

Production of calcium carbonate from phosphogypsum wastes

By

Lilian Urlain Ondo Ndjimbi

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Supervisor: Dr E.M van der Merwe

Co-supervisor: Dr Frédéric Doucet

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I Lilian Urlain Ondo Ndjimbi declare that the dissertation, which I hereby submit for the degree of Magister Scientiae at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at another university.

.....

Signature

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Date

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Abstract

Phosphogypsum is a waste generated during the production of wet phosphoric acid from phosphate rocks. Numerous studies have attempted to find applications for phosphogypsum, but its composition is generally limiting its reuse. For instance, depending on the origin of the phosphate rocks it originates from, phosphogypsum can contain environmentally-problematic elements such as radionuclides or fluoride.

In this study, the potential of using a South African phosphogypsum waste for the production of calcium carbonate was investigated. The sample was collected from the Rustenburg plant of Omnia and was characterised by a number of analytical techniques. Two different processes of mineral carbonation were studied.

The first method, which can be described as an indirect mineral carbonation route, involved the reaction between phosphogypsum and an aqueous NaOH solution to form Ca(OH)_2 where after the Ca(OH)_2 was converted into CaCO_3 using CO_2 . During the first step of this process, the impurities contained in the phosphogypsum sample was transferred to the Ca(OH)_2 precipitate. Upon carbonation, a low grade CaCO_3 product, containing more than 10% impurities (such as unreacted gypsum and portlandite) was obtained.

Using the optimised reaction conditions, the effect varying the solid to liquid ratio and merging of the two steps applied during the indirect mineral carbonation route was studied. XRD analysis indicated that most of the carbonated products contained mainly two polymorphs of CaCO_3 , calcite and vaterite, in varying quantities. Only one set of reaction conditions was effective in both inducing a complete conversion of phosphogypsum into carbonate, and producing a single polymorph of CaCO_3 (calcite). The obtained calcite was defined as high-grade, containing close to 100% CaCO_3 . Its particles were spherical and contained the rare earth elements originally contained in the untreated phosphogypsum.

The second process used in this study, defined as the Merseburg process, involved the reaction between phosphogypsum and an $(\text{NH}_4)_2\text{CO}_3$ solution. The effect of varying the reaction time and temperature was studied on the conversion of phosphogypsum into calcium carbonate. The reactions were studied at 3 different temperatures (25°C, 40°C and 65°C) for 1 to 4 hours. It was found that a temperature of 65°C was required to yield the complete conversion of phosphogypsum into high-grade ($\text{CaCO}_3 > 99\%$) calcite. The time had no effect on the conversion rate at this temperature (65°C). The calcite particles formed had cube-like and plate-like structures and

contained significant amounts of the rare earth elements contained in the untreated phosphogypsum as impurities.

This study shows that both these processes are able to produce calcite particles which contain most of the rare earth elements (REE) originally present in the untreated phosphogypsum sample. The process involving the use of NaOH may not be suitable for large-scale industrial applications due to cost implications, whereas the Merseburg process may prove to be more favourable.

Table of contents

CHAPTER ONE

INTRODUCTION.....	1
1.1 Background.....	1
1.2 South-African phosphate ores and rocks: properties and origin.....	1
1.2.1 Igneous phosphates.....	1
1.2.2 Sedimentary phosphates.....	2
1.3 Phosphogypsum.....	3
1.3.1 Production of phosphogypsum.....	3
1.3.2 Disposal of phosphogypsum.....	5
1.3.3 Impact of phosphogypsum on the environment.....	5
1.3.4 Treatment and utilization of phosphogypsum.....	6
1.4 Calcium carbonate.....	7
1.4.1 Formation of calcium carbonate.....	7
1.4.2 Applications for calcium carbonate.....	9
1.4.3 Demand for calcium carbonate.....	9
1.4.3 Structure and morphology of phosphogypsum.....	11
1.5 Study objectives.....	12
1.6 References.....	13

CHAPTER TWO

ANALYSIS TECHNIQUES APPLIED IN THIS STUDY.....	18
2.1 Introduction.....	18
2.2 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for major element oxides (CGS, 2009b).....	18
2.3 X-ray powder diffraction analysis (XRD).....	19
2.3.1 Principles.....	19
2.3.2 Instrument and identification.....	20
2.4 Thermogravimetric analysis (TGA).....	21
2.4.1 Principles.....	21

2.4.2 TGA coupled to Fourier Transform Infrared Spectroscopy (TGA-FTIR).....	23
2.5 Field Emission Scanning Electron Microscopy (FESEM).....	23
2.5.1 Sample preparation.....	24
2.6 Particle Size Distribution (PSD).....	26
2.6.1 Principles.....	26
2.6.2 Instrument.....	27
2.7 The Brunauer, Emmet and Teller (BET) surface area analysis.....	27
2.7.1 Adsorption (Lowell, 2006).....	27
2.7.2 BET surface area.....	28
2.8 Inductively Coupled Plasma Mass-Spectrometry analysis (ICP-MS).....	29
2.8.1 ICP-MS for rare earth elements (REE) (CGS, 2006).....	31
2.8.2 Inductively Coupled Plasma 4-acid Method (CGS, 2011).....	31
2.9 Carbon and Sulphur analysis.....	33
2.10 Ion chromatography for water soluble anions (CGS, 2009c).....	33
2.11 Experimental equipment.....	34
2.12 References.....	36

CHAPTER THREE

CHARACTERIZATION OF PHOSPHOGYPSUM.....	38
3.1 Sampling.....	38
3.2 Physicochemical characterization of phosphogypsum, synthetic gypsum and natural gypsum.....	40
3.2.1 X-ray powder diffraction analysis (XRD).....	42
3.2.2 Carbon and sulphur analysis on phosphogypsum, synthetic gypsum and natural gypsum.....	44
3.2.3 Determination of anions in the gypsum samples by ion chromatography.....	45
3.2.4 Field Emission Scanning Microscopy of phosphogypsum, synthetic gypsum and natural gypsum.....	46
3.2.5 Particle size distribution (PSD) of phosphogypsum, synthetic gypsum and natural gypsum.....	49
3.2.6 BET surface area analysis of phosphogypsum, synthetic gypsum and natural gypsum.....	51
3.3 Thermogravimetric analysis (TGA).....	52
3.3.1 Literature study and calculation of the decomposition weight loss percentages of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3 and $\text{Ca}(\text{OH})_2$	52

3.3.2 TGA and XRD analysis of CaCO_3 and $\text{Ca}(\text{OH})_2$	55
3.3.3 Thermogravimetric analysis of the gypsum samples used in this study.....	62
3.4 Solubility studies performed phosphogypsum, synthetic gypsum and natural gypsum.....	69
3.5 ICP-MS analyses performed on phosphogypsum, synthetic gypsum and natural gypsum.....	73
3.5.1 ICP-MS 4-acid analysis performed on phosphogypsum, synthetic gypsum and natural gypsum for the determination of the different major and trace elements.....	73
3.5.2 ICP-MS analysis performed on phosphogypsum, synthetic gypsum and natural gypsum for the determination of Rare Earth Elements (REE).....	74
3.6 Inductively Coupled Plasma-Optical Emission Spectroscopy analyses performed on phosphogypsum, synthetic gypsum and natural gypsum for major oxide elements (ICP-OES).....	77
3.7 Conclusion.....	78
3.8 References.....	79

CHAPTER FOUR

MINERAL CARBONATION OF PHOSPHOGYPSUM.....	82
4.1 Introduction.....	82
4.1.1 Cardenas-Escudero process (Cardenas-Escudero et al, 2011).....	82
4.1.2 NaOH solution and hydroxide ions (OH^-).....	83
4.2 Experimental.....	84
4.2.1 Conversion of gypsum into $\text{Ca}(\text{OH})_2$	84
4.2.2 Synthesis of $\text{Ca}(\text{OH})_2$ and CaCO_3 (controls) from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	85
4.2.3 Carbonation of $\text{Ca}(\text{OH})_2$ formed from gypsum.....	86
4.3 Results and discussion.....	86
4.3.1 Results of the reactions between gypsum and NaOH.....	86
4.3.1.1 Changes in solution pH with time for the reactions of all 3 types of gypsum with NaOH.....	86
4.3.1.2 Weights of the precipitates formed from the reactions between NaOH and the gypsum samples.....	91
4.3.1.3 XRD analyses of the precipitates formed from the reaction between NaOH and the gypsum samples.....	92
4.3.1.4 Extent of conversion of the precipitates formed from the reaction between NaOH and the gypsum samples.....	94

4.3.1.5 Elemental compositions (majors) of the precipitates formed at different temperatures.....	96
4.3.1.6 Carbon and Sulphur analysis of the precipitates formed at different temperatures.....	101
4.3.2 Synthesis of $\text{Ca}(\text{OH})_2$ and CaCO_3 from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	102
4.3.2.1 Variations of pH with time for the reactions between $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ with NaOH	103
4.3.2.2 Variations of pH with time for the carbonation of the $\text{Ca}(\text{OH})_2$ precipitates made from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH	104
4.3.2.3 XRD analysis of the precipitates formed from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	105
4.3.2.4 Extent of conversion of the precipitates formed from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	107
4.3.3 Carbonation of $\text{Ca}(\text{OH})_2$ precipitates formed from phosphogypsum, synthetic gypsum and natural gypsum.....	108
4.3.3.1 Variations of pH with time for the carbonation reactions of the $\text{Ca}(\text{OH})_2$ formed from the gypsum samples.....	109
4.3.3.2 XRD analyses the carbonated $\text{Ca}(\text{OH})_2$ precipitates obtained from the gypsum samples.....	112
4.3.3.3 Extent of conversion of the $\text{Ca}(\text{OH})_2$ precipitates formed from the gypsum samples into CaCO_3	113
4.3.3.4 Thermogravimetric analyses of the carbonated $\text{Ca}(\text{OH})_2$ precipitates made from the gypsum samples.....	114
4.4 Conclusion.....	117
4.5 Future work.....	118
4.6 References.....	118

CHAPTER FIVE

A FURTHER STUDY ON THE MINERAL CARBONATION OF PHOSPHOGYPSUM...120

5.1 Introduction.....	120
5.2 Experimental.....	120
5.3 Results and discussion.....	122
5.3.1 The variation of pH with time for the carbonation of phosphogypsum.....	122
5.3.2 X-ray powder diffraction analysis (XRD) of the precipitates formed.....	124
5.3.3 Further characterization of the CaCO_3 precipitates formed using 5 g of phosphogypsum into 20 ml of solution (Experiment 1).....	127
5.3.3.1 Extent of conversion of the calcite precipitate formed using 5 g of phosphogypsum into 20 ml of solution (Experiment 1).....	127

