



Making sense of our mining wastes: removal of heavy metals from AMD using sulphidation media derived from waste gypsum

by J. Mulopo*

Synopsis

This study investigates the recovery of water and the selective removal of valuable metals from acid mine drainage (AMD) using sulphidation media (CaS) derived from waste gypsum. AMD systems containing Fe(II), Ni, Co, Zn, and Pb were investigated using CaS produced from the carbothermal reduction of Anglo Coal waste gypsum at 1025°C to precipitate metals as insoluble metal sulphides. The results show a sulphidation dependence on the pH, sulphide dosage, and metal concentration. The selective sulphidation of metals also showed significant dependence on the respective metal sulphide solubility order as a function of pH. According to the Department of Environmental Affairs' South African Waste Information Centre, over 42 million cubic metres of general waste is generated every year in South Africa and mining waste is by far the biggest contributor to the solid waste (about 72%). Although alarming, these vast quantities of waste also present an opportunity for integrated economic development, particularly in the recycling sector. The major argument has always been that the mining sector generates a large number of waste streams which show strong differences in time, in their treatment methodologies, or even in their spatial distribution. This paper presents a case of a simple strategy for integrated recycling of two mining waste streams and highlights the need for the mining industry to break away from the traditional 'linear' *cul-de-sac* disposal of wastes and think of new sustainable ways of waste management.

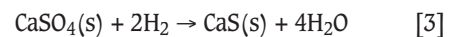
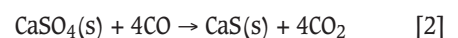
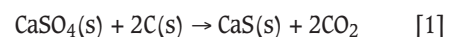
Keywords

acid mine drainage, waste gypsum, CaS, metals removal.

Introduction

Gypsum is a waste product generated by various industries, such as the mining, power generation, and fertiliser industries. For instance, phosphate fertilizer production using the 'wet process' generates phosphoric acid which in turn generates around 4.5 t of waste gypsum per ton of phosphoric acid. Foskor, the only current producer of phosphoric acid in South Africa, operates a fertilizer complex at Richards Bay with a capacity of 780 000 t/a of phosphoric acid (<http://www.sulphuric-acid.com/sulphuric-acid-on-the-web/>). The waste gypsum generated at this plant is pumped into the sea, representing a lost opportunity partially due to the lack of waste gypsum beneficiation or treatment. A total of 55–70 Mt of waste gypsum is currently stockpiled in South Africa at various sites, and indications are that the amounts of waste gypsum generated in South Africa are going

to increase substantially in the future as a result of the treatment of acid mine water and of flue gases in coal-burning operations. Disposal of waste gypsum to landfill is not a viable option due to the shortage of landfill space and the formation of hazardous and toxic gaseous emissions in the form of hydrogen sulphide (H₂S), when gypsum is landfilled with biodegradable wastes. Moreover, legislative requirements for landfill disposal methods, such as the National Environmental Management Waste Act (NEMWA) 59 of 2008, are projected to be more stringent in future, resulting in the need to develop alternative waste management approaches. Previous studies have shown the potential of thermal reduction of waste gypsum at 900 to 1100°C to produce calcium sulphide (CaS) using reducing agents, including solid carbon materials such as coal or activated carbon (Equation [1]) (Kato *et al.*, 2012; Ma *et al.*, 2011; Mihara *et al.*, 2008; Nengovhela *et al.*, 2007), carbon monoxide gas (Equation [2]) (Miao *et al.*, 2012; Zhang *et al.*, 2012; Tian and Guo, 2009; Li and Zhuang, 1999), or hydrogen gas (Equation [3]) (Ning *et al.*, 2011):



Wastewater containing toxic as well as valuable metals is discharged as acid mine drainage (AMD) in major mining and industrial operations. This has led to a sharp increase in metal contamination of water reserves and a potential risk of decant water

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Table I

Composition of the Anglo Coal waste gypsum as determined by XRF analysis

| | | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Cr % | Mn % | Fe % | Co ppm | Ni ppm | Cu ppm | Zn ppm | Ga ppm | Ge ppm | As ppm |
| 0.027 | 0.007 | 0.029 | 24.1 | 11.1 | 8.200 | 16.4 | 7.3 | <0.9 | 0.4 |
| Br ppm | Rb ppm | Sr ppm | Y ppm | Zr ppm | Ag ppm | Cd ppm | Sn ppm | Sb ppm | Te ppm |
| 2.400 | 1.6 | 661.60 | <0.7 | <4.8 | <0.5 | <0.5 | <0.8 | 1.7 | <1.0 |
| Cs ppm | Ba ppm | La ppm | Ce ppm | Hf ppm | Ta ppm | W ppm | Tl ppm | Pb ppm | Th ppm |
| 4.8 | 8.80 | 12.70 | <13.0 | 5.50 | <4.10 | 41.4 | 1.40 | 4.90 | <0.9 |
| Al % | Na % | Mg % | Si % | P % | S % | K % | Ca % | Ti % | V % |
| 0.089 | <0.420 | 0.341 | 0.127 | 0.031 | 16.110 | <0.01 | 21.11 | <0.003 | 0.003 |

