

Recovery of calcium carbonate from steelmaking slag and utilization for acid mine drainage pre-treatment

J. Mulopo, M. Mashego and J. N. Zvimba

ABSTRACT

The conversion of steelmaking slag (a waste product of the steelmaking process) to calcium carbonate (CaCO_3) was tested using hydrochloric acid, ammonium hydroxide and carbon dioxide via a pH-swing process. Batch reactors were used to assess the technical feasibility of calcium carbonate recovery and its use for pre-treatment of Acid Mine Drainage (AMD) from coal mines. The effect of key process parameters, such as the amount of acid (HCl/Calcium molar ratio), the pH and the CO_2 flow rate were considered. It was observed that calcium extraction from steelmaking slag significantly increased with increase in the amount of hydrochloric acid. The CO_2 flow rate also had a positive effect of the carbonation reaction rate but did not affect the morphology of the calcium carbonate produced for values less than 2 L/min. The CaCO_3 recovered from the bench scale batch reactor demonstrated effective neutralization ability during AMD pre-treatment compared to the commercial laboratory grade CaCO_3 .

Key words | Acid Mine Drainage, calcium carbonate, carbonation, extraction, steelmaking slag

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INTRODUCTION

During steel production, for every ton of crude steel produced, about 100–600 kg of slag is generated in the form of waste by the Steel industry in South Africa. For instance ArcelorMittal Steel South Africa generates globally about 4 million tons of by-products each year, including 600,000 tons of waste in the form of steelmaking slag. However the steelmaking slag is only partially reprocessed in the steel making process and a significant proportion is stockpiled at various sites across the country, for instance, at Vanderbijlpark and New Castle. Worldwide fifty million tons per year of steel slag are produced as a residue (Altun 2002), whereas in Europe every year nearly 12 million tons of steel slag are produced (Motz & Geiseler 2001). There is no doubt that the utilization of steel slag is a subject of great environmental interest worldwide.

Globally an understanding of reusing and recycling of steelmaking has made significant progress in the past years with various studies conducted (Huijgen *et al.* 2005; Teir *et al.* 2007; Bonenfant *et al.* 2008; Doucet *et al.* 2010). In some of these studies the recycling of the waste slag into the steel making process to recover the fluxing compounds such as CaO and MgO in the slag as well as the iron units has been considered. However this recycling is restricted

because of the high P_2O_5 content as most of the phosphorous in the steelmaking slag reverts back to the hot metal in the blast furnace limiting the quantity of waste slag that can be charged back to the blast furnace (Topkaya *et al.* 2004). The use of steelmaking slag as an aggregate in road ballast has been considered as well as it provides excellent anti-skid properties. However in recent years its use for road ballast has fallen into disfavour because of the free lime present in steelmaking slag which subsequently hydrates, causing expansion and disintegration of the roadbed (Shi & Day 1999; Motz & Geiseler 2001) but also because of environmental concerns with regards to the leaching of hyper-alkaline waters and potential toxic trace elements (Chaurand *et al.* 2007).

On the other hand, Security of water supply has become a key strategic issue for the sustained economic growth of South Africa as it is a water-stressed country. Although the South African mining sector is one of the critical pillars and drivers of the South African economy, mining activities are also associated with environmental pollution such as acid mine drainage (AMD). The gold mining industry in South Africa (principally the Witwatersrand Goldfield) is in decline, but the post-closure decant of AMD represents

an enormous threat. For example, the potential volume of AMD for the Witwatersrand Goldfield alone amounts to an estimated 350 mL/day (Duane *et al.* 1997; Naicker *et al.* 2003). Recently the government of South Africa has recently established the inter-ministerial committee on AMD, with a primary focus on coordinating strategies for treatment/prevention of acid and toxic mine drainage (AMD) from abandoned mines. It is against this background that we believe there exists tremendous opportunities for assessing the production of calcium carbonate from steel slag in order to expand the existing market of calcium carbonate, preserve natural resources of calcium carbonate and integrate waste management by recycling a waste for the treatment of another waste. One may mention that the potential value of lime-rich industrial by-products for AMD neutralization has been also globally considered: (1) Fly Ash (FA), (2) Flue gas desulfurization (FGD) by-products and (3) Steel slag have shown potential utility for the sealing of inoperative mines and/or the containment and neutralization of AMD waters especially as passive treatment options. The neutralization of AMD occurs as a result of dissolution of the alkaline solids present in their respective matrix (Kopsick & Angino 1981; Abbot *et al.* 2001; Rudisell *et al.* 2001; Simmons *et al.* 2002; Xenidis *et al.* 2002). However:

- The active treatment of AMD with FA, FGD by-products or steel slag will generate excessive solid residues that will require disposal.
- FA, FGD by-products and steel slag are all enriched with many trace of hazardous elements such as fluoride, chromium and vanadium which can mobilize in water bodies.

