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RESEARCH ARTICLE

Management of Acid Rock Drainage Based on Geochemical Characterisation of Waste Rock Material, Study Case: Gold Mining With High Sulfidation Ephithermal (HS) Deposits

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Abstract

Acid rock drainage (ARD), also known as acid mine drainage (AMD), is a significant challenge for the global gold mining industry, necessitating specialized treatment to prevent its occurrence. Rambajoring deposits, located at the Martabe gold mine in North Sumatra, represent an epithermal deposit of a high-sulfidation system. A crucial step in managing AMD involves identifying whether rocks have the potential to produce acid water when in contact with water and oxygen. Static testing is used to estimate the potential acidity that rock samples can generate based on their composition. These rocks are classified as either Potentially Acid Forming (PAF) or Non-Acid Forming (NAF). Laboratory analyses, including Acid Base Accounting (ABA), Net Acid Generating (NAG) tests, and paste pH measurements, identified all lithologies as belonging to an uncertain category. This uncertainty arises from the presence of significant non-pyritic or non-acid-forming sulfide sulfur minerals, such as alunite ($KAl_3(SO_4)_2(OH)_6$). The presence of these minerals can lead to erroneously high estimations of total sulfur (S) and an increase in calculated Net Acid Producing Potential (NAPP). The long-term implications of non-pyritic sulfide include their potential to oxidize slowly, leading to delayed acid generation not reflected in static NAPP calculations. To validate static test results and analysed the geochemical behaviour of the rocks, supplementary testing was conducted using the Field Column Leach Test (FCLT) method. Over an eight-month monitoring period, FCLT tests confirmed that all lithologies exhibited a lag time before significant acidity was produced and classified as PAF rocks material. The final pH measurements for each lithology were as follows: Scree (SCR) had a pH of 5.56, Phreatomagmatic Breccia (BPM) had a pH of 3.26, and Hornblende Andesite Intrusive (VANh) had a pH of 3.44. The leachates also exhibited the highest dissolved concentrations of metals i.e. iron (Fe), copper (Cu), and zinc (Zn).

Keywords: AMD, ABA, Geochemical Charateristic, Kinetic Test, Static Test

1. Introduction

The mining industry has the potential to damage the environment due to the nature of its activities, which can significantly alter the natural landscape. One of the major environmental impacts is the potential production of acid water. Acid Mine Drainage (AMD) is a term used to describe the acidic water pollution that occurs around mining activities. It is characterized by high levels of acidity, typically with a pH between 1.5 and 3. AMD is produced by the oxidation of sulfide minerals in the presence of water. This process results in water with extremely high acidity levels, elevated concentrations of dissolved metals (e.g., iron, aluminum, manganese, cadmium, copper, lead, zinc, arsenic, and mercury), and low concentrations of dissolved oxygen (Gautama, 2014; Afandi, 2016).

The presence of AMD can negatively impact ecosystems by decreasing water quality and causing environmental degradation (Sandan et al., 2023).

Waste rocks are broadly categorized based on their risk level, including higher risk and lower risk Potentially Acid Forming (PAF) materials, Non Acid Forming (NAF) materials, and PAF materials that may have a lag time before acid generation occurs. A common technique for managing AMD involves encapsulating PAF materials with sealing layers of NAF material to reduce oxygen ingress and minimize contact between PAF rocks and surface water. These methods are widely used in the mining industry as part of an integrated waste management strategy, typically implemented in waste and tailings storage facilities (TSF) or waste dumps to control AMD generation (Henim & Pearce, 2020).

The first and most important stage in preventing AMD is identifying the classification of waste rocks. Determining whether rocks are PAF or NAF can be achieved through static testing, which involves analyzing acid balance calculations (Amira, 2002; Gautama, 2014; Afandi, 2016; Pearce, 2018).

The methodological approach to interpreting Acid Based Accounting (ABA) data focuses on two key area, potential acidity and stored acidity. Potential acidity is associated with unreacted sulfide minerals that release acidity following oxidation. It is typically determined using ABA methodologies. Stored acidity refers to the acidity already present within the waste rock, formed as a result of sulfide oxidation processes. Stored acidity can be identified through methods such as paste pH testing and Acid Neutralizing Capacity (ANC) testing (Amira, 2002; Pearce, 2018).

