



Challenges of Processing Sulphide Copper Ore Tailings Aiming at Minimizing the Occurrence of Acid Mine Drainage and Metal Leaching

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AGENDA

- ❖ INTRODUCTION.
- ❖ COPPER TAILING GENERATION.
- ❖ VALE'S MINERAL DEVELOPMENT CENTRE INFRASTRUTURE.
- ❖ CASE STUDY RESULTS.



INTRODUCTION

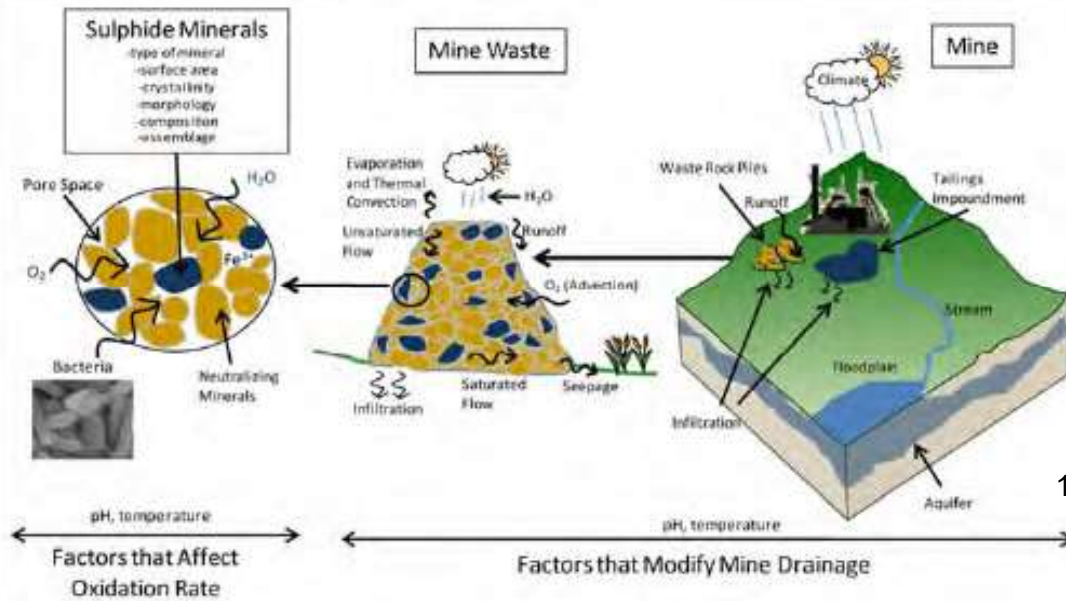
- ❖ Copper is an important metal in the construction, appliance, and energy industries.
- ❖ Main Cu-bearing minerals aiming the production of copper metal are chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4), chalcocite (Cu_2S), enargite (Cu_3AsS_4), and covellite (CuS).
- ❖ Most copper sulphides mines generate a large amount of tailing after its concentration (flotation).
- ❖ 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.



(GARD, 2014)

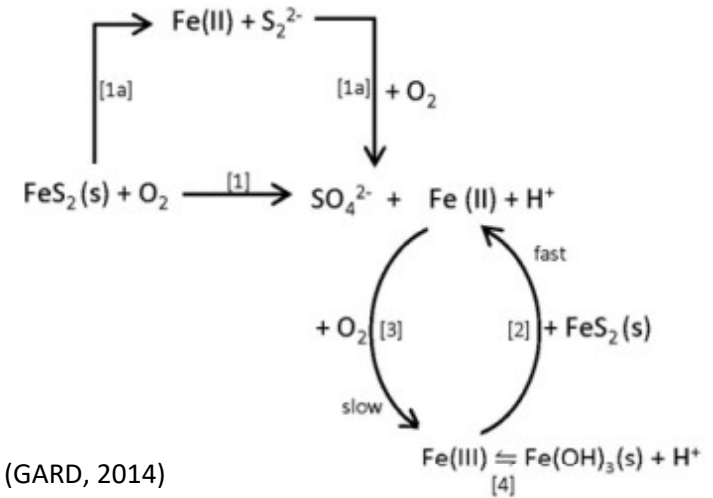


INTRODUCTION

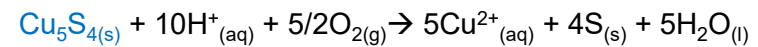
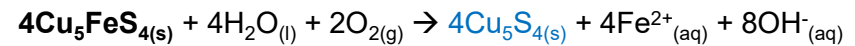
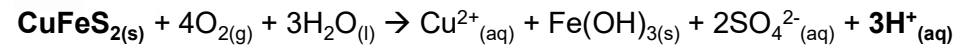
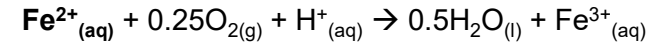
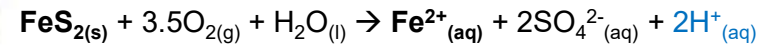


(GARD, 2014)

Other sulphides minerals: Pyrrhotite (Fe_{1-x}S), Enargite (Cu_3AsS_4).

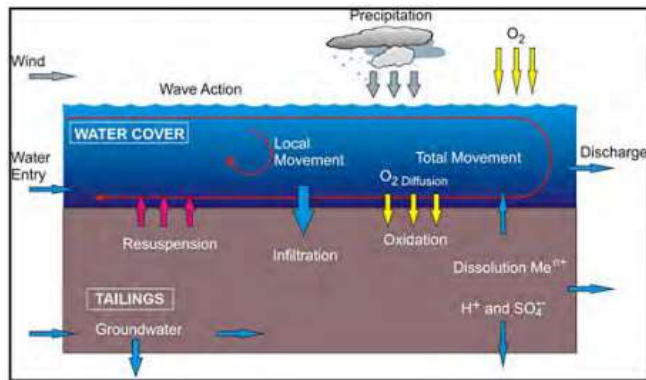
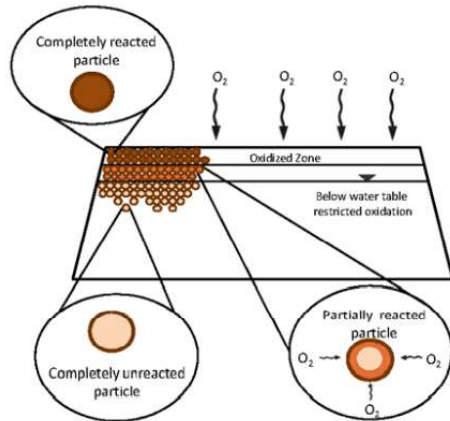


(GARD, 2014)



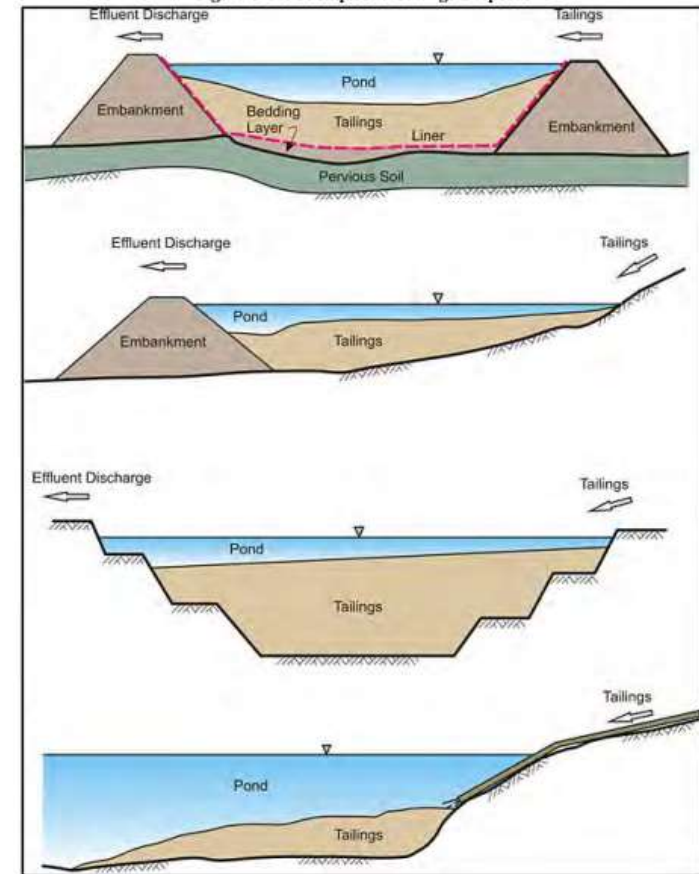


INTRODUCTION



- ❖ Water covers limit the exposure of PAF (**Potential Acid Forming**) material to oxygen.
- ❖ Sufficient depth of water over PAF material must be provided to account for mixing of the water column and to prevent resuspension of wastes by wind or wave action.

