Integrating Treatment of Neutralization with Sulfidic Natural Water (SNW) to Capture Dissolved Copper (Cu^{2+}) from Acid Mine Drainage (AMD) at Batu Hijau Site, Sumbawa Island Indonesia

Surya Hadi*, **Ni Made Sri Suliartini, Lely Kurniawati, and Surayyal Hizmi**

Department of Chemistry, University of Mataram, Jl. Majapahit No. 62, Mataram-83125, Indonesia

Received September 12, 2017; Accepted March 13, 2018

ABSTRACT

The overall objectives of the research were (1) to study the capability of sodium hydrosulfide (NaHS) and sulfidic natural water (SNW) of Sebau in recovery of Cu^{2+}, (2) to investigate the potency of integrating treatments of neutralization with sulfidization using SNW of Sebau in removing Cu^{2+} from acid mine drainage (AMD) collected from Batu Hijau site. The first objective was achieved by separately reacting (in situ) NaHS and SNW with a Cu^{2+} solution at pH 5.5. The second objective was answered by conducting treatments of lime-neutralization by the use of three levels of pH (4.0; 5.5; 7.0) and sulfidization using SNW collected from Sebau, Lombok Island at three sampling points. The result showed that NaHS (61.6 mg/L) could precipitate Cu^{2+} solution (44.45 mg/L) up to 71.3%, while SNW of Sebau could precipitate Cu^{2+} solution (44.45 mg/L) for almost 100% at pH 5.5. The results also revealed that SNW could precipitate the remained Cu^{2+} in the AMD from the neutralization treatment (pH 4 = 113.5 mg/L; pH 5.5 = 85.01 mg/L; and pH 7.0 = 2.372 mg/L) to 83.84% (pH = 4.0) and 100% (pH = 5.5 and 7.0). Although both pH 5.5 and 7.0 could completely precipitate Cu^{2+} in the AMD, by comparing the experimental result with the stoichiometric analysis, it was predicted that pH 5.5 was an optimum pH level for the reaction between AMD and SNW to recover Cu^{2+} in the AMD. Without neutralization treatment, SNW showed potentiality to recover Cu^{2+} since the combination treatments of neutralization at pH 4 with SNW collected from three sample points resulted in a high percent recovery of Cu^{2+}.

Keywords: *acid main drainage (AMD); sulfidic natural water*

ABSTRAK

Tujuan keseluruhan dari penelitian ini adalah: (1) untuk mempelajari kemampuan dari natrium hidrosulfida (NaHS) dan air belerang alami (SNW) dari Sebau dalam mengendapkan Cu^{2+}, (2) untuk menginvestigasi potensi dari pengintegrasian perlakuan pada netralisasi dengan sulfidisasi menggunakan SNW dari Sebau dalam menghilangkan Cu^{2+} terlarut yang berasal dari air asam tambang (AMD) dari Batu Hijau. Tujuan pertama telah tercapai dengan mereaksikan secara in situ NaHS dan SNW dengan larutan Cu^{2+} secara terpisah pada pH 5,5. Tujuan kedua telah tercapai dengan melakukan perlakuan netralisasi dengan penggunakan tiga level pH (4, 5, 7) dan sulfidisasi menggunakan SNW yang diperoleh dari Sebau pada tiga titik sampel. Hasil menunjukkan bahwa NaHS (61,6 mg/L) dapat mengendapkan Cu^{2+} (44,45 mg/L) sampai dengan 71,3%, sementara SNW dari Sebau dapat mengendapkan larutan Cu^{2+} (44,45 mg/L) sampai dengan 100% pada pH 5,5. Hasil juga telah menunjukkan bahwa SNW dapat mengendapkan sisa Cu^{2+} dalam AMD dari perlakuan netralisasi (pH 4 = 113,5 mg L; pH 5,5 = 85,01 mg /L; dan pH 7,0 = 2,372 mg/L) sampai dengan 83,84% (pH = 4) dan 100% (pH = 5,5 dan 7,0). Meskipun kedua pH 5,5 dan 7,0 dapat secara sempurna mengendapkan Cu^{2+} dalam AMD, dengan membandingkan hasil eksperimen dengan analisis stoikiometri, diperkirakan bahwa pH 5,5 merupakan pH optimal untuk reaksi antara AMD dan SNW dalam mengendapkan Cu^{2+} di dalam AMD. Tanpa perlakuan netralisasi, SNW menunjukkan potensi dalam mengendapkan Cu^{2+} dikarenakan kombinasi perlakuan netralisasi pada pH 4 dengan SNW yang diperoleh dari tiga titik sampel manghasilkan konsentrasi yang tinggi dalam mengendapkan Cu^{2+}.

Kata Kunci: *air asam tambang; air belerang alami*

INTRODUCTION

Batu Hijau site is an open-pit mining located in West Sumbawa, Indonesia. This mining has operated since 1999 to obtain copper and gold as the major commodities [1]. The high intensity of exploration for gold and copper at Batu Hijau site has caused a large amount of disposed waste generating acid mine drainage (AMD). AMD is polluted water generated from a coal or metal mine, which is naturally formed by exposing sulfide minerals,

* Corresponding author.
Email address : sur_hadi88@yahoo.com

DOI: 10.22146/ijc.28223

such as Pyrite (FeS_2), with oxygen and water [2]. This process yields acidic sulfate and metal-bearing leachate as shown in the equation below [3]:

$$4FeS_2 + 14H_2O + 15O_2 \rightleftarrows 8H_2SO_4 + 4Fe(OH)_3 \quad (1)$$

FeS_2 is not the only source of sulfide minerals, but other minerals, namely Covellite (CuS), Chalcopyrite ($CuFeS_2$), Pyrrhotite and Marcasite, can also form AMD [4].