While ABA methodology and the assessment of acidic salt content provide general tools for characterizing waste rock in terms of its potential to generate acidity including both potential acidity and stored acidity, they do not account for the potential for metalliferous drainage.

Supplementary tests, such as kinetic testing, can be used to validate and confirm static test results, address uncertain classifications, and evaluate geochemical behavior over the long term (Weber et al., 2006;).

2. Location and Site Backgorund

Situated in North Sumatra, South Tapanuli, Indonesia, the Martabe Mine Cluster (MMC) is an epithermal acid sulfate volcanogenic gold deposit developed using open pit mining (Sutopo, 2013;). Accurately and efficiently classifying waste rocks to prepare a fit-for-purpose waste management schedule is challenging due to the geological complexity and significant variation in the AMD characteristics of the materials being mined at the MMC (Pearce et al., 2017).

Pit Rambajoring is one of three active pits in the Martabe project, hosting a high sulfidation epithermal gold deposit (Henim, 2020). The geology broadly comprises two major lithological units, Hornblende Andesite Intrusive (VANh) and Phreatomagmatic Breccia (BPM). The alteration is predominantly advanced argillic (AA), argillic (AR), and silica (SI), with a minor presence of propylitic alteration (PP).

3. Methodology

In this research, static testing was conducted at the mine site. Sampling was performed in phases, with an initial selection of 166 samples from the Rambajoring Pit. These samples were chosen from the drilling database, which contained analysis results from the on site laboratory operated and certified by Intertek Utama Services (ITS). The selected samples represented a cross-section of lithologies and alteration types defined at the Rambajoring Pit at the time.

The samples were analyzed for Acid Base Accounting (Table 1), including net acid generation (NAG) pH test, NAG 4,5 acidity, NAG 7,0 acidity, paste pH, and total sulfur (S).

Table 1. Summary of Static Test Methods

Test	Method	Used to Identify
	Acid-neutralising properties	
ANC	Aggressive sobek-type test	Carbonates and silicates
	Acid-generating properties	
Sulfur	LECO	Total of sulfides and sulfates
MPA	Calculation formula MPA = Total S (%) x 30,62	Estimate of acidity generation potential
NAPP	Calculation formula NAPP = MPA - ANC	Estimate of sample ABA properties
Paste pH	Mixing 1 part of pulverised rock (<75um) and 2 part deionised water	Immediate acid-base nature of samples

3.1 MPA (Maximum Potential of Acidity)

The Maximum Potential Acidity (MPA) value indicates the maximum acidity that can be generated by sulfide minerals (Amira, 2002). This value is determined based on the total sulfur (S) content in the sample. The MPA calculation is performed using the following formula:

$$MPA = \text{Total S (\%)} \times 30{,}62 \quad (1)$$

Where S represents the total sulfur content, measure with LECO method and expressed in %. MPA is expressed in Kg H_2SO_4 per ton of rock.

3.2 ANC (Acid Neutralizing Capacity)

ANC is a method used to determine the amount of neutralizing minerals (generally carbonates, CO_3^{2-}) present in rock samples that can react with acidifying minerals (generally sulfates, SO_4^{2-}). This method involves reacting the sample with a standard HCl acid solution, followed by back-titration with a 0.1 M NaOH solution. The amount of acid neutralized by the NaOH during the titration represents the ANC value (Amira, 2002; Pearce, 2018; Tonny et al., 2021).

3.3 NAPP (Net Acid Producing Potential)

NAPP is a method used to identify rock acidity, taking into account the rocks ability to produce acid and the rocks ability to neutralize it (Amira, 2002). The NAPP value is calculated using the formula below and expressed in Kg H_2SO_4 per ton of rock.

$$NAPP = MPA - ANC \quad (2)$$

3.4 Paste pH

The purpose of paste pH testing is to indicate the amount of natural oxides present in the sample, which is done by mixing the sample with distilled water it (Amira, 2002).

3.5 NAG (Net Acid Generating) test

The NAG (Net Acid Generation) test is conducted to evaluate the potential for sulfuric acid generation from sulfides. This test involves reacting the sample with an oxidizing solution, specifically hydrogen peroxide (H_2O_2), to accelerate the complete oxidation of all sulfide minerals present in the rock sample. During the oxidation process, both acid generation and neutralization reactions may occur simultaneously. The result of this test reflects the net amount of acid produced by the rock sample, expressed in kg H_2SO_4 per ton of rock (Amira, 2002).

