

# Determining Acid and Metalliferous Drainage Potential of Waste Rock on a Mine\*

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## Abstract

Acid and Metalliferous Drainage (AMD) is recognised as serious environmental problem in the mining industry. This is because environmental issue of AMD poses serious threat to water quality, vegetation cover and social licence of the mining operations. AMD occurs when reactive sulphide bearing materials are exposed to oxidising conditions. It has now become imperative for some mining companies to test sulphide bearing minerals for their AMD potential before major mining excavations are done. This work determines the AMD potential of fifty (50) waste rock samples from a Mine using Acid Base Accounting (ABA) techniques. Mineralogical studies on the sample indicated that the major sulphide mineral assemblages present were pyrite, arsenopyrite and chalcocopyrite. Paste pH showed that 20% of the samples had undergone weathering and as such AMD generation had already started. Approximately 22% of the sample had conductivity levels between 1000 to 10,000  $\mu\text{S}/\text{cm}$  and this shows a typical AMD chemical characteristic of high salinity. Acid Base Accounting showed that 32% of the samples were acid generating. Exactly 16% were non-acid forming and 52% were uncertain. The analysis showed that the potential for AMD generation exists for the waste rock material and can affect the local environment, specifically water quality if preventive measures are not taken.

**Keywords:** Sulphide, Waste Rock, Acid Base Accounting, Paste pH, Conductivity

## 1 Introduction

One of the major problems facing most mining site environs is the spontaneous acidic effluent discharges into community waters close to mining companies as a result of the mining activities. The discharge termed as Acid and Metalliferous Drainage (AMD) is generated when reactive sulphide minerals (Table 1) chiefly pyrite are exposed to atmospheric oxygen, water and microbial action (Johnson and Hallberg, 2005; Akcil and Koldas, 2006; Kalin *et al.*, 2006; Dold, 2008; Dold, 2017). Sulphide mineral like pyrites go through a binary stage oxidation process, firstly generating ferrous sulphur and sulphuric acid and thereafter, ferric hydroxide (Fig. 1) that is reddish orange with additional sulphuric acid (Naidu *et al.*, 2019).

AMD occurs naturally but mining and land disturbances facilitate its generation rate by increasing the amount of exposed sulphide-bearing materials. The attributes of AMD tend to rely on varying site conditions such as weather, geomorphology and amount of waste materials (Schneider *et al.*, 2014; Nieva *et al.*, 2018). Chemical, biological and physical factors that mainly impact the level of AMD generation includes air (oxygen), rain drop temperature and water saturation levels, microbial activity and degree of metal sulphide exposure (Akcil and Koldas, 2006) Fig. 2. Naturally-occurring bacteria can also accelerate the generation of AMD by aiding in the breakdown of sulphide materials (Akcil and Koldas, 2006; Qureshi *et al.*, 2016).

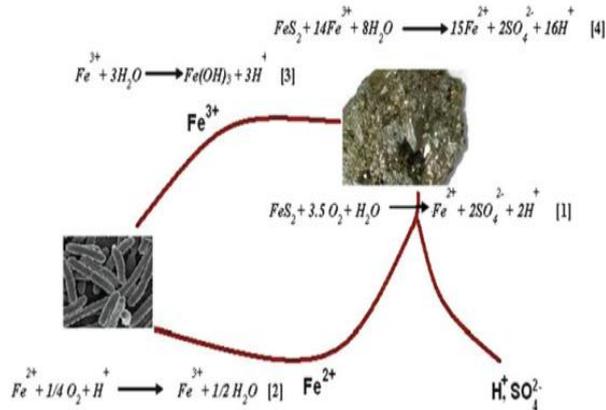
**Table 1 Metal Sulphides with Predominant Acid Producers.**

Metal sulphide	Chemical formula
Pyrite	$\text{FeS}_2$
Marcasite	$\text{FeS}_2$
Pyrrhotite	$\text{Fe}_{1-x}\text{S}$
Chalcocite	$\text{Cu}_2\text{S}$
Covellite	$\text{CuS}$
Chalcocopyrite	$\text{CuFeS}_2$
Molybdenite	$\text{MoS}_2$
Millerite	$\text{NiS}$
Galena	$\text{PbS}$
Sphalerite	$\text{ZnS}$
Arsenopyrite	$\text{FeAsS}$

**Source:** (Skousen, 1995; Simate and Ndlovu, 2014)

Due to the mineral composition of the sulphide-bearing rock, that is, the acid generating minerals, a study of the mineralogy and analysis of the relative percentages of acidic and basic minerals of the rock can be used to predict its acid generating potential (Ofori-Sarpong *et al.*, 2013). With the evolution of metal extraction technologies, the amount of mine wastes produced have increased tremendously, a trend, which will increase even more in the future (Dold, 2017).

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**Fig. 1 Pyrite Oxidation Process**  
 Source: (Kleinmann *et al.*, 1981)

The oxidation of sulphide mine waste and the corresponding acidic effluent discharges have been described as the major environmental pollutant of water in many countries that have historic or current mining activities. This is because once an acid-generating rock is exposed to oxygen and water, the reaction process is difficult to contain or stop, and can continue for years until the sulphide minerals are exhausted (Simate and Ndlovu, 2014; Kefeni *et al.*, 2017). Hence using a more precise method to predicts AMD potential to take proactive measures to prevent its effect on environment is of paramount importance.

Generally, in low pH, water variable concentrations of heavy metals and metalloids are mobilised.

