Combination of CaCO$_3$ and Ca(OH)$_2$ as agents for treatment acid mine drainage

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Abstract. Acid mine drainage (AMD) has characteristic very low pH solution and containing metal ions in high concentration. This paper presents the use of CaCO$_3$, Ca(OH)$_2$ and the combination of both to increase the pH and decreased the concentration of Fe and Mn ions for acid mine drainage. The research variables are the effect of reactant dosage, contact time and temperature by batch studies. The AMD before treatment has pH solution of 3.38, Fe and Mn ions concentration of 44.6 and 7.19 mg/L, respectively. The dosage of CaCO$_3$ to increased pH solution about 7.0 was found 2400 mg/L at contact time 60 minutes and temperature 40 ^{0}C. The amount of Ca(OH)$_2$ for the neutralization of AMD solution smaller than CaCO$_3$ is 210 mg/L at contact time 45 minutes and temperature 40 ^{0}C. The combination dosage of CaCO$_3$ 1000 mg/L and Ca(OH)$_2$ 90 mg/L can increased the pH of AMD solution to 7.10 and reduction concentration of Fe to 3.53 and Mn to 4.51 mg/L. Therefore, the integrated of CaCO$_3$ and Ca(OH)$_2$ has the potential to be applied to treatment acid mine drainage.

1 Introduction

Acid mine drainage (AMD) is an important problem in the environment and a serious concern in many countries. The AMD contains of heavy metal from the oxidation of sulphidic minerals and producing low of pH solution. The treatment of AMD must be done on the exhaust into the environment because this substance is harmful to aquatic life at low concentration, not biodegradable and media surroundings. The AMD contains a lot of heavy metal ions such as Cu^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}. The heavy metal ions are not biodegrable and tends to accumulate in the bodies in living organis [1]..

The AMD solution usually is orange colour from precipitation of iron oxide and hydroxide [2]. Characteristic of AMD of each region is different depending on typical mine water for the individual deposits [3]. The characteristic of AMD solution is influenced by several factors such as bacteria, temperature, starting pH and alternative oxidants like iron or manganese [4].

The treatment of AMD must be efficient and continual [5]. The method is often used for AMD treatment is oxidation, coagulation/flocculation, neutralization and precipitation of metal ions. The oxidants for the AMD such as Ca(OCl)$_2$, NaClO, CaO$_2$, H$_2$O$_2$, whereas coagulands often to treatment of AMD are Al$_2$(SO$_4$)$_3$, FeSO$_4$, Fe$_2$(SO$_4$)$_3$, NaAlO$_2$ [2].

Some materials can be used for the neutralization process such as CaCO$_3$ [3, 6], Mg(OH)$_2$ [7], fly ash [8], NaOH [9]. The use of CaCO$_3$ for the neutralization process of AMD was patented by the US Geological Survey Leetown Science Center [10]. It has been reported that the pH of AMD treatment using CaCO$_3$ (limestone) more economical but slow rate of dissolution with effectiveness $\pm$ 30%) [11]. The other research, effect neutralization of AMD with limestone in the reactor during 48 hours produced an armor coating in the bottom [6]. It causes the decline in the effectiveness of the use of CaCO$_3$. Two step reaction process of limestone with sulfuric acid in the AMD as follows:

$$CaCO_3 + H_2SO_4 \rightarrow CaHSO_4^+ + HCO_3^- \qquad (1)$$
$$HCO_3^- + CaHSO_4^+ \rightarrow CO_2 + H_2O + CaSO_4 \qquad (2)$$
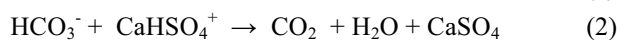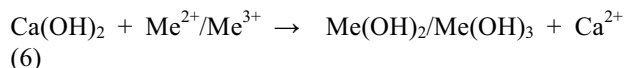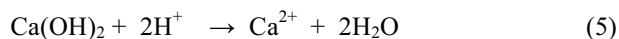
At the end of the reaction occurs of precipitated calcium sulfate. The other studies have shown that calcium carbonate to raise the pH by consuming hydrogen ions and adding alkanity to form bicarbonate ions, according the following reaction: [12]

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2 \qquad (3)$$
$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \qquad (4)$$
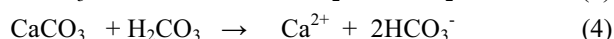
The metal ions can be precipitate to form hydroxides or oxyhydrosides.