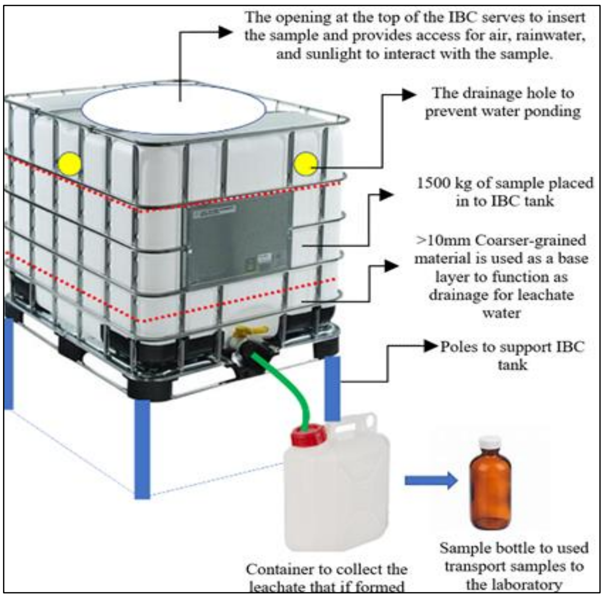

Fig. 1. Field column leach test (FCLT)

3.6 FCLT (Field Column Leach Test)

Kinetic testing is conducted to simulate oxidation reactions on a laboratory scale, adjusted to field conditions with create a column reactor (Fig. 1) to study the chemical processes involved. This test aims to provide insights into sulfide mineral reactivity, oxidation reaction rates, metal solubility, and the characteristics of leachate water (Pearce, 2018).

3.7 AMD Classification

A typical approach for AMD sample characterization is to plot NAG pH versus NAPP (Fig.2). If there is a strong correlation between NAG pH and NAPP, a clear classification process can be developed to identify NAF and PAF samples (Amira, 2002).

Meanwhile, if the correlation between NAG pH and NAPP is not strong, it will give results as uncertain. An uncertain (UC) classification plot can often occur in the upper right UC quadrant in some cases, such as when there is significant non pyritic or non-acid forming sulfate sulfur. Other case can happen if there are significant iron carbonates and insufficient H_2O_2 to oxidize all sulfide minerals within the sample, which may buffer any acidity before the exhaustion of the H_2O_2. A plot in the lower left-hand UC quadrant may occur if significant organic acidity is produced in the samples (Weber et al., 2004).

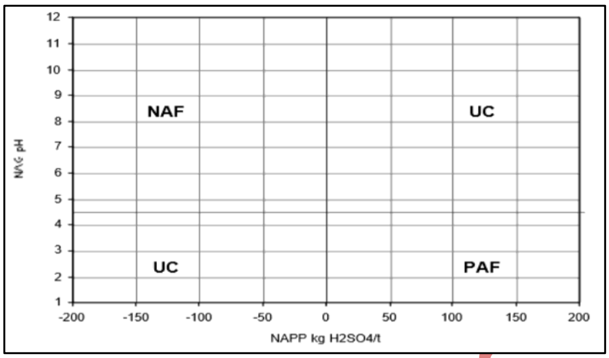

Fig. 2. Acid Generation Potential Classification system using NAPP and NAG pH Data

4. Result and Discussion

4.1 Geology

A typical approach for AMD sample characterization is to plot NAG pH versus NAPP (Fig.3). If there is a strong correlation between NAG pH and NAPP, a clear classification process can be developed to identify NAF and PAF samples (Amira, 2002).

