

Neutralization and Attenuation of Metal Species in Acid Mine Drainage and Mine Leachates Using Magnesite: a Batch Experimental Approach

V. Masindi^{1,3}, W.M. Gitari¹, H. Tutu², M. De Beer³, N. Nekhwevha¹

*1 Environmental Remediation and Pollution Chemistry Group, University of Venda,
mugera.gitari@univen.ac.za; mugeraw@gmail.com*

2 Department of Chemistry, University of Witwatersrand, hlanganani.tutu@wits.ac.za

3 CSIR (Council of Scientific and Industrial Research): mdebeer@csir.co.za, Vmasindi@csir.co.za

Abstract This paper evaluates the potential application of amorphous magnesite for remediation of Acid Mine Drainage (AMD). Magnesite was mixed with simulated AMD at specific S/L ratios and agitated in an orbital shaker and its capacity to remove metals and neutralize the acidity assessed over time. XRF analysis showed that magnesite contains MgO (88.54 %) as the major element. XRD revealed that magnesite is amorphous and contains periclase as major mineral phase. Results indicate that contact of AMD with magnesite leads to an increase in pH (pH \geq 10), and a reduction in EC, TDS and metal concentration to below DWAF guidelines. PHREEQC geochemical modeling predicted precipitation of Al, Fe, Mn, Mg bearing mineral phases could be responsible for attenuation of most metal species. However a high proportion of alkali and alkaline earth metals remained in the treated water which might require post treatment polishing.

Keywords acid mine drainage, magnesite, metal species, neutralization

Introduction

Mineral exploitation contributes to socio-economic development of a country. In 1995, mining contributed to 7.7 % of GDP of South Africa (Wilson et al. 1998). However mineral resources exploitation can leave in its wake disastrous environmental consequences that require mitigation long after the mineral extraction has stopped. Some of the environmental consequences of mining include: dewatering and disposal of poor quality water pumped from underground mine workings. Of major concern is huge volume of acidic water (acid mine drainage-AMD) which is generated in active and old abandoned mines underground workings. This water requires treatment to DWA/DWAF (1996) set guidelines. Several technologies have been advanced for treatment of AMD. These are, limestone and lime treatment, biological sulphate reduction and passive treatment in alkalinity generating artificially constructed wetlands. Magnesite has the potential to neutralize and precipitate heavy metals in acidic solutions such as AMD. Due to the high solubility of MgSO₄ (260 g/L) only metal hydroxides precipitate with little sulphates. Magnesite also has the capability of raising the pH to 10 which is sufficient for removal of metals like manganese and zinc that cannot be removed with limestone (Bologo et al, 2012). This study evaluates the capacity of magnesite to neutralize acidity and attenuate metal species in AMD. It's the first part of a planned series of experiments to evaluate the feasibility of a magnesite based technology for remediation of AMD and acidic tailing leachates for coal, copper and phosphate mines based in Limpopo. Significant deposits of magnesite are available in Limpopo province of South Africa.

Materials and methods

Sample collection and preparation

The treatment of AMD with magnesite was optimized using synthetic acid mine drainage solutions while final treatment at optimized conditions used AMD from Krugersdorp Gold mine in Gauteng, South Africa. Magnesite was collected from Folovhodwe magnesite mine

in Limpopo province. Synthetic AMD solution was simulated by dissolving the following quantities of salts in 1000 mL of ultra-pure water, 7.48 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 2.46 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, and 0.48 g MnCl_2 to give a solution of 2000 mg/L Fe^{2+} , 200 mg/L Al^{3+} and 200 mg/L Mn^{2+} . A 5 mL of 0.05 M H_2SO_4 was added to make up SO_4^{2-} concentration to 6000 mg/L. Magnesite samples were milled into fine powder using Retsch RS 200 miller and passed through a 32 μm particle size sieve.

