# Alternative neutralisation materials for acid mine drainage treatment

Gurkiran Kaur, Sara J. Couperthwaite*, Bradley W. Hatton-Jones, Graeme J. Millar

*School of Chemistry, Physics & Mechanical Engineering and Institute for Future Environments, Science and Engineering Faculty, Queensland University of Technology (QUT), Brisbane, Queensland, 4000, Australia*

### 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 ($Ca(OH)_2$), 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 ($Fe(OH)_3$) (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].

$$2FeS_{2(s)} + 2H_2O_{(l)} + 7O_{2(g)} \rightarrow 2Fe^{2+}_{(aq)} + 4SO_4^{2-}_{(aq)} + 4H^+_{(aq)} \quad (1)$$

$$2Fe^{2+}_{(aq)} + 2H^+_{(aq)} + \frac{1}{2}O_{2(g)} \rightarrow 2Fe^{3+}_{(aq)} + H_2O_{(l)} \quad (2)$$

$$15Fe^{2+}_{(aq)} + 16H^+_{(aq)} + 2SO_4^{2-}_{(aq)} \rightarrow 2Fe^{3+}_{(aq)} + H_2O_{(l)} \quad (3)$$

$$2Fe^{3+}_{(aq)} + 6H_2O_{(l)} \rightarrow 2Fe(OH)_{3(s)} + 6H^+_{(aq)} \quad (4)$$

$$MS_{(s)} + 2H_2O_{(l)} + O_{2(g)} \rightarrow M^{2+}_{(aq)} + SO_4^{2-}_{(aq)} + 4H^+_{(aq)} \quad (5)$$
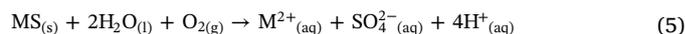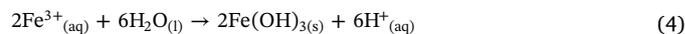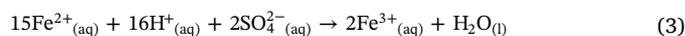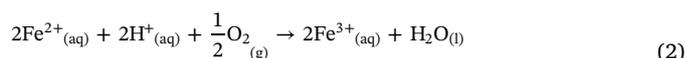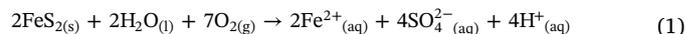
The various methods used to treat acid mine drainage can be classified as active or passive systems based on their requirements for chemical addition, infrastructure, maintenance and monitoring. A variety of passive treatment systems such as aerobic wetlands, anaerobic or compost wetlands [8], vertical 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 pH $\geq$ 5 but this element enters back into solution at pH 9.0 as soluble aluminate ions ($Al(OH)_4^-$) [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 ($Ca(OH)_2$), 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 ($Mg_6Al_2(OH)_{16}(CO_3)\cdot4H_2O$) 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 alkali's. 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)<br>< 1 mg/L (cattle)<br>< 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 |

## 2.2. AMD solutions and chemicals

Acid mine drainage water samples were collected from the open cut pit at the Mount Morgan mine, located in central Queensland, August 2014. Note, at the time of this investigation, AMD water used in the water treatment plant (lime neutralisation) was piped from approximately 3 m below the surface. The compositions of surface water and water from 3 m depth were compared, and it was confirmed that minimal variations in concentrations of metals were present. Lime, sodium hydroxide and sodium carbonate used in this research were of AR grade and supplied by Labtek. Bayer liquor and Bayer precipitates were synthesised in the laboratory as outlined below.

## 2.3. Synthesis of Bayer liquor

10 g/L Bayer liquor solution was prepared by the dilution of a highly concentrated Bayer liquor (saturated evaporative liquor − 96 g/L $Al_2O_3$) provided by an Australian alumina refinery. This latter solution was prepared by addition of 1 L of deionised (DI) water to a 2 L volumetric flask to which 21.13 g of sodium carbonate ($Na_2CO_3$) was dissolved before the addition of 29.99 g of sodium hydroxide (NaOH). Once the $Na_2CO_3$ and NaOH were dissolved, 212 mL of saturated evaporative liquor was added to the volumetric flask and additional DI water added until the final solution volume was 2 L. The mixture was then inverted several times to ensure homogeneity.

## 2.4. Synthesis of Bayer precipitates

Bayer precipitate was synthesised by the addition of seawater to 1L of the 10 g/L Bayer liquor until a pH of 9.25 was obtained. This latter pH value was achieved by placing the Bayer liquor into a 10 L container equipped with an overhead stirrer (IKA, RW20) with a 4 propeller paddle stirrer placed into solution. The stirrer was set to 400 rpm to ensure uniform mixing, while seawater was pumped into the beaker using a Watson and Marlow 520U pump set to 1.5 mL/min using Marprene tubing (diameter 6.4 mm). Once a pH of 9.25 was obtained, the solution was allowed to stir for a further 24 h before being vacuum filtered. The precipitate was then placed in an oven (90 °C) overnight before being crushed to a fine powder (< 125 μm) using a Fritsch agate ball mill.

## 2.5. Acid mine drainage neutralisation

The treatment of mine pit water involved the addition of known amounts of lime, Bayer hydrotalcite, Bayer liquor, sodium carbonate and sodium hydroxide to 25 mL of acid mine drainage water at ambient temperature. The resultant mixture was then allowed to agitate for 24 h before being centrifuged using a Thermofischer Scientific X1 Series centrifuge for 5 min at 2500 rpm. We note that the selected time of 24 h may not be the optimum time in terms of practical application of this technology, but for this bench study this approach was sufficient to determine the chemistry occurring. The neutralisation process most probably was rapid and amenable to potential commercial application. The supernatant was then transferred into a sample container, while the solid component was washed with 30 mL of DI water before being centrifuged again. The solid component was placed in an oven overnight at 90 °C to dry and then crushed to a fine powder using an agate mortar and pestle. The pH and conductivity of treated AMD were monitored using calibrated TPS meters and probes. Solutions for ICP–OES were syringe filtered using a 0.45 μm nylon filter prior to analysis.

## 2.6. Leaching of precipitates

Precipitates obtained after the treatment of mine pit water with different alkalis were leached using DI water and water from Mount Morgan's open pit. Measured amounts of the obtained precipitates were added to either 20 mL of DI water or mine pit water and then stirred for 24 h before being centrifuged using a Thermo Fischer Scientific X1 Series centrifuge for 5 min at 2500 rpm. The supernatant was then transferred into a sample container, while the solid component was placed in an oven at 90 °C overnight to dry. The pH and conductivity of treated AMD were monitored using calibrated TPS meter and probes. Solutions for ICP–OES were syringe filtered using a 0.45 μm nylon filter prior to analysis.

## 2.7. Characterisation techniques

### 2.7.1. Inductively coupled plasma − optical emission spectroscopy (ICP-OES)

Solutions were analysed using a VISTA-MPX CCD simultaneous ICP-OES instrument using an integration time of 0.15 s with 3 replications, using the following wavelengths (nm): Al (308.215), Ca (317.933), Mg (285.213), Na(589.592), Co (230.786), Cu (327.393), Fe (259.939), Mn (257.610), Ni (341.476), Be (313.07), Cd (214.440), Si (251.611), Zn (213.857), Cr (267.716), K (766.490), As (197.197), B (249.677) and Ba (455.403). A certified standard from Australian Chemical Reagents (ACR) containing 1000 mg/L of aluminium, calcium, magnesium, and sodium was diluted to form a multi-level calibration curve using a Hamilton auto-diluter.

### 2.7.2. X-ray diffraction (XRD)

X-ray diffraction patterns were collected using a Panalytical X'pert wide angle X-Ray diffractometer, operating in step scan mode, with Co Kα radiation (1.7903 Å). Patterns were collected in the range 5–90° 2θ with a step size of 0.02° and a rate of 30 s per step. Samples were prepared as Vaseline thin films on silica wafers, which were then placed onto aluminium sample holders. The XRD patterns were matched with ICSD reference patterns using the software package HighScore Plus. The profile fitting option of the software used a model that employed twelve intrinsic parameters to describe the profile, the instrumental aberration, and wavelength dependent contributions to the profile.