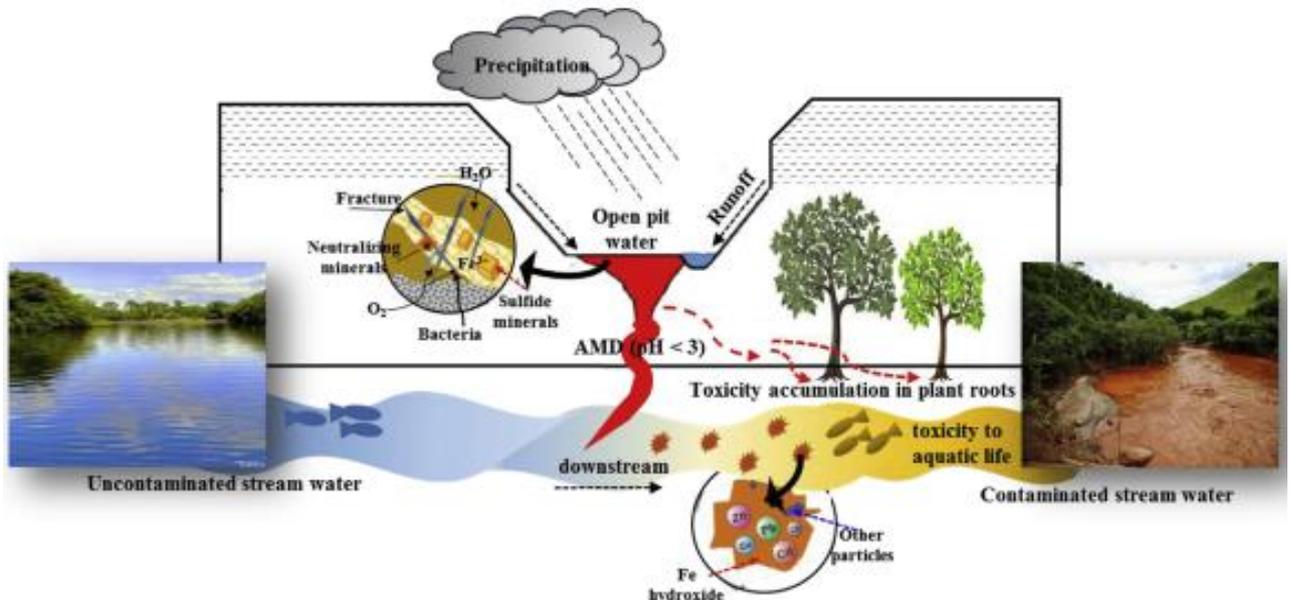
These characteristics can lead to pollution or contamination of both surface and groundwater as well as soils, which consequently affect the biodiversity of the affected area (Nleya *et al.*, 2016) (Fig. 2).

This work seeks to determine the acid and metalliferous drainage potential of waste rock from a mineral bearing concession in Ghana using Acid Base Accounting (ABA) as the predictive tool, which can help to effectively employ preventive measures to curb the menace, protect ecological properties at the mine and surrounding communities.

## 2 Resources and Methods Used

### 2.1 Sample Preparation

Fifty (50) waste rock samples from the mine were received in sample bags. The samples were weathered materials with an average size of 8 mm. Portions of the as-received samples were split for mineralogical studies, total sulphur content and paste pH determination. The samples were crushed and pulverized to 80% passing 75 µm after which ABA was done to ascertain the acid production potential, neutralization potential and net neutralising potential of the samples in accordance with the Australian Mineral Industries Research Association Limited (AMIRA) protocol (Anon, 2002).



**Fig. 2 AMD Generation and Related Contamination Pathway**  
 Source: (Naidu *et al.*, 2019)

## 2.2 Mineralogical Analysis

Mineralogical studies were done by thin and polish section microscopy and XRD determination. Thin section microscopy was done using a LEICA DMC EP Polarizing Microscope. Polish sections were conducted using a Leitz Optical Microscope. Quantitative X-ray diffraction (QXRD) quantified and identified the various mineral phases in the waste rock sample. Prior to the XRD analysis, the samples were placed into a sample cup ensuring that it was packed, flat and levelled with the top of the cup before analysing with Scintag ARL X'tra diffractometer and Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). XRD traces were collected between  $2^\circ$  and  $90^\circ 2\theta$  at  $0.02$  intervals at the rate of  $0.24^\circ$  per minute. All the mineral peaks were identified using X Powder software and then quantified using SIROQUANT V3 software.

## 2.3 Past pH and Conductivity of Samples

Paste pH of all the fifty (50) samples was done to determine the current acidity status of the sample (Weber *et al.*, 2006). In this test, 10 g of each sample was pulped with 20 mL of deionized water in a beaker. The mixture was allowed to stand for 10 mins, after which the pH and conductivity values were recorded as the values became stable.

## 2.4 Acid Base Accounting (ABA)

Acid Base Accounting is an analytical technique that generates values to help predict the acid generation and acid-neutralizing potential of rock prior to mining and other large excavations (Anon, 1994). It is also a theoretical balance between the potential for a sample to generate acid and neutralise acid. The ABA's simplest form is known as the Net Acid Producing Potential (NAPP). It involves determining the maximum potential acidity (MPA) and the inherent acid-neutralising capacity (ANC). The procedure helps in determining post-mining water quality. In the acid base accounting technique utilized, the following terms were applied: PAF - Potential Acid Forming, PLC - Potential Acid Forming Low Capacity, NAF - Non-Acid Forming, U - Uncertain.

### 2.4.1 Determination of maximum potential acidity (MPA)

The MPA can be deduced from the sulphur content of a sample. The MPA is determined by multiplying the total sulphur content of the sample by a conversion factor of 30.6 in units of kg H<sub>2</sub>SO<sub>4</sub>/t, i.e. (MPA = 30.6 \* %S) (Weber *et al.*, 2004). The calculation assumes that the measured sulphur content occurs as pyrite reacts under oxidising conditions to produce acid (Anon, 2002).

### 2.4.2 Determination of total Sulphur in the samples

Total sulphur content of a sample is commonly determined by high temperature combustion volumetric technique using LECO SC-144 Titrator.

