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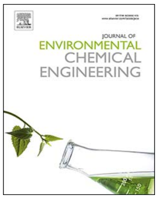

Research paper

Comparison of mine water neutralisation efficiencies of different alkaline generating agents

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ABSTRACT

Acid mine drainage is formed from the oxidation and hydro-geo-chemical weathering of sulphide bearing minerals. These minerals originate from mining and natural processes. This has led to the formation of a very acidic mine drainage enriched with Al, Fe, Mn and sulphate. The low pH of mine water promotes the leaching of residual toxic and hazardous chemical species from the surrounding parent rocks. Due to the potency of AMD to harm the environment and degrade its intrinsic values, this mine effluent requires a prudent management and an effective treatment option prior release to different receiving compartments of the environment. The present study was therefore designed with the aim of evaluating the efficiencies of different alkaline generating agents for acid mine drainage (AMD) treatment. To fulfil the goals of this study, a comparative study was undertaken using limestone, lime, hydrated lime, magnesite, periclase, brucite, soda ash and caustic soda. Bench scale laboratory studies were undertaken. The experiments were done at 60 mins of mixing, 1 g: 100 mL S/L ratios, and ± 25 °C room temperature and mixing at 650 rpm using overhead stirrers. The experimental results revealed that the pH of AMD increased after contacting different neutralizing agents. Chemical species were also removed from an aqueous system using different agents. Using pH as an indicator, the neutralisation efficiencies varied as follow: caustic soda ≥ hydrated lime ≥ lime ≥ cryptocrystalline magnesite ≥ periclase ≥ soda ash ≥ brucite ≥ limestone. This study advised on the best and effective pre-treatment agents and options that can be used by different mining houses.

1. Introduction

The environment has been severely affected by the release of acid mine drainage (AMD) to different environmental compartments. This has led to a long-term impairment and degradation of terrestrial and aquatic ecosystems [1]. AMD results from the bio-hydro-geochemical weathering of pyrite (FeS_2) (Eqs. (1)–(3)) and other reactive sulphide-bearing minerals when exposed to oxidising conditions [2–8]. The formation of AMD can be represented by the following reactions Eqs. (1)–(3)) [2,9–13]:

$$2FeS_{2(s)} + O_{2(g)} + 2H_2O_l \rightarrow 2Fe^{2+}_{(aq)} + 4SO^{2-}_{4(aq)} + H^+_{(aq)} \quad (1)$$

The oxidation of sulphide to sulphate solubilises the ferrous iron (Fe(II)) (Eq. (1)), which is subsequently oxidised to ferric iron (Fe(II)) (Eq. (2)):

$$4Fe^{2+}_{(aq)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 4Fe^{3+}_{(aq)} + 2H_2O_{(l)} \quad (2)$$

These reactions can occur spontaneously or can be catalysed by microorganisms (Sulphur and iron oxidising bacteria) that derive energy from the oxidation reaction. The ferric cations produced can also oxidise additional pyrite and itself being reduced into ferrous ions (Eq. (3)):

$$FeS_{(s)} + 14Fe^{3+}_{(aq)} + 8H_2O_{(l)} \rightarrow 15Fe^{2+}_{(aq)} + 2SO^{2}_{4(aq)} + 16H^+_{(aq)} \quad (3)$$

The net effect of these reactions is to produce H^+ and maintain the solubility of the ferric iron. This has led to the formation of acidic mine drainage that is characterised of pH ≤ 2, and high content of Fe (II) and (III), Al (III), Mn (II) and sulphate. High acidity in the resultant water increases the solubility, mobility and bio-availability of toxic and hazardous chemical species, thus, raising their concentration to unacceptable and often toxic levels as reported by different toxicological studies [2,14–16]. As such, the release of this drainage to adjacent

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surface and subsurface ecosystems can adversely affects the water quality and its ability to support life [17]. The most visual legacy of AMD is undoubtedly the precipitation of ferric (Fe^{3+}) hydroxide and oxy-hydroxide complexes as a yellow or orange coating in stream channels hence affecting the aquatic habitat and benthic organisms. These precipitates lead to a reduction of dissolved oxygen in affected water bodies during their formation, and ultimately the reduction in biodiversity [18,19].

In a quest for holistic and multidisciplinary approach, a number of treatment methods, both passive and active, have been developed, proposed and used for abating AMD [14,15,20–25] and they include ion-exchange [26–28], adsorption [29–34], bio-sorption [35–39], neutralisation [24,40–45], coagulation and precipitation [46–51].

The extent of application of most of these methods has largely been limited by factors such as cost and generation of excessive secondary sludge that is toxic and expensive to dispose and efficiencies [9,11,15,27,52–55]. To date, precipitation technologies have been predominantly used in the treatment of acid mine drainage due to their versatility, ability to treat large volume of water, easiness to recover valuable minerals [7]. Adsorption and ion exchange have shortcomings in terms of selective removal of pollutants, poor performance at high concentration and regeneration demands [56]. Membranes are effective but energy intensive and they generate brines that cause another environmental problem that requires disposal permits and costs [11].

