

Efficiencies of different alkaline generating agents for the treatment of acid mine drainage: A comparative study and techno-economic appraisals

* Vhangwele Masindi¹, Vhangwele Akinwekomi²,
Johannes Philippus Maree³, Khathutshelo Lilith Muedi³

¹Council for Scientific and Industrial Research (CSIR), Built Environment (BE), Hydraulic Infrastructure Engineering (HIE), P.O Box 395, Pretoria, 0001, South Africa, VMasindi@csir.co.za,

¹Department of Environmental Sciences, School of Agriculture and Environmental Sciences, University of South Africa (UNISA), P. O. Box 392, Florida, 1710, South Africa, masindivhangwele@gmail.com; khathumuedi@gmail.com

²Department of Environmental, Water and Earth Sciences, Faculty of Science, Tshwane University of Technology, Private Bag X680, Pretoria, 0001, South Africa, bologov@tut.ac.za

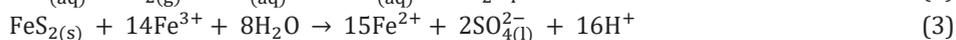
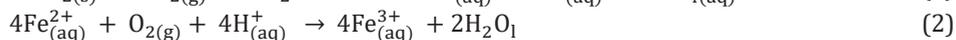
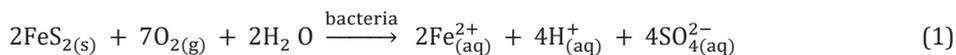
³ROC Water Technologies, P O Box 70075, Die Wilgers, 0041, Pretoria, South Africa, maree.jannie@gmail.com

Abstract This comparative study aims at evaluating the efficiencies of different alkaline generating agents for neutralising acid mine drainage. Batch laboratory experiments (at 1:10 S/L ratio) were used to achieve the goal of this study. Neutralisation studies revealed that: hydrated lime, Periclase, magnesite and caustic soda achieved pH ≥ 9 , and $\geq 99\%$, metals removal respectively whereas the use of soda ash, limestone, lime and brucite yielded pH ≥ 6 , Al and Fe $\geq 99\%$, and Mn $\geq 60\%$. Techno-economic evaluations revealed that hydrated lime is the cheapest and most effective material for mine water neutralisation.

Key words Acid mine drainage, Alkaline generating agents, precipitation

Introduction

Depending on the sources and the host rocks, mine drainages are categorised under different types and they include: acid, neutral and basic mine drainage (Nordstrom et al. 2015). Of prime concern is acid mine drainage which results from the weathering of pyrite (FeS_2) and other reactive sulphide-bearing minerals when exposed to oxidising conditions as shown by equation 1 – 4 (Masindi 2016):



The reactions are also mediated by micro-organisms (Nordstrom et al. 2015). The most visual legacy of AMD is undoubtedly the precipitation of ferric (Fe^{3+}) hydroxide and oxy-hydroxide and oxy-hydrosulphates complexes as a yellow or orange coating in stream channels. These precipitates lead to a reduction in dissolved oxygen concentrations in affected water bodies during their formation, and have abrasive effects on biota and clog stream-

beds. Acid mine drainage is mainly characterised of $\text{pH} < 3$ and elevated levels of Al, Fe, Mn and sulphate in addition trace of other components (Masindi et al. 2015).

Worldwide, a number of treatment methods, both passive and active, have been proposed and used for abating AMD (Zipper and Skousen 2010) and they include ion-exchange (Torres and Auleda 2013), adsorption (Falayi and Ntuli 2014), bio-sorption (Çabuk et al. 2013), neutralisation (Alakangas et al. 2013), coagulation and precipitation (Zhao et al. 2012). The extent of application of most of these methods has largely been limited by factors such as cost and generation of excessive secondary sludge that is toxic and expensive to dispose (Simate and Ndlovu 2014). Effectiveness and efficiency of a given material also affect its industrial deployment. This pioneer and ground breaking comparative study was, therefore, developed and designed with the aim of appraising the efficiency and effectiveness of different alkaline generating agents for mine water pre-treatment and develops a guide for mine houses and respective industries.