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Several methods have been developed for treatment of AMD. In this paper, integrated of limestone ($CaCO_3$) and hydrated lime ($Ca(OH)_2$) was used for neutralization of AMD solution. Effectiveness $Ca(OH)_2$ for AMD treatment three times greater than $CaCO_3$, but the cost of processing using these materials more expensive [11]. Hydrated lime has the ability to raise the pH quickly and precipitate the metal ions as hydroxide such as manganese at pH 9 to 9.5. Reaction of $Ca(OH)_2$ with hydrogen ions or metal ios as follow: [13]

$$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_2O \qquad (5)$$
$$Ca(OH)_2 + Me^{2+}/Me^{3+} \rightarrow Me(OH)_2/Me(OH)_3 + Ca^{2+} \qquad (6)$$

The other research, the use of $CaCO_3$ on AMD treatment can increase the pH solution from 2.9 to over 7 at the contact time of 48 hours [6]. Beside that, the addition of $Ca(OH)_2$ do not only neutralized, but also the OH^- anionic ions increased the rate of speciation with reaction to metal ions and increased the pH of AMD. $CaCO_3$ and $Ca(OH)_2$ can also destabilize the hydrolysis of acid mine drainage so that the value of TSS decrease [14].

At present, the combination of $CaCO_3$ and $Ca(OH)_2$ to treatment of AMD $_2$ is expected to increase the pH and reduction the heavy metal ions at the faster contact time. $Ca(OH)_2$ has a greater solubility than $CaCO_3$ are 1850 and 14 mg/L, respectively [7]. The parameters of studied are the effect of reactant dosage, contact time and temperature by batch studies.

2 Experimental details

2.1.1 Materials

The reagents such as $CaCO_3$, $Ca(OH)_2$ were analytical grade by Merck and all solution were prepare with deionized water. Acid mine drainage collected from a mine in Tanjung Enim, South Sumatera, Indonesia.

2.1.2 Effect of dosage, contact time and temperature

The effect of dosage was added of $CaCO_3$ and $Ca(OH)_2$ to 1 L of AMD solution at constant stiring (120 rpm) at room temperature for 60 minutes. The amount of $CaCO_3$ was added from 100-2500 mg/L (interval 100 mg) and $Ca(OH)_2$ 10-240 mg/L (interval 10 mg). The data of effect contact time obtained from 0-100 minutes with interval 5 minutes. The effect of the temperature was performed using thermostatic water bath at temperature of 30-90 ^{0}C. Data is the observed pH of the solution. The pH solution is obtained using pH meter Orion star A2111.

### 2.1.3 Neutralization of AMD using combination $CaCO_3$ and $Ca(OH)_2$

For this purpose $CaCO_3$ and $Ca(OH)_2$ were added to 1 L of AMD. The amount of $CaCO_3$ 1000 mg while the $Ca(OH)_2$ in the range 10-120 mg (interval 10 mg) with contact time and temperature using the latest result of previous studies. Determination of metal ions (Fe and Mn) in AMD before and after treatment were determined using Atomic Absorption Spectroscopy Shimadzu AA 7000 with atomization by N_2O-acetilene flame. The wave number for obtaining Fe and Mn ions at 248.3 and 279.8 nm, respectively.

3 Result and discussion

There are two technologies for treatment of acid mine drainage (AMD), these are active treatment and passive treatment processes. The active treatment method is the addition of chemicals to raise the pH and precipitate the metal ions. The active treatment using chemical reagents. This method is very effective for the treatment of AMD. The passive treatment includes aerobic and anaerobic wetland. This method is natural process.

