

Alternative neutralisation materials for acid mine drainage treatment

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ARTICLE INFO

Keywords:

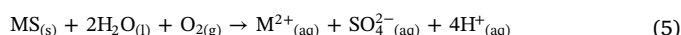
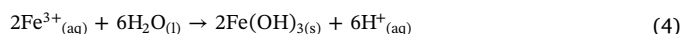
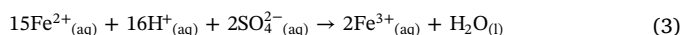
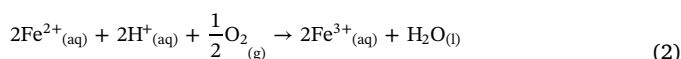
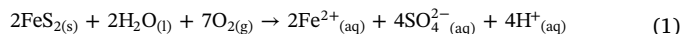
Acid mine drainage
Bauxite residue
Neutralisation
Bayer liquor
Bayer precipitates

ABSTRACT

This study reports the novel use of alkaline waste material from the alumina refining industry (Bayer liquor and precipitates formed by the seawater neutralisation of Bayer liquor), for the neutralisation of acid mine drainage (AMD) water. The hypothesis was that utilization of waste to treat waste can potentially result in environmental and economic benefits. The performance of Bayer liquor and Bayer precipitate was compared with conventional alkalis used for AMD neutralisation such as lime ($\text{Ca}(\text{OH})_2$), sodium hydroxide (NaOH), and sodium carbonate (Na_2CO_3). Target ions to remove from the AMD solution included Al (1233 mg/L), Cu (77.26 mg/L), Fe (16.7 mg/L), Ni (1.54 mg/L), Mn (161.5 mg/L) and Zn (48.89 mg/L). Both alumina industry wastes were shown to produce treated water with acceptable discharge limits for all metals except Mn. Nevertheless, Bayer precipitate was shown to have an enhanced ability to remove manganese at lower pH (6.5–7.5) relative to lime, with residual Mn concentrations of 32.30 and 85.40 mg/L, respectively. Manganese discharge limits were challenging to meet due to pH values > 9 being required wherein not only aluminium species redissolved but also the pH was not compatible with discharge regulations. Mechanistically, larger precipitates were found to positively influence the removal of heavy metals, with lime and Bayer precipitates forming the largest precipitates. Overall, Bayer precipitate was found to be a potential alternative for the treatment of AMD water.

1. Introduction

Acid mine drainage (AMD) is a challenging environmental problem created by numerous mining operations [1,2]. In the presence of oxygen, water and oxidising bacteria, the oxidation of pyrite and other sulphide minerals in mine wastes occur which leads to the formation of acid mine drainage [1,3]. The pyrite oxidation is a complex process resulting in release of hydrogen, sulphate and ferrous ions (Eq. (1)) [4]. In oxygenated water ferrous iron (Fe^{2+}) is oxidised to ferric iron (Fe^{3+}) (Eq. (2)) which either further reacts with pyrite to produce more ferrous iron and acidity (Eq. (3)) or precipitates as ochre ($\text{Fe}(\text{OH})_3$) (Eq. (4)) [4]. In waste rocks a variety of other metal sulphides can also be oxidised in the presence of oxygen and water (Eq. (5)) and may release metals such as arsenic, cadmium, zinc, copper and lead which can ultimately contaminate groundwater; making it unsuitable for drinking and agricultural purposes [5]. Nearby waterways can also be affected if run off events occur and situations exist wherein significant fish and crustacean kills have been observed due to low pH conditions [6,7]. The toxic characteristics of AMD can permanently damage surrounding ecosystems, thus suitable management and treatment methods to remediate affected water bodies are required [5].