5.3.3.2 Field Emission Scanning Electron Microscopy (FESEM).....	128
5.3.3.3 Particle size distribution (PSD) of the precipitates obtained in Experiment 1.....	129
5.3.3.4 ICP-MS 4-acid analysis performed on the calcite precipitates formed for the determination of the different major and trace elements.....	131
5.3.3.5 ICP-MS analysis performed on the calcite precipitates obtained from (Experiment 1) for the determination of Rare Earth Elements (REE).....	133
5.3.3.6 Carbon and Sulphur analysis of the calcite precipitates formed in Experiment 1.....	135
5.4 Conclusion.....	136
5.5 Future work.....	136
5.6 References.....	136

CHAPTER SIX

THE MERSEBURG PROCESS.....	138
6.1 Introduction.....	138
6.1.1 Description of the Merseburg process (Burnett et al, 1996).....	138
6.1.2 Ionic species in solution during the reaction between gypsum and ammonium carbonate.....	138
6.2 Experimental.....	140
6.2.1 Chemistry of commercial-grade ammonium carbonate.....	140
6.2.2 Conversion of phosphogypsum into CaCO_3	141
6.3 Results and discussion.....	141
6.3.1 XRD analysis of the precipitates formed from the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$	141
6.3.2 Thermogravimetric analyses of the precipitates formed from the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$ at different temperatures.....	145
6.3.3 Further characterization of the calcite precipitates formed at 65 °C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 1 hour and 30 minutes and 2 hours of reaction.....	155
6.3.3.1 Extent of conversion of the calcite precipitates formed at 65 °C.....	156
6.3.3.2 Field Emission Scanning Electron Microscopy (FESEM) of the calcite precipitates formed at 65 °C.....	157
6.3.3.3 Particle size distribution (PSD) analysis of the calcite precipitates formed at 65 °C....	164
6.3.3.4 ICP-MS 4-acid analysis performed on the calcite precipitates formed at 65°C for the determination of the different major and trace elements.....	166
6.3.3.5 ICP-MS analysis performed on the calcite precipitates formed at 65°C for the determination of rare earth elements (REE).....	168

6.3.3.6 Carbon and Sulphur analysis of the calcite precipitates formed at 65°C.....	171
6.4 Conclusion.....	172
6.5 Future work.....	172
6.6 References.....	173

CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS.....	175
7.1 Conclusions and recommendations.....	175
7.2 References.....	176

List of abbreviations

%T	Percentage of Transmittance
BET	Brunauer, Emmet, and Teller
CGS	Council for Geoscience
CSD	Cambridge Structure Database
D (v, 0.1)	Size of the particles below which 10 % of the sample lies
D (v, 0.5)	Mass Median Diameter (MMD); It is the size in microns at which 50% of the sample is smaller and 50 % is larger
D (v, 0.9)	Size of particles below which 90 % of the sample lies
D [3, 2]	Sauter Mean Diameter; It is the Surface Area Mean Diameter and represents the diameter of theoretical spherical particles that have the same surface area as the original particles.
D [4, 3]	Volume Weight Mean Diameter and represents the diameter of theoretical spherical particles occupying the same volume as the original particles
DTG	Derivative Thermogravimetry
Eqn	Equation
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
GCC	Ground Calcium Carbonate
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ICSD	Inorganic Crystal Structure Database
L.O.I	Loss of Ignition
PCC	Precipitated Calcium Carbonate
PET	Polyethylene
PP	Polypropylene
PSD	Particle Size Distribution
PVC	Polyvinyl Chloride or Polychloroethene
REE	Rare Earth Element
TGA	Thermogravimetric Analysis
TGA-FTIR	Thermogravimetric Analysis with Fourier Transform Infrared
XRD	X-ray Diffraction

List of chemical formulae

$(\text{Mg, Al})_2(\text{Si}_4)\text{O}_{10}(\text{OH}) \cdot 4\text{H}_2\text{O}$	Palygorskite
$(\text{NH}_4)_2\text{CO}_3$	Ammonium carbonate
Al	Aluminium
Al_2O_3	Aluminium (III) Oxide; Alumina (page 8)
Au	Gold
Ba	Barium
C	Carbon
Ca	Calcium
$\text{Ca}(\text{OH})_2$	Calcium Hydroxide; Portlandite
Ca^{2+}	Calcium ion
$\text{Ca}_5\text{F}(\text{PO}_4)_3$	Calcium Fluorophosphates also named Apatite
CaC_2O_4	Calcium oxalate
$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	Calcium oxalate monohydrate
CaCO_3	Calcium Carbonate
CaO	Calcium Oxide
CaSiO_3	Calcium Silicate; slag (page 8)
CaSO_4	Calcium sulfate also known as anhydrite
$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	Calcium sulfate hemihydrate also known as bassanite
$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Calcium Sulfate dihydrate also designated as phosphogypsum or gypsum
Ce	Cerium
Cl^-	Chlorine
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
Cr	Chromium
Cr_2O_3	Chromium (III) Oxide
Cu	Copper
Dy	Dysprosium
Er	Erbium
Eu	Europium
F^-	Fluorine
Fe_2O_3	Iron (III) Oxide
Fe_2O_3	Iron (III) Oxide
FeCO_3	Iron (II) Carbonate; Siderite (page 8)
Gd	Gadolinium
H_2CO_3	Carbonic acid
H_2O	Water
H_2O_2	Hydrogen peroxide
H_2PO_4^-	Dihydrogen Phosphate ion
H_2SO_4	Sulfuric acid
H_3O^+	Hydronium ion
H_3PO_4	Phosphoric acid
HCl	Hydrochloric acid
HClO_4	Perchloric acid

HCO_3^-	Hydrogen carbonate
HF	Hydrogen Fluoride or Hydrofluoric acid
HNO_3	Nitric acid
Ho	Holmium
HSO_4^-	Hydrogen sulfate ion
K	Potassium
K_2O	Potassium oxide
KBr	Potassium Bromide
$\text{KFeMg}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	Mica
KH_2PO_4	Potassium Hydrogen Phosphate
La	Lanthanum
Lu	Lutetium
$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$	Sepiolite
MgO	Magnesium oxide
MnO	Manganese (II) Oxide
N_2	Nitrogen
Na	Sodium
$\text{Na}_2(\text{SO})_4$	Sodium Sulfate
Na_2O	Sodium oxide
NaCl	Sodium Chloride
NaF	Sodium Fluoride
NaNO_2	Sodium Nitrite
NaNO_3	Sodium Nitrate
NaOH	Sodium Hydroxide
Nd	Neodymium
$\text{NH}_4\text{CO}_2\text{NH}_2$	Ammonium carbamate
NH_4HCO_3	Ammonium bicarbonate
$\text{NH}_4\text{HCO}_3 \cdot \text{NH}_4\text{CO}_2\text{NH}_2$	Commercial reagent grade of ammonium carbonate
NO_2^-	Nitrite
NO_3^-	Nitrate
O_2	Oxygen
OH^-	Hydroxide
P_2O_5	Phosphorus pentoxide
pH	Measure of the acidity or basicity of an aqueous solution
PO_4^{3-}	Phosphate ion
Pr	Praseodymium
Pt	Platinum
S	Sulfur
SiO_2	Silicon (IV) Oxide also known as silica or Silicon dioxide; Molecular formula of quartz
Sm	Samarium
SO_2	Sulfur dioxide
SO_3	Sulfur Trioxide
SO_4^{2-}	Sulfate ion
Tb	Terbium
Th	Thorium
TiO_2	Titanium dioxide
Tm	Thulium

U	Uranium
Y	Yttrium
Yb	Ytterbium
Zr	Zirconium

List of units

°C	Degree Celsius
µg/kg	micro gram per kilogram,
µm	micrometre or micron
µs	microsecond
cm	centimeter
cm ⁻¹	Wavenumber
g	gram
g/ mol	gram per mole
g/100 ml	gram per 100 milliliters
g/cm ³	gram per cubic centimeter
Km	Kilometer
kv	kilovolt
kw	kilowatt
m	meter
M	Molar
m ² .g ⁻¹	Square meter per gram
mA	milliampere
mg	milligram
Mg	Magnesium
mg /kg	milligram per kilo gram
ml	millilitre
ml/ min	milliliter per minute
Mt	Million tons
mv	millivolt
MΩ	Megaohm
N	Normality
ppb	Part per billion
ppm	Part per million
ppt	Part per trillion
v/v	Volume per volume
w/w	Weight by weight
wt %	Weight percent
µS/cmA	micro siemens per centimeter

List of figures

Figure 1.1: Typical wet process acid plant showing the three stages, involved in the production of phosphoric acid and formation of gypsum.....	4
Figure 2.1: X-ray diffraction.....	20
Figure 2.2: TGA curves of different chemical reactions.....	22
Figure 2.3: A thermograph: Stepwise decomposition of calcium oxalate monohydrate.....	23
Figure 2.4: Carbon tabs with samples mounted on an aluminium plate before being coated.....	24
Figure 2.5: Emitech K950X Carbon coater used for coating the samples.....	25
Figure 2.6: Carbon tabs with samples mounted on an aluminium plate after being coated.....	25
Figure 2.7: Zeiss Ultra Plus Field Scanning Electron Microscope instrument used for imaging....	26
Figure 2.8: Components of a commercial ICP-MS system.....	30
Figure 2.9: Experimental equipment used to perform reactions in this study.....	35
Figure 3.1: Photograph showing the phosphoric acid production plant of Omnia at Rustenburg, South-Africa (<i>source: Omnia</i>).....	38
Figure 3.2: Photograph showing the phosphogypsum stockpile at OMNIA's phosphoric acid production plant in Rustenburg (<i>source: Omnia</i>).....	39
Figure 3.3: Photograph showing the rotary splitter used for the splitting of phosphogypsum into representative homogeneous subsamples.....	40
Figure 3.4: Samples of raw phosphogypsum, synthetic gypsum and natural gypsum.....	41
Figure 3.5: FESEM images of phosphogypsum, synthetic gypsum and natural gypsum particles...	44
Figure 3.6: Particles of phosphogypsum, synthetic gypsum and natural gypsum observed under scanning electron microscopy at higher magnification.....	48
Figure 3.7: The frequency curve of the particle size distribution of phosphogypsum, synthetic gypsum and natural gypsum.....	49
Figure 3.8: The TGA curve of CaCO_3 and its first derivative (DTG).....	56
Figure 3.9: The TGA curve of CaCO_3 and its first derivative (DTG).....	57