In traditional treatment of AMD, $CaCO_3$ has been used for neutralization of AMD in many countries. There used in anoxic limestone drain and open limestone channel [9]. In this study, the combination of $CaCO_3$ and $Ca(OH)_2$ to treatment of AMD was evaluated. Before integrating of both, investigated the optimum conditions of treatment in each material includes the effect of dosage of $CaCO_3$ and $Ca(OH)_2$, contact time and temperature.

Neutralization of AMD using $CaCO_3$ and $Ca(OH)_2$ are presented in Fig 1. and Fig 2. The AMD solution has initial pH of 3.38. The AMD is classified as types of 1 that has pH solution very lower. In the AMD, pyrite is oxidized to soluble iron and sulphuric acid as follows : [15]

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \qquad (7)$$
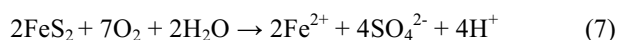
Fe^{2+} is oxidaxed to Fe^{3+} by oxygen and hydrogen and oxidation of sulfure by Thiobacillus and Ferroplasma bacteria.

The oxidation process is influenced by pH solution, this reaction occurs fast at low pH (<4). Ferrous hydroxide formed is namely *yellow boy*. [5,16]

$$2Fe^{2+} + 7O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4H_2O \qquad (8)$$
$$4Fe^{3+} + 12 H_2O \rightarrow 4Fe(OH)_3 + 12H^+ \qquad (9)$$
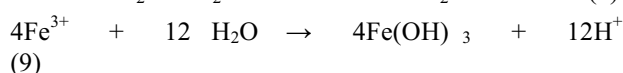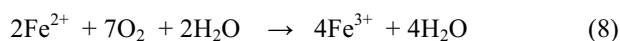
The result obtained that the increased dosage of $CaCO_3$ and $Ca(OH)_2$ increased of pH and reached at pH 7 on the addition $CaCO_3$ of 2400 mg while $Ca(OH)_2$ of

210 mg. Ca $(OH)_2$ has the ability to increase the pH solution of AMD better than $CaCO_3$. The positive correlation that fact with increasing dosage of neutralization agents, more hydrogen ions can be neutralized using $CaCO_3$ and $Ca(OH)_2$.

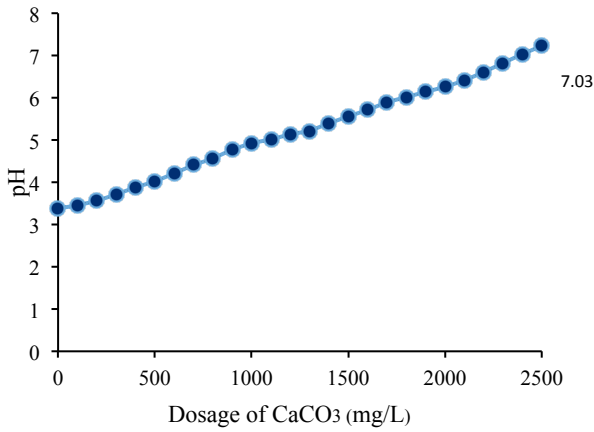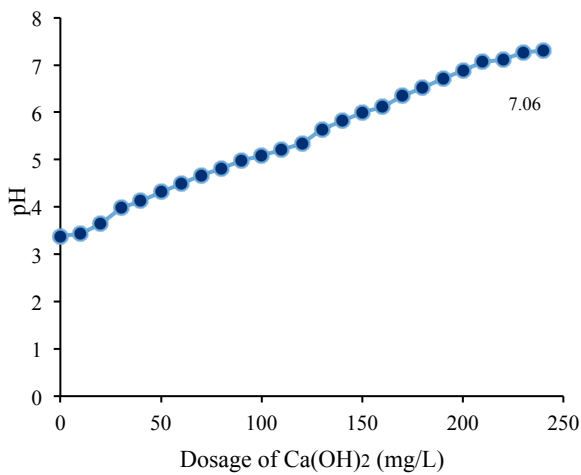**Fig. 1.** Effect of dosage $CaCO_3$ for pH solution

Fig. 2. Effect of dosage $Ca(OH)_2$ for pH solution

The both of agents have the same acid equivalent is 2 but $Ca(OH)_2$ has an efficiency factor of 0.8 higher than $CaCO_3$ of 0.4 [17]. Efficiency factor is an empirical estimate for neutralizing acidity. Besides than, $Ca(OH)_2$ is a strong alkaline has a neutralization efficiency of 90 % greater than $CaCO_3$ only 30 % [11]. The alkaline necessary to raise the pH solution and produce hydroxide to precipated with metal ions.