from closed mines is looming in the Western, Central, and Eastern basins of the Witwatersrand, South Africa. Because of their toxicity, any of these metals in excessive quantities will adversely interfere with many beneficial uses of the water, such as human consumption and crop irrigation.

Current methods for the removal of heavy metals from wastewater generally require the use of chemical reagents for precipitation of these metals from solution. For instance, lime could be used to precipitate soluble metals in their insoluble hydroxide forms in an alkaline environment (Barnes *et al.*, 1986). Other methods used for removal of metals from AMD include coagulation-flocculation, electro-coagulation, cementation, membrane separation, membrane filtration, solvent extraction, ion exchange, adsorption, and bio-sorption (Meunier *et al.*, 2006; Kurniawan *et al.*, 2006). Among these methods, chemical precipitation with NaOH or Ca(OH)₂ followed by filtration is by far the most widely used process to remove metals from wastewater. However, the major setback with hydroxide precipitation lies in the difficulty of efficiently dewatering the sludge, which leads to generation of enormous volumes of hydroxide sludge.

Other treatment methods such as sulphidation have attracted several researchers (Tokuda *et al.*, 2008; Lewis *et al.*, 2006; Maruyama *et al.*, 1975; Kim, 1980; Bhattacharyya *et al.*, 1979, 1981). The use of sulphidation media derived from waste gypsum as sulphide sources for metal precipitation has been reported by Mihara *et al.* (2008) and Soya *et al.* (2008) as a recycling process for gypsum boards in Japan. This study considers the use of CaS produced by carbothermal reduction of waste gypsum for the treatment of AMD in an attempt to integrate the treatment of two waste streams that poses major challenges to the South African mining industry.

Materials and methods

Feedstock

Waste gypsum from Anglo Coal (Landau Colliery) (Figure 1) was collected. XRD analysis showed that the sample contained 33.65% CaO, 51.38% SO₃, 5.02% MgO, 0.02% Na₂O, 0.15% P₂O₅, 0.03% Fe₂O₃, 0.01% Al₂O₃, and 0.01% SiO₂. The waste sludge was sized to less than 250 µm. X-ray

fluorescence (XRF) analysis was also used to identify the elemental composition in waste gypsum samples. Table I shows the trace metal contents in weight (%) or ppm. Industrial coke from George (South Africa) was used for thermal treatment with composition 60.1% fixed carbon, 2.8% moisture, 10.5% ash content, and 26.7% volatile matters. Acid minewater was collected from Shaft 8, or Winze 18, Harmony Gold Mine (Table II) and the Navigation Coal Mines (Table III). The sulphide precipitation agent (CaS) was obtained by the reductive decomposition of the waste gypsum.

Equipment

A tubular furnace consisting of a 750 mm long, 24 mm diameter mullite tube mounted horizontally and equipped with a temperature controller was used for the thermal reduction of waste gypsum to calcium sulphide. All precipitation experiments were carried out in 1 litre batch plastic beakers equipped with overhead stirrers fitted with radial turbine impellers. A Metrohm 691 pH meter was used to monitor and measure pH. A Perkin Elmer Analyst 700 atomic absorption spectrometer was used to determine Pb, Zn, Ni, and Co.

Table II

Chemical composition of the Harmony Gold Mine water

| Parameter | Feed (mg/L) |
|-----------|-------------|
| pH | 3.1 |
| Sulphate | 4510 |
| Chloride | 37 |
| Free acid | 500 |
| Sodium | 96 |
| Potassium | 3 |
| Magnesium | 113 |
| Calcium | 559 |
| Pb | 16 |
| Manganese | 174 |
| Iron(II) | 1196 |
| Aluminium | 6 |
| Zinc | 49 |
| Nickel | 43 |
| Cobalt | 85 |

