An evaluation of waste gypsum-based precipitated calcium carbonate for acid mine drainage neutralization

J. N. Zvimba, J. Mulopo, L. T. Bologo and M. Mathye

ABSTRACT

Precipitated $CaCO_3$ compounds recovered from pulped waste gypsum using some carbonate and hydroxide-based reagents were evaluated for their utilization in acid mine drainage (AMD) neutralization. The neutralization potentials, acid neutralization capacities and compositions of the $CaCO_3$ compounds were determined and compared with some commercial $CaCO_3$. It was observed that $CaCO_3$ recovered from waste gypsum using Na_2CO_3 significantly neutralized AMD compared with commercial $CaCO_3$ and that recovered using both $(NH_4)_2CO_3$ or NH_4OH-CO_2 reagents. Moreover, a higher acid neutralization capacity of 1,370 kg H_2SO_4/t was determined for $CaCO_3$ recovered from waste gypsum using Na_2CO_3 compared with an average of 721 and 1,081 kg H_2SO_4/t for ammonium-based $CaCO_3$ and commercial $CaCO_3$ respectively. The inorganic carbon content for the $CaCO_3$ recovered using Na_2CO_3 and ammonium-based reagents of 49 and 34% respectively confirmed their observed neutralization potentials and acid neutralization capacities, while energy dispersive X-ray fluorescence suggested absence of major oxide impurities, with the exception of residual SO_4^{2-} and Na_2O which still requires further reduction in the respective compounds.

Key words | acid mine drainage, acid neutralization capacity, acid neutralization potential, calcium carbonate, gypsum

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INTRODUCTION

Globally, acid mine drainage (AMD) has been identified as a major environmental problem facing the mineral industry (Ribet *et al.* 1995), resulting in serious and sometimes permanent ecological damage (Micera & Dessi 1988). In this regard, a wide range of AMD treatment technologies has been developed and proven (Arnold 1991; Ackman & Kleinmann 1991; Akcil & Koldas 2006; Zhuang 2009). Generally, chemical treatment of AMD is broadly classified into two options. These options include pH control with partial sulfate removal using limestone such as in the integrated limestone/lime neutralization process (Geldenhuys *et al.* 2003) and the more advanced desalination technologies such as SAVMIN, reverse osmosis (RO) and the Alkaline–Barium–Calcium (ABC) processes (Smit 1999; Hlabela *et al.* 2007; Motaung *et al.* 2008), which focus not only on neutralization, but also achieve significant sulfate removal. Desalination technologies such as RO currently utilized commercially in South Africa, however, also require pre-treatment, thereby consuming significant quantities of limestone. Recently, a report (Coetzee *et al.* 2010) prepared by a team of experts for the South African Government-appointed Inter-Ministerial Committee on AMD recommended construction of a 20 ML/d emergency neutralization plant for AMD treatment as one of the short-term interventions to deal with large quantities of uncontrolled AMD already decanting from the Witwatersrand's Western Basin. In this regard, such short-term measures have significant potential for putting pressure on the current South African limestone market with significant increase in generation of waste gypsum.

Despite previous extensive investigations based on the Merseberg approach (Robinson & Okla 1953), over the last two decades there has been resurgence in waste gypsum beneficiation (Meng *et al.* 2005; Yang *et al.* 2008; Abbas 2011). Although it is well established that sulfur can be recovered from waste gypsum thermally (Turkdogan & Vinters 1976; Nengovhela *et al.* 2007), the use of the Merseberg-based approach for waste gypsum beneficiation in South Africa still remains an attractive option due to its low

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energy input. In this regard, our recent investigations have demonstrated the feasibility of waste gypsum beneficiation using different aqueous reagents (Mulopo *et al.* 2011). However, it has become imperative that the behaviour and properties of the valuable by-products from waste gypsum beneficiation be evaluated and compared with their commercial equivalents so as to identify their key applications in the South African market. Moreover, such an evaluation is currently viewed as a critical innovative requirement for identification and ascertaining some possible novel applications likely to be associated with these by-products.

