

Thermochemical reduction of pelletized gypsum mixed with carbonaceous reductants

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ABSTRACT

The recovery of better quality waste gypsum during acid mine drainage (AMD) neutralization is one step closer to achieving downstream waste gypsum beneficiation for recovery of valuable materials. This can facilitate recovery of treatment costs and prevention of environmental pollution from gypsum waste-dumps. Thermal reduction using rotary kilns to recover valuable materials from waste gypsum remains a critical and controversial process because of waste gypsum handling problems, environmental pollution due to dust and gaseous emissions and poor conversion yields. In order to mitigate these problems and improve waste gypsum conversion yields, pelletization of waste gypsum in the presence of binders (starch and cellulose) was investigated. A laboratory-scale disc pelletizer was used to produce pellets from a mixture of coal and commercial gypsum or waste gypsum, generated during AMD neutralization, with starch and micro-crystalline cellulose used as binders. The pellets were subjected to high-temperature thermal treatment in a tube furnace to generate calcium sulphide (CaS), an important intermediate for waste gypsum beneficiation. The kinetics of thermal conversion of pelletized waste gypsum to CaS were found to be highly dependent on furnace temperature. Results also showed that pelletization affords improved handling of waste gypsum while use of binders as additives significantly improved the CaS yield, with starch giving the better yield compared to cellulose.

Keywords: waste gypsum, binders, pelletization, tube furnace

INTRODUCTION

CaSO₄ formed during pre-treatment of acid mine drainage (AMD) with hydrated lime is a resource that can be converted to CaS, an important intermediate for synthesis of a number of calcium compounds including CaCO₃, which is a feed stock for AMD neutralization. Other saleable products such as sulphur may also be produced downstream and the recovery of these feed materials promotes the cost effectiveness of AMD treatment. The recovery of sulphur from waste gypsum in particular is very critical from a South African context for two reasons. Firstly, South Africa imports more than R1 billion worth of sulphur from Canada and other oil-producing countries (Maree, 2013) and, secondly, AMD remediation is currently under the spotlight as various stakeholders come together to find a lasting solution. A report prepared by a team of experts (Coetzee et al., 2012) appointed by the South African Government-appointed Inter-Ministerial Committee on AMD has 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 decanting from the Witwatersrand's Western Basin. This short-term intervention plan provides an opportunity for recovery of saleable materials from waste gypsum generated during AMD neutralization, thereby contributing towards providing economically sustainable AMD remediation. Therefore the treatment and recycling of this material is beneficial. Zvimba et al. (2011, 2012) reported some opportunities for the treatment and recycling of gypsum whereby CaCO₃ is recovered.

Thermal decomposition is the process used for the conversion of waste gypsum (hydrated CaSO₄) to CaS, from which saleable products such as CaCO₃, MgCO₃ and S can be recovered. Several authors have studied the conversion of CaSO₄ into CaS through the carbothermal reaction (Zheng et al., 2013, Zheng et al., 2011, Nengovhela et al., 2007, Van der Merwe et al., 1999). Strydom et al. (1997) confirmed the need to perform thermal reduction of CaSO₄ using carbon as a reducing agent in the absence of air, as air was observed to impact negatively on the conversion of CaSO₄ to CaS. While challenges to CaSO₄ thermal reduction such as those reported by Strydom et al. (1997) are well known, further challenges generally not encountered at laboratory scale are likely upon scaling up of the process to full-scale application. One of these challenges to be overcome is the form in which the feed-stocks are introduced into the rotary kiln. In this regard, it may be necessary to introduce the feed-stocks in a compacted form to facilitate handling of waste gypsum and also to avoid the formation of dust in the kiln.