The AMD has become an environmental issue in global mining industries for decades [2,5-6]. Due to high contents of heavy metals (e.g. Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) and strong acidity, the AMD has caused severe environmental pollutions, reduction of water quality, and death of many aquatic organisms [5-8]. A high concentration of heavy metals especially dissolved Cu (Cu^{2+}) in the AMD of Batu Hijau site has caused long-term detrimental impacts to aquatic environments, fish, plants, and other organisms [9-10].

Adjusting pH using lime ($Ca(OH)_2$) is a common method used to remove metals from acid mine drainage (AMD) through precipitation [11-13]. The dissolved metals will form insoluble hydroxide precipitates after the addition of $Ca(OH)_2$, which is commercially called neutralization treatment [2,10,14-15]. Although $Ca(OH)_2$ can precipitate dissolved metals, the treatment using $Ca(OH)_2$ cannot completely remove Cu^{2+} at acidic condition [2]. To optimize the precipitation of Cu^{2+}, this method has currently been combined with sulfidization [2]. The sulfidization is a commercial method that commonly used to recover metals from the AMD.

A recent study found that sodium hydrosulfide (NaHS) can optimize the metal removals from the AMD by integrating sulfidization with neutralization treatment [2]. The result of this method was not only to improve the quality of AMD, but the result (precipitates) can also be retreated to obtain other industrial chemicals. The amount and types of metals resulted from integrating that treatment depends on the pH level [2,16-19]. Despite the benefit, NaHS cannot be used effectively in small mining industries since it has been categorized as an expensive agent. Besides using NaHS, many mining industries apply other chemical reagents containing sulfide, such as Na_2S, FeS, $(NH_4)_2S$, BaS, and H_2S, to precipitate metals from AMD. Precipitation using sulfide reagents generate a better metal recovery in AMD or effluents than precipitation using hydroxide reagents [17,20-21]. However, using these sulfide reagents can increase the expenses of mining companies. Considering a high treatment cost of AMD, it is necessary to find another alternative low-cost technology to recover Cu^{2+} in AMD of Batu Hijau site. One of the potential alternative sulfidization agents is sulfidic natural water (SNW) from Sebau, East Lombok, Indonesia. SNW contains sulfide compound that might be used to capture Cu^{2+} from AMD. Therefore, the study observed the capability of NaHS and SNW of Sebau in the recovery of Cu^{2+} and investigated the potency of integrating treatment of neutralization with sulfidization using SNW of Sebau in removing Cu^{2+} from the AMD collected from Batu Hijau site.

EXPERIMENTAL SECTION

Materials

The materials used for this study were samples of Acid Mine Drainage (AMD) collected from Batu Hijau site and SNW collected from Sebau hot springs. For the first experiment, the materials used were: $CuO_{(s)}$ to make a Cu^{2+} solution and NaHS (granule) to make NaHS solution.

In the characterization of AMD and SNW, the materials used were: $K_2Cr_2O_7$ (0.25 N), standard solution of Iodine (I_2) 0.025 N, sodium thiosulfate solution ($Na_2S_2O_3$) 0.025N, sulfuric acid reagent (Ag_2SO_4, concentrated H_2SO_4), standard solution of KHP/Potassium Hydrogen Phthalate ($HOOCC_6H_4COOK$), Ferro Ammonium sulfate (FAS) 0.1 N, and Ferroin indicators for COD analysis. Sulfuric acid (H_2SO_4), oxidizing/digesting solution ($K_2Cr_2O_7$, concentrated H_2SO_4, $HgSO_4$), HCl 6 N and 2% Starch Indicators were used for sulfide analysis. To determine the sulfate-containing in the samples, the analyses used Natrium sulfate (Na_2SO_4), barium chloride $BaCl_2$(s), and a buffer solution ($MgCl_2.6H_2O$, $CH_3COONa.3H_2O$, KNO_3, and CH_3COOH (99%)).

In AMD lime-neutralization integrated with sulfidization, $Ca(OH)_2$ 0.1 M and HCl 0.1 M were used for setting up different pH levels of AMD.

Instrumentation

The instruments used in this study were: vacuum pumps Hach S/N 970600016119 and filter paper (125 mm) for refining AMD and SNW samples before characterization.

The characterization experiments used analytical balance Sartorius BP210S, pH meter WTW pH 192, thermometer glass, conductivity meter Jenway 470, UV-Vis spectrophotometer Hitachi UH 5300 to measure the sulfate, and atomic absorption spectrophotometers (AAS) PerkinElmer AAnalyst 400 to measure Cu^{2+} in the samples.

The instrument used for COD analysis were: COD reactor Hach S/N 970600016119, Pyrex glassware and rubber bulb D&N, while for BOD Analysis used DO meter HACH Sension + DO6, and incubators FOC 215E.

To determine TSS and TDS levels, the instruments used were: porcelain dish 150 cc, desiccator Duran 250 L, oven UNB Memert and Cellulose Nitrate porous membrane filter Whatman 0.45 μm. Magnetic stirrer-hot

