

Cavitation of Acid Mine Drainage-Magnesite Mixtures: A Promising Acid Mine Drainage Treatment Technology

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Abstract

Cavitation of AMD-magnesite mixtures was induced using a sonotrode and the chemical species removal, and neutralization potential of the magnesite evaluated. This process was repeated using the conventional agitation by a magnetic stirrer. SEM images showed new morphologies indicating formation of new mineral phases while XRF results indicated increased concentration of Fe, S, Al and Mn in residues indicating formation of Fe, S, Al and Mn bearing mineral phases and deposition on unreacted magnesite grains. Contact of magnesite with AMD for 60 mins with conventional agitation led to increase in pH to 9.4. Al, Mn, Fe and Zn were removed to levels > 99% while SO_4^{2-} were removed to levels $\geq 50\%$. Cavitation treatment of the same AMD-magnesite mixtures for 60 mins led to an increase in pH to 8.6 and sulphate removal $\geq 90\%$. Cavitation treatment was observed to induce fast kinetics, final alkaline pH was attained in a shorter time than conventional shaking and was also superior in terms of sulphate removal. Cavitation seems to introduce superior mechanical aspects that enhanced sulphate removal and can be enhanced through seeding with various salts for recovery of beneficial salt products

Keywords: Acid Mine Drainage, Metal Species, Sulphate, Magnesite, Cavitation, pH, precipitation

Introduction

South Africa is endowed with large quantities mineral deposits. These include gold, diamond, platinum, manganese, copper, coal and chromium among others. However exploitation of these mineral deposits have positive and negative effect. Exploitation of these mineral have deposits contributes to social and economic development. However, the mining processes generate waste that could have negative effect on the environment if not adequately managed (Name 2014). Acid mine drainage (AMD) is an inevitable waste effluent resulting from the mineral deposit exploitation, its strongly acidic in nature and contains substantial levels of inorganic contaminants such as Fe, Al, Mn, Zn, Pb and SO_4^{2-} ions. Acid mine drainage results from oxidation of sulphide rock in presence of water during mineral deposit exploitation, the oxidation in presence of water and oxygen leads to formation of sulphuric acid (Watten 2015). Release of these effluents to

the environment can have negative effect on surface and groundwater resources. Most government have regulations that require these effluents to be treated to acceptable levels before release into the environment. Many treatment technologies that are currently in use have limitations which include, cost factor, treatment inefficiencies, implementation inconveniences and material availability (Masindi 2016). There is thus a constant search for cheaper and more efficient technologies for effective management of AMD. Moreover for the technologies to be sustainable, the treatment process needs to include material recovery from the treatment process in addition to using locally available liming agents. Magnesite, a locally available liming agent was used in this study. Magnesite (MgCO_3) occurs in two forms crystalline and cryptocrystalline. The application of cryptocrystalline magnesite for treatment of AMD has been reported in our previous work (Masindi 2016) which reported

effective removal of inorganic contaminants. This study was designed to develop a novel technology that uses ultrasonic technology to drive the mass transfer kinetics between magnesite and the AMD during the mixing process. Due to the ability of ultrasonication to create cavitation phenomena, it was envisaged this aspect will introduce superior mechanistic aspects that will lead to more efficient and faster treatment process. This would in turn result in less contact time and liming agent required for the treatment process. Our previous work using jet loop reactor that employs cavitation and impingement provided superior mixing that enhanced the treatment process leading to a more efficient contaminants removal (Madzivire 2013). An attempt was also made to compare the efficiency of this new novel technology with the conventional agitation of the reaction mixtures.

Methods

Magnesite was collected from Follovhondwe magnesite mine Limpopo province, South Africa. The magnesite was crushed using a hammer and milled into fine powder. The samples were kept in a zip-lock plastic bag until use.

A simulated AMD solution was prepared as described by Gitari [15]. The AMD was formulated by dissolving the following quantities of salts in 1000 mL of MilliQ water (18M Ω), 0.895g Fe₂(SO₄)₃·H₂O, 2.685g FeSO₄, 0.494g Al₂(SO₄)₃·18H₂O, 0.08015 g MnCl₂·4H₂O, 1.1393g MgSO₄, 2.421g, CaCl₂·2H₂O, 0.08793g ZnSO₄·7H₂O and 0.03 ml H₂SO₄. This was expected to give 250 mg/L Fe³⁺, 540 mg/L Fe²⁺, 40 mg/L Al³⁺ and 35 mg/L Mn²⁺, 230 mg/L Mg²⁺, 660 mg/L Ca²⁺, 20 mg/L Zn²⁺ and 524 mg/L SO₄²⁻ in solution.

