

Fractional and sequential recovery of inorganic contaminants from acid mine drainage using cryptocrystalline magnesite

Vhangwele Masindi^{1,2,3}; John G. Ndiritu¹

¹*School of Civil and Environmental Engineering, University of the Witwatersrand, Private Bag 3, WITS 2050, South Africa, john.ndiritu@wits.ac.za*

²*Council for Scientific and Industrial Research (CSIR), Built Environment (BE), Hydraulic Infrastructure Engineering (HIE), P.O Box 395, Pretoria, 0001, South Africa, Tel: +2712 841 4107, Fax: +27128414847, VMasindi@csir.co.za, masindivhahangwele@gmail.com*

³*Department of Environmental Sciences, School of Agriculture and Environmental Sciences, University of South Africa (UNISA), P. O. Box 392, Florida, 1710, South Africa*

Abstract This study evaluated the fractional and sequential recovery of inorganic contaminants from acid mine drainage (AMD) using cryptocrystalline magnesite. Batch experimental approach was used to fulfil the goals of this study. The obtained results revealed that $\geq 99.9\%$ of metals were recovered. Experimental and Geochemical modelling revealed that Fe was recovered at $\text{pH} \geq 3.5$, Al at $\text{pH} \geq 4.5$, Mn at $\text{pH} \geq 9$, Cu at $\text{pH} \geq 7$, Zn at $\text{pH} \geq 8$, Pb at $\text{pH} \geq 8$ and Ni at $\text{pH} \geq 9$. This study successfully proved that metal species can be fractionally and sequentially recovered from acid mine drainage using cryptocrystalline magnesite.

Key words Acid mine drainage, cryptocrystalline magnesite, neutralisation, recovery, precipitation

Introduction

Availability of Fe, Al, Mn and sulphate in acid mine drainage at elevated levels makes a valuable source of recoverable minerals. The genesis of these major metals and anions in acid mine drainage is as a result of hydro-geochemical weathering of pyrite and other sulphide bearing lithologies. The presence of toxic chemical species in AMD has raised environmental concerns at regional, national and international scientific communities (Masindi et al. 2017). The resultant water is very acidic hence dissolving the metals in the surrounding rocks. As a result, AMD has $\text{pH} \leq 2$, high dissolved metals and electrical conductivity (Masindi 2016). Chemical species leached to the surrounding aqueous solution include Al, Fe, Mn and SO_4^{2-} , and traces of Cu, Zn, Pb, and Ni. Toxicity and epidemiological studies reported that these metals are hazardous to terrestrial and aquatic organisms on exposure (Masindi et al. 2015), as such, they require treatment prior release to the environment and different end-users.

Passive and active technologies have been developed to treat AMD but downstream products limit their applications. Research studies have been in a quest to come-up with pragmatic and prudent technologies that can be employed for the recovery of valuable minerals (Seo et al. 2017a). The recovery of elements from acid mine drainage will generate some revenues that will aid in off-setting the running cost of the treatment process through commercialisation of the recovered resources (Masindi et al. 2015; Seo et al. 2017a).

Numerous methods have been developed and adopted for the recovery of metals from acid mine drainage and they include: neutralisation, adsorption, filtration, solvent extraction and electro dialysis (Seo et al. 2017a; Simate and Ndlovu 2014). Precipitation has been a commonly used method for metals recovery (Seo et al. 2017a). Precipitators commonly used are sodium hydroxide, sodium carbonate and lime (Seo et al. 2017a). Using these precipitators, metals will be recovered as hydroxides (Masindi et al. 2017). The use of cryptocrystalline magnesite for fractional and sequential recovery of metals from acid mine drainage has never been explored, as such, this is the first study in design and execution to explore the efficiency and feasibility of using cryptocrystalline magnesite to fractionally and sequentially recover potentially toxic metals from acid mine drainage. PHREEQC geochemical model was also employed to complement the experimental results.