### 2.4.3 Determination of Acid Neutralisation Capacity (ANC)

The ANC is commonly determined by the Sobek method. This method involves the addition of a known amount of hydrochloric acid (HCl) to an accurately weighed sample, allowing the sample time to react (by heating) and back titrating the mixture with standardized sodium hydroxide (NaOH) to determine the amount of unreacted HCl (Sobek *et al.*, 1978). A fizz test was performed to determine the volume and concentration of both acid and caustic to be used in the analysis as shown in Table 2. The appropriate volume and concentration of acid as deduced from the fizz test was added to 2 g of the sample together with 20 mL of deionized water. The mixture was heated for approximately 2 hrs and titrated with standardized sodium hydroxide. Blanks were prepared in the same manner (Anon, 2002). The ANC value (in kg H<sub>2</sub>SO<sub>4</sub>/t) was calculated using Eq.1:

$$ANC = [Y \times \frac{M_{HCl}}{wt}] \times C \quad (1)$$

where; Y = (Volume of HCl added) – (Volume of NaOH titrated  $\times$  B), B = (Volume of HCl in Blank) / (Volume of NaOH titrated against Blank), M<sub>HCl</sub> = Molarity of HCl, wt = Weight of sample in grams C = Conversion factor (49.0).

**Table 2 Amount of HCl and NaOH used in the ANC Test**

Reaction	Fizz Rating	HCl		NaOH
		Molarity (M)	Volume (mL)	Molarity (M)
No	0	0.5	4	0.1
Slight	1	0.5	8	0.1
Moderate	2	0.5	20	0.5
Strong	3	0.5	40	0.5
Very Strong	4	0.1	40	0.5
	5	0.1	60	0.5

Source: (Anon, 2002)

### 2.4.4 Determination of Net Acid Generation (NAG)

This static method uses hydrogen peroxide to oxidise any sulphides present in the sample. 250 mL of 15% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was added to 2.5 g of the sample. The mixture was left undisturbed for 24 hrs after which it was heated for 2 hr.

Deionized water was added to achieve a total volume of 250 mL after which pH ( $NAG_{pH}$ ) and conductivity values were recorded (Anon, 2002). The NAG (in kg  $H_2SO_4/t$ ) value was calculated using Eq. 2:

$$NAG = (49 \times V \times M) / W \quad (2)$$

where; V = Volume of NaOH used in titration, M = Concentration of NaOH used, W = Weight of sample.

#### 2.4.5 Determination of Net Acid Production Potential (NAPP)

NAPP is a theoretical calculation commonly used to indicate if a material has a potential to generate AMD. It represents the balance between the capacity of a sample to generate acid (MPA) and its capacity to neutralize acid (ANC). The NAPP was determined by subtracting the ANC from the MPA. Fig. 3 shows the procedure for the NAPP determination of the samples.

### 3 Results and Discussion

#### 3.1 Mineralogy

Result of mineralogical analysis is shown in Fig. 4. Some of the mineral assemblages identified were pyrite, arsenopyrite, chalcopyrite and magnetite. The presence of magnetite in the sample could be as result of pyrite alteration, implying that sulphide oxidation leading to acid generation has already begun. A, B, C, D depicts arsenopyrite, magnetite, pyrite, and chalcopyrite respectively. This implies that the ore-bearing materials contain sulphide and hence have the potential of generating acid.

Results of the quantitative XRD mineral analysis of the sample are shown in Table 3. The mineralogy of the sample is complex with several mineral phases. Apart from the sulphide minerals phases, there are also important acid neutralisation minerals such as dolomite, quartz and muscovites (Table 3). According to Sverdrup (1990), at pH range 5 to 7, these minerals have relative reactivity in acid neutralisation capacity in the order; dolomite (1.0) > muscovite (0.01) >> quartz (0.004) and tend to buffer the system in a circum-neutral pH value.

#### Sample Preparation

#### Basic Screening Tools

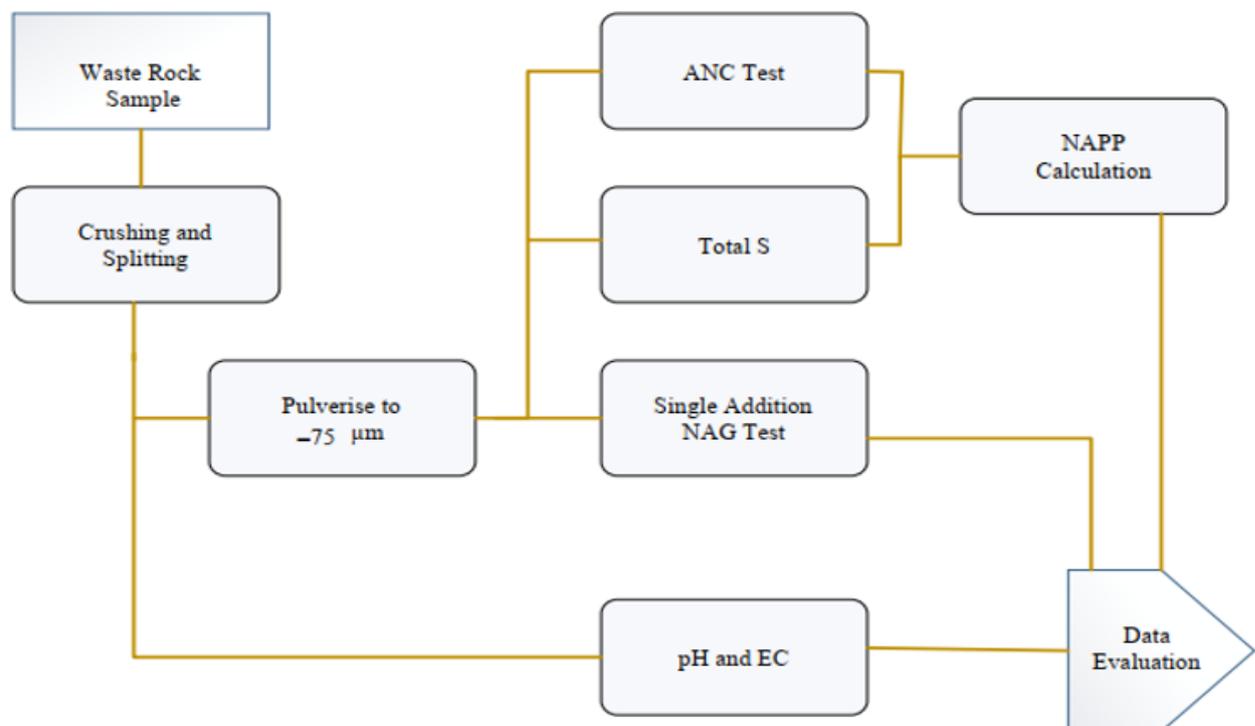
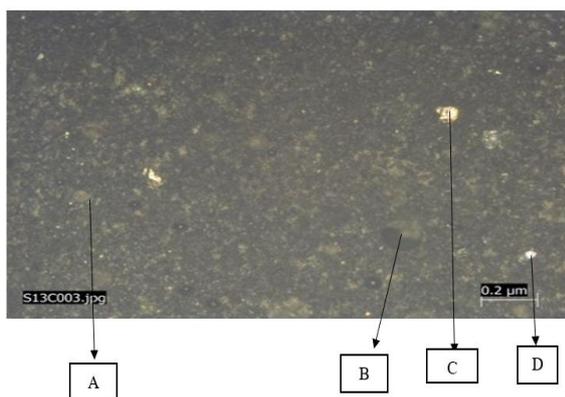