### 2.7.3. Optical imaging of precipitates

Light microscopy images were captured using a Leica M125 Light Microscope fitted with a Leica DFC490 digital camera. Flocculation samples were inverted slowly 5 times and allowed to flocculate for one minute, where 30 μL of suspension was transferred between two glass slides. The slides were viewed at 32× magnification. Subsequent images were analysed using the software package ImageJ. Images were made binary (black and white) and average particle size and area coverage of the flocculated particles was measured.

### 2.7.4. Freeze drying of Mount Morgan lime neutralisation sludge

Approximately 600 g of sludge was collected as a slurry from the Mount Morgan mine lime neutralisation plant, and this material was freeze dried in a −80 freezer and then placed into the main chamber of the freeze dryer unit until dry. The freeze dryer unit was operated at 0.013 mbar pressure with a condenser temperature of −55 °C. Average moisture loss for the sludge samples was approximately 72% with a slight variation noted between sub-samples. The sludge sample was freeze dried as the high amounts of gypsum present would convert to bassanite ($CaSO_4 \cdot 0.5H_2O$) if the samples were oven baked.

### 2.7.5. X-Ray fluorescence

Samples for Wavelength Dispersive X-Ray Fluorescence (WDXRF) major element analysis were prepared by weighing 1.15 g of the sample into a 95/5% Pt/Au crucible followed by

8.85 g of vitreous 50:50 lithium tetraborate:lithium metaborate flux containing 0.5% lithium iodide as a non-wetting agent (Claisse Scientific). This sample was then mixed carefully in the crucible before being placed into an automatic six position fusion instrument (TheOx,

Claisse Scientific). The samples were fused for 20 min at 1050 °C with constant agitation before the melts were poured automatically into 40 mm Pt/Au casting dishes and then cooled by a stream of air. The resultant glass disks were then analysed using a PANalytical Axios WDXRF equipped with a 1 kW Rh tube calibrated for the analysis of 21 major elements using the PANalytical WROXI protocol and associated standards. LOI was determined by igniting a separate sample portion in a muffle furnace at 1050 °C for 30 min.

### 2.7.6. Acid digestion

Accurately weighed samples of the precipitates obtained after treatment of AMD with different alkali were acid digested using 2 mL $HCl$, 1 mL $HNO_3$ and 2 mL DI water. The sample mixture was then heated at 80 °C for one hour. The samples were then cooled prior to DI water being added to the sample solutions to make final volume 50 mL. Digested samples were then diluted to 1:10 and 1:100 before being analysed by ICP-OES using above discussed method (Section 2.7.1).

### 2.8. Process simulation using AqMB software

The commercially available AqMB water treatment software was used to simulate the current lime neutralisation plant conditions used at Mount Morgan to provide insights into the theoretical mineralogical phases that make up the lime sludge. The simulation used a doser to add lime or sodium hydroxide (caustic) to the mine pit water (Table 2 using sulphate corrections for mass balance) up to pH 7.5. A thickener was then used for the solid-liquid separation process, with design specifications as follows: minimum underflow solids 5% w/v, feed pump duty pressure of 100 kPa, 120 min contact zone, 9000 mm mixer impeller diameter, and 1 rpm rake arm rotation speed.

## 3. Results and discussion

### 3.1. Characterisation of Bayer precipitate

The XRD pattern of Bayer precipitate employed in this study (Fig. 1) revealed that the material was composed of a number of mineralogical phases including: 1) hydrotalcite ($Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$); 2) calcite ($CaCO_3$–rhombohedral); 3) aragonite ($CaCO_3$–orthorhombic); and 4) magnesium hydroxide ($Mg(OH)_2$). These detected materials were consistent with phases previously observed in precipitates formed from the seawater neutralisation of Bayer liquor [35,45,46]. However, it was noted that brucite ($Mg(OH)_2$) is normally only observed when magnesium is more prevalent than aluminium at pH values greater than 10 [11,47]. The broadness of the $d_{003}$ and $d_{006}$ peaks (approximately 12 and 25° 2θ) was characteristic of hydrotalcite and indicated that this material had a poorly crystalline structure probably due to hydroxide layers being partially askew [48]. The Bayer hydrotalcite formed had a d-spacing of 7.8 Å, typical of a carbonate hydrotalcite material [49]. Based on the mineralogical composition of Bayer precipitate, species involved in the neutralisation of AMD would be majorly hydrotalcite and calcium carbonate.



**Fig. 1.** XRD pattern of Bayer precipitate formed by the seawater neutralisation of Bayer liquor.

### 3.2. AMD characteristics

The mine pit water contained relatively high concentrations of dissolved metals and displayed a characteristic low pH value of 3.74 (Table 2), typical of AMD waters. Compared to the values observed by Bosman [23], Mount Morgan mine pit water had a high sulphate concentration (17,430 mg/L), low iron concentration (16.7 mg/L), and significantly higher concentrations of aluminium (1233 mg/L) and magnesium (2265 mg/L). Based on the geological study performed by Taube [50], the primary sources of aluminium and magnesium were probably from feldspar and dolomite. A previous study of Mount Morgan mine pit water in 2002, also showed major differences to the water composition in this study; an increase in pH (2.7–3.74), $SO_4$ (13600–17430 mg/L), Al (780–1233 mg/L), Mg (1280–2265 mg/L), Cu (44.54–77.26 mg/L), Mn (71.28–161.5 mg/L) and Zn (21.97–48.89 mg/L), and reductions in Fe (253–16.7 mg/L) and Na (830–648 mg/L). The reduction in iron concentration from 2002 to 2014, was believed to be due to the precipitation of $Fe(OH)_3$, which occurs at pH values above 3.5 in oxygenated waters caused by turbulence [51]. A sediment sample

**Table 2**
Composition of mine pit water from Mount Morgan, August 2014.

| pH | Conductivity (mS) | | Turbidity (NTU) | | | $SO_4$ (mg/L) | TSS (g/L) | TDS (g/L) | $Cl^-$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|
| 3.74 | 14.86 | | 8.29 | | | 17430 | 25.44 | 0.015 | 14.59 |
| Concentration (mg/L) | | | | | | | | | |
| Al | Fe | Mn | Cu | Zn | | Co | Ni | Cd | Cr |
| 1233 | 16.7 | 161.5 | 77.26 | 48.89 | | 4.05 | 1.54 | 0.19 | 0.06 |
| Concentration (mg/L) | | | | | | | | | |
| S | Mg | Ca | Na | Si | | K | Li | Sr | B |
| 5703 | 2265 | 534.3 | 647.8 | 36.94 | | 6.24 | 0.39 | 0.77 | 0.06 |

taken from the open pit also showed the presence of jarosite $(KFe_3^{3+}(OH)_6(SO_4)_2)$.

The rise in metal concentrations (Cu, Mn and Zn) in open pit water was probably a by-product of the lime dosing plant built in 2006 to reduce water volumes in the open pit [52]. The lime neutralising plant treats the mine pit water by raising the pH to 7.5, causing the precipitation of heavy metals before discharging the metal free water into the Dee River. The heavy metal rich sludge is transferred to an adjacent tailings beach [53]. It is therefore proposed, the decreasing water volumes and leaching of metals from the metal rich sludge has caused an increase in metals in the mine pit water over time. The possibility for release of metals from the sludge when exposed to the open pit AMD water has been confirmed in this study (Section 3.5).

