

Chapter 1. Introduction and outline of thesis

1.1 Background

Limestone is a natural resource defined as a calcareous material or rock with a calcium carbonate content of at least 70% (Oates 1998). Although there are extensive reserves of limestone worldwide, very few deposits are of sufficient quality to provide raw materials for specialised industrial applications and uses. Their commercial exploitation is dependent on the purity, homogeneity, colour and thickness of the deposit (Oates 1998).

From an industrial perspective, the term CaCO_3 of “high quality” includes two groups of substances, namely ground calcium carbonate (GCC) and synthetic or precipitated calcium carbonate (PCC). Ground calcium carbonate results directly from the exploitation of pure carbonate ore bodies and is a mechanically crushed, finely ground pure calcium carbonate product. PCC is synthesised via a chemical precipitation process (Mark et al. 1978). The advantage of PCC over GCC is that impurities from the limestone rock can be removed in the production process and the properties of the precipitated products can be controlled (Renaudin et al. 2008). The PCC products are therefore characterised by a higher degree of chemical purity, and by finer and more uniform particle sizes with narrower particle size distributions than GCC.

CaCO_3 has many uses in a wide variety of industrial and commercial applications. GCC is used for purposes such as manufacturing concrete or Portland cement, for producing lime to be used in, for example, soil stabilization and acid neutralization, for water treatment, and flue gas desulphurization (Oates 1998). Worldwide, PCC is mainly used as a filler and coating pigment in paper, plastics, paints, rubbers and adhesives. Other uses include manufacturing of glass, textiles, putties, chalks, sealant, inks, varnishes, food, cosmetics, chemicals and pharmaceuticals (Zhang et al. 2010; Windholz 1983). The variety of industrial applications requires that PCC is supplied commercially with various physical and chemical properties, among which are: chemical purity, particle size, specific surface area, density and morphology are of critical importance (Chakraborty & Bhatia 1996; Chakraborty et al. 1994; Tai & Chen 1998).

The world consumption of filler-grade CaCO_3 was 74 mega-tonnes in 2011, comprising of 60 mega-tonnes of ground (GCC) and 14 mega-tonnes of precipitated (PCC) material (Roskill 2012). Figure 1.1 shows the combined consumption (2011) and forecast demand (2016) for GCC and PCC by end users.

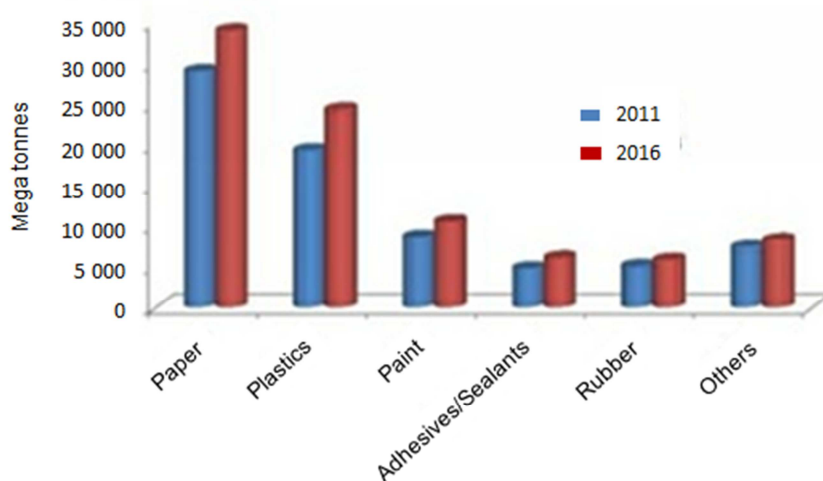


Figure 1.1 World consumption (2011) and forecast demand (2016) for the GCC and PCC by end users (Roskill 2012)

The South African lime industry differs significantly from the lime industries of the main industrialised countries where limestone deposits are widespread and of good quality. Only isolated deposits of high-grade limestone occur in South Africa (SA) (Mabuza et al. 2012). The principal use of limestone in SA is in the manufacture of cement, followed by metallurgical applications as a fluxing agent in steel making, the manufacture of lime, and agricultural uses. The use of PCC is limited to the paper industry and a fine-ground CaCO_3 (FGCC) of very high purity is used in the plastics, paint and rubber industries.

