Contents lists available at ScienceDirect

Heliyon

The comparison of 7.5 and 15% hydrogen peroxide as oxidizing agent in static tests of acid mine drainage potential in Indonesia

Muhammad Sonny Abfertiawan [a],[*], Yoseph Palinggi [b], Mindriany Syafila [a], Marisa Handajani [a], Kris Pranoto [b]

[a] Water and Wastewater Engineering Research Group, Faculty of Civil and Environmental Engineering, Bandung Institute of Technology, Indonesia
[b] Environmental Department, Kaltim Prima Coal, Indonesia

ARTICLE INFO

ABSTRACT

Static tests of acid mine drainage potential are an important part of mining water management. Net acid generation (NAG) test is widely used in Indonesian coal mines because of its convenience. This test uses H_2O_2 to oxidize sulfide minerals within rock samples to determine their net acid-forming capacity. This study aimed to determine the difference between H_2O_2 at concentrations of 7.5% (the standard in several Indonesian coal mines) and 15% (the standard of the Acid Rock Drainage Test Handbook and Indonesian National Standard) in categorizing rocks as potentially acid-forming and non-acid-forming and in terms of NAG solution characteristics. A total of 564 rock samples collected from two Indonesian coal mining sites were analyzed using pH, NAG, total sulfur, and acid-base-accounting tests. The results of the study showed that there was no significant difference in rock classification or the behavior of contaminants in the NAG solution between 7.5% and 15% H_2O_2. The characteristics of sulfide minerals in Indonesian coal mines were the main factors influencing the results of the NAG test and behavior of contaminants in the NAG solution. Therefore, H_2O_2 at a concentration of 7.5% can be used in Indonesian coal mines with relatively low total sulfur concentrations ($<5\%$) and minerals in framboidal form.

1. Introduction

Acid mine drainage (AMD) is one of the major environmental issues in the coal and mineral mining industries [1–3]. It also leads to social tensions and is often the primary reason for communities rejecting mining projects [4,5]. AMD is formed when sulfide minerals contained in overburden or waste rock are exposed and oxidized by oxygen in the air during excavation and stockpiling activities. However, AMD will only form if insufficient amounts of acid neutralizing alkalinity are produced [6–8]. The oxidation of sulfide minerals, generally dominated by pyrite minerals, produces products such as SO_4, Fe^{2+}, Fe^{3+}, Al, Mn, and other metals that can be carried to surface water and groundwater [9]. The pH of AMD can reach as low as -3.6 [10] and associated high metal concentrations have a negative impact on aquatic life [11,12]. Therefore, AMD prevention is key to successful environmental management in coal and mineral open-pit mines.

AMD prevention can be achieved using wet and dry cover approaches, each of which has advantages and disadvantages [13,14]. Several studies have been conducted on AMD prevention using the wet cover method [15,16] and dry cover method using existing

---

* Corresponding author.
  E-mail address: msa@itb.ac.id (M.S. Abfertiawan).

non-acid-forming (NAF) material [1,17] as well as other alkaline materials such as lime, ash from coal power plants [18–20] and alkaline/cementitious amendments [21,22]. During mine planning, particularly excavation and overburden stockpiling, priority should be given to the implementation of appropriate preventive techniques. Prevention efforts can only be carried out after identifying the potential for AMD generation, which must be carried out in the exploration stage so that rock geochemical models can be developed as the basis for mining planning.

The prediction of potential AMD generation through various laboratory tests and at different scales in the field has developed over the last 50 years. AMD prediction can be grouped into two methods: static and kinetic tests [23–28]. The static test determines the potential for AMD generation from sulfide minerals and the potential for neutralization due to the presence of minerals such as carbonates in the sample. This test can be performed in a laboratory in a relatively short time, usually hours or days. In contrast, kinetic tests are carried out over a long period (several months to years) and use leaching to determine the rate of generation, behavior, weathering of rocks, and metal mobility in relation to AMD. Therefore, kinetic tests are usually only used to validate static tests, not to identify rocks at the operational scale of the mining industry.

Several static test methods have been reported to predict AMD, two of which are commonly used: acid-base accounting (ABA) and net acid generation (NAG) tests. The ABA method was first developed by Smith et al. at West Virginia University in 1965 [29,30]. This method was further refined in the late 1960s and 1970s [31]. After inclusion in a manual by the US EPA in 1978, ABA testing procedures were widely adopted to identify potential AMD generation [32]. Since then, the ABA method has been further modified and implemented by several researchers [26,33–35]. In general, the ABA method comprises total sulfur (TS) and neutralization potential. TS is measured using high-temperature combustion to determine the maximum potential acidity (MPA) produced from the sample. MPA is calculated using a stoichiometric approach, where 1% pyrite mineral is equivalent to 30.6 kg H_2SO_4/ton. The TS method does not distinguish between different forms of S and assumes that all S contained in the sample is in the form of pyrite sulfide [1]. Acid neutralizing capacity (ANC) is determined using the Sobek method [36] by adding a standard amount of HCl to the sample and heating it to catalyze the reaction. Next, the solution is titrated with NaOH to determine the amount of unreacted HCl. Net acid-producing potential (NAPP) is the difference between the MPA and ANC.

The NAG test, first introduced and developed by Ref. [37], uses H_2O_2 to measure potential AMD generation from sulfide minerals contained in the overburden of coal and mineral mines. This method directly measures NAG in the sample after the addition of the strong oxidizing agent, H_2O_2. Other researchers have also investigated the use of H_2O_2 to measure the sulfide content and acid potential of mining activities [33,36,38–40]. In the early 1990s, Environmental Geochemistry International (EGI) Pty Ltd., funded by the Australian Mining Industry Research Association (AMIRA), conducted case studies in 17 mining sites in Australia, New Guinea, and Indonesia to develop a simple and low-cost procedure for testing AMD generation potential [41]. EGI and the Ian Wark Research Institute were subsequently involved in Project P387A on Prediction and Kinetic Control of Acid Mine Drainage, funded by AMIRA in 2002, to produce the Acid Rock Drainage (ARD) Test Handbook, which has been used in many countries, including the Indonesian National Standard (SNI) 6597:2011. The ARD Test Handbook combines ABA and NAG analyses to determine the characteristics of potentially acid-forming (PAF) and NAF rocks. During this period, EGI co-developed a standard operating procedure for measuring AMD generation in Kaltim Prima Coal (KPC), Indonesia's largest coal mine, which is still used today. KPC is one of the few Indonesian companies that controls potential AMD generation by comparing NAF materials with PAF materials.

The NAG tests developed by EGI in the ARD Test Handbook and KPC in the 1990s differ. The ARD Test Handbook adopts the method of Finkelman and Giffin in 1986 [37], using 250 mL of 15% H_2O_2 to oxidize sulfide minerals in a 2.5 g pulverized sample. The H_2O_2 solution then reacts with the sample overnight, after which it is slowly heated to near-boiling temperature for at least 2 h using a hotplate. Deionized water is added to maintain the solution volume, if necessary. This heating removes excess H_2O_2 and releases the neutralizing agent (carbonate buffer). Next, the solution is allowed to cool to room temperature (at approximately 25 °C), and its pH is measured. NAG capacity is also calculated from the consumption of NaOH during titration to pH 4.5 and 7.0 and expressed as equivalent kg H_2SO_4/ton [26]. The KPC NAG test uses 250 mL of 7.5% H_2O_2 and a 2.5 g pulverized sample. Rock classification also differ from those developed in the late 1980s and early 1990s. For operational management purposes, the KPC rock types identified via the NAG test are categorized into four types: Type 1 (NAF), Type 2 (low PAF capacity <2 kg H_2SO_4/t; Type 3 (moderate PAF capacity = 2–10 kg H_2SO_4/t; and Type 4 (high PAF capacity >10 kg H_2SO_4/t).