Materials and Methods

Materials

Raw magnesite rock was collected from the Folovhodwe Magnesite Mine in Limpopo Province, South Africa. Field AMD samples were collected from a coal mine in Mpumalanga province, South Africa. Before the experiments, magnesite samples were milled to a fine powder for 15 minutes at 800 rpm using a Retsch RS 200 vibratory ball mill and passed through a 32 µm particle size sieve. The samples were kept in a zip-lock plastic bag until utilization for sensitivity study and the recovery of metals.

Characterization

Aqueous samples were analysed using ICP-MS (7500ce, Agilent, Alpharetta, GA, USA). The accuracy of the analysis was monitored by analysis of National Institute of Standards and Technology (NIST) water standards. Three replicate measurements were made on each sample and results are reported as mean average. Morphological properties were examined using Scanning Electron Microscopy (SEM) (JEOL JSM – 840, Hitachi, Tokyo, Japan). PHREEQC geochemical model was used to model the precipitation of chemical species from acid mine drainage.

Results and discussions

Morphology by Scanning Electron Microscopy (SEM)

The morphological properties of raw cryptocrystalline magnesite and AMD-reacted magnesite are shown in fig. 1.

Cryptocrystalline magnesite was observed to contain octagonal sheet and leafy-like structures on its surface (Fig. 1A). This is an indication that the material is heterogeneous. After contacting acid mine drainage (AMD), there was a transformation on the morphological properties of the recovered sludge hence indicating a possible dissolution and a subsequent deposition of chemical species. The sheet and leafy-like structures were observed on the surface of a secondary residue. The morphology was similar throughout the surface hence denoting that the recovered material is homogeneous.

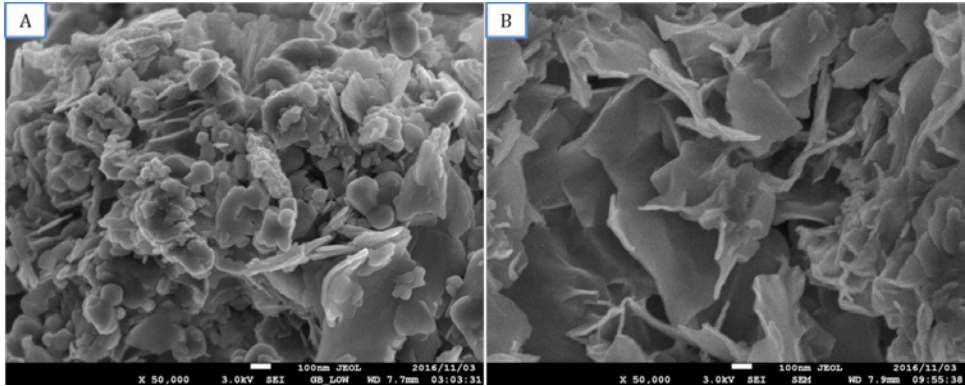


Figure 1 Morphological property of raw magnesite and AMD-reacted magnesite

Effect of pH on the removal of ions

An increase in pH and variation in percentage removal of chemical species during interaction of magnesite with AMD is shown in fig. 2.