Limestone has been the commonly used as a main feed for acid mine drainage neutralisation but it has a challenge of raising the pH to < 7 which is not suitable for the removal of all the pollutants in mine water [57]. It also generates a heterogeneous and complex sludge that is difficult to recover [58]. Low solubility of limestone and lime will also affect their suitable since they compromise the efficiency of the plant. Caustic soda has been applied for the recovery of magnetite. It has good neutralisation capacity but can only raise the pH < 10 [7]. Soda ash and caustic soda has the cost implications. Magnesite has the advantage of raising the pH to > 10 which suitable for the removal of all the metals. It has an advantage of forming a magnesium sulphate complex hence making it much easier to recover metals. This materially is readily and locally available in South Africa [17,59] hence making it the best replacement for limestone and lime.

This study was, therefore, developed with the aim of appraising the efficiency of different alkaline generating agents for mine water pre-treatment. Several alkaline generating agents as pre-treatment options were used and they include: limestone, lime, hydrated lime, magnesite, periclase, brucite, soda ash and caustic soda. Potgieter-Vermaak, et al. [57] conducted a similar study but their work was only limited to limestone, dolomite and fly ash. This will be an update study. This study will also inform environmental engineers about the user-friendly pre-treatment option for membranes technology or a synergy of those.

2. Materials and methods

2.1. Materials

Field AMD samples were collected from Coal mine in Mpumalanga Province, South Africa. The samples were stored in closed High Density Polyethylene (HDPE) bottles to prevent further oxidation and precipitation of metals, and kept in 4 °C until utilisation in neutralisation experiments. Prior utilisation, the AMD samples were filtered through 0.4 μm perforated filter. The neutralisation reagents were of analytical grade from Lab consumables Pty (Ltd).

2.2. Quality control/quality assurance

A QC/A programme was established and implemented to ensure the production of trustworthy results. The QC/A process entailed conducting the experiments in triplicate and reporting the data as mean value. Data was considered acceptable when percentage difference within triplicate samples and percent error were below 10%. The analytical values below detection limit (BDL) were managed in according to EPA guideline [56]. The accuracy of the analysis was monitored by analysis of National Institute of Standards and Technology (NIST) water standards. Inter-laboratory analysis was also done to further verify the validity of the results.

2.3. Characterization

Aqueous samples were analysed using inductively coupled plasma mass spectrometry (ICP-MS) (7500ce, Agilent, Alpharetta, GA, USA). Elemental composition was determined using X-ray fluorescence (XRF). Morphology was determined using SEM-EDS (JOEL JSM − 840, Hitachi, Tokyo, Japan).

2.4. Batch experiments

2.4.1. Neutralization of AMD using different dosages

Arrays of published studies have investigated the use of different alkaline generating agents for mine water treatment. However, time requirement to reach the desired pH is an issue of concern to designers and water process engineers. They require quick, effective and efficient reagents. In neutralization reaction, pH is the major factor that dictates the precipitation of difference chemical components in an aqueous system.

Potgieter-Vermaak, et al. [57] reported that 6 h of contact time is required for limestone and dolomite to raise the pH of mine water to > 7. Tolonen, et al. [60] documented that lime and hydrated lime can reach a maximum pH of 9.5 within 30 mins of equilibration on contact with AMD. Akinwekomi, et al. [7] pointed out that sodium carbonate can increase the pH of AMD to > 10 within an hour of equilibration. [61] reported that caustic soda can increase the pH of mine water to > 13 within an hour. Masindi [8] revealed that cryptocrystalline magnesite can increase the pH of acid mine drainage to > 10 at 60 mins of mixing. For the purpose of this study, it was therefore decided that the neutralization experiments will run for a maximum time of 60 mins since all material can perform best except for limestone.

Aliquots of 1L, each of AMD, were pipetted into 1L beaker flasks and varying masses the required dosage (0–20 g) of alkaline reagents was added into the flask. The mixtures were mixed using an overhead stirrer for 60 min at > 250 rpm. The time was based on the optimum conditions reported by Masindi, et al. [17]. After mixing, the mixtures were filtered through a 0.45 μm perforated nitrate cellulose filter membrane. pH/EC/Temp and TDS were monitored using CRISON MM40 multimeter probe.

3. Results and discussions

3.1. Water reaction chemistry

3.1.1. Effect of different alkaline dosage on the pH of AMD

Variations of pH with varying dosages for different neutralization agents are shown in Fig. 1.

As shown in Fig. 1, there was an increase in pH with an increase in dosage. This may be attributed to dissolution of the feed chemicals and the release of hydroxyl ions (OH^-) (Eqs. (4)–(5)).

$$MgO + H_2O \rightarrow Mg^{2+} + 2OH^- \tag{4}$$

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \tag{5}$$

Caustic soda was observed to have increased the pH from 1.8 to: 2 at 1 g/L, 7 at 5 g/L, 12.9 at 10 g/L, 13.2 at 15 g/L and 13.3 at 20 g/L. After 10 g/L, there was no significant change in pH that was observed. Soda ash was observed to have increased the pH from 1.8 to: 1.9 at 1 g/L, 3.7 at 5 g/L, 6.6 at 10 g/L, 7.7 at 15 g/L, 9.2 at 20 g/L. Similar results were reported by Akinwekomi, et al. [7]. Periclase was observed to