Dubey and Das in 1981 [42], as reported by Finkelman and Giffin in 1986 [37], stated that 15% H_2O_2 is the most effective solution for oxidizing pyrite minerals. However, since adopting the NAG procedure in the 1990s, KPC has reported more efficient potential AMD identification using 7.5% H_2O_2. This procedure has also been adopted by several other Indonesian coal mining companies. The total cost for NAG Test using the 7.5% of H_2O_2 were reported as approximately US$20 per sample. The use of these two concentrations has implications on the cost of AMD management in Indonesian coal mining companies. The realistic and cost-effective of static test for AMD management is important to be determined so that all companies can carry out plans to prevent the AMD generation effectively and efficiently. Therefore, this study aims to compare the effects of 7.5% and 15% H_2O_2 on the NAG test. Based on the results of this study, we aim to recommend a reliable, low-cost static test method for predicting potential AMD to the mining industry, particularly coal mines and government.

2. Materials and methods

2.1. Materials

Rock core samples were taken from the Sangatta and Bengalon mining sites of KPC, located in the East Kutai Regency, East Kalimantan, Indonesia. A total of 564 NAF and PAF samples from exploration activities were obtained from different lithologies. These

samples were categorized based on AMD potential using the procedure of KPC, as shown in Table 1. Core samples (core dia. 6 cm), with density 2210 - 2360 kg/m^3, were crushed using a jaw crusher with an opening of approximately 2 cm, and samples were collected using a splitter. Next, the samples were finely pulverized to a particle size of 200 mesh (<75 μm), and 2.5 g of each sample was collected according to the standard static test method.

2.2. Methods

2.2.1. Static tests procedures

Static tests were performed to determine the AMD generation capacity of the rock samples. These included the paste pH, TS, ABA, and NAG tests. NAG tests were performed using an H_2O_2 concentration of 7.5% according to the standard operating procedure of KPC and 15% in accordance with the ARD Test Handbook [26] and SNI 6597:2011. Tests were also performed on the NAG solution after the addition of H_2O_2 by analyzing the concentrations of metals (Fe, Mn, and Al) and SO_4^{2-} and changes in temperature. Sample classification was based on NAG capacity (kg H_2SO_4/t): NAF, low PAF, moderate PAF, and high PAF capacity. These four NAG categories employed by KPC are not significantly different from those used by Miller in 1996 [43] and Smart et al., in 2002 [27]: NAF, low PAF, high PAF, and uncertain capacity. NAG tests were also performed at pH 4.5 and 7.0 to understand the acid-forming behavior of the samples. This also informed rock classification, such that pH < 4.5 and pH > 4.5 were categorized as PAF and NAF, respectively. The TS analysis was conducted using high-temperature combustion, without differentiating between different forms of S that might be contained in the samples, such as sulfides (pyrite or other sulfide minerals), sulfates, and S. ABA analysis was conducted for selected samples to determine the consistency of AMD generation. These tests on NAG solutions were also aimed at determining the differences in the formation and mobility of contaminants potentially contained in AMD when mixed with 7.5% and 15% H_2O_2 [44]. Water quality analysis was performed with reference to the Standard Methods of Analysis of Water and Waste from the American Public Health Association (APHA). The NAG solution was analyzed according to its pH, temperature, total dissolved solid, oxidation reduction potential, conductivity and concentrations of total Fe and total Mn.

2.3. Chemical and mineralogical characterization

Mineralogical analyses were performed to determine the type and form of sulfide minerals in the rock samples, which represent the characteristics of PAF and NAF, using XRD (Siemens rotating-anode instrument) and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM/EDS). XRD patterns of pulverized samples were analyzed at Hydrogeology and Hydrogeochemistry Laboratory, Bandung Institute of Technology, using Rigaku Smart Lab from 5 to 90° for 2-θ value using Cu K-α radiation (1.54059 Å), step size 0.01°, 40 kV voltage, 30 mA. The diffractograms were analyzed using the International Centre for Diffraction Database (ICDD) PDF-4 and PDXL software. The SEMD/EDS JEOL-JSM-6510LV was operated with an accelerating voltage of 20 kV and a probe current of 7.45 nA. A counting time of 40 s was used for quantitative analysis, work distance of 15 mm, and detection limit 1%.

3. Results and discussion

3.1. pH, NAG, TS, and ABA test results

Table 2 lists the results of the paste pH, TS, ABA, and NAG tests. The results of the NAG test comprised 154 samples classified as Type 1 (NAF), 109 classified as Type 2 (low PAF capacity), 150 classified as Type 3 (moderate PAF capacity), and 151 classified as Type 4 (high PAF capacity). Type 1 ranged from 0 to 1.96 kg and 0–3.92 kg H_2SO_4/t, with an average of 0.01 and 0.27 kg H_2SO_4/t, respectively. In contrast, the $NAG_{4.5}$ and $NAG_{7.0}$ capacities of Type 4 ranged from 9.80 to 152.88 and 2.15–158.76 kg H_2SO_4/t, with an average of 51.26 and 17.28 kg H_2SO_4/t, respectively. $NAG_{4.5}$ test results revealed a capacity for H_2SO_4 generation from sulfide oxidation products and the hydrolysis of dissolved Al and Fe [26,41,45], whereas those of $NAG_{7.0}$ indicated that the net remaining acid could be due to the presence of dissolved metals such as Cu and Zn and other metal ions potentially present as hydroxides [26,45].

Table 2 and Fig. 1a-c show a 1:1 correlation between the results of the NAG test using H_2O_2 concentrations of 7.5% and 15%. The average NAG pH values obtained using 7.5% and 15% H_2O_2 were 7.45 and 7.59 (Type 1), 3.76 and 3.75 (Type 2), 3.11 and 3.06 (Type

Table 1
Number of samples used in each method of acid mine drainage potential.

Samples		Rock Type		Total Samples	Number of Samples (each analysis)					
Group	ID Range				A		B	C	D	E
					A1	A2				
A	A1 to A154	NAF	Type 1	154	154	154	5	5	1	5
B	B1 to B109	PAF (Low)	Type 2	109	109	109	5	5	–	5
C	C1 to C150	PAF (Moderate)	Type 3	150	150	150	5	5	–	5
D	D1 to D151	PAF (High)	Type 4	151	151	151	5	5	1	5
Total Samples				564	564	564	20	20	2	20

A, net acid generation (NAG) test; A1, NAG test using 7.5% H_2O_2; A2, NAG test using 15% H_2O_2; B, total sulfur; C, acid neutralizing capacity; D, mineralogy; E, characteristics of NAG solution.

Table 2
Descriptive statistics of rock samples representing acid mine drainage generation.

Acid-Base Accounting Test								
	Type 1		Type 2		Type 3		Type 4	
	R	A	R	A	R	A	R	A
ANC	255.62 to 264.82	259.44	242.83 to 260.57	252.99	38.68 to 52.57	47.11	33.72 to 41.66	38.08
TS	0.38 to 1.18	0.716	0.05 to 0.06	0.054	0.22 to 1.67	0.98	1.23 to 2.44	1.7
MPA	11.63 to 36.13	21.92	1.53 to 1.83	1.65	6.73 to 51.13	30	37.66 to 74.71	52.17
NAPP	−248.23 to −228.7	−237.53	−259.04 to 245.33	−252.82	−31.94 to −1.43	−17.1	−1.01 to 38.01	14.088
ANC/MPA	7.32 to 22.33	13.57	143.53 to 170.20	155.21	1.02 to 5.74	2.48	0.49 to 1.02	0.79

