

Chapter 6. Conclusions and recommendations for further work

6.1 Consolidation of work done

CaCO₃ plays an important role in a broad range of industrial applications. The application of PCC particles is determined by a large number of strictly defined parameters and as such the purity and crystal structure of these products determine their market value.

The objective of the research was to investigate the possibility for the production of high-purity PCC by utilizing calcium sulphide (CaS), an intermediate product in the process of the recovery of elemental sulphur from waste gypsum, as raw material. The suitability of a direct aqueous CaS carbonation (one-step) process was first tested. Although only a low-grade CaCO₃ could be produced, experimental results on the characteristics of CaS in the presence of CO₂ in the CaS-H₂O-CO₂ system showed that the reaction proceeded in two distinct stages. In the first stage, CaS dissolution takes place and H₂S stripping in the second stage. Calcium carbonation and the subsequent precipitation of CaCO₃ are concurrent with the CaS dissolution and the H₂S stripping reactions.

The influence of process parameters, including an increase in stirring rate and the increase in the CO₂ flow-rate were shown to shorten the overall reaction time due to faster reaction kinetics for both the CaS dissolution stage and H₂S stripping stage. Although the CaCO₃ content of the products produced at different CO₂ flow-rates did not show major variations in their total CaCO₃ content (86~88 mass%), the distribution ratio of the CaCO₃ polymorphs (calcite to vaterite) was greatly influenced by the CO₂ flow-rate. At low CO₂ flow-rates, the CaCO₃ phase consisted mainly of calcite, the most stable polymorph of CaCO₃. At higher CO₂ flow-rates, binary mixtures of calcite and vaterite were produced. The increase in CO₂ flow-rates led to a decrease in the CaCO₃ polymorph ratio (calcite : vaterite). The direct aqueous carbonation of CaS led to a low-grade CaCO₃ product (< 90 mass% as CaCO₃) with very limited opportunities for useful applications.

Since the production of high-purity CaCO₃ could not be obtained via the direct aqueous CaS carbonation process, a two-step or indirect carbonation process route was also developed. Acid gases, either CO₂ or H₂S were used to induce CaS dissolution in the first step of the treatment process. This was followed by the carbonation of the solubilized calcium (Ca(HS)₂ solution) in the second step.

When CO_2 gas was used for CaS dissolution, a low-grade CaCO_3 (< 90 mass% as CaCO_3) was generated in the first step and a high-purity CaCO_3 product (> 99 mass% as CaCO_3) was formed in the second step. However, the yield of the high-purity product was very low, varying between 12-23 %. The products, consisting of only the calcite polymorph, were micron-sized, spherical interpenetrated, rhombohedral cubes of calcite with smooth surfaces. Figure 6.1 shows the simplified process diagram and mass balance of the indirect CaS process using CO_2 gas for CaS dissolution.

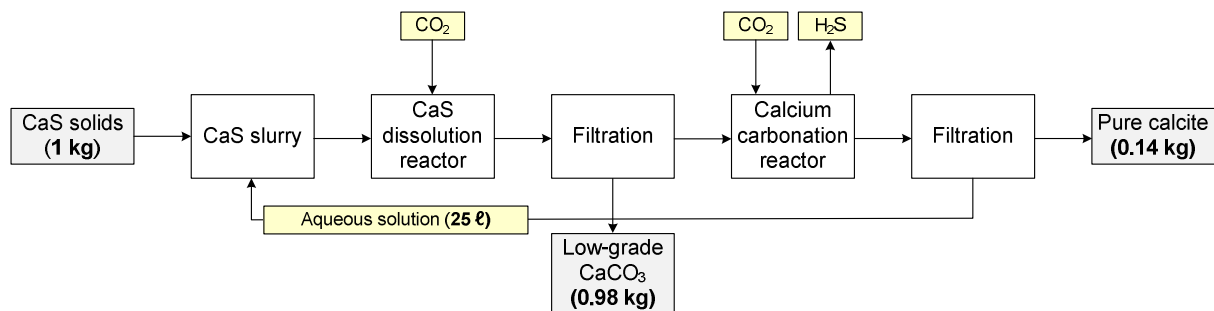


Figure 6.1 Simplified schematic process diagram and mass balance of the indirect CaS process using CO_2 gas for CaS dissolution

