

Pre-treatment of coal dump leachate with MgO for pigment recovery

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Abstract

Mine water rich in metals requires sustainable and cost effective treatment that leads to recovery of resources. Consequently, this investigation was aimed at identifying a process for recovering clean water and saleable products such as pigments from iron-rich acid mine water. For this, MgO was used to remove iron as $\text{Fe}(\text{OH})_3$, which was converted through drying at 80°C to goethite (yellow) and at 700°C to haematite (red). Na_2CO_3 was used for removal of the remaining metals (Mn^{2+} and Ca^{2+}) as carbonates. The pre-treated water is desalinated with RO to produce a permeate (TDS = 105 mg/L) and a brine of 85 069 mg/L. The brine is further concentrated by freeze crystallization up to a TDS of 336 820 mg/L. This is concentrated enough for the recovery of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Key words: Acid mine water, ROC process, Freeze crystallization, pigment, magnesium oxide, magnesium sulphate

Background

Acid mine drainage (AMD) from mining activities is a major environmental concern in South Africa as it requires neutralisation and desalination. Sludges generated during neutralization are rich in metals such as Fe^{2+} , Fe^{3+} , Al^{3+} , Mn^{2+} , Co^{2+} and Ni^{2+} and needs to be handled as toxic waste. Furthermore, the sludge generated during desalination is often rich in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$. Legislation requires that mine water should be treated to drinking water quality and ideally, there should be zero-waste. These requirements imply that both neutralization and desalination are to be implemented and that any waste needs to be transported to a registered and approved toxic waste disposal site. Near zero-waste processes have a further benefit in that they allow for the recycling of a large portion of the treatment chemicals. This recycling has the benefit of generating income through the recovery of saleable by-products, thereby reducing operational costs of treatment.

In the reverse osmosis/cooling (ROC) process (see **Figure 1**), acidic or neutral

mine water is treated with Na_2CO_3 and/or NaOH and/or MgO in the pre-treatment stage to allow selective precipitation of metals ($\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, CaCO_3 , MnO_2 and $\text{Mg}(\text{OH})_2$) (Akinwekomi, et al., 2016; Maree & Mtombeni, 2018; Maree, et al., 2018; Magagane, et al., 2019). After pre-treatment, the sodium-rich water is passed through a membrane stage to produce drinking water and brine. The brine has a concentration high enough to allow Na_2SO_4 crystallization upon cooling. In the improved ROC process MgO is used in the pre-treatment stage with the aim to recover MgSO_4 from the brine treatment stage, which can be used as raw material for fertilizer manufacturing.

Objectives

This project attempted to answer the following questions, which can also be formulated differently as objectives: (i) Can MgCO_3 or MgO be used for neutralization of acid mine water?; (ii) Can pigment be recovered from iron-rich mine water when neutralized with MgO?; and (iii) can magnesium sulphate be recovered from the brine after neutralized

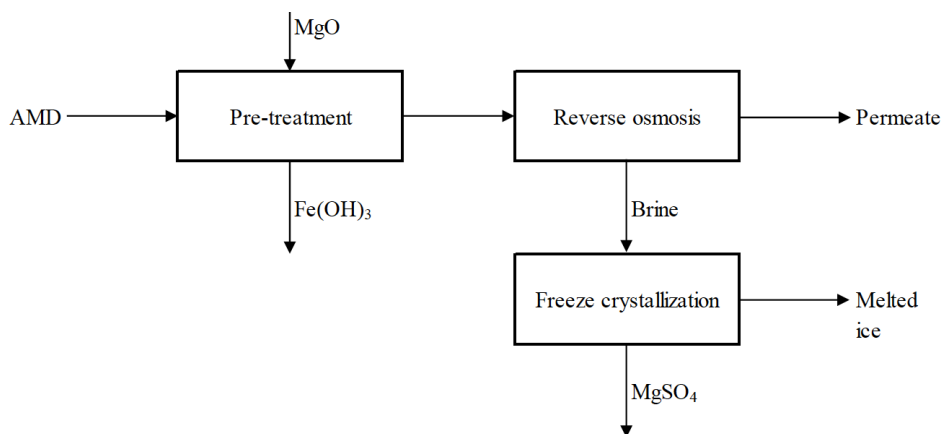


Figure 1. Process configuration of the ROC (Reverse osmosis/Cooling) process

water is desalinated with RO and the RO brine is further treated with freeze crystallization?