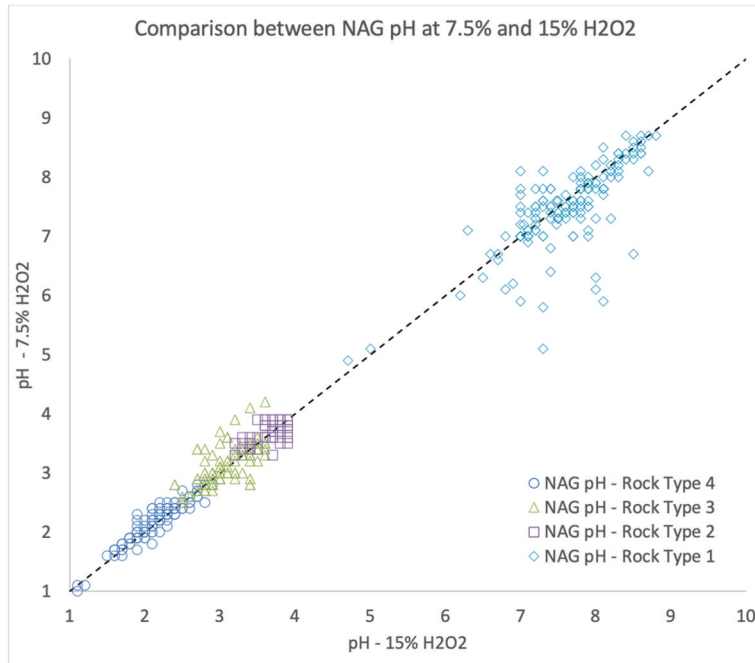| Net Acid Generation (NAG) Test															
	Type 1				Type 2				Type 3				Type 4			
	7.5% H_2O_2		15% H_2O_2		7.5% H_2O_2		15% H_2O_2		7.5% H_2O_2		15% H_2O_2		7.5% H_2O_2		15% H_2O_2	
	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A
NAG pH	4.9 to 8.7	7.45	4.7 to 8.8	7.59	3.30 to 3.90	3.76	3.2 to 3.9	3.75	2.5 to 4.2	3.11	2.4 to 3.6	3.06	1.00 to 3.30	2.17	1.10 to 2.90	2.13
$NAG_{4.5}$	0 to 1.96	0.01	0 to 1.96	0.01	1.95 to 1.96	1.96	1.96	1.96	0 to 11.76	6.2	1.96 to 13.72	6.27	3.92 to 145.04	50.69	9.80 to 152.88	51.26
$NAG_{7.0}$	0 to 3.92	0.27	0 to 9.8	0.26	3.92 to 21.56	10.37	3.92 to 25.48	10.95	0 to 27.44	16.08	5.88 to 25.48	15.85	17.64 to 166.6	70.39	2.15 to 158.76	17.28
$NAG_{4.5}$/ NAPP	0	0	0	0	−0.1	−0.1	−0.1	−0.1	−0.12 to −2.73	−0.82	−0.18 to −4.09	−1.21	−1283 to 10	10.15	−1166 to 11.60	−235.97

*ANC, acid neutralizing capacity; TS, total sulfur; MPA, maximum potential acidity; NAPP, net acid-producing potential; $NAG_{4.5}$ and $NAG_{7.0}$, NAG at pH 4.5 and 7.0, respectively; all values measured in kg H_2SO_4/t.

** Type 1, non-acid-forming (NAF); Type 2, potential acid-forming (PAF)—low capacity (NAG <2 kg H_2SO_4/t); Type 3, PAF—moderate capacity (NAG = 2–10 kg H_2SO_4/t); Type 4, PAF—high capacity (NAG >10 kg H_2SO_4/t).

***R, Range of values; A, Average value.

3), and 2.17 and 2.13 (Type 4), respectively. The average $NAG_{4.5}$ capacities observed when using 7.5% and 15% H_2O_2 were 0.01 and 0.01 kg H_2SO_4/t (Type 1), 1.96 and 1.96 kg H_2SO_4/t (Type 2), 6.20 and 6.27 kg H_2SO_4/t (Type 3), and 50.69 and 51.26 kg H_2SO_4/t (Type 4), respectively. Similarly, the average $NAG_{7.0}$ capacities observed when using 7.5% and 15% H_2O_2 were 0.27 and 0.26 kg H_2SO_4/t (Type 1), 10.37 and 10.95 kg H_2SO_4/t (Type 2), and 16.08 and 15.58 kg H_2SO_4/t (Type 3). Average $NAG_{7.0}$ capacities only differed between 7.5% and 15% H_2O_2 in Type 4 samples, at 70.39 and 17.28 kg H_2SO_4/t, respectively. These results demonstrate that sulfide minerals exhibit the same characteristics and behavior when reacting with different concentrations of H_2O_2.

The NAG test remains a reliable method of identifying potential AMD in mining operations at different scales. This is because the NAG test is easy to perform and does not require a TS test using modern equipment [46]. However, this test has the disadvantage of not measuring potential neutralizing capacity because of the presence of carbonate minerals. Several studies have reported that the

(a)
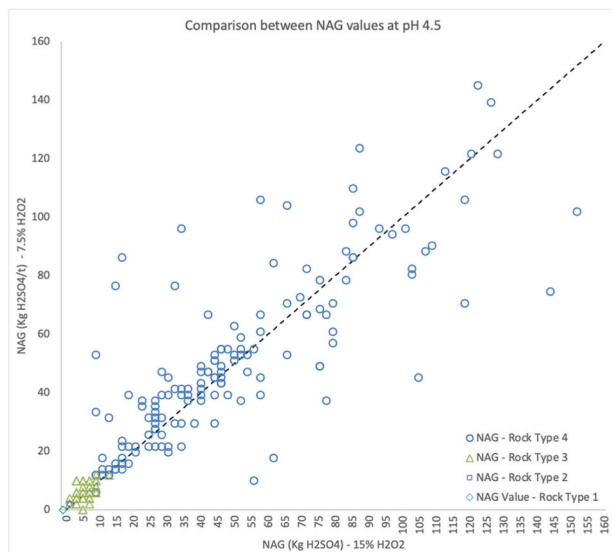
(b)
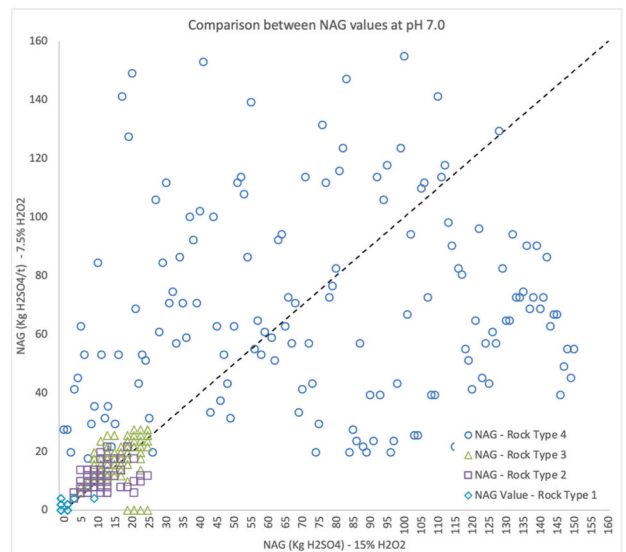
(c)

Fig. 1. Scatter plot of the relationship between net acid generation (NAG) test results obtained using H_2O_2 concentrations of 7.5% and 15%: (a) NAG pH; (b) $NAG_{4.5}$; and (c) $NAG_{7.0}$.

presence of high amounts of carbonate minerals such as siderite can lead to invalid potential acid capacities [45,47–49].

The TS concentrations of NAF and high-capacity PAF rocks range from 0.38% to 1.18% and 1.23%–2.44%, respectively. Several researchers have recorded relatively low TS concentrations ranging from 0.1% to 5.0% in the overburden of Indonesian coal mines [1, 50–52], with a predominantly framboidal form. Framboidal pyrite minerals are more reactive than euhedral forms [53]. This potentially explains the insignificant difference between the results of NAG tests using 7.5% and 15% H_2O_2.

Fig. 2 shows the geochemical classification of the samples with classification based on the NAG test. The Type 1 rock sample (Group A) had an NAPP range of -248.23 to -228.7 kg H_2SO_4/t, which indicates that the sample was dominated by carbonate minerals with an ANC value of 259.44 kg H_2SO_4/t, it was classified as an NAF rock. The average NAPP values of Types 2, 3, and 4 were -252.82, -17.1, and 14.088 kg H_2SO_4/t, respectively. As shown in Fig. 2, the samples classified as Types 2 and 3 were in the uncertainty quadrant because they had a negative average NAPP, but NAG pH below 4.5. Average NAG capacity is very likely to be greater than average NAPP because NAPP includes a stoichiometric maximum acidity based on S analysis and pyrite oxidation [54]. In addition, this phenomenon occurs because organic matter in the sample reacts during oxidation and produces organic acids that can be titrated during the NAG test.