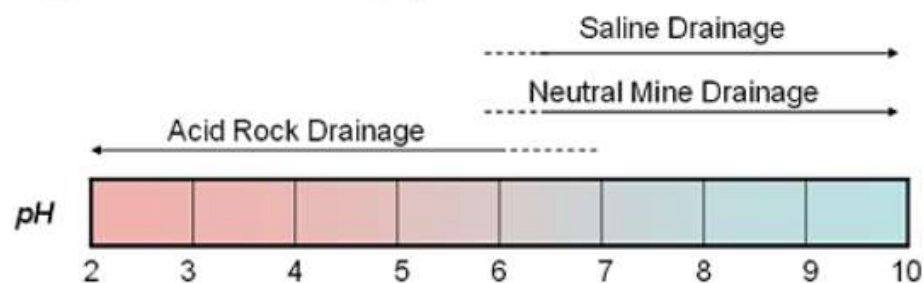
(GARD, 2014)





INTRODUCTION

Typical relation to drainage pH:



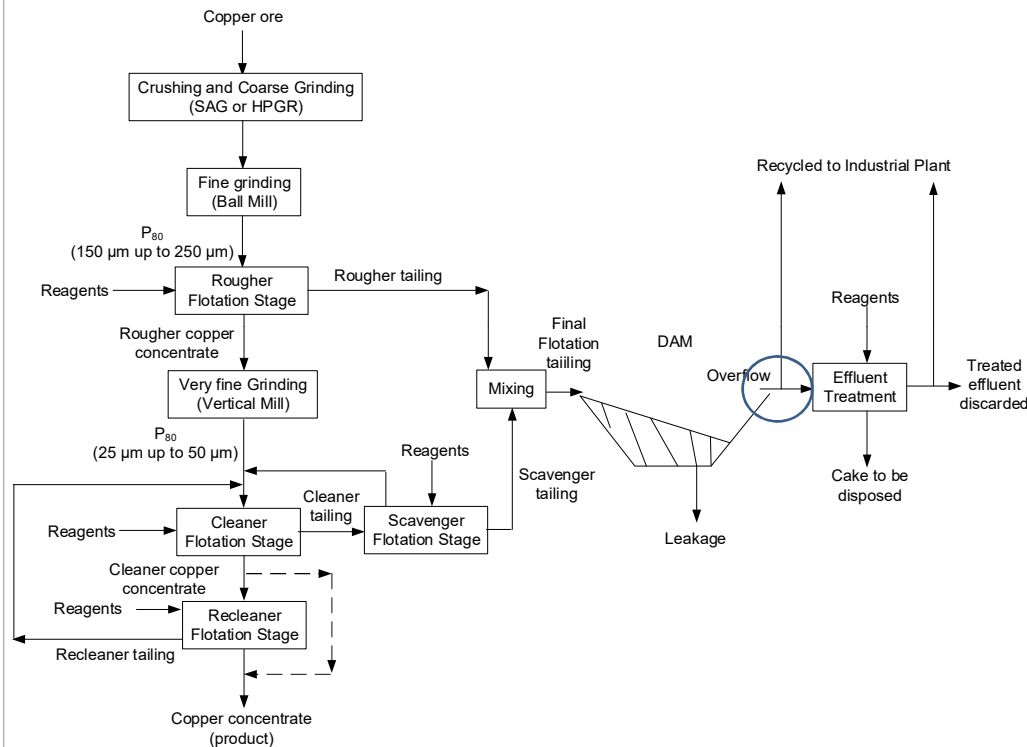
Typical drainage characteristics:

Acid Rock Drainage:	Neutral Mine Drainage:	Saline Drainage:
<ul style="list-style-type: none">• acidic pH• moderate to elevated metals• elevated sulphate• treat for acid neutralization and metal and sulphate removal	<ul style="list-style-type: none">• near neutral to alkaline pH• low to moderate metals. May have elevated zinc, cadmium, manganese, antimony, arsenic or selenium.• low to moderate sulphate• treat for metal and sometimes sulphate removal	<ul style="list-style-type: none">• neutral to alkaline pH• low metals. May have moderate iron.• moderate sulphate, magnesium and calcium• treat for sulphate and sometimes metal removal

- ❖ The **drainage produced** from the oxidation process may be **neutral to acidic**, with or without dissolved metals, but always contains sulfate.
- ❖ When sufficient base minerals are present to neutralize the acid rock drainage, **neutral mine or saline drainages** may result from oxidation process.
- ❖ **Neutral mine drainage** is characterized by **elevated metals in solutions at circumneutral pH**, while **saline drainage** contains **high levels of sulfate at neutral pH without significant dissolved metals concentrations**.



COPPER TAILING GENERATION



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 the industrial plant.



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VALE'S MINERAL DEVELOPMENT CENTRE INFRASTRUCTURE

50 Humidity Cells Test (HCT), being 25 with height 20 cm and diameter 10 cm (Coarser samples) and 25 hct: Height 10 cm and Diameter 20 cm (Fines samples); 2 Air Dryer; 2 manifold with the capacity to run 38 humidity cells.

- ❖ To determine long-term weathering rates under oxygenated conditions.
- ❖ To evaluate lag time to acid generation.
- ❖ To provide reaction rates for geochemical modeling.
- ❖ Provides kinetic and steady-state leaching information and is recommended tests for determination of weathering rates of primary minerals.
- ❖ Not suitable to evaluate of saturated materials.
- ❖ Grain size reduction may increase reactivity.



Humidity Cells in operation in CDM



Designation: D5744 – 13^{e1}

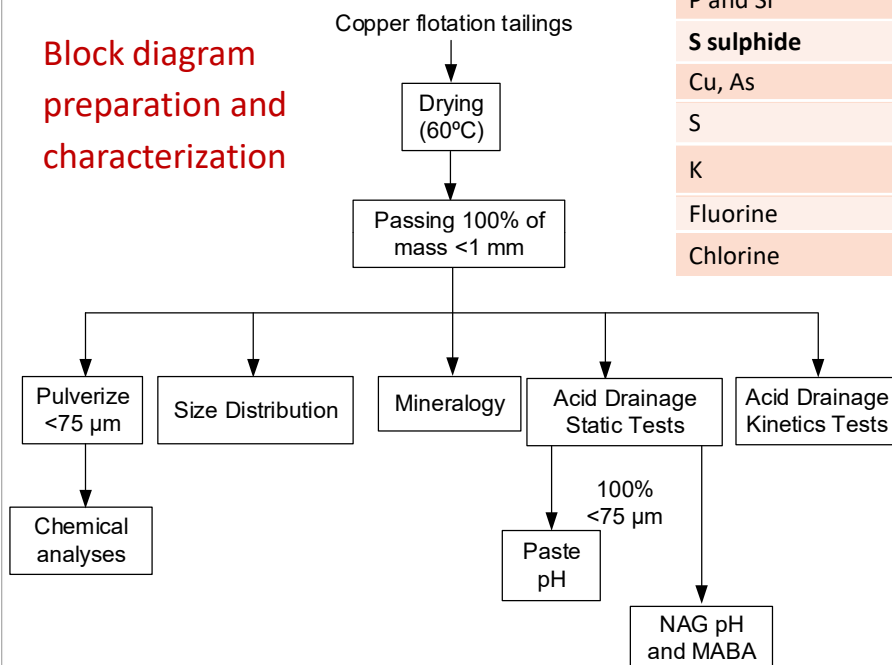
Standard Test Method for
Laboratory Weathering of Solid Materials Using a Humidity
Cell¹



CASE STUDY RESULTS

Static Tests

Block diagram
preparation and
characterization



Analytical procedures for assays for solids samples

Element	Analytical methodology
Ca, Mg, Al, Fe, Mn, P and Si	Calcination 600°C, fusion Na ₂ CO ₃ /Na ₂ B ₄ O 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	Total 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.