Materials and Methods

Feedstock

Leachate from a waste coal disposal dump was used as iron source. $\text{Mg}(\text{OH})_2$ (analytical grade), magnesite (MgCO_3) and MgO were used as magnesium alkalis. Charmotte Holdings supplied the magnesite and MgO .

Equipment

The following pieces of equipment were used: Beakers (600mL), pH meter (Ohaus, Starter3100m), mechanical stirrers (IKA, RW 20 digital), thermometer and hot plate stirrers (Heidolph MR 3001k).

Procedure

Gran titrations were carried out by titrating 5 g of a magnesium alkali salt in 100 mL water with 0.05 mol/L H_2SO_4 . Beaker studies were carried out to determine the rate of neutralization with magnesium alkalis. Beakers (600 mL) were filled with acid water (500 mL) and stirred at 250 rpm. At time zero the magnesium alkali was added. Samples were taken at regular intervals (10, 30, 60 and 120 minutes), filtered, pH recorded and analysed for acidity conductivity, Fe and Mg. Further, the effects of the following parameters were investigated over the given reaction time: $\text{Mg}(\text{OH})_2$ dosage, MgO dosage and temperature (20°C to 80°C).

Analysis

Samples were collected at various stages in the treatment process, filtered (Whatman No 1), pH recorded and analysed for, acidity and magnesium using standard procedures (APHA, 2012). Acidity was determined by titration to pH 8.3 using standard 0.1 M NaOH. The magnesium concentration was analysed using ICP.

Modelling

The *OLI ESP* software program was used to predict the behaviour of metals dissolved in water when treated with alkalis such as MgO and NaOH (OLI, 2015). *OLI* is an aqueous equilibrium chemistry estimator with an interactive and self-instructive interface for clarifying reactions, the ability to work with all kinds of common equilibrium reactions, a strong solution algorithm, expressive and easily understandable displays for results, and the ability to produce results in multiple formats according to different uses. The Stream Analyzer of *OLI* was used to perform single point equilibrium calculations, multiple point survey calculations for calculating a complete trend analysis for characteristics such as temperature, pressure, pH and composition effects, and simple mix and separate capability. The calculations provide liquid- and solid-phase separations for a specialized model.

The *OLI Analyser 9.0 System* was used to simulate the reactions by running a

simulated AMD sample with assumed values of temperature, pressure and pH. The base titrants used were Na_2CO_3 , MgCO_3 , $\text{Mg}(\text{OH})_2$ and MgO . The effect of temperature on the solubility of MgSO_4 and Na_2SO_4 was determined for when MgO was used for neutralization to pH 3.2, followed by Na_2CO_3 to raise the pH to 8.6. Once the input values were run in the *OLI Systems Chem Analyzer*, a calculated summary of the simulated results would appear. This could be used to predict the actual reactions to use in the treatment methods according to the specific characteristics. Thus it was used to optimize a neutralisation-precipitation-desalination process for AMD.

Results and Discussion

Neutralization with magnesium alkalis

In the ROC process sodium or magnesium alkalis can be used during pre-treatment of sulphate-rich acidic effluents. Both Na_2SO_4 and MgSO_4 have high solubilities (Na_2SO_4 , 262.4 g/L and MgSO_4 , 226.1 g/L at 25 °C) and therefore no chemical scaling will form on the membrane in the subsequent RO stage. As MgSO_4 is a raw material for fertilizer manufacturing it is the preferred alkali to use. A limitation of magnesium alkalis is their low solubilities. In pure water at 25°C MgCO_3 has a solubility of 12.04 mmol/L (292.6 mg/L) (as Mg) and MgO a solubility of 0.1 mmol/L (2.43 mg/L) (as Mg). OLI software showed that MgCO_3 is converted to $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (nesquehonite) and $\text{Mg}(\text{OH})_2$ (brucite) when contacted with water.

OLI software predicted that, according to thermodynamic data, all magnesium salts will react with H_2SO_4 . Gran titrations (Figure 2) show the behaviour of 123.7 mol/L MgCO_3 (magnesite) and MgO , when reacted with H_2SO_4 . Predicted values with OLI software showed that with MgO the pH gradually dropped from 10.3 to 9.2 when the H_2SO_4 dosage was increased from 0 to 123.7 mol/L. Thereafter the pH dropped rapidly to 2.2 and lower, as expected when a strong acid is reacted with a strong alkali. Figure 2 also compared the effect of MgO on pH (as predicted by OLI and when carried out experimentally). In the case of actual MgO (85%; 75µm particle size) it was determined

that 62% of the mass of MgO reacted with H_2SO_4 . The utilization of MgO amounted to 74% (62.9 / 85.0 × 100). Unreacted MgO particles were observed. It was concluded that fine MgO with a particle size of less than 20 µm needs to be used for neutralization.