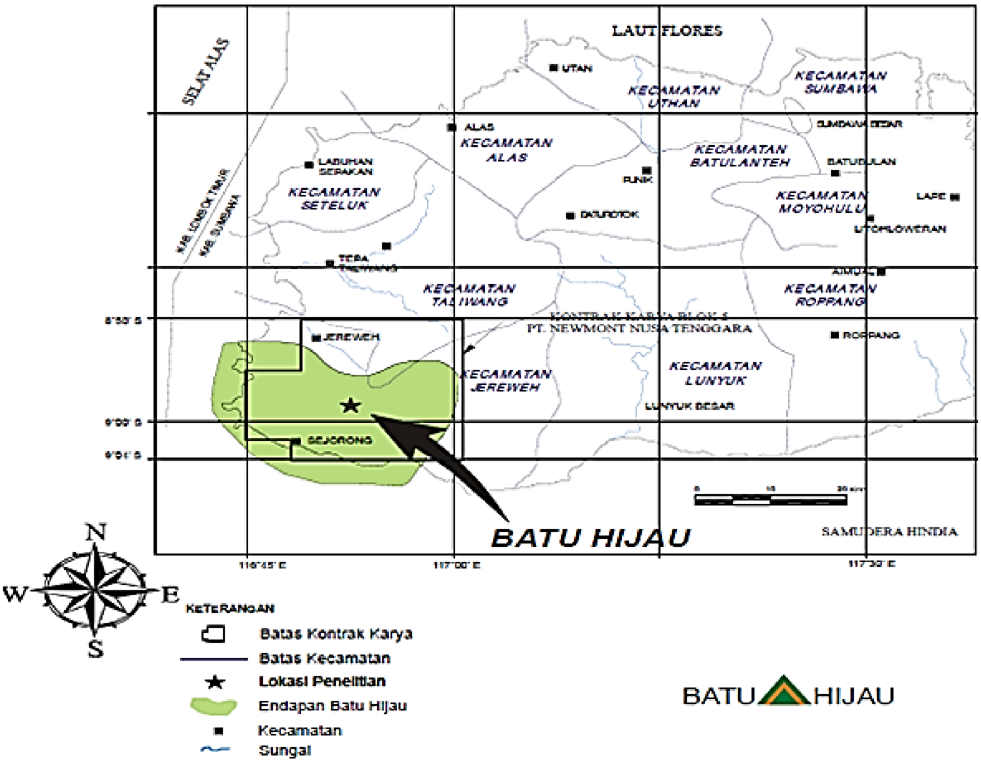

Fig 1. The location of Batu Hijau site

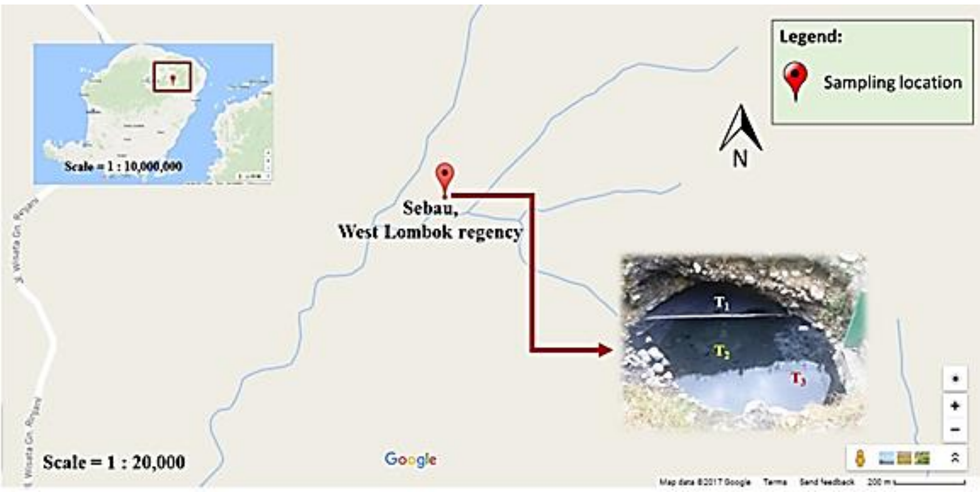

Fig 2. Map and the sampling points (T1, T2, and T3) of SNW in Sebau, East Lombok Regency

plate CAT:CH2090 001 was used for setting up different pH of AMD.

Procedure

Procedure for sampling

The AMD sample was taken from the outlet pipe of copper mine pit located in Batu Hijau site of West Sumbawa Regency, Indonesia (Fig. 1). This sample was collected by using a high-density polyethylene (HDPE) bottle with screw cap and the sample was then transported to Water Laboratory of West Nusa Tenggara Province, Indonesia, for characterization. SNW for sulfidization was taken from a pond of natural sulfur hot springs in Sebau, East Lombok Regency, Indonesia (Fig. 2). The SNW samples were collected from three sampling points, namely T1 (cove/steady point), T2 (source of SNW) and T3 (outlet). All samples were put into high-density polyethylene (HDPE) bottles and the samples were then transported to the laboratory for

Table 1. The combination reactions between AMD in three different pH levels with SNW collected from the three sampling points

pH of AMD	Sampling points of SNW		
	T1	T2	T3
4.0 (H1)	H1T1	H1T2	H1T3
5.5 (H2)	H2T1	H2T2	H2T3
7.0 (H3)	H3T1	H3T2	H3T3

characterization purposes.

The capability of NaHS and SNW in precipitating Cu^{2+}

To study the capability of SNW and NaHS in recovery of Cu^{2+}, two experiments were set up by reacting NaHS and SNW with Cu^{2+} solution separately. Both experiments were conducted *in situ* at room temperature (T = 300K) and pH 5.5. Descriptions of the experiments were described below.

Experiment 1: Reaction between NaHS and Cu^{2+}solution. NaHS solution was set into three different concentrations: 16.8, 39.2, and 61.6 mg/L. Each concentration was then reacted with a Cu^{2+} solution (44.45 mg/L) generated from CuO and the ratio was 1:1. Each reaction was filtrated using filter paper (0.45 µm). Then, the remained Cu^{2+} in the filtrate was measured by using Atomic Absorption Spectrophotometer (AAS) AAnalyst 400 at the Analytical Chemistry Laboratory.

Experiment 2: Reaction between SNW and Cu^{2+} solution. The second experiment was conducted by adding SNW collected from three sampling points (T1, T2, and T3, see Fig. 2) to the Cu^{2+} solution (44.45 mg/L) respectively with ratio 1:1 at pH 5.5. Similar to the previous experiment, each result (T1-Cu^{2+}, T2-Cu^{2+}, and T3-Cu^{2+}) was filtrated using filter paper (0.45 µm) and the remained Cu^{2+} from the filtrate was then analyzed using AAS Analyst 400 at the Analytical Chemistry Laboratory.