Pelletization is one of the techniques used to compact powdered material to make it handleable. Nengovhela et al. (2007) investigated and concluded that pelletization of gypsum-coal mixtures resulted in a higher CaS yield as compared to non-pelletized mixtures. However, the pellets need to be of acceptable mechanical strength to minimize disintegration during handling, transportation, storage and, eventually, thermal reduction. Binders such as starch and cellulose are known to improve the mechanical properties of agglomerates such as pellets. Moreover, starch and cellulose also act as reducing agents because of their carbon content, further increasing the reducing components in the pellets. Avicel PH 101, a brand of microcrystalline cellulose, though expensive, was used in this study, since Azubuike and Okhamafe (2012) reported that the physico-chemical and thermal properties of low-cost microcrystalline

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powders derived from agricultural residues such as maize cobs are comparable to those of the commercial products such as Avicel PH 101. Starch is composed of carbon, hydrogen and oxygen in the ratio 6:10:5, respectively. Alex et al. (1997) pelletized gypsum, coal and laterite mixtures and compared the effects of starch, bentonite and sodium silicate as binders. The authors found that starch and bentonite improved the strength of the pellets. The current study investigated waste gypsum pelletization and the effects of using binders as well as binder content during thermal reduction in a tube furnace. The kinetic data were measured and a macrokinetic model of the CaSO_4 thermal reduction by a mixture of carbon-containing components, formed as pellets, was proposed. The model allowed for the prediction of conversion rates for various process temperatures and could provide insight into the process when used together with a heat transfer model.

MATERIALS AND METHODS

Feedstock

Waste gypsum (95.54 %) precipitated during AMD neutralization and commercial CaSO_4 (Merck; 98.5%) were used as feed-stocks in this study. Bituminous coal (60% carbon content) of particle size $<750 \mu\text{m}$ from Mpumalanga Province (South Africa) was used as reducing agent by preparing a sample mixture of 2.5:1 C: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ molar ratio in the case of commercial CaSO_4 and 1.9:1 C: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the case of the precipitated gypsum. Food-grade starch (Protea Chemicals) and commercial microcrystalline cellulose (Fluka) were used as binders.

Equipment

A disc pelletizer (Fig. 1) operated at 20 r/min was used to prepare the pellets. An Elite tube furnace with a quartz protective

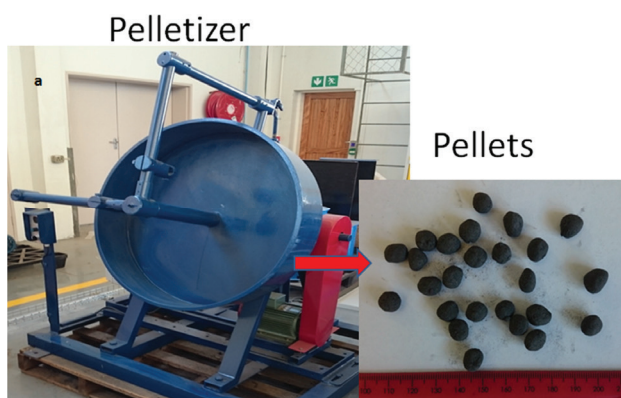


Figure 1

Pelletization of waste gypsum in a disc pelletizer

Table 1 Proximate analysis of coal sample	
Parameter	Coal
Inherent moisture (%)	2.9
Ash (%)	12.3
Volatile matter (%)	23.7
Fixed carbon (%)	61.1

tube was used for the thermal reduction tests. Reagents were introduced in quartz boats into the tube furnace.

Experimental procedure

A sample made up of coal and commercial CaSO_4 in the molar ratio 2.5:1 was divided into 6 portions. The 6 portions were mixed with 0%, 1%, 2%, 4%, and 8%, by mass, corn starch or microcrystalline cellulose (MCC), respectively. These mixtures were pelletized using a disk pelletizer with tap water simultaneously sprayed onto the sample to aid pellet formation. The average moisture content of the pellets was 25%. The moisture content was determined by drying the pellets to a constant mass in an oven with a temperature pre-set at 105°C in an oven. The pellets were weighed into quartz boats before subjecting them to high-temperature thermal reduction in the tube furnace. Samples were heated for 5, 10, 15, and 20 min. All of the samples were tested at 900°C , 1000°C , 1050°C and 1100°C . Waste gypsum, precipitated during AMD neutralization, was also mixed with coal and 2.9% (by mass; based on the results in Fig. 2) starch and heated in the tube furnace at 900°C , 1000°C , 1050°C and 1100°C . The time intervals were 5, 10, 15, and 20 min for each temperature range.