Kinetics of neutralization

MgCO_3 has a higher solubility than MgO (12.04 mmol/L versus 0.10 mmol/L). It was expected that MgCO_3 would be the preferred magnesium alkali for neutralization of iron-rich acid water. Surprisingly, it was found that MgCO_3 did not neutralize acid water rich in iron. It was assumed that MgCO_3 reacted with Fe^{3+} and formed a layer of $\text{Fe}_2(\text{CO}_3)_3$ on the surface of MgCO_3 particles, to prevent further dissolution. The focus was then shifted to $\text{Mg}(\text{OH})_2$ and MgO for neutralization.

Figures 3 and 4 show that both $\text{Mg}(\text{OH})_2$ and MgO can be used for neutralization of acid water rich in Fe^{3+} . Figure 3 shows the effect of $\text{Mg}(\text{OH})_2/\text{H}_2\text{SO}_4$ mol ratio on the rate of neutralization of a mine water containing 6 000 mg/L acidity (as CaCO_3) at 25 °C. It was noted that the rate of neutralization was related to the concentration. At a mol ratio of 1.0 a long reaction time of more than 120 min was required. This can be ascribed to the low solubility of $\text{Mg}(\text{OH})_2$ of 2.43 mg/L (as $\text{Mg}(\text{OH})_2$). This was expected and the reason why alkalis with higher solubilities are normally used for neutralization such as $\text{Ca}(\text{OH})_2$ (0.173 g/L), Na_2CO_3 (21.5 g/L) and NaOH (109 g/L). This shortcoming of $\text{Mg}(\text{OH})_2$ as an alkali can be overcome at increased temperatures and extending reaction times. Complete neutralization was achieved after 1 440 min at a $\text{Mg}(\text{OH})_2/\text{Acidity}$ mol ratio of 1.3.

Figure 4 shows the effect of the $\text{MgO}/\text{H}_2\text{SO}_4$ mol ratio on the rate of neutralization of mine water at 60°C containing 6 000 mg/L acidity (as CaCO_3). The particle size of the MgO was 75µm, i.e. larger than the 20µm of the $\text{Mg}(\text{OH})_2$ used as depicted in Figure 3. It was noted that the increased $\text{MgO}/\text{Acidity}$ mol ratio resulted in an increased rate of neutralization. MgO like $\text{Mg}(\text{OH})_2$ can be used for neutralization, provided that a long reaction time is provided, fine particle size is used and the temperature is increased. Figure

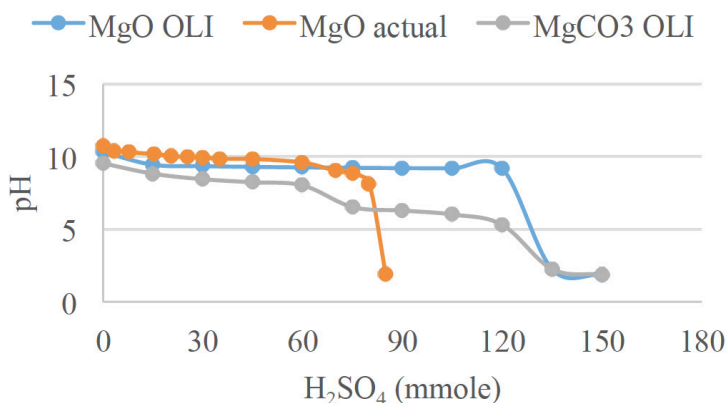


Figure 2. Gran titration when 5 g/L (123.7 mmol/L) magnesium alkali is treated with H_2SO_4

5 shows that at 60°C complete neutralization was achieved after 120 min compared to much longer times required at 25°C.

Pigment recovery

The $Fe(OH)_3$ was produced by adjusting the coal leachate with MgO to pH 3. After separation of the $Fe(OH)_3$ from the water, the $Fe(OH)_3$ -sludge was dried and heated to various temperatures. Goethite (yellow) was produced at 80°C, haematite (red) at 650°C and magnetite at pH 10 and 100°C (Figure 6).