Physicochemical and mineralogical characterization

For X-ray diffraction Analysis (XRD) a back loading preparation method. A PANalyticalX'Pert Pro powder diffractometer with X'Celerator detector was used. For X-ray fluorescence (XRF) analysis, a Thermo Fisher ARL9400 XP+ Sequential XRF with WinXRF software was used for analysis. Morphology of raw and reacted magnesite was examined using Hitachi X-650 scanning electron micro-analyzer.

Treatment of AMD with magnesite: optimization of reaction conditions

Nine, 100 mL samples of 2000 mg/L Fe^{3+} , 100 mg/L Al^{3+} and 50 mg/L Mn^{2+} , and 12000 mg/L SO_4^{2-} solution was pipetted into nine, 250 mL bottles and 1g of magnesite added. The mixture was agitated at varying contact time. pH, Temp, EC, and TDS was measured before and after agitation and then filtered through a 0.45 μm pore nitrate cellulose filter membrane. Two drops of concentrated HNO_3 acid were added to prevent aging and immediate precipitation of Al^{3+} , Fe^{3+} , and Mn^{2+} ions. The samples were refrigerated at 4°C until analysis by NexION 300 Inductively coupled plasma mass spectrometer (ICP-MS). SO_4^{2-} was analysed using ion chromatography.

Nine, 100 mL solutions of 1000 mg/L Fe^{3+} , 1000 mg/L Al^{3+} and 500 mg/L Mn^{2+} , and 12000 mg/L SO_4^{2-} was pipetted into nine, 250 mL bottles and varying masses of magnesite added. The mixtures were agitated for an optimum time of 60 minutes at 250 rpm using the Stuart reciprocating shaker. pH, Temp, EC, and TDS was measured using a CRISON multimeter MM40 probe before and after agitation. The filtered samples were treated as discussed previously.

Treatment of field sampled AMD with magnesite at the optimized conditions

One gram of magnesite was added to 100 mL of field AMD sample and agitated for a time of 120 minutes at 250 rpm using the Stuart reciprocating shaker. Measurement of pH, Temp, EC, and TDS was done by CRISON multimeter MM40 probe before and after agitation. The filtered samples were treated as discussed previously

Results and discussions

Physicochemical and mineralogical characterization

XRF results showed that the main component of magnesite is MgO with trace components of SiO_2 , CaO, Al_2O_3 and Fe_2O_3 . XRD revealed that magnesite is composed of periclase (88 %), brucite (9%) and forsterite (3%). The presence of forsterite is an indication that this geological material has been formed from the evaporation and replacement of Fe from FeCO_3 (Siderite) and feldspars by Mg. These results also verify findings from the XRF analysis. A change in morphology was observed for AMD reacted magnesite particles with increased agglomeration being observed. New elongated structures were also observed indicating formation of new mineral phases.

Treatment of AMD as a function of contact time

Results for variation of various parameters evaluated with contact time are presented in figure 1. An increase in pH with an increase in contact time is observed, an indication that the amorphous magnesite dissolution releases alkalinity on interacting with the acidic solution. A corresponding decrease in Al^{3+} , Fe^{2+} , Mn^{2+} and TDS is observed. At $pH > 10$, Al^{3+} , Fe^{2+} and Mn^{2+} precipitates as metal hydroxides and oxyhydroxides. In presence of high concentration of sulphates, Fe^{2+} and Al^{3+} can precipitate out as oxyhydroxysulphates (Gitari et al. 2008).