The next experiment was to change Cu^{2+} solution with AMD collected from Batu Hijau site. This experiment was firstly characterized SNW from Sebau and AMD from Batu Hijau site, which is described below.

Study integrating lime-neutralization with sulfidizing treatment

Characterization of SNW and AMD. Characterization of SNW and AMD was to obtain preliminary data of physical and chemical characteristics of AMD in Batu Hijau site and SNW in Sebau. The SNW and AMD were characterized for the physical and chemical parameters based on the Indonesian National Standard procedure (SNI). These parameters were temperature (SNI 06-6989.23: 2005), EC (SNI 06-6989.1: 2004), Total Suspended Solid/TSS (SNI 06-6989.3: 2004), TDS (SNI 06-6989.27: 2005), pH (SNI 06-6989.11: 2004), Dissolved Oxygen/DO (SNI 06-6989.14: 2004), Biological Oxygen Demand/BOD (SNI 06-6989.72: 2009), and Chemical Oxygen Demand/COD (SNI 06- 6989.73: 2009). This study only determined sulfate (SNI 06-6989.20-2004) and sulfide (SNI 06-6989.75: 2009) for the chemical contents of SNW as both compounds have important roles in sulfidization treatment, whereas Cu^{2+} was only measured in the AMD. All analyses for both physical and chemical parameters were conducted in Analytical Chemistry Laboratory, University of Mataram and Water Laboratory at Department of General Works of West Nusa Tenggara Province, Indonesia.

Neutralization treatment on the AMD. In this experiment, five different pH levels (4.0, 5.5, 7.0, 8.5, and 10.0) were set by adding $Ca(OH)_2$ to the AMD. Once AMD reached the coveted pH level, it was filtered using filter paper (0.45 µm) to obtain the precipitate. The filtrates were then measured for the EC level using conductivity meter, TDS level using TDS meter, and concentration of Cu^{2+} using PerkinElmer Atomic Absorption Spectrophotometer (AAS) Analyst 400. All analyses were conducted in the Analytical Chemistry Laboratory, University of Mataram. Filtrates (with several pH levels) found to still contain Cu^{2+} would be treated to the sulfidization treatment.

Sulfidization treatment using SNW of Sebau. This experiment was conducted by adding pure SNW from three sampling points (T1, T2, and T3) to the AMD with three different pH levels in 1:1 ratio reaction. This reaction was conducted at room temperature (around 300K) in the Analytical Chemistry Laboratory. The combination reactions between SNW and AMD are shown in Table 1.

RESULT AND DISCUSSION

The Capability of NaHS and SNW in the Recovery of Cu^{2+}

The recovery of Cu^{2+} by using NaHS and SNW can be seen in Fig. 3. NaHS with concentration of 16.8 mg/L could precipitate Cu^{2+} solution (44.45 mg/L) to 54.84%, while 61.6 mg/L NaHS could precipitate Cu^{2+} solution for more than 70%. On the other hand, the reaction between SNW of Sebau from T1, T2, and T3 and Cu^{2+} solution with the ratio 1:1 was able to recover Cu^{2+} solution (44.45 mg/L) for almost 100%. The two experiments indicated that SNW of Sebau has also potency to recover Cu^{2+} solution. How the SNW of Sebau was able to be applied to the AMD of Batu Hijau site below described.

Characterization of AMD and SNW

The AMD collected from Batu Hijau of West Sumbawa was characterized by warm temperature

(36 °C); acidic condition (pH = 3.99); high EC (4,734 µmhos/cm), TDS (3,658 mg/L) and Cu^{2+} (151.4 mg/L); low BOD (0.27 mg/L) and DO (< 2) (see Table 2). These characteristics were the same as AMDs from previous studies even though the studies were conducted in different geographical areas. For example, a high concentration of Cu found in the AMD of Richmond mine, USA (Cu = 120–650 mg/L) and Cantareras, Spain (160 mg/L) [22]; and a typically low pH level of the AMD was also found in Wheal Jane, England (pH = 3.4), King's mine, Norway (pH = 2.7), Parys mine, Wales (pH = 2.5), Cantareras, Spain (pH = 2.7) and Richmond mine, USA (pH = 0.5–1) [22].

The SNW of Sebau was characterized by warm temperatures (37–39 °C), slightly alkaline condition (pH = 7.20–7.25), high EC (2330–2370 µmhos/cm), high sulfide concentration (13.58–16.79 mg/L), and sulfate (4.08–6.38 mg/L, Table 2). Other parameters, namely DO, BOD and COD, were heterogeneous. For example, BOD and COD in T1 were far lower than those of T2 and T3, while DO in T1 was higher than those of T2 and T3. The level of BOD and COD are associated with the existence of microorganisms and chemical matters, as well as the abundance of dissolved oxygen in the SNW of Sebau. Therefore, the higher the number of microorganisms or chemical matters, the higher the BOD and COD level in the solution. Varied results of DO, BOD and COD analyses in the SNW of Sebau demonstrated that the existence of biological or chemical matters was higher in T2 and T3 than that of in T1. This means that the sampling points affected the presence of chemical matters and microorganisms. Many microorganisms and chemical matters tend to exist in the area where water flows from the source (T2) to the outlet (T3).

Precipitation of Cu^{2+} on the AMD Using Neutralization Treatment

The increase of AMD pH value due to the addition of $Cu(OH)_2$ was found to bring down EC and TDS value as well as Cu^{2+} concentration. At several pH levels (4.0, 5.5, 7.0, 8.5, and 10), EC value went from 4,734 µmhos/cm to 4,550–4,110 µmhos/cm; TDS value went from 3,658 mg/L to 2,730–2,460 mg/L; and Cu^{2+} was completely precipitated at pH > 8.5 (Fig. 4).