Because of the high flow rate of AMD decant in the western basin (350 mL/day). The preferred option in the short term is the active neutralization of AMD in an integrated limestone/lime process where the AMD is firstly neutralized with limestone with a resulting decrease in acidity, increase in pH, gypsum precipitation and sulphate load reduction. Sulphate removal is then later maximized by raising the pH to >12 with lime resulting in magnesium precipitation and gypsum crystallization. There are a number of reviews on different treatment methods that have been developed for the treatment of acid mine waters using limestone (Maree *et al.* 1992; Hedin *et al.* 1994; Maree *et al.* 1994; Maree *et al.* 1996). The use of limestone for AMD treatment requires that its calcium content be as high as possible to reduce the drawbacks of using limestone which include slow reaction time. In an attempt to provide for the excessive amount of limestone with high calcium content, the

CSIR has developed a pH-swing process to produce high quality calcium carbonate from steelmaking slag with the following steps: (a) Dissolution of the calcium containing solid waste in hydrochloric acid (b) Neutralization of the resulting calcium rich solution under ambient conditions (c) Carbonation of the neutralized calcium rich solution at ambient temperature and atmospheric pressure.

MATERIALS AND METHODS

Waste slag characteristics

Chemical analysis on the homogenized sample waste slag from ArcelorMittal Steel South Africa Vanderbijlpark gave the following compositions (%): 0.11 Na₂O; 10.33 MgO; 2.86 Al₂O₃; 16.9 SiO₂; 0.12 S; 36.28 CaO; 0.78 MnO; 0.01 Zn; 0.03 Pb; 0.11 Cr; 0.03 Sr; 0.09 Ba; 0.11 F; <0.01 As; 0.04 V; 0.01 Sn. XRD Analysis in Table 1 shows that the steelmaking slag contains mostly dicalcium larnite (Ca₂SiO₄), wuestite (FeO), magnetite, CaO and brownmillerite (Ca₂FeAlO₅) with lesser amounts of mayenite (Ca₁₂Al₁₄O₃₃), CaO and free lime (Ca(OH)₂) as shown in Table 1.

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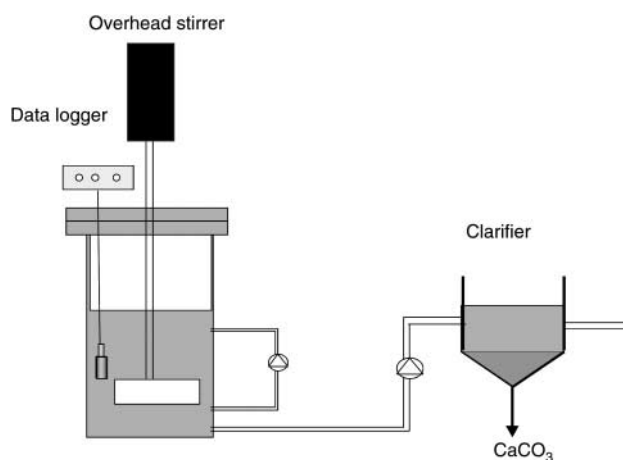
Twenty kilograms of waste steelmaking slag was collected from the Vanderbijlpark slag dump. The sample of waste slag was well mixed by repeated coning and quartering and finally a homogenized sample (5 kg) was prepared by using a laboratory sample divider (Retsch PT 100) for chemical and mineralogical analysis. One particle size fractions of waste slag: <6 mm was used in this study. Hydrochloric acid (32% and density of 1.13) and Ammonium Hydroxide (32% and density of 0.88) were purchased from Sigma-Aldrich. CO₂ (30%, balance nitrogen) was purchased from Air Liquid.