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).

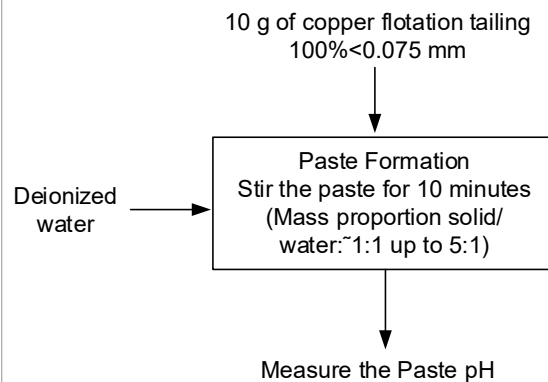
- ❖ Mineralogical: QEMSCAN. Mineral data were correlated with chemical assays.
- ❖ Size distribution followed conventional sieving for particles bigger than 45 µm and hydrocyclone loop for particles smaller than 45 µm.



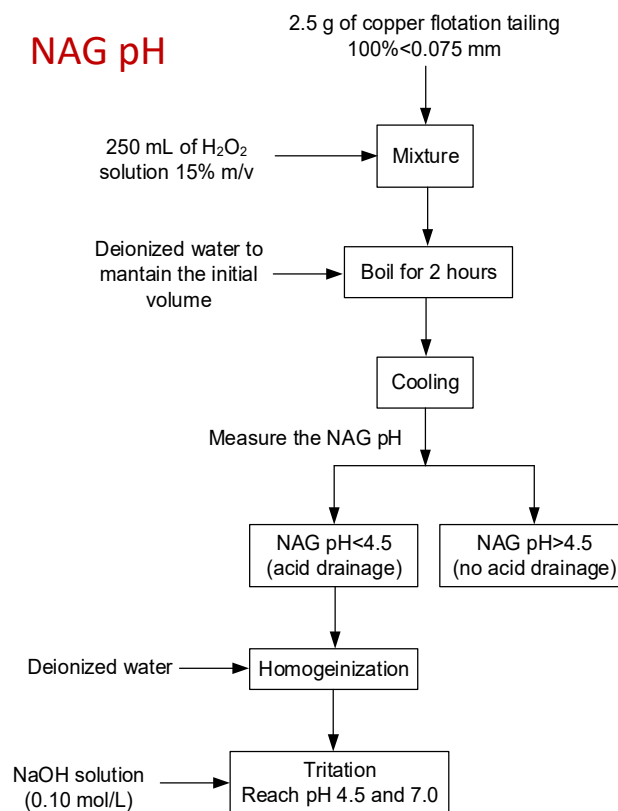
CASE STUDY RESULTS

Static Tests

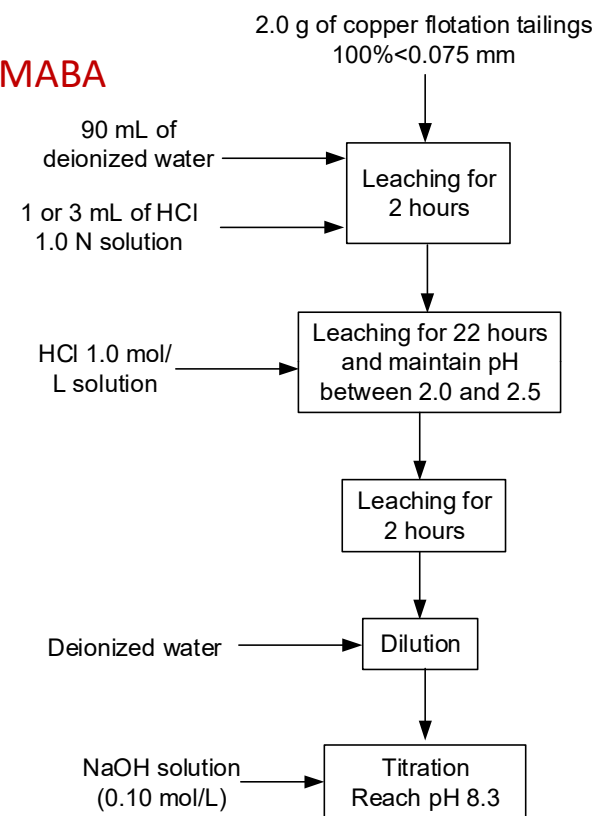
Paste pH



NAG pH



MABA





CASE STUDY RESULTS

Static Tests

Samples

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

❖ **Samples I and II** are final flotation tailings from two different copper sulphide ores which the main Cu-bearing mineral being chalcopyrite (CuFeS_2). These final tailings are a mixture of 90 wt% of rougher tailing and 10 wt% of scavenger tailing.

❖ **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 is the final tailing, (70 wt% of sample III and 30 wt% of sample IV).

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

Chemical assays

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	<u>0.18</u>	0.05	<u>0.51</u>	<u>0.19</u>
S total (wt%)	0.09	0.22	3.79	26.40	10.30
S sulphide (wt%)	0.07	0.09	0.08	<u>23.57</u>	<u>7.87</u>
K ₂ O total (wt%)	2.18	<u>0.94</u>	3.37	2.25	3.00
Al ₂ O ₃ total (wt%)	<u>1.71</u>	8.00	9.45	7.53	8.79
CaO total (wt%)	<u>7.58</u>	2.74	0.10	<0.09	0.09
Fe ₂ O ₃ total (wt%)	15.77	<u>29.02</u>	0.98	<u>29.01</u>	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 ₂ O ₅ total (wt%)	1.81	0.44	0.12	0.13	<0.12
SiO ₂ total (wt%)	48.07	45.73	<u>73.65</u>	35.44	<u>62.31</u>
F total (mg/kg)	1080	<u>1226</u>	416	308	365
Cl total (mg/kg)	<u>6042</u>	685	434	596	445
As total (mg/kg)	<4	10	10	<u>146</u>	<u>65</u>
S sulphide/ S total mass ratio	0.80	0.40	0.02	0.89	0.76
K ₂ O+CaO+MgO (wt%)	14.32	8.18	<3.50	<3.50	<3.50



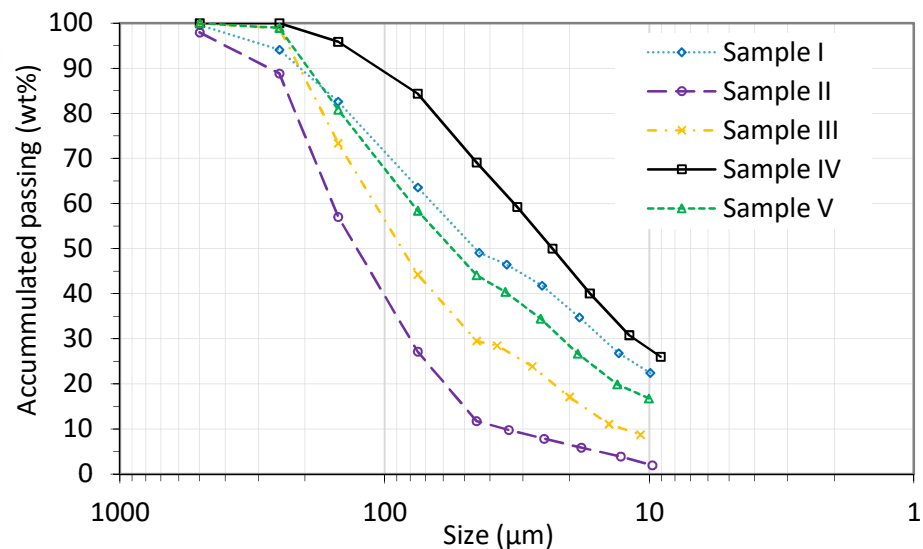
CASE STUDY RESULTS

Static Tests

Size Distribution

Size distribution of samples (accumulated passing, wt%)