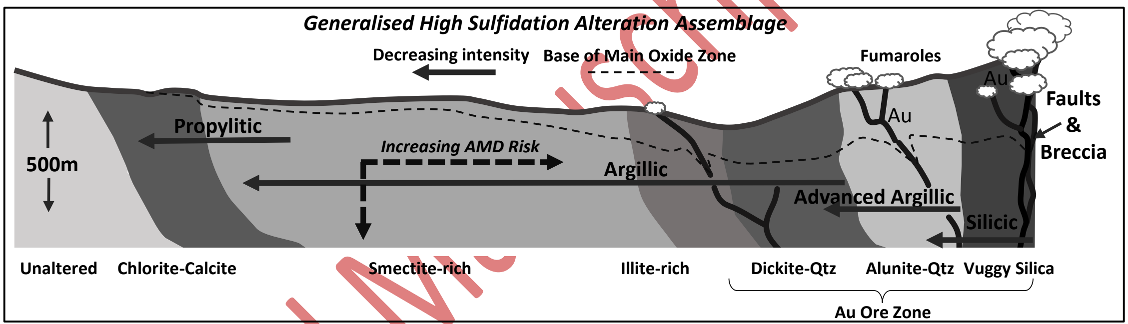

Fig. 3. Generalized high-sulfidation alteration assemblage at the MMC (Mandradewi et al. 2014)

The zones are partially coincident with breccia zones, although they are not a primary control on mineralisation. The geology comprises broadly of two major lithological units, Hornblende andesite intrusive (VANh) with code lithdom 0, small portion Scree (SCR) lithology with code lithdom 1, and Phreatomagmatic Breccia (BPM) with code lithdom 2 (Fig.4). Alteration (Fig. 5) consists predominantly of advanced argillic (AA) with altdom 2, Argillic (AR) with altdom 0 and Silica (SI) with altdom 1, with small unit of Propylitic alteration (PP) with altdom 3.

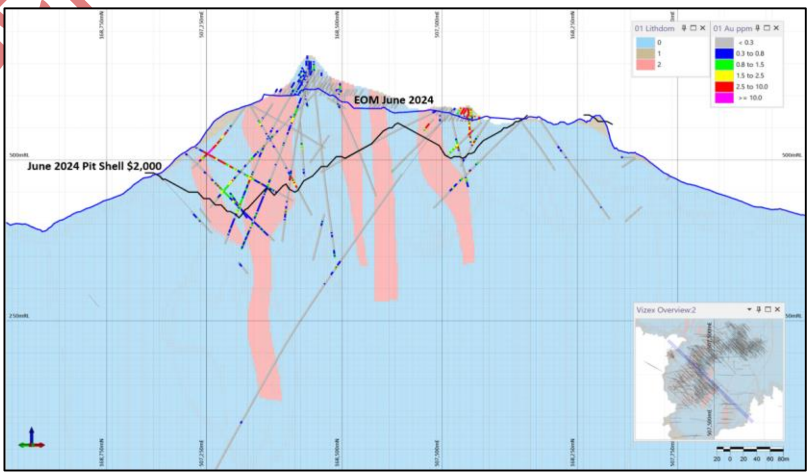

Fig. 4. Domain Lithology Rambajoring (Cross section at 507,500 mE)

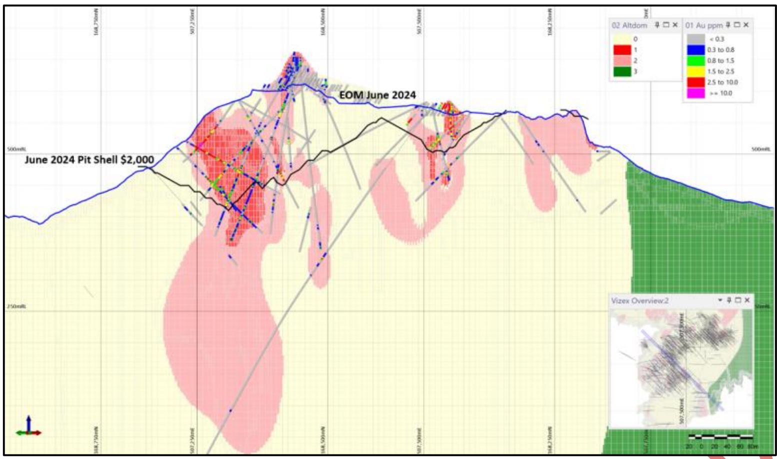

Fig. 5. Domain Alteration Rambajoring (Cross section at 507,500 mE)

4.2 Static Test Result

The results of the static testing for acid generation and base neutralization potential or ABA for each rock lithology, i.e., VANh, BPM, and SCR, in the Rambajoring pit are as follows (Table 2).

Table 2. Static Test Result Rambajoring.