Figure 3.10: The TGA curve of $\text{Ca}(\text{OH})_2$ and its first derivative (DTG) obtained from TGA-FTIR analysis.....	58
Figure 3.11: Graph of the Gram-Schmidt Absorbance versus time profile obtained for the gaseous decomposition products of the $\text{Ca}(\text{OH})_2$ sample.....	59
Figure 3.12: FTIR spectrum obtained from the gaseous TGA decomposition products taken at 350 seconds.....	60
Figure 3.13: FTIR spectrum obtained from the gaseous TGA decomposition products taken at 437 seconds.....	61
Figure 3.14: The TGA curve of synthetic gypsum and its first derivative (DTG).....	63
Figure 3.15: The TGA curve of phosphogypsum and its first derivative (DTG).....	64
Figure 3.16: The TGA curve of natural gypsum and its first derivative (DTG).....	65
Figure 3.17: Changes in conductivity of aqueous solution upon addition of phosphogypsum, synthetic gypsum and natural gypsum over time.....	70
Figure 3.18: Changes in solution pH upon addition of phosphogypsum, synthetic gypsum and natural gypsum over time.....	71
Figure 4.1: pH changes of the reaction between phosphogypsum and NaOH over time.....	87
Figure 4.2: pH changes of the reaction between synthetic gypsum and NaOH over time.....	88
Figure 4.3: pH changes of the reaction between natural gypsum and NaOH over time.....	90
Figure 4.4: pH variations of the reaction between $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH at 40 °C.....	103
Figure 4.5: pH variations for the carbonation of the $\text{Ca}(\text{OH})_2$ precipitates made at 40 °C from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH.....	104
Figure 4.6: Variation of pH for the carbonation of the $\text{Ca}(\text{OH})_2$ precipitates obtained at 25 °C from phosphogypsum and NaOH.....	109
Figure 4.7: Variation of pH for the carbonation of the $\text{Ca}(\text{OH})_2$ precipitates obtained at 40 °C from synthetic gypsum and NaOH.....	110
Figure 4.8: Variation of pH for the carbonation of the $\text{Ca}(\text{OH})_2$ precipitates obtained at 70 °C from natural gypsum and NaOH.....	110

Figure 4.9: The TGA curve and the first derivative (DTG) obtained for the carbonated $\text{Ca}(\text{OH})_2$ sample from the reaction between phosphogypsum and NaOH at 25°C.....	114
Figure 5.1: Variation in pH for the carbonation of 5 g of phosphogypsum in 20 ml of NaOH solution (Experiment 1).....	122
Figure 5.2: Variation in pH for the carbonation of 5 g of phosphogypsum into 100 ml of NaOH solution (Experiment 2).....	123
Figure 5.3: Variation of pH for the carbonation of 2 g of phosphogypsum in 40 ml of NaOH solution (Experiment 3).....	124
Figure 5.4(a): FESEM images of the calcite formed using 5 g of phosphogypsum in 20 ml of solution (Experiment 1) at a magnification of $3000 \times$ (a) and $17500 \times$ (b).....	128
Figure 5.4(b): FESEM image of a single crystal of calcite formed.....	129
Figure 5.5: The frequency curve of the particle size distribution of calcite formed using 5 g of phosphogypsum in 20 ml of NaOH solution (Experiment 1).....	130
Figure 5.6: Calculated percentage of rare earth elements which was transferred from phosphogypsum to the calcite precipitate.....	135
Figure 6.1: The TGA curve of a precipitate formed from the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$ at 25 °C during 1 hour of reaction ($\text{M}_{4-25^\circ\text{C}-1\text{h}}$) and its first derivative (DTG).....	146
Figure 6.2: FTIR spectrum obtained from the gaseous TGA decomposition between 40 °C and 241 °C of the precipitate ($\text{M}_{4-25^\circ\text{C}-1\text{h}}$) formed at 25 °C during an 1 hour reaction.....	147
Figure 6.3: FTIR spectrum obtained from the gaseous TGA decomposition taking place after 241 °C of the precipitate ($\text{M}_{4-25^\circ\text{C}-1\text{h}}$) formed at 25 °C during an 1 hour reaction.....	148
Figure 6.4a: FESEM images of the calcite crystals formed at 65 °C after 1 hour of reaction at a magnification of $3200 \times$	158
Figure 6.4b: FESEM images of the calcite crystals formed at 65 °C after 1 hour and 30 minutes of reaction at a magnification of $2500 \times$	159
Figure 6.4c: FESEM images of the calcite crystals formed at 65 °C after 2 hours of reaction at a magnification of $2500 \times$	160

Figure 6.5a: Cubic and plate-like crystals formed from the reactions at 65°C between phosphogypsum and ammonium carbonate during an 1 hour reaction at a magnification of 16000 ×.....	161
Figure 6.5b: Cubic and plate-like crystals formed from the reactions at 65°C between phosphogypsum and ammonium carbonate during an 1 hour and 30 minutes of reaction at a magnification of 19000 ×.....	162
Figure 6.5c: Cubic and plate-like crystals formed from the reactions at 65°C between phosphogypsum and ammonium carbonate during an 2 hours of reaction at a magnification of 17000 ×.....	163
Figure 6.6: The frequency curve of the calcite precipitates formed at 65 °C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 1 hour and 30 minutes and 2 hours of reaction.....	165
Figure 6.7: Calculated percentage of rare earth elements which was transferred from phosphogypsum to the calcite precipitate obtained at 65°C after 1 hour of reaction.....	170
Figure 6.8: Calculated percentage of rare earth elements which was transferred from phosphogypsum to the calcite precipitate obtained at 65°C after 1 hour and 30 minutes of reaction.....	170
Figure 6.12: Calculated percentage of rare earth elements which was transferred from phosphogypsum to the calcite precipitate obtained at 65°C after 2 hours of reaction.....	171

List of tables

Table 3.1: Summary of the moisture content present in each gypsum sample.....	42
Table 3.2: XRD results of untreated phosphogypsum, synthetic gypsum and natural gypsum.....	43
Table 3.3: Estimated carbon and sulphur contents in phosphogypsum, synthetic gypsum and natural gypsum, as calculated from XRD data.....	44
Table 3.4: Measured carbon and sulphur in phosphogypsum, synthetic gypsum and natural gypsum, as determined using the Carbon and Sulphur analyser.....	44
Table 3.5: Concentration of anions in solution for the three gypsum samples (mg /kg).....	45
Table 3.6: Relationship between sulphate from ion chromatography and sulphur trioxide contents...	46
Table 3.7: Calculated diameters of phosphogypsum, synthetic gypsum and natural gypsum particles.....	50
Table 3.8: Summary of the results obtained for the BET surface area measurements of phosphogypsum, synthetic gypsum and natural gypsum.....	51
Table 3.9: Theoretical weight percentages of the decomposition products of pure calcium sulphate dehydrate.....	53
Table 3.10: Theoretical weight percentages of the decomposition products of $\text{Ca}(\text{OH})_2$	54
Table 3.11: Theoretical weight percentages of the decomposition products of CaCO_3	54
Table 3.12: Quantitative XRD results of $\text{Ca}(\text{OH})_2$ and CaCO_3 obtained from Merck.....	55
Table 3.13: Quantitative TG analysis of the gypsum samples used in this study.....	67
Table 3.14: Concentration of the major and trace elements in solution reported in part per billion ($\mu\text{g}/\text{kg}$).....	73
Table 3.15: Concentrations of rare earth elements in phosphogypsum, synthetic gypsum and natural gypsum as determined by ICP-MS, reported in parts per billion ($\mu\text{g}/\text{kg}$).....	76
Table 3.16: ICP-OES of major oxide elements contained in the studied gypsum samples reported in (wt %).....	77
Table 4.1: Weights of the precipitates formed at the different temperatures for the reaction between the gypsum samples and NaOH	91

Table 4.2: Mineral compositions of the precipitates formed from the reaction between the gypsum samples and NaOH at different temperatures, reported as weight percentage (wt %).....	93
Table: 4.3: Extent of conversion of the calcium contained in the gypsum samples into $\text{Ca}(\text{OH})_2$	95
Table 4.4: ICP-OES of major elements (wt % oxide) of the precipitates formed from phosphogypsum.....	96
Table 4.5: Amount of CaO in the $\text{Ca}(\text{OH})_2$ precipitates made from phosphogypsum as determined from XRD.....	97
Table 4.6: ICP-OES of major elements (wt % oxide) of the precipitates formed from synthetic gypsum.....	98
Table 4.7: Amount of CaO in the $\text{Ca}(\text{OH})_2$ precipitates made from synthetic gypsum as determined from XRD.....	99
Table 4.8: ICP-OES of major elements (wt % oxide) of the precipitates formed from natural gypsum.....	100
Table 4.9: Carbon and Sulphur analysis of the $\text{Ca}(\text{OH})_2$ precipitates formed from the three gypsum samples.....	101
Table 4.10: XRD results of the precipitates formed at 40 °C between $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH.....	106
Table 4.11: Mineral compositions of the carbonated $\text{Ca}(\text{OH})_2$ precipitates.....	106
Table 4.12: Weights of the $\text{Ca}(\text{OH})_2$ precipitates formed at 40 °C from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH.....	107
Table 4.13: Weights of the carbonated $\text{Ca}(\text{OH})_2$ precipitates made from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	108
Table 4.14: XRD results of carbonated $\text{Ca}(\text{OH})_2$ samples obtained from phosphogypsum, synthetic gypsum and natural gypsum.....	112
Table 4.15: weights of the carbonated $\text{Ca}(\text{OH})_2$ precipitates obtained from the gypsum samples.....	113
Table 4.16: Quantitative TG analysis of the carbonated $\text{Ca}(\text{OH})_2$ samples.....	116
Table 4.17: Comparisons of the total CaCO_3 as calculated from TGA versus the amount of CaCO_3 detected by XRD in each precipitate formed from the gypsum samples.....	117
Table 5.1: XRD analyses of the precipitates formed from the mineral carbonation of phosphogypsum, using different solid to liquid ratios.....	125