Although a number of tests useful in the identification of calcium carbonate containing materials are known and readily available (Sobek *et al.* 1978), we envisage utilizing the strength of a combination of tests to give important insights into the innovative nature of the behaviour and properties of the recovered products. Typically, the application of titration-type tests for acid–base accounting is well known (Sobek *et al.* 1978; Skousen *et al.* 1997; Weber *et al.* 2004) in providing acid neutralization capacity (ANC) despite associated uncertainties challenges (Paktunc *et al.* 2001); and this process is typified as given in Equation (1).

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O\,(\,pH < 6.4) \qquad (1)$$

Moreover numerous AMD neutralization kinetics studies using calcium carbonate have been widely published (McDonald & Grandt 1981; Geldenhuys *et al.* 2003) while several material composition determination techniques are available. To this end, we have utilized the combined innovative strength of three tests (acid–base accounting, AMD neutralization kinetics and compositional determination and measurements) as a simple, but robust scientific approach in the evaluation of the nature and behaviour of precipitated calcium compounds (PCCs) recovered from waste gypsum. The study further compared the PCC with commercially available calcium compounds for their respective AMD neutralization.

MATERIALS AND METHODS

Feedstock

AMD containing 2,000 mg/L SO_4^{2-}, pH of 2.0–3.0 and acidity of 1,000 mg/L was collected from Emalahleni Reclamation Plant and used as feed water. Precipitated calcium carbonate recovered from waste gypsum materials of composition given in Table 1, using various reagents ($(NH_4)_2CO_3$, NH_4OH-CO_2 and Na_2CO_3) as well as commercial $CaCO_3$ from Merck and Sappi were used. HCl (1.0 mol/L) and NaOH (0.5 mol/L) reagents were prepared using titrisol ampoules from Merck.

Equipment

AMD neutralization experiments were carried out batchwise using a closed 1 L perspex reactor as given in Figure 1. The reactor had four equally spaced baffles and was equipped with an overhead stirrer with two radial turbine impellers used for mixing. A Hanna HI 2829 multiparameter data logger was used to continuously record reactor solution pH, while a Toledo Auto-titrator was used for acidity determination. A magnetic stirrer heating block was used to digest samples for ANC determinations.

Experimental procedure

The AMD neutralization experiments were carried out batch-wise by dosing similar quantities of $CaCO_3$ directly into 1 L of AMD, with a data logger to record pH, immersed into the vessel mixture. Sample aliquots were collected at specific time points during neutralization for the determination of acidity. The Modified Sobek ANC based on the original methodology by Sobek *et al.* (1978) was used to determine quantitative ANC for all the precipitated $CaCO_3$. Fizz rating was used to determine the acid quantities and molarities to be used in the ANC test in accordance with Weber *et al.* (2004).

Table 1 | Composition (wt %) of major oxides and inorganic carbon in three waste gypsum materials as determined by XRF and LECO analysis

Sample	Inorg. C wt%	SiO_2 wt%	SO_4^{2-} wt%	Al_2O_3 wt%	Fe_2O_3 wt%	MgO wt%	CaO wt%	Na_2O wt%	K_2O wt%	Cr_2O_3 wt%	MnO wt%
Gypsum (A)	0.24	0.27	32.19	0.17	0.04	0.57	29.5	0.57	0.02	0.04	0.01
Gypsum (S)	0.04	0.8	33.21	0.64	0.06	1.46	30.6	7.54	0.02	0.03	0.01
Gypsum (F)	0.05	0.74	39.28	0.03	0.09	0.12	35.7	0.61	0.02	0.04	0.01

(A), (S) and (F) denotes Anglo Coal, Sasol and Foskor respectively as sources of waste gypsum.

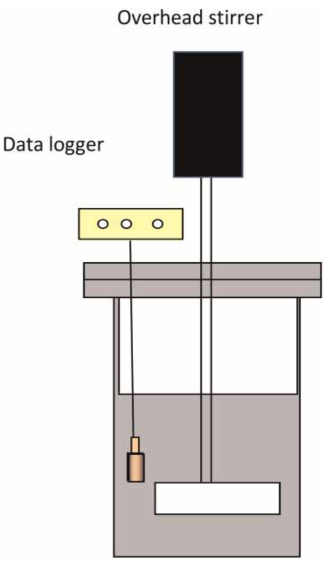

Figure 1 | Schematic representation of the experimental setup.