3.2. NAG solution characteristics

Fig. 3 shows the pH (Fig. 3a), total dissolved solids (Fig. 3b), oxidation reduction potential (Fig. 3c), conductivity (Fig. 3d), and Fe (Fig. 3e) and Mn (Fig. 3d) concentrations of the NAG solution. There was no significant difference in these parameters between samples treated with 7.5% and 15% H_2O_2. For example, the average pH values of the four rock types with the addition of 7.5% and 15% H_2O_2 were 7.65 and 7.78 (Type 1), 4.12 and 4.44 (Type 2), 2.96 and 2.91 (Type 3), and 2.51 and 2.58 (Type 4), respectively.

As shown in Fig. 3e, the lowest concentration of Fe (1.65 mg/L) was recorded in Type 1. In contrast, relatively high Fe concentrations were recorded in the NAG solution of Type 4. With the use of 7.5% and 15% H_2O_2, Fe concentrations ranged from 15.8 to 112 and 15.8–85 mg/L, respectively. Fe was one of the pyrite mineral oxidation products found in PAF rocks in Sangatta and Bengalon. XRD analysis was done to determine the phase composition of the dried and pulverized rock core samples. Based on XRD results in Fig. 4, PAF rock samples (Types 2–4) contained various minerals, namely quartz (SiO_2), pyrite (FeS_2), halloysite ($Al_2Si_2O_5(OH)_4$), jarosite ($(K,H_3O)Fe_3(SO_4)_2(OH)_6$), kaolinite ($Al(Si_2O_5)(OH)_4$), albite ($(Na,Ca)Al(Si,Al)_3O_8$), butlerite ($Fe(SO_4)(OH)(H_2O)_2$), and anatase ($TiO_2$). The mineralogy of the PAF (Type 4) is relatively complex with several mineral phases. Pyrite is known to be one of the minerals which was detected in the PAF (type 4) sample. In addition, there are also minerals that potentially can neutralize acids such as silicate minerals (quartz) and albite. However, according to Ref. [55] stated that silicate minerals do not contain neutralizing cations and albite has a very low dissolution rate and a minor cation exchange capacity. This causes the presence of these minerals does not contribute significantly to neutralize acid mine drainage, especially in PAF samples (Type 4). From Fig. 5b, EDS spectrum analysis of PAF (Type 4) sample detected peaks corresponding to Fe (mass 47.76%) and S (mass 52.24%). Both are the main elements contained in the mineral pyrite. In addition, the elements Fe and S of the PAF sample surface by SEM mapping analysis was shown in Fig. 5a. It was
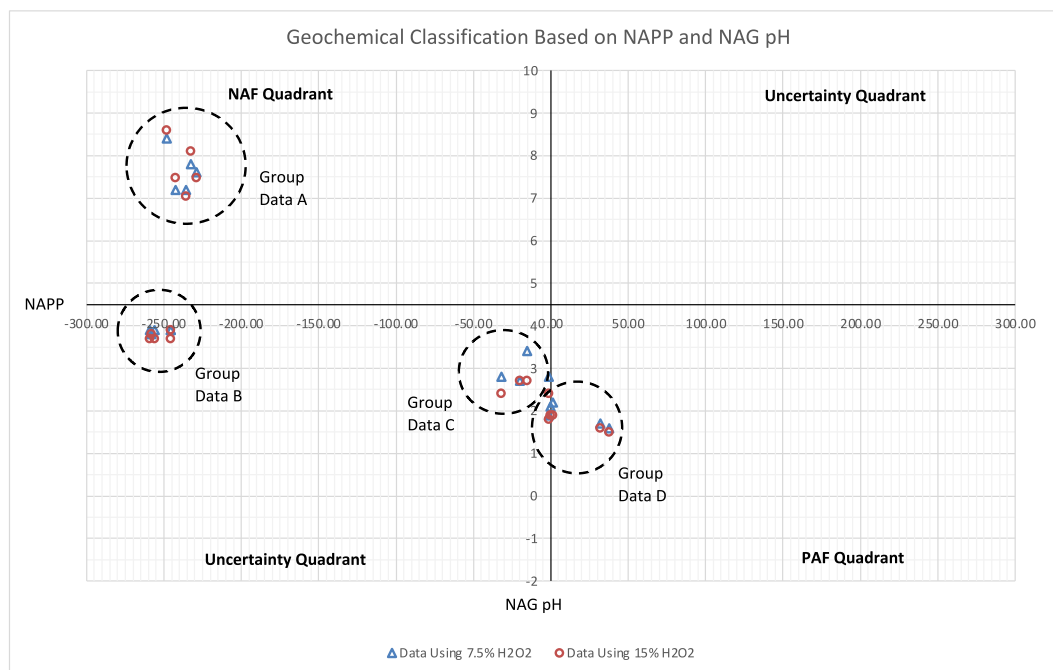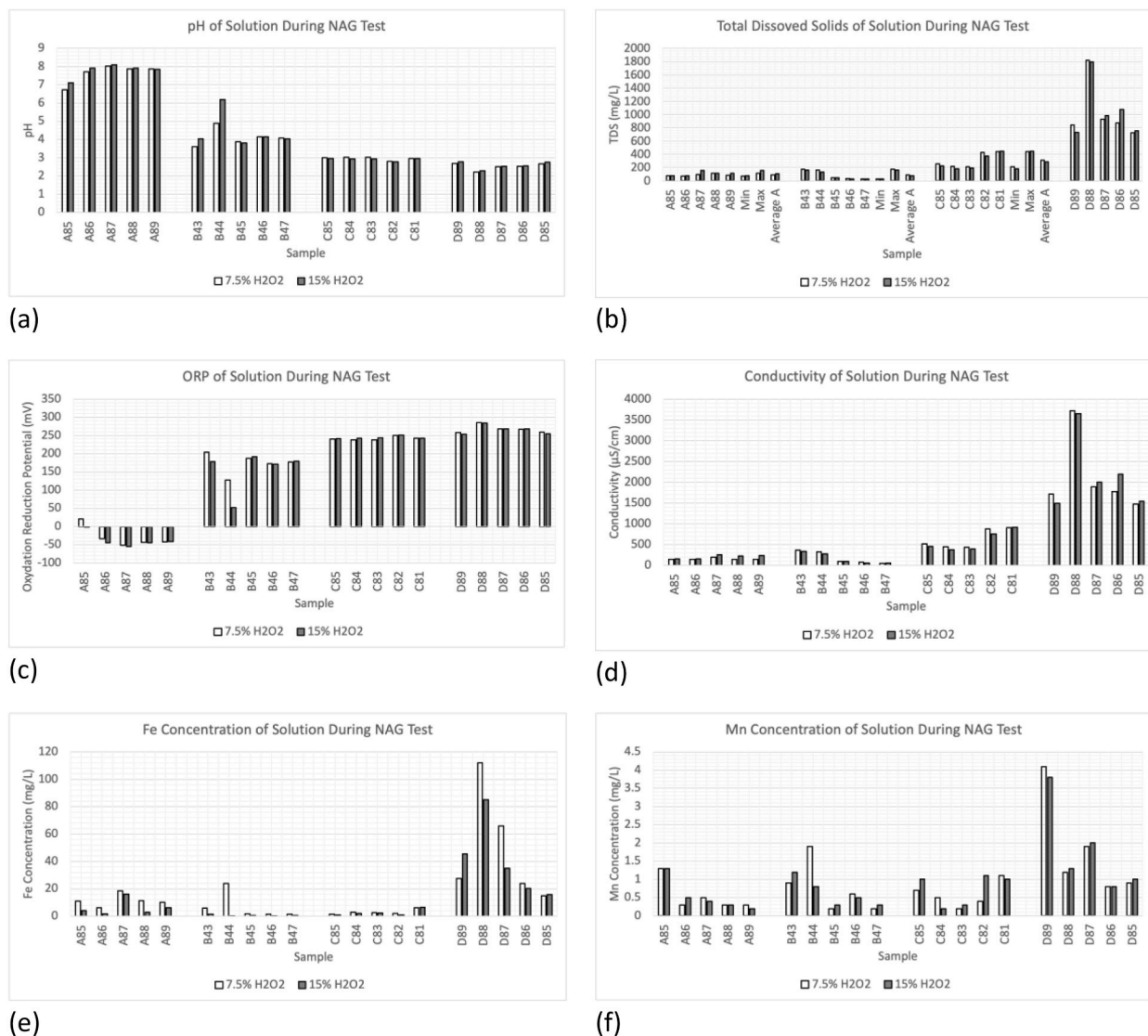

Fig. 2. Geochemical classification based on net acid-producing potential (NAPP) and net acid generation (NAG) pH using H_2O_2 at concentrations of 7.5% and 15%. Notes: NAF, non-acid-forming; PAF, potentially acid-forming.