Element/ ID	Sample I	Sample II	Sample III	Sample IV	Sample V
500	100	100	100	100	100
250	94	89	99	100	99
150	83	57	73	96	81
75	64	27	44	84	58
45	49	12	30	69	44
35	46	10	29	59	40
25	42	8	24	50	35
18	35	6	17	40	27
13	27	4	11	31	20
9	22	2	9	26	17
<9	0	0	0	0	0
P ₅₀ (µm)	46	132	90	23	57
P ₈₀ (µm)	140	222	176	66	147



Size distribution of copper sulphide flotation tailings

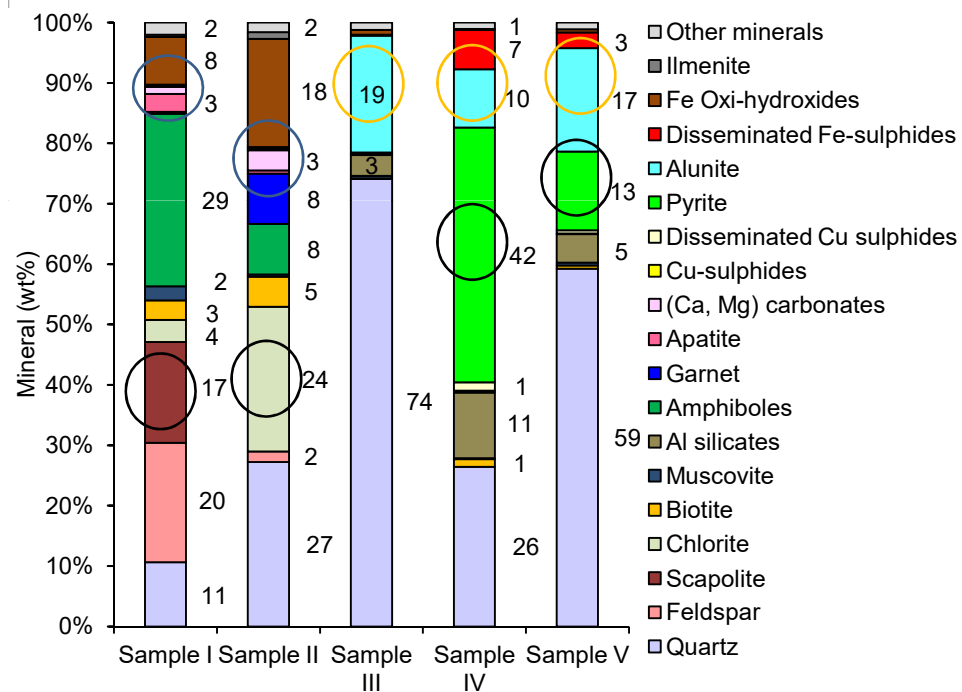
Sample IV was the finest and sample II was the coarsest with 80 wt% of particles (P_{80}) below 66 and 222 µm, respectively. The samples I, III, and V presented intermediate size distributions, with P_{80} of 140, 176, and 147 µm, respectively. The particle size is an important parameter because it impacts the kinetics of metals dissolution.



CASE STUDY RESULTS

Static Tests

Mineralogy



- ❖ Samples I and II present the most complex mineral assemblage, both have many Fe-Al silicates and Fe oxo-hydroxides.
- ❖ The main minerals in sample I are amphiboles, feldspar, scapolite, quartz, and Fe oxo-hydroxides, totalizing 84 wt% of the total mass.
- ❖ Sample II has quartz, chlorite, Fe oxo-hydroxides, amphiboles, and garnet, which correspond to 86 wt% of the total mass.
- ❖ Basically, sample III is composed of quartz and alunite, representing 93 wt% of the total mass.
- ❖ Sample IV contains pyrite, quartz, aluminum silicates, alunite, and disseminated Fe-sulphides, 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.
- ❖ No pyrite in Samples I and II, only 0.3 wt% of pyrite in Sample III.

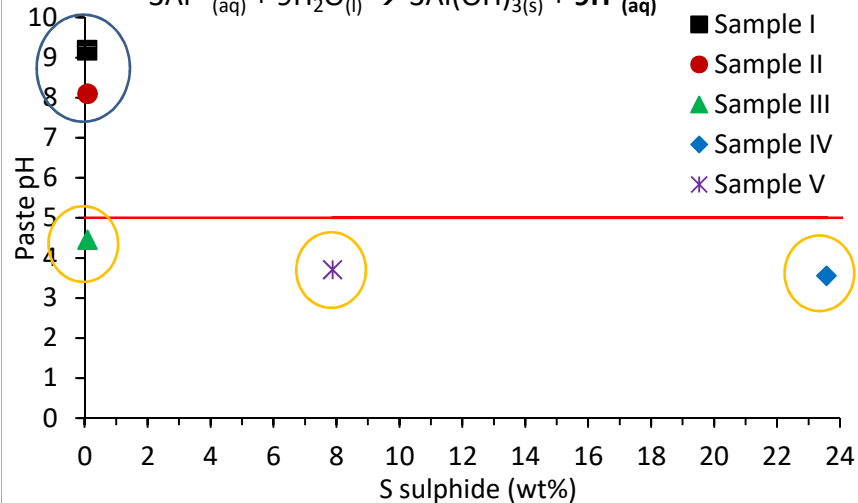
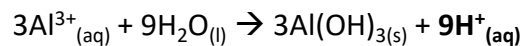
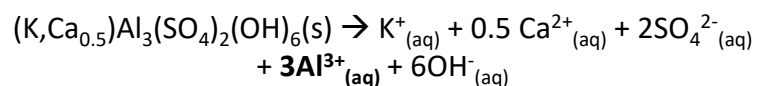


Paste pH of five copper sulphide flotation tailings

CASE STUDY RESULTS

Static Tests

Paste pH



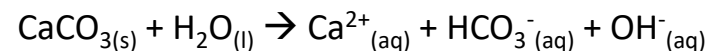
Paste pH versus S sulphide grades for samples

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.

❖ 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 high alunite content in sample III seem to be the reason for the low Paste pH.





CASE STUDY RESULTS

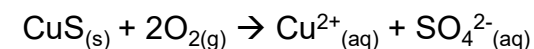
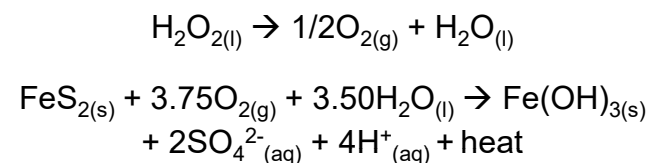
Static Tests

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

NAG pH

- ❖ High pyrite content in samples IV and V, which are 42.2 wt% and 13.0 wt% of pyrite, respectively. 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;
- ❖ Chalcopyrite and covellite can also be oxidized;
- ❖ The lowest NAG pH obtained with sample III can be explained by the presence of pyrite (~0.3 wt%), which was oxidized, generating H⁺ ions, and lowering the pH.
- ❖ Additionally, the absence of calcium carbonate in sample III does not allow the neutralization of its acidity with the addition of hydrogen peroxide.



High formation of gases Samples IV and V



CASE STUDY RESULTS

Static Tests

MABA

MABA results of five copper sulphide flotation tailings

ID	S as sulphide (wt%)	AP (kg CaCO ₃ /t sample)	NP (kg CaCO ₃ /t sample)
Sample I	0.07	2.31	59.76
Sample II	0.09	2.71	34.39
Sample III	0.08	2.50	16.26
Sample IV	23.57	736.43	26.95
Sample V	7.87	245.95	46.00