Materials and methods

Materials and Characterization

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. The samples were stored in closed High Density Polyethylene (HDPE) bottles to prevent further oxidation and precipitation of metals, and kept in 4°C until utilisation in neutralisation experiments. Prior utilisation, the AMD samples were filtered through $0.4\mu\text{m}$ perforated filter. The chemical compositions of the Eight (8) neutralizing agents and they include: lime, limestone, hydrated lime, soda ash, caustic soda, periclase, brucite and magnesite. All other chemicals were of analytical grade quality. Water samples were analysed using inductively coupled plasma mass spectrometer (ICP-MS) (7500ce, Agilent, Alpharetta, GA, USA). Elemental composition was determined using X-ray fluorescence (XRF).

Quality control/quality assurance

A QA/QC programme was established and implemented to ensure the production of trustworthy results. The QA/QC process entailed conducting the experiments in triplicate and reporting the data as mean value. Data was considered acceptable when percentage difference within triplicate samples and percent error were below 10%. The analytical values below detection limit (BDL) were managed in according to EPA guideline. The accuracy of the analysis was monitored by analysis of National Institute of Standards and Technology (NIST) water standards. Inter-laboratory analysis was also done to further verify the validity of the results.

Neutralisation experiments

Aliquots of 1L, each of AMD, were pipetted into 1L beaker flasks and 1 g of each alkaline reagent was added into each flask. The mixtures were mixed using an overhead stirrer for 60 min at >250 rpm. The shaking speed and optimum time were obtained from a study

conducted by Masindi et al. (2015). After mixing, the mixtures were filtered through a 0.45 µm pore nitrate cellulose filter membrane. After filtration, the filtrates were preserved by adding two drops of concentrated HNO₃ acid to prevent aging and immediate precipitation of Al, Fe and Mn, and refrigerated at 4 °C prior to analysis. The pH, before and after agitation, was measured using the CRISON multimeter probe (model MM40).

Results and discussions

Reaction of AMD with different neutralizing agents

The chemical profiles of raw AMD and AMD after contacting different alkaline generating agents at optimized conditions are shown in tab. 1.

Table 1 Chemical profiles of AMD after contacting different alkaline generating agents at optimized conditions

Parameters	AMD	Caustic soda	Soda ash	Periclase	Brucite	Magnesite	Lime	Hydrated lime	Lime-stone
pH	<2	13	7	10	6	9	6	11	6
Acidity (mg/L CaCO ₃)	8133	<5,0	473	<5,0	1564	<5,0	29	<5,0	117
Alkalinity (mg/L CaCO ₃)	<5,0	3565	1398	71	<5,0	56	<5,0	57	354
Aluminium (mg/L Al)	300	95	BDL	BDL	BDL	BDL	BDL	5	BDL
Calcium (mg/L Ca)	337	<50	232	316	320	683	549	630	594
Electrical Conductivity (mS/m [25°C])	547	1635	959	599	646	619	441	218	433
Iron (mg/L Fe)	1800	5	45	BDL	450	BDL	BDL	BDL	BDL
Magnesium (mg/L Mg)	273	<40	278	1693	1590	1565	621	<40	652
Manganese (mg/L Mn)	75	0.4	50	BDL	75	BDL	55	BDL	65
Potassium (mg/L K)	<60	<60	<60	<60	<60	<60	<60	<60	<60
Sodium (mg/L Na)	<30	5836	4035	<30	<30	<30	<30	54	40
Sulphate (mg/L SO ₄)	33705	33700	33700	30705	32705	20705	3705	3005	9000
Total Dissolved Solids	3556	10628	6234	3894	4199	4024	2867	1417	2815
Total Hardness (mg/L)	1965	<290	1724	7759	7345	8149	3928	1738	4168