Fig. 3. Characteristics of NAG solution treated with 7.5% and 15% H_2O_2: (a) pH; (b) total dissolved solids; (c) oxidation reduction potential (ORP); (d) conductivity; (e) Fe concentration; and (f) Mn concentration.

confirmed that these elements were present on the surface of PAF (type 4) sample. In contrast, the NAF rock sample (Type 1) comprised fewer minerals, namely quartz (SiO_2), siderite ($Fe(CO_3)$), Anatase (TiO_2), Anatase (TiO_2), kaolinite ($Al_2Si_2O_5(OH)_4$), albite ($(Na,Ca)Al(Si,Al)_3O_8$), kaolinite ($Al_2Si_2O_5(OH)_4$), Vaterite ($CaCO_3$), and Rutile (TiO_2). Pyrite occurred in PAF rock samples in a rounded, very fine, and framboidal form (Fig. 5a). This framboidal shape is believed to be an important factor in the solution's reaction with 7.5% and 15% H_2O_2. Ref. [56] described the reaction between mineral pyrite and hydrogen peroxide solution as follows:

$$FeS_2 + 15\left/2\right. H_2O_2 \rightarrow Fe^{3+} + 2SO_4^{2-} + H^+ + 7H_2O$$
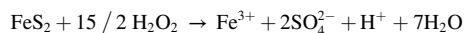
As shown in Fig. 3f, the concentration of Mn in PAF was also highest in Type 4, ranging from 0.8 to 4.1 and 0.8–3.8 mg/L when using 7.5% and 15% H_2O_2, respectively. However, Mn concentrations were lower than those of Fe.

Several studies have highlighted the importance of performing mineralogical analysis alongside static testing to determine the behavior of rock samples during AMD potential tests [28,45,47,53,57–59]. Fig. 6(a–d) shows the change in temperature and pH of different rock samples over time when reacting with 7.5% and 15% H_2O_2. The two H_2O_2 concentrations yielded similar changes in pH, but significantly different changes in temperature. The addition of 15% H_2O_2 to Type 4 increased the temperature of the NAG solution to a maximum of 71.3 °C in 42 min, whereas the addition of 7.5% H_2O_2 increased temperature to a maximum of only 43.1 °C in 54 min. Maximum temperatures were reached when all other sulfide and sulfide minerals were oxidized. The oxidation of pyrite by the strong oxidizing agent H_2O_2 is a catalytic exothermic decomposition reaction that releases thermal energy [60,61]. The catalytic decomposition phase of the NAG test was triggered by metals such as Pb, Cu, Mn, and Fe [62–64]. According to Ref. [53], pyrite mineral

(a)

(b)
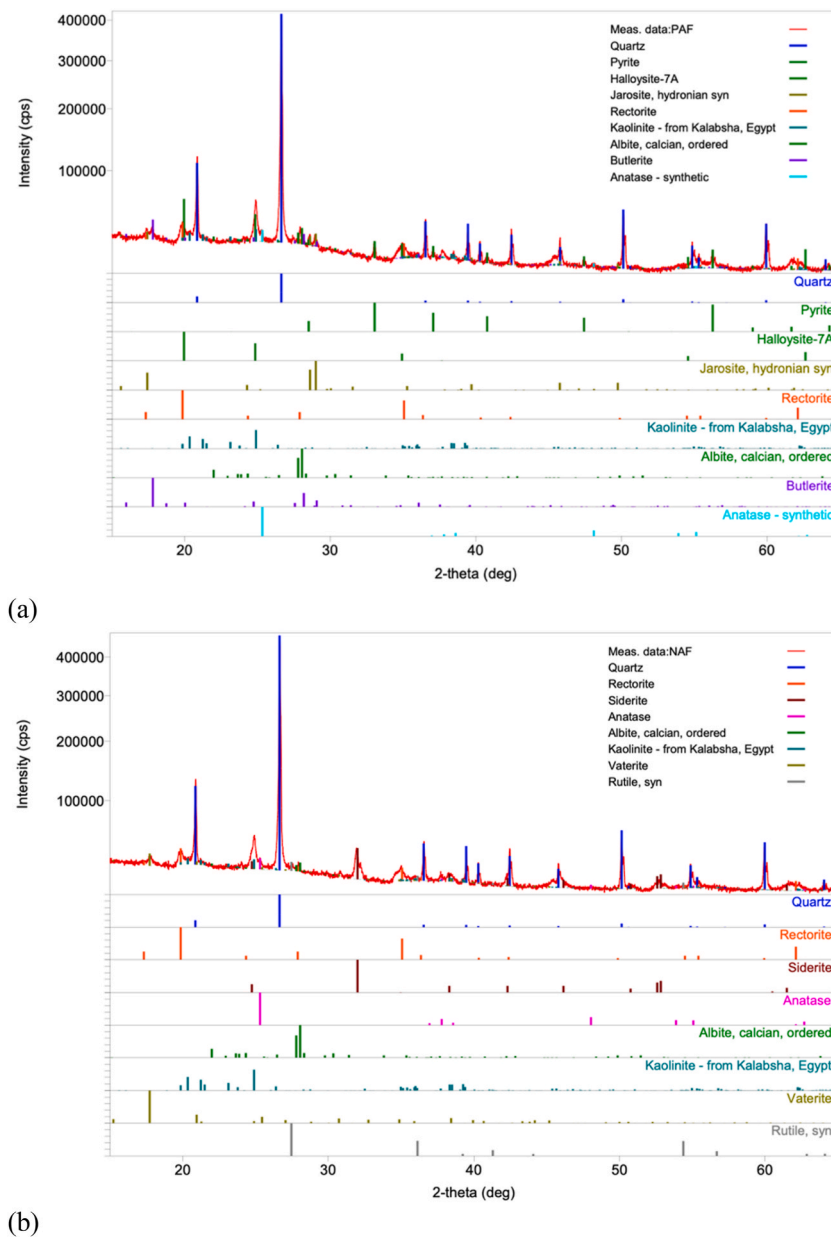
Fig. 4. X-ray diffraction profile of one of the samples categorized as (a) PAF (Type 4); and (b) NAF (Type 1) from rock core sample.

oxidation ceases when H_2O_2 decomposition is complete. Both scenarios in Fig. 6a-d show that the solution required 150–180 min to return to its initial temperature.

Although different in magnitude, all PAF samples (Types 2–4) exhibited similar temperature curves with the addition of 7.5% and 15% H_2O_2. This could be due to the relatively low TS concentration and framboidal minerals, which stimulated oxidation. Ref. [37] concluded that the rate of pyrite mineral oxidation in the presence of H_2O_2 is affected by several factors, namely particle size, sulfates, organic material, clay rock type, temperature, other sulfides, unreacted pyrite, and the presence of carbonate minerals in the sample. Therefore, H_2O_2 with a concentration of 7.5% can be used for reliable, low-cost NAG tests in Indonesian coal mines with relatively low TS concentrations (<5%) and minerals in framboidal form.
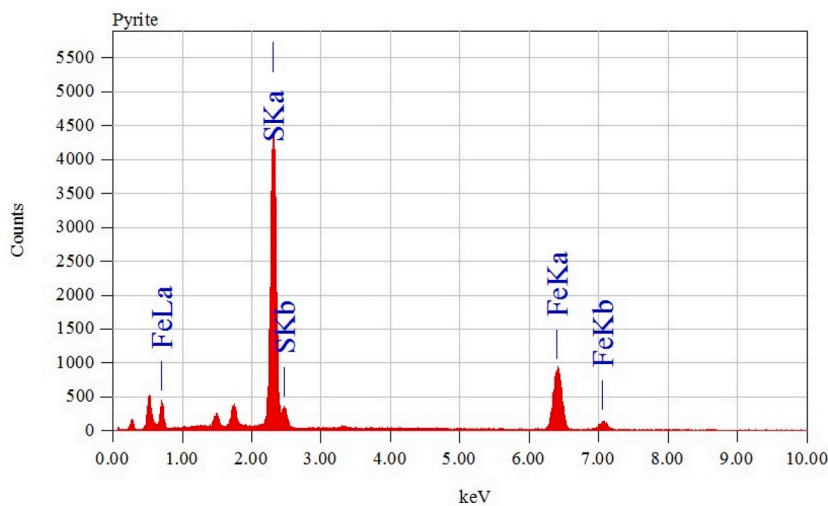
4. Conclusion