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Table III

Chemical composition of the Navigation Coal Mine water

| | Units | |
|------------|------------------------|------|
| pH | | 3.00 |
| Acidity | mg/L CaCO ₃ | 700 |
| Alkalinity | mg/L CaCO ₃ | 0 |
| Sulphate | mg/L | 3200 |
| Aluminium | mg/L | 43 |
| Calcium | mg/L | 447 |
| Fe (II) | mg/L | 840 |
| Co | mg/L | 75 |
| Ni | mg/L | 93 |
| Pb | mg/L | 0.09 |
| Zinc | mg/L | 75 |



Figure 1 – Photograph of the Anglo Coal waste gypsum

Experimental procedure

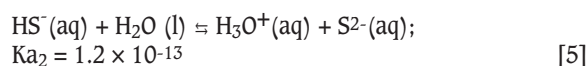
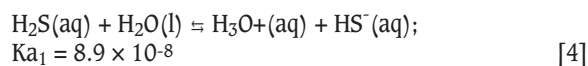
The two AMD samples were submitted for Pb, Zn, Ni, and Co analysis by atomic absorption spectrometry (AAS) in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA, 1992). Fe(II) in the AMD was determined in-house by iodometry. The amount of CaS required to remove the metals from the AMD was calculated from the total metal analyses using a sulphide/total metal ratio of 1.0.

CaS was produced by carbothermal reduction of waste gypsum in a muffle furnace at a temperature of 1025–1030°C for 45 minutes using a C/CaSO₄ molar ratio of 2. The CaS yield was about 78%, as shown in Table IV. The effect of sulphide addition to the AMD system was investigated using sulphide/total metal mole ratios of 0, 0.5, 0.75, 1.0, 1.5, 2.0, and 2.5. Appropriate amounts of CaS were added to the AMD

to give a total of 1 L mixture and batch equilibrium removal experiments were run at appropriate pH values using a pH cascading approach. The metal removal batch experiments were carried out for at least 5 minutes at a particular pH or until a steady pH was attained. At each pH used a 50 ml sample was collected, filtered using Whatman 12.5 cm qualitative filter papers, acidified with 2.5 ml concentrated HCl, and left overnight to drive out any residual sulphide and preserve the metals. A portion of the sample was used for Fe(II) determination while the rest of the sample was used for the determination of Pb, Zn, Ni, and Co by AAS. The residue was submitted for XRD analysis using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence and fixed receiving slits with Fe-filtered Co-K α radiation on a back-loading preparation method. The phases were identified using X'Pert Highscore Plus software.

Results and discussion

The extent of metal sulphide precipitation in multi-metal systems such as AMD is expected to be a function of pH, reaction time, initial metal concentration, sulphide dosage, and the presence of chelating agents and other interfering ions. With some metals such as nickel and cobalt, the precipitation is also dependent on the reactor system (closed or open). The effect of pH on solubility can be used to separate metal ions by sulphide precipitation. Many metal sulphides are insoluble in water but dissolve in acidic solution. Qualitative analysis uses this change in solubility of the metal sulphides with pH to separate a mixture of metal ions. Hydrogen sulphide is a stronger acid than water, ionizing in water as a diprotic acid according to Equations [4] and [5]:



The ionization forms bisulphide ion, HS⁻, and sulphide ion, S²⁻, which can combine with the metal ions to precipitate the metal sulphides. However, the S²⁻ ion is a strong base (K_b approx. 10⁵) and will react immediately to form HS⁻ and a hydroxide ion. The true concentration of S²⁻ in solution therefore is negligible.

By adjusting the pH in an aqueous solution, one can adjust the sulphide ion concentration in order to precipitate the least soluble metal sulphide while maintaining the other metal ions in solution. For instance, the solubility product constant of lead (II) sulphide is much smaller than that of zinc sulphide, therefore lead sulphide will be expected to precipitate before zinc sulphide.

In order to investigate the interactions between different metal ions and observe the possible differences in individual metal sulphide precipitation in typical AMD wastewater containing Pb, Zn, Ni, Co, and Fe(II),

Table IV

XRD analysis of CaS produced by the thermal reduction of gypsum

| CaSO ₄ % | CaS % | CaO % | MgO % | Ca ₂ Al ₂ SiO ₇ % | MgAl ₂ O ₄ % | Ca ₅ (PO ₄) ₃ OH % |
|---------------------|-------|-------|-------|--|------------------------------------|--|
| 0 | 78 | 6 | 4 | 5 | 5 | 2 |