Analytical procedure

Coal proximate analyses was performed by the South African Bureau of Standards using the SANS 5925:2007, ISO 11712010, ISO 5622010 for the inherent moisture, ash and volatile matter, respectively. X-ray diffraction (XRD) analysis was performed using a PANalytical x-ray diffractometer equipped with a PIXel detector and fixed slits with iron-filtered cobalt $\text{K}\alpha$ radiation. Phase identification was achieved using X'Pert Highscore Plus software. The relative phase amounts were estimated using the Rietveld method in percentage form. Sulphide was determined by standard iodometry (APHA, 1992), in which excess iodine which is mixed with the sample solution is titrated using sodium thiosulphate in the presence of starch indicator.

RESULTS AND DISCUSSION

Feedstock characterization

Waste gypsum was characterized by XRD and was found to be composed of 95.5% gypsum, 1% calcite and 3.5% hydrated MgSO_4 (Epsomite). The proximate analyses of the reducing agent used in this study are presented in Table 1. As much as the carbon content is the main driving force of the carbothermal reduction process, the volatile matter is also expected to influence this reaction since most of the volatiles are composed of hydrocarbons and some sulphur. Solid-solid reactions are known to be slower; as a result the contribution by gaseous reactions from the constituents of the volatile matter will improve the rate of the reaction. Several authors have reported the main reducing agent during the thermal reduction process to be the gaseous intermediate (Gorkan et al., 2000; Oh and Whelock, 1990).

Starch and cellulose as thermal reduction additives

Figure 2 shows the effects of starch and cellulose (MCC) as thermal reduction additives while Fig. 3 shows the waste gypsum sludge thermo-reduction conversion curves. The CaS percentage yield in Fig. 2 was calculated using the Rietveld software. Corn starch is seen in Fig. 2 to be more effective in comparison to

MCC in promoting thermal reduction when used as an additive during pelletization of waste gypsum. The carbon content of both starch and MCC appear to be beneficial in terms of increasing the conversion of waste gypsum to CaS during thermal decomposition. Therefore one can conclude that, in addition to improving the pellet's compactness, the two binders, starch and MCC, may also have catalytic effects on the decomposition reaction. In this regard, the addition of starch and MCC as binders is observed to have a positive effect on the conversion of waste gypsum to CaS, as given in Fig. 2. Several factors are known to have either a positive or negative effect on the conversion of gypsum to CaS. The presence of O₂ and CO₂ are undesirable since both favour the formation of CaO and CaSO₄. Oh and Wheelock (1990) have reported that the presence of SO₂ and CO₂ at higher levels relative to CO favoured the formation of CaO. Therefore, the desirable reaction condition for the effective thermal reduction of CaSO₄ to CaS is excess amounts of CO in the kiln (Jagtap et al., 1990). Finney et al. (2009) have also reported that the addition of starch as a binder increased the percentage of CO in a reactor by more than 50% and decreased the oxygen content by up to 44% during the combustion of fuel pellets. This finding partly explains the improved yield of CaS during the thermal reduction of waste gypsum pellets using starch as an additive instead of MCC. Alternatively, the poor conversion of waste gypsum to CaS during thermal reduction using MCC as an additive relative to starch may also be attributed to the aromatic structure of MCC (Adel et al., 2011) that may not easily break to release carbon, hydrogen or oxygen during the thermal reaction.