The NAG test can be used to determine AMD generation potential. This method is considered the easiest to use in mining operations because it does not require TS analysis, allowing it to be conducted quicker and more easily than other tests. In this study, NAG tests
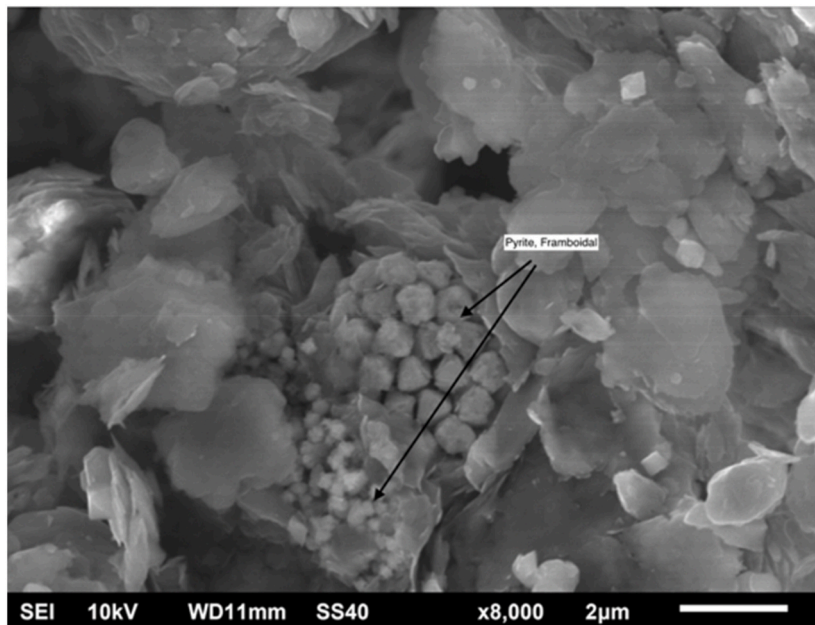
(a)

(b)

Fig. 5. (a) Scanning electron microscope images of typical pyrite framboids observed in potentially acid-forming samples (Types 4) and (b) EDS spectrum of pyrite in graphic of pulverized rock core sample categorized as PAF (Type 4).

were performed on 564 rock samples from Sangatta and Bengalon to determine the differences in behavior and results between sample reactions with 7.5% and 15% H_2O_2. Results showed that 7.5% and 15% H_2O_2 did not significantly differ in their effect on the potential AMD generation classification of rock samples. In addition, the behavior of the NAG solution did not significantly differ between the two H_2O_2 concentrations. This could be due to the relatively low TS concentration and framboidal minerals, which stimulated oxidation. Therefore, H_2O_2 with a concentration of 7.5% can be used for reliable, low-cost NAG tests in Indonesian coal mines with relatively low TS concentrations ($<5\%$) and minerals in framboidal form. Further testing is required to determine the effect of different H_2O_2 concentrations on sulfide minerals from mines with different characteristics.

Author contribution statement

Muhammad Sonny Abfertiawan: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.
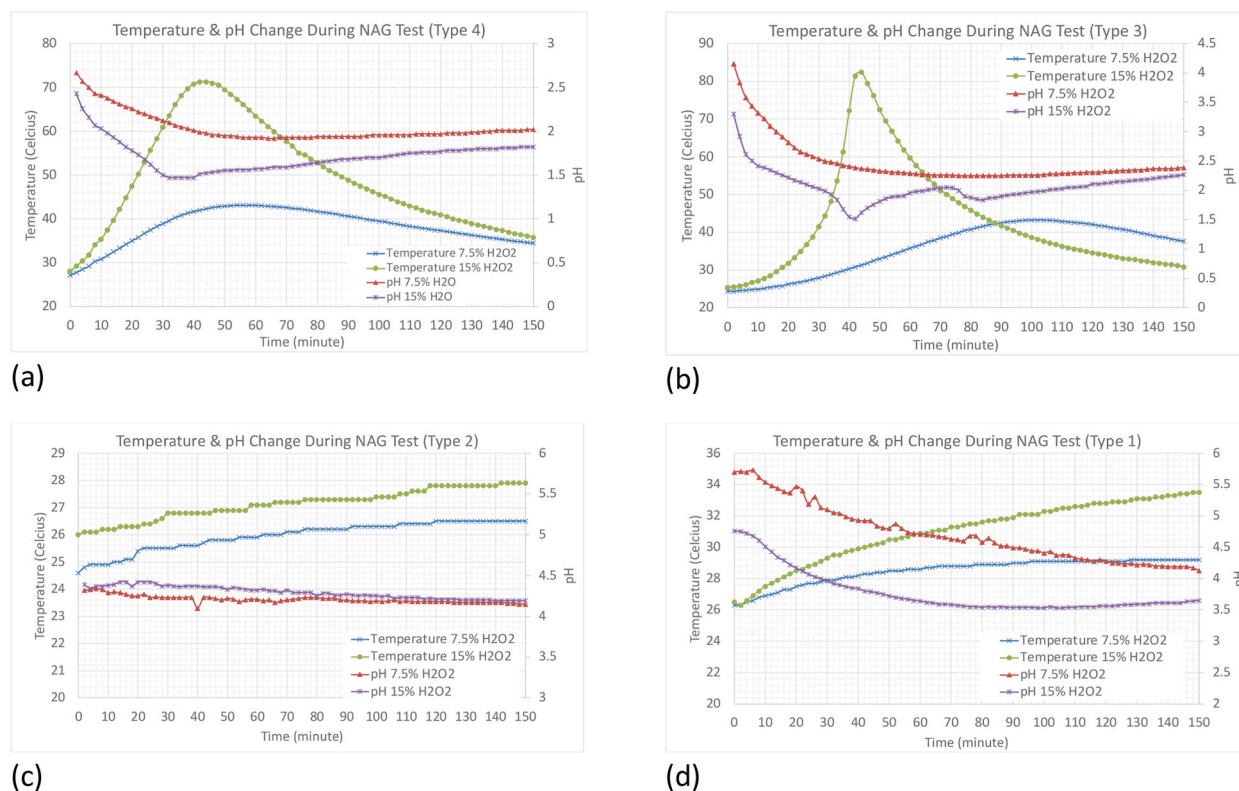
Fig. 6. Temperature and pH change of different rock samples during the net acid generation (NAG) test using 7.5% and 15% H_2O_2: (a) Type 4; (b) Type 3; (c) Type 2; (d) Type 1.

Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

References

[1] M.S. Abfertiawan, Y. Palinggi, M. Handajani, K. Pranoto, A. Atmaja, Evaluation of Non-Acid-Forming material layering for the prevention of acid mine drainage of pyrite and jarosite, Heliyon 6 (11) (2020), e05590, https://doi.org/10.1016/j.heliyon.2020.e0559.

[2] C. Vasilatos, N. Koukouzas, D. Alexopoulos, Geochemical control of acid mine drainage in abandoned mines: the case of ermioni mine, Greece, Procedia Earth and Planetary Science 15 (2015) 945–950, https://doi.org/10.1016/j.proeps.2015.08.151.

[3] Z. Wang, Y. Xu, Z. Zhang, Y. Zhang, Review: acid mine drainage (AMD) in abandoned coal mines of shanxi, China, Water 13 (2021) 8, https://doi.org/10.3390/w13010008.