Table 1 shows some of the materials used to raise the pH solution of AMD. Compared to the data in table, the results of this research requires fewer doses to increase pH of AMD. The type and dosage of materials have effect to the increase of pH solution.

Figure 3 showed effect contact time of $CaCO_3$ and $Ca(OH)_2$ on the neutralization of AMD. The data obtained that the equilibrium time required for the neutralization was almost 60 minutes for $CaCO_3$ and 45 minutes for $Ca(OH)_2$.

Table 1. The materials to treatment of AMD

Materials	Dosage	pH of Acid mine drainage	
		Initial pH	Final pH
$Mg(OH)_2$ [7]	0.25 g/L	3.4	8.3
$Ba(OH)_2.8H_2O$ [7]	7.35 g/L	3.4	12
Fly ash [8]	AMD:Fly ash (2:1)	2.7	11.5
Fly ash [8]	AMD:Fly ash (1:1)	2.7	11.5
Fly ash [8]	AMD:Fly ash (3:1)	2.7	9.5
Limestone [6]	-	2.9	6.5
Bentonite [18]	1 g/L	2.7	7.5

The contact time affect the number of hydrogen ions that can be neutralized by chemical agents. The longer the contact time so the more hydrogen ions that can be neutralized. From the result, the neutralization using $Ca(OH)_2$ faster than $CaCO_3$. In this work indicated that an increase in contact time resulted in increased of pH solution. After the equilibrium time, the pH relatively constant at pH 7. It is clear that the pH value dependence of contact time. The longer of the contact time, the more neutralization process. Furthermore, pH relatively constant at about pH 7 for a limited amount of reagents.

To compare the other research, the optimal dosage to reach at pH 7 on acid mine water in the locality of Jiří Mine in the Sokolov Region is 150 mg/L of $Ca(OH)_2$ with contact time 30 minutes [3]. The reduction of sulfate from AMD also dependent dosage of $CaCO_3$ and $Ca(OH)_2$. The research indicated that the relationship between sulfate solubilization and pH was direct and linear [19].
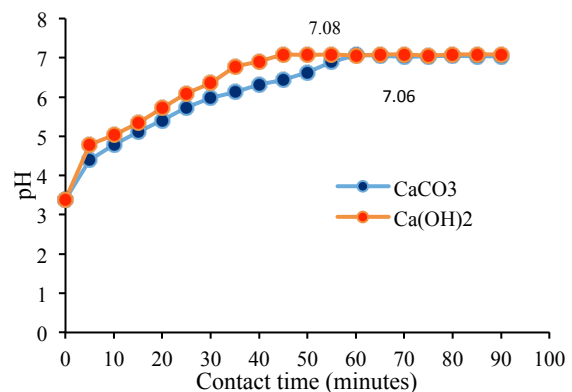

Fig. 3. Effect of contact time for Ph solution

The effect of temperature for AMD neutralization is presented in Fig 4. On evaluating the result, it was clear

that an increase of pH at the temperature 20-40 ^{0}C, and then the pH decreased at higher temperature. The solubility indicated the maximum concentration of substance that can be dissolved at solution (ussulaly at room temperature). Beside pH solution, the solubility of compound is also dependent by temperature. The increase of temperature so the greater solubility of compounds.
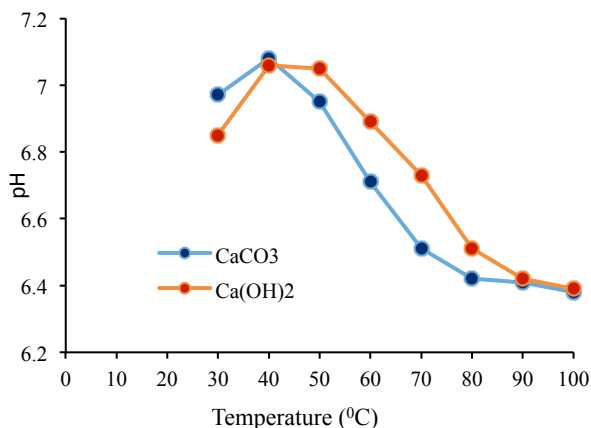

