

The production of precipitated calcium carbonate from industrial gypsum wastes

M. de Beer
13087398

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Promoter: Prof. L. Liebenberg
Co-Promoter: Dr F.J. Doucet

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Abstract

Precipitated calcium carbonate (PCC) is a material of great interest due to its large range of applications in polymer composites, as rubber filler, additive for plastics, paints and paper, and in pharmaceuticals. PCC is also known as purified or synthetic calcium carbonate and has the same chemical formula (CaCO_3) as other types of calcium carbonate such as limestone, marble and chalk. CaCO_3 crystallizes in several different schemes of atomic arrangements, called polymorphs. The typical morphologies of CaCO_3 polymorphs are generally classified as rhombohedral calcite, spherical vaterite and needle-like aragonite. The application of PCC is mainly determined by a number of strictly defined parameters, such as purity, particle morphology, and structure. On industrial scale, limestone rock is the preferred raw material for the production of PCC.

However, gypsum is an industrial solid waste product generated in various industrial processes such as phosphoric, hydrofluoric, citric and boric acid production, treatment of waste from desulphurisation of flue gases from coal-fired power stations, ore smelting, and acid mine water treatment. Large stockpiles of gypsum waste exist with little or no usage and commercial applications.

The objective of the research was to investigate the possibility of producing high-purity PCC from calcium sulphide (CaS), an intermediate product in the process of the recovery of elemental sulphur from waste gypsum. At first, the suitability of a direct aqueous CaS carbonation (one-step) process was tested. Although only a low-grade CaCO_3 product (86-88 mass% as CaCO_3) could be produced, experimental results on the characteristics of CaS in the presence of CO_2 in the CaS- H_2O - CO_2 system showed that the reaction proceeded in two distinct stages. In the first stage, CaS dissolution took place, with H_2S stripping occurring in the second stage. Calcium carbonation and the resulting precipitation of CaCO_3 were concurrent with the CaS dissolution and the H_2S stripping reactions.

Because the production of high-purity CaCO_3 could not be obtained via the direct aqueous CaS carbonation process, a two-step or indirect carbonation process route was also developed and tested. In the first step, either CO_2 gas or H_2S gas was used to induce CaS dissolution. This was followed by the separate carbonation of the solubilized calcium (in the form of $\text{Ca}(\text{HS})_2$ solution). 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. Importantly, the H_2S -based 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 effects of various process conditions and experimental techniques were applied in order to control the morphology, structure and characteristics of the formed PCC.

The control of the purity and the crystal structure of the carbonate products derived from waste gypsum in a mineral carbonation process were demonstrated. 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) product, which was often made up of two polymorphs, calcite and vaterite, in varying proportions. Approximately 0.62 kg of the high-grade CaCO_3 was produced from every 1 kg CaS processed, while 0.43 kg residue was generated.

The use of calcium-rich solid wastes (gypsum in this study) as primary material in replacement to mined limestone for the production of PCC could not only alleviate waste disposal problems but could also convert significant volumes of waste materials into marketable commodities.

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Publications based on work described in this thesis

M. de Beer, and S. Eggers. Production of high-grade CaCO₃ from waste gypsum. 2013. *51st annual Microscopy Society of Southern Africa Conference*, Farmhill Inn, Pretoria. 3-6 December 2013.

M. de Beer, J.P. Maree, L. Liebenberg, and F.J. Doucet. Conversion of calcium sulphide into calcium carbonate during the process of recovery of elemental sulphur from waste gypsum. *Waste Management* (final draft submitted)

M. de Beer, J.P. Maree, L. Liebenberg, and F.J. Doucet. Production of calcium carbonate of different grades from calcium sulphide. *Journal of Materials Chemistry A* (in preparation)

M. de Beer, L. Liebenberg, and F.J. Doucet. Production of high-purity CaCO₃ via the indirect calcium sulphide carbonation process. (in preparation)