Lith.	Qty Samples	NAG pH	Total S %	Sulfide %
		Average		
SCR	9	5,90	3,64	1,24
BPM	64	4,95	2,81	1,21
VANh	93	4,84	3,15	1,54
		Median		
SCR	9	5,90	3,64	1,24
BPM	64	4,95	2,81	1,21
VANh	93	4,84	3,15	1,54

Lith.	Qty Samples	Paste pH	MPA Kg H_2SO_4/t	ANC Kg H_2SO_4/t
		Average		
SCR	9	5,77	111	23
BPM	64	5,32	86	11
VANh	93	5,48	96	12
		Median		
SCR	9	5,60	100	0,3
BPM	64	5,10	68	0,3
VANh	93	5,20	73	0,3

Referring to the calculation using (formula 2), the result of NAPP in Kg H2SO4/ton rock and NAG pH for Rambajoring are as follows (Table 3).

Table 3. NAPP & NAG pH Values.

Lithology	Qty Samples	NAPP	NAG pH
		Average	
SCR	9	89	5,90
BPM	64	75	4,95
VANh	93	85	4,85
		Median	
SCR	9	97	5,60
BPM	64	61	5,10
VANh	93	65	5,20

If the NAPP and NAG pH, based on the average data of samples (Fig. 6) and based on median data of samples (Fig. 7) are plotted into the AMD classification quadrant, the lithologies Scree (SCR), Phreatomagmatic Breccia (BPM), and Hornblende Andesite Intrusive (VANh) cannot be clearly classified based on NAG pH and NAPP values, as they fall into the Uncertain Category (UC) in the upper-right quadrant.

This uncertainty is generally due to sulfur content that does not contribute to acid formation. This is supported by the high total sulfur values, where not all sulfur is acid-generating, as indicated by the NAG test and paste pH results, which do not show low acidity levels (pH below 4.5).

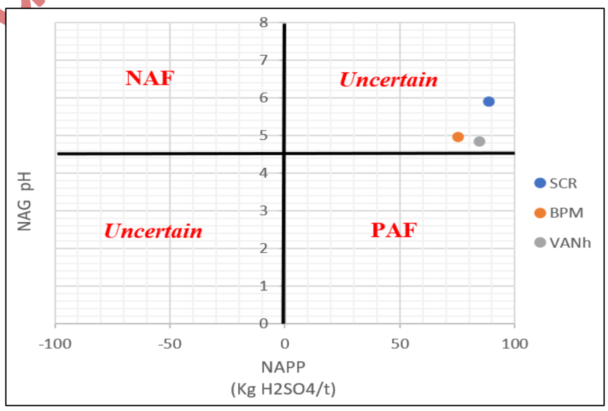

Fig. 6. AMD classification based on average data

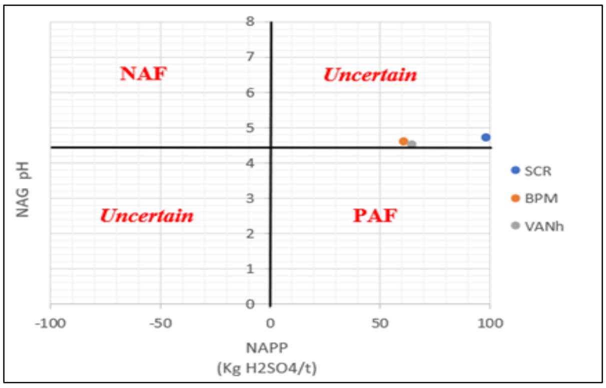

Fig. 7. AMD classification based on median data

All lithology samples from the Rambajoring Pit show there is no strong correlation of coefficient determination (R^2 0,49) between the NAPP calculation results and the NAG test (Fig. 8).