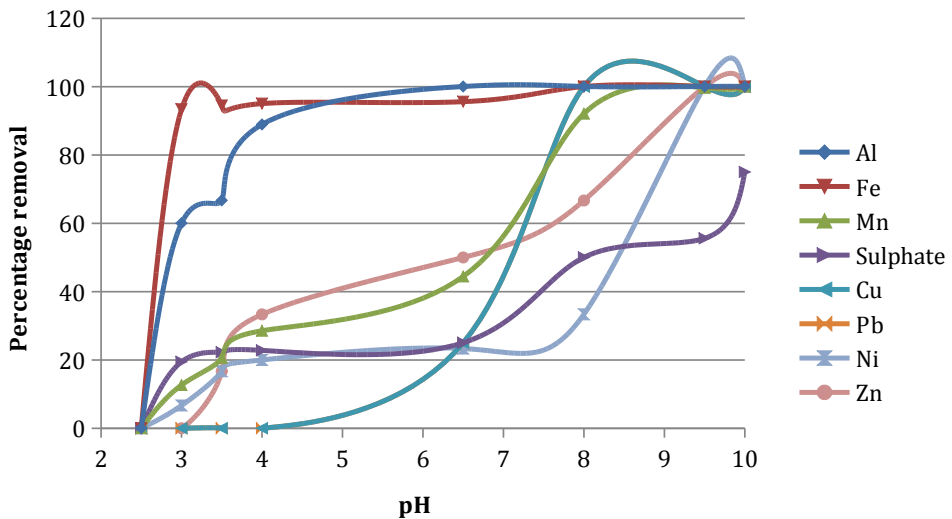


Figure 2 Variation of pH and heavy metals concentration with adsorbent dosage (Conditions: 100 mL solution, 250 rpm shaking speed, <math><32\ \mu\text{m}</math> particle size, 60 min reaction, 26 °C temperature).

As shown in fig. 2, the chemical species removal efficiencies were directly proportional to the pH of the supernatant solution. As the pH was increasing, the metal removal efficiency was also observed to increase, however, this was anticipated. An increase in pH may be attributed to dissolution of CaO and MgO from the magnesite matrices hence leading to an increase in pH. Similar results were reported by Masindi et al. (2015). Furthermore, Figure 2 points out that the chemical species were totally removed from the aqueous solution

($\geq 99.9\%$) with Fe-species removed at $\text{pH} > \approx 4$, Al-species removed at $\text{pH} > \approx 6$ and Mn species removed at $\text{pH} > \approx 9$. The result of this study are consistent with the results obtained by Wei and Viadero Jr (2007). This is an indication of optimum pH suitable for the recovery of this chemical species. Trace elements were observed to precipitate at varying pH regimes with Cu at $\text{pH} \geq 7$, Zn at $\text{pH} \geq 8$, Pb at $\text{pH} \geq 8$, and Ni at $\text{pH} \geq 9$. Similar results were reported by Park et al. (2013). Close to 100% removal efficiency was achieved for all the metals at a given pH gradient except for sulphate. Cu, Ni, Pb and Zn are insignificant due to minute concentration, as such; there is no metal recovery potential for those species.

Geochemical modelling of chemical species removal with varying pH gradients

The PHREEQC modelled Variation in percentage removal of chemical species in AMD is shown in fig. 3.

As shown in fig. 3, the PHREEQC geochemical model simulations indicated that the Fe(III) was removed at $\text{pH} \geq 3.5$. This is due to the fact that AMD was oxidised already on decant and the addition of magnesite increased the pH to > 10 hence making the Fe(III) to precipitate. Fe(II) was observed to precipitate at $\text{pH} > 8.5$. Similar results were reported by Petrilakova et al. (2014). Mn was simulated to precipitate at $\text{pH} 9.5$. Zn was predicted to precipitate at $\text{pH} 10$, Cu was predicted to precipitate at $\text{pH} 8$. These results were consistent to the studies by Petrilakova et al. (2014) and Seo et al. (2017b). Ni and Pb were observed to precipitate at $\text{pH} 8$. Sulphate was observed to precipitate from $\text{pH} 4$ to $\text{pH} 12$. A similar study was reported by Masindi et al. (2016).