Water quality

Table 1 shows the water quality before acid mine water was treated with MgO for neutralization and pigment recovery, RO for desalination and freeze crystallization for brine treatment and $MgSO_4$ recovery. It was noted that $Fe(OH)_3$ can be recovered by raising the pH with MgO to pH 3, pure water

can be recovered through RO treatment, and brine with a high TDS of 80 g/L can be produced. The brine can be further treated with freeze crystallization to produce solid $MgSO_4 \cdot 7H_2O$ (72 284 mg/L) and a brine containing 54 479 g/L Mg^{2+} , 21 737 mg/L Na^+ and 256 791 mg/L SO_4^{2-} .

Conclusions

It was found that MgO can be used for removal of iron from iron-rich mine water as $Fe(OH)_3$. $Fe(OH)_3$ can be converted to goethite (yellow pigment) by drying at 80°C and to haematite (red pigment) at 700°C. Na_2CO_3 can be used for the removal of the remaining metals (Mn^{2+} and Ca^{2+}) as carbonates. The pre-treated water can be desalinated with RO to produce a permeate with a TDS of 104.7 mg/L and a brine with a TDS of 85 069 mg/L. The brine can be further concentrated by freeze crystallization to

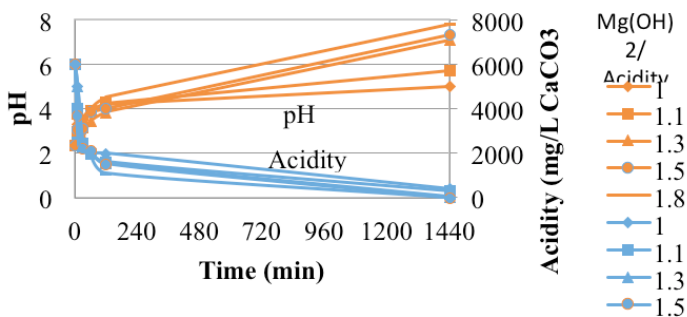


Figure 3. Effect of $Mg(OH)_2$ /Acidity ratio on neutralization rate (Temp = 25°C; $Mg(OH)_2$, Particle size = 25 μm ; $Mg(OH)_2$ purity = 92%)

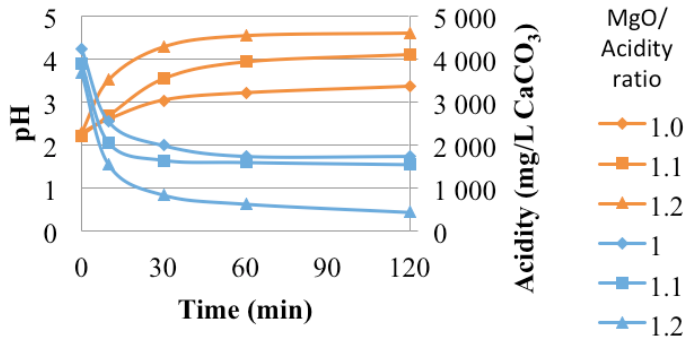


Figure 4. Effect of MgO/Acidity ratio on neutralization rate (Temp = 60°C; MgO, particle size = 75 µm; MgO, purity = 75%; MgO/Acidity ratio =1.0)

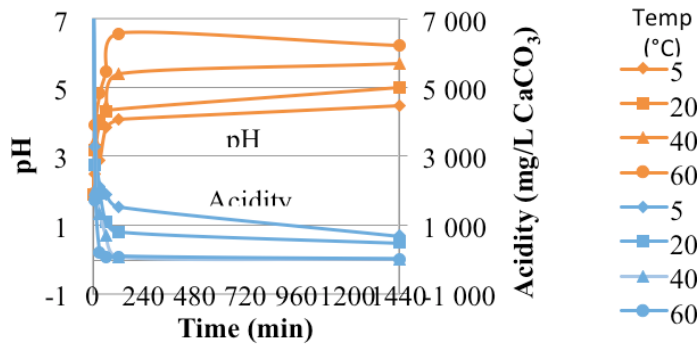


Figure 5. Effect of temperature on neutralization rate (MgO particle size = 75 µm; MgO purity = 75%; MgO/Acidity ratio =1.0)