Analytical procedure

The acidity of the AMD during neutralization was determined using a Toledo Auto-titrator.

Semi-quantitative scans for bulk elemental composition were determined by X-ray fluorescence (XRF) using a Spectro X-Lab 2000 Energy-Dispersive instrument. The fizz test using HCl was used to test for the presence of carbonates, which was validated by a LECO CS200 carbon/sulfur analyser for the C analyses to determine the inorganic C content.

RESULTS AND DISCUSSION

In order to evaluate the acid neutralization potential kinetics of the precipitated $CaCO_3$ (PCC), AMD with an initial acidic pH averaging 2.0–3.0 was neutralized over a period of 1 h. Figures 2 and 3 show the changes in pH and acidity during neutralization of AMD using the various PCCs recovered from waste gypsum over a period of 1 h. These data were compared with the acid neutralization potential kinetics for commercial and Sappi PCC. Table 2 shows the composition (wt %) in terms of major oxides and inorganic carbon as well as ANC data for the various calcium compounds evaluated in this study as determined by XRF, LECO analysis and the ANC test respectively.

Acid neutralization potential kinetics

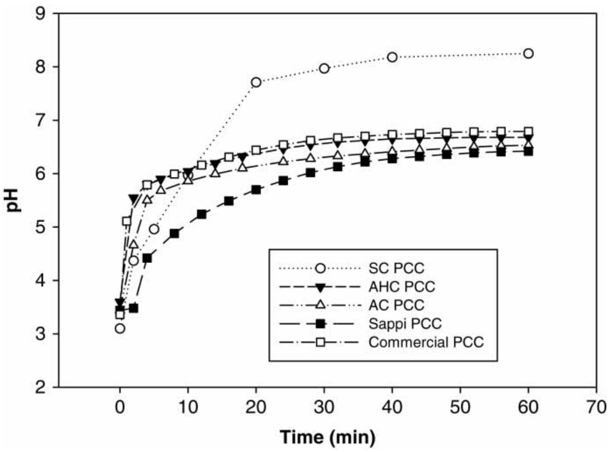

Figure 2 | pH as a function of time during neutralization of AMD using various PCCs recovered from waste gypsum, commercial PCC and Sappi PCC. Conditions: feed water volume = 1 L; PCC mass = 2 g.

From Figure 2, the initial pH of the acidic feed water averaging 2.0–3.0 increases to a maximum pH value of 8.0 over a period of 30 min upon neutralization using PCC recovered from waste gypsum using sodium carbonate (SC PCC). On the other hand, maximum pH values within the range 6.4–6.8 were achieved upon neutralization using Sappi PCC, commercial PCC and PCC recovered from waste gypsum using $(NH_4)_2CO_3$ (AC PCC), NH_4OH-CO_2 (AHC PCC) over 1 h.

From these data, the AHC PCC appears to exhibit neutralization potential quite comparable with the commercial PCC used in this study as a reference. On the other hand, AC PCC exhibited slightly better neutralization potentials compared with the Sappi PCC, also used as a reference. It is quite possible that both AHC PCC and AC PCC contain residual hydroxide and ammonia on their surfaces thereby contributing to their respective improved neutralization

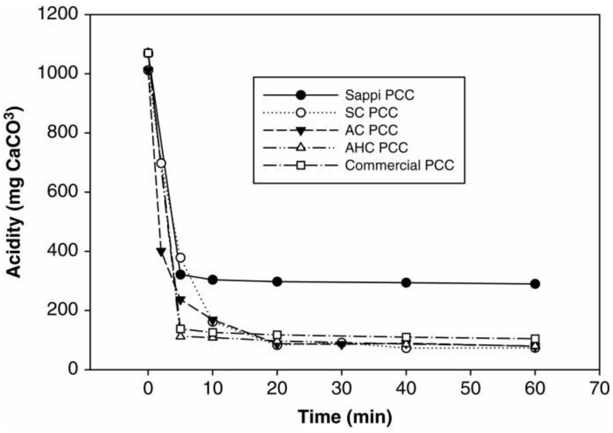

Figure 3 | Acidity as a function of time during neutralization of AMD using PCC recovered from waste gypsum, commercial PCC and Sappi PCC. Conditions: Feed water volume = 1 L; PCC mass = 2 g.