Idwala Carbonates (Idwala 2013), which is located near Port Shepstone (South Africa), produces FGCC by means of a limestone crushing and flotation process (Figure 1.2). This operation quarries a scarce, white, high purity calcitic and dolomitic limestone deposit. The production is energy-intensive, as it involves processes such as crushers, mills, and electric driers.

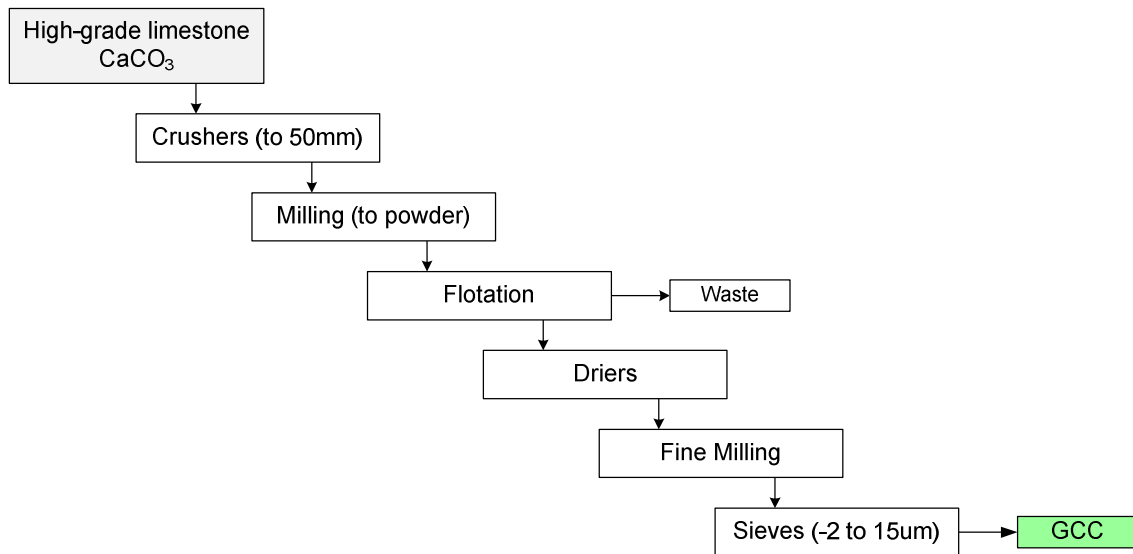


Figure 1.2 Fine-ground calcium carbonate (FGCC) production via the mechanical treatment of natural minerals used by Idwala Carbonates (Idwala 2013)

Speciality Minerals Inc. (SMI) is an international producer of high-quality minerals including PCC, GCC and lime (SMI 2013). A satellite PCC production facility (Figure 1.3), operated at Mondi Merebank by Speciality Minerals South Africa (SMSA), is the only dedicated PCC production plant in SA. The concept of satellite production facilities is used to implement research and development activities that are geared towards improving the quality of paper produced, as well as reducing cost. This is mainly achieved by improving the PCC properties, as well as increasing the percentage of PCC in the paper. This lowers the paper cost, but increases the amount of PCC used. SMI currently manufactures several customized PCC products using proprietary processes. It starts the production of lime from high-quality limestone sources. In the case of SA, Speciality Minerals imports high-quality quicklime (CaO) as feedstock for their PCC production plant (SMI 2013).