Table 5.2: Extent of conversion of the calcium contained in the gypsum samples into CaCO_3	127
Table 5.3: Summary of the particle size distribution of the calcite samples formed using 5 g of phosphogypsum into 20 ml of solution (Experiment 1).....	130
Table 5.4: Concentration of the major and trace elements in the calcite precipitates formed in Experiment 1 reported in part per billion ($\mu\text{g/kg}$).....	131
Table 5.5: Percentage of calcium in the calcite precipitates formed in Experiment 1 as estimated from the XRD data.....	132
Table 5.6: Concentrations of rare earth elements in the calcite precipitates obtained from Experiment 1 as determined by ICP-MS, reported in parts per billion ($\mu\text{g/kg}$).....	134
Table 5.7: Carbon & Sulfur analysis of the CaCO_3 precipitates obtained from 5 g of phosphogypsum and 20 ml of solution expressed in weight percentage (wt%).....	135
Table 6.1: XRD analyses of the precipitates formed from the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$ at 25 °C.....	142
Table 6.2: XRD analyses of the precipitates formed from the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$ at 40 °C.....	143
Table 6.3: XRD analyses of the precipitates formed from the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$ at 65 °C.....	144
Table 6.4: Quantitative TG analysis of the precipitates formed at 25 °C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 2 hours 3 hours and 4 hours of reaction.....	150
Table 6.5: Quantitative TG analysis of the precipitates formed at 40 °C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 1 hour and 30 minutes and 2 hours of reaction.....	151
Table 6.6: Quantitative TG analysis of the precipitates formed at 65 °C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 1 hour and 30 minutes and 2 hours of reaction.....	152
Table 6.7: Comparisons of the total CaCO_3 detected by TGA against the total CaCO_3 detected by XRD of the precipitates formed at 25 °C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 2 hours 3 hours and 4 hours of reaction.....	153

Table 6.8: Comparisons of the total CaCO_3 detected by TGA against the total CaCO_3 detected by XRD of the precipitates formed at 40 °C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 1 hour and 30 minutes and 2 hours of reaction....	154
Table 6.9: Comparisons of the total CaCO_3 detected by TGA against the total CaCO_3 detected by XRD of the precipitates formed at 65 °C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 1 hour and 30 minutes and 2 hours of reaction....	155
Table 6.10: Extent of conversion of the calcium contained in the gypsum samples into CaCO_3	156
Table 6.11: Summary of the particle size distribution of the calcite samples formed at 65 °C.....	165
Table 6.12: Concentration of the different major and trace elements contained in the calcite precipitates obtained at 65 °C in part per billion ($\mu\text{g}/\text{kg}$).....	166
Table 6.13: Percentage of calcium in the calcite precipitates obtained at 65°C as estimated from the XRD data.....	167
Table 6.14: Percentage of calcium in the calcite precipitates obtained at 65°C as estimated from the ICP-MS 4-acid analysis.....	167
Table 6.15: Concentration of rare earth elements contained in the calcite precipitates obtained at 65 °C, reported in parts per billion ($\mu\text{g}/\text{kg}$).....	169
Table 6.16: Carbon and Sulphur analysis of the calcite precipitates obtained at 65 °C.....	171

CHAPTER ONE: INTRODUCTION

1.1 Background

All over the world and in South-Africa more precisely, phosphate rocks are used for the production of phosphate fertilizers. During the process of manufacturing phosphate fertilizers, phosphoric acid is produced and phosphogypsum is obtained as waste product. The disposal and handling of this phosphogypsum by-product have been a major concern around the world due to its impacts on the environment and on the health of the human population, with South-Africa not deviating from it (Mulopo and Ikhu-Omoregbe, 2012). The utilization of phosphogypsum may provide economic and social benefits in terms of profits which can be made from it, as well as the reduction of its polluting effects on the environment. As such, developing methods for the recycling of this waste product have been prioritized (Tayibi et al, 2009; van der Merwe, 2001).

1.2 South-African phosphate ores and rocks: properties and origin

Phosphate rocks have played a significant role in the agricultural development of South Africa. They are an important source of commercial phosphorus and have been invaluable for their direct application to soils presenting deficiencies in nutrients, such as phosphorus. As such, local resources of phosphate rocks have been developed for the production of fertilizers. The types of phosphate rocks encountered in South Africa can be divided into two main categories; namely, igneous phosphate with its main mineral being apatite, and sedimentary phosphate rocks (Wilson, and Anhaeusser, 1998). The properties of these types of phosphate rocks are discussed in the next sections. The phosphate content of phosphate rocks is commonly reported as phosphorus pentoxide (P_2O_5), and this may average as little as 3.8% in commercial deposits. A minimum of around 28% of P_2O_5 is recommended by manufacturers of both phosphoric acid and phosphatic fertilizers. Most marketed grades of phosphate rocks contain more than 30% of P_2O_5 . In order to meet this requirement, phosphate ores need to undergo beneficiation (Nothol et al, 1989).

1.2.1 Igneous phosphates

Igneous phosphates are mainly found in the Northern Province of South-Africa, specifically at the Phalaborwa complex, which represents the largest reserve of igneous phosphate in South-Africa (Wilson, and Anhaeusser, 1998).

The main body of the Phalaborwa complex has a kidney shape, measuring 1.5 to 3.5km in width and 6.5km in length divided into three lobes named: Northern pyroxenite, Loolekop and Southern pyroxenite (Roux et al, 1989). This igneous complex is made of three major types of rocks: the carbonatite, the phoscorite and the pyroxenite (Wilson, and Anhaeusser, 1998).

Coetzee (1976) defines the carbonatite as an igneous rock containing varying amounts of magnetite, apatite and serpentinised olivine. The average P_2O_5 content found in this rock is reported to be 3.5%. However, this low percentage in phosphate content does not qualify it as a phosphate ore (Roux et al, 1989).

Roux (1989) also describes phoscorite as an igneous rock consisting of minerals such as serpentine, magnetite, calcite, dolomite and apatite with a P_2O_5 content of 10% and an apatite content of 25%. According to the same author, pyroxenite is defined as an igneous rock consisting essentially of minerals of the pyroxene group such as, diopside phlogopite and apatite. The P_2O_5 content of pyroxenite varies between 6 and 7.5% while its content in apatite varies between 15 and 19%.

1.2.2 Sedimentary phosphates

The nature of sedimentary phosphates in South Africa has been described thoroughly by Roux et al (1989). Briefly, sedimentary phosphates mainly come from the western and southern coastal regions as offshore and onshore deposits.

The onshore deposits occur sporadically from Saldanha in the south, to Lamberts Bay in the north. The deposits in this region, which are reported to have an ore grade varying between 8.0% and 12.5% of P_2O_5 , consist of phosphatic sand horizons overlain by limestone and/or younger sand. The phosphate occurs as carbonate apatite soluble in citric acid making it suitable as a direct-application fertilizer.

The deposits met in the New Varswater ore body found in the vicinity of Langebaan have an average grade of 15% P_2O_5 . In this region, the phosphate is present as cement binding the quartz.

The offshore deposits on the other hand occur on the continental shelf at Agulhas Bank, extending from Cape Town eastwards as far as Port Elizabeth and shelf off the west coast from Cape Town northwards as far as Lamberts Bay. The deposits consist of scattered nodules and sands found at depths ranging from 100 m to over 1000 m. They are reported to have an average of 16% P_2O_5 which is considered to be relatively low, making them not readily open to upgrading.

Despite the progress in the offshore mining technology, there is doubt as to whether these deposits can be exploited economically, due to the difficulties in finding a market for such low-grade material.

1.3 Phosphogypsum

1.3.1 Production of phosphogypsum

Phosphogypsum is a waste product generated during the wet phosphoric acid process (Cárdenas-Escudero et al, 2011). During this process, phosphate rocks also known as apatites react with sulphuric acid and water to produce a slurry mixture made up of phosphoric acid and phosphogypsum (Schorr et al, 2010). The slurry mixture is then filtered and phosphogypsum is separated from the acid. The acid is concentrated by evaporation while phosphogypsum is stockpiled on large available land areas (Cárdenas-Escudero et al, 2011). About 15% of the world phosphogypsum production, which is estimated to be between 100 million tons and 280 million tons per year, is being recycled (Tayibi et al, 2009; Yang et al, 2009; Parreira et al, 2003). The production of phosphogypsum is described by the chemical equation below:



The characteristics of the phosphogypsum produced are influenced by several parameters, such as the nature of the phosphate ores used during the wet phosphoric acid process, the plant operation, the disposal method, and the age and location of the stack where the phosphogypsum is dumped (Tayibi et al, 2009). Depending on the nature of the apatite rock used in the wet phosphoric acid process, whether it is fluorapatite, chlorapatite or hydroxylapatite in solution, phosphogypsum could contain a significant concentration of anions, such as fluorine (F⁻), chlorine (Cl⁻) or hydroxide (OH⁻) (Tayibi et al, 2009).

Figure 1.1 illustrates the phosphoric acid process from which phosphogypsum is produced as a waste material.

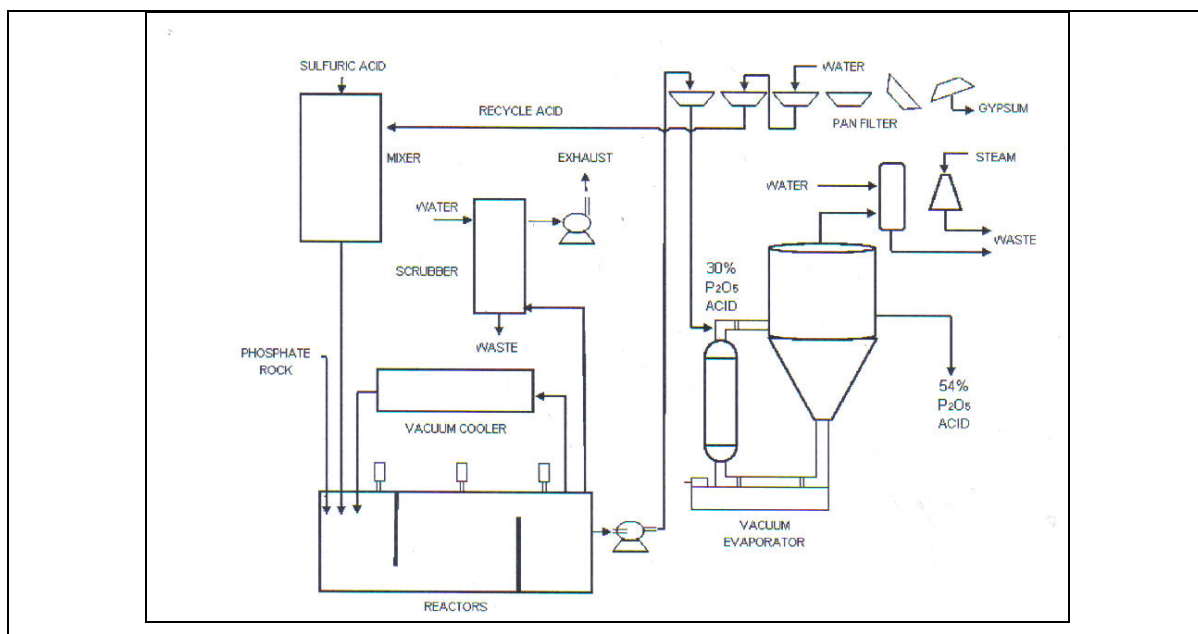


Figure 1.1: Typical wet process acid plant showing the three stages involved in the production of phosphoric acid and the formation of phosphogypsum (Schorr et al, 2010).