Fig. 3 Representation of Sample Preparation and Screening Tools for ABA  
Source: (Anon, 2002)



**Fig. 4 Photomicrographs (polish sections) Showing Mineralogical Analysis**

**Table 3 The Distribution of Major Mineral in the Waste Rock Sample as Defined by QXRD**

Minerals	Mass fraction (% w/w)
Pyrite	5.20
Arsenopyrite	4.70
Chalcopyrite	1.00
Dolomite	13.01
Quartz	56.37
Muscovite	18.90
Magnetite	0.82
Total	100

### 3.2 Paste pH and Conductivity

#### 3.2.1 Paste pH

Table 4 shows the paste pH result of the samples. Out of the 50 samples, 20% (i.e., samples 1, 3, 4, 17, 22, 28, 31, 32, 35 and 39) had paste pH below 6.5, implying that, these samples have the potential of generating AMD. Table 4 shows that 80% of the samples had a paste pH above 6.5. Paste pH is a preliminary test conducted to determine the “natural” pH or the current acidity of the rock mineral sample (Weber *et al.*, 2006). The test is non-vigorous as such only soluble salts and reactive minerals are assessed. Paste pH provides no indication of the sample’s total capacity to generate acidity or alkalinity, but rather provides an indication of the immediate pH characteristics of the sample should it be mixed with water (Sobek *et al.*, 1978; Ferguson and Morin, 1991). Paste pH may give an indication of the extent of sulphide oxidation in the sample, which is also a sign of potential weathering of the sample (Weber *et al.*, 2006). According to Weber *et al.* (2004), samples with paste pH < 6.5 have already undergone weathering and therefore would contain acidic sulphate salts.

Such samples will readily release acidity when in contact with water.

#### 3.2.2 Conductivity

Fig. 5 shows the conductivity values recorded during the test. 22% of the samples (i.e., samples 3, 4, 21, 22, 24, 31, 32, 35, 36 and 39) had electrical conductivity (6160, 6700, 2810, 4530, 1002, 2110, 1652, 1505, 2440 and 3610  $\mu\text{S}/\text{cm}$  respectively). Conductivity values can be used as a predictive measure to forecast the potential of samples to produce acid and consequently release ions even before analysis to determine the acid generation and neutralising potential of samples are conducted. AMD is associated with electrical conductivity levels between 1000 to 20000  $\mu\text{S}/\text{cm}$ , as such, samples with electrical conductivity within this range have the potential of releasing high levels of metal concentrations should AMD occur (Sephton and Webb, 2017). Again, the conductivity values of the above-mentioned samples fall within the range of AMD electrical conductivity.

Results from the pH and electrical conductivity values can be used to predict samples with the potential of generating AMD, even before Acid Base Accounting techniques are employed. It was noticed that samples 3, 4, 22, 31, 32, 35 and 39 had a paste pH (6.02, 6.22, 6.25, 3.19, 6.15, 6.21 and 6.43 respectively) less than 6.5 and conductivity between 1000 to 20000  $\mu\text{S}/\text{cm}$ , as such these samples (i.e., samples 3, 4, 22, 31, 32, 35, and 39) have a potential of releasing acidic effluent when exposed to oxidizing conditions.