As shown in tab. 1, AMD had the pH of < 2 which is suitable for dissolution of metals. It had high content of Fe and sulphate, hence showing that it might have been formed from the oxidation of pyrite. Caustic soda managed to increase the pH to > 13 and remove all the

metals except al. and sulphate. Soda ash managed to increase the pH to > 7 and remove Al, with partial removal of Fe and Mn. Periclase removed all the metals from the aqueous system, except the sulphate. It also increased the pH to > 10. Brucite managed to increase the pH to > 6 and partially removed the metals from the mine water. It managed to achieve > 90% removal for al. and partial removal of Fe and Mn. Magnesite raised the pH to > 9 which is suitable for all the metals to precipitate. It removed > 99% of Al, Mn and Fe and 40% sulphate. Ca-based reagents managed to removed > 80 sulphate from acid mine drainage. Lime managed to remove 99% of Fe and al. from mine water and 70% Mn. Hydrated lime managed to remove > 99% of all the metals from acid mine drainage. Limestone managed to remove > 99% of al. and Fe but failed to remove Mn which was only 20% removal.

Elemental composition of different alkaline agents after contacting AMD

The Elemental compositions of different alkaline generating agents after contacting AMD are shown in tab. 2.

Table 2 Elemental compositions of different alkaline generating agents after contacting acid mine drainage

Element	Caustic soda		Soda ash		Periclase		Brucite		Magnesite		Lime		Hydrated lime		Limestone	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
SiO ₂	<0,01	9.33	<0,01	4	<0,01	0.33	<0,01	0.57	5	3.4	<0,01	1.25	<0,01	0.56	<0,01	0.19
TiO ₂	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Al ₂ O ₃	<0,01	4.84	<0,01	7.56	<0,01	2.52	<0,01	2.71	<0,01	3.08	<0,01	3.23	<0,01	2.84	<0,01	4.18
Fe ₂ O ₃	<0,01	38.5	<0,01	33	<0,01	11.1	<0,01	12.5	<0,01	14.2	<0,01	7.08	<0,01	6.15	<0,01	10.9
MnO	<0,01	1.24	<0,01	1.03	<0,01	0.38	<0,01	0.16	<0,01	0.47	<0,01	0.34	<0,01	0.22	<0,01	0.16
MgO	<0,01	6.12	<0,01	3.04	98	51.5	70	52.4	80	46.5	<0,01	3.18	2	2.94	8	0.42
CaO	<0,01	6.36	<0,01	5.36	0.5	0.46	4	0.28	9	2.98	95	39.7	77	29.8	80	43.5
Na ₂ O	90	7.2	96	10.1	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
K ₂ O	2	0.1	<0,01	0.42	0.5	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
P ₂ O ₅	<0,01	<0,01	1	0.01	<0,01	<0,01	<0,01	<0,01	1	<0,01	1	0.01	1	<0,01	<0,01	0.01
Cr ₂ O ₃	<0,01	0.02	<0,01	0.01	<0,01	0.02	<0,01	0.05	<0,01	0.05	<0,01	0.04	<0,01	0.04	<0,01	0.05
NiO	<0,01	0.03	<0,01	0.02	<0,01	0.02	<0,01	0.02	<0,01	0.04	<0,01	0.02	<0,01	0.02	<0,01	0.02
V ₂ O ₅	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	1	<0,01	<0,01	<0,01	<0,01	<0,01	1	<0,01	2	<0,01
SO ₃	<0,01	2.79	<0,01	7.34	<0,01	0.08	<0,01	0.11	<0,01	2.79	<0,01	22.8	<0,01	22.3	<0,01	16.5
BaO	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
CuO	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	0.02	<0,01	0.02	<0,01	0.04
ZnO	<0,01	0.08	<0,01	0.09	<0,01	0.03	<0,01	0.03	<0,01	0.03	<0,01	0.02	<0,01	0.02	<0,01	0.03
LOI	7	23.2	3	27.9	1	33.6	15	31.2	5	26.5	4	22.3	20	35.1	10	23.8
Total	99	99.93	100	100.02	100	100.04	90	100.03	100	100.06	100	99.99	101	100.02	100	99.81