Firstly, phosphate rocks are introduced into a reactor along with sulphuric acid and water. From that reactor emerges a slurry mixture made up of phosphogypsum and phosphoric acid. The mixture is filtered in a pan filter to separate gypsum, which is then discarded as a waste product, from the phosphoric acid containing about 30% P_2O_5 . The phosphoric acid solution is then introduced into a second reactor and concentrated by evaporation to produce a commercial phosphoric acid containing about 54% P_2O_5 . Further evaporation of water contained in the phosphoric acid might occur to yield superphosphoric acid with a P_2O_5 content of 70%.

South-Africa has a highly-developed domestic and export oriented phosphate industry which results into the production of large quantities of phosphogypsum as waste product. Once produced, phosphogypsum consists of about 20 to 30% of free water, and is either pumped into the sea or stockpiled on large land areas (Mulopo and Ikhu-Omoregbe, 2012) with a very small portion of it being used in some industries such as the cement industry and/or in agriculture. For instance, about 10000 tonnes of phosphogypsum are produced every day by the Richard Bay plant all alone against 40000 tonnes being sold to the agricultural sector and other 200000 tonnes being upgraded for use in the cement industry every year by the Omnia group (Mulopo and Ikhu-Omoregbe, 2012).

1.3.2 Disposal of phosphogypsum

The disposal of phosphogypsum has been regarded as an important challenge, for many years, by the phosphoric acid industry, ecologists and all those concerned with the disposal of this waste product such as government and civil society in South-Africa as it poses a threat to the environment as well as to human health (Mulopo and Ikhu-Omoregbe, 2012). The threat arises from the fact that the impurities contained in phosphogypsum piles, under the action of percolating waters such as rain water and/ or storage water could be leached from the stockpile and enter nearby soils and/or ground waters and creating an environmental hazard.

The disposal of phosphogypsum requires large available land areas where it is stacked using a dry or wet technique (van der Merwe, 2001). The dry technique consists of transporting the phosphogypsum filter cake, after being separated from the phosphoric acid, to the disposal facilities using conveyor belts or trucks (de Freitas and Albuquerque, 1991; Ghafoori and Chang, 1993; Morris 1993).

The wet technique used for the disposal of phosphogypsum consists of slurring and pumping the phosphogypsum filter cake with waste water from the phosphoric acid process plant to a nearby settling pond (van der Merwe, 2001; Cárdenas-Escudero et al, 2011). In this case, the phosphogypsum slurry consists of about 30% solids and 70% process water. The overflowing water falling from the phosphogypsum stack is collected in process ponds located near the gypsum stack. These process ponds also act as flood ponds to store rain water falling over the phosphogypsum stack for a subsequent evaporation and as cooling ponds to allow recirculation of process water (van der Merwe, 2001).

1.3.3 Impact of phosphogypsum on the environment

If not treated prior to its disposal, phosphogypsum can cause serious environmental contamination of the atmosphere, soil and water (Tayibi et al, 2009).

Bolivar et al (2000) for instance found that 90% of Polonium and Radium formerly present in the phosphate rocks remain in phosphogypsum. According to Szlauer et al (1990), the negative atmospheric impacts of phosphogypsum disposal can be caused by the erosion of the pile causing the release of highly polluting substances due to the formation of hazardous vapours containing heavy metals, sulphates and hydrogen fluoride as well as phosphorus and cadmium (Marovic and Sencar, 1995). Tayibi et al (2009) further stated that atmospheric agents such as strong winds play

an important role in the contamination of the atmosphere by transporting the contaminations to neighbouring areas therefore putting human beings at risk.

Other authors agree on the fact that the contamination of ground water underlying phosphogypsum stacks can occur from the leachability of hazardous elements naturally contained in the phosphogypsum (May and Sweeney, 1982; Carter and Scheiner, 1992; Berish 1990). The leachability of these elements from the phosphogypsum pile can result into their dissolution and deposit in nearby soils followed by their transfer to waters and then living organisms (Reinjnders, 2007).

Among the impurities contained in South-African phosphogypsum, Rutherford et al., 1994 listed the presences of fluorides, sulphates, acids, organics, trace metals and naturally occurring radionuclides (U, Cd, etc.). They found, for instance, that phosphogypsum wastes that were produced at Kynoch and Omnia contained 0.12% and 0.03% by mass of fluoride respectively. According to Coetzee et al (2003), South-Africa has a drinking water standard in fluorine of 1.5 mg/l. However, levels of fluoride as high as 30 mg/l were found in ground waters of provinces such as North West, Northern Cape and Limpopo and were at the cause of dental fluorosis found in affected inhabitants who source drinking water from untreated groundwater (Coetzee et al., 2003). With the purpose of reducing the potential threat of those impurities, Motalane and Strydom (2004) suggested that waste disposal facilities should firstly be built in such a manner that the environment is being protected then phosphogypsum wastes should be treated with sulfuric acid before being stockpiled away from the plant of production, then and finally the level of fluoride in the vicinity of the phosphogypsum stockpile should be controlled regularly.

1.3.4 Treatment and utilization of phosphogypsum

Prior to its utilization, phosphogypsum has to be treated in order to considerably reduce the amount of impurities it contains. Treatments range from washing to drying and from chemical to thermal extractions (Tayibi et al, 2009). Manjit et al (1993 and 2002) and Potgieter et al (2003) reported that washing phosphogypsum, either with water, acidic or basic solution, then drying it at low or high temperatures, considerably reduces almost all types of impurities it might contain. Tayibi (2009) reported that the treatment of phosphogypsum by heat converts calcium sulphate dihydrate contained in phosphogypsum directly into anhydrite which is ideal for applications in the cement industry as well as in the manufacturing of building materials.

Lately there has been great interest in the utilization of phosphogypsum as an alternative material in many applications. Like gypsum, phosphogypsum could be used for the production of building materials such as cement, bitumen lime etc. It is used in the cement industry, instead of natural gypsum, as a setting regulator (Akin and Yesmin, 2004). It can be used for the making of plaster and plaster-derived products (van der Merwe, 2001). Phosphogypsum is also useful for the recovery of elemental sulphur, either through the production of sulphuric acid, or ammonium sulphate (van der Merwe, 2001). Furthermore, it is considered as a source of calcium for the production of precipitated calcium carbonate for the paper industry, where it is used as coating (Roberts, 1996), and for the reduction of high levels of toxic soluble aluminium in soils by supplying calcium (Wirsching, 1978).

1.4 Calcium carbonate

Calcium carbonate is a mineral, which is fine and white in appearance, with the chemical formula CaCO_3 , a molar mass of 100.0869g/ mol, and a density of 2.711g/cm³. At room temperature, its solubility in water is 0.0013g/100 ml. It exists as three predominant anhydrous phases: as calcite with a trigonal crystal structure, as aragonite with an orthorhombic crystal structure, and as vaterite with a hexagonal crystal structure (Boynnton, 1980; Maciejewski et al, 1994). Calcite is the most stable among the three while aragonite and vaterite are metastable (Day et al, 2013). Vaterite can serve as a precursor phase of aragonite and calcite (Nehrke et al, 2006); it easily transforms in aqueous solution at low temperatures into stable calcite, a phenomenon which is not observed in the case of aragonite (Maciejewski et al, 1994).

1.4.1 Formation of calcium carbonate

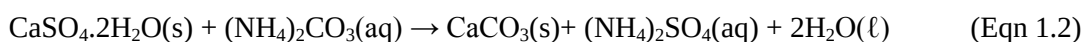
According to the Paper Industry Technical association (2013), two types of calcium carbonate exist; ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC). Ground calcium carbonate is manufactured when either limestone or marble is ground. Precipitated calcium carbonate is formed by carbonation processes (Fernando and Thomas, 2007).

In nature, calcium carbonate is found in rocks as well as in plants and animals which have in common the calcium carbonate cycle (Banth et al, 2008). Its formation starts with the sedimentation of crustacea, coccoliths, algae and corals on sea-beds from which chalk and limestone are initially made. At the completion of the sedimentation, limestone and chalk are formed. However, chalk is a poorly compacted sedimentary calcium carbonate rock whose diagenesis is incomplete. If the sedimentation occurs in waters containing magnesium, this will

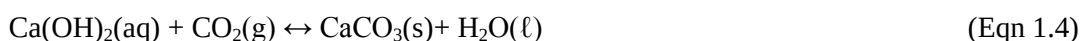
result into the formation of dolomite where magnesium ions replace part of the calcium ions contained in the crystal lattice. Limestone, chalk and dolomite carbonate rocks are in turn exposed to erosion under the influence of wind, acidic water (resulting from the reaction between rain water and gases such as CO₂ and SO₂ from the atmosphere) and temperatures that dissolve them back into the sea-beds. That dissolved calcium carbonate will then be absorbed by plants and animals which use it to build their shells and skeletons. After their deaths, plants and animals will form sedimentary deposits on sea-beds opening doors to the formation of new calcium carbonate rocks (Banth et al, 2008).

The conventional route for the industrial production of PCC starts by the calcination of limestone at high temperatures (between 800°C and 1000°C). The calcined limestone is then combined with water to produce a “milk-of-lime” suspension, with all the initial contaminants contained in the limestone present. Carbon dioxide is then reacted with the milk-of-lime suspension to precipitate calcium carbonate (Equity development, 2005).