[4] P.J.C. Favas, S.K. Sarkar, D. Rakshit, P. Venkatachalam, M.N.V. Prasad, Acid mine drainages from abandoned mines, in: Environmental Materials and Waste, Elsevier, 2016, pp. 413–462, https://doi.org/10.1016/b978-0-12-803837-6.00017-2.

[5] S. Matsumoto, H. Shimada, T. Sasaoka, The key factor of acid mine drainage (AMD) in the history of the contribution of mining industry to the prosperity of the United States and South Africa: a review, Nat. Resour. 7 (2016) 445–460, https://doi.org/10.4236/nr.2016.77039.

[6] A. Elghali, M. Benzaazoua, H. Bouzahzah, M. Abdelmoula, J.J. Dynes, H.E. Jamieson, Role of secondary minerals in the acid generating potential of weathered mine tailings: crystal-chemistry characterization and closed mine site management involvement, Elsevier BV, Sci. Total Environ. 784 (2021), 147105, https://doi.org/10.1016/j.scitotenv.2021.147105.

[7] A. Petrilakova, M. Balintova, M. Holub, Precipitation of heavy metals from acid mine drainage and their geochemical modeling, Walter de Gruyter GmbH, Sel. Sci. Pap. J. Civ. Eng. 9 (1) (2014) 79–86, https://doi.org/10.2478/sspjce-2014-0009.

[8] A. Parbhakar-Fox, B.G. Lottermoser, A critical review of acid rock drainage prediction methods and practices, Elsevier BV, Miner. Eng. 82 (2015) 107–124, https://doi.org/10.1016/j.mineng.2015.03.015.

[9] S. Shirin, A. Jamal, C. Emmanouil, A.K. Yadav, Assessment of characteristics of acid mine drainage treated with fly ash, Appl. Sci. 11 (2021) 3910, https://doi.org/10.3390/app11093910.

[10] D.K. Nordstrom, C.N. Alpers, C.J. Ptacek, D.W. Blowes, Negative pH and Extremely Acidic Mine Waters from Iron Mountain, Web, California, United States: N. p., 2000, https://doi.org/10.1021/es990646v.

[11] M.S. Abfertiawan, R.S. Gautama, S.B. Kusuma, S. Notosiswoyo, Hydrology simulation of ukud river in lati coal mine, Kyushu University, Evergreen 3 (1) (2016) 21–31, https://doi.org/10.5109/1657737.

[12] G. Robb, James D.F. Robinson, Acid drainage from mines, Geogr. J. 161 (1) (1995) 47–54, https://doi.org/10.2307/3059927.

[13] International Network for Acid Prevention (INAP). The global acid rock drainage guide, 2009. Available at, http://www.gardguide.com.

[14] P.K. Sahoo, K. Kim, S.M. Equeenuddin, M.A. Powell, Current approaches for mitigating acid mine drainage, Rev. Environ. Contam. Toxicol. 226 (2013) 1–32, https://doi.org/10.1007/978-1-4614-6898-1_1. PMID: 23625128.

[15] T. Cochrane, R.V. Nicholson, A. Small, P. Babulic, May, in: Proceedings of the 9th International Conference on Acid Rock Drainage, Ottawa, 2012, pp. 20–26, 2012.

[16] Sjoberg-Dobchuk, B., Wilson, G.W., and M. Aubertin, 2003. Evaluation of a single-layer desulfurised tailings cover. In: Proceedings of 6th International Conference Acid Rock Drainage (ICARD), July 14-17, Cairns, QLD, Australia, AusIMM.

[17] R.S. Gautama, M.S. Abfertiawan, G.J. Kusuma, F. Gunawan, Comparison of Leach Column Experiment from Laboratory Bench to Mine Site for Coal Mine Overburden, ICARD IMWA, Santiago, Chile, 2015.

[18] H. Shimada, G.J. Kusuma, K. Hiroto, T. Sasaoka, K. Matsui, R.S. Gautama, B. Sulistianto, Development of a new covering strategy in Indonesian coal mines to control acid mine drainage generation: a laboratory-scale result, Int. J. Min. Reclamat. Environ. 26 (1) (2012) 74–89, https://doi.org/10.1080/17480930.2011.608505.

[19] T.S. Win, S. Dwiki, A. Hamanaka, T. Sasaoka, H. Shimada, S. Mastumoto, G.J. Kusuma, Application of fly ash and organic material as dry cover system in prevention of acid mine drainage generation, J. Geosci. Environ. Protect. 8 (2020) 56–64, https://doi.org/10.4236/gep.2020.85004.

[20] Y. Zhou, M.D. Short, J. Li, R.C. Schumann, R.S.C. Smart, A.R. Gerson, G. Qian, Potential strategies for sustainable control of acid generation from pyrite oxidation, 25-30 June, in: C. Wolkersdorfer, L. Sartz, M. Sillanpää, A. Häkkinen (Eds.), 13th International Mine Water Association Congress - Mine Water & Circular Economy, Lappeenranta, Finland, LUT Scientific and Expertise Publications, 2017.

[21] R. Ciccu, M. Ghiani, A. Serci, S. Fadda, R. Peretti, A. Zucca, Heavy metal immobilization in the mining-contaminated soils using various industrial wastes, Elsevier BV, Miner. Eng. 16 (3) (2003) 187–192, https://doi.org/10.1016/s0892-6875(03)00003-7.

[22] A. Elghali, M. Benzaazoua, B. Bussière, T. Genty, In situ effectiveness of alkaline and cementitious amendments to stabilize oxidized acid-generating tailings, MDPI AG, Minerals 9 (5) (2019) 314, https://doi.org/10.3390/min9050314.

[23] K.J. Bethune, D.A. Lockington, D.J. Williams, Acid mine drainage: comparison of laboratory testing to mine site conditions, 31 May to 6 June. vol. 1, in: Proceeding of the 4th International Conference on Acid Rock Drainage, British Columbia, Vancouver, 1997, pp. 305–318.

[24] MEND, Acid rock drainage prediction manual, in: Canmet – MSL Division, Department of Energy, Mines, and Resources. Canada, 1991, p. 77. MEND project 1.16.1b.

[25] W.A. Price, K. Morin, N. Hutt, Guidelines for the prediction of acid rock drainage and metal leaching for mines in British Columbia: Part II – recommended procedures for static and kinetic testing, in: 4th International Conference on Acid Rock Drainage (ICARD), Vancouver, Canada, 1997, pp. 15–30.

[26] R.StC. Smart, W.M. Skinner, G. Levay, A.R. Gerson, J.E. Thomas, H. Sobieraj, R. Schumann, C.G. Weisener, P.A. Weber, S.D. Miller, W.A. Stewart, ARD Test Handbook. Amira P387a Project: Prediction and Kinetic Control of Acid Mine Drainage, Amira International, Melbourne, Australia, 2002. http://www.amira.com.au.

[27] EPA, Acid Mine Drainage Prediction, U.S. Environmental Protection Agency, 1994. Technical Report EPA530-R-94-036.

[28] W.W. White, K.A. Lapakko, R.L. Cox, Static-test methods most commonly used to predict acid mine drainage: practical guidelines for use and interpretation, 228, in: G.S. Plumlee, M. Logsdon (Eds.), The Environmental Geochemistry of Mineral Deposits, Part A: Theory and Background, Reviews in Economic Geology, 7A, 1999, p. 325.

[29] E. Perry, Interpretation of acid-base accounting. Chapter 11, in: Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, PA Department of Environmental Protection, Harrisburg, PA, 1998.

[30] J. Skousen, , Simmons, L.M. McDonald, P. Ziemkiewicz, Acid-base accounting to predict post-mining drainage quality on surface mines, J. Environ. Qual. 31 (6) (2002) 2034.

[31] R.M. Smith, A.A. Sobek, T. Arkle, J.C. Sencindiver, J.R. Freeman, Extensive Overburden Potentials for Soil and Water Quality, Field and Laboratory Methods Applicabla to Overburden and Minesoil, Cincinnati, OH, 1976. EPA-600/2-76-184.

[32] A.A. Sobek, J.G. Skousen, S.E. Fisher Jr., Chemical and physical properties of overburdens and minesoils, in: Reclamation of Drastically Disturbed Lands, Agronomy No. 41, American Society of Agronomy, Madison, WI, 2000, pp. 77–104.