## 3.3. AMD neutralisation using various alkalis

Treatment efficiency of AMD by different alkaline materials depends upon various factors such as concentration and oxidation state of metals, pH of AMD water and hydrolysis reactions that occur upon addition of alkali to AMD [54]. Fig. 2 shows the pH behaviour as a function of the different alkali species during treatment of mine pit water. Neutralisation was assumed to be predominantly through the buffering capacity of hydroxyl and carbonate groups in alkali [11]. It was evident that increasing the pH of AMD water consumed a substantial amount of alkalinity agent, for example, to achieve a pH between 6 and 7 for 25 mL of AMD water, 1.6 mmol lime, 4.7 mmol sodium hydroxide, 1.7 mmol of sodium carbonate, 2.5 mL of 10 g/L Bayer liquor and 0.5025 g of Bayer precipitate were required. The dissolution of alkali increased the pH and promoted the formation of insoluble metal hydroxide and carbonate precipitates that could potentially be removed by a solid-liquid separation process [55].

Table 3 provides a snapshot of the concentrations of Al, Mg, Mn, Cu, Zn, Si, Fe and Ni at 3 stages during treatment as a function of solution pH (metal concentrations at approximately pH 3.5, 6.5 and 9). The full range of pH values tested (Fig. 2), corresponding AMD water compositions, and curves related to the removal of metals for each alkali at a particular pH is shown in

Fig. 3. In order to evaluate the effectiveness of various alkalis for treatment in removing metals from AMD, the metal ion removal results (Table 3) were compared with Australian and New Zealand guidelines (Table 2) [43]. Increasing the pH of mine pit water showed the precipitation of metal hydroxide and carbonate precipitates occurred in the following order: Fe, Al, Cu, Zn, Ni and then Mn. It was possible that iron and manganese could be selectively precipitated out of solution, however for the remaining metals, overlap in the precipitation pH range existed.

### 3.3.1. Iron removal

Iron species in acid mine drainage waters are normally in the ferric $(Fe^{3+})$ state due to oxygenation by turbulence. However, deeper water that has not been disturbed can have iron in the ferrous $(Fe^{2+})$ state [51]. The water collected in this study was from a depth of only 3 m (with the deepest section of the open pit being 40 m), therefore it is reasonable to assume that the majority of the 16.7 mg/L iron existed as $Fe^{3+}$. As the pH of the mine pit water was gradually increased to in excess of 6, iron precipitated to the point it was below detection limits.

The removal of iron was relatively rapid with a sharp decline in iron concentration in the pH range 3 and 4, observed for all alkalis investigated (Fig. 3). For all alkali tested, 99.7% of iron was removed from the open pit AMD waters; thus meeting water quality guidelines outlined by ANZECC (Table 1) [43]. Iron in the ferric state should readily precipitate as oxyhydroxide compounds (FeO(OH)) as shown in Eq. (6) at pH values greater than 3.5 [10].

$$Fe^{3+}_{(aq)} + 2OH^-_{(aq)} \rightarrow FeOOH_{(s)} + H^+_{(aq)} \tag{6}$$
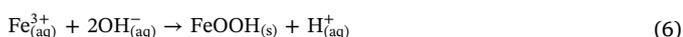
Formation of oxyhydroxides of Fe tends to effect the mobility of other metals like Mn, Ni, As and Mo through sorption or co-precipitation [14,56]. At pH 8, most of the Mn can be removed if the Fe concentration is more than four times the concentration of Mn in water [22]. However, Fe concentration in the mine pit water was too low (16.7 mg/L) and thus there was not enough iron present to promote the co-precipitation of Mn, Ni, As and Mo (Table 3).

### 3.3.2. Aluminium removal

Aluminium was the second metal found to precipitate out of solution within a pH range 4–7 (Fig. 3). The average initial concentration of aluminium in the mine pit water was 1212 mg/L. Treatment results for all alkali materials showed maximum removal of aluminium between pH 7 and 8, with a slight increase in aluminium concentration at pH values above 8.5. At pH 5.5, Al begins to precipitate as $Al(OH)_3$ (Eq. (7)), however this species can redissolve when the pH is increased to 8.5 as aluminate ions $(Al(OH)_4^-)$ as shown in Eq. (8) [17].

$$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Al(OH)_{3(s)} \tag{7}$$

$$Al(OH)_{3(s)} + OH^-_{(aq)} \rightarrow [Al(OH)_4]^-_{(aq)} \tag{8}$$
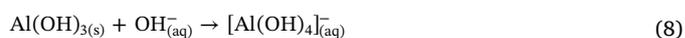
Current acceptable release limits of aluminium into waterways from industry have been reported to be 5 mg/L [43]. All alkalis achieved a water discharge quality (aluminium removal percentage of greater than 99.5%) with acceptable aluminium concentrations in the pH range 6.5–8.5 based on ANZECC guidelines (Table 1) [43], with lime showing a significantly greater retention of aluminium in the solid phase at pH values above 9. This is proposed to be due to the formation of calcium aluminium hydroxide co-precipitates based on the work by Packter and Khaw [57], who showed precipitation of this latter mineral with increasing calcium concentrations in mixed cation solutions (Eq. (9)).

$$2Ca^{2+}_{(aq)} + 2OH^-_{(aq)} + 2[Al(OH)_4]^-_{(aq)} + nH_2O_{(l)} \rightarrow Ca_2(H_2O)_n[Al_2(OH)_{10}]_{(s)} \tag{9}$$
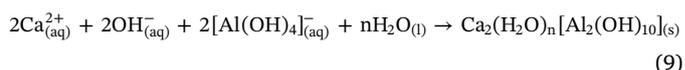
### 3.3.3. Copper removal

Based on the $E_h$-pH curves of a Cu-S-$H_2O$ system at pH 3.5–4, it is believed $Cu^{2+}$ ions are present as the dominant species [58]. The average initial concentration of copper in the mine pit water was 79.32 mg/L, which was substantially above the ANZECC water quality guidelines for copper ($< 5$ mg/L) [43]. However, the results in Table 3 showed that by increasing the pH above 4 (Fig. 3), greater than 95% removal of copper for all alkali materials was achieved; which resulted in concentrations less than those stipulated by ANZECC guidelines (Table 1).

In the case of lime, Bayer liquor, and Bayer precipitates, the concentration of copper fell below instrumental detection limits of 0.05 mg/L (Table 3). Baltpurvins et al. [59] conducted a study on the solubility domains of copper hydroxide precipitate using lime, and found that multiple phases formed depending on the $Cu^{2+}$:$SO_4^{2-}$:$OH^-$ ratio, temperature, and reaction time. The precipitation of copper hydroxides from sulphate rich solutions typically results in the formation of brochantite $(Cu_4SO_4(OH)_6)$ as shown in Eq. (10) and tenorite (CuO) (Eq. (11)), as other phases such as posnjakite $[Cu_4SO_4(OH)_6 \cdot H_2O]$ and spertiniite $(Cu(OH)_2)$ are precursors to these more thermodynamically preferred minerals, respectively [60]. Baltpurvins et al. [59] further found that gypsum $(CaSO_4 \cdot 2H_2O$ − most dominant species precipitated during lime neutralisation) had little influence on the formation of brochantite and tenorite.

$$Cu^{2+}_{(aq)} + SO_4^{2-}_{(aq)} + 6OH^-_{(aq)} \leftrightarrow Cu(SO_4)(OH)_{6(s)} \tag{10}$$

$$CuSO_{4(aq)} + 2OH^-_{(aq)} \leftrightarrow CuO_{(s)} + SO_4^{2-}_{(aq)} + H_2O_{(l)} \tag{11}$$
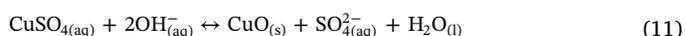
### 3.3.4. Zinc removal