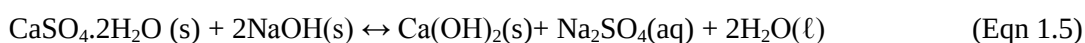
Calcium carbonate can be produced in the laboratory using the Merseburg process. This involves the reaction between calcium sulphate dihydrate and ammonium carbonate (Abbas, 2011), as shown in Equation 1.2

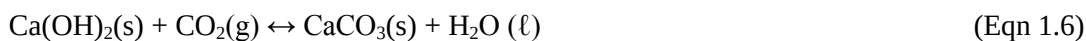


Calcium carbonate can also be made by direct mineral carbonation of calcium oxide in an aqueous solution (Koukouzas et al, 2007). Water is firstly added to calcium oxide to form a calcium hydroxide solution. The calcium hydroxide solution is then carbonated with CO₂ to precipitate calcium carbonate as shown by Equations 1.3 and 1.4



Another mineral carbonation process from which calcium carbonate can be produced industrially involves the reaction between calcium sulphate dihydrate, the mineral mainly found in phosphogypsum, with NaOH and CO₂ (Cardenas-Escudero et al, 2011) as shown by the chemical equations below:





In the first reaction of this process (Eqn 1.5), phosphogypsum reacts with sodium hydroxide to produce Ca(OH)_2 and $\text{Na}_2(\text{SO})_4$. The calcium hydroxide produced is then made to react with CO_2 in water to produce CaCO_3 during the second reaction of the process.

1.4.2 Applications for calcium carbonate

Calcium carbonate finds its use in several fields. It is used in the manufacture of paper and plastic, in the treatment of water, in the production of cement as well as in the metallurgy of iron (Railroad Industries Incorporated 2010; Zumdahl and Zumdahl, 2006).

Calcium carbonate is commonly used in the paper industry where it serves as filler and/or pigment and it accounts for as much as 50% of the paper while in the plastic industry, it is used in rigid PVC, rubber, latex sealants and adhesives where it accounts for less than 5% of a product's mass (Railroad Industries Incorporated 2010).

In the treatment of water, calcium carbonate is used to remove impurities and acidity contained in water, using water and sewer treatment plants, where it has the advantage to be used in its natural form and does not need to be ground very finely (Railroad Industries Incorporated 2010).

Calcium carbonate is also used in cement as a filler to increase the durability and aesthetic appeal of concrete (Railroad Industries Incorporated 2010)

Calcium carbonate is used to purify metals for use in construction applications. In the metallurgy of iron, calcium carbonate is part of the raw materials used during the refining of siderite (FeCO_3). Calcium carbonate loses CO_2 in the furnace to combine with SiO_2 and other impurities to form a slag which consists mostly of molten calcium silicate and alumina (Al_2O_3) (Zumdahl and Zumdahl, 2006) as shown by Equation 1.7:



1.4.3 Demand for calcium carbonate

Demand and production of calcium carbonate are growing in Asia as the more traditional market, while Europe and North America face their own challenges. Asia is now the fastest growing

regional market for GCC and PCC because of the expansion of the Chinese paper and plastic sectors. According to the latest report from Roskill (2012), Asia consumed about half of the GCC and PCC global demand of 74 Mt in 2011, with China alone consuming over 20% (PR Newswire 2010)

The overall world demand for GCC and PCC is expected to rise by more than 3% per year from 74 Mt in 2011 to 90 Mt in 2016. The paper industry is expected to remain the leading market for both GCC and PCC until 2016. Growth in this market is estimated at 3.1% per year, with strong growth in Asia, due to a rise paper production and higher filler loadings (PR Newswire 2010).

In the plastic industry, growth in the world demand for GCC and PCC is expected to rise by 5% per year through to 2016, with 80% of this additional demand allocated to Asia. In China, over 100 Mt per year of new PVC capacity is planned to come on-stream over the next few years. By 2016, China and India are expected to account for more than 45% of the world PVC demand (PR Newswire 2010).

According to the Department of Minerals and Energy through their report published in 2005, carbonates in South-Africa are used in five principal applications: cement (58%), aggregate construction (13%), metallurgical (11%), agriculture (6%) and lime manufacture (6%). Smaller market places include: fillers, refractories, paper pulping, chemical manufacture, sugar processing, paint and glass applications, which represent less than 5% of the total applications.

The reserves of local carbonate deposits in South-Africa are extremely large. A reserve base of 2.17 billion tons has been calculated for active carbonate operations estimated to be sufficient for a minimum of 77 years. Eleven medium to large-scale mines have life of mine plans of over 100 years each. Several medium/high grade deposits have been searched in KwaZulu-Natal, Limpopo province and the Western Cape, although continuity and consistency have not been determined (Department of Minerals and Energy of South-Africa, 2005).

The local GCC products have existed since the 1950's. Its brightness improved over the years from an initial 90-92% to 98-99%. The production of fine fractions of GCC has added to the appeal of such high-purity products. The current GCC volumes exceed 416 kiloton per annum, with all fine-grade products with particle sizes below 10 μm , representing about 25% of total GCC sales while ultra-fine grades with particle sizes less than 2 μm represent about 13% of total GCC sales (Department of Minerals and Energy of South-Africa, 2005).

The same report (Department of Minerals and Energy of South-Africa, 2005) stated that research have been conducted on the production of precipitated calcium carbonate (PCC) from impure CaO using the Calcitech method, which permits the formation of the narrowest particle size distribution of PCC. In this method of production of PCC, carbide lime is dissolved with water in a digester along with a proprietary promoter which selectively dissolves the calcium, leaving the impurities as insoluble solids which are then removed. The pure calcium solution is then made to react with CO₂ in a reactor to precipitate calcium carbonate (Equity development, 2005).

1.4.4 Structure and morphology of calcite

Calcite has a hexagonal structure which consists of alternating layers of calcium and carbonate groups perpendicular to the c-axis with interionic bonding between layers. Within a layer, carbonate groups are all co-planar with the same orientation. Consecutive layers are rotated 180° with respect to the layers above and below. If the conformation of a cleavage surface is consistent with the mineral's bulk structure, it should consist of alternating rows of calcium (Ca²⁺) and carbonate (CO₃²⁻) groups. All CO₃²⁻ groups should be inclined to the plane in such a way that one oxygen atom (O) lies above it, one in it and one below it (Alan et al, 1992).

Furthermore, the morphologies of calcite particles are numerous. It can adopt spherical, plate-like or even needle-like morphologies with a corresponding increase or decrease in diameter. Such morphologies are influenced by factors such as impurities, degree of supersaturation and the temperature of formation.

Wen et al (2002) suggested that the morphology of calcite crystals could be influenced by factors such as the concentration of Ca(OH)₂ and CO₂ and the temperature. They found that an increase in the initial concentration of Ca(OH)₂ resulted into the change in the shape of crystals. These changed from regular plate-like crystals to spherical shapes when the concentration of Ca(OH)₂ was varied from 0.10% (m/v) to 0.40% (m/v). An increase in the concentration of CO₂ from 25% (v/v) to 50% (v/v) also progressively changed the morphology of the calcite particles which departed from granular shapes to plate-like. When this concentration was then increased up to 100% (v/v), the plate-like particles became more uniform. A further increase in the concentration of CO₂ from 100 to 600ml/min made the particles bigger and thicker. They also found that the temperature influenced the morphology of the calcite particles in the sense that an increase in temperature from 20°C, where the particles were reported to have a regular plate-like morphology with bigger diameter but smaller thickness, to 40°C, resulted in the appearance of granular particles.

1.5 Study objectives

With the purpose of managing industrial wastes such as phosphogypsum, the overall objective of this study was to convert phosphogypsum wastes into calcium carbonate using two separate processes: (i) mineral carbonation and (ii) the Merseburg process and to compare them.

1.6 Thesis outline

Chapter one gives an overview of the path taken by phosphogypsum waste from its production using phosphate rocks, its disposal and impact on the environment as well as its treatment prior to its transformation into valuable products such as calcium carbonate. The formation, applications and demand for calcium carbonate worldwide, including in South-Africa, are furthermore discussed in this chapter.

Chapter two gives a description of the different analysis techniques used in this study, used to characterize the raw materials and the final products used and formed respectively.

Chapter three provides a physical and chemical description of the gypsum samples used during the study.

In chapter four, parameters such as the temperature, the time of reaction as well as the CO₂ flow rate required to transform phosphogypsum waste into calcium carbonate are identified and the products formed are characterized. In this section, an indirect mineral carbonation method, as developed by Cardenas-Escudero et al (2011), is followed on the gypsum samples characterized in chapter three.

In Chapter five, the indirect mineral carbonation method, as developed by Cardenas-Escudero et al (2011), and applied in chapter four is applied solely on the phosphogypsum sample described in chapter three. This is done by varying the mass of solid and volume of solution and using the same parameters such as the temperature, the time of reaction and the CO₂ flow rate identified in chapter four.

Chapter six is an attempt to transform phosphogypsum waste, obtained from OMNIA, into calcium carbonate using the Merseburg process (Chen and Chen, 1990). The products formed were characterized by a number of physical and chemical techniques.

Chapter seven is a general conclusion as well as some recommendations for future work.

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CHAPTER TWO: ANALYTICAL TECHNIQUES

2.1 Introduction

A combination of complementary analytical techniques was used to characterize solid and liquid samples in this study. These techniques are: Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), X-ray powder diffraction analysis (XRD), Thermogravimetric Analysis (TGA), Field Emission Scanning Electron Microscopy (FESEM), Particle Size Distribution (PSD), BET surface area analysis, Inductively coupled Plasma Mass Spectroscopy analysis (ICP-MS), Carbon and Sulphur analysis and Ion chromatography.

2.2 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for major element oxides (CGS, 2009b)

This analysis was performed to determine the major oxide elements which might be present in the samples.

The instrument used for this analysis was a Varian Liberty 200 ICP-OES which was equipped with a V-groove nebulizer and an acid resistant spray chamber. The instrument was optimized according to the manufacturer's specifications.

Terbium (Tb) was used as internal standard. It was added to samples and calibration solutions to correct for any instrument drifts and factors which can influence the physical introduction of sample.

For sample preparation, 0.5g of rock powder milled to below 75 microns and 1.5g of dried AR grade 12 : 22 X-ray Flux (35.3% Lithium Tetraborate : 64.7% Lithium Metaborate) was weighed into a 25 ml Platinum-Gold (Pt-Au) crucible and fused for approximately 30 minutes at 1000°C in a muffle furnace. The crucibles were cooled afterwards and the sample was then leached in 200ml of a 10% nitric acid (HNO₃) solution using a 250ml wide mouth, disposable, PET plastic bottle. The solution was stirred on a 15 position magnetic stirrer until complete dissolution of the glass beads. This solution was then diluted 5 times in volumetric flasks to which 1 ppm Terbium (Tb) was added as internal standard, filled up to the mark with ultra pure water and analyzed by ICP-

OES. Analysis of the solution should follow immediately as the solution could form a gel if standing for too long.