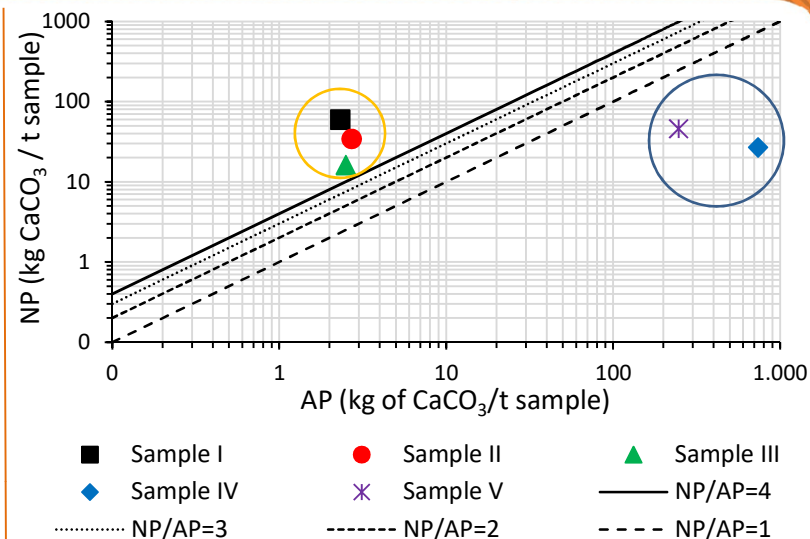
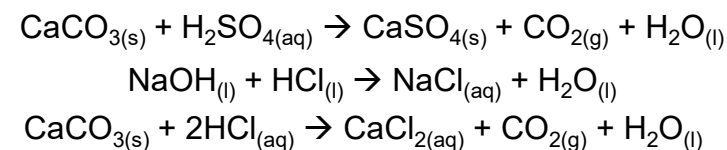


Figure 7. NP versus AP for five copper flotation tailings



According to the MABA tests results, 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 these low NP/AP mass ratios is the respective high AP, being approximately 736 kg CaCO₃/t for sample IV and 246 kg CaCO₃/t for sample V.



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

CASE STUDY RESULTS

Static Tests

Classification of acid mine drainage (AMD) potential

Table 8. Classification of samples for acid drainage potential

ID	Paste pH (pH<5, acid; pH>7, neutral)	NAG pH (pH<4.5, acid; pH>4.5, no acid)	MABA NPR=(NP/AP) (kg CaCO ₃ / t sample) (NP/AP<1, acid; NP/AP>4, no acid)	Classification with MABA results
Sample I	9.19	8.15	>4	NAF
Sample II	8.10	8.18	>4	NAF
Sample III	4.46	5.30	>4	NAF
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.



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CASE STUDY RESULTS

Kinetic Tests

Procedure

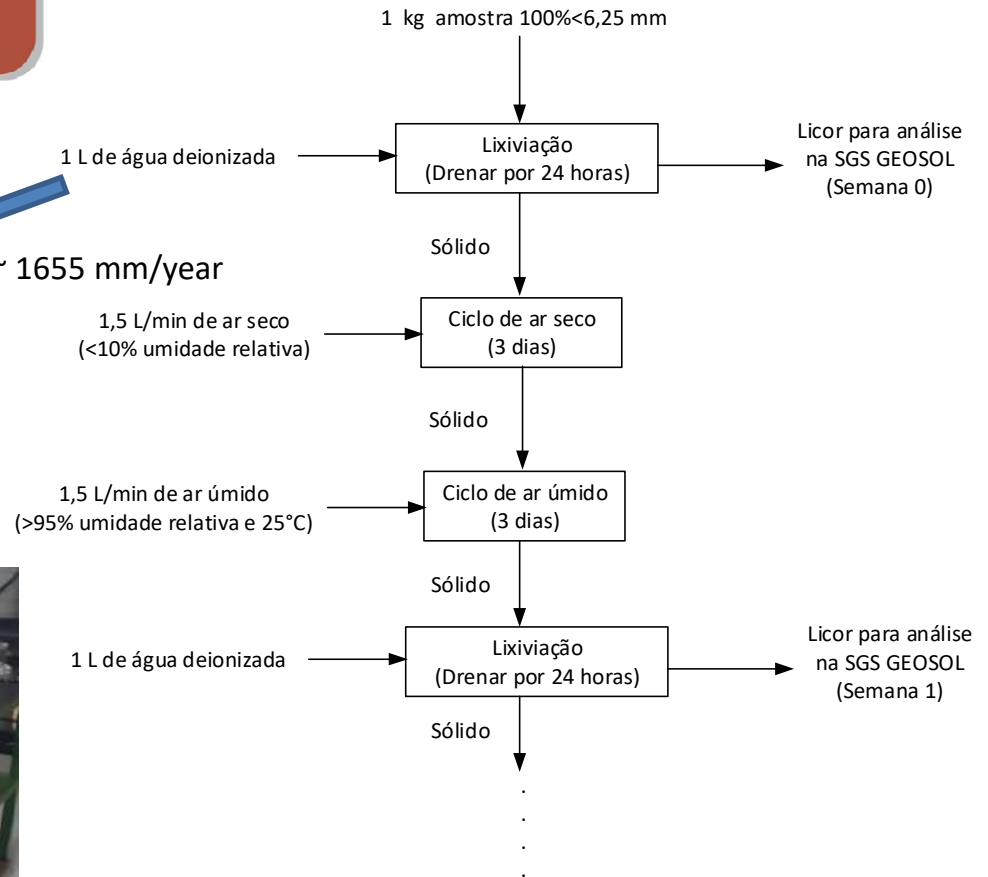
Diameter= 20 cm;
Area=0.0314 m²

(1 L/week/0.0314 m² x 52 weeks/year) ~ 1655 mm/year



Designation: D5744 - 13^e

Standard Test Method for
Laboratory Weathering of Solid Materials Using a Humidity
Cell¹

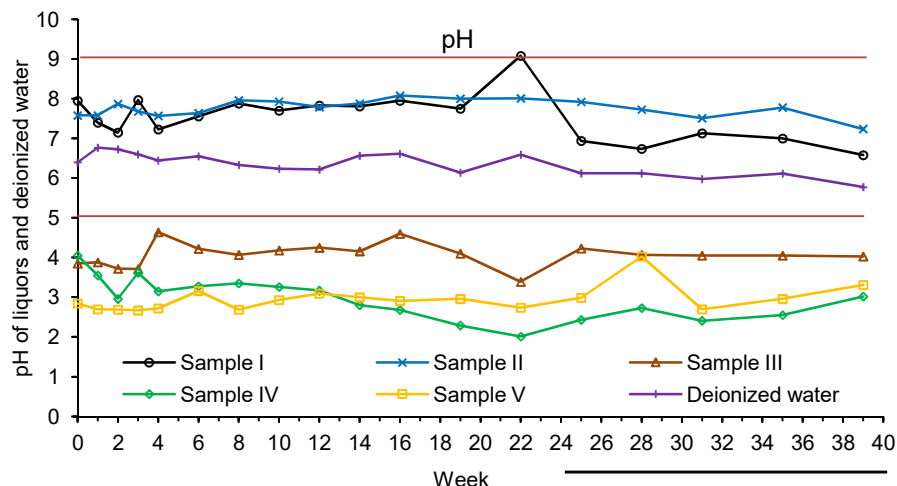


Envio dos licores das semana 0, 1, 2, 3, 4, 6, 8, 10, 12, 14, 16, 19, 22, 25, 28, 31, 35, 39, 43, 47 e 51