[33] Coastech Research Inc, Investigation of Prediction Techniques for Acid Mine Drainage. MEND Project 1.16.1 a, Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources Canada, 1989, p. 61 (p. plus appendices).

[34] R.W. Lawrence, Prediction of the behaviour of mining and processing wastes in the environment, in: F. Doyle (Ed.), Proc. Western Regional Symposium on Mining and Mineral Processing Wastes, Soc. For Mining, Metallurgy, and Exploration, Inc., Littleton, CO, 1990, pp. 115–121.

[35] R.W. Lawrence, Y. Wang, Determination of neutralization potential for acid rock drainage prediction. MEND Project, 38 p. plus figures, tables and appendices 1 (3) (1996) 16.

[36] A.A. Sobek, W.A. Schuller, J.R. Freeman, R.M. Smith, Field and Laboratory Methods Applicabla to Overburden and Minesoil, U.S. Environmental Protection Agency, Cincinati, Ohio, 1978, pp. 47–50, 45268. EPA-600/2-78-054.

[37] R.B. Finkelman, D.E. Giffin, Hydrogen peroxide oxidation: an improved method for rapidly assessing acidgenerating potential of sediments and sedimentary rocks, Recreation and Revegetation Research 5 (1986) 521–534.

[38] R.M. Smith, W.E. Grube, T. Arkle, A. Sobek, Mine Spoil Potentials for Soil and Water Quality, U.S. EPA, Cincinanti, OH, 1974. EPA-670/2-74-070: 303.

[39] T.A. O'Shay, L.R. Hossner, The determination of potential acidity of overburden sediments, in: Proceedings of Surface Mine Reclamation Workshop, San Antonio, TX, 1984, pp. 13–14. October 9-10).

[40] T. O'Shay, L.R. Hossner, J.B. Dixon, A modified hydrogen peroxide oxidation method for determination of potential acidity in pyritic overburden, J. Environ. Qual. 19 (1990) 778–782.

[41] S.D. Miller, J. Jeffery, T.A. Donohue, Developments in predicting and management of acid forming mine wastes in Australia and southeast asia, Journal of the American Society of Mining and Reclamation, 1994 (1994) 177–184.

[42] S.N. Dubey, C.N. Das, Studies on sulphur and ash reduction in Assam coal through hydrogen peroxide treatment, Indian Journal of Mines, Metals, and Fuels, September-October (1981) 280–284.

[43] S.D. Miller, Advances in Acid Mine Drainage Prediction and Implications for Risk Management. In Proceeding of the 3rd International and the 21st Annual Minerals Councils of Australia, Environmental Workshop, Canbera, 149-57 vol. 1, Mineral Council of Australia, October, Newcastle, Australia, 1996, pp. 14–18.

[44] T. Karlsson, L. Alakangas, P. Kauppila, et al., A test of two methods for waste rock drainage quality prediction: aqua regia extraction and single-addition net-acid generation test leachate analysis, Mine Water Environ. 40 (2021) 736–751, https://doi.org/10.1007/s10230-021-00784-0.

[45] M.L. Räisänen, P.M. Kauppila, T. Myöhänen, Suitability of static tests for acid rock drainage assessment of mine waste rock, Bull. Geol. Soc. Finland 82 (2010) (2010) 101–111.

[46] K. Lapakko, Metal mine rock and waste characterization tools: an overview, Mining, Minerals and Sustainable Development (MMSD) working paper 67 (2002) 31.

[47] J.L. Jambor, Mine-waste mineralogy and mineralogical perspectives of acid-base accounting, in: J.L. Jambor, D.W. Blowes, A.I.M. Ritchie (Eds.), Environmental Aspects of Mine Wastes, Mineralogical Association of Canada, Short Course Series, vol. 31, 2003, pp. 117–145.

[48] F.A. Meek, Development of a procedure to accurately account for the presence of siderite during mining overburden analysis, in: Proc., WV Surface Mine Drainage Task Force Symp, Morgantown, WV, 1981.

[49] J. Skousen, J. Renton, H. Brown, P. Evans, B. Leavitt, K. Brady, L. Dohen, P. Ziemkiewicz, Neutralization potential of overburden samples containing siderite, J. Environ. Qual. 26 (3) (1997) 673–681.

[50] R.S. Gautama, Acid Water Problem in Bukit Asam Coal Mine, South Sumatra, Indonesia. – Proceedings (Nottingham) vol. 2, 5th International Mine Water Congress, Nottingham, U.K, 1994, pp. 533–542, 5 fig., 2 tab.

[51] R.S. Gautama, G.J. Kusuma, Evaluation of geochemical tests in predicting acid mine drainage potential in coal surface mine, in: N. Rapantova, Z. Hrkal (Eds.), Mine Water and the Environment. –, VSB – Technical University of Ostrava, Ostrava, 2008, pp. 271–274.

[52] M. Ramli, N. Situru, M. Thamrin, November 30). Prediksi laju pembentukan air asam tambang dengan metode column leaching test, Jurnal Penelitian Enjiniring 23 (2) (2019) 129–135, https://doi.org/10.25042/jpe.112019.06.

[53] P. Weber, W.A. Stewart, W.M. Skinner, C. Weisener, J. Thomas, R.S.C. Smart, Geo-chemical effects of oxidation products and framboidal pyrite oxidation in acid mine drainage prediction techniques, Appl. Geochem. 19 (2004) 1953–1974, https://doi.org/10.1016/j.apgeochem.2004.05.002.

[54] J.E. Pope, P. Weber, A.P. Mackenzie, N. Newman, R. Rait, Correlation of acid base accounting characteristics with the Geology of commonly mined coal measures, West Coast and Southland, New Zealand, N. Z. J. Geol. Geophys. 53 (2–3) (2010) 153–166, https://doi.org/10.1080/00288306.2010.498404.

[55] P.A. Weber, J.E. Thomas, W.M. Skinner, R. St C. Smart, A methodology to determine the acid-neutralization capacity of rock samples, Can. Mineral. 43 (Issue 4) (2005) 1183–1192, https://doi.org/10.2113/gscanmin.43.4.1183. Mineralogical Association of Canada.

[56] P. Chirita, Pyrite oxidation by hydrogen peroxide in phosphoric acid solutions, Eur. J. Miner. Process. Environ. 4 (2004) 203–209.

[57] P.M. Heikkinen, Active Sulphide Mine Tailings Impoundments as Sources of Contaminated Drainage: Controlling Factors, Methods of Characterization and Geochemical Constraints for Mitigation, Academic Dissertation. Geological Survey of Finland, Espoo, 2009, p. 38.

[58] R.W. Lawrence, M. Scheske, A method to calculate the neutralization potential of mining wastes, Environ. Geol. 32 (1997) 100–106.

[59] L. Lei, R. Watkins, Acid drainage reassessment of mining tailings, black swan nickel mine, kalgoorlie, western Australia, Appl. Geochem. 20 (2005) 661–667.

[60] M. Knobloch, B.G. Lottermoser, Infrared thermography: a method to visualise and analyse sulphide oxidation, MDPI AG, Minerals 10 (11) (2020) 933, https://doi.org/10.3390/min10110933.

[61] W.A. Stewart, S.D. Miller, R.S.T.C. Smart, A.R. Gerson, J.E. Thomas, W.M. Skinner, G.M. Levay, R.C. Schumann, Use of the Net Acid Generation (NAG) test for evaluating and quantifying the acid generating capacity of sulphide minerals, Proc. Sixth Int. Conf. on Acid Rock Drainage (Cairns) (2003) 617–625.

[62] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, fifth ed., Wiley-Interscience, New York, 1988.

[63] S.K. Thisani, D.V.V. Kallon, P. Byrne, Geochemical classification of global mine water drainage, Sustainability 12 (2020), 10244, https://doi.org/10.3390/su122410244.

[64] M.B.J. Lindsay, M.C. Moncur, J.G. Bain, J.L. Jambor, C.J. Ptacek, D.W. Blowes, Geochemical and mineralogical aspects of sulfide mine tailings, Appl. Geochem. 57 (2015) 157–177, https://doi.org/10.1016/j.apgeochem.2015.01.009.