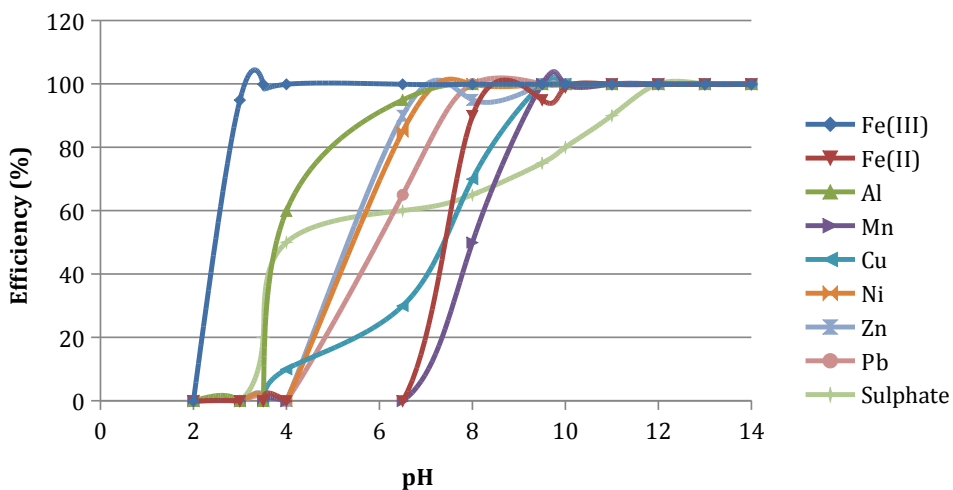


Figure 3 Variations of chemical species concentration with the pH using PHREEQC geochemical modelling.

Sensitivity analysis of cryptocrystalline magnesite to AMD ratios

Sensitivity of acid mine drainage to certain dosages of cryptocrystalline magnesite is shown in fig. 4.

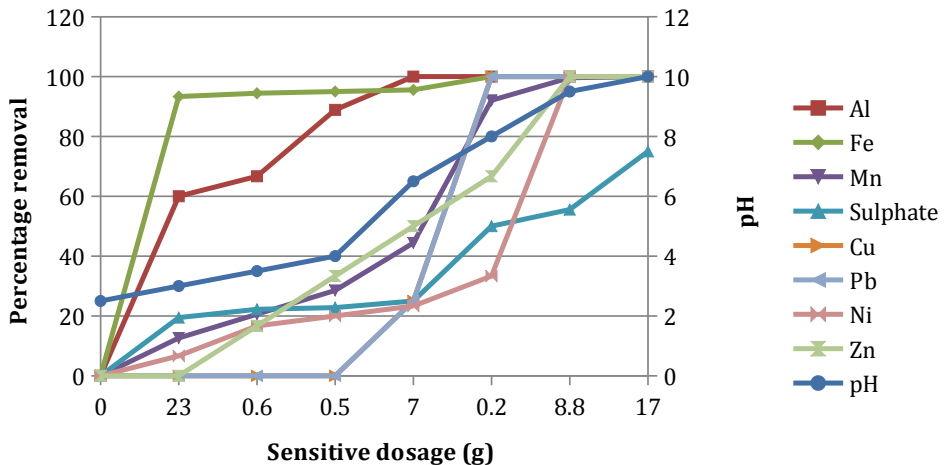


Figure 4 Sensitivity test and ions removal efficiency for AMD and calcine cryptocrystalline magnesite.

The chemical species concentration in AMD water before and after contacting varying dosages of calcined cryptocrystalline magnesite as shown in fig. 4, this will assist in showing the dosage requirement for different mine drainages and their respective pH. The initial pH required 23 g of calcined cryptocrystalline magnesite to increase the pH from 2 to ≈ 3 . This may be attributed to neutralisation of free acidity in an aqueous system. Similar results were reported by Bologo et al. (2012). After that, the dose requirement was significantly reduces. pH was also observed to increase with an increase in dosage. This may be due to addition of extra alkalinity when adding more of calcined cryptocrystalline magnesite. The pH trend is directly related to the metal removal trend as predicted by PHREEQC geochemical modelling.