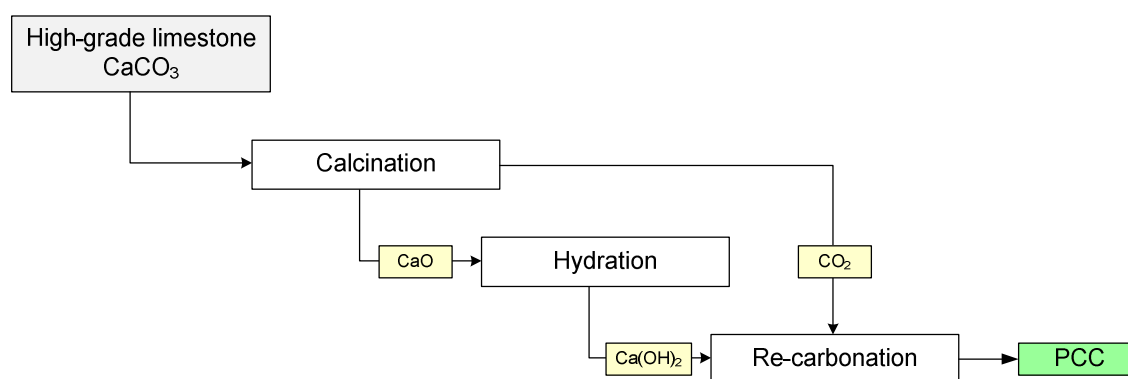
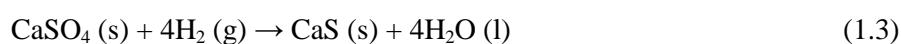
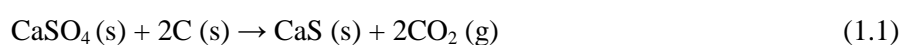


Figure 1.3 The precipitated calcium carbonate (PCC) production route via the conventional carbonation process used by Speciality Minerals South Africa (SMI 2013)

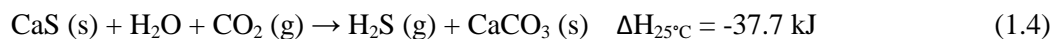
On industrial scale, high-grade limestone rock is currently the preferred raw material for the production of both PCC and GCC. However, the replacement of this natural raw mineral as feedstock by calcium-rich, waste-derived products in the manufacture of PCC may contribute towards a more sustainable use of a country's natural resources. The conversion of such solid wastes into PCC via industrial mineral carbonation can therefore represent a potentially-viable strategy for the re-exploitation of industrial wastes, but it can also contribute towards the mitigation of carbon dioxide emissions since industrial mineral carbonation could make use of industrial CO₂ streams as feedstocks.

The Council for Scientific and Industrial Research (CSIR, Pretoria, SA) has developed a novel technological process for the conversion of waste gypsum (CaSO₄·2H₂O) into high-value elemental sulphur with a low-grade CaCO₃ being generated as a by-product (Maree 2005). The technology has been patented in several countries under the following title: *Conversion of a sulphur-containing waste material into a sulphur-containing product*. The multi-step process (Figure 1.4) of sulphur recovery can be described as follows (Mbhele et al. 2009; Nengovhela et al. 2007):

- Thermal reduction (900 to 1100°C) of waste gypsum to produce calcium sulphide (CaS) using reducing agents, including solid carbon materials such as coal or activated carbon (Eq. (1.1)) (Kato et al. 2012; Ma et al. 2011; Mihara et al. 2008; Nengovhela et al. 2007), carbon monoxide gas (Eq. (1.2)) (Miao et al. 2012; Zhang et al. 2012; Tian & Guo 2009; Li & Zhuang 1999), or hydrogen gas (Eq. (1.3)) (Ning et al. 2011):



- Direct aqueous carbonation of CaS to produce hydrogen sulphide (H₂S), and low-grade CaCO₃ as a by-product. The reaction proceeds according to equation (1.4).



- Recovery of elemental sulphur from H₂S via the commercially available, chemical catalytic Claus process (Mark et al. 1978)