2.3 X-ray powder diffraction analysis (XRD)

X-ray powder diffraction is a semi-quantitative method of analysis used to determine the mineral compositions of samples by identifying only the crystalline compounds present in a solid sample (Skoog et al, 2007).

2.3.1 Principles

The sample to be analyzed is firstly micronised to a fine homogeneous powder in order to orient in every possible direction the enormous number of crystallites the solid sample may contain. A representative sub-sample is obtained and placed in a small disc-like container with its surface carefully flattened. The sample holder is then inserted in the instrument on one axis of the diffractometer and tilted by an angle θ (Skoog et al, 2007).

The sample is then radiated by x-ray photons coming from the x-ray tube through a Beryllium window. When reaching the sample, the x-ray photons can be completely absorbed by the sample, scattered when passing through it or reflected by it. When the x-rays striking the sample have the same wavelength than those being scattered by the sample; this results into coherent scattering. These x-rays then reach the sample by a deviation angle θ as shown in Figure 2.1. Coherent scattering between the rays and the sample occurs when Bragg's law, which is defined by Bragg's equation, is satisfied. These coherent rays are then deviated and dispersed by the crystalline compounds contained in the sample, via a deviation angle of 2θ and reach the detector for measurement (Skoog et al, 2007).

During analysis, each crystalline compound has a unique X-ray diffraction pattern. Therefore, if an exact match is found between the pattern of an authentic sample and an unknown, identification of the unknown is certain (Skoog et al, 2007).

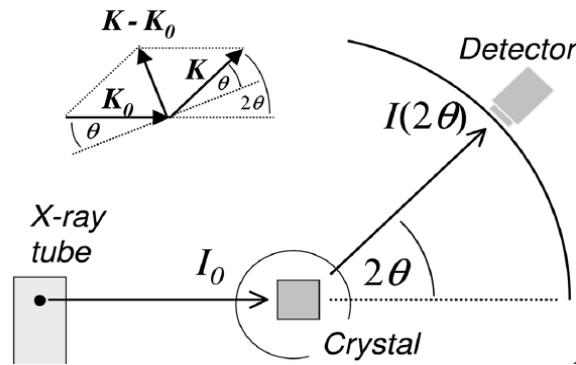


Figure 2.1: X-ray diffraction (Birkholz, 2006)

$$\text{Bragg's equation: } n\lambda = 2d \sin\theta \quad (\text{Eqn 2.1})$$

Where:

d represents the interplanar distance of the crystal.

θ is the angle which the ray beam strikes the crystal surface at.

λ is the wavelength of the incident beam.

n is an integer.

2.3.2 Instrument and identification

For all the XRD analyses performed in this study, the British Standard for non-destructive testing of polycrystalline and amorphous materials (XRD: BS EN 13925 - 2003) was used. Each measurement was done using a Bruker DS Advance instrument, coupled with 2.2 KW Cu long fine focus tube (Cu $K\alpha$, $\lambda = 1.54060$) and 90 position sample changer, and set with a LynxEye detector with 3.7° active area. Samples were scanned with a 2θ ranging from 2 to 70° at a speed of 0.02° 2θ steps/3 sec and generator settings of 40 kv and 40 mA.

The identification of mineral phases was done using the Bruker DIFFRACplus EVA evaluation program; and the PDF-2 release in 2006 from the ICDD (JCPDS) inorganic/organic database was used for phase searching. The Rietveld method was applied using the DIFFRACplus TOPAS software for quantification purposes with accuracy in the range of $\pm 1\%$; the different structure databases were the Cambridge Structure database (CSD), the Inorganic Crystal Structure Database (ICSD) and the TOPAS structure database obtained from the instrument software supplier.

2.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a technique used to determine and quantify the composition of a sample by measuring the weight of the sample against the temperature or the time.

2.4.1 Principles

The sample is placed in an inert pan and heated at a constant heating rate in an environment which consists of an inert or reactive gas.

During the analysis, the changes in weight of the sample are measured against the time or the temperature and presented as a graph. Each change in weight of the sample is represented by a step on the graph and each change occurs over a specific range of time or temperature and represents a specific sample composition over that range (Gabbot, 2008).

In humidity controlled experiments, the increase in weight of the sample can be due to the uptake of volatiles such as water. If the environment of the analysis is air or oxygen, the decrease in weight of the sample can be due to the evaporation of volatile elements such as water contained in the sample, or due to an oxidation reaction of metals or an oxidative decomposition of organic substances contained in the sample. If an inert gas such as nitrogen (N_2) is composing the atmosphere, the decrease in weight of the sample is simply due to a thermal decomposition which is accompanied by the formation of gaseous products (Gabbot, 2008).

Figure 2.2 represents the different types of decomposition steps which might occur during a thermogravimetric analysis.

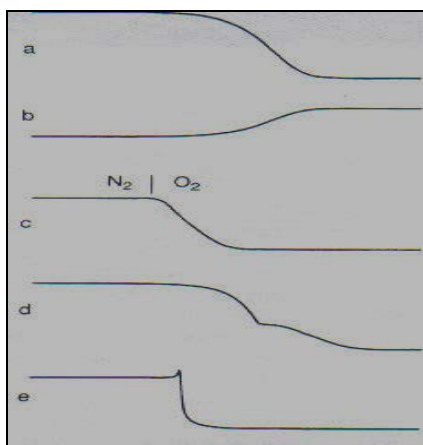


Figure 2.2 : TGA curves of different chemical reactions (Gabbot, 2008)

Curve (a) shows a thermal decomposition accompanied with the formation of volatile reaction products. Curve (b) shows an increase in weight of the sample, and represents the oxidation reaction of metals characterized by the formation of non-volatile oxides. Curve (c) shows the combustion of carbon black, on switching from an environment made up of an inert gas, N_2 , to an environment with a reactive gas, (O_2). Curve (d) is described as a multi-step decomposition while curve (e) refers to an explosive decomposition with recoil effect (Gabbott, 2008).

Figure 2.3 shows the variations of the weight percentage of calcium oxalate monohydrate, ($CaC_2O_4 \cdot H_2O$) with temperature during a thermogravimetric analysis.

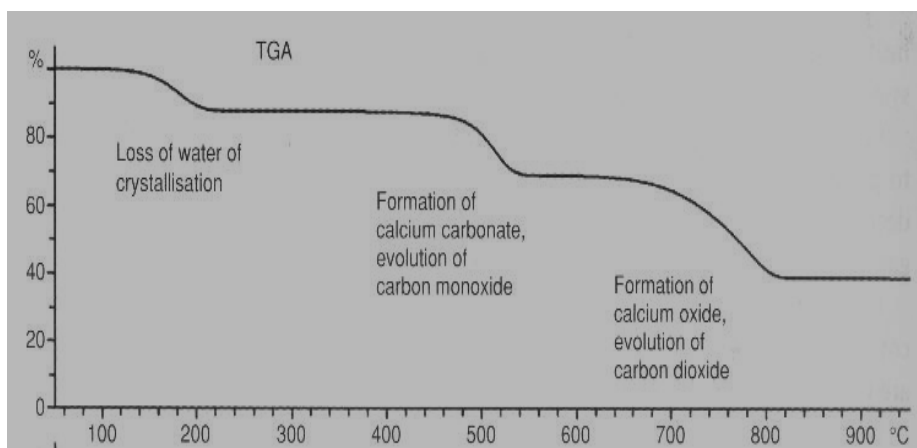


Figure 2.3 : A thermograph: Stepwise decomposition of calcium oxalate monohydrate (Gabbot, 2008)

This figure shows that the first weight loss of the sample occurs below 200°C with the loss of water of crystallization contained in the molecular structure of the sample to produce CaC_2O_4 . The second weight loss occurs between 380°C and 600°C with the release of carbon monoxide (CO) from the CaC_2O_4 formed to produce calcium carbonate (CaCO_3). The last weight loss occurs between 620°C and 820°C with the release of carbon dioxide (CO_2) from previously formed calcium carbonate to produce calcium oxide, CaO (Gabbot, 2008).

The thermogravimetric analyses performed in this study were done using a simultaneous TGA / SDTA 851^e METTLER TOLEDO instrument, with alumina pan of size 150µl. For each analysis, a sample mass of about 20 mg was used. A heating rate of 10°C/min was used in an air atmosphere with flow rate of 50ml/min. The maximum heating temperature during the analyses was defined according to the capacity of the instrument.

2.4.2 TGA coupled to Fourier Transform Infrared Spectroscopy (TGA-FTIR)

FTIR can be used for the identification of gases (Lephardt and Fenner, 1980). A combination of TGA with FTIR permits a complete analysis of samples with the quantitative weight data from TGA and the identification of the gases evolved by FTIR (Wieboldt et al, 1988).

During the analysis, the gases evolved in the thermogravimetric analysis experiment are swept by a heated transfer line to an FTIR spectrometer. The infrared spectra of the evolved gases are then recorded and compared to a database library for identification of the species being given off (Akinade et al, 1994).

The TGA-FTIR analyses of samples in this study were performed using a Perkin Elmer TGA 4000 coupled with a Perkin Elmer Spectrum 100. The samples in the TGA were exposed to a heating rate of 10°C/min between 35°C and 950°C using a nitrogen flow rate of 20ml/min. The transfer line was kept at a constant temperature of 225°C to avoid condensation of the gases. The optics used in the FTIR instrument was potassium bromine with a sample pathlength of 10cm.

2.5 Field Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscopy (FESEM) is a technique which uses electrons to obtain morphological and topographic information about a sample. Information about the sample such as its morphology, texture, chemical composition and crystallographic information can be obtained by scanning the sample with a high-energy beam of electrons (Skoog et al, 2007).

However, the analysis requires the sample to be conductive. Non conductive samples are coated with a thin layer of conductive materials using a device called a sputter coater.

2.5.1 Sample preparation

The samples to analyze were spread on carbon tabs which were in turn fixed over a carbon tab mounted on an aluminium plate. Nitrogen gas was then blown over the carbon tabs containing the samples to remove any excess sample not sticking to the tabs. A picture of the prepared plate is shown in Figure 2.4. The aluminium plate containing the filled carbon tabs was then placed in a carbon sputter coater (Emitech K950X) to which 4 coatings of carbon was applied to make the samples conductive for imaging purposes. A picture of the carbon sputter coater is shown in Figure 2.5 and that of the coated plate in Figure 2.6. After coating, the aluminium plate was inserted in the Field Emission Scanning Electron Microscope (Zeiss Ultra Plus) shown in Figure 2.7.