The data given in Fig. 3 were generated from thermal reduction of pelletized waste gypsum precipitated during AMD neutralization with gypsum and starch in the ratio 1:2.9. The percentage yield of CaS during thermal reduction of waste gypsum from AMD neutralization, as given in Fig. 3, showed improved conversion as the reduction temperature was increased. Lower conversion of gypsum to CaS was observed at a temperature of 900°C, even at the maximum reaction time (20 min). In contrast, a higher yield of >80% CaS was obtained at temperatures of 1 000°C, 1 050°C and 1 100°C using thermal reduction times of 20 min, 15 min and 10 min, respectively. Temperature plays an important role in the thermal decomposition studies of gypsum (Yan et al., 2014).

The XRD peaks presented in Fig. 4 showed that CaS was the predominant product under the experimental conditions used.

Macrokinetic model of gypsum reduction by coal in the presence of starch and cellulose

It was assumed that reduction of CaSO₄ to CaS in the pellets, where the mixture of coal starch and cellulose serves as carbon source, takes place in the matrix of carbon-containing materials during gasification of these materials:



In this set of reactions the initial reduction of CaSO₄ with carbon takes place according to Reaction 1. The generated CO diffuses and reacts with CaSO₄, which is not in contact with carbon, according to Reaction 2. Further, the CO₂ evolved

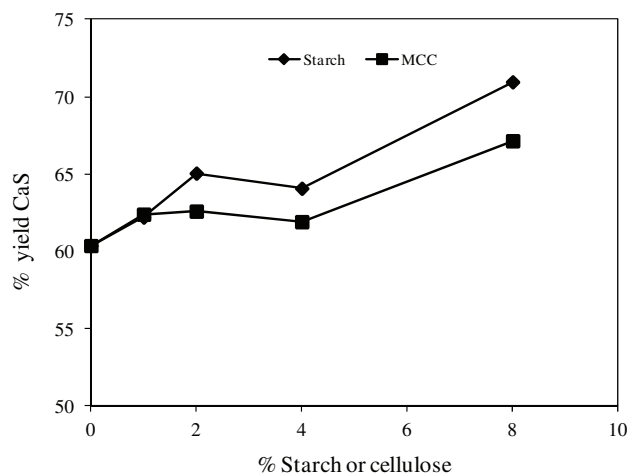


Figure 2
Effects of starch and cellulose (MCC) as thermal reduction additives

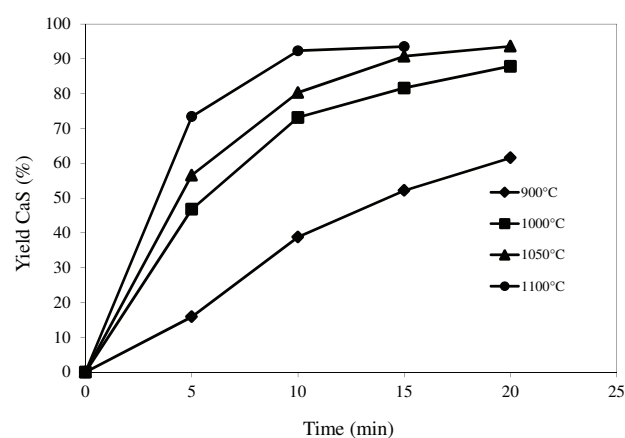


Figure 3
Conversion curves of thermo-reduction studies of waste gypsum sludge from AMD neutralization

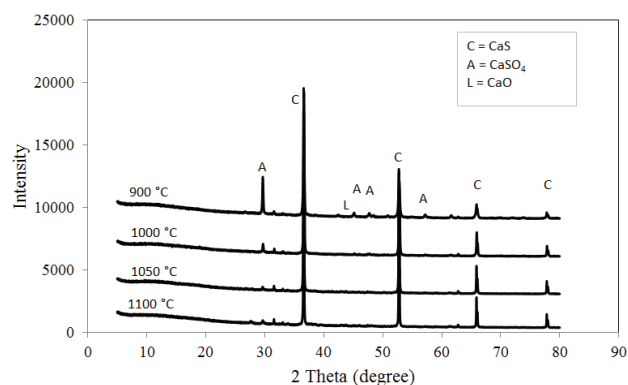


Figure 4
XRD characterization of the products of the thermal decomposition experiments

diffuses back into carbonaceous materials to generate more CO according to the Boudouard reaction (Reaction 3). The proposed mechanism is similar to the mechanism of barite reduction by coal, discussed by Jagtap et al. (1990). Ma et al. (2011) reported that increasing the concentration of CO in the reactor favours the formation of CaS relative to CaO.