Equipment

Calcium extraction experiments were carried out batch-wise using a 3 L Perspex reactor. The reactor had four equally spaced baffles and was equipped with an outer flow jacket for reaction temperature regulation connected to a water bath. An overhead stirrer equipped with a radial turbine impeller was used for mixing. The experimental setup used is shown in Figure 1. A Hanna HI2829 multi-parameter meter was used to log reactor electrical conductivity, pH

Table 1 | XRD Analysis of the starting waste steelmaking slag and extraction product for HCl/Ca = 5.13 mol/mol and time = 90 min

Phases		Raw waste slag	Extraction product
Amorphous	Relative amount (%)	12	58.22
	Error (%)	4.8	2.7
Mayenite $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	Relative amount (%)	2.75	1.01
	Error (%)	1.2	0.78
Larnite $\beta\text{-Ca}_2\text{SiO}_4$	Relative amount (%)	33.64	1.74
	Error (%)	2.82	1.11
Brownmillerite $\text{Ca}_2(\text{Al},\text{Fe})_2\text{O}_5$	Relative amount (%)	17.28	17.07
	Error (%)	1.77	1.56
CaO	Relative amount (%)	5.32	0.16
	Error (%)	0.57	0.33
Magnetite Fe_3O_4	Relative amount (%)	2.21	3.34
	Error (%)	0.69	0.6
Portlandite $\text{Ca}(\text{OH})_2$	Relative amount (%)	0.77	0
	Error (%)	0.36	0
Wuestite FeO	Relative amount (%)	26.06	18.46
	Error (%)	1.77	1.17

**Figure 1** | Bench scale experimental setup.

and temperature data. A hypodermic syringe was used to draw out sample aliquots from the reactor. A Perkin Elmer Analyst 700 Atomic Absorption Spectrometer (AAS) and a Varian Inductively Coupled Plasma (ICP) spectrometry were used to analyse for Ca, Mg, Fe, Si and Al during extraction. The samples for XRD analysis were prepared using a back loading preparation method or a zero background sample holder, depending on the amount of sample available.

Experimental procedure

The steelmaking slag material was crushed and pulverized to minus <6 mm. Steelmaking slag (50–150 g) was loaded

into the reactor charged with HCl at different acid to calcium molar ratios. The dissolved samples were filtered using Whatman filter paper before analysis. NH_4OH was added to the calcium-rich leachate at 25 °C until pH of 10, followed by filtration. The neutralized calcium-rich filtrate was carbonated using CO_2 to precipitate CaCO_3 . The precipitated CaCO_3 was filtered and dried at 120 °C. The correlative calculation of the calcium leaching efficiency applied to all the experimental data is as follows:

$$\text{Ca leaching efficiency}(\%) = (\text{Ca in extraction filtrate} / \text{Ca in feed sample}) \times 10$$

RESULTS AND DISCUSSION

Extraction

The effect of hydrochloric acid amount on the dissolution of 50 g slag dissolution was investigated at 25 °C with <6 mm particle size. From Figure 1 it can be seen that hydrochloric acid is efficient to dissolve steelmaking slag and over 95% of calcium has been leached from the waste steelmaking slag matrix within 90 min at a temperature of 25 °C and HCl/Ca = 5.13 (mol/mol). The calcium extraction efficiency increases with increasing the amount of hydrochloric acid.

The weakest acid solution HCl/Ca = 0.3 mol/mol leached out a maximum of 10% calcium from the BOF slag

during 90 min of leaching, while the more concentrated acid solution HCl/Ca = 5.13 mol/mol leached out 96% calcium within a shorter time of 60 min. It is therefore clear that the extent of the leaching reaction is controlled in the first place by the proportion of acid to steelmaking slag. Since all these experiments of Figure 2 are at the same temperature, the rate of reaction (the slope of the curves) is controlled by the pH, being higher when one starts with a stronger acid as shown in Figure 2. The pH of the solutions increases significantly at longer reaction times when using weaker acids (lower amount HCl/amount Ca). The amount of acid required for complete calcium leaching efficiency is more than the stoichiometric required amount because the leachable elements include Al, Fe and Mg which are in significant quantities in the waste slag considered and probably some trace elements as well.

The changes in composition during extraction with HCl were examined using XRD analysis for HCl/Ca = 5.13 mol/mol as shown in Table 1. The results show that after 90 min, calcium containing phases react in different proportions. For example larnite is the most reactive phase whereas brownmillerite did not react.

Neutralization and Carbonation

The initial pH of the filtrate from the leaching stage was quite low (pH ~0.1–0.7). In order to promote carbonation, alkaline conditions are preferred as CO₂ dissolution and speciation into HCO₃⁻ and CO₃²⁻ occurs under such conditions. Moreover, the neutralization step ensures removal