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List of chemical reactions

- $\text{CaSO}_4(\text{s}) + 2\text{C}(\text{s}) \rightarrow \text{CaS}(\text{s}) + 2\text{CO}_2(\text{g})$ (1.1)
 $\text{CaSO}_4(\text{s}) + 4\text{CO}(\text{g}) \rightarrow \text{CaS}(\text{s}) + 4\text{CO}_2(\text{g})$ (1.2)
 $\text{CaSO}_4(\text{s}) + 4\text{H}_2(\text{g}) \rightarrow \text{CaS}(\text{s}) + 4\text{H}_2\text{O}(\text{l})$ (1.3)
 $\text{CaS}(\text{s}) + \text{H}_2\text{O} + \text{CO}_2(\text{g}) \rightarrow \text{H}_2\text{S}(\text{g}) + \text{CaCO}_3(\text{s})$ (1.4)
 $\text{Ca}(\text{OH})_2(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l})$ (1.5)
 $2\text{CaS}(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \rightarrow \text{Ca}(\text{HS})_2(\text{aq}) + \text{CaCO}_3(\text{s})$ (1.6)
 $\text{CaS}(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{Ca}(\text{HS})_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$ (1.7)
 $\text{Ca}(\text{HS})_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s}) + 2\text{H}_2\text{S}(\text{g})$ (1.8)
 $\text{CaCO}_3(\text{s}) + \text{heat} \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ (2.1)
 $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{aq})$ (2.2)
 $\text{Ca}(\text{OH})_2(\text{aq}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l})$ (2.3)
 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s}) + 2\text{C}(\text{s}) \rightarrow \text{CaS}(\text{s}) + 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}$ (4.1)
 $\text{CaS}(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \rightarrow \text{H}_2\text{S}(\text{g}) + \text{CaCO}_3(\text{s})$ (4.2)
 $2\text{H}_2\text{S}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{S}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$ (4.3)
 $2\text{CaS}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{Ca}(\text{HS})_2(\text{aq}) + \text{Ca}(\text{OH})_2(\text{aq})$ (4.4)
 $\text{CaS} \leftrightarrow \text{Ca}^{2+} + \text{S}^{2-}$ (4.5)
 $\text{S}^{2-} + \text{H}_2\text{O} \leftrightarrow \text{HS}^- + \text{OH}^-$ (4.6)
 $\text{HS}^- + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{S} + \text{OH}^-$ (4.7)
 $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$ (4.8)
 $\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_2\text{CO}_3(\text{aq})$ (4.9)
 $\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$ (4.10)
 $\text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ (4.11)
 $2\text{CaS}(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{aq}) \leftrightarrow \text{Ca}(\text{HS})_2(\text{aq}) + \text{CaCO}_3(\text{s})$ (4.12)
 $\text{Ca}(\text{HS})_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow 2\text{H}_2\text{S}(\text{g}) + \text{CaCO}_3(\text{s})$ (4.13)
 $\text{H}_2\text{S}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{HS}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}); \quad \text{pK}_{\text{a}1} = 7.04$ (4.14)
 $\text{HS}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{S}^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}); \quad \text{pK}_{\text{a}2} = 11.96$ (4.15)
 $\text{CaS}(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{H}_2\text{S}(\text{aq}) \rightarrow \text{Ca}(\text{HS})_2 + \text{H}_2\text{O}(\text{l})$ (5.1)

Nomenclature

Abbreviations and Acronyms

AMD	Acid mine drainage
ACC	Amorphous calcium carbonate
ATR	Attenuated total reflectance
BET	Brunauer, Emmett & Teller
CCS	Carbon capture and storage
CTAB	Cetyl trimethylammonium bromide
CSTR	Completely stirred tank reactor
CSIR	Council for Scientific and Industrial Research
EDX	Energy dispersive X-Ray analysis
EDS	Energy dispersive X-ray spectrometry
EDTA	Ethylenediamine tetraacetate
FGCC	Fine-ground calcium carbonate
FGD	Flue gas desulphurization gypsum
FTIR	Fourier transform infrared spectroscopy
GCC	Ground calcium carbonate
ICP-AES	Inductively coupled plasma-atomic emission spectrometry
LD	Laser diffraction
NCC	Natural calcium carbonate
PSA	Particle size analyser
PSD	Particle size distribution
PCC	Precipitated calcium carbonate
SEM	Scanning electron microscope
SA	South Africa
SMI	Speciality Minerals Inc.
SMSA	Speciality Minerals South Africa
SS	Supersaturation
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy

Chemical compounds and minerals

Ca(HS)_2	Calcium bisulphide; calcium hydrosulphide
Ca(OH)_2	Calcium hydroxide; milk of lime
CaCO_3	Calcium carbonate; limestone
$\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$	Ikaite
$\text{CaCO}_3 \cdot \text{H}_2\text{O}$	Monohydrocalcite
CaO	Calcium oxide; lime
CaS	Calcium sulphide
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Calcium sulphate dihydrate; gypsum
CO	Carbon monoxide
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
H_2	Hydrogen
H_2CO_3	Carbonic acid
H_2O	Water
H_2S	Hydrogen sulphide
HCO_3^-	Bicarbonate ion
N_2	Nitrogen
S	Elemental sulphur