A reduction of Cu^{2+} was caused by the precipitation of Cu^{2+} to form $Cu(OH)_2$ through the reaction with ion OH^- from $Ca(OH)_2$ (eq. 2).

$$Cu^{2+}(aq) + 2OH^{-}(aq) \rightleftarrows Cu(OH)_2(s) \quad (2)$$

The reaction between Cu^{2+} and OH^- was reversible especially at pH < 8.5, in which the reaction did not completely form $Cu(OH)_2$. The product ($Cu(OH)_2$) was unstable and could reform Cu^{2+} and OH^- ions due to its high solubility. This result can cause difficulties on separating Cu from the other metals in the AMD. Therefore, additional treatment, such as sulfidization, is required to prevent the occurrence of the reformation process [2].

The Reaction between SNW and the Filtrates from Neutralization Treatment

The addition of SNW and EC reduction

The addition of SNW to the filtrates from neutralization treatment resulted in a reduction of EC value, where the initial EC values (4,550–4,250 µmhos/cm). Although EC values from this treatment were lower than those of the neutralization treatment, the EC values in all pH levels were still high (Fig.5). It was assumed that there were other metals besides Cu^{2+} in AMD affected the EC values.

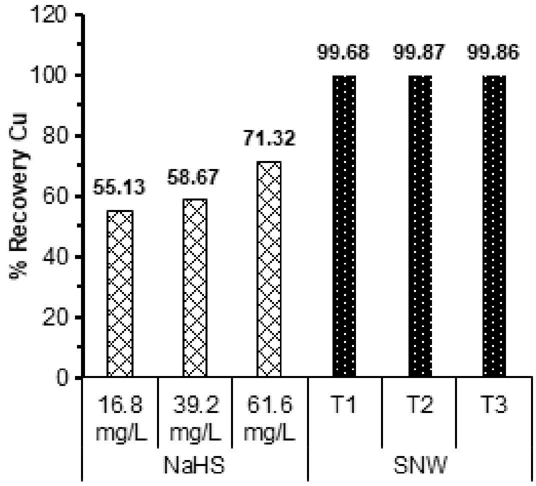

Fig 3. The recovery of Cu^{2+} by using NaHS and SNW

Table 2. Physical and chemical parameters of AMD and SNW

Type of sample	Parameter										
	TTS mg/L	TDS mg/L	EC µmhos/cm	Temperature °C	pH	DO mg/L	BOD mg/L	COD mg/L	Sulfide mg/L	Sulphate mg/L	Cu^{2+} mg/L
AMD	27	3658	4734	36	3.99	5.03	0.27	< 2	-	-	151.4
T1	30	1586	2370	38	7.78	5.82	9.72	15.84	13.58	6.38	0.004
T2	32	1485.5	2350	39	8.06	3.39	26.75	31.68	16.08	5.30	ND
T3	32	1558	2330	37	6.74	3.38	26.82	31.68	16.79	4.08	ND

