A comparison of the acid mine drainage (AMD) neutralization potential of low grade nickel laterite and other alkaline-generating materials

C. Turingan, G. Singson, B. Melchor, R. Alorro, A. Beltran, A. Orbecido

Chemical Engineering Department, De La Salle University, 1004, Philippines

Department of Mining Engineering and Metallurgical Engineering, Faculty of Science and Engineering, Curtin University, Australia

*e-mail: aileen.orbecido@dlsu.edu.ph

Abstract. Acid mine drainage (AMD) is a serious environmental problem caused by the weathering of sulfur-rich minerals found in mine sites, typically pyrite. Passive treatment methods have been extensively studied exploring various materials and treatment systems. Limestone is typically used as neutralizing media through open channels or anoxic limestone drains. However, the armouring that occurs when heavy metals precipitate on the surface restricts the lifespan of limestone treatment systems to 15-20 years. Goethite has been characterized to be a good adsorbent of heavy metals found in wastewater. It is abundant in a layer of nickel laterite deposit which are considered mine wastes due to the low amount of nickel present. This study investigates the performance of locally available nickel laterite ore rock, limestone, fly ash, and cement waste as media for AMD neutralization. The treatment efficiency are evaluated based on the physiochemical properties of the AMD, namely: pH, redox potential (ORP), conductivity, total dissolved solids (TDS), and dissolved oxygen (DO).

Keywords: nickel laterite, fly ash, cement waste, acid mine drainage, passive treatment

Introduction

Philippines is the fifth most mineral-rich country in the world for gold, nickel, copper, and chromite with about nine million hectares of high mineral potential land (Quintans, 2017). However, these sites produce acid mine drainage (AMD), an environmental problem second only to climate change according to the United Nations, as a byproduct of the mining process. The oxidation of the ores leads to the formation of sulfates which turns the water acidic allowing it to dissolve various heavy metals along its path. Pyrite (FeS₂) is one of the most common sulfide minerals involved in AMD generation. Eq. 1-3 shows the chemical reactions that allow the formation of AMD at different environments (Kefeni et al., 2017; Pierre Louis et al., 2015; Chen et al., 2015):

\[
\begin{align*}
\text{FeS}_2 + 15/4\text{O}_2 + 1/2\text{H}_2\text{O} & \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + \text{H}^+  \\
\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} & \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+  \\
\text{FeS}_2 + 15/2\text{O}_2 + 7/2\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+
\end{align*}
\]

Eq. 1 shows the oxidation reaction which occurs when the water supply is limited. In the presence of excess water, Eq. 3 makes use of Fe³⁺ as an oxidizing agent and proceeds at a faster rate than Eq. 2. So, while AMD may form under natural circumstances, the exposure of pyrite due to mining heightens the problem to a degree wherein the contamination of bodies of water consequentially endangers the surrounding flora and fauna (Simate & Ndlovu, 2014). Therefore, treatment of acid mine drainage discharge is necessary during and after operations in a mining site.

Acid mine drainage treatment can be achieved through the conventional chemical treatments or the use of passive treatment systems. Passive treatments include but not limited to anoxic and oxic limestone drains (ALD, OLD), open limestone channel (OLC), and successive alkalinity-producing
system (SAPS) (Bernier, 2005). Limestone has been the traditional treatment media used in passive treatment since it is a safe and cheap alternative. However, its use is limited by its low solubility and armoring, that occurs when the heavy metals found in AMD precipitate on the surface of the limestone, rendering the treatment media inert (Skousen et al., 2019). Other alternatives such as blast furnace slag (Feng et al., 2004), fly ash (Petrik et al., 2003; Potgieter-Vermaak et al., 2005), and serpentinite (Bernier, 2005; Kamal and Sulaiman, 2014) were also investigated. Petrik et al. (2003) and Potgieter-Vermaak et al. (2005) stated that fly ash alone can be used to neutralize acid mine drainage and can be considered as a cost effective alternative alkaline generating material for AMD treatment. Additionally, serpentinite as an alternative for AMD neutralization is also possible but would need more studies to be conducted (Bernier, 2005).