As shown in tab. 2, there was high content of Si, Al, Fe, Mn, Ca, Mg, Na and S in the secondary sludge. These are the main components in acid mine drainage. These results complement the ICP-MS results. Similar results were obtained for soda ash except the levels of those inorganic contaminants. Results also revealed that Na-based salts are the best candidates for Mg and Ca removal. They are also suitable for the recovery of Fe from acid mine drainage. Magnesium based salts removed Al, Fe, Mn from acid mine drainage since they are the major constituents. High content of Ca was also observed in magnesite. This might have contributed to the reduction of sulphate in the product water after contacting the acid mine drainage with magnesite. The Ca-based reagents removed Al, Fe, Mn and elevated levels of sulphate from acid mine drainage. Ca was present because it is part of the seeding material that is being used for neutralization. From this XRF results, one could conclude that an integrated approach can be derived from this treatment process. Mg-based salts can be used for neutralization of acid mine drainage and leave the residual sulphate in solution. Ca-based reagents can be used to remove the residual sulphate to form gypsum.

Techno-economic appraisals

Economic and technical efficiency of different alkaline generating materials as pre-treatment of acid mine drainage are shown in tab. 3.

Table 3 Economic and technical efficiency of different alkaline generating materials

Material	Caustic soda	Soda ash	Periclase	Brucite	Magnesite	Lime	Hydrated lime	Limestone
Price (R gram ⁻¹)	0.26	0.3	0.41	0.5	0.64	0.34	0.12	0.24
Dosages	10 g	10 g	10 g	10 g	10 g	10 g	10 g	10 g
Liquid	1 L	1 L	1 L	1 L	1 L	1 L	1 L	1 L
S/L ratio	1:100	1:100	1:100	1:100	1:100	1:100	1:100	1:100
Cost (RL ⁻¹)	2.6	3	4.1	5	6.4	3.4	1.2	2.4
Particle size	<100 µm	<100 µm	<100 µm	<100 µm	<100 µm	<100 µm	<100 µm	<100 µm
Contact time	60 mins	60 mins	60 mins	60 mins	60 mins	60 mins	60 mins	60 mins
Final pH	13	7	10	6	9	6	11	6
Fe (mgL ⁻¹)	3.5	45	0.9	461	0.9	0.9	0.9	0.9
Al (mgL ⁻¹)	94	0.7	0.7	0.7	0.7	0.7	4.5	0.7
Mn (mgL ⁻¹)	0.4	50	0.25	75	0.25	55.6	0.25	65.7
Sulphate (mgL ⁻¹)	33700	33700	30705	32705	20705	3705	3005	9000
Host metal (mgL ⁻¹)	5836	4035	1693	1590	1565	549	630	594

As shown in tab. 3, the results obtained from the treatment of acid mine drainage with Caustic soda, Soda ash, Periclase, Brucite, Magnesite, Lime, Hydrated lime and Limestone when contacted with them for 60 min and their respective costs. Magnesium-based agents are more expensive than Na-based and Ca-based agents. Caustic soda, periclase, magnesite and hydrated lime were efficient in the removal of Mn from AMD. Magnesite and periclase were effective for all the chemical species in AMD except the sulphate. This can be removed by a polishing step. Hydrated lime was the most effective, efficient and economic viable way for the treatment of acid mine drainage. It is also much cheaper than all the other neutralizing agents. Lime and limestone could remove Fe and Al. completely and partially remove sulphate except Mn. This may be attributed to pH of the secondary solution.