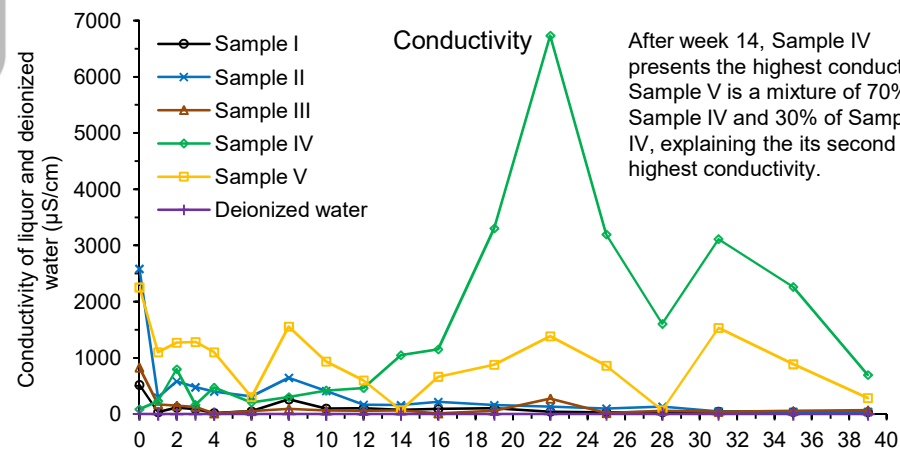
CASE STUDY RESULTS

Kinetic Tests

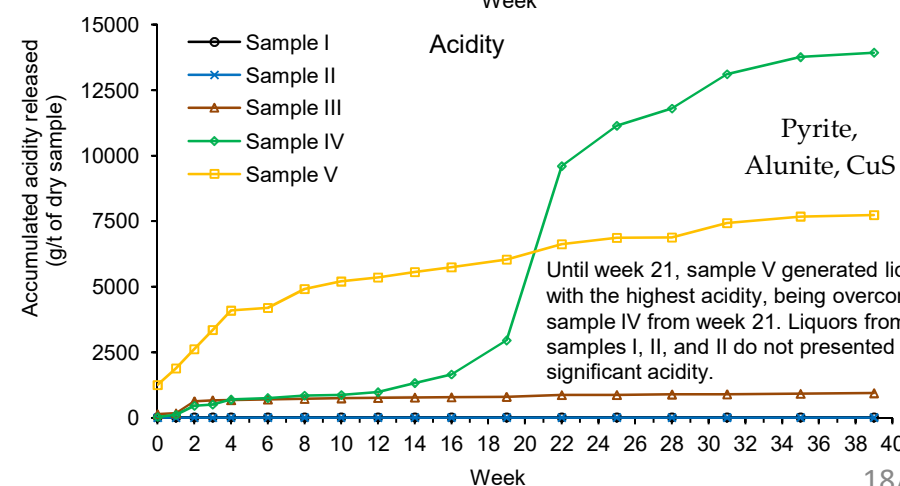


Samples I and II generated an alkaline liquors, with pH above 6.50, whereas the liquors from samples III, IV, and V show a pH below 5.50, which means to be acidity liquors. As expected, no significant variation of pH of deionized water used to leach the samples in each week, which pH was (5.96±0.20), value in the range 5.50 and 6.50.

ID	NAG pH
Sample I	8.15
Sample II	8.18
Sample III	5.30
Sample IV	Not
Sample V	Not



After week 14, Sample IV presents the highest conductivity. Sample V is a mixture of 70% Sample IV and 30% of Sample IV, explaining the its second highest conductivity.



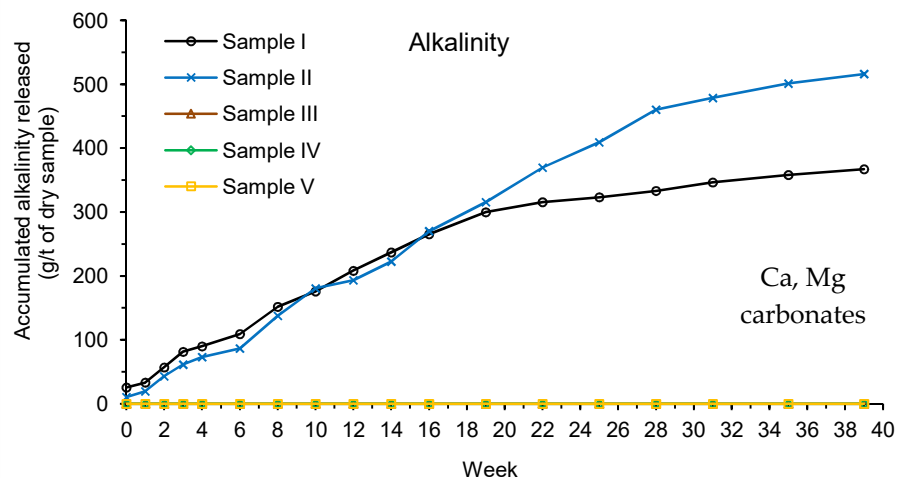
Until week 21, sample V generated liquors with the highest acidity, being overcome by sample IV from week 21. Liquors from samples I, II, and III do not presented significant acidity.

Pyrite, Alunite, CuS

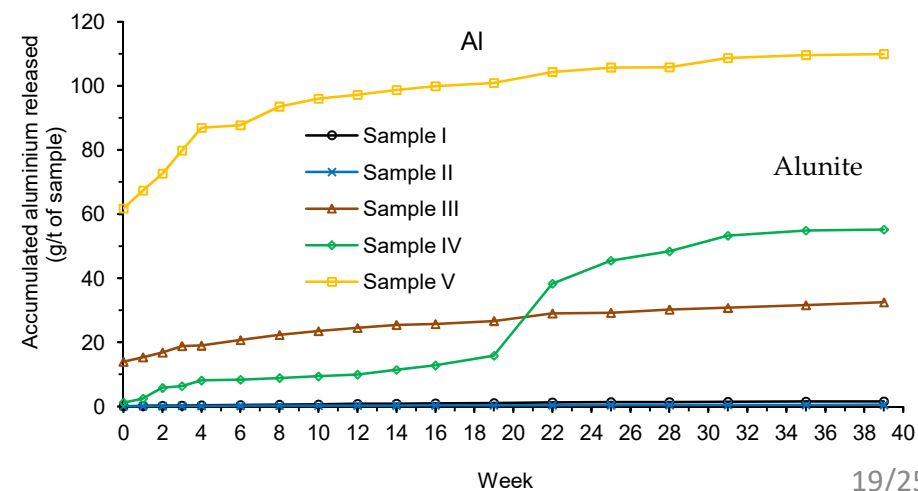
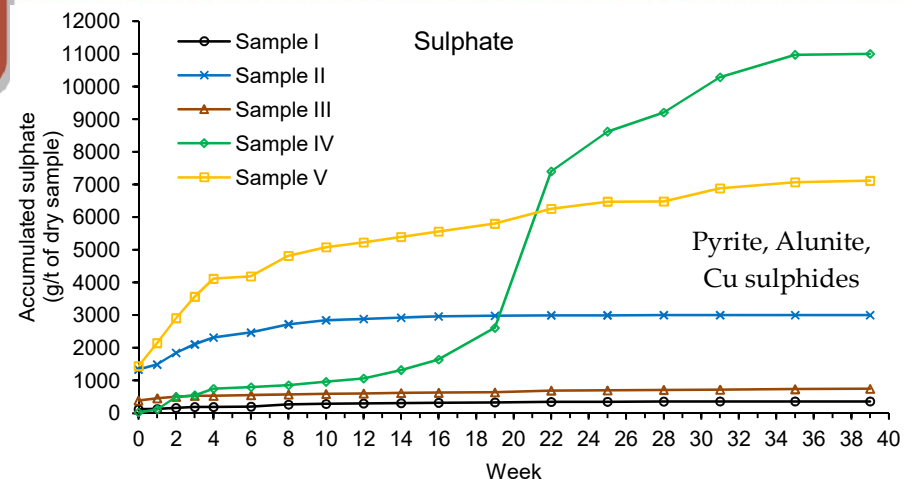


CASE STUDY RESULTS

Kinetic Tests



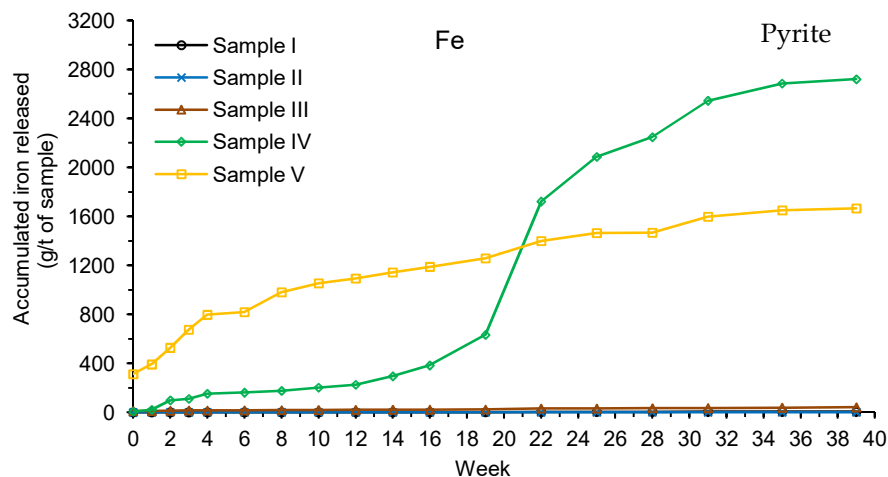
No alkaline liquors with samples III, IV, and V. Same alkalinity for liquors obtained with samples I and II until week 19. The alkalinity of liquor with sample I was overcome by liquor with sample II from week 19.