The average initial concentration of zinc in the mine pit water was
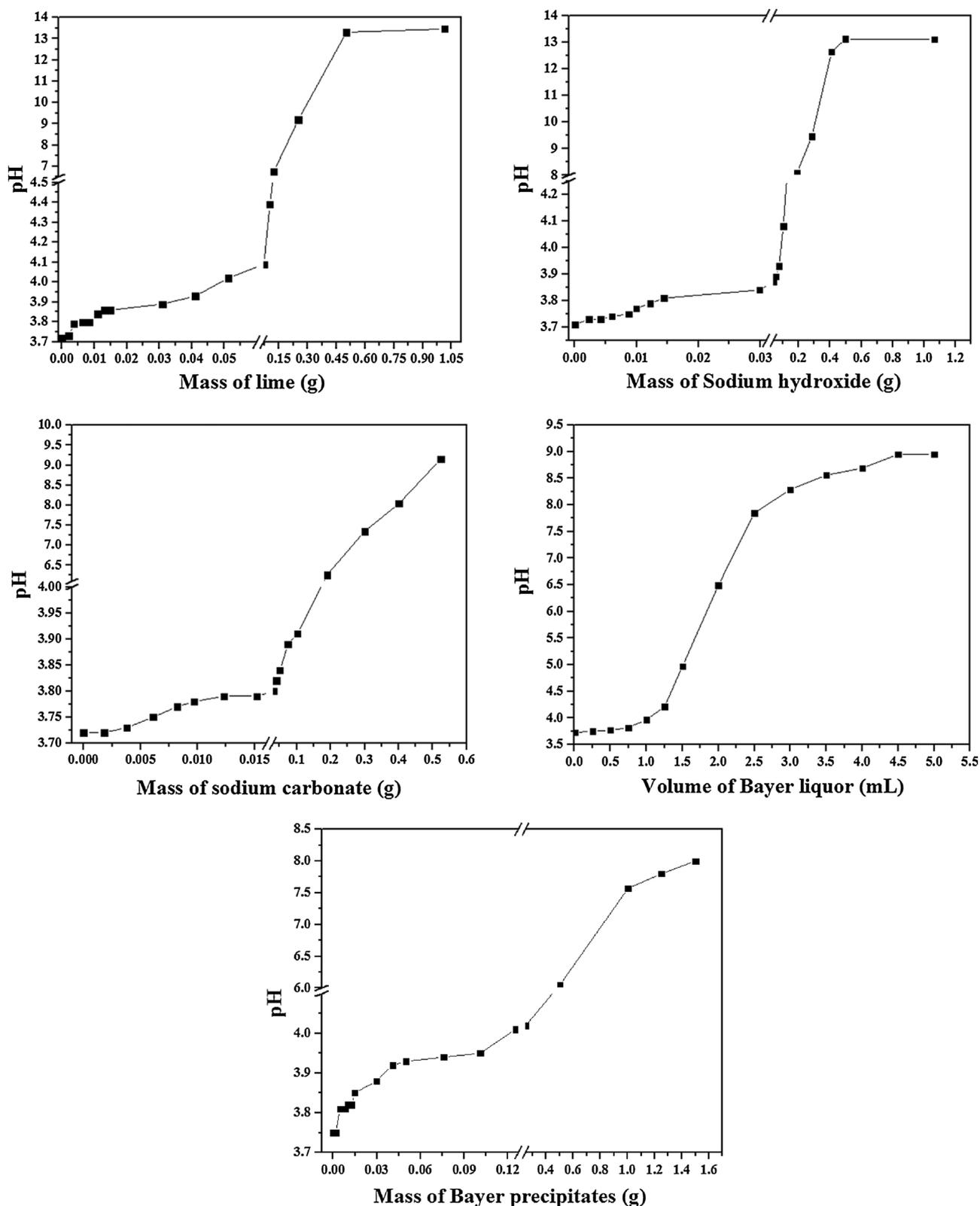
**Fig. 2.** Neutralisation curves for different alkaline materials as indicated.

48.62 mg/L, which was in excess of ANZECC guidelines (Table 1) for discharge [43]. In aerobic natural waters, zinc can form various complexes with numerous ions (carbonate and hydroxyls) present in water [61]. Below pH 7, zinc exists as $Zn^{2+}$ and in the pH range 7–8.2 ionic zinc gets converted to a hydroxycarbonate precipitate termed hydrozincite ($Zn_5(CO_3)_2(OH)_6$) (Eq. (12)). In sulphate rich environments,

zinc forms $ZnSO_4$ (Eq. (13)) at pH < 7 [18]. Therefore, the > 95% removal of zinc in this study is proposed to be due to the formation of $ZnSO_4$ which was converted to hydrozincite at higher pH. The treatment of mine pit water with lime, sodium carbonate, Bayer liquor and Bayer precipitates reduced the concentration of zinc below the instrumental detection limit of 0.05 mg/L (Table 3) and ANZECC guidelines

**Table 3**
Mount Morgan mine pit water treatment using various alkaline materials and their metal removal capacity in mg/L.

| Alkali | pH | Amount added | Concentration (mg/L) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Al | Mn | Cu | Zn | Fe | Ni |
| Lime | 3.72 | 0.0 mmol | 1233 | 161.5 | 77.26 | 48.89 | 16.70 | 1.54 |
| | 6.75 | 1.6 mmol | 0.53 | 85.40 | 0.11 | 0.75 | 0.05 | < 0.05 |
| | 9.19 | 3.3 mmol | 0.60 | 0.45 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| Percentage removed (%) | | | 99.9 | 99.7 | 99.9 | 99.9 | 99.7 | 96.8 |
| Sodium hydroxide | 3.71 | 0.0 mmol | 1233 | 161.5 | 77.26 | 48.89 | 16.70 | 1.54 |
| | 6.80 | 3.12 mmol | 0.11 | 136.8 | 0.757 | 10.67 | < 0.05 | < 0.05 |
| | 9.46 | 7.1 mmol | 3.46 | < 0.05 | 2.59 | < 0.05 | < 0.05 | < 0.05 |
| Percentage removed (%) | | | 99.7 | 99.9 | 96.64 | 99.9 | 99.7 | 96.8 |
| Sodium carbonate | 3.72 | 0.0 mmol | 1233 | 161.5 | 77.26 | 48.89 | 16.70 | 1.54 |
| | 6.26 | 1.7 mmol | 2.97 | 131.60 | 3.53 | 21.34 | < 0.05 | 1.37 |
| | 9.15 | 4.9 mmol | 1.95 | 6.80 | 3.24 | < 0.05 | < 0.05 | < 0.05 |
| Percentage removed (%) | | | 99.8 | 95.8 | 95.8 | 99.9 | 99.7 | 96.8 |
| Bayer liquor | 3.69 | 0.0 mL | 1233 | 161.5 | 77.26 | 48.89 | 16.70 | 1.54 |
| | 6.49 | 2.5 mL | 2.28 | 111.70 | 2.99 | 23.80 | < 0.05 | 1.07 |
| | 8.95 | 5.0 mL | 4.77 | 3.78 | 0.55 | < 0.05 | < 0.05 | < 0.05 |
| Percentage removed (%) | | | 99.6 | 97.6 | 99.3 | 99.9 | 99.7 | 96.8 |
| Bayer precipitates | 3.75 | 0.0000 g | 1233 | 161.5 | 77.26 | 48.89 | 16.70 | 1.54 |
| | 6.05 | 0.5025 g | 2.65 | 67.20 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| | 8.00 | 1.5000 g | 0.91 | 27.74 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| Percentage Removed (%) | | | 99.9 | 82.82 | 99.9 | 99.9 | 99.7 | 96.8 |

(Table 1) [43].

$$Zn^{2+}_{(aq)} + 2CO_3^{2-}_{(aq)} + 6OH^-_{(aq)} \rightarrow Zn_5(CO_3)_2(OH)_{6(s)} \qquad (12)$$

$$Zn^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \rightarrow ZnSO_{4(s)} \qquad (13)$$
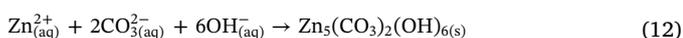
Lime and Bayer precipitate were discovered to be particularly effective at removing zinc from the mine pit water at a lower pH range (pH 6–7) than the other alkaline materials (pH 8.5–9.5) (Table 3). The calcium content in lime and Bayer precipitates (as $CaCO_3$) resulted in an increase in the amount of gypsum that formed during the neutralisation of acid mine drainage water (XRD in Section 3.4.2). A study by Huang et al. [62] found that the formation of gypsum flocs from a sulphate wastewater and lime had a zinc uptake capacity of 0.06 mg/g at pH 6 and 0.10 mg/g at pH 7. Therefore, a similar adsorption and encapsulation process is proposed to be occurring in the neutralisation of AMD water for lime and Bayer precipitates.