Fig.4. Effect of temperature for pH solution

The chemical reagents of $CaCO_3$ and $Ca(OH)_2$ have the same pattern of obtained pH 7 at temperature 40 ^{0}C. If the temperature is increased, the average kinetics also increases, it destabilized the solid state and thus the dissolve of the precipitate. This causes solubility of hydrogen ions and then the pH solution is decreased. The same result observed the influence of temperature for neutralization of AMD solution using NaOH. The optimum temperature at 20 ^{0}C, there was no change in pH at temperature 40 and 60 ^{0}C. The pH dropped to 2.2 at temperature 90 ^{0}C [9].
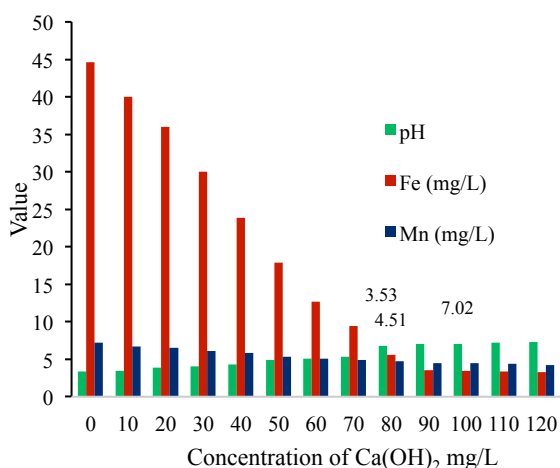

Fig. 5. Combination of $CaCO_3$ with $Ca(OH)_2$ to treatment of AMD solution

The combined of $CaCO_3$ and $Ca(OH)_2$ is expected to reduce the dosage of $CaCO_3$ and improve efficiency process and economical. The concentration of Fe and Mn ions in AMD solution during the addition of 1000 mg/L $CaCO_3$ and variation dosage of $Ca(OH)_2$ from 10-120 mg/L showed in Fig 5.

The process at contact time 45 minutes and temperature 40 ^{0}C. The AMD have contain of Fe is 44.6 mg/L while the Mn is 7.19 mg/L. Characteristic of AMD solution exceeds of acid mine drainage quality standard. The maximum of Fe is 7 mg/L, Mn is 4 mg/L and pH solution in the range 6-9 [20]. We can see that after neutralization using $CaCO_3$ and $Ca(OH)_2$ was reached Fe and Mn ions of 3.53 and 4.51 mg/L, respectively.

The pH solution increased from 3.38 to 7.02. The effectively decrease of Fe and Mn ions were 92.42 and 37.27 %. The effectivity to removal Fe ions from AMD greater than Mn ions. The oxidixed and precipitation of Fe ions about at pH 7.0 while Mn ions at higher pH is 8. The other studies shows that $CaCO_3$ and $Ca(OH)_2$ effectif to reduced TSS by mechanism coagulation and floculation [21]. The study also investigated interaction double layer metal ions on both reagents of the aqua-colloids.

The use of bottom ash, bentonite and fly ash to reduce the concentration of iron ions obtained at the optimum weight of 3, 4, 4 g in 100 mL of AMD solution, respectively [18]. In this study, has a smaller dosage than the result. Another study shows that adsorption capacity for adsorption of Mn ions in AMD is 6.03 mg/g using bone char [22].

The AMD solution is very complex, there is competition between the metal ions to form precipitate. The metal ions form precipitates depending value of Solubility Product Constant (KSP). The Ksp is the equilibrium constant, indicated that saturated solutions of ionic dissolving in an aqueous. The metal ions have small solubility product constants will be precipitated first. Example, Ksp $Fe(OH)_3 = 6.10^{-38}$ smaller than Ksp $Mn(OH)_2 = 2.10^{-13}$, so Fe ions to form precipitate earlier than Mn ions [23].