The indirect carbonation process, when H_2S gas was used for CaS dissolution, yielded only one carbonate product in the form of a high-purity CaCO_3 (> 99 mass% as CaCO_3) and no low-grade CaCO_3 was formed, although the high-purity CaCO_3 was often made up of two polymorphs, calcite and vaterite, in varying proportions. Approximately, 0.62 kg high-grade CaCO_3 and 0.43 kg residue were produced for every 1 kg CaS processed. Figure 6.2 shows the simplified process diagram and mass balance of the indirect CaS process using H_2S gas for CaS dissolution.

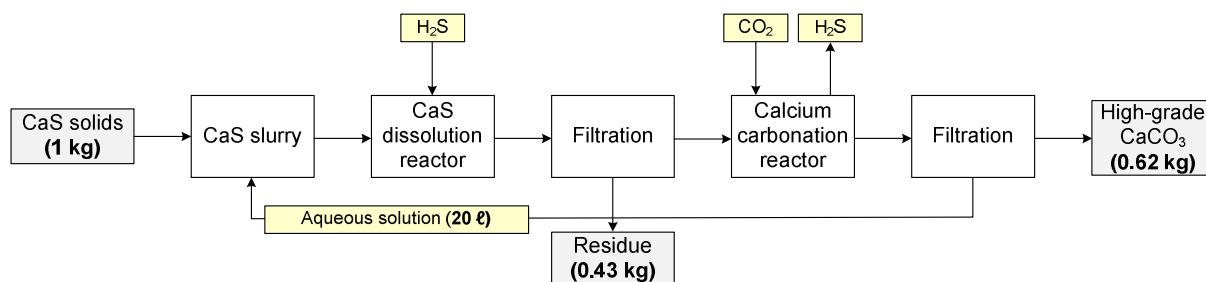


Figure 6.2 Simplified schematic process diagram and mass balance of the indirect CaS process using H_2S gas for CaS dissolution

The effect of various process parameters including gas flow-rate, mixing rate and mixing mode (mechanical agitation or ultrasound irradiation) were evaluated in order to control the reaction kinetics, the morphology, structure and characteristics of the PCC end products. Increasing the gas flow-rate or the mixing rate was successful in increasing the kinetics of the CaS dissolution, CaCO_3 precipitation and H_2S stripping reactions. However, the nature of the CaCO_3 products in terms of the CaCO_3 polymorph ratios (vaterite to calcite) was affected by the CO_2 flow-rate as well as the mode of mixing. The ratio of vaterite to calcite increased with increased flow-rates and the amount of vaterite formed under ultrasound irradiation was generally higher and consequently the polymorph ratios of CaCO_3 compared to mechanical agitation. Higher ratios of vaterite to calcite produced products of higher specific surface area and lower densities.

Table 6.1 gives a summary of the different grades of CaCO_3 produced via direct versus indirect CaS carbonation processes.

Table 6.1 Characteristics of the CaCO₃ products produced via the direct and indirect mineral carbonation processes