### 3.3.5. Nickel removal

The average initial concentration of nickel in the mine pit water was only 1.49 mg/L, which was considerably less than other metal species present; nevertheless, according to ANZECC guidelines discharge requires concentration levels < 0.2 mg/L (Table 1) [43]. In aqueous systems, Ni is present as ionic nickel below pH 6.6, while between 6.6 and 8.2 ionic Ni changes to species such as $NiCO_3$ (Eq. (14)) or $NiSO_4$ (Eq. (15)) depending upon the sulphate concentration in solution [18]. Treatment of mine pit water with all alkali materials showed the removal of Ni to below instrumental detection limits < 0.05 mg/L at pH values around 8. In the case of lime, sodium hydroxide and Bayer precipitate, acceptable discharge limits were achieved at pH values greater than 6. Based on the work by Olds et al. [63], increased removal of nickel at lower pH values for lime, sodium hydroxide and Bayer precipitate may be due to the greater surface area of precipitates that form when using these alkali materials (See Section 3.4.3 for more details).

$$Ni^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow NiCO_{3(s)} \qquad (14)$$

$$Ni^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \rightarrow NiSO_{4(s)} \qquad (15)$$

### 3.3.6. Manganese removal

The removal of manganese from complex water matrices such as AMD water using chemical precipitation can be problematic due to the

highly alkaline conditions (greater than 9) required to produce manganese precipitates [17]. Issues with raising the pH this high relate to concerns about excessive chemical usage, failure to comply with discharge water pH requirements and the dissolution of aluminium hydroxide. Theoretically, Mn can exist in numerous oxidation states, but in natural waters only $Mn^{2+}$ and $Mn^{4+}$ are relatively stable [64]. Depending upon pH conditions manganese can form oxides, hydroxides, or carbonate compounds [65]; however, between pH 9 and 9.5 Mn is precipitated as hydroxides as shown in Eq. (16) [17] with complete removal of Mn requiring a pH of 10.5 [66].

$$Mn^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Mn(OH)_{2(s)} \qquad (16)$$

The average initial concentration of manganese in the mine pit water was 162 mg/L, which was above acceptable release limits. Sodium hydroxide decreased the concentration of Mn to acceptable levels (< 0.2 mg/L) at pH 9.46; however, slight increases in aluminium concentration were observed (Table 3 shows aluminium concentration increased to 3.46 mg/L at pH 9.46 from 0.82 mg/L at pH 8.10). Bayer precipitates were able to remove 57% of manganese (67.2 mg/L remaining in solution) at pH 6.05 compared to 45.6% removal at pH 6.75 for lime (next best performing alkali). This result clearly showed that Bayer precipitates perform better at the removal of manganese at lower pH values than the more conventionally used lime. It is proposed that the incorporation of manganese in reformed hydrotalcite (substitution of Mg with Mn in the structure) enabled the removal of manganese at lower pH than the other alkalis. A more in-depth study (outside the scope of the current work) will be required to confirm this proposed mechanism, in particular, the reformation of hydrotalcite at pH 6–7 after dissolution in acid and the degree of Mn inclusion in the structure.

### 3.4. Precipitate analysis

#### 3.4.1. Elemental composition

The precipitates obtained after the treatment of mine pit water with different alkalis to a pH between 6.5 and 7.5 were analysed using ICP–OES to determine their elemental composition (Table 4). The Bayer precipitate had the highest concentration of magnesium (105.13 mg/g) compared to the other alkaline materials wherein Mg ranged from 16.68 to 34.70 mg/g. This was probably due to magnesium content present in Bayer precipitates in the form of hydrotalcite ($Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$). In acidic conditions, hydrotalcite in Bayer
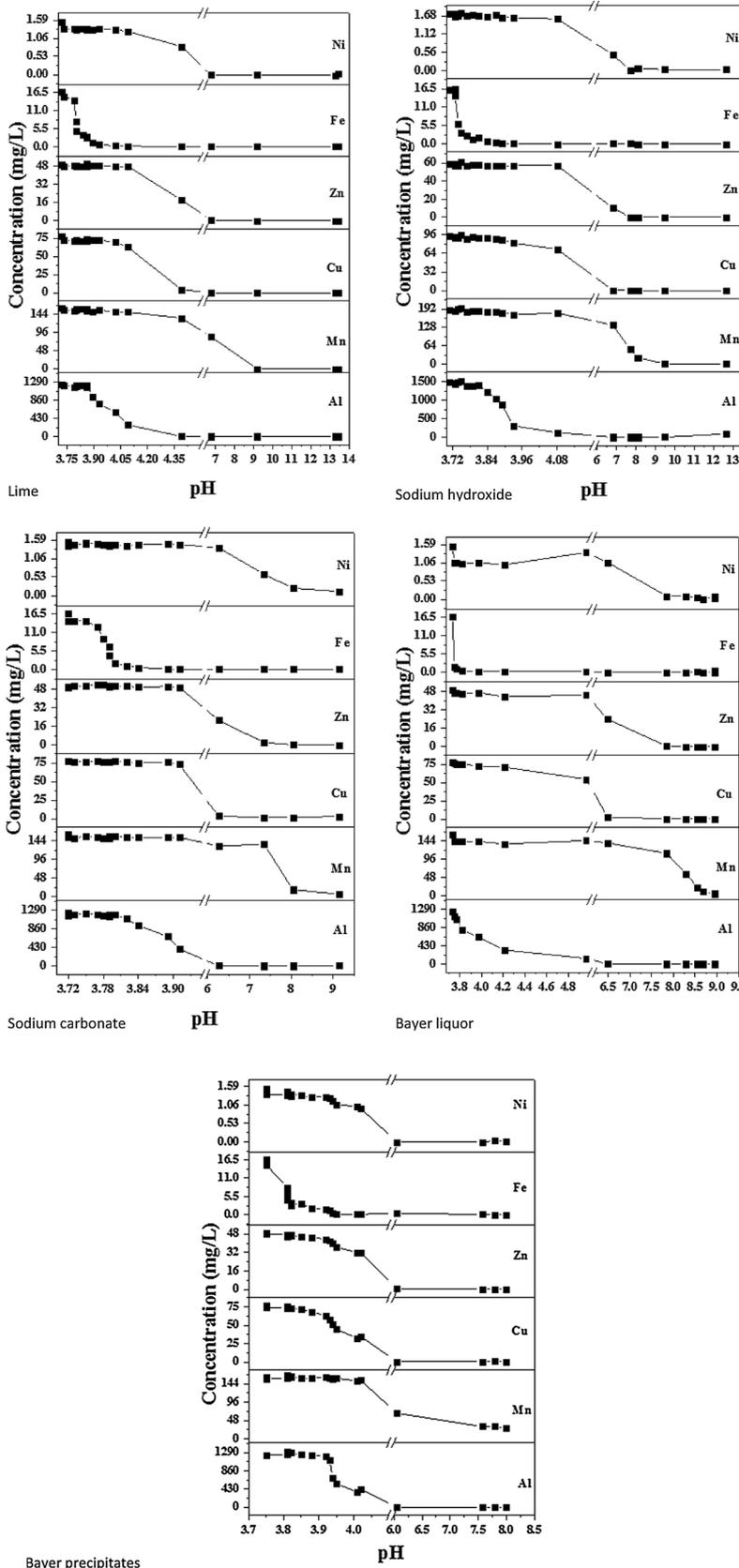
**Fig. 3.** Trends for Al, Mg, Mn, Cu, Zn, Si, Fe and Ni removal from Mount Morgan mine pit water when using different alkaline materials.