In this paper, a comparative study was conducted to determine the efficiency of various alternative alkaline-generating materials such as low-grade nickel laterite ore, limestone, fly ash, and cement waste in the neutralization of acid mine drainage. The study aims to evaluate the treatment efficiency of the locally available waste materials in relation to limestone. The increase in pH and other physicochemical properties, namely: redox potential (ORP), dissolved oxygen (DO), total dissolved solids (TDS), and conductivity, are compared for the different materials using a synthetic AMD solution.

Materials and Methods

Materials Low grade nickel laterite ores (LGO), characterized by having less than 1.4% Ni, and limestone were collected from a nickel ore mine site in Agusan del Norte, Philippines. Cement waste was obtained from a local construction site in Manila, Philippines. Fly ash was obtained from a coal-fired power plant located in Bataan, Philippines.

The synthetic AMD was prepared with analytical grade reagents shown in Table 1. The physicochemical properties of the solution were the following: a pH of 2.25, oxidation-reduction potential (ORP) of 268.9 mV, dissolved oxygen (DO) concentration of 4.75 mg/L, total dissolved solids (TDS) of 2.660 parts per thousand (ppt), and a conductivity of 5.427 mS/cm.

| Table 1. Reagents needed for synthetic AMD preparation |
|------------------------------------------------------|
| **Reagents** | **Mass (g)** |
| FeSO₄•7H₂O | 65.46 |
| Al₃(SO₄)₁₈H₂O | 17.28 |
| NiSO₄•6H₂O | 9.39 |
| CuSO₄•5H₂O | 1.4 |
| MnSO₄•H₂O | 1.4 |
| MgSO₄•7H₂O | 1.4 |
| 1.5 M H₂SO₄ | 60 mL |

Methodology Jar test (Lovibond Floc Tester) was used to evaluate the efficiency of the alkaline-generating materials in neutralizing synthetic AMD using various water/rock ratios of 0.75, 1.0, 1.5, and 2.0 mL/g. Four beakers were filled with 200 mL synthetic AMD solution along with the corresponding amounts of the alkaline-generating materials based on the ratio. The mixture was steadily stirred using the jar test apparatus for 60 min at 180 rpm (Fig. 1). All the tests were conducted in duplicates. Afterwards, the mixtures were allowed to settle for 30 min before filtering and collecting
50 mL of the supernatant for analysis. The pH and ORP were measured using Orion Star A211 pH Benchtop meter. Orion Star A212 Conductivity was used to measure the conductivity and total dissolved solids, while the dissolved oxygen concentration was measured using Orion Star A213 DO meter.

![Figure 1](image)

**Figure 1.** Jar test of various alkaline-generating materials

### Results and Discussion

#### Change in pH and ORP

The study makes use of the same materials as Fabella & Sadol (2019) and Tigue et al. (2018); unfortunately, no data was available on the chemical composition of the cement waste. Table 2 shows a summary of the chemical composition of the materials in comparison to other studies. Masindi et al. (2017) reports a similar calcium content for limestone – a calcium carbonate (CaCO₃) mineral. Tigue et al. (2018) uses a sample of fly ash wholly different than what was used by Jones & Cetin (2017).

**Table 2.** Oxide Content by % weight of LGO, limestone, and fly ash

| Material   | LGO | Limestone | Limestone | Cement Waste | Fly Ash | Fly Ash |
|------------|-----|-----------|-----------|--------------|---------|---------|
| Author     | Fabella, D. & Sadol, K. (2019) | Masindi et al. (2017) | Jones, S. & Cetin, B. (2017) | Tigue et al. (2018) |
| Al₂O₃      | 4.19 | 0.93      | <0.01     | 3.20          | 25.50   | 8.55    |
| CaO        | 4.56 | 85.66     | 80.00     | 45.10         | 12.50   | 16.04   |
| Fe₂O₃      | 54.07| 7.59      | <0.01     | 6.10          | 13.70   | 44.63   |
| MgO        | 7.96 | 0.02      | 8.00      | 2.00          | 1.90    | n/a     |
| SiO₂       | 23.87| 1.78      | <0.01     | 37.90         | 50.40   | 24.65   |
| NiO        | 2.13 | 0.76      | <0.01     | n/a           | n/a     | n/a     |
| Others     | 3.22 | 3.26      | 12.00     | n/a           | n/a     | 6.13    |