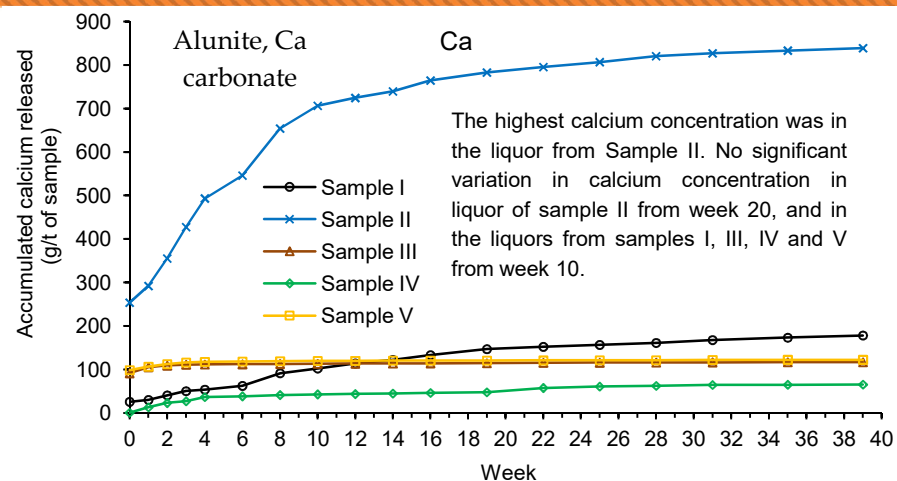


CASE STUDY RESULTS

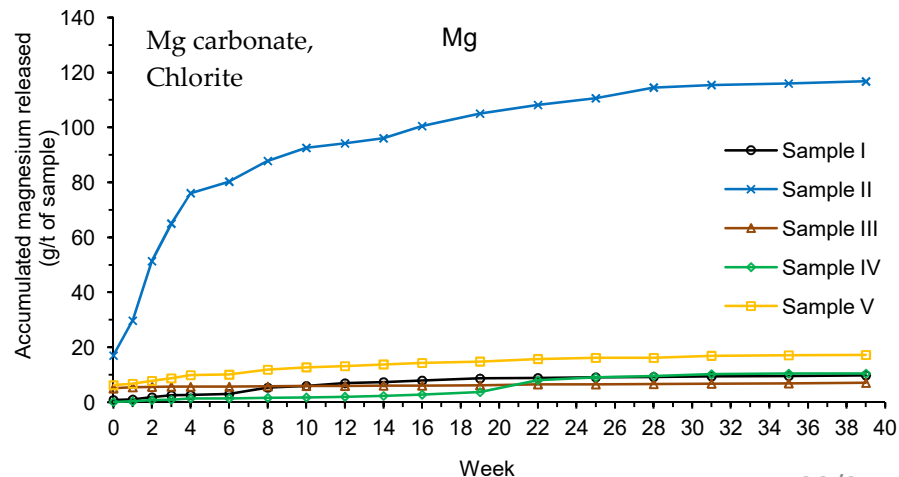
Kinetic Tests



No significant concentration of iron in liquors from samples I, II, and III. The iron concentration in liquor from sample V was overcome by liquor from sample IV in the week 21, same behavior observed for aluminium.



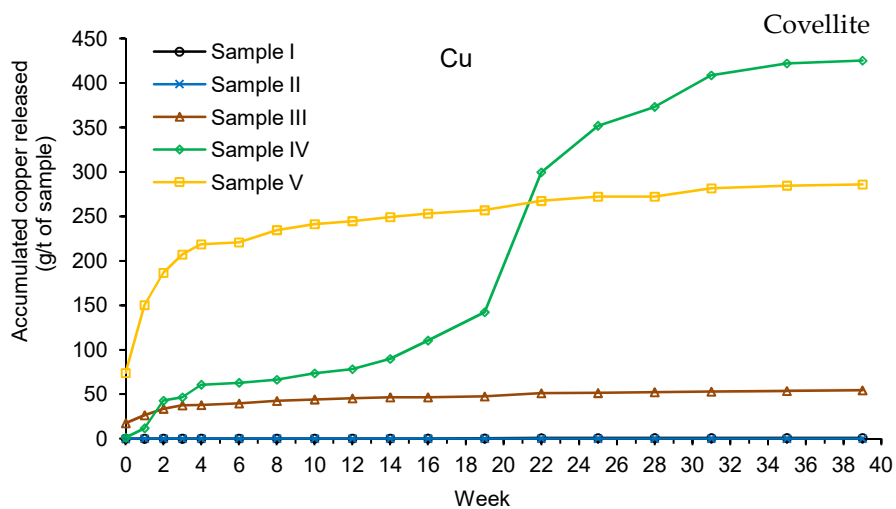
The highest calcium concentration was in the liquor from Sample II. No significant variation in calcium concentration in liquor of sample II from week 20, and in the liquors from samples I, III, IV and V from week 10.



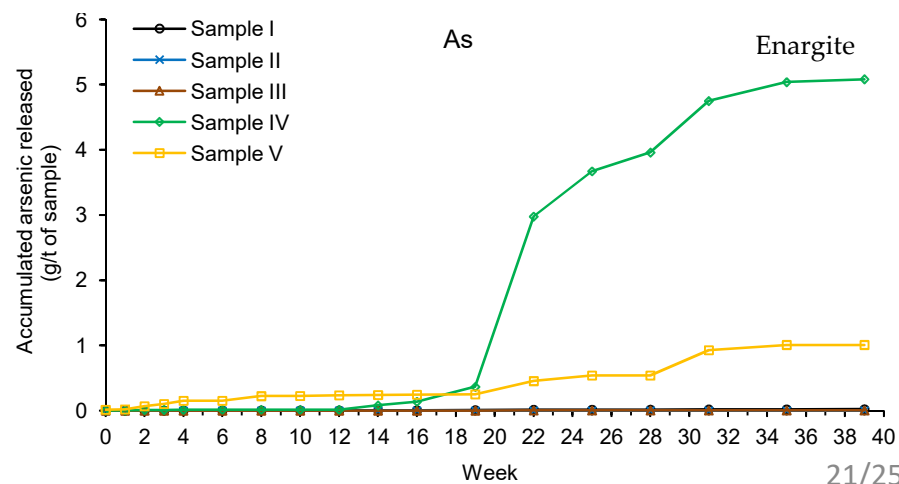
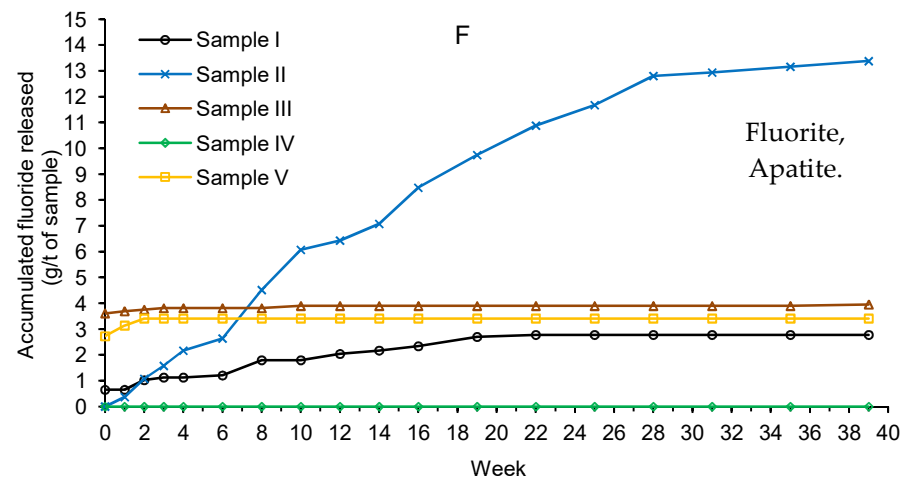


CASE STUDY RESULTS

Kinetic Tests



The highest copper concentration was in the liquor from Sample V. The accumulated copper released from sample V was overcome by sample V in the week 21.