precipitate dissociates [11,67] and thus releases hydroxyl units required for the neutralisation of acid mine drainage waters. Magnesium in the precipitates formed after neutralisation, was most likely some form of magnesium hydroxide species or even could be due to the

reformation of the hydrotalcite structure [68]. All precipitates had very high concentrations of Al, Fe, Cu, Zn, Si and Mn as shown in Table 4. The concentration of aluminium in lime (59.75 mg/g) and Bayer precipitates (96.87 mg/g) was significantly lower than sodium hydroxide

**Table 4**
Metal concentrations (mg/g) in precipitates between pH 6.5 and 7.5.

| Alkali | pH | Mg | Ca | Al | Mn | Cu | Zn | Si | Fe |
|---|---|---|---|---|---|---|---|---|---|
| Lime | 6.75 | 16.68 | 141.2 | 59.75 | 4.05 | 3.89 | 2.46 | 2.21 | 0.87 |
| Sodium hydroxide | 6.70 | 24.57 | 5.78 | 122.6 | 3.24 | 7.95 | 3.86 | 3.30 | 0.81 |
| Sodium carbonate | 7.37 | 27.11 | 31.94 | 157.0 | 6.18 | 10.11 | 6.16 | 4.53 | 1.95 |
| Bayer liquor | 6.49 | 34.70 | 10.35 | 133.9 | 4.46 | 6.42 | 3.90 | 3.90 | 1.27 |
| Bayer precipitates | 7.57 | 105.1 | 44.41 | 96.87 | 3.33 | 2.76 | 1.80 | 2.56 | 0.86 |
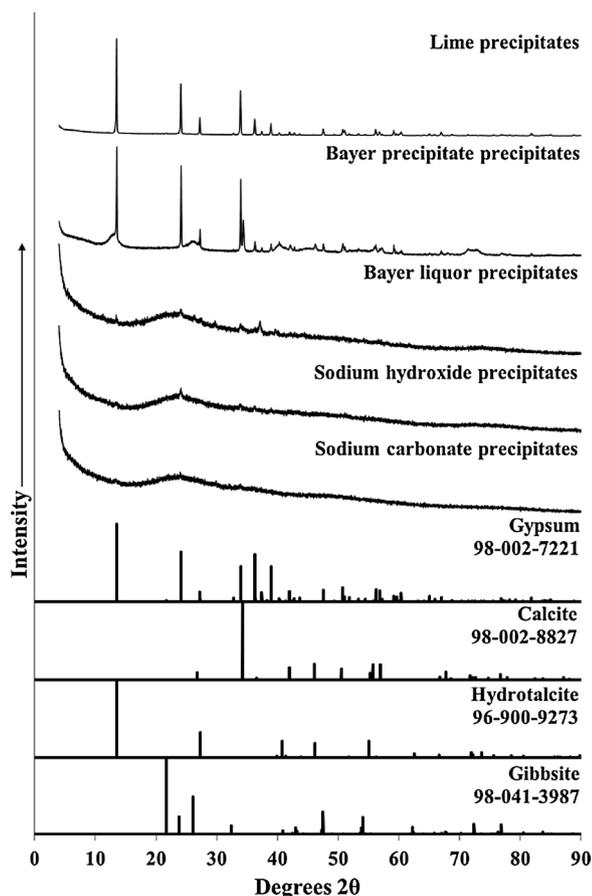


**Fig. 4.** XRD pattern of precipitates obtained from treatment of Mount Morgan mine pit water with different alkaline materials.

(122.57 mg/g), sodium carbonate (157.02 mg/g) and Bayer liquor (133.94 mg/g). In the absence of excess Ca, gibbsite (Al(OH)$_3$) was the primary phase found for sodium hydroxide, sodium carbonate and Bayer liquor precipitates (Section 3.4.2).

*3.4.2. X-ray diffraction*

The addition of lime to mine pit water resulted in gypsum (CaSO$_4$·2H$_2$O – reference 98-002-7221) being the primary phase formed (Fig. 4), which agreed with the composition of the lime sludge sample collected at the Mount Morgan lime neutralisation tanks (Supplementary Information). Gypsum was also a dominant phase formed with the addition of Bayer precipitate to the AMD water, however calcite (CaCO$_3$) and hydrotalcite were also detected in the precipitates formed. The presence of hydrotalcite in the precipitate showed that hydrotalcites can reform after they undergo dissolution in AMD water. These assignments were supported by the infrared spectra of the precipitates (dominated by sulphate bands between 1200 and 900 cm$^{-1}$ and 700 and 500 cm$^{-1}$–Supporting Information), as well as by high concentrations of Mg, Ca and Al found in the acid digested precipitates (Table 4).

The remaining alkaline materials used to neutralise the mine pit

**Table 5**
Possible phases precipitated at pH 7.5 using lime and sodium hydroxide based on AqMB simulations.

| Mineral phase | Chemical Formula | Lime (mol/hr) | Sodium hydroxide (mol/hr) |
|---|---|---|---|
| Birnessite | Mn$_7$O$_{13}$ | 1.00 | 0.49 |
| Copper hydroxide | Cu(OH)$_2$ | 16.96 | 24.47 |
| Copper carbonate | CuCO$_3$ | 12.66 | 5.67 |
| Ferrihydrite | Fe$_2$O$_3$·0·5H$_2$O | 3.71 | 3.76 |
| Gibbsite | Al(OH)$_3$ | 812.1 | 822.1 |
| Gypsum | CaSO$_4$·2H$_2$O | 2052 | 77.26 |
| Hydrotalcite-CO$_3$ | Mg$_6$Al$_2$(OH)$_{16}$(CO$_3$)·4H$_2$O | 93.6 | 94.36 |
| Muscovite | KAl$_3$Si$_3$O$_{10}$(OH)$_{1.8}$ F$_{0.2}$ | 3.87 | 0 |
| Paragonite | NaAl$_3$Si$_3$O$_{10}$(OH)$_2$ | 0 | 4.34 |
| Zinc carbonate | ZnCO$_3$·H$_2$O | 15.29 | 15.81 |

water (Bayer liquor, sodium hydroxide and sodium carbonate), produced precipitates with similar XRD patterns that primarily consisted of amorphous material and gypsum. Gypsum forms for mine pit water treated with sodium carbonate and sodium hydroxide due to the presence of 460 mg/L of calcium in the untreated mine pit water (Table 2). Based on the location of the broad band in Fig. 4, with respect to the gibbsite reference pattern 98-041-3987, water chemistry and simulations performed using caustic additions using AqMB software (Table 5), it is proposed that the amorphous phase was primarily gibbsite (Al (OH)$_3$).

AqMB simulations were also able to provide more details regarding the mineralogical phases which were difficult to characterise by XRD (due to the presence of highly crystalline gypsum which exhibited intense reflections which obscured other peaks) (Table 5). Simulations were run for lime and sodium hydroxide, with Mount Morgan mine pit water dosed to pH 7.5 and allowed to react for 2 h prior to solid-liquid separation. Gypsum was the primary phase formed by the addition of lime, at a rate of 2052 mol/h, followed by gibbsite (812 mol/h) and hydrotalcite (93.6 mol/h). This was an interesting finding as the XRD patterns of the lime precipitates were unable to identify the formation of gibbsite. The addition of caustic in the simulation found gibbsite to be the primary phase formed, at a rate of 812 mol/h, followed by hydrotalcite (194 mol/hr) and gypsum (77.26 mol/hr). These results support the details in the XRD pattern shown in Fig. 4. Based on the concentrations of sulphate in the feed (18630 mg/L) and resultant thickener overflow in AqMB, the addition of lime results in a 42% reduction of sulphate in the discharge water (10780 mg/L) compared to a 1.6% reduction for caustic (18310 mg/L). Interestingly, different aluminosilicates were predicted by AqMB simulations to precipitate based on the alkaline material used; in the case of lime, muscovite formed (KAl$_3$Si$_3$O$_{10}$(OH)$_{1.8}$ F$_{0.2}$), while for caustic solutions paragonite formed (NaAl$_3$Si$_3$O$_{10}$(OH)$_2$). This latter situation was consistent with the dependency of the formation of paragonite and muscovite on the ratio of sodium (Na) and Potassium (K) [69].