The milled magnesite and the AMD-reacted magnesite were characterized using XRF. Magnesite powder pellets were prepared by pressing the powder mixed with 15-20 g boric acid as a binding agent in a Die set of 40 mm diameter. The pellets were then placed in plastic cups for XRF analysis (S2 Ranger, Bruker Bench top XRF). The morphology of the raw magnesite and AMD-reacted magnesite was examined using scanning electron microscopy (SEM) and SEM-EDX at the University of Cape Town, South Africa.

Temperature, electrical conductivity and pH of aqueous samples were measured using an Orion multi-parameter analyser. Simulated and treated AMD samples were divided into two, the first half was acidified with 3 drops of concentrated HNO₃ to prevent aging and immediate precipitation of Al, Fe, Mn and SO₄²⁻ ions and stored in a refrigerator at 4 °C until analysis for cations using ICP-MS and the second half left unacidified and stored in a refrigerator at 4°C until analysis for anions using metrohm professional 850 IC.

To evaluate the chemistry and kinetics of the treatment process several operational parameters were evaluated. These were agitation time, sonication time, amplitude and cycle time of sonicator and liming agent dosage. For the effect of agitation time 9 samples of 100 mL each of the simulated AMD were pipetted into 9 HDPE bottles of 250 mL and 1g of magnesite added to each. The mixtures were agitated for 1, 5, 10, 15, 30, 60, 90, 120 and 180 minutes at 250 rpm using the Stuart reciprocating shaker. To study the effect of sonication time 9 samples containing 100 mL of the simulated AMD solution were pipetted into 9 bottles of 250 mL and 1g of magnesite was added to each sample. The mixtures were sonicated for 1, 5, 10, 15, 30, 60, 90, 120 and 180 minutes at 60% amplitude and a cycle time of 50%, using the ultrasonic processor UP400S. The mixtures were then filtered through 0.45 μ m pore membrane filters and analysed for cations and anions as previously described.

Results and discussions

Physicochemical characterization of magnesite, magnesite residues, AMD and product water

Table 1 present the chemical composition of magnesite and AMD treatment residues. MgO is a major component of the magnesite while SiO₂ and CaO occur in minor quantities. After AMD treatment a decrease in MgO was observed. This is as a result of MgCO₃ dissolution on interaction with the acidic media. There was an increase in Mn, Al and Fe oxides in an AMD reacted magnesite. An increase in Fe, Ca, Al and Mn indicates the precipitation of Fe, Al, Mn bearing mineral phases such oxyhydroxides, oxyhydroxysulphates and carbonates.

The increase in Ca could be attributed to the formation of gypsum due to the high concentration of SO_4^{2-} in the simulated AMD. Our previous studies reported formation of these mineral phases on interacting Fe, Al, Mn, Ca and sulphate rich AMD with highly alkaline and Ca rich fly ash (Gitari 2008). For trace components Ni, S, Zn and Cr had the highest concentration in raw magnesite and were also observed to increase in the residues. This is again an indication of formation of new mineral phases bearing these elements. Of notable importance is the substantial increase in S and Zn content in the residues. Sr, Yb, Ba and Zr were observed

to decrease in the residues as compared to the raw magnesite indicating their release into solution. Our previous studies reported release of such chemical species on reacting AMD with highly alkaline and Ca, Ba, Sr rich coal fly ash (Gitari 2006). This would be of concern in this treatment technology and would require detailed investigation.

Morphology of the raw and reacted magnesite by Scanning Electron Microscope and Scanning Electron Microscopy Energy Dispersive Spectroscopy

Figure 1 shows the SEM and SEM-EDS spectra of raw magnesite and AMD reacted magnesite residues.

Table 1 Chemical composition of magnesite and residues

	Major oxides (% w/w)		Trace element (mg/kg)		
	Magnesite	Residues		Magnesite	Residues
MgO	87.3	52.3	Ni	482	258.3
SiO ₂	8.66	8.36	Sr	279.6	120.1
CaO	1.84	3.44	S	261.1	2136.5
Fe ₂ O ₃	0.38	10.08	Yb	177.2	109.2
Al ₂ O ₃	BDL	1.60	Ba	88	77.3
TiO ₂	0.04	0.048	Zr	50.1	24.5
K ₂ O	0.02	0.04	Cr	23.5	35.6
P ₂ O ₅	0.036	0.056	Zn	7.8	2738.2
MnO	0.011				