Product characteristics	Direct carbonation	Indirect carbonation					
	CO ₂ -gas route	CO ₂ -gas route		H ₂ S-gas route			
Solid material	Low-grade CaCO ₃	Low-grade CaCO ₃	High-grade CaCO ₃	Residue	High-grade CaCO ₃		
Reaction	CaS dissolution and carbonation	CaS dissolution	Ca(HS) ₂ carbonation	CaS dissolution	Ca(HS) ₂ carbonation		
Reactor configuration	CSTR	CSTR	CSTR	CSTR	CSTR	Glass beaker	Glass beaker
Mode of mixing	Overhead stirrer	Overhead stirrer	Overhead stirrer	Overhead stirrer	Overhead stirrer	Magnetic stirrer	Ultrasonic irradiation
Actual mass (g/100g calcine)	95.0 ± 1.2	90.6 ± 7.6	18.3 ± 5.3	43.1 ± 1.6	46.1 ± 1.6	45.8 ± 0.9	45.9 ± 1.3
CaCO ₃ (mass%)	86.9 ± 0.6	86.3 ± 4.8	99.4 ± 0.5	-	99.5 ± 0.03	99.4 ± 0.20	99.5 ± 0.04
Colour	Greyish-white	Greyish-white	Pure white	Dark grey	Pure white	Pure white	Pure white
Mineral phase (Polymorph)	Rhombohedral calcite and lens-shaped vaterite	-	Calcite	Various structures	Calcite	Mixture of calcite rhombs and spherical vaterite	Mixture of calcite rhombs and spherical vaterite
Geo. Mean size (µm)	¹ 14.4 to 22.2	-	31.85 ± 1.6	15.3 ± 3.0	22.5 ± 2.0	25.4 ± 1.7	22.5 ± 2.0
BET surface area (m ² /g)	-	-	¹ 1.19 to 1.95	-	-	¹ 0.26 to 0.22	¹ 2.01 to 4.33
Density (g/m ³)	-	-	2.72 ± 0.004	-	-	2.71 ± 0.040	2.62 ± 0.003

¹ Depends on the CO₂ flow rate during the carbonation reaction

6.2 Validation in terms of objectives

An important aspect for the economics of mineral carbonation is the end-use of the carbonate product and the purity and crystal structure which determines its market value. The objective of the research was to study a mineral carbonation process that could be used for the production of high-quality PCC from CaS, the intermediate product of a waste gypsum treatment process, as the starting material. The research focus was on the assessment of process conditions (direct *versus* indirect mineral carbonation reactions) and the control of the end-product quality including chemical purity and the physical qualities (structure and shape) of the carbonate products.

The research hypothesis of this study was validated by showing that **high-grade PCC** with a CaCO₃ content of greater than 99 mass% with **variable physical properties** i.e. comprised of calcite and vaterite polymorphs, can be produced from waste gypsum *via* the **intermediate CaS** product in an **indirect mineral carbonation process**.

6.3 Significance of work / contributions to the field

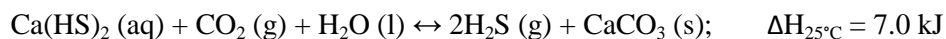
PCC is widely used in industrial processes and consequently its existing production routes on large scale are well known. Currently, PCC is produced by three different processes: a caustic soda process, a calcium chloride process, and the conventional carbonation process. In the caustic soda and calcium chloride processes, both the calcium and carbonate ions are supplied in the form of soluble reagents (liquid-liquid reaction) in the Ca²⁺-H₂O-CO₃²⁻ reaction system. However, the most prevalent route followed for industrial-scale PCC production is through the carbonation process in the Ca(OH)₂-H₂O-CO₂ reaction system. This conventional carbonation process uses mined, crushed limestone as raw material and CaCO₃ is precipitated through a gas-solid reaction in an aqueous medium.

This work showed that high-grade PCC, with variable crystal structures and morphologies, in the form of rhombohedral calcite and spherical vaterite, can be produced through a liquid-gas reaction in a sulphide medium, using calcium sulphide (CaS) as the calcium source in the Ca(HS)₂-H₂O-CO₂ reaction system and with minimum energy requirements at ambient temperature and atmospheric pressure.