Figure 2 shows consistent trends for all alkaline materials wherein the highest pH was attained when the water/rock ratio was lowest; however, the pH range of each material for different ratios is small. This indicates that the difference in the ratio of water and neutralizing material had minimal effect to the treatment of AMD. Moreover, the values reported were similar to those of other studies
(Fabella & Sadol, 2019; Jones & Cetin, 2017; Masindi et al., 2017) for each material despite the difference in methodology.

Assuming the cement waste used has a similar chemical composition to the one used by Jones & Cetin (2017), limestone is reported to have the highest alkaline content – calcium and magnesium – among the materials. LGO had the lowest alkaline content, which could explain its poor performance in neutralizing the AMD solution. Furthermore, the neutralization of AMD using LGO can be attributed to its metal hydroxide content, specifically goethite (FeOOH), which is the main component of LGO (Fabella & Sadol, 2019). Hydroxides of metals, such as magnesium, iron, bismuth, nickel, cobalt, and copper, also have the ability to neutralize acids (Encyclopaedia Britannica & Gaur, 2017). Nonetheless, the results show cement waste as the best neutralizing media in terms of pH followed by fly ash, then limestone. Additionally, the result obtained for the AMD treated with limestone was expected and was consistent with its capacity to neutralize acidic solution to a pH range of 6.0 to 7.5 (Pearson & McDonnell, 1975). Using fly ash increased the pH to around 9 despite having low alkaline content close to LGO. This indicates that a larger amount of the alkaline content of fly ash is free to react with the AMD solution contrary to that of limestone which only raised the pH above 6.
Meanwhile, Figure 3 shows that from a very high redox potential, treatment with fly ash and cement waste had greatly reduced the AMD solution’s redox potential to negative, while the redox potential of AMD treated with both LGO and limestone had very low but remained at a positive value. This is due to the fact that fly ash and cement waste were the materials that were able to raise the pH to at least above neutral (7) level. The negative ORP value for the AMD solution treated with both fly ash and cement waste could be further explained by the possible reaction of heavy metals with water to form metal precipitates (Fabella & Sadol, 2019). For the LGO and limestone-treated AMD solution, it was still considered to be acidic as its pH did not go beyond 7, thus, oxidizing agents would still be present in the solution.

Figure 4. Conductivity as a function of water/rock ratio for different materials
Change in Conductivity and TDS The order of materials with respect to the magnitude of effluent conductivity and TDS is the same for pH as seen in Figure 2, 4, and 5. The AMD solution treated by cement waste shows a general downward trend, for fly ash maintains a relatively constant value, and for limestone and LGO, a higher AMD-to-media ratio results to lower values for both parameters. Figure 4 and 5 show similar graphs for conductivity and TDS which may be due to the use of one probe to measure both parameters. Different trends observed may indicate that each material neutralizes the AMD solution with varying mechanisms. Neutralization using limestone generally involves the dissolution of the alkaline material; hence, a smaller particle size is preferred (Mendelez et al., 2000). This may not be the case for LGO which is mainly composed of goethite (α-FeOOH) – a mineral known for its capacity to adsorb heavy metals (Fabella & Sadol, 2019).

Change in Dissolved Oxygen Figure 6 shows a decrease in the dissolved oxygen levels of the effluent at a lower ratio with the exception of LGO. There is minimal difference between the initial and final DO levels for the AMD samples treated with LGO. The change in DO levels is almost constant for the other three neutralizing media. Given the aerobic nature of the jar test, no definite conclusion can be drawn from Figure 6. Nevertheless, it may be indicative of the aforementioned difference in neutralization mechanism.
Conclusions

Acid mine drainage is commonly treated with the use of passive systems wherein naturally occurring alkaline-generating materials such as lime is used to neutralize the acidic water and eventually promoting heavy metal removal through precipitation. However, such materials are deemed unsustainable due to high economic costs. These costs can be usually reduced by using alternative alkaline-generating materials such as low grade nickel laterite ore (LGO), limestone, fly ash, and cement waste. In addition, the use of these materials also helps waste minimization in other industries such as fly ash which is a by-product of coal combustion and cement waste which is cement blocks commonly found in construction sites.