of other metals leached alongside calcium as metal hydroxides. Some of the major elements of the steel slag namely Fe, Al and Mn have potential to precipitate at circumneutral pH as amorphous (oxy) hydroxides (Mayes *et al.* 2011). These precipitates probably behave also as sink for some trace elements leached from the slag. The carbonation of the neutralized calcium-rich solution shows that in the first 10–15 min over 80% of the calcium is carbonated while only an extra 18% gets carbonated when the reaction time is increased to just over 30 min. The declining carbonation reaction rate beyond 20 min shows that the precipitation of CaCO₃ is unlikely the rate-determining step for this process. In that case, the CaCO₃ initially precipitated would have served as nuclei and enhanced further precipitation and subsequently improve the carbonation efficiency. The carbonation medium pH profile forms a plateau after 25 min as the pH gradually decreases from 9.9 to 8.6. This gradual decrease in pH upon carbonation is attributed to formation of the HCO₃⁻ species in the carbonation medium and subsequent replacement of the H⁺ in the HCO₃⁻ species by Ca²⁺ resulting in CaCO₃ precipitation and loss of proton and decrease in the pH of the carbonation solution. This is consistent with the pH data profile given in Figure 3. We found as well that increasing the CO₂ flow rate significantly improves the carbonation reaction rate. However, this should be considered in view of the known effect of CO₂ flow rate on precipitated CaCO₃ morphology as reported by Han *et al.* (2005).

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According to the X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) analyses all the precipitates

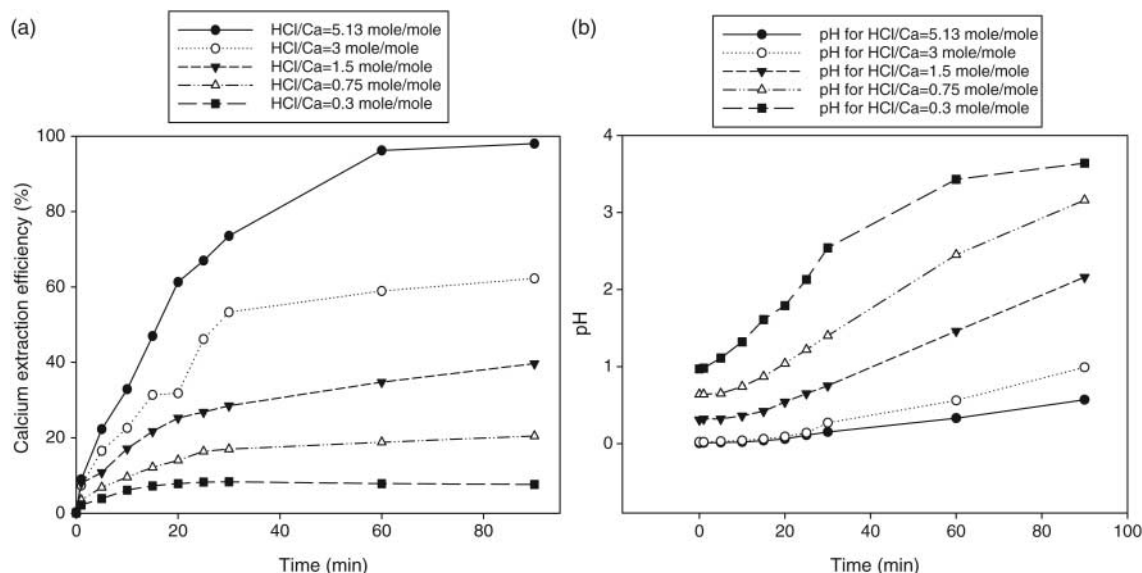


Figure 2 | Effect of HCl amount on (a) Calcium extraction efficiency and (b) pH for 50 g steelmaking slag at 25 °C.

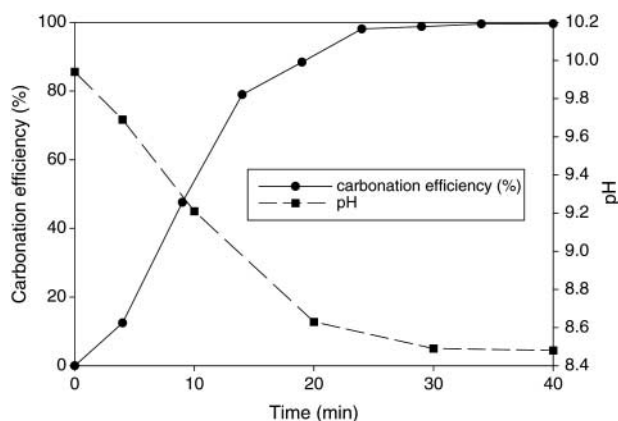


Figure 3 | Carbonation efficiency and pH over time during carbonation (CO_2 flow rate = 0.3 L/min; stirring rate = 186 rpm).

formed from the carbonation of the calcium-rich solutions contained CaCO_3 phases as a mixture of calcite and vaterite, thus 100% CaCO_3 content, with rhombohedra and hexagonal particle shapes. The CO_2 flow rate exhibited insignificant impact on the morphology of CaCO_3 for values less than 2 L/min. It is probable that below a certain threshold flow rate, CO_2 diffusion does not control the nucleation process and the morphology of CaCO_3 crystals. In this regard, calcite and vaterite content of the precipitates was determined to be 94.52 and 5.4 wt-% respectively at a CO_2 flow rate of 0.3 L/min and 95.52 and 4.48 wt-% at a flow rate of 1.2 L/min.