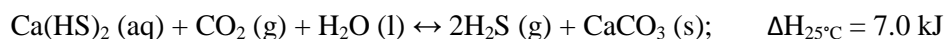
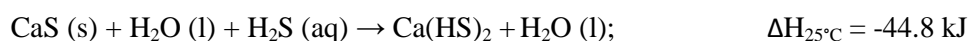
Direct aqueous CaS carbonation process:



Indirect CaS carbonation process, CO₂-gas route:



Indirect CaS carbonation process, H₂S-gas route:



The use of a calcium-rich solid waste i.e. gypsum *via* the CaS intermediate product as primary material in place of mined limestone for the production of PCC, may not only alleviate waste disposal problems but could also convert significant tonnages of waste material into marketable commodities (From 2.6kg of gypsum waste, 0.43kg of residue is generated, a six fold reduction in the volume of waste and 0.46kg of high-grade CaCO₃ is produced). Large amounts of waste gypsum are generated in South Africa and indications are that the amounts are going to increase substantially in the future as a result of the treatment of acid mine water and of flue gases in coal burning operations. Disposal of waste gypsum to landfill is not a viable option due to the shortage of landfill space and the formation of hazardous and toxic, gaseous emissions in the form of H₂S, when gypsum is landfilled with biodegradable wastes. Moreover, legislative requirements for landfill disposal methods such as the National Environmental Management Waste Act (NEMWA) 59 of 2008 are projected to be more stringent in future, resulting in the need to develop alternative waste management approaches. In this regard, the gypsum waste generating industry provides a cheap source of raw material for the indirect CaS carbonation process for the production of valuable pure CaCO₃ (PCC).

While only one source of waste gypsum produced at a specific acid mine water neutralisation facility was used during this study, the indirect processes developed and tested, as described in this thesis, are expected to be applicable to other sources of waste gypsum and calcium sulphide waste products. Typical examples of industries that generate large amounts of potentially, suitable waste gypsum include the fertiliser industry (phosphogypsum) and coal-fired power stations (FGD gypsum).

Therefore, this work may also contribute to the environmentally sound management of solid gypsum wastes and form part of the development of sustainable solid waste management practices.

6.4 Aspects meriting further investigation

The production of high-grade CaCO_3 from waste gypsum, *via* the intermediate CaS product in an indirect mineral carbonation process, is possible. However, the suitability of the CaCO_3 produced for use as a commercial product or liming agent has to be explored further. PCC formed with the required properties e.g. small particle size, larger specific surface area, controlled morphology, would need to be tested in the chosen application and compared with currently used commercial PCC.

The full characterization of the residue in terms of the mineral and elemental composition is needed to determine the quality of the waste material generated in the process. From 2.6kg of gypsum waste, 0.43kg of residue is generated, a six fold reduction in the volume of waste. The necessary following steps in investigating the process are to calculate the commercial feasibility and viability of the technology, followed by a full techno-economic feasibility analysis including operational, environmental and cost performances as well as a detailed market study. Depending on the commercial potential, the design and construction of a scaled-up process, combined with a detailed analysis of chemical kinetics and reaction mechanisms should follow.

6.5 Conclusion

The potential for the product of high-purity CaCO_3 from industrial waste gypsum was demonstrated in this study. At first, a direct aqueous CaS carbonation (one-step) process was tested but only a low-grade CaCO_3 product could be produced. An indirect CaS carbonation (two-step) process was then developed and tested. The indirect process using CO_2 as ‘ CaS dissolution catalyst’ produced two separate CaCO_3 products of different grades, *i.e.* a low-purity CaCO_3 product (< 90 mass% as CaCO_3) in the first step and a high-purity CaCO_3 product (> 99 mass% as CaCO_3) in the second step. Since only low yields of the high-grade CaCO_3 product were obtained, the study was expanded to an H_2S -based process for the CaS dissolution. This process was successful in producing a single CaCO_3 product, which formed in the second step and was of high purity (> 99 mass% as CaCO_3). The effect of various process conditions and experimental techniques were applied in order to control the morphology, structure and characteristics of the PCC. This study was the first to demonstrate the

feasibility of the production of high-purity CaCO_3 from industrial gypsum wastes *via* the intermediate CaS calcination product.

Reference

National Environmental Management Waste Act (NEMWA) 59 of 2008. Available from: https://www.environment.gov.za/sites/default/files/legislations/nema_amendment_act59 [accessed 8/21/2013].