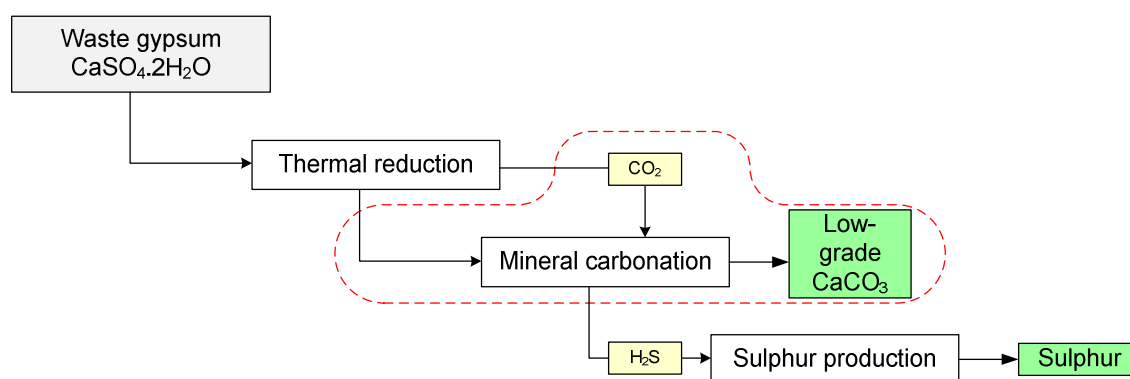
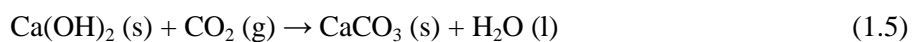


Figure 1.4 Elemental sulphur production from waste gypsum. (the area highlighted in red delineates the part of the process where low-grade CaCO₃ is produced, and represents the focus of this study)

CaS is an intermediate product generated in the first step of the process. Although the conversion of CaS into H₂S has been studied (Brooks & Lynn 1997; Nishev & Pelovski 1993; Biswas et al. 1976), little, if any, effort has been given to the controlled production of commercial-grade CaCO₃ during the second step of the process.

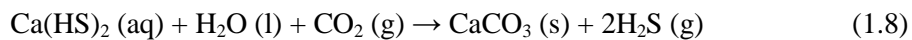
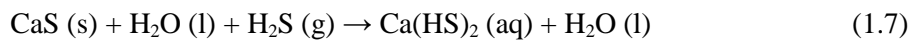
1.2 Hypothesis and statement of originality

The commercial technology for producing PCC in an aqueous medium using Ca(OH)₂ as the calcium source (Eq. (1.5)) (the Ca(OH)₂-H₂O-CO₂ reaction system) is used on industrial scale (Souto et al. 2008), but the carbonation of alkaline waste materials requires processes other than those used for the carbonation of a Ca(OH)₂ slurry.



The research hypothesis is that **high-grade PCC** (product containing greater than 99 mass% as CaCO_3) with **variable physicochemical properties** (morphology and particle characteristics, including particle size, surface area and density) can be produced from waste gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) via the intermediate **CaS product** (Eq. (1.4)) in a **mineral carbonation process** by controlling operating parameters and conditions during the calcium carbonation step (Figure 1.4, highlighted area).

This study, therefore, focused on the production of high-grade PCC in a sulphide medium, using calcium sulphide (CaS) as the calcium source in the CaS- H_2O - CO_2 reaction system. A one-step, direct aqueous mineral carbonation (Eq. (1.4)) and a two-step, indirect mineral carbonation process route was used. For the indirect mineral carbonation process, CaS dissolution was induced by either CO_2 (Eq. (1.6)) or H_2S (Eq. (1.7)); this step was followed by the precipitation of solubilized calcium (Eq. (1.8)) in a separate reactor.



1.3 Objectives

The objective of this project was to study a 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 (area highlighted in Figure 1.4). The experimental focus was on the control of the crystallization process during the carbonation stage to produce high quality CaCO_3 particles with specific physical properties. Specific areas of interest were the:

- chemical purity of the carbonate product;
- physical properties of the products (particle size, morphology or shape, density, surface area, porosity and crystallinity);
- minimization of additional chemical requirements and overall energy input into the carbonation reaction; and
- minimum production of wastes or by-products.

The specific objectives were:

- To produce PCC, and via a Claus process, elemental sulphur from waste gypsum
- To assess process conditions controlling the end-product quality (direct vs indirect mineral carbonation reaction using CO₂).

The use of industrial gypsum wastes as primary material, replacing mined limestone for the production of PCC would not only alleviate gypsum waste disposal problems, but would also convert significant volumes of this waste material into marketable commodities. The purity and crystal structure of the carbonate products determine their market value and, therefore, the proposed mineral carbonation process of waste products will control the characteristics of the final product.