### 3.3 Acid Base Accounting (ABA)

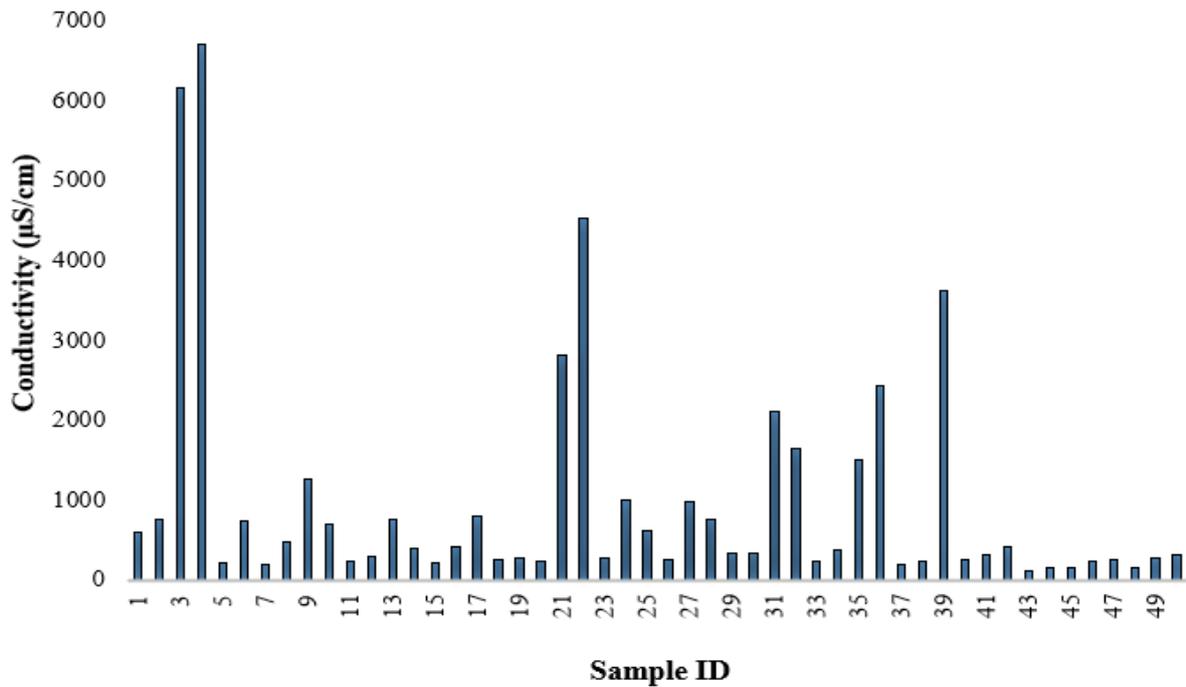
#### 3.3.1 Net acid producing potential (NAPP)

NAPP values can be used as a preliminary indication to determine if a sample will generate acid or not (Anon, 2002). It is also a qualitative measure of the difference between the capacity of a sample to generate acid (MPA) and its capacity to neutralise acid (ANC). A negative NAPP value implies that there are enough neutralizing minerals in the sample to prevent the generation of acid, (i.e.  $\text{MPA} < \text{ANC}$ ) and vice versa.

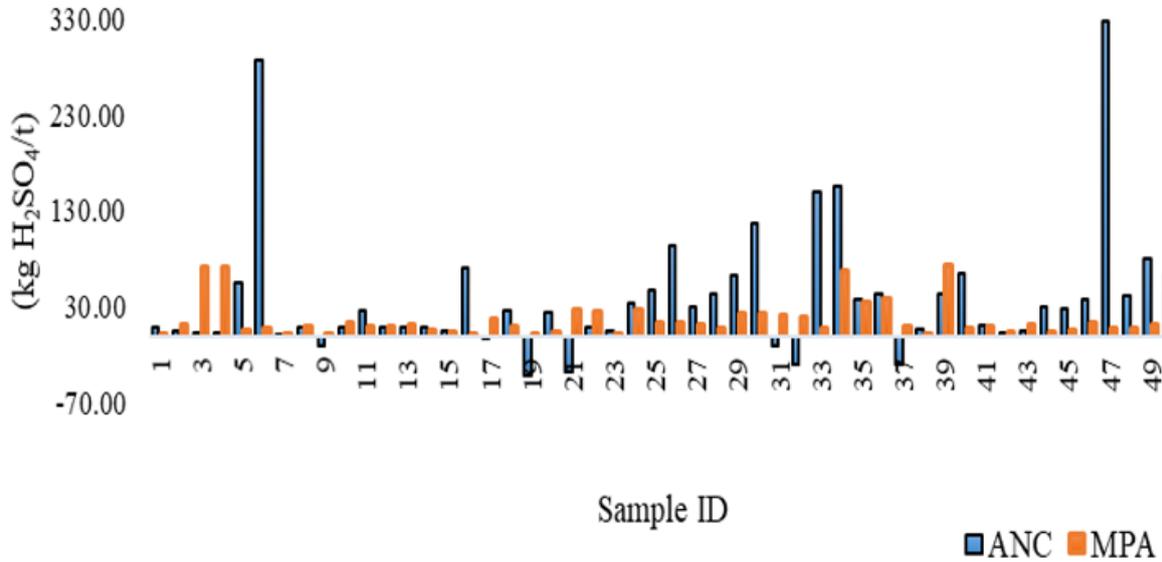
Fig. 6 shows the ANC and MPA values obtained. Sample 47 recorded the highest ANC value of 327.97  $\text{kg H}_2\text{SO}_4/\text{t}$  with corresponding MPA value of 8.32  $\text{kg H}_2\text{SO}_4/\text{t}$ . Sample 39 recorded the highest MPA value of 74.358  $\text{kg H}_2\text{SO}_4/\text{t}$  with corresponding ANC value of 43.40  $\text{kg H}_2\text{SO}_4/\text{t}$ .

**Table 4 Paste pH of Samples**

Sample ID	pH	Sample ID	pH
1	5.68	26	7.94
2	6.92	27	6.73
3	6.02	28	6.32
4	6.22	29	8.20
5	8.04	30	8.25
6	7.01	31	3.19
7	7.15	32	6.15
8	6.97	33	8.58
9	7.12	34	8.35
10	7.62	35	6.21
11	7.72	36	6.93
12	7.67	37	8.13
13	6.70	38	7.00
14	7.30	39	6.43
15	7.81	40	8.33
16	7.79	41	7.82
17	5.77	42	9.91
18	8.24	43	7.75
19	8.14	44	7.47
20	8.40	45	8.13
21	7.00	46	7.85
22	6.25	47	9.03
23	7.45	48	7.92
24	7.42	49	9.05
25	7.73	50	8.69