CASE STUDY RESULTS

Kinetic Tests

Metal Released Rate R_M (g/t)

ID	Sulphate	Al	Ba	Fe	Ca	Mg	Cu	F	As
Sample I	5,33	0,06	0,001	0,17	4,89	0,16	0,01	0,05	0,002
Sample II	7,21	0,02	0,003	0,05	7,70	1,47	0,00	0,43	0,000
Sample III	12,02	0,77	0,005	2,59	0,29	0,15	0,78	0,06	0,000
Sample IV	506,90	1,94	0,004	119,74	1,03	0,42	13,62	0,00	0,280
Sample V	127,54	0,83	0,002	38,28	0,34	0,34	2,56	0,00	0,089

$$R_M = (C_{M \text{ kinetic tests}} \times V_L) \text{ (mg/kg or g/t)}$$

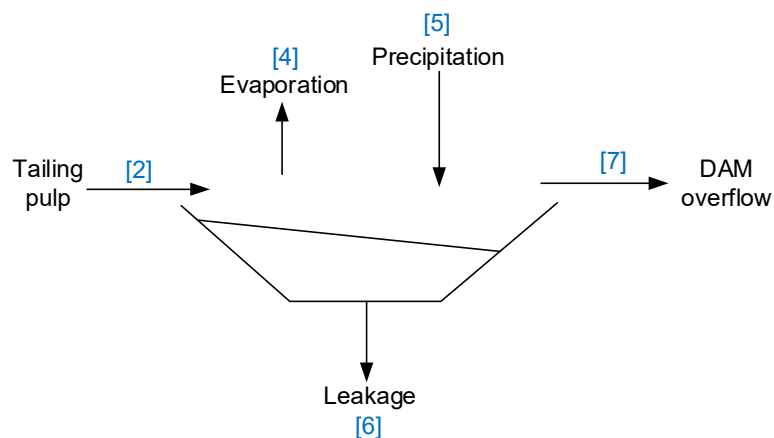
$C_{M \text{ kinetic tests}}$: Mean value from kinetic tests (mg/L);
 V_L : Mean Volume of Liquor in Kinetic Tests (L/kg of dry sample).



CASE STUDY RESULTS

Estimation of Liquor Concentration C_M (mg/L)

Stream	Solids Flow in Tailing Pulp (Mtpy) [1]	Sectional Area DAM (km ²)	Solids content in tailing pulp (%)	Tailing Pulp Mass Flow (Mtpy) [2]	Water Flow in the Tailing Pulp (Mm ³ /year) [3]	Evaporated water (Mm ³ /year) [4]	Precipitated water (Mm ³ /year) [5]	Leakage (Mm ³ /year) [6]	Liquid water in the DAM (Mm ³ /year)	DAM Overflow (Mm ³ /year) [7]	Liquor Concentration [7]							
											Sulphate (mg/L)	Al (mg/L)	Fe (mg/L)	Ca (mg/L)	Mg (mg/L)	Cu (mg/L)	F (mg/L)	As (mg/L)
Sample I	12,61	13,00	35,00	36,03	23,42	6,50	13,00	0,00	29,92	29,92	2,29	0,02	0,06	1,92	0,06	0,003	0,02	0,001
Sample II	4,85	5,00	35,00	13,86	9,01	2,50	5,00	0,00	11,51	11,51	2,95	0,01	0,02	2,89	0,52	0,001	0,15	0,000
Sample III	24,01	24,75	35,00	68,60	44,59	12,38	24,75	0,00	56,97	56,97	5,02	0,32	1,06	0,12	0,06	0,318	0,02	0,000
Sample IV	10,29	10,61	35,00	29,40	19,11	5,30	10,61	0,00	24,41	24,41	183,11	0,69	42,55	0,42	0,17	4,755	0,00	0,099
Sample V	34,30	35,36	35,00	98,00	63,70	17,68	35,36	0,00	81,38	81,38	46,47	0,30	13,56	0,12	0,14	0,905	0,00	0,031

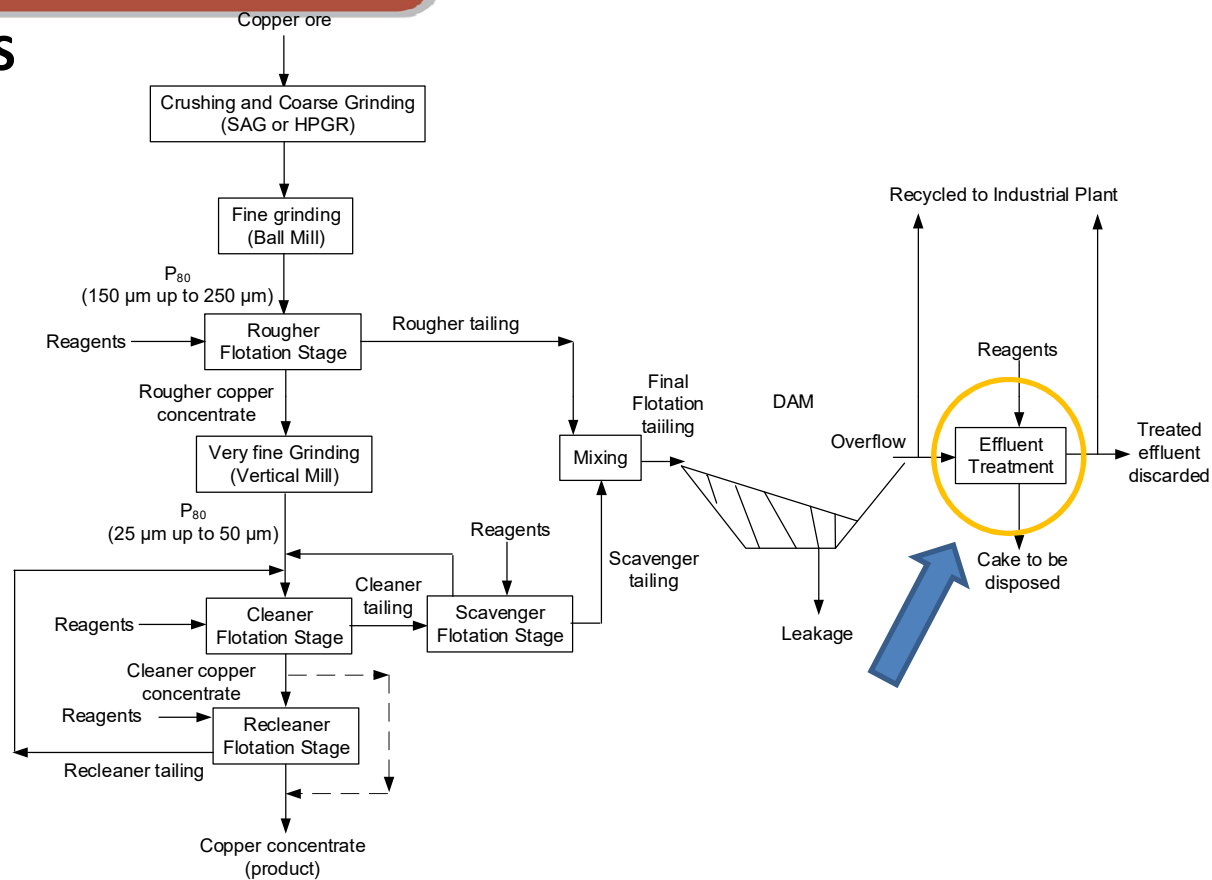


- ❖ 35% of solids in pulp (Assumed);
- ❖ Evaporation rate: 500 mm/year and Precipitation rate: 1500 mm/year (Assumed);
- ❖ $[2] = ([1]/35\%)$;
- ❖ $[3] = [2] - [1]$;
- ❖ $[4] = 500 \times \text{Sectional Area} / 1000$;
- ❖ $[5] = 1500 \times \text{Sectional Area} / 1000$;
- ❖ $[6] = 0$, assumed;
- ❖ $[7] = [3] + [5] - [4] - [6]$
- ❖ $C_M = (\text{Solids Flow} \times R_M / [7])$

In red values above 357 CONAMA Brazilian Law Class II



CASE STUDY RESULTS





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THANK YOU

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