Based on mineralogical identification in the Rambajoring Pit, there is a significant presence of non acid forming sulfate minerals as alunite ($KAl_3(SO4)_5(OH)_6$). Alunite is a sulfate mineral composed primarily of potassium and aluminum, t is typically found in volcanic rocks and hydrothermal deposits, often in areas with acidic conditions. Alunite is relatively non-reactive in the context of acid mine drainage (AMD) compared to other sulfide minerals, like pyrite. Alunite chemical structure is relatively stable under natural conditions. It contains aluminum, potassium, sulfate, and hydroxide, but these elements do not easily break down to form sulfuric acid, a key component of acid mine drainage. In contrast, sulfide minerals like pyrite (FeS_2) undergo oxidation when exposed to air and water, producing sulfuric acid (H_2SO_4) and iron (Fe) that can lead to the formation of acidic. Alunite is a sulfate mineral, meaning its sulfur is already chemically bound in a stable form (as sulfate, SO_4^{2-}), rather than in the reactive sulfide (S^{2-}) form found in pyrite and other sulfide minerals. Sulfate minerals like alunite do not readily contribute to the production of sulfuric acid upon oxidation. For alunite to contribute to acid production, it would need to undergo significant weathering, but this process is much slower and less aggressive than the oxidation of sulfide minerals. Thus, it doesn't readily release acid and metals into the environment like pyrite does.

Presence of Alunite disturbed the interpretation of Acid Base Accounting (ABA) and other static test results due to their behaviour in releasing acidity and their potential for storing latent acidity. Alunite is less reactive in NAG test and make underestimating its contribution to future acid generation. Alunite dissolves slowly, static test (short term evaluations) may not fully capture this long term acid generation.

The analytical spectrum divices (ASD) previously conducted at Rambajoring pit (Henim, 2021), identified correlation between associated mineral and alteration type. Strong AA alteration associated with alunite-dickite-calcium minerals, moderate AA alteration associated with alunite-kaolinite-dickite minerals and weak AA alteration associated with dickite-kaolinite minerals. Rock sample with moderate AR alteration are associated with illite-smectite-kaolinite-gypsum minerals and weak AR alteration associated with smectite minerals.