This study showed that the AMD solution is best neutralized using a ratio of 0.75 mL/g. Limestone, fly ash, and cement waste were all successful in raising the pH of the synthetic AMD solution to at least neutral level (7.0) in a duration of 60 minutes reaction time. Cement waste was the best performing alkaline-generating material as it successfully raised the AMD solution to at most pH 12.51 followed by fly ash and limestone. Lastly, LGO had a poor performance in neutralizing the synthetic AMD solution as it only managed to raise the pH to a maximum of 4.71. This is explained by the possible pyrite dissolute coming from the nickel laterite since it may contain goethite minerals (Butt and Cluzel, 2013). Yet, its effluent had the lowest levels of conductivity and TDS signifying lower amounts of heavy metals remaining after treatment.

This investigation proved that among the four materials, cement waste and fly ash can be considered as cost effective alternative alkaline-generating materials for neutralizing acid mine drainage. Moreover, the capability of LGO may be coupled with the neutralization potential of the other materials to address the acidity and high heavy metal content of AMD in mine sites. If integrated before the more alkaline-generating materials, armoring may be lessened which can result to passive treatment systems with longer lifespans.

The minimal difference in pH as the ratio changes show that each material may be capable of neutralizing more AMD while achieving the same effluent characteristics. Further studies are recommended to determine the maximum treatment capacity of each material before seeing a decrease in efficiency. Also, the treatment mechanism of each material, especially LGO, may be investigated to aid the design of treatment systems that would make use of the different media.

References

Bernier, L.R. (2005). The potential use of serpentinite in the passive treatment of acid mine drainage: batch experiments. Environmental Geology, 47(5), 670-684. https://doi.org/10.1007/s00254-004-1195-9
Butt, C.R.M., & Cluzel, D. (2013). Nickel laterite ore deposits: weathered serpentinites. Elements, 9(2), 123-128. https://doi.org/10.2113/gselements.9.2.123
Chen, M., Lu, G., Guo, C., Yang, C., Wu, J., Huang, W., Yee, N., Dang, Z. (2015). Sulfate migration in a river affected by acid mine drainage from the Dabaoshan mining area, South China. Chemosphere, 119, 734–743. doi:10.1016/j.chemosphere.2014.07.094
Feng, D., van Deventer, J.S.J., & Aldrich, C. (2004). Removal of pollutants from acid mine wastewater using metallurgical by-product slags. Separation and Purification Technology, 40(1), 61-67. https://doi.org/10.1016/j.seppur.2004.01.003
Fabella, D. & Sadol, K. (2019). Synthetic acid mine drainage treatment using low-grade ore from nickel laterite mines. (Unpublished bachelor thesis). De La Salle University, Manila, Philippines
Jones, S. N., & Cetin, B. (2017). Evaluation of waste materials for acid mine drainage remediation. Fuel,188, 294-309. doi:10.1016/j.fuel.2016.10.018.
Kamal, N.M., & Sulaiman, S.K. (2014). Bench-scale study of acid mine drainage treatment using local neutralisation agents. Malaysian Journal of Fundamental and Applied Sciences, 10(3), 150-153. https://doi.org/10.11113/mjfas.v10n3.272
Kefeni KK, Msagati TAM, Mamba BB, Acid mine drainage: prevention, treatment options, and resource recovery: A review, Journal of Cleaner Production (2017), doi: 10.1016/
Acknowledgments

This is to acknowledge the financial support provided by the Department of Science Technology (DOST) Philippine Council for Industry, Energy and Emerging Technology Research and Development (PCIEERD) given under the 3R Program.