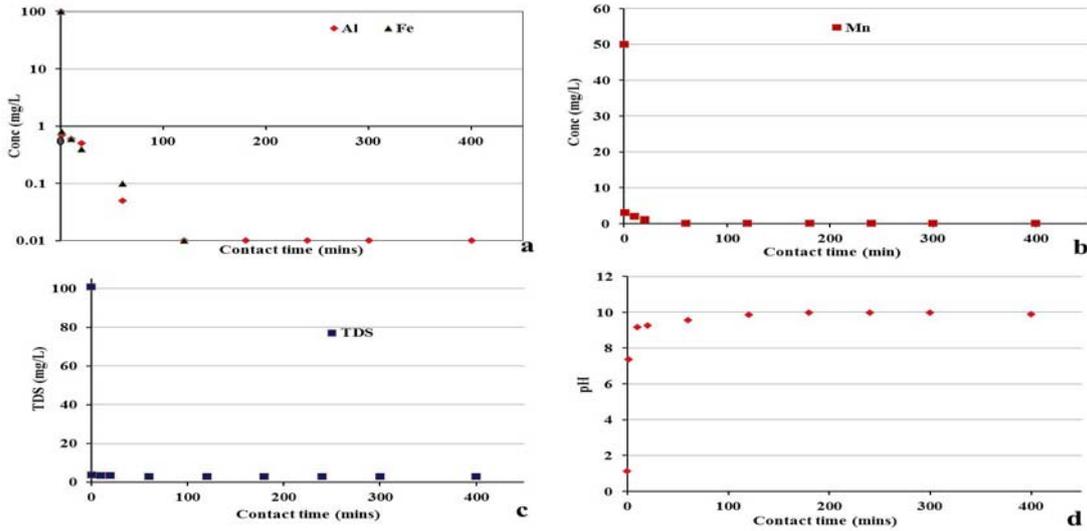


Fig. 1 Variation of pH, TDS, Al^{3+} , Mn^{2+} and Fe^{2+} with contact time (1g/100 mL, Fe^{2+} :-100 mg/L, Al^{3+} :- 100 mg/L, Mn^{2+} :-50 mg/L, rpm=250)

In presence of oxygen Fe^{2+} undergoes oxidation with subsequent precipitation of amorphous $Fe(OH)_3$ (Maree et al. 1992). In presence of CO_3^{2-} from magnesite dissolution Fe^{2+} , Mn^{2+} could precipitate as metal carbonates.

Treatment of AMD as a function of magnesite dosage

Results for variation of various parameters evaluated with dosage of magnesite are presented in fig. 2.

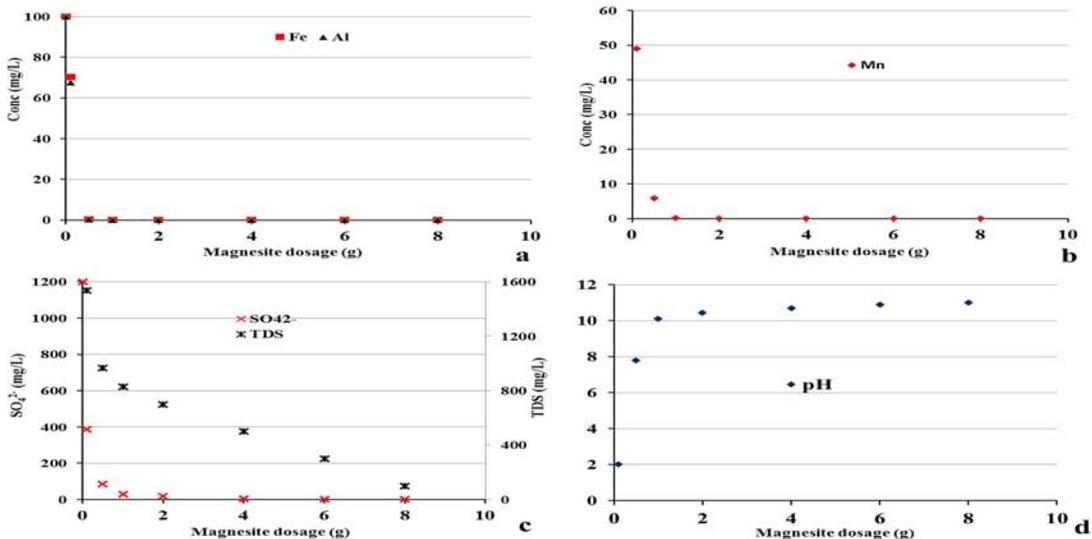


Fig. 2 Variation of pH, TDS, Al^{3+} , Mn^{2+} , SO_4^{2-} and Fe^{2+} with dosage (1g/100 mL, Fe^{2+} :-100 mg/L, Al^{3+} :- 100 mg/L, Mn^{2+} :-50 mg/L, SO_4^{2-} :-1200 mg/L, rpm=250, agitation time= 60 mins)

Results from fig. 2d shows that a magnesite dosage of 0.5 g or greater can increase the pH of the acidic solution to values ≥ 8 . This is attributed to increased dissolution of magnesite with a subsequent release of alkalinity.