Conclusions

From this comparative study, it can be concluded that acid mine drainage was successfully treated using different alkaline agents and the techno-economic appraisals were successfully executed. At 60 mins of equilibration, 10 g/L solid/Liquid ratio, >250 agitation speed and $\leq 100 \mu\text{m}$ particle sizes, the following results were obtained: pH ≥ 13 , metal species removal $\geq 90\%$ and sulphate $\geq 10\%$ for caustic soda. pH ≥ 7 , Al $\geq 99\%$, Fe $\geq 60\%$, Mn $\geq 30\%$ and sulphate $\geq 30\%$ for soda ash. pH ≥ 10 , metal removal efficiency $\geq 99\%$ and $\geq 10\%$ sulphate removal for periclase. pH ≥ 6 , Al $\geq 99\%$, Fe $\geq 60\%$, Mn $\geq 40\%$ and sulphate $\geq 10\%$ for brucite. pH ≥ 9 , Al $\geq 99\%$, Fe $\geq 99\%$, Mn $\geq 99\%$ and sulphate $\geq 40\%$ for magnesite. pH ≥ 6 , Al $\geq 99\%$, Fe $\geq 60\%$, Mn $\geq 30\%$ and sulphate $\geq 60\%$ for lime. pH ≥ 11 , Al $\geq 60\%$, Fe $\geq 99\%$, Mn $\geq 99\%$ and sulphate $\geq 90\%$ for hydrated lime. pH ≥ 6 , Al $\geq 99\%$, Fe $\geq 99\%$, Mn $\geq 60\%$ and sulphate $\geq 80\%$ for limestone. Regarding cost, Caustic soda, Soda ash, Periclase, Brucite, Magnesite, Lime, Hydrated lime and Limestone are valued at R 2.6 L⁻¹, R 3 L⁻¹, R 4.1 L⁻¹, R 5 L⁻¹, R 6.4 L⁻¹, R 3.4 L⁻¹, R 1.2 L⁻¹, R 2.4 L⁻¹ respectively.

Acknowledgements

The authors thank Council for scientific and Industrial Research for supporting this project financially and Tshwane University of technology for providing laboratory space. The authors would also like to thank NRF for funding this project.

References

- Alakangas L, Andersson E, Mueller S (2013) Neutralization/prevention of acid rock drainage using mixtures of alkaline by-products and sulfidic mine wastes. *Environmental Science and Pollution Research* 20:7907-7916
- Çabuk A, Aytar P, Gedikli S, Özel YK, Kocabiyyik E (2013) Biosorption of acidic textile dyestuffs from aqueous solution by *Paecilomyces* sp. isolated from acidic mine drainage. *Environmental Science and Pollution Research* 20:4540-4550
- Falayi T, Ntuli F (2014) Removal of heavy metals and neutralisation of acid mine drainage with un-activated attapulgite. *Journal of Industrial and Engineering Chemistry* 20:1285-1292, doi:<http://dx.doi.org/10.1016/j.jiec.2013.07.007>
- 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

- Nordstrom DK, Blowes DW, Ptacek CJ (2015) Hydrogeochemistry and microbiology of mine drainage: An update. *Appl Geochem* 57:3-16, doi:<http://dx.doi.org/10.1016/j.apgeochem.2015.02.008>
- Simate GS, Ndlovu S (2014) Acid mine drainage: Challenges and opportunities. *Journal of Environmental Chemical Engineering* 2:1785-1803, doi:<http://doi.org/10.1016/j.jece.2014.07.021>
- Torres E, Auleda M (2013) A sequential extraction procedure for sediments affected by acid mine drainage. *Journal of Geochemical Exploration* 128:35-41
- Zhao H, Xia B, Qin J, Zhang J (2012) Hydrogeochemical and mineralogical characteristics related to heavy metal attenuation in a stream polluted by acid mine drainage: A case study in Dabaoshan Mine, China. *Journal of Environmental Sciences* 24:979-989, doi:[http://dx.doi.org/10.1016/S1001-0742\(11\)60868-1](http://dx.doi.org/10.1016/S1001-0742(11)60868-1)
- Zipper CE, Skousen JG (2010) Influent water quality affects performance of passive treatment systems for acid mine drainage. *Mine Water Environ* 29:135-143