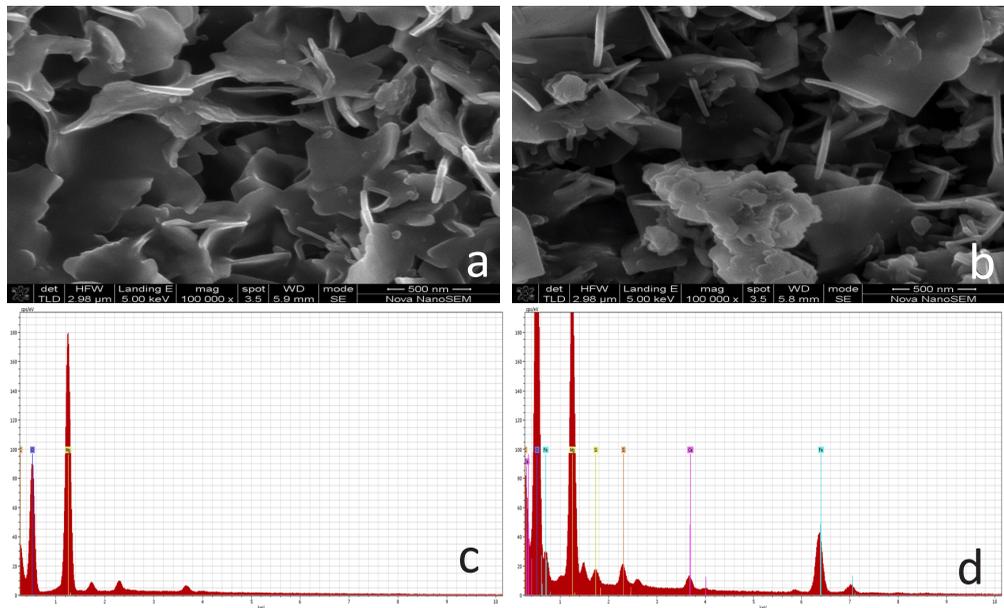


Figure 1 SEM Images (a) raw magnesite, (b) AMD reacted magnesite residues, (c) SEM-EDS for raw magnesite and (d) SEM-EDS of AMD reacted magnesite residues.

The SEM images reveal that magnesite has a leafy like-petals like morphology and with rod shaped hedges. The leafy like structures are folded to form a confining like structure (bowl like depth). The surfaces of these structures appear smooth (fig. 1a). After contact with AMD, new structures with completely different morphology appear to be deposited on the flower like structures. A substantial portion of the original magnesite morphology are still present (fig. 1b). This indicates that only a small portion of the magnesite appear to have reacted, majority of it remaining unreacted. The SEM-EDS gives surface elemental composition of a material. In figure 1c and d we see new chemical species present in AMD appearing the surface of the AMD reacted magnesite indicating possible incorporation of mineral phases bearing these elements on the surface of the magnesite. This was also confirmed through bulky analysis of the raw magnesite and AMD reacted magnesite residues by XRF (tab. 1). There is emergency of Fe, Si, S and Ca peaks that were not present in the raw magnesite (fig.1b) confirming deposition of mineral phases bearing these chemical species on the surfaces of the unreacted magnesite.

Contaminants removal trends as a function of operation parameters

Effect of contact time

Figure 2a and b shows the % metal removal and change in pH as a function of shaking and sonication time respectively.

An increase in pH was observed for both treatment systems, for the conventional agitation the pH stabilized at ≈ 9.8 after 60 minutes (fig.a) while for the sonication

system it stabilized at ≈ 8.97 after 1 minute (fig b). This indicates the superior mechanistic aspects introduced by sonication of the reaction mixtures. This rapid increase in pH is accompanied by rapid removal of the metal contaminants Fe, Al, Zn and Mn to near $\approx 100\%$ within 5 minutes. The removal of the metal contaminants is attributed to precipitation as metal hydroxides, oxyhydroxides and oxyhydroxysulphates. Ca removal followed the same trend as the metal contaminants which could suggest incorporation in the metal bearing mineral phases. Our previous studies have shown the formation of Fe, Al oxyhydroxides and oxyhydroxysulphates when AMD solutions were treated with high alkaline coal fly ash (Gitari 2008). In addition gypsum precipitation was observed to account for removal of Ca and sulphate too. We note the enhanced removal of Ca and sulphate in the sonication system as compared to the conventional agitation system. Experiments conducted using lime to treat AMD through the conventional agitation and sonication didn't show any difference interms of pH and metal removal trends (data not shown). Its interesting to note that experiments conducted with limestone to treat AMD through conventional agitation and sonication system showed similar trends to those of magnesite. Both magnesite and limestone are form of carbonates and are less soluble than lime, during treatment of AMD with limestone and magnesite armoring occurs which renders further contact of reactive surface with AMD impossible hence no release of alkalinity. Its