Kinetic parameters were obtained from the conversion curve presented in Fig. 3. The kinetic model equation proposed by Kasaoka and Sakata (1984) was used:

$$x = 1 - \exp(-a \cdot \theta^b) \quad (4)$$

where: x is the fractional conversion, θ is the time in seconds, and a and b are constant parameters.

This type of model is based on the shrinking core model and is capable of capturing the kinetic-controlled region, where reduction is controlled by gas phase reactions, which is the formation of gaseous intermediates such as CO. Parameter a is related to the kinetic rate constant of the reaction and parameter b to the physical changes occurring in the carbon matrix. The linearization of Eq. 4 gives:

$$\ln(-\ln(1-x)) = \ln(a) + b \cdot \ln(\theta) \quad (5)$$

The linearized equation is plotted in Fig. 5. The slope of the graph is equal to b and intercept is equal to a .

The conversion data given in Fig. 5 by Eqs 4 and 5 allow solving for a and b for each temperature, T (see Table 2).

The rate of gasification of carbonaceous materials varies continuously with time due to continuous structural changes in the pellet. In such situations the reaction rate $k(x)$ will vary with time, and some average value should be used.

According to Kasaoka et al. (1983) the expression for the average rate constant, $k(x)$, s^{-1} is given by:

$$k(x) = a^{(1/b)} b [-\ln(1-x)]^{(b-1)/b} \quad (6)$$

As an indicator of the process rate, the typical conversion of 50% can be used to estimate the average reaction rate $k(x=0.5)$. The variation of the average reaction rate with temperature is given in Table 2.

Activation energy of the CaSO_4 conversion, E , and pre-exponential factor, A , can be determined from the Arrhenius plot (Fig. 6).

The 'averaged' activation energy of CaSO_4 reduction is equal to 90.0 kJ/mol, and pre-exponent A is equal to 7.39. This lower activation energy may be attributed to the presence of starch, which was shown in Fig. 2 to be increasing the rate of the reaction. These values are different to the data reported by Kato et al. (2012) where another reaction mechanism (excluding gas phase reduction) was postulated and the activation energies of 370–400 kJ/mol were reported for CaSO_4 powder (sieve, 61 μm) reduction by solid coal particles (31 μm) in a nitrogen atmosphere. As shown in Fig. 7, the macrokinetic model developed predicted conversion trends similar to the experimental kinetic data curves.

The model coefficients a and b vary with temperature. These highly nonlinear dependences can be represented by a neural network, similar to the case of Fe_2O_3 to FeO reduction process kinetics, reported by Piotrowski et al. (2005). Together with the energy balance model, the kinetic model can serve as a tool to investigate process trends and improve operation and design of furnaces and eventually pilot- and full-scale rotary kilns for CaSO_4 reduction by carbon-containing materials.

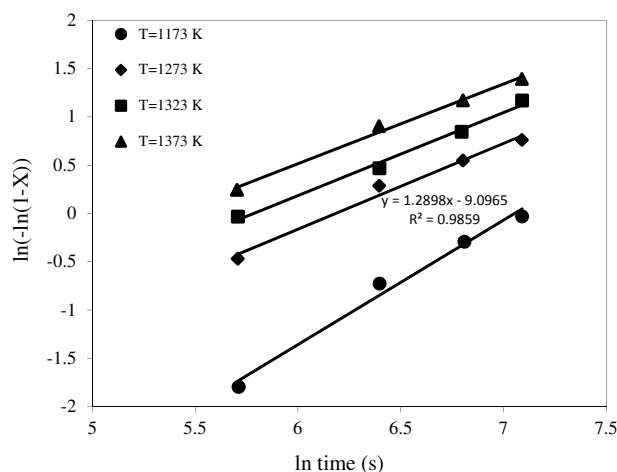


Figure 5

Conversion of CaSO_4 represented by the linearized kinetic equation (Eq. 5)