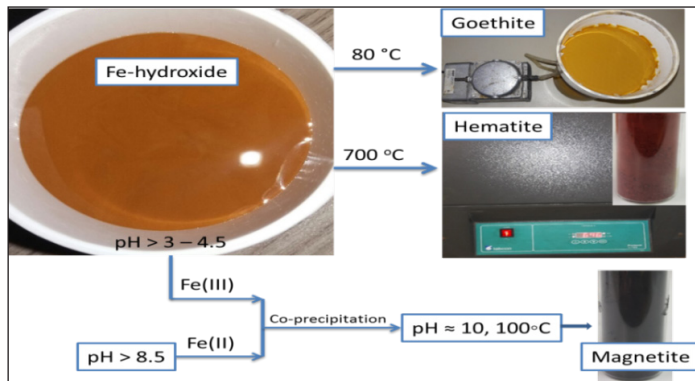


Figure 6. A furnace was used for calcination to produce goethite (yellow pigment) and haematite (red pigment). Haematite can be produced from goethite. Magnetite is produced as shown (Akinwekomi et al. 2016)

produce a brine with a TDS of 336 820 mg/L and 72 284 mg/L $MgSO_4 \cdot 7H_2O$ (epsomite).

Acknowledgements

The authors express their gratitude to Department of Trade and Industry (THRIP

Programme) for financial support, Tshwane University of Technology for providing laboratory facilities to conduct this study, Anglo American Thermal Coal for providing acid mine water and F. Carlsson for editing of the document.

Table 1. Predicted water quality (OLI software)

Parameter	Concentration (mg/L)							
	Feed	MgO		Na ₂ CO ₃	RO		Freeze	
					Permeate	Brine	Melted ice	Brine
Flow (m ³ /h)	1.00	1.00	1.00	1.00	0.88	0.122	0.09	0.032
pH	2.3	3.5	4.1	9.3		6.9		7.1
Dosage (mg/L)		2 199	2 751	1 349				
H ₂ O	1.0	1.0	1.0	1.0		997 842		
Na ⁺	22	22	22	607.6	6.1	4 962	198	21 738
Mg ²⁺	166	1 327	1 660	1 722.4	17.2	14 063	563	54 479
Ca ²⁺	369	369	369	10.4	0.1	85	3	221
Mn ²⁺	50	50	50	0.2	0.0	2.0	0.1	8.6
Fe ²⁺	168	168	168	0.5	0.0		-	
Fe ³⁺	1 798	6.0	0.4	-	-		-	
Al ³⁺	246	246	8	1	0.0		-	
SO ₄ ²⁻	7 793	7 798	7 805	7 814	78.1	65 139	2 606	256 791
Cl ⁻	100.0	100.0	100.0	100.0	1.0	818	33	3 582
Alk	-	-	-	176.3	1.8		-	
TDS	10 712	10 085	10 182	10 471	105	85 069	3 403	336 820
Cations (meq/L)	165	164	165	169	2	1378	55	5440
Anions (meq/L)	165	165	165	169	2	1380	55	5451
Solids								
Fe(OH) ₃ (Bernalite)		3 431.9	687.4	0.7				
Al(OH) ₃ (Gibbsite)		-						
FeCO ₃ (Siderite)				348				
CaCO ₃ (Calcite)				646				
Mg(OH) ₂ (Brucite)				38				
MnCO ₃ (Rhodochrosite)				104				
MgSO ₄ ·7H ₂ O (Epsomite)								72 284
CaSO ₄ ·2H ₂ O (Gypsum)								643
Suspended solids	-	3 432	687	1 137	-	-	-	72 927
Osmotic pressure (bar)							17.2	71
Salt removal (%)					99.0		96.0	

References

- Akinwekomi, V., Maree, J. P., Strydom, A. & Zvinowanda, C., 2016. *Recovery of magnetite from iron-rich mine water*. WISA Biennial Conference, Durban, South Africa.
- APHA, 2012. *Standard methods for the examination of water and wastewater*, 12th ed. Washington, DC: American Public health Association.
- Magagane, N. et al., 2019. Facile thermal activation of non-reactive cryptocrystalline magnesite and its application on the treatment of acid mine drainage. *Journal of Environmental Management*, Volume 236, pp. 499-509.
- Maree, J. P. & Mtombeni, T., 2018. *Treatment of brine for the recovery of drinking water, calcium carbonate and sodium sulphate*. Proceedings of the 2018 WISA biennial conference, Cape Town, South Africa, 24 – 27 June.
- Maree, J. P., Mtombeni, T., Ramothole, P. & Letjiane, S. L., 2018. *Treatment of copper leachate for the recovery of valuable products*. CSIR Conference Centre, 11 th ICARD/IMWA/AMD Conference – Risk to Opportunity, Pretoria, South Africa, 10-14 September .
- OLI, 2015. [http://www.olisystems.com/..](http://www.olisystems.com/) [Online] [Accessed 2015].