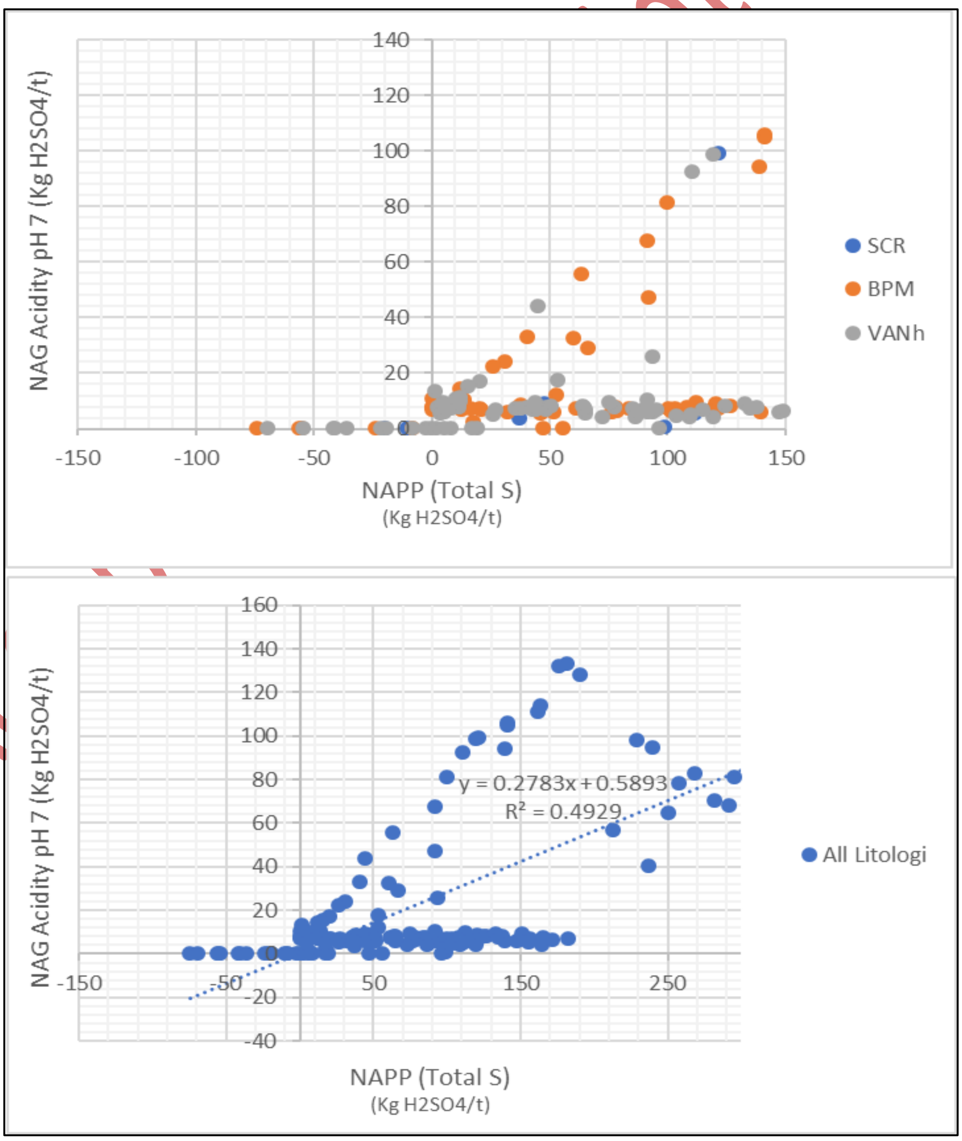

Fig. 8. Correlation NAPP vs NAG pH

The analysis shows that the presence of alunite can distort the results of static testing, leading to an uncertain classification of rock types. This is supported by mineral identification testing using the X-Ray Diffraction (XRD) method, which reveals a high presence of alunite mineral (Table 4).

Table 4. XRD Mineral Identification

Mineral Identification	Rietveld Refinement WT%		
	AR 2004212	AR 2004234	AR 2004236
Alunite	20,2	19,3	21,5
Anastase	1,2	-	-
Iron	-	0,4	0,3
Gibbsite	-	-	1.2
Goethite	4,4	-	2.5
Hematite	20,1	-	2.6
Kaolinite	-	-	2.9
Montmorillonite	12,5	-	-
Pyrite	9,2	0,6	0,5
Quartz	32,4	79,7	68,5

Alunite is a significant component in each of these samples, with its weight percentage ranging between 19.3% and 21.5%.

4.3 Kinetic Testing Result

The kinetic test was conducted using samples from each rock lithology (VANh, BPM and SCR) and was carried out over a period of eight months, with the leachate measured every month.

The results of the kinetic test (Table 5) confirm the static test, showing that over a long reaction period, the rocks at Rambajoring are classified as PAF (Potentially Acid-Forming) rocks. The pH values are low for both BPM (3,44) and VANh (3,26), which are strongly acidic. A low pH is a critical sign that the rock could generate acidic conditions. A pH below 4,5 is often associated with the formation of acid mine drainage, a characteristic of PAF rocks. SCR has a higher pH (5,56), which is closer to neutral due to higher alkalinity (37 mg/L) and has a greater potential to buffer acids.

Fig. 9. Kinetic Test (Field Column Leach Test)

Table 5. NAPP & NAG pH Values

Parameters	SCR	BPM	VANh
Final pH	5,56	3,44	3,26
Avidity Total, mg/L	94	134	124
Alkalinity Total, mg/L	37	8	8

In the early period, all samples had an average pH above 4,5, consistent with static test measurements. No significant pH decrease was observed, which can be attributed to the rocks ability to neutralize acid. The SCR lithology at Rambajoring shows better acid neutralization capacity, as indicated by the high ANC value, which averaged 23 kg H_2SO_4/ton. For the BPM and VANh lithologies, the pH gradually decreased. This was due to the presence of non-pyrite or non-acid-forming sulfate sulfur minerals, such as alunite, which undergo a slow acid formation process and began to oxidize. By the end of the measurement period, the pH had decreased to an average of 3.26 – 3.44.

The changes in pH values during the measurement period are consistent with the total acidity and total alkalinity produced (Fig. 11). The pH and acidity show a positive relationship, as the pH decreases, total acidity increases due to the production of more acid. Conversely, as the alkalinity increases, the pH will also increase to.