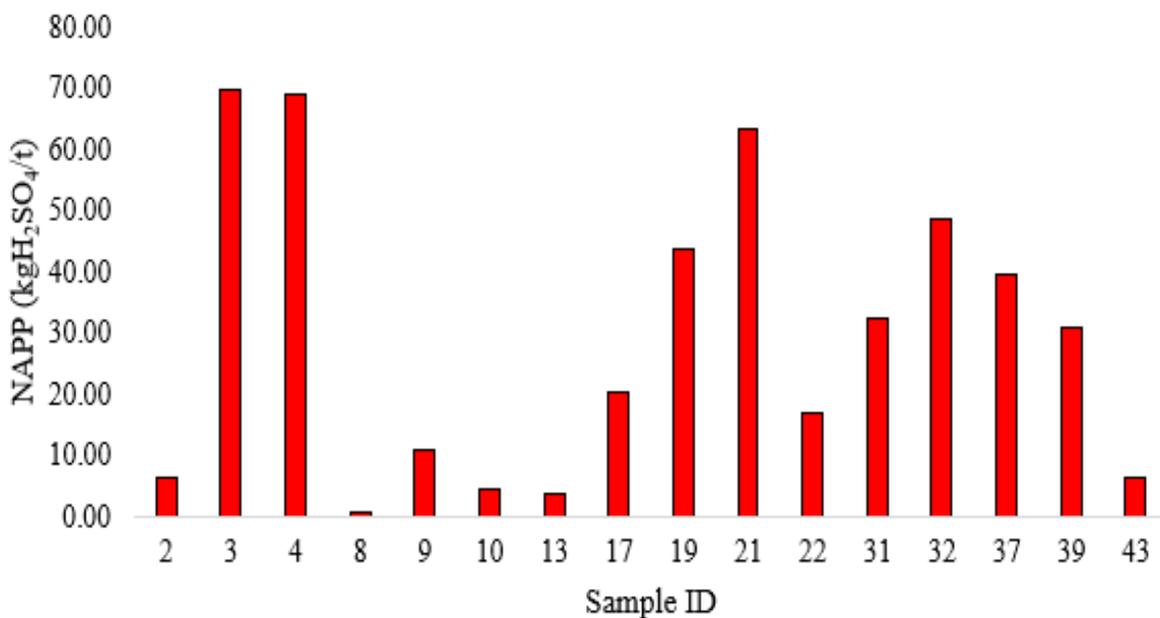
**Fig. 5 Conductivity of Samples**



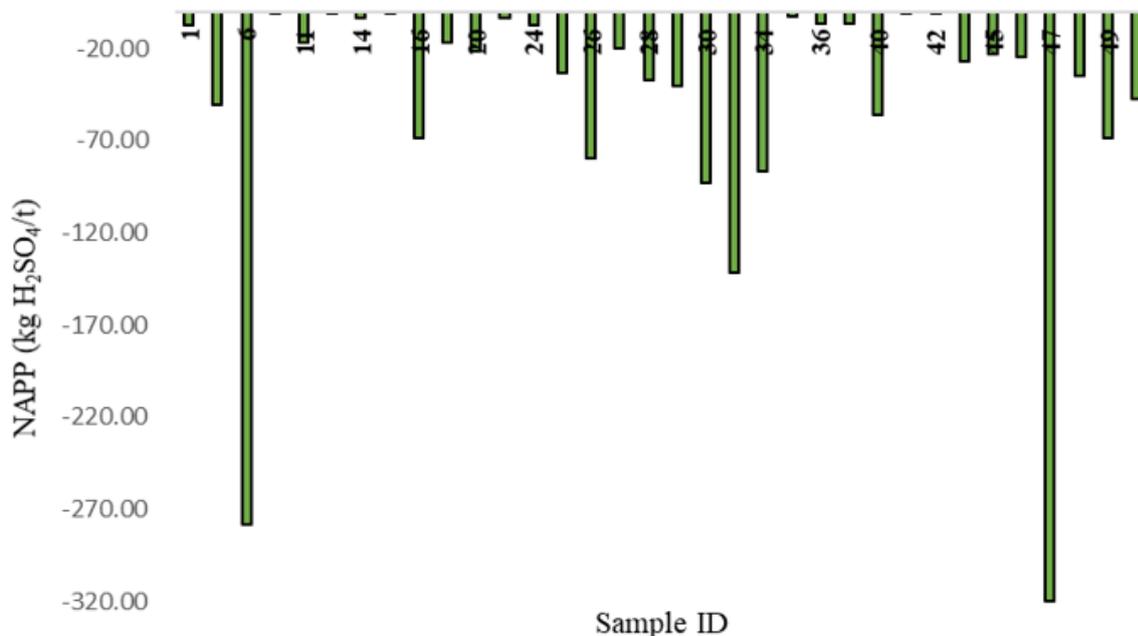
**Fig. 6 ANC and MPA Values of the Samples**

From Fig. 6 it can be seen that, samples with high ANC values have low MPA values and vice versa. This affirms the work done by numerous researchers (Schumann *et al.*, 2012; Olds *et al.*, 2016; Assawincharoenkij *et al.*, 2017), indicating that once neutralising minerals are dominant in a sample, little or no acid is produced, since these minerals such as dolomite are able to buffer the acid produced. Similarly, once the MPA values are higher than that of ANC, it implies that the dominant minerals are acid generating hence, acid may be produced upon exposure to favourable

oxidising conditions. Figs. 7 and 8 which are graphical representations of the balance between MPA and ANC (MPA – ANC) show in details, samples with the potential of generating acid or not. Fig. 7 shows that 32% of the samples (i.e., samples 2, 3, 4, 8, 9, 10, 13, 17, 19, 21, 22, 31, 32, 37, 39 and 43) have the potential to generate acid with corresponding NAPP values (6.41, 69.79, 69.18, 0.81, 11.05, 4.36, 3.59, 20.25, 43.66, 63.49, 16.98, 32.35, 48.51, 39.69, 30.96 and 6.54 kgH<sub>2</sub>SO<sub>4</sub>/t respectively). This implies that, these samples had a higher MPA than ANC.