1.4 Thesis outline/overview

To contextualise the study, a general background is given in Chapter 1 regarding the industrial and commercial applications of natural and synthetic CaCO₃. An overview of the South African lime industry is given together with a brief discussion on the CSIR's waste gypsum treatment process. The hypothesis, statement of originality and objectives of the study are formulated.

A literature overview on PCC is given in Chapter 2. The existing PCC production routes as well as the use of industrial solid wastes as alternative feedstocks for PCC production are discussed. The application of PCC is determined by a number of strictly defined parameters and therefore the effect of process conditions on the physicochemical properties of PCC is also included in the literature review.

Chapter 3 contains a detailed description of all the experimental and analytical methods used during this study. This is followed by two chapters containing experimental results. Chapter 4 describes the direct aqueous CaS carbonation (one-step) process and experimental results pertaining to the characteristics of CaS in the presence of CO₂ in the CaS-H₂O-CO₂ system.

Chapter 5 describes the indirect (or two-step) process for the production of high-purity CaCO₃. The thesis is consolidated with overall conclusions, and recommendations are made for aspects meriting further investigation (Chapter 6) Appendix A contains a list of experimental equipment and range of experimental uncertainties. Appendix B lists the test matrix that was followed.

1.5 Originality of this work

The study focused on the production of precipitated calcium carbonate from industrial gypsum wastes. Precipitated calcium carbonate is normally produced by contacting CO₂ with lime (Ca(OH)₂). This study focused on the following new and innovative approaches for the formation and characterization of precipitated calcium carbonate:

- Waste gypsum is used as raw material.
- Two configurations were studied. In the first configuration, CaCO₃ contaminated with coal impurities was produced. A second configuration was proposed as an improvement to the first configuration which made the production of a chemically pure CaCO₃ possible. Another original input was to identify the conditions needed to manipulate the morphology.

References

- Biswas, S.C., Sabharwal, V.P. and Dutta, B.K., 1976. Hydrogen sulphide from reduced gypsum. *Fertilizer Technology*, 13(4), 255-258.
- Brooks, M.W. and Lynn, S., 1997. Recovery of calcium carbonate and hydrogen sulphide from waste calcium sulphide. *Industrial and Engineering Chemistry Research*, 36(10), 4236-4242.
- Chakraborty, D., Agarwal, V.K., Bhatia, S.K. and Bellare, J., 1994. Steady-state transitions and polymorph transformations in continuous precipitation of calcium carbonate. *Industrial and Engineering Chemistry Research*, 33(9), 2187-2197.
- Chakraborty, D. and Bhatia, S.K., 1996. Formation and aggregation of polymorphs in continuous precipitation. 2. Kinetics of CaCO₃ precipitation. *Industrial and Engineering Chemistry Research*, 35(6), 1995-2006.
- IDWALA, 2013. Idwala Carbonates. Port Shepstone. Available from: <http://www.idwala.co.za/our-operations-listing/idwala-carbonates/> [accessed 8/21/2013].
- Kato, T., Murakami, K. and Sugawara, K., 2012. Carbon reduction of gypsum produced from flue gas desulphurization. *Chemical Engineering Transactions*, 29(1), 805-810.
- Li, H.J. and Zhuang, Y.H., 1999. Catalytic reduction of calcium sulphate to calcium sulphide by carbon monoxide. *Industrial & Engineering Chemistry Research*, 38(1), 3333-3337.
- Ma, L., Niu, X., Hou, J., Zheng, S. and Xu, W., 2011. Reaction mechanism and influence factors analysis for calcium sulphide generation in the process of phospho-gypsum decomposition. *Thermochimica Acta*, 526(1-2), 163-168.
- Mabuza, M., Mohale, S., Mwape, P., Dlambulo, N., Malebo, L., Ikaneng, M. and Motsie, R., (eds.), 2012. *South Africa's minerals industry 2011/2012: 29th Edition*. Pretoria, South Africa: Directorate: Minerals Economics.