Treatment of field AMD under the optimized batch conditions

Table 1 presents the chemical composition of field AMD samples and treated effluent with magnesite at optimized conditions.

Table 1 Chemical composition of field AMD samples and treated effluent

Parameter	Field AMD	After Treatment
pH	2.30	10.30
TDS	10237.30	4345.21
EC ($\mu\text{S}/\text{cm}$)	22713.12	4635.60
Na	248.40	245.40
K	21.60	21.10
Mg	2.30	285.80
Ca	710.82	281.00
Al	134.40	0.10
Fe	1243.60	0.30
Mn	91.50	0.12
Cu	7.80	0.21
Zn	7.90	0.13
Pb	6.30	0.21
Co	41.30	0.24
Ni	16.60	0.50
Si	1.49	5.67
SO ₄ ²⁻	4635.6	1912.9

NOTE All chemical species are in mg/L except EC

The treatment of field AMD samples with amorphous magnesite was effective in lowering the EC and TDS. Most of the metal species have been reduced to below detection limits and DWAF guidelines. A disadvantage of the technology could be the alkali and alkaline earth metal cations that remains largely in solution and will require post secondary treatment. Precipitation of the metal cations as hydroxides/oxyhydroxides is suggested as the main mechanism of the metal cations removal.

Geochemical modelling

Calculation of saturation indices with PHREEQC geochemical code suggested the following mineral phases are likely to precipitate during treatment as the pH increases. These include: Fe bearing mineral phases such as ferrihydrite, Fe(OH)₃ (a), Hematite, K-jarosite, Na-jarosite, siderite, Fe(OH)SO₄, Al bearing mineral phases such as alunite, basaluminite, jurbanite, boehmite, Al(OH)₃(a), diaspora gibbsite, Mn bearing mineral phases such as rhodochrosite, pyrolusite and manganite, other mineral phases predicted include: anhydrite, brucite, barite, MgSO₄·7H₂O, and gypsum. The precipitation of these mineral phases could contribute to attenuation of these metal cations as pH increases

Conclusion

Results of this study indicate that contact of AMD with magnesite leads to an increase in pH ($\text{pH} \geq 10$), and a reduction in EC, TDS and metal concentration in treated product water. PHREEQC geochemical modeling predicted Al, Fe, Mn and Mg bearing mineral phases could be responsible for attenuation of most metal species. However a high proportion of alkali and alkaline earth metals remained in the treated water which might require post treatment polishing. This preliminary work demonstrates that magnesite could be a potential reagent for remediation of AMD and acidic tailing leachates.

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References

- Department of Water Affairs and Forestry (DWAF) (1996) Water Quality guidelines
- Gitari MW, Petrik LF, Etchebers O, Key DL, Okujeni C (2008) Utilization of fly ash for treatment of coal mines wastewater: Solubility controls on major inorganic contaminants Fuel 87: 2450-2462
- Maree JP, Plessis Pdu, van der Watt CJ (1992) Treatment of acidic effluents with limestone instead of lime. Water Science Technology 26: 345-355
- Mulopo J, Mashego M, Zvimba JN (2012) Recovery of calcium carbonate from steelmaking slag and utilization for acid mine drainage pre-treatment. Water Science and Technology
- Wilson MGC, Robb VM, Robb LJ, Tosen GR, Conlin JB, Viljoen MJ (1998) Mining in South Africa: Legislation and Environmental Considerations. In: Wilson MGC, Auhaeusser CR, (Eds), The Mineral Resources of South Africa, Handbook, Council for Geoscience 16: 40-45