**Fig. 7 Samples with the Potential of Generating Acid**



**Fig. 8 Samples Unlikely to Generating Acid**

Results from Fig. 6 confirmed to an extent that paste pH and electrical conductivity can be used as a preliminary AMD predictive tool. This is because from Fig. 6, samples 3, 4, 17, 22, 31 and 39 have been indicated to have the potential to generate AMD. These samples recorded paste pH values below 6.5 (6.02, 6.22, 5.77, 6.25, 3.19 and 6.43 respectively) and electrical conductivity values between 1000 and 20000  $\mu\text{S}/\text{cm}$  (6160, 6700, 1000, 4530, 2110 and 3610  $\mu\text{S}/\text{cm}$  respectively). Fig. 8 shows that 68% of the samples may not produce acid. That is to say that, samples 1, 5, 6, 7, 11, 12, 14, 15, 16, 18, 20, 23 and 24 just to mention a few, had a greater ANC than MPA, hence a negative NAPP value of -7.57, 50.25, -277.96, -0.54, -16.44, -0.08, -3.36, -1.12, -68.85, 17.06, -21.10, 3.31 and -7.60  $\text{kgH}_2\text{SO}_4/\text{t}$  respectively.

### 3.3.2 Sample Categorisation

The Net Acid Generation (NAG) together with the NAPP was used to classify samples into PAF, NAF and Uncertain, following the logical flowchart of Fig. 9 (Anon, 2002). A sample is termed a potential acid forming (PAF) when its NAPP is positive, NAGpH is less than 4.5 and NAG value at a NAGpH of 4.5 is greater than 5. A sample is termed a potential acid forming with low capacity (PLC) when its NAPP is positive, its NAGpH is less than 4.5 and its NAG value at a NAGpH of 4.5 is less than 5. A sample is termed a non-acid forming (NAF) when its NAPP is negative, and NAGpH  $\geq$  4.5. On the other hand, an uncertain classification is used when there is an apparent conflict between the NAPP and NAG values. (i.e. samples with a positive NAPP and a NAGpH  $\geq$  4.5 or a negative NAPP with

a NAGpH  $<$  4.5). Fig. 10 is a graph of NAGpH against NAPP, it depicts the results deduced from categorizing the samples.

The comparison between NAPP and NAGpH indicated that, samples 3, 4, 9, 13, 17, 19, 21, 22, 32, 37, and 39 had a positive NAPP, a NAGpH less than 4.5 and a NAG value at NAGpH 4.5 greater than 5, hence Potential Acid Forming (PAF). Samples 2, 8, 10, 31 and 43 had a positive NAPP, a NAGpH less than 4.5 but a NAG value at NAGpH 4.5 less than 5, hence the samples had a low capacity of producing acid (PLC). Samples 16, 18, 33, 40, 47, 49 and 50 had a negative NAPP and a NAGpH greater than 4.5 hence, Non-acid Forming (NAF). Samples 1, 5, 6, 7, 11, 12, 14, 15, 20, 23, 24, 25, 26, 27, 28, 29, 30, and 35 had a negative NAPP and a NAGpH less than 4.5, hence fall under uncertain classification.

Fig. 10 is a geochemical classification plot showing NAGpH versus the NAPP value for the 50 waste rock samples. Potential Acid Forming (PAF), Non-Acid Forming (NAF) and Uncertain Classification (UC) domains are indicated. Even though many samples fall within the PAF, that is 22% of the samples have the potential of producing acid (PAF), 10% had a low-capacity potential of producing acid (PLC), 16% were non-acid forming (NAF), but there a number of samples that fall within in the uncertain domain, that is 52% were uncertain. Hence the NAG test has shown to be a more reliable measure of the acid generating capacity than the NAPP.

