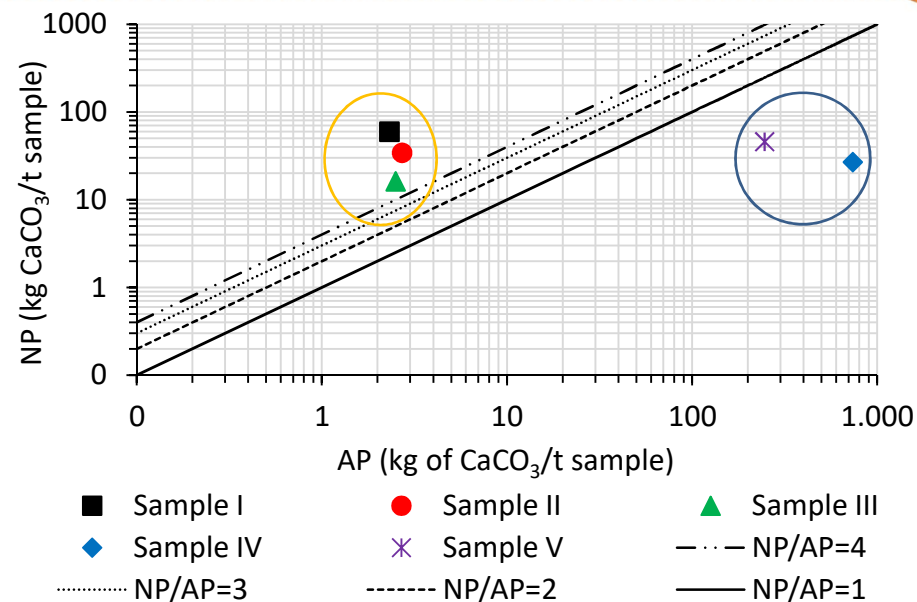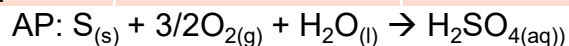
Figure 7. NP versus AP for five copper flotation tailings

NP: $NaOH_{(l)} + HCl_{(l)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

NP: $CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$
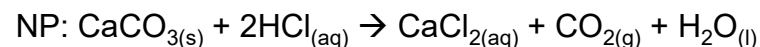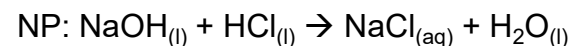
Only samples IV and V present acid drainage potential since these two samples show NP/AP mass ratios lower than 1. The main reason for low NP/AP mass ratios is the respective high AP, being approximately 736 kg CaCO$_3$/t for sample IV and 246 kg CaCO$_3$/t for sample V.

RESULTS AND DISCUSSION

Classification of acid mine drainage (AMD) potential

NAF and PAF stand for Non-Acid Forming and Potential Acid Forming, respectively

Table 8. Classification of samples for acid drainage potential

ID	Paste pH (pH<5, AMD; pH>7, neutral	NAG pH (pH<4.5, AMD; pH>4.5, no AMD)	MABA NPR=(NP/AP) (kg CaCO$_3$/ t sample) (NP/AP<1, AMD; NP/AP>4, no AMD)	Classification
Sample I	9.19	8.15	>4	NAF
Sample II	8.10	8.18	>4	NAF
Sample III	4.46	5.30	>4	PAF
Sample IV	3.56	Not possible to measure	<1	PAF
Sample V	3.71	Not possible to measure	<1	PAF

❖ Only samples IV and V could be classified as PAF or with a high potential to generate acidity liquor, and certainly with a high amount of metal dissolved.

❖ According 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 sulphide 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.

CONCLUSION

❖ **Only samples III, IV, and V show Paste pH results lower than 5.0**. The 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.

❖ **The NAG pH of Samples IV and V (high pyrite contents) were not possible to measure.** The low NAG pH obtained with sample III was due to presence of covellite (CuS) in its composition. **The high NAG pH for samples I and II are explained by the high K$_2$O+CaO+MgO in their compositions.**

❖ According to the **MABA tests results**, **only samples IV and V present acid drainage potential** because these two samples show NP/AP<1. On the other hand, **samples I, II, and III** present NP/AP>4, **not showing potential to generate acid drainage**.

❖ Based on the results of static acid drainage tests, only **samples III, IV and V could be classified as Potential Acid Forming (PAF),** showing a high potential to generate acidity liquor, and certainly with a high amount of metal dissolved. **The samples I and II were classified as Non-Acid Forming (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 sulphide oxidation, dissolution and neutralizing minerals, trace metal release, under oxygenated conditions, to evaluate lag time to acid generation and to provide reaction rates for geochemical modeling.