- Maree, J.P., 2005. *Conversion of sulphur-containing waste material into a sulphur-containing product*. Australia: AU 2005201759 patent. Available from: <http://ip.com/patfam/en/35455786>.
- Mark, H.F., Othmer, D.F., Overberger, C.G. and Seaborg, G.T., (eds.), 1978. *Kirk-Othmer: Encyclopedia of Chemical Technology* (22, 276): 3rd Edition. New York: Wiley-Interscience.
- Mark, H.F., Othmer, D.F., Overberger, C.G. and Seaborg, G.T., (eds.), 1978. *Kirk-Othmer: Encyclopedia of Chemical Technology* (4, 428): 3rd Edition. New York: Wiley-Interscience.
- Mbhele, N.R., Van der Merwe, W., Maree, J.P. and Theron, D., 2009. Recovery of sulphur from waste gypsum, *Proceedings of the International Mine Water Conference*, 19-23 October 2009, pp. 622-630.
- Miao, Z., Yang, H., Wu, Y., Zhang, H. and Zhang, X., 2012. Experimental studies on decomposing properties of desulphurization gypsum in a thermogravimetric analyzer and multiatmosphere fluidized beds. *Industrial and Engineering Chemistry Research*, 51(15), 5419-5423.
- Mihara, N., Soya, K., Kuchar, D., Fukuta, T. and Matsuda, H., 2008. Utilization of calcium sulphide derived from waste gypsum board for metal-containing wastewater treatment. *Global Nest Journal*, 10(1), 101-107.
- Nengovhela, N.R., Strydom, C.A., Maree, J.P., Oosthuizen, S. and Theron, D.J., 2007. Recovery of sulphur and calcium carbonate from waste gypsum. *Water SA*, 33(5), 741-747.
- Ning, P., Zheng, S.C., Ma, L.P., Du, Y.L., Zhang, W., Niu, X.K. and Wang, F.Y., 2011. Kinetics and thermodynamics studies on the decompositions of phospho-gypsum in different atmospheres. *Advanced Materials Research*, 160-162(1), 842-848.
- Nishev, T. and Pelovski, Y., 1993. Kinetics of carbonization of calcium sulphide in water suspension. *Journal of Chemical Technology and Biotechnology*, 56(3), 271-272.
- Oates, J.A.H., 1998. *Lime and limestone: Chemistry and technology, production and uses*: Weinheim: Wiley-VCH Verlag GmbH.
- Renaudin, G., Bertrand, A., Dubois, M., Gomes, S., Chevalier, P. and Labrosse, A., 2008. A study of water releases in ground (GCC) and precipitated (PCC) calcium carbonates. *Journal of Physics and Chemistry of Solids*, 69(7), 1603-1614.
- Roskill, 2012. *The economics of precipitated calcium carbonate*. Seventh Edition. Roskill Information Services Ltd.
- SMSA, 2013. Specialty Minerals SA (Pty) Ltd. Merebank. Available from: <http://www.specialtyminerals.com/> [accessed 8/21/2013].
- Souto, E.C.S. Damasceno, J.J.R. Hori, C.E., 2008. Study of operational conditions for the precipitated calcium carbonate production. *Materials Science Forum*, 591-593, 526-530.
- Tai, C.Y. and Chen, F.B., 1998. Polymorphism of CaCO₃ precipitated in a constant-composition environment. *AIChE Journal*, 44(8), 1790-1798.

Tian, H. and Guo, Q., 2009. Investigation into the behaviour of reductive decomposition of calcium sulphate by carbon monoxide in chemical-looping combustion. *Industrial and Engineering Chemistry Research*, 48(12), 5624-5632.

Windholz, M., (ed.), 1983. *The Merck Index*: 10th Edition. New Jersey, U.S.A.: Merck & Co., Inc.

Zhang, W., Li, X., Qu, Z., Zhao, Q. and Chen, G., 2010. Facile solution synthesis and characterization of CaCO₃ microspheres with urchin-shaped structure. *Materials Letters*, 64(1), 71-73.

Zhang, X., Song, X., Sun, Z., Li, P. and Yu, J., 2012. Density functional theory study on the mechanism of calcium sulphate reductive decomposition by carbon monoxide. *Industrial and Engineering Chemistry Research*, 51(18), 6563-6570.