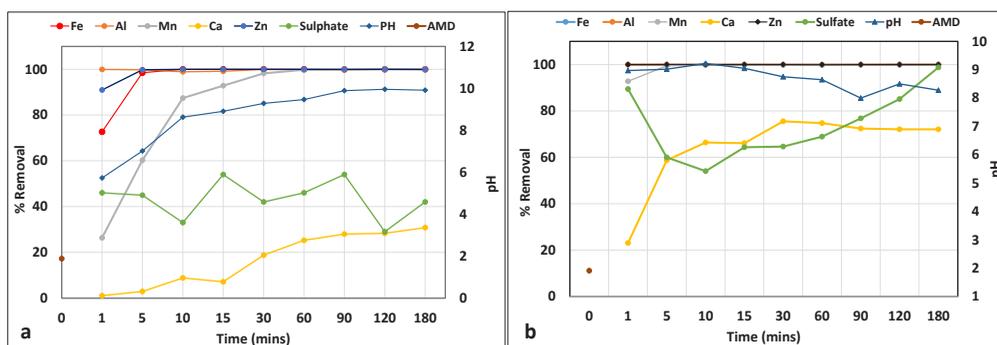


Figure 2: (a) Variation of Al, Fe, Mn pH and sulphate with increasing shaking time (b) Variation of pH and sulphate with increasing sonication time Cycle 0.5, Amplitude 60%, magnesite dosage=1g/100ml).

our hypothesis that sonication disrupts this phenomena leading to increased contact of AMD with fresh surfaces of magnesite and limestone particles. This is still subject of our continued investigation.

Conclusion

Acid mine drainage treatment with magnesite liming agent was evaluated using a conventional agitation of the reaction mixtures and compared to a sonication system. Solid residues from both agitation systems showed increased concentration of Fe, S, Al and Mn indicating formation of Fe, S, Al and Mn bearing mineral phases and deposition on unreacted magnesite grains. Contact of magnesite with AMD at S/L of 1g/100 mL for 60 mins of conventional agitation led to an increase in pH to 9.4 while for sonication pH increased to 8.97 within 1 minute. Al, Mn, Fe and Zn were removed to levels > 99% with both systems. However Ca and sulphate removal with agitation system was low as compared to sonication. For sonication system metal contaminants were removed to levels > 99 % with 1 minute of treatment. Cavitation treatment was observed to induce fast kinetics, final alkaline pH was attained in a shorter time than conventional shaking and was also superior interms of sulphate removal. Cavitation treatment was observed to introduce superior mechanistic aspects that enhanced sulphate removal and can be enhanced through selective seeding with various salts to enhance sequential chemical species removal and recovery of beneficial salt products. This will be the subject of further investigation in this project

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References

- Gitari WM, Petrik LF, Etchebers O, Key DL, Iwuoha E, Okujeni C (2008) Utilization of Fly Ash for Treatment of coal mines waste water: Solubility controls on major inorganic contaminants. *Fuel* 87: 2450–2462, doi.org/10.1016/j.fuel.2008.03.018
- Gitari WM, Petrik LF, Etchebers O, Key DL, Iwuoha E, Okujeni C (2006) Treatment of acid mine drainage with fly ash: Removal of major contaminants and trace elements. *Journal of Environmental Science and Health-Part A* 8: 1729–47, doi.org/10.1080/10934520600754425
- Madzivire G, Gitari WM, Vadapalli VRK, Petrik LF (2013) Jet loop reactor application for mine water treatment using fly ash, lime and aluminium hydroxide. *Int. J. Environ. Sci. Technol* 12: 173–182, DOI 10.1007/s13762-013-0417-7
- Masindi V (2016) A novel technology for neutralizing acidity and attenuating toxic chemical species from acid mine drainage using cryptocrystalline magnesite tailing. *J of Water Process Engineering* 10: 67–77, doi.org/10.1016/j.jwpe.2016.02.002
- Name T, Sheridan C (2014) Remediation of acid mine drainage using metallurgical slags. *Minerals Engineering* 64: 15–22, doi.org/10.1016/j.mineng.2014.03.024
- Watten BJ, Sibrell PL, Schwartz MF (2005) Acid neutralization within limestone sand reactors receiving coal mine drainage. *Environmental Pollution* 137: 295–304, doi.org/10.1016/j.envpol.2005.01.026