ACID MINE DRAINAGE TREATMENT

We have assessed the quality and the neutralization potential of the precipitated calcium carbonate produced steelmaking slag. In the case of limestone, the AMD neutralization process can be described as the replacement of the undesirable cation components (H^+ , Fe^{2+} , Fe^{3+}) in AMD by Ca^{2+} according to the following set of reactions:



Reactions 2 and 3 take place only below a pH of about 6.4, but reaction 1 can proceed to pH 8.3, where solid CaCO_3 is in equilibrium with the normal atmosphere. The calcium carbonate used in this evaluation was prepared using the following conditions: time = 60 min,

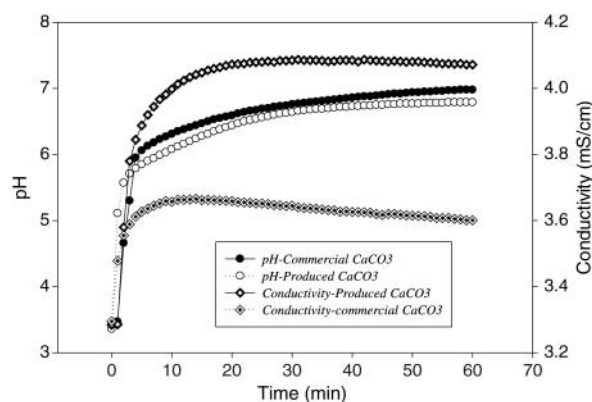


Figure 4 | pH and conductivity profiles during neutralization of AMD with produced calcium carbonate and commercial calcium carbonate (Conditions: 2 g calcium carbonate/1,000 mL AMD-315 rpm).

Temperature = 25 °C, HCl/Calcium molar ratio = 5.13, CO_2 Flow rate = 1.2 L/min and stirring rate = 180 rpm. The calcium carbonate precipitated contains 96.2%, 3.8% vaterite.

The main objective of this section was to compare the neutralizing potential of the produced calcium carbonate *vis-à-vis* the commercial calcium carbonate. The AMD treated has a pH of 3.01, an acidity of 125 mg CaCO_3 and the following chemical compositions (mg/L): 2,700 SO_4^{2-} , 468 Ca, 246 Fe, 135 Mg, 70 Mn, 82 Na, 2.6 Al, 45 Cl^- .

The main results of the batch tests performed are presented in Figure 4 where one can see a rapid increase of pH during the first 2 min from 3.2 to 5.3 for produced calcium carbonate and to 5.6 for commercial calcium carbonate. Then a slight difference in the neutralization potential between these two calcium carbonates is monitored until 60 min. These results confirm that the neutralizing potential of the produced calcium carbonate presents similar neutralization characteristics in the long run to that of commercial calcium carbonate. One also notice that the high electronic conductivity of the produced calcium carbonate compared to the commercial (laboratory grade) calcium carbonate which may be due to the presence of contaminant ionic compounds in the produced calcium carbonate. Steel slag may possess significant amount of trace elements (Mayes et al. 2011), which in theory can be transferred to the calcium carbonate precipitated and remobilized upon addition to an acid wastewater stream.

CONCLUSIONS

The conditions of calcium carbonate production from waste steelmaking slag were considered. The batch generation of

CaCO₃ from waste steelmaking slag using HCl under ambient conditions has been demonstrated to be significantly dependent on the amount of acid (HCl/Calcium molar ratio) and the CO₂ flow rate. The effect of acid concentration and CO₂ were studied in order to provide a framework for optimization of the calcium extraction and carbonation efficiencies. Because of the energy consumption and costs associated particularly with the grinding of steelmaking slag to a small particle size and HCl consumption, further research is required to help assess the energetic and economic feasibility of calcium carbonate production from steelmaking slag using the approach developed in this work. This study further demonstrated that the produced CaCO₃ exhibits effective neutralization ability during AMD pre-treatment compared to commercial laboratory grade CaCO₃. However the fate of toxic trace elements in the steel slag leached during extraction with HCl will require further experimentation.

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