N.B.: - = did not undertake, ND = not detected

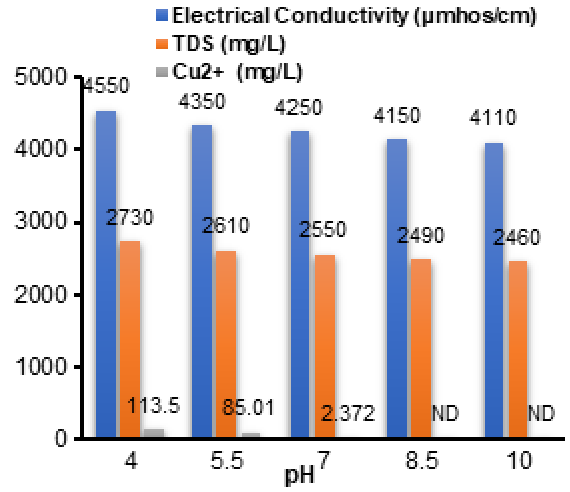

Fig 4. The effect of pH on electrical conductivity, TDS, and Cu^{2+} in AMD

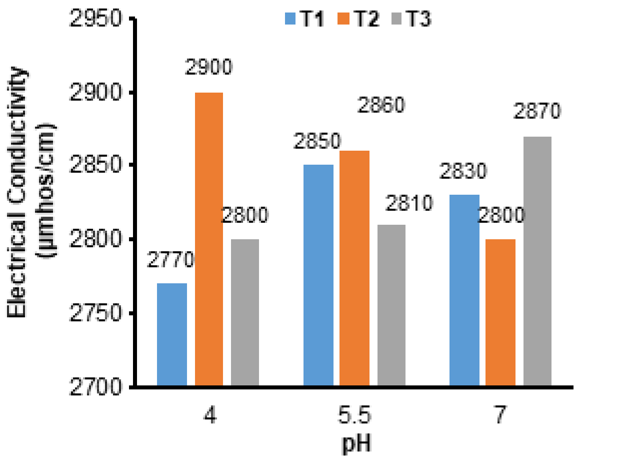

Fig 5. The effect of reaction between SNW and AMD on EC value

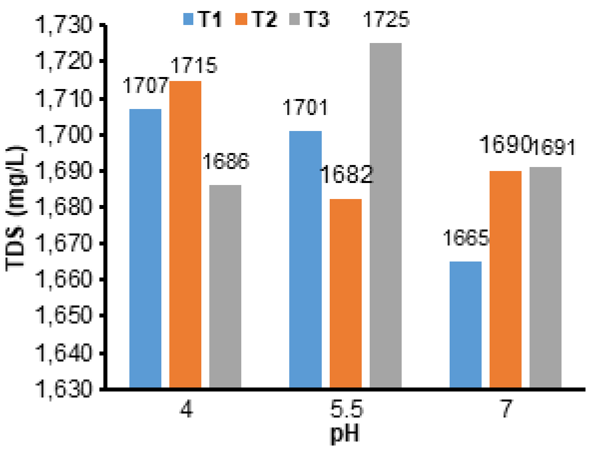

Fig 6. The effect of reaction between SNW and AMD on TDS value

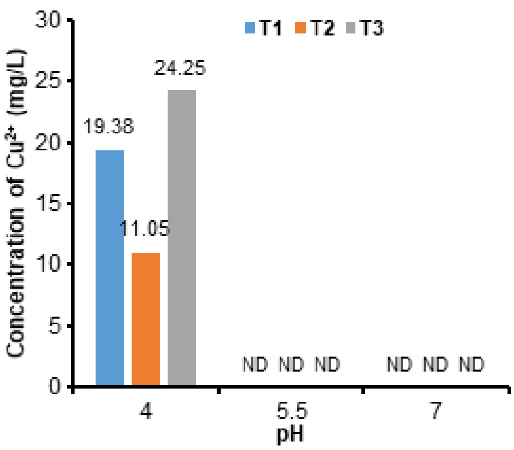

Fig 7. The effect of reaction between SNW and AMD on the concentration of Cu^{2+}

The addition of SNW and TDS reduction

A similar trend also showed in the TDS values after the reaction between SNW and the filtrates from neutralization treatment. TDS values went from 2,360–2,730 to 1,665–1,725 mg/L, in which these values were still higher than the expectation (Fig.6). Based on the investigation, it is found that there is an anomaly of chemical elements of Au, Fe, Pb, Zn, Ag, Mn, Sb located in Sumbawa regency [1]. This means that the existence of other chemical elements might cause high TDS values in the reaction between SNW and AMD from Batu Hijau site.

The addition of SNW and concentration of Cu^{2+}

The addition of SNW to the filtrate from neutralization treatment could precipitate the remained Cu^{2+} (Fig. 7). The study found that there was no Cu^{2+} detected at pH 5.5 and 7, which means Cu^{2+} was completely removed. In addition, referring to the EC and TDS values were still high, it was assumed that the SNW was mostly precipitate Cu^{2+} while other metals remained in the solution.

A reduction of Cu^{2+} on the AMD indicated that there was a reaction between Cu^{2+} in the AMD and S^{2-} from the SNW, which was supported by the existence of a black precipitate as a final product. The previous studies [2,15,23] found that sulfidizing agent like NaHS could exist as H_2S, HS^- and S^{2-} (eq. 3 and 4). This means that sulfide from SNW of Sebau might exist as those ions.

$$H_2S(aq) \rightleftarrows H^+(aq) + HS^-(aq) \quad (3)$$

$$HS^-(aq) \rightleftarrows H^+(aq) + S^{2-}(aq) \quad (4)$$

However, the ion abundances on the SNW depend on the pH level. It is estimated that S^{2-} was a dominant ion in SNW, which was supported by the form of black precipitate as a final result. The higher pH levels, the higher concentration of S^{2-} that would react with a metal ion (Cu^{2+}) to form CuS as shown by the eq. 5 [15,24]:

Table 3. The percentage recovery of Cu^{2+} from the experiment and stoichiometric analysis on the various treatments

Treatments	Initial $[Cu^{2+}]$ (mg/L)	Experiment		Stoichiometric analysis		
		Remained $[Cu^{2+}]$ (mg/L)	Recovery of Cu^{2+} (%)	Remained S^{2-} (mg/L)	Remained $[Cu^{2+}]$ (mg/L)	Recovery of Cu^{2+} (%)
H1T1	113.5	19.38	82.30	0	86.5315	23.76
H1T2		11.05	90.60	0	81.5721	28.13
H1T3		24.25	78.63	0	80.1560	29.38
H2T1	85.01	ND	100	0	58.8835	31.67
H2T2		ND	100	0	53.1214	37.51
H2T3		ND	100	0	51.7081	39.17
H3T1	2.372	ND	100	12.38	0	100
H3T2		ND	100	14.88	0	100
H3T3		ND	100	15.59	0	100

$$Cu^{2+}(aq) + S^{2-}(aq) \rightleftarrows CuS(s) \quad (5)$$

The high concentration of S^{2-} in the SNW was probably not only from sulfide, but a reduction of sulfate due to the existence of bacteria and alkaline condition (the addition of $Ca(OH)_2$) could also form S^{2-} [24-30].

In the application of NaHS as a sulfidizing agent, the reaction was not only between Cu and sulfide. Other metals, such as mercury (Hg), lead (Pb), chromium (Cr), zinc (Zn), arsenic (As), and nickel (Ni), could also be precipitated from the AMD by setting the reaction at the typical pH condition of each metal [31]. The possible reaction between NaHS and other metals (M) is shown in eq. 6 [32].

$$NaSH + M^{2+} \downarrow \ \rightarrow MS + Na^{+} + H^{+} \quad (6)$$

Considering the possibility of other metals occurs in the AMD of Batu Hijau Site, it is suspected that other reactions might also occur among SNW and other metals. Similar to NaHS, the SNW of Sebau might also recover other metals by setting up the reaction at specific pH condition. To obtain the potential other reactions between SNW and other metals in the AMD of Batu Hijau site, further study is required.