The various methods used to treat acid mine drainage can be classified as active or passive systems based on their requirements for chemical addition, infrastructure, maintenance and monitoring. A variety of passive treatment systems such as aerobic wetlands, anaerobic or compost wetlands [8], vertical flow wetlands, AMD treatment ponds, bioreactors and permeable reactive barriers [5,9,10] are available to treat acid mine drainage. However, the requirement of relatively large land area, high installation cost and system failure (poor design, winter conditions or due to accumulation of metal hydroxides) are the major disadvantages associated with these treatment systems.

Active treatment methods of acid mine drainage water typically involve alkali addition in order to raise the pH to between 6 and 9 [11–13].

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In this latter pH range the concentrations of dissolved metals generally decreases due to the formation of insoluble metal hydroxides and oxy-hydroxides [14,15]. The rate and degree of metal precipitation depends upon their concentration, identity and complex interaction between dissolved species in water [16]. For example, in an oxygen rich environment the recommended pH for iron (Fe^{3+}) precipitation is 3.5–4.0, while in oxygen poor environments a pH of 8.5 is required [14]. Manganese (Mn) precipitation is dependent upon the oxidation state present, but will generally precipitate at pH 9, a value which is typically higher than recommended water discharge limits [14]. If the iron concentration in water is significantly higher than manganese, it may be removed with iron at pH 8 due to co-precipitation [14]. Aluminium (Al) generally precipitates at $\text{pH} \geq 5$ but this element enters back into solution at pH 9.0 as soluble aluminate ions ($\text{Al}(\text{OH})_4^-$) [17]. Therefore, increasing the pH to 9 to remove Mn can result in the dissolution of aluminium precipitates. Divalent metal ions such as nickel (Ni^{2+}) and zinc (Zn^{2+}) precipitate at pH values ranging from 8 to 9 [18]. Various alkalis like lime ($\text{Ca}(\text{OH})_2$), sodium hydroxide (NaOH), and sodium carbonate (Na_2CO_3) have been used to modify pH and remove heavy metals from AMD water as precipitates [19,20]. In some cases, limestone (CaCO_3) was employed and removed 90% of heavy metals such as Cd, Pb, Zn, Ni, Cu and Cr(III) from solutions at pH 8.5 [21].

Lime is arguably the most widely used alkali applied to remediate acid mine drainage solutions [22], due mainly to its relatively low cost, availability and simplicity of treatment plant [23]. A disadvantage of the process is the voluminous sludge that is produced; sludge typically settles slowly to 10% of the volume of water treated albeit as much as 50% sludge volume has been observed [23]. The combination of slow settling rate, low sludge density, and excessive volumes of sludge formed from the neutralisation process can result in a costly process.

Bosman [23] reviewed the variability of mine water and resultant sludge compositions, and the benefits of using high density sludge recovery methods to improve sludge characteristics. An analysis of AMD water compositions from six different South African mines showed large variations in pH (1.8–5.0), calcium (30–800 mg/L), magnesium (10–660 mg/L), ferrous iron (5–1250 mg/L), ferric iron (5–3350 mg/L), aluminium (2–200 mg/L) and sulphate (600–13390 mg/L); concentrations of heavy metals were not provided [23]. This variability in AMD water quality illustrates the difficulties in developing a single treatment process for all AMD waters. The problem is further escalated when variations in mine water compositions at the same mine site are considered, as reported by Edraki et al. [16] for ten water holding areas at Mount Morgan mine. The following variations were observed across the ten sites at Mount Morgan; pH (2.6–3.8), sulphate (8390–56240 mg/L), aluminium (209–3074 mg/L), calcium (426–514 mg/L), magnesium (1051–6101 mg/L), iron (13–1487 mg/L), sodium (106–830 mg/L), copper (3.27–138 mg/L), manganese (51.1–355 mg/L), and zinc (7.11–81.4 mg/L).