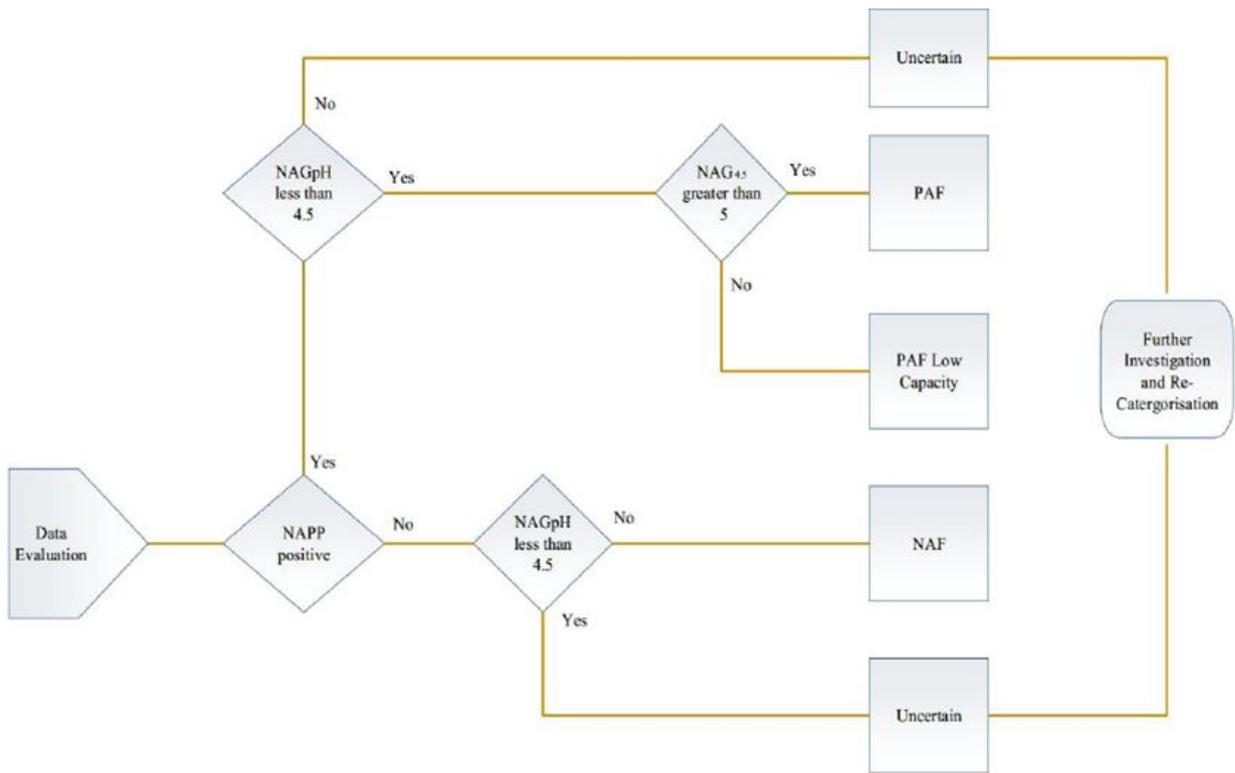


Fig. 9 Flowchart Conditions for Sample Categorisation  
Source: (Anon, 2002)

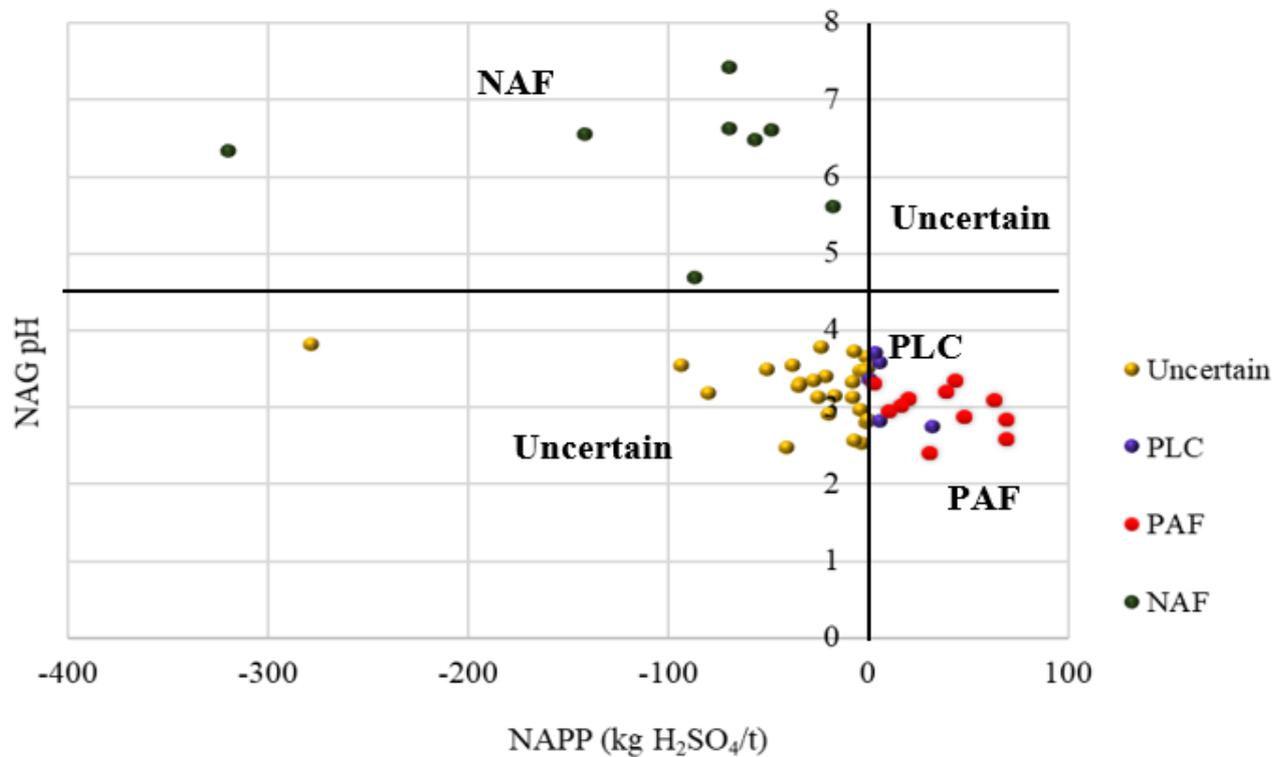


Fig. 10 Geochemical Plot for the Waste Rock Samples showing NAGpH versus NAPP, with AMD Classification Domains Indicated

## 4 Conclusions and Recommendation

### 4.1 Conclusions

The study investigated the acid and metalliferous drainage potential of waste rocks of a Mine in Ghana using Acid Base Accounting (ABA) as a predictive tool. From the mineralogical analysis of the waste rocks the presence of magnetite could be as result of alteration of pyrite, signifying sulphide oxidation and commencement of acid generation.

The most common sulphide minerals with potential to generate acid identified in the waste rocks were pyrite, arsenopyrite and chalcopyrite. The mineral group identified with the potential to neutralise acid was carbonate (dolomite).

Paste pH showed that about 20% of the samples had pH below 6.5 and had already began generating acid. 22% of the samples (i.e. samples 3, 4, 21, 22, 24, 31, 32, 35, 36 and 39) had electrical conductivity associated with AMD in the range of 1000 to 20000 µS/cm. Paste pH and electrical conductivity can be used as a preliminary AMD predictive tool

Results from Acid Base Accounting showed that 22% of the samples had the potential of generating acid, 16% were non- acid forming and 52% were uncertain. Although more than half of the total samples had uncertain classification, the potential of Acid Mine Drainage exists for the waste rock on the mine.

### 4.2 Recommendation

It is recommended that kinetic test should be done on samples with uncertain classification to accurately predict their potential of AMD.

### Acknowledgements

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