Metal hydroxide phases could not be detected by XRD, however, heavy metals were present in the precipitates based on ICP-OES for the acid digested precipitate samples. The AqMB simulations predicted that the main metal phases forming were copper hydroxide and carbonate, zinc carbonate, and birnessite (Table 5). In the presence of lime, copper was precipitated out in relatively similar amounts of hydroxide

(16.96 mol/h) and carbonate (12.66 mol/h), while the use of caustic in the neutralisation process favoured the formation of copper hydroxide (24.47 mol/h). Both lime and caustic removed similar quantities of zinc (15.29 and 15.81 mol/h, respectively), while lime precipitated out approximately double the amount of manganese than caustic at the same pH (1.00 compared to 0.49 mol/h). These simulation results appeared to reflect the trends observed in the actual treatment of the Mount Morgan mine pit water at pH 7.5 using lime and sodium hydroxide (Fig. 3). It was thus apparent that the sludge composition was complex and this must be taken into account when determining how to handle, reuse, or store this material. The analysis provided in this study provides a guide to future means of addressing this waste in the most practical manner.

The most effective alkali materials for the removal of metals were found to be lime and Bayer precipitates; high gypsum generating precipitates after the neutralisation of mine pit water. Huang et al. [62] studied the removal of nickel, copper and zinc from a sulphate wastewater using gypsum and determined the removal mechanism to be a combination of adsorption on gypsum colloids followed by encapsulation during the subsequent precipitation processes. An increase in metal removal was found when there was a high $Ca^{2+}:SO_4$ ratio, solution pH, ionic strength and surface area [62]. It was noted, that the addition of gypsum had a negligible adsorption of heavy metals, but rather it was the formation of high surface area gypsum flocs from metal rich sulphate wastewaters that allowed for their removal [62]. Therefore, the increased removal efficiency of heavy metals for lime and Bayer precipitates was postulated as due to gypsum being the major mineralogical phase formed.

### 3.4.3. Particle size analysis

Sorption of metals on aluminium/iron hydroxide precipitates has been reported to be related to their surface area [70], while the uptake of Ni, Cu and Zn from sulphate wastewaters has been linked to the surface area of gypsum flocs [62]. Magnesium hydroxides have also been found to show metal uptake capacity through adsorption onto the surface of $Mg(OH)_2$ particles [71]. As the concentration of iron in the mine pit water was only 16.7 mg/L, while the magnesium, aluminium and calcium concentrations were 2265, 1233 and 534 mg/L, respectively, it is proposed that metal uptake was through adsorption on

different phases of magnesium and aluminium hydroxide (more prevalent in Bayer precipitates compared to lime), and gypsum (to a much greater extent for lime). The dissolution of hydrotalcite in Bayer precipitates, increases the amount of aluminium and magnesium available to form $Mg(OH)_2$ and $Al(OH)_3$ precipitates as the pH becomes alkaline [11,67].

Optical images and Image J values for the average size (μm) of the precipitates that formed during the neutralisation of mine pit water with lime, sodium hydroxide, sodium carbonate, Bayer liquor and Bayer precipitates are shown in Fig. 5. Average particle size of the precipitates formed was in the order lime (730 μm) > Bayer precipitates (184 μm) > sodium carbonate (62 μm) > sodium hydroxide (59 μm) > Bayer liquor (20 μm). Based on the size of the flocs that formed for the different alkali, it appeared that surface area alone was not driving the metal uptake capacity. Therefore, based on the work by Huang et al. [62], it was believed that the encapsulation of metals in larger flocs (precipitates) was a key factor in metal removal.

### 3.5. Performance versus operational considerations

The hydrochemical and geochemical behaviour of metals in solids must be considered during the treatment of mine pit water to avoid the release of metal contaminants once disposed of [19,72]. Depending upon the site conditions, in some cases, sludges are further treated for metal recovery or can be converted into an inert material via stabilisation or solidification prior to disposal to avoid further contamination [72,73]. Currently at Mount Morgan, lime neutralised precipitates (sludge) are disposed of on a tailings beach that has periods of immersion with open pit water. This form of disposal was chosen to utilise any residual caustic remaining in the sludge to slowly raise the pH of the water in the open pit. However, XRF analysis of samples collected at the Mount Morgan tailings beach (Table 6) shows that the metals have been leached back into the mine pit water (reductions in Cu – 92%, Mn – 87%, and Zn – 96%), and thus are being recirculated through the neutralisation tanks. Only slight reductions in calcium were observed (22.2 compared to 20.9%).

Precipitates obtained after the treatment of mine pit water with different alkalis were leached using deionised water and mine pit water to determine the extent of metal leaching, and thus precipitate stability.



| (a) Average size 730μm | (b) Average size 59μm | (c) Average size 62μm |
| (d) Average size 20μm | (e) Average size 184μm | |
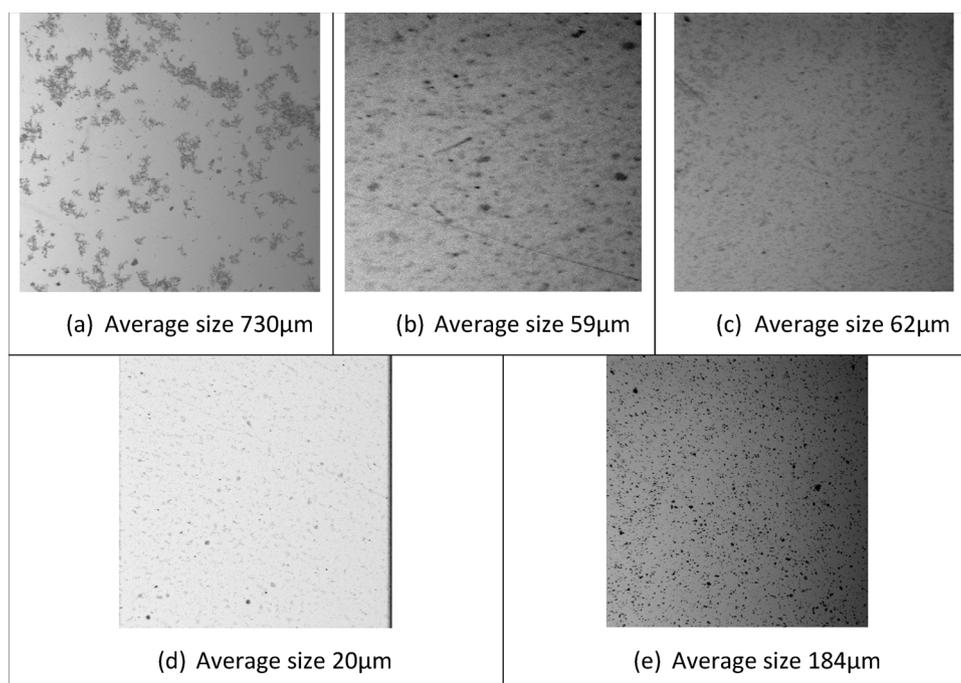
Fig. 5. Image J particle size analysis of optical images of precipitates formed during Mount Morgan mine pit water treatment; a) with lime at pH 6.75, b) sodium hydroxide at pH 6.80, c) sodium carbonate at pH 6.26, d) Bayer liquor at pH 6.49, and e) Bayer precipitates at pH 6.50.