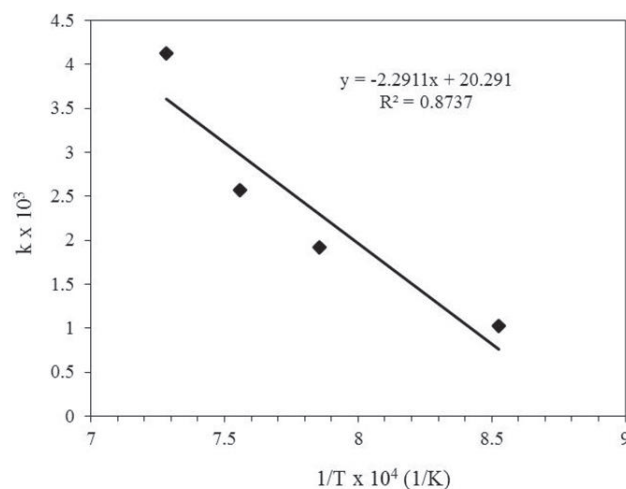


Figure 6

Arrhenius plot for the reduction of CaSO_4 by carbonaceous materials

Temperature, K	a	b	k, s^{-1}
1 173	1.12×10^{-4}	1.29	1.02×10^{-3}
1 273	4.15×10^{-3}	0.89	1.92×10^{-3}
1 350	4.59×10^{-3}	0.91	2.57×10^{-3}
1 373	1.18×10^{-2}	0.83	4.13×10^{-3}

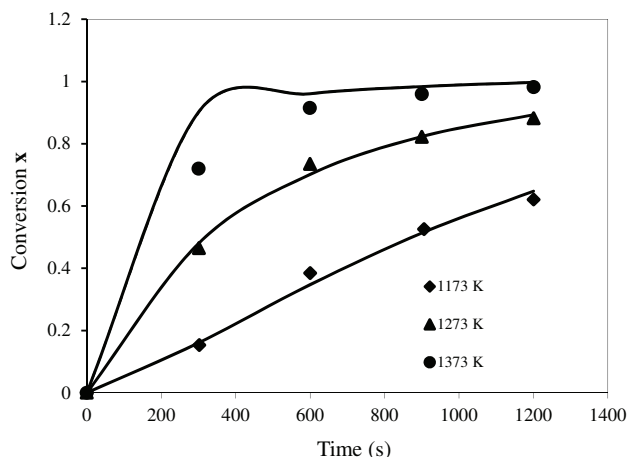


Figure 7

Conversion of CaSO_4 at various temperatures.

Dots = experimental data (Fig. 3); solid lines = prediction by Eq. 5

CONCLUSIONS

This study has investigated pelletization of waste gypsum mixed with carbonaceous reductants as a means of improving handling of gypsum during thermal reduction to recover CaS, as well as promoting better conversion of the feed material. The effects of using binders, starch and microcrystalline cellulose were also investigated. In this regard, starch and MCC were observed to exhibit synergistic effects on the thermal reduction of the gypsum-coal pellets. The hetero-hydrocarbon structure of both starch and MCC appeared to be responsible for the promotion of the desired environment during the thermal reduction, as their decomposition results in the presence of extra C, resulting in increased amounts of CO and decreased O_2 levels. Starch was more effective compared to MCC in terms of improving the conversion rate of waste gypsum to CaS. The study also confirmed that pelletization of waste gypsum is possible and therefore facilitates waste gypsum handling. A maximum of 2.9% starch, by mass, was identified as suitable for waste gypsum pelletization.

As expected, temperature was confirmed to be the driving force for the thermal reduction. In this regard, low conversions were observed at 900°C , with acceptable conversions realised when the temperature was increased to between $1\,000^\circ\text{C}$ and $1\,100^\circ\text{C}$.

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