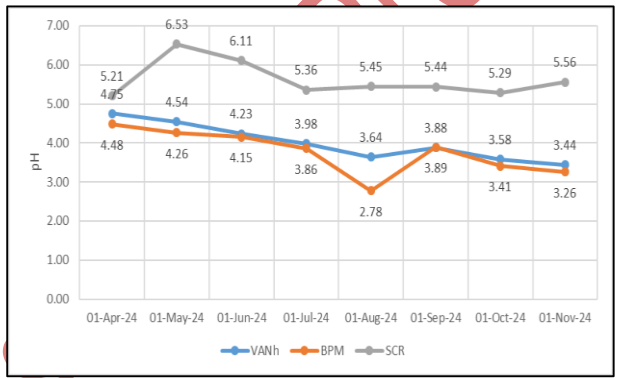

Fig. 10. Trend of pH changing per period

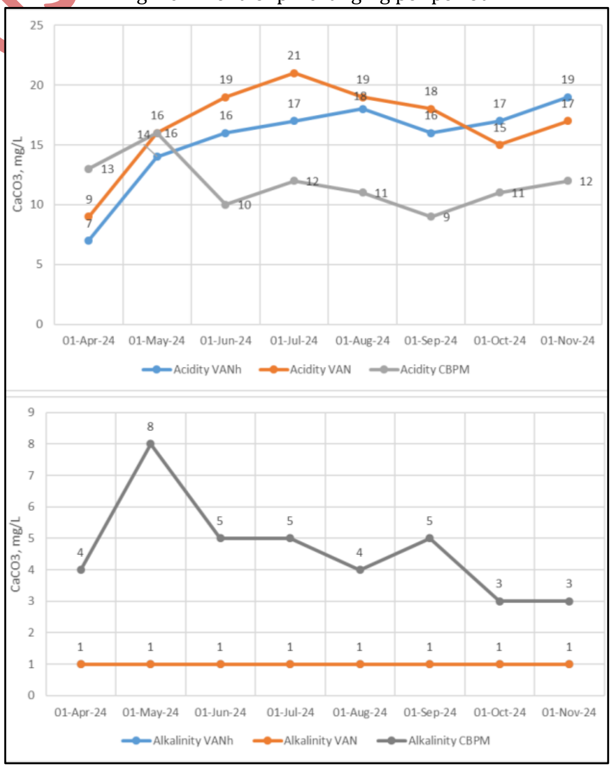

Fig. 11. Formation Trend for Acidity (above) and Alkalinity (Below) Total Kinetic Test

4.4 Characteristics of Leachate

The measurement of leachate in kinetic testing using samples from the Rambajoring pit contains several dissolved metals, with iron (Fe) being the highest dissolved metal for all lithologies VANh, BPM and SCR at total 1,12 mg/L, followed by zinc (Zn) at total 0,28 mg/L and arsenic (As) at total 0,05 mg/L. Other metal dissolved with small total concentration i.e. copper (Cu) at 0,03 mg/L. nickel (Ni) at 0,01 mg/L, chromium (Cr), mercury (Hg), cadmium (Cd) and lead (Pb), each with a metal dissolved concentration below 0,01 mg/L.

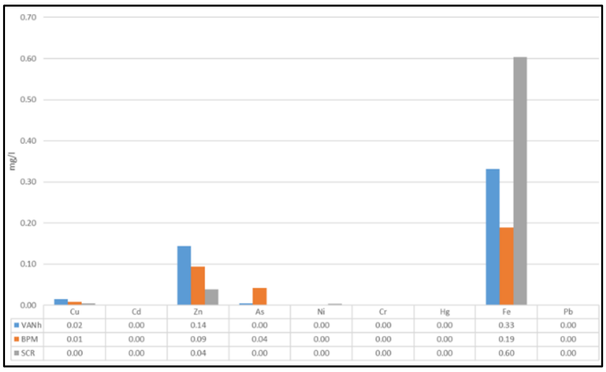

Fig. 12. Total metal concentration on leachate

5. Conclusion

Based on the analysis conducted, it can be concluded that the Rambajoring pit contains the following lithologies: Hornblende andesite intrusive (VANh), Phreatomagmatic Breccia (BPM), and Scree (SCR). The static testing results classified the samples as uncertain (UC) due to the presence of alunite minerals. However, after confirmation through kinetic testing over a longer period, the geochemical trends of each sample became clearer. This led to the conclusion that the SCR, VANh, and BPM lithologies in the Rambajoring pit are classified as Potential Acid Forming (PAF). These lithologies contain several dissolved metals, with iron (Fe) being the highest at 1.12 mg/L, followed by zinc (Zn) at 0.28 mg/L and arsenic (As) at 0.05 mg/L.

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