**Table 6**
XRF data of freeze dried tailings beach and lime neutralisation plant sludge from Mount Morgan.

| Measurement | Lime neutralisation plant sludge | Tailings beach sludge |
|---|---|---|
| Initial (g) | 1.15 | 1.16 |
| Final (g) | 10.0 | 10.0 |
| Loss On Ignition (%) | 27.0 | 23.8 |
| Sum | 101.6 | 100.6 |
| $SiO_2$ (%) | 0.617 | 8.58 |
| $Al_2O_3$ (%) | 13.4 | 7.07 |
| $Fe_2O_3$ (%) | 0.137 | 3.61 |
| $Na_2O$ (%) | 0.305 | 0.183 |
| MgO (%) | 1.47 | 0.577 |
| $K_2O$ (%) | 0.003 | 0.032 |
| CaO (%) | 22.2 | 20.9 |
| $TiO_2$ (%) | 0.004 | 0.023 |
| $Mn_3O_4$ (%) | 0.391 | 0.052 |
| $P_2O_5$ (%) | 0.01 | 0.028 |
| $SO_3$ (%) | 35.2 | 35.6 |
| ZnO (%) | 0.303 | 0.012 |
| CuO (%) | 0.521 | 0.040 |
| NiO (%) | 0.008 | 0.001 |

Concentration of metals (mg/L) in DI water and mine pit water after 24 h contact are provided in Tables 7 and 8, respectively. In DI water, the Bayer precipitates appeared to be the most stable with leached Al, Cu, Zn and Fe concentrations being less than 0.05 mg/L (detection limit), while only 1.30 mg/L of Mn leached. Minimal changes in pH were also observed (remained neutral at around 7.25). Bayer liquor and sodium hydroxide also showed minimal leached Al, Cu, Zn and Fe, however at pH values of 6.04 and 5.67, respectively, an increased amount of Mn was leached (18.3 and 25.3 mg/L) compared to the Bayer precipitates (1.30 mg/L). Interestingly, the Mn concentration for lime, which had the lowest pH value of 5.46, only observed 7.99 mg/L. The main mineralogical difference between Bayer precipitates and lime with the other alkaline materials was the content of gypsum, therefore, the increased stability of Mn in these precipitates was thought to be related to adsorption mechanisms previously explained [62]. Overall, lime and sodium carbonate released the greatest amount of Cu (2.10 and 2.19 mg/L) and Zn (3.83 and 2.29 mg/L) back into solution.

The exposure of the precipitates to mine pit water for 24 h showed greater amounts of leached species. Precipitates obtained after mine pit water treatment with Bayer precipitates had the greatest pH buffering capacity (5.73 after 24 h), due to the formation of hydrotalcite and calcite as shown in Fig. 4; compared to all other alkaline materials whose pH was similar to the original 3.75 of the mine pit water (between 3.80 and 3.90). This pH buffering capacity of Bayer precipitates, meant that Bayer precipitates were able to reduce the concentrations of Cu from 77.3 to 16.2 mg/L, Zn from 48.9 to 34.7 mg/L and Al from 1233 to 42.9 mg/L from mine pit water compared to other alkaline materials which showed an increase in the metal concentrations due to leaching Table 8.

However, for all the tested alkaline materials including Bayer precipitates this was not the case for Mn when leaching the precipitates with mine pit water. Table 8 showed leaching for all tested alkaline

**Table 8**
Metals concentration in Mount Morgan mine pit water from precipitates obtained after treatment with different alkali.

| Alkali | pH | Concentrations (mg/L) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 3.75 | Mg | Ca | Al | Mn | Cu | Zn | Fe |
| Mine pit water | 3.75 | 2265 | 535 | 1233 | 162 | 77.3 | 48.9 | 16.7 |
| Lime | 3.80 | 2547 | 483 | 1284 | 158 | 121 | 63.1 | 1.24 |
| Sodium hydroxide | 3.82 | 2542 | 562 | 609 | 194 | 192 | 145 | < 0.05 |
| Sodium carbonate | 3.87 | 2386 | 579 | 634 | 163 | 209 | 92.8 | < 0.05 |
| Bayer liquor | 3.90 | 2616 | 567 | 583 | 187 | 154 | 115 | < 0.05 |
| Bayer precipitates | 5.73 | 3332 | 517 | 42.9 | 168 | 16.2 | 34.7 | < 0.05 |

materials (due to low pH) which resulted in enhanced Mn concentrations ranging from 158 to 194 mg/L. In acidic conditions hydrotalcite present in Bayer precipitates dissociates, hence why Bayer precipitates showed the highest concentration of leached Mg (resulted in increase in concentration to 3332 from 2265 mg/L compared to concentrations ranging from 2386 to 2616 mg/L for other alkaline materials). It should be noted, that the concentrations of Mg, Cu, Mn and Zn were significantly higher than the original mine pit water, which supported the theory that the increased concentrations observed in this study compared to Edraki, et al. [16] were due to the dissolution of precipitates in the disposed lime sludge. Overall, Bayer precipitates were the most stable in the presence of AMD water.

This study has found Bayer precipitates to perform as well as lime, with the added benefits of increased sludge stability and the removal of manganese at lower pH. However, the mass required for attaining the desired pH is higher for Bayer precipitates (40 g/L to attain pH 7.5), compared to lime (6.16 g/L to attain pH 7.7), and thus associated plant neutralising capacities would be negatively affected. An added incentive for using Bayer precipitates is that they are a waste by-product of the alumina industry; prepared from seawater neutralised residual Bayer liquor. Bayer precipitates are also highly soluble in acidic conditions, whereas the hydrophobic properties of lime means extensive mixing is required [19,22]. By taking into account the cost and behaviour of lime, it is suggested that using Bayer precipitates for AMD neutralisation and removal of metals is an attractive alternative both in terms of effectiveness and that one industry waste can be used to treat another's waste. Consideration into transportation costs and its feasibility requires further investigation.

## 4. Conclusions

This study evaluated the hypothesis that waste Bayer liquor and Bayer precipitates from the alumina refining industry for the neutralisation of acid mine drainage. The first question was whether the waste alkali materials could enhance the pH to achieve water discharge limits. All investigated alkaline materials successfully raised the pH of treated mine pit water to meet discharge limits *i.e.* pH 6.5-8.5. The second research question was in relation to the effectiveness of removal of dissolved metal concentrations to satisfy regulations. This study found that lime and Bayer precipitates were more effective in removing the metals present in Mount Morgan mine pit water than either sodium

**Table 7**
Metals leached in DI water from precipitates obtained after treatment of Mount Morgan mine pit water with different alkali.

| Alkali | pH | Concentrations (mg/L) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Mg | Ca | Al | Mn | Cu | Zn | Fe |
| Lime | 5.46 | 108 | 569 | < 0.05 | 7.99 | 2.10 | 3.83 | < 0.05 |
| Sodium hydroxide | 5.67 | 244 | 73.1 | < 0.05 | 25.3 | < 0.05 | < 0.05 | < 0.05 |
| Sodium carbonate | 5.78 | 177 | 86.9 | < 0.05 | 13.7 | 2.19 | 2.29 | < 0.05 |
| Bayer liquor | 6.04 | 298 | 94.0 | < 0.05 | 18.3 | < 0.05 | < 0.05 | < 0.05 |
| Bayer precipitates | 7.25 | 147 | 209 | < 0.05 | 1.30 | < 0.05 | < 0.05 | < 0.05 |

hydroxide, sodium carbonate or Bayer liquor. The removal capacity of Bayer precipitates and lime was approximately the same for Al, Cu, Fe, Zn and Ni and shown to achieve acceptable discharge limits, whereas in the case of Mn, at lower pH (6.5–7.5) Bayer precipitates were more efficient than lime to decrease its concentration. For complete Mn removal, pH > 9 was required. However, raising the pH > 9 was not viewed as acceptable; since not only was the caustic nature of the water elevated but also aluminium content increased due to dissolution events. Therefore, satisfying discharge limits for Mn remains challenging.

The final research question concerned the search for a scientific explanation to explain differences in performance for the various alkali's. The ability of the precipitates to encapsulate heavy metals was determined to be more important than surface area. Sludge produced after treatment with Bayer precipitates was more stable and showed minimum metal leaching as compared to sludge produced after treatment with other alkali. The mass of material required for attaining the desired pH was higher for Bayer precipitates compared to lime, but the capital cost for a system using lime was considered high due to its hydrophobic nature and the resultant extensive mixing required.

By considering the cost and behaviour of lime, it was suggested that the use of tailings for the treatment of another mining waste was an interesting prospect that has the potential to reduce the footprint of both industries, and therefore making them more sustainable.

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