Table 2 | Composition (wt %) of major oxides, inorganic carbon and ANC as determined by XRF, LECO analysis and Modified Sobek ANC test respectively

Sample	Fizz rating	Inorg. C wt%	SiO_2 wt%	SO_4^{2-} wt%	Al_2O_3 wt%	Fe_2O_3 wt%	MgO wt%	CaO wt%	Na_2O wt%	K_2O wt%	Cr_2O_3 wt%	MnO wt%	ANC kg H_2SO_4/t
Sappi PCC	5	52.8	0.92	0.07	0.29	0.21	1.04	55.9	0.202	0.01	0.04	0.62	1,060
Com. PCC	5	54.3	0.49	0.07	0.26	0.07	0.19	58.1	0.162	0.01	0.04	0.03	1,102
AC PCC	5	34.1	1.44	9.46	0.37	0.07	0.25	46.7	0.337	0.01	0.03	0.02	728
AHC PCC	5	33.2	1.47	9.88	0.53	0.09	0.07	46.3	2.55	0.01	0.04	0.02	714
SC PCC	5	48.9	1.63	2.41	0.36	0.099	0.05	46.8	2.49	0.01	0.04	0.02	1,370

potentials. The SC PCC exhibits superior neutralization potential kinetics compared with all the PCC evaluated, achieving a maximum neutralization pH value of 8.0. Such a high maximum neutralization pH value is however quite unusual considering that the calcium compound here is calcium carbonate, with a theoretically known maximum neutralization pH value of 6.4 due to pH buffering by CO_2 during AMD neutralization (Akcil & Koldas 2006; Motaung *et al.* 2008; Zhuang 2009).

From Figure 3, acidity is removed from an initial value of about 1,000 mg/L $CaCO_3$ to 300 mg/L $CaCO_3$ using Sappi PCC. The use of AC PCC, SC PCC, AHC PCC and commercial PCC, resulted in removal of acidity from 1,000 mg/L $CaCO_3$ to about 100 mg/L $CaCO_3$ in less than 20 min. The acidity data indicate that all the PCC generated from waste gypsum are quite comparable with commercially available PCC but slightly better than Sappi PCC in their ability to remove AMD acidity. In this regard, the acidity data given in Figure 3 further support the pH data given in Figure 2. It is worthy noting that neutralization beyond 20 min in all cases does not change the AMD acidity content, and there may be no need to carry out the AMD neutralization for longer than this.

However, as acidity and pH are related, more independent data would still be required to positively confirm the observed acid neutralization potential kinetics associated with the various PCC recovered from waste gypsum. In this regard, a more quantitative approach based on ANC and compositional (major oxides and inorganic carbon) determinations was explored.

Acid neutralization capacity and compositional determination

ANC, inorganic carbon and major oxides content for all the PCC evaluated are shown in Table 2. The ANC determined using the Modified Sobek ANC test (Sobek *et al.* 1978) was based on a Fizz rating of 5 (carbonate reaction). The ANC data for all the six PCC compounds were also based on the same grain size of less than 75 μm as this is known to significantly affect ANC data, with greater ANC values previously reported for smaller grain-size fractions (White *et al.* 1999; Jambor *et al.* 2002). Moreover, according to Loewenthal *et al.* (1986), the rate of $CaCO_3$ dissolution as described by the following equation:

$$-\mathrm{d}[\mathrm{Ca}^{2+}]/\mathrm{d}t = kS\left\{(\mathrm{Ca}^{2+})^{0.5}(\mathrm{CO}_3{}^{2-})^{0.5} - K_{\mathrm{sp}}{}^{0.5}\right\}^2 \qquad (2)$$

where k is the dissolution rate constant, S the surface area of $CaCO_3$ dissolution sites and the activity in mol/L, depends on k, S and the terms within curly brackets (Loewenthal & Marais 1976). Although k is affected to an unknown extent by crystal structure, S is dependent on the size, mass and structure of the crystals. Therefore, by controlling S and the degree of super-saturation, the rate of dissolution of $CaCO_3$ is controllable during neutralization resulting in acceptable ANC determinations.