Referring to the reaction between SNW from three sampling points and AMD with three different pH levels, although Cu^{2+} was completely precipitated at pH 5.5 and 7.0, the precipitation of Cu^{2+} was not complete at treatment H1T1–H1T3 (Table 3). This was because of the addition of $Ca(OH)_2$ to reach pH = 4.0 was lower than other treatment at pH 5.5 and 7.0. Among treatments at pH 4.0 (H1T1–H1T3), the highest precipitation was found in the source (H1T2) with 90.6% of the Cu^{2+} precipitate. This is because the T2 sample point (source of SNW) contained more S^{2-} than in the cove (T1) or outlet (T3, see Fig. 2).

A stoichiometric analysis of the reaction between Cu^{2+} in AMD and S^{2-} in the SNW was conducted to compare the results of the experiment and theory. As shown in Table 3, there was no similarity for percent recovery between stoichiometric analysis and the experiment result. Cu^{2+} was completely removed at pH 5.5 and 7.0, while the optimal precipitation from stoichiometric analysis only occurred at pH 7.0. Different acquisition of percent recovery from both experimental and stoichiometric analyses might be affected by other compounds in the SNW. This is required further study to determine the details of chemical compounds in the SNW. Although maximum precipitation of Cu^{2+} occurred at pH 7.0 for both experimental and stoichiometric analyses, it was predicted that 5.5 was an optimum pH level for Cu^{2+} precipitation since there was no S^{2-} residual from the reaction between Cu^{2+} and S^{2-}. The reaction between S^{2-} and Cu^{2+} at pH 7.0 generated plenty of the S^{2-} residual, i.e., 12.38 mg/L (H3T1); 14.88 mg/L (H3T2) and 15.59 mg /L (H3T3, see Table 3).

Referring to the experimental results, SNW of Sebau has a potency to recover Cu^{2+} from AMD similar to the sulfidizing agent (e.g. NaHS). This was because the SNW can precipitate Cu^{2+} with the percentage of 78.63% (H1T1), 82.3% (H1T2) and 90.6% (H1T3) at pH = 4.0, where there was a very low addition of $Ca(OH)_2$ to AMD (initial pH = 3.99) at neutralization treatment. Without neutralization treatment, it was expected that SNW can be used to recover Cu^{2+} and the optimum recovery of Cu^{2+} will be in T2, the source of SNW. In addition, the EC and TDS values from the experiments were still high, indicated that other metals in AMD affected the values.

Possibility other reactions between AMD and SNW can occur depending on the species of chemical compositions. To study the potential reactions, details characterization of chemical compounds containing in SNW and its potency to recover metals from AMD require further research and the results will be published in the next paper.

CONCLUSION

The AMD was characterized by the low pH and high concentration of Cu^{2+}, which were the same as results found in the previous studies from different location of AMD. The SNW of Sebau was specifically characterized by a slightly alkaline condition, warm temperature, and high concentration of sulfide. The separated reaction of NaHS and SNW of Sebau with Cu^{2+} solution revealed the potentiality of SNW to recover Cu^{2+}. The addition of $Ca(OH)_2$ in neutralization treatment of the AMD lowered the values of electrical conductivity, TDS, and Cu^{2+}. These values were further reduced by the addition of SNW to the AMD. Although TDS and EC also reduced in the SNW treatment, the values were still high. The high values of EC and TDS indicated that there were other metals or particles occurred in the solution. At pH 5.5 and 7.0 of the treatments, Cu^{2+} was completely precipitated. This result also demonstrated that SNW could be potentially used to recover Cu^{2+}. By comparing the experimental result with the stoichiometric analysis, it was predicted that pH 5.5 was an optimum pH level for the reaction between AMD and SNW to recover Cu^{2+} in the AMD. Without neutralization treatment, SNW showed potentiality to recover Cu^{2+} since the combination treatments of neutralization at pH 4 with SNW collected from three sample points resulted in a high percent recovery of Cu^{2+}.

ACKNOWLEDGEMENT

We would like to acknowledge, Mr. Idris, the technician of Laboratory of Analytical Chemistry Faculty of Mathematics and Natural Sciences University of Mataram, for his assistance in AAS analysis, and the staff from Water Laboratory for their assistance in sampling process and characterization of the SNW from Sebau.