AMD is characterised of Fe(II) and Fe(III), this makes it the best candidate for the recovery of magnetite. At $\text{pH} > 3$, most of Fe(III) were removed and $\text{pH} > 8$, most of Fe(II) are removed. This can be seen by the pH trend and Fe removal trend as shown in fig. 2. The results corroborate what has been reported in literature (Akinwekomi et al. 2017; Wei and Viadero Jr 2007). Al was optimally removed at $\text{pH} > 6.5$. Similar results were reported by Hedrich and Johnson (2014), Seo et al. (2017a), and Akinwekomi et al. (2017). Cu and Pb were observed to precipitate at $\text{pH} \geq 7.5$. This was similar to the studies conducted by Park et al. (2013), Oh et al. (2016) and Masindi et al. (2016). Ni and Zn precipitated at $\text{pH} \geq \approx 9$. This indicates that this technology can be applied to water with any pH gradient and recover valuable minerals that have commercial value.

Saturation index using PHREEQC geochemical modelling

The saturation indices (SI) of different selected potentially toxic metals at varying final pH are shown in fig. 5.

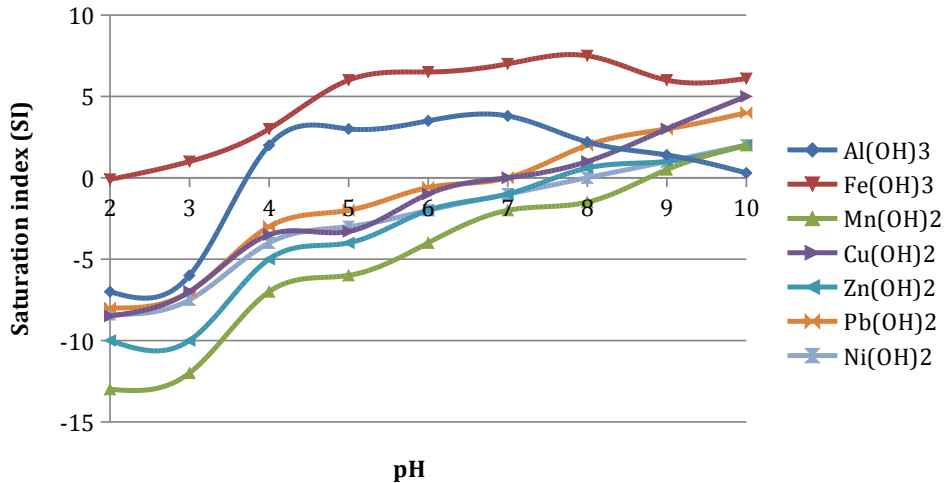


Figure 5 Saturation indices (SI) of different selected potentially toxic metals at varying final pH

As shown in fig. 5, PHREEQC geochemical model was used to complement experimental results and to point out species that are more likely to precipitate during the interaction of magnesite with acid mine drainage. The anticipated sludge were hematite, diaspore, bronchitite, hydrozincite and nickel carbonate. Zn and Ni were expected to precipitate together hence seeking more metallurgical processes for the recovery. This results were also anticipated in a number of published studies such as Masindi et al. (2017) and Park et al. (2013). The obtained results revealed that Fe was recovered at $\text{pH} \geq 3.5$, Al at $\text{pH} \geq 4.5$, Cu at $\text{pH} \geq 7$, Zn at $\text{pH} \geq 8$, Pb at $\text{pH} \geq 8$, Mn at $\text{pH} \geq 9$, and Ni at $\text{pH} \geq 9$. This has proven that metal species in acid mine drainage can be fractionally recovered at varying pH gradients in a sequential manner. The PHREEQC geochemical model results were consistent to the experimental results hence commending and attesting that the obtained results were valid and reputable. This was also confirmed by SEM-EDS.

Conclusions and recommendations

In this study, the recovery efficiency of potentially toxic metals from acid mine drainage by magnesite at varying dosages and pH gradients were successfully evaluated at 60 mins of equilibration. Magnesite increased the pH of acid mine drainage from pH 2 -10 with an increase in dosage. The removal sequence was observed to be pH 3.5 for Fe, pH 4.5 for Al, pH 7 for Cu, pH 8 for Zn, pH 8 for Pb, pH 9 for Mn and Ni. The sequence can be as follow: Fe > Al > Cu > Zn > Pb > Mn > Ni in order. Close to 100% metals removal efficiency was achieved. Further research work is underway to determine the purity of recovered potentially toxic metals.