The ANC values presented in Table 2 for the Sappi and commercial PCC are much higher than the ANC values determined for both AC PCC and AHC PCC. In this regard, Sappi PCC, commercial PCC, AC PCC and AHC PCC consume 1,060, 1,102, 728 and 714 kg of H_2SO_4 per tonne of PCC used. On the contrary, 1,370 kg of H_2SO_4 is consumed per tonne of SC PCC. The significantly high CaO content as the major oxide ranging from 46–47% for all the PCC compounds recovered from waste gypsum and insignificant levels of most major oxides are a clear indication that calcium based compounds of high quality were produced. The high inorganic carbon content ranging from 34 to 49% for all PCC compounds confirms that $CaCO_3$ is the typical major calcium based compound recovered, and therefore the PCC would be applicable for AMD neutralization as previously shown in Figure 2. The $CaCO_3$ in these compounds as shown in Equation (1) is mainly responsible for acid neutralization and therefore its quantity significantly influences the ANC data as given in Table 2. The major oxides content shows that the AC PCC, AHC PCC and SC PCC contain insignificant quantities of most impurities, with the exception of SO_4^{2-} and Na_2O. However, a low SO_4^{2-} content of 2.41% for the SC PCC compared with an average ranging 9.5–9.9% in both AC PCC and AHC PCC suggest that better quality calcium carbonate is recovered from waste gypsum using Na_2CO_3 rather than the Merseberg-based reagents (Robinson & Okla 1953).

CONCLUSIONS

Based on the current study, $CaCO_3$ recovered from waste gypsum using Na_2CO_3 exhibited significant AMD neutralization potential compared with the PCC recovered using $(NH_4)_2CO_3$ or NH_4OH and CO_2. In this regard, the $CaCO_3$ recovered from waste gypsum using Na_2CO_3 achieved neutralization of AMD to a maximum pH value of 8.0, while the $(NH_4)_2CO_3$ or NH_4OH and CO_2 – based PCC only achieved a maximum pH of not more than 6.5. The maximum pH achieved using SC PCC is rather unusual considering that AMD neutralization using $CaCO_3$ is buffered by CO_2. However, based on the quantitative data (ANC, inorganic carbon and major oxides content), it was concluded that the $CaCO_3$ recovered from waste gypsum using Na_2CO_3 would consume more acid in AMD per ton of PCC used; contains more CO_3^{2-} species and less residual SO_4^{2-} compared with $CaCO_3$ recovered from waste gypsum using $(NH_4)_2CO_3$ or NH_4OH and CO_2. Moreover, its ANC is also significantly higher than the commercially based PCC used in this study for comparison. In this regard, this study confirms that there is merit in waste gypsum beneficiation for the recovery of valuable by-products such as $CaCO_3$ useful in AMD treatment as demonstrated in this study. However, residual SO_4^{2-} and Na_2O content in the SC PCC still require reduction to further improve the quality of the $CaCO_3$ recovered from waste gypsum and this is the subject for future focus. Overall, the current study has laid the basis for evaluation of waste gypsum beneficiation by-products and therefore presents a great opportunity for identification of new applications for the recovered products. It is therefore imperative to build on this study in future studies seeking further development and establishment of an even more robust product evaluation protocol applicable to a wide range of waste beneficiation by-products. In this context, new industrial applications for precipitated $CaCO_3$ recovered from waste gypsum such as SO_2 scrubbing as currently applied for the Flue Gas Desulfurization (FGD) technology widely used in the power generation industry in South Africa, also require evaluation and incorporation into the product assessment.

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