4 Conclusions

The combination of $CaCO_3$ and $Ca(OH)_2$ can be used for neutralization and reduce metal ions on acid mine drainage (AMD) solution. Integrated of both with a dosage of $CaCO_3$ 1000 mg/L and $Ca(OH)_2$ 90 mg/L can raise the pH solution from 3.38 to 7.02 and decrease of Fe and Mn ions with efficiency 92.42 and 37.27 %, respectively. In this study show that combination of $CaCO_3$ and $Ca(OH)_2$ an effectif to treatment of AMD.

References

1. N. Moreno, X. Querol, X., C. Ayora. Environm. Sci. and Tech., **35**, 3526-3534 (2001)
2. T. Motsi. Thesis. University of Birmingham, United Kingdom (2010)
3. D. Kirby. Dissertation. Marshall University, Virginia (2014)
4. S. Heviankova, I. Bestova, M. Kyncl, L. Simkova, M. Zechner. J. of the Polish Mineral Eng. Soc., 159-166 (2013)
5. C. Zipper, J. Skousen, C. Jage. Virginia Cooperative Extension. Powell River Project, 1-14 (2011)
6. J.M. Hammarstrom, P.L. Sibrell, H.E. Belkin, Appl. Geochem., **18**, 1705-1721 (2003)
7. V. Bologo, J.P. Maree, C.M. Zwinovanda. Proceeding of the International Mine water Conference, Pretoria, South Africa, 372-380 (2009)
8. V.R.K. Vadapalli, M.J. Klink, O. Etchebers, L.F. Petrik, W. Gitari, R.A. White, D. Key, E. Iwuoha, S AFR J SCL, **104**, 317-322 (2008)
9. E. Michalkova, M. Schwarz, P. Pulisova, B. Masa, P. Sudovsky, Pol. J. Environt Stud., **22(4)**, 1111-1118 (2013)
10. B.J. Watten. US patent No. 5.914.046. US Department of Commerce, Washington DC, (1999)
11. J. Skousen. T. Hilton, B. Faulkner, American Society of Agronomy and the American Society for Surface Mining and Reclamation, (1997)
12. Y. Paul, S.A. Banwart, Hedin, S. Robert, Kluwer Academic Press, Netherlands, (2002)
13. B. Lottermoser, Springer Berlin Heilderberg, London-New York, (2010)
14. I.O. Ntwampe, F.B. Waanders, J.R. Bunt, J. Chem. Eng. Mater. Sci., **6(3)**, **15-33** (2015)
15. C.N. Sawyer, Mc Catty, P.L., G.F. Parkin. Mc Graww Hill International Editions, (1994)
16. H.L. Yadav, A. Jamal, Intern. J. New Tech. Sci. Eng., **2(3)**, 77-84 (2015)
17. C.A. Cravotta, D.L. Parkhurst, B. Means, R. Mc Kenzie, W. Arthur. Proceeding of National Meeting of The American Society of Mining and Reclamation, Pittsburgh, PA Bridging Reclamation, Scince and the Community, 1413-1436 (2010)
18. E.O. Orakwue, V. Asokbunyarat, E.R. Rene, P.N.L. Lens, A. Annachhatre, Water Air Soil Pollut, **227(74)**, 1-12 (2016)
19. S. Rose, W. C. Elliot. Appl. Geochem., **15**, 27-34 (2000)
20. Governor Regulation in South Sumatera No 8 (2012).
21. I.O. Ntwampe, F.B. Waanders, J.R. Bunt, J. Chem. Eng. Mater. Sci., **6(3)**, 34-51 (2015)
22. D.C. Sicupira, T.T. Silva, A.C.Q. Ladeira, M.B. Mansur, Brazilian J. Chem. Eng., **32(02)**, 577-584 (2015)
23. W.B. Euler, L.J. Kirschenbaum, B. Ruekberg, Jour. Chem. Ed., **77(8)**, 1039-1040