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Effect of pH

The pH values required for selective sulphidation of Pb, Zn, Ni, Co, and Fe (II) in typical AMD wastewater were determined based on the results reported by previous workers (Soya *et al.*, 2008). The basis of metal sulphide solubility as a function of pH was also taken into consideration. In this regard, the pH range 3.0–10.0 was targeted for selective sulphidation of Pb, Zn, Ni, Co, and Fe(II) in AMD wastewater. The selective sulphidation of the various metals was carried out using a pH cascade approach. Figures 2 and 3 show the change in Zn, Ni, Co, and Fe (II) concentrations in the filtrate. For reasons of clarity, the results for Pb are not plotted. It can be seen that the Zn concentration was reduced to a value below 1.0 mg/L for all AMD wastewaters studied at a molar ratio of sulphide to Zn of about 1.0. As the pH increased, selective removal of Ni was achieved at an average pH range of 5.0–7.0. From Figures 2 and 3, it can be seen that Ni is 90% removed at pH 5.0 from Harmony AMD and at pH 7.0 from Navigation AMD. To achieve the same removal efficiency, both the Harmony would require a pH value of

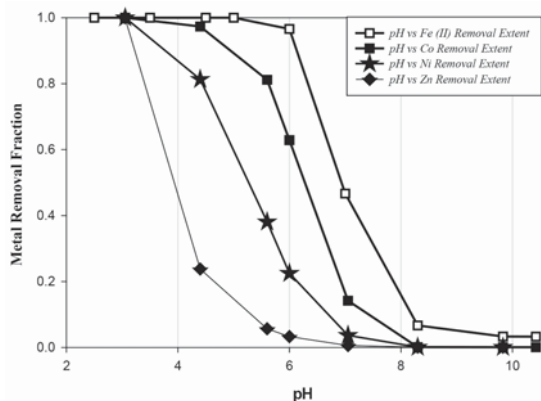


Figure 2 – Effect of pH on selective removal of metals from Newcastle AMD in a pH cascade experiment (5 minutes' reaction time per unit pH). Initial metal concentrations were 75 mg/L Zn, 93 mg/L Ni, 75 mg/L Co, and 840 mg/L Fe. The metal removal fraction is defined as the ratio of the metal concentration at time t (mg/L) and the initial metal concentration (mg/L)

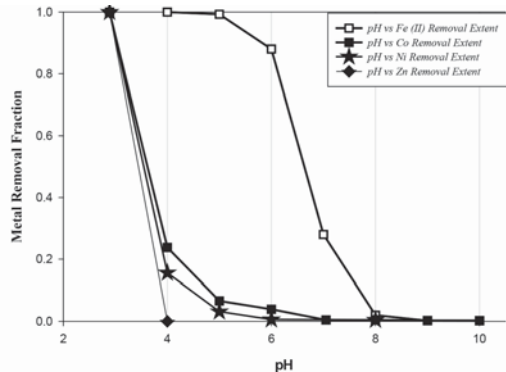


Figure 3 – Effect of pH on selective removal of metals from Harmony AMD in a pH cascade experiment (5 minutes' reaction time per unit pH). Initial metal concentrations were 49 mg/L Zn, 43 mg/L Ni, 85 mg/L Co, and 1396 mg/L Fe. The metal removal fraction is defined as the ratio of the metal concentration at time t (mg/L) and the initial metal concentration (mg/L)

6.0. The next metal to be removed from AMD was Co. Figures 2 and 3 show that Co is more than 80% removed at pH values above 7.0 for from Navigation AMD, while for the Harmony AMD the same removal is achieved at a lower pH of slightly greater than 4.0. Figures 2 and 3 show that significant Fe(II) removal occurs only at pH values higher than around 6.0.

To achieve 90% Fe(II) removal, the pH of the AMD wastewater had to be increased to an average of 8.0. Fe(II) is removed to less than 50 mg/L at pH 9.0 from both types of AMD wastewater used in this study. At this pH, more than 99% of the Zn, Ni, and Co have already been completely removed.

Despite using an open reactor system, which is prone to atmospheric oxidation, no evidence for nickel sulphide and cobalt sulphide dissolution was observed. This could be due to the short retention times for the metal sulphide residue in the AMD wastewater.