Acknowledgements

The authors thank would like to thank National Research Foundation (NRF), University of the Witwatersrand and the Council for scientific and industrial research for sponsoring this project.

References

- Akinwekomi V, Maree JP, Zvinowanda C, Masindi V (2017) Synthesis of magnetite from iron-rich mine water using sodium carbonate. *Journal of Environmental Chemical Engineering*, doi:10.1016/j.jece.2017.05.025
- Bologo V, Maree JP, Carlsson F (2012) Application of magnesium hydroxide and barium hydroxide for the removal of metals and sulphate from mine water. *Water SA* 38:23-28
- Hedrich S, Johnson DB (2014) Remediation and Selective Recovery of Metals from Acidic Mine Waters Using Novel Modular Bioreactors. *Environ Sci Technol* 48:12206-12212, doi:10.1021/es5030367
- Masindi V (2016) A novel technology for neutralizing acidity and attenuating toxic chemical species from acid mine drainage using cryptocrystalline magnesite tailings. *Journal of Water Process Engineering* 10:67-77, doi:10.1016/j.jwpe.2016.02.002
- Masindi V, Gitari MW, Tutu H, De Beer M (2015) Passive remediation of acid mine drainage using cryptocrystalline magnesite: A batch experimental and geochemical modelling approach. *Water SA* 41:677-682, doi:10.4314/wsa.v41i5.10
- Masindi V, Gitari MW, Tutu H, De Beer M (2016) Fate of inorganic contaminants post treatment of acid mine drainage by cryptocrystalline magnesite: Complimenting experimental results with a geochemical model. *Journal of Environmental Chemical Engineering* 4:4846-4856, doi:10.1016/j.jece.2016.03.020
- Masindi V, Gitari MW, Tutu H, DeBeer M (2017) Synthesis of cryptocrystalline magnesite–bentonite clay composite and its application for neutralization and attenuation of inorganic contaminants in acidic and metalliferous mine drainage. *Journal of Water Process Engineering* 15:2-17, doi:10.1016/j.jwpe.2015.11.007
- Oh C, Han Y-S, Park JH, Bok S, Cheong Y, Yim G, Ji S (2016) Field application of selective precipitation for recovering Cu and Zn in drainage discharged from an operating mine. *Sci Total Environ* 557–558:212-220, doi:10.1016/j.scitotenv.2016.02.209
- Park SM, Yoo JC, Ji SW, Yang JS, Baek K (2013) Selective recovery of Cu, Zn, and Ni from acid mine drainage. *Environ Geochem Health* 35:735-743
- Petrilakova A, Balintova M, Holub M (2014) Precipitation of heavy metals from acid mine drainage and their geochemical modeling vol 9. doi:10.2478/sspjce-2014-0009
- Seo EY, Cheong YW, Yim GJ, Min KW, Geroni JN (2017a) Recovery of Fe, Al and Mn in acid coal mine drainage by sequential selective precipitation with control of pH. *CATENA* 148, Part 1:11-16, doi:10.1016/j.catena.2016.07.022
- Seo EY, Cheong YW, Yim GJ, Min KW, Geroni JN (2017b) Recovery of Fe, Al and Mn in acid coal mine drainage by sequential selective precipitation with control of pH. *CATENA* 148:11-16, doi:10.1016/j.catena.2016.07.022
- Simate GS, Ndlovu S (2014) Acid mine drainage: Challenges and opportunities. *Journal of Environmental Chemical Engineering* 2:1785-1803, doi:10.1016/j.jece.2014.07.021
- Wei X, Viadero Jr RC (2007) Synthesis of magnetite nanoparticles with ferric iron recovered from acid mine drainage: Implications for environmental engineering. *Colloids Surf Physicochem Eng Aspects* 294:280-286, doi:10.1016/j.colsurfa.2006.07.060