From the previous discussion, it can be seen that AMD solutions are inherently composed of many dissolved components [24] and thus the optimal alkali addition strategy may not be the same for all AMD types. Additionally, the question arises as to the potential benefits of employing alternate alkaline solutions or materials [19,25,26]. An innovative means of treating AMD solutions may involve the application of alkaline solutions or materials produced as waste products from other major industries. For example, bauxite refining produces large volumes of highly alkaline (pH 13) waste (1–1.5 t of red mud slurry produced for every tonne of alumina produced) [27,28]. Many researchers have reported the use of bauxite refinery residue (solid portion of red mud) to treat acid mine drainage; neutralisation of the acid and precipitation or adsorption of heavy metals, however large volumes of solid waste is produced that requires subsequent disposal and capping to prevent metals leaching [29–33]. Very little research has been completed on the use of red mud liquor and seawater derivatives (Bayer precipitate) to treat acid mine drainage [34], as well as comparisons of the performance of bauxite refinery wastes with commercially used

materials. Therefore, this research will focus on comparing the use of Bayer liquor and Bayer precipitates to treat AMD with conventionally used alkali.

Seawater neutralisation of Bayer liquor results in the formation of Bayer precipitates comprising of hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)_4\text{H}_2\text{O}$) and calcium carbonate species (CaCO_3) [35,36]. Due to the causticity of these waste materials, they may prove an interesting alternative to the traditional application of lime for treating AMD waters [11,34]. It is envisioned that the use of these “cleaner” wastes from bauxite residues will produce similar volumes of waste to traditional neutralisation agents, such as lime, with similar or improved metal removal capacities due to the presence of hydrotalcite in the Bayer precipitate (a known adsorbent material) [37]. The fact that a region such as Queensland contains not only a substantial bauxite refining industry [38,39] but also numerous acid mine drainage problems generated by the mining industry [40–42], makes this outlined approach attractive.

Therefore, the aim of this study was to compare the performance of Bayer liquor and Bayer precipitates, with respect to material requirements and discharge water quality, with commercially available alkali commonly used in the treatment of acid mine drainage water. The fundamental hypothesis was that waste alkaline materials may provide both performance and economic benefits in relation to AMD treatment. The research questions addressed were: (1) can the waste alkali materials raise the pH to the required levels to meet water discharge limits; (2) is it possible to reduce dissolved metal concentrations to satisfy regulations; and (3) what is scientific explanation for differences in performance for the various alkalis. The Australian and New Zealand Environment Conservation Council (ANZECC) guidelines were used to determine the required discharge water quality values for this study [43]. Bench scale tests were conducted using acid mine drainage water collected from the open pit at the abandoned Mount Morgan mine in Queensland, Australia. Lime neutralisation is currently being used at Mount Morgan to control the volume of AMD in the open pit to avoid overflow events [44]. This process involves the neutralisation of the mine pit water using slaked lime to increase the pH to between 6.5 and 8.5 to facilitate the precipitation of metals as metal hydroxides. After approximately 2 h of residence time in the neutralisation tanks, the slurry is dosed with a flocculating agent prior to clarification and disposal. The treated water is ultimately discharged into the adjoining Dee River if water quality requirements are met.

2. Materials and methods

2.1. Water quality standards

The ANZECC guidelines for fresh and marine water which were used to determine the effectiveness of the alkali addition strategies in this study are outlined in Table 1 [43].

In addition, sulphate ion discharge limit was assumed to be 1000 mg/L which is the upper limit for most environments and jurisdictions.

Table 1
ANZECC water quality guidelines relevant to Mount Morgan Mine Pit water.

| Water quality parameter | Agricultural irrigation water | Livestock drinking water |
|-------------------------|-------------------------------|--|
| pH | 6.5 to 8.5 | 6.5 to 8.5 |
| Al | < 5 mg/L | < 5 mg/L |
| Fe | < 0.2 mg/L | Not sufficiently toxic |
| Cu | < 0.2 mg/L | < 0.4 mg/L (sheep) < 1 mg/L (cattle) < 5 mg/L (pigs and poultry) |
| Ni | < 0.2 mg/L | < 1 mg/L |
| Mn | < 0.2 mg/L | Not sufficiently toxic |
| Zn | < 2 mg/L | < 20 mg/L |

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