REFERENCES

[1] Moe'tamar and Ernowo, 2011, *Penyelidikan logam emas kabupaten Sumbawa, provinsi Nusa Tenggara Barat*, The Geological Resource Center Activities, Bandung.
[2] Wang, L.P., Ponou, J., Matsuo, S., Okaya, K., Dodbiba, G., Nazuka, T., and Fujita, T., 2013, Integrating sulfidization with neutralization treatment for selective recovery of copper and zinc over iron from acid mine drainage, *Miner. Eng.*, 45, 100–107.
[3] Hesketh, A.H., Broadhurst, J.L., and Harrison, S.T.L., 2010, Mitigating the generation of acid mine drainage from copper sulfide tailings impoundments in perpetuity: A case study for an integrated management strategy, *Miner. Eng*., 23 (3), 225–229.
[4] Karapınar, N., 2016, Removal of heavy metal ions by ferrihydrite: An opportunity to the treatment of acid mine drainage, *Water Air Soil Pollut*., 227 (6), 193.
[5] Davies, H., Weber, P., Lindsay, P., Craw, D., and Pope, J., 2011, Characterisation of acid mine drainage in a high rainfall mountain environment, New Zealand, *Sci. Total Environ*., 409 (15), 2971–2980.
[6] Galván, L., Olías, M., Cánovas, C.R., Torres, E., Ayora, C., Nieto, J.M., and Sarmiento, A.M., 2012, Refining the estimation of metal loads dissolved in acid mine drainage by continuous monitoring of specific conductivity and water level, *Appl. Geochem*., 27 (10), 1932–1943.
[7] Chen, T., Yan, B., Lei, C., and Xiao, X., 2014, Pollution control and metal resource recovery for acid mine drainage, *Hydrometallurgy*, 147-148, 112–119.
[8] Seo, E.Y., Cheong, Y.W., Yim, G.J., Min, K.W., and Geroni, J.N., 2017, Recovery of Fe, Al and Mn in acid coal mine drainage by sequential selective precipitation with control of pH, *CATENA,* 148, 11–16.
[9] U.S. EPA, 1993, *Wildlife Exposure Factors Handbook vol. I*, EPA/600/R-93/187a.
[10] U.S. Department of Health and Human Services, 2004, *Toxicological Profile for Copper, Agency for Toxic Substances and Disease Registry*, Division of Toxicology/Toxicology Information Branch, Atlanta, Georgia.
[11] Othman, A., Sulaiman, A., and Sulaiman, S.K., 2017, Carbide lime in acid mine drainage treatment, *J. Water Process Eng*., 15, 31–36.
[12] Blake, D.A., Blake, R.C., Khosraviani, M., and Pavlov, A.R., 1998, Immunoassays for metal ions, *Anal. Chim. Acta*, 376 (1), 13–19.
[13] Kurniawan, T.A., Chan, G.Y.S., Lo, W.H., and Babel, S., 2006, Physico-chemical treatment techniques for wastewater laden with heavy metals, *Chem. Eng. J.*, 118 (1-2), 83–98.
[14] Ayeche, R., and Hamdaoui, O., 2012, Valorization of carbide lime waste, a by-product of acetylene manufacture, in wastewater treatment, *Desalin. Water Treat*., 50 (1-3), 87–94.
[15] Sánchez-Andrea, I., Sanz, J.L., Bijmans, M.F.M., and Stams, A.J.M., 2014, Sulfate reduction at low pH to remediate acid mine drainage, *J. Hazard. Mater.,* 269, 98–109.
[16] Park, S.M., Yoo, J.C., Ji, S.W., Yang, J.S., and Baek, K., 2015, Selective recovery of dissolved Fe, Al, Cu, and Zn in acid mine drainage based on modeling to predict precipitation pH, *Environ. Sci. Pollut. Res*., 22 (4), 3013–3022.
[17] Harimu, L., Matsjeh, S., Siswanta, D., and Santosa, S.J., 2010, Separation of Fe(III), Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) metal ions using poly(eugenyl oxyacetic acid) as an ion carrier by a liquid membrane transport method, *Indones. J. Chem*., 10 (1), 69–74.
[18] Buhani and Suharso, 2006, The influence of pH towards multiple metal ion adsorption of Cu(II), Zn(II), Mn(II), and Fe(II) on humic acid, *Indones. J. Chem*., 6 (1), 43–4611.

[19] Shofiyani, A., and Gusrizal, 2006, Determination of pH effect and capacity of heavy metals adsorption by water hyacinth (*Eichhornia crassipes*) biomass, *Indones. J. Chem*., 6 (1), 56–60.
[20] Yanful, E.K., Wheeland, K.G., St-Arnaud, L., and Kuyucak, N., 1991, Overview of Noranda research on prevention and control of acid mine drainage, *AMIC Workshop*, Perth, Australia, October 1991.
[21] Kuyucak, N., 2000, Microorganisms, biotechnology and acid rock drainage – Emphasis on passive-biological control and treatment methods, *Miner. Metall. Process.*, 17 (2), 85–95.
[22] Hallberg, K.B., 2010, New perspectives in acid mine drainage microbiology, *Hydrometallurgy*, 104 (3-4), 448–453.
[23] Kolmert, Å., and Johnson, D.B., 2001, Remediation of acidic waste waters using immobilised, acidophilic sulfate-reducing bacteria, *J. Chem. Technol. Biotechnol.*, 76 (8), 836–843.
[24] Sampaio, R.M.M., Timmers, R.A., Xu, Y., Keesman, K.J., and Lens, P.N.L., 2009, Selective precipitation of Cu from Zn in a pS controlled continuously stirred tank reactor, *J. Hazard. Mater.,* 165 (1-3), 256–265.
[25] Fishbain, S., Dillon, J.G., Gough, H.L., and Stahl, D.A., 2003, Linkage of high rates of sulfate reduction in Yellowstone hot springs to unique sequence types in the dissimilatory sulfate respiration pathway, *Appl. Environ. Microbiol.*, 69 (6), 3663–3667.
[26] Kimura, S., Hallberg, K.B., and Johnson, D.B., 2006, Sulfidogenesis in low pH (3.8–4.2) media by a mixed population of acidophilic bacteria, *Biodegradation*, 17 (2), 159–167.
[27] Koschorreck, M., 2008, Microbial sulphate reduction at a low pH, *FEMS Microbiol. Ecol*., 64 (3), 329–342.
[28] Luptakova, A., Ubaldini, S., Macingova, E., Fornari, P., and Giuliano, V., 2012, Application of physical–chemical and biological–chemical methods for heavy metals removal from acid mine drainage, *Process Biochem*., 47 (11), 1633–1639.
[29] Meier, J., Piva, A., and Fortin, D., 2012, Enrichment of sulfate-reducing bacteria and resulting mineral formation in media mimicking pore water metal ion concentrations and pH conditions of acidic pit lakes, *FEMS Microbiol. Ecol*., 79 (1), 69–84.
[30] Retnaningrum, E., and Wilopo, W., 2017, Removal of sulphate and manganese on synthetic wastewater in sulphate reducing bioreactor using Indonesian natural zeolite, *Indones. J. Chem.*, 17 (2), 203–210.
[31] Wang, L.K., Hung, Y.T., and Shammas, N.K., 2009, *Handbook of Advanced Industrial and Hazardous Wastes Treatment*, CRC Press, Boca Raton, FL.
[32] Fu, F., and Wang, Q., 2011, Removal of heavy metal ions from wastewaters: A review, *J. Environ. Manage*., 92 (3), 407–418.