The selective removal data trends for the two AMD wastewaters studied indicate the critical role of metal sulphide solubility and pH on the removal efficiency. The solubilities of the metal sulphides under consideration are in the order $PbS < ZnS < NiS < CoS < FeS$. In this regard, the least soluble metal sulphides (PbS and ZnS) are precipitated first while the most soluble metal sulphide (FeS) is precipitated last in a pH cascade experiment. NiS and CoS, with comparable solubilities, are removed within a narrow pH range. From these results, it was also inferred that under low pH conditions ($pH < 4.0$), $H_2S(aq)$ was the predominant species (García-Calzada *et al.*, 2000; Peters *et al.*, 1985), and part of the H_2S is released from the solution as H_2S gas due to the poor precipitation of the metal sulphides in an acidic solution. Moreover, from molecular orbital theory, the highest occupied molecular orbital (HOMO) for HS^- has been calculated to be -2.37 eV, which compares well with the experimental value of -2.31 eV (Drzaić *et al.* 1984; Radzig and Smirnov 1985). The HOMO for HS^- is less stable than that for H_2S (-10.47 eV), indicating that HS^- is more nucleophilic and basic than H_2S , which is consistent with the observed reactivity for metal sulphide precipitation observed in this study. Thus, H_2S is not a strong electron donor because the HOMO is so stable.

Effect of sulphide addition

Figure 4 shows the changes in the Pb, Zn, Ni, Co, and Fe(II) concentrations in filtrates obtained from Harmony AMD wastewater at different sulphide to total metal molar ratios over a period of 90 minutes. The order of metal removal follows the order of solubility of the respective metal sulphides, with the least soluble metal sulphide precipitated first. In the case of Pb, Zn, Ni, and Co, it can be seen that the metal concentrations in the filtrate were reduced to below 5% using a sulphide to total metal ratio of 1.0. In contrast, at this same sulphide to total metal molar ratio, less than 80% of Fe(II) is removed. At a sulphide to total metal ratio of 1.5, Pb, Zn, Ni, and Co in the filtrate were reduced to a value below 1.0 mg/L, representing more than 99% metal removal. Less than 40% of the Fe(II) was removed using this sulphide to total metal molar ratio. Thus the addition of the CaS agent at a sulphide to total metal ratio of 2.0 was necessary to achieve more than 70% Fe(II) removal in the filtrate.

The poor Fe(II) removal at sulphide to total metal ratios of 1–1.5 can be explained in two ways. Firstly, Fe(II) forms the least soluble metal sulphide compared to all the other metals,

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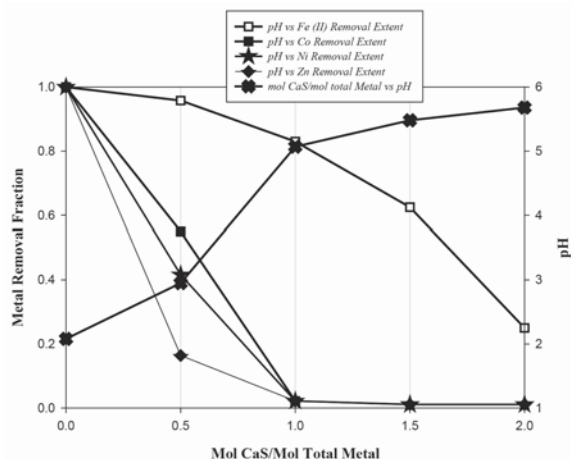


Figure 4 – Effect of sulphide addition on selective removal of metals from Harmony AMD using CaS as sulphide source over a reaction time of 90 minutes per sulphide dosage addition. Initial metal concentrations: 1340 mg/l Fe(II), 136 mg/l Ni, 136 mg/l Co, 136 mg/l Zn, and 74 mg/l Pb

Pb, Zn, Ni, and Co. In this regard, FeS is not expected to precipitate at pH values lower than 5.5, as shown by the pH profile for the sulphide to total metal ratios of 1.0–1.5. Secondly, rapid precipitation of both PbS and ZnS on the CaS particles could have brought about encapsulation of unreacted CaS inside the PbS and ZnS particles. As a consequence, a higher molar ratio of CaS to total metal was needed to achieve more than 70% removal of Fe(II) in the filtrate. Similar CaS encapsulation by CuS precipitation at low pH has been reported by Soya *et al.* (2008).

Conclusions

The sulphidation behaviour of Fe (II) using CaS derived from waste gypsum as a sulphidation agent was investigated, together with the possibility of selective precipitation of Pb, Zn, Ni, Co, and Fe(II) from various AMD solutions. It was found that Pb, Zn, Ni, and Co can be removed as metal sulphides at lower pH values while Fe(II) stays in solution – enabling the ferrous iron to be separated from the other metals, which is a great advantage for metal recovery. Selective metal removal and recovery as metal sulphides may be achieved conveniently using CaS as the sulphidation medium. However, the purity of CaS obtained by the thermal reduction of waste gypsum and mass transfer limitations associated with the AMD–CaS system may be critical for process development. Moreover, the settling characteristics of the precipitates are poor, but this could probably be improved by the use of an anionic polymer at low pH.

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