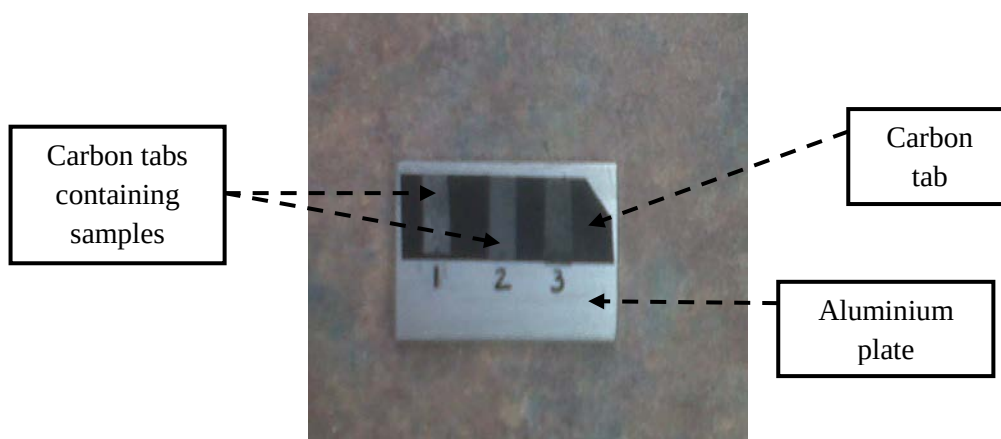


Figure 2.4: Carbon tabs with samples mounted on an aluminium plate before being coated.



Figure 2.5 : Emitech K950X Carbon coater used for coating the samples

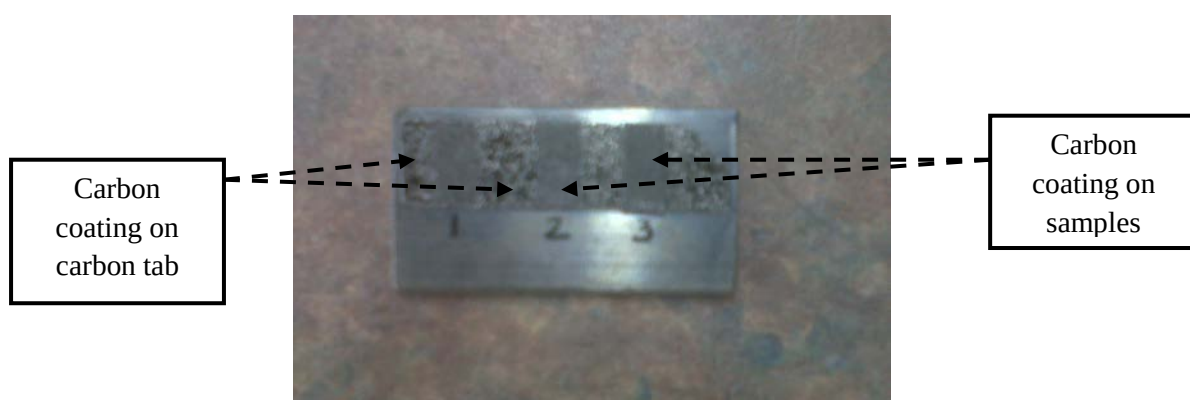


Figure 2.6 : Carbon tabs with samples mounted on an aluminium plate after being coated

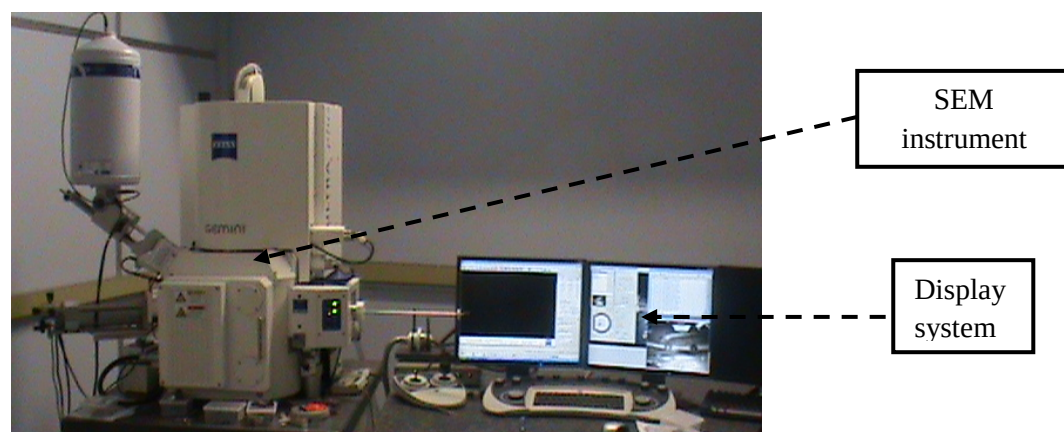


Figure 2.7 : Zeiss Ultra Plus Field Emission scanning electron microscope instrument used for imaging

2.6 Particle Size Distribution (PSD)

Particle sizing is a measurement technique used to determine and report the size range of the particles of powder samples.

2.6.1 Principles

The particle sizes of the sample are measured by laser diffraction which allows measuring the particle size and size distribution from $0.02\mu\text{m}$ to $2000\mu\text{m}$. During the analysis, particles of a sample are passed through a laser beam and scatter light at an angle that is directly related to their respective size. Large particles scatter light at narrow angles with high intensity while small particles scatter the light at wider angles and with low intensity (Skoog et al, 2007).

The particle size distributions are then calculated by comparing the scattering pattern of a sample with that of an appropriate optical model. The optical model in used in present days is the Mie theory, which allows measuring the size of all particles: small, large, transparent or opaque by predicting their scattering intensities (Skoog et al, 2007).

The results of this analysis are volume based, and are displayed on a frequency curve where the volume in percentage is plotted against the particle size (μm). The presence of a peak in the graph indicates the presence of particles with a specific size within the sample. If, for example, the result of a distribution size analysis indicates that 10% of the distribution is in the size category (8.97-

9.75) microns, this means that the total volume of all particles with diameters in the range of (8.97-9.75) microns represents 10% of the total volume of all particles in the distribution.

The following calculated diameters assist in interpreting the results of a particle size distribution analysis on a frequency curve.

1. **D (v, 0.5)** , also known as the Mass Median Diameter (MMD), is the size in microns at which 50% of the sample is smaller and 50% is larger.
2. **D (v, 0.1)** is the size of the particles below which 10% of the sample lies.
3. **D (v, 0.9)** gives the size of particles below which 90% of the sample lies.
4. **D [4, 3]** is the Volume Weight Mean Diameter and represents the diameter of theoretical spherical particles occupying the same volume as the original particles.
5. **D [3, 2]** also known as the Sauter Mean Diameter, is the Surface Area Mean Diameter and represents the diameter of theoretical spherical particles that have the same surface area as the original particles.

2.6.2 Instrument

The particle size distribution for each sample was obtained by laser diffraction (Malvern Mastersizer 2000 fitted with a Hydro 2000G dispersion unit, Malvern Instrument Ltd, Worcester, UK). Scattered light data were recorded from 2000 to 5000 snapshots of 10 μ s. A polydisperse mode of analysis and a refractive index of 1.533 with an adsorption of 0.1 were chosen. Calcium carbonate samples were analysed using a refractive index of 1.57235 and an absorption index of 0.1. Size data collection was performed at constant obscuration in the range 10-20%.

2.7 The Brunauer, Emmet and Teller (BET) surface area analysis

The BET surface area analysis was performed on samples in order to measure the specific surface area they will make available when involved in a reaction.

2.7.1 Adsorption (Lowell, 2006)

Adsorption is a surface-based process referring to the adhesion of molecules, atoms or ions from a solid, gas or liquid to a surface. The molecules, ions, liquid or gas are defined as adsorbate while

the solid surface is defined as the adsorbent. We distinguish two types of adsorption processes: chemical adsorption and physical adsorption.

Chemical adsorption or chemisorption is an irreversible process where the adsorbate is chemically bonded to the adsorbent. It occurs at temperatures above the critical temperature of the adsorbate. It requires activation energy and is restricted to a single layer, making the adsorbate more localized on the surface.

Physical adsorption on the other hand is a reversible process and takes place when an absorbable gas is brought in contact with the surface of the adsorbent. Unlike chemisorption, it can lead to the coverage of the surface of the adsorbent by one or more layers of adsorbate and no activation energy is required, making it suitable for the calculation of surface areas of samples.

Adsorption is described through isotherms, which refers to the amount of adsorbate on the adsorbent as a function of its pressure in the case where the adsorbate is a gas. If the adsorbate is a liquid; it is described at constant temperature.

2.7.2 BET surface area

The BET is a gas adsorption procedure used to measure the surface area of ultra-fine powders and porous materials (Stanley-Wood and Lines, 1992).

Before measuring the surface area of the sample, an empty sample cell to which was inserted a piece of cotton wool, was calibrated (Gregg and Sing, 1982). The calibration of the empty cell is a process lasting about 35 minutes.

The sample cell, containing the sample, is then inserted simultaneously in the instrument and a heating mantle is used for a degassing process which in the case of our experiments lasted 2 hours at 80°C. This process, which is a requirement for measuring the surface area of the sample, should remove all previously physisorbed material from the surface of the adsorbent; including adsorbed water (Gregg and Sing, 1982). The surface area of the sample is then measured in units of $\text{m}^2 \cdot \text{g}^{-1}$ by the instrument.

The BET equation is summarized by the mathematical equation below:

$$\left[\frac{P}{n(P^\circ - P)} \right] = \left[\frac{1}{(n_m C)} \right] + \left[\frac{(C - 1)}{(n_m C)} \right] \cdot \left[\frac{P}{P^\circ} \right] \quad (\text{Eqn 2.1})$$

n is the amount of adsorbed at P/P^0 , P/P^0 is the relative pressure, n_m is the amount of gas or solute required to cover the surface with a complete single layer of adsorbed molecules and C is an empirical constant. It follows that there should be a linear relation between $P/n(P^0 - P)$ and P/P^0 for the BET plot (Stanley-Wood and Lines, 1992)

The surface areas of the samples used in this study were determined using a NOVA Quantachrome 1000e instrument, a computer equipped with NOVWIN software, liquid nitrogen, nitrogen gas, an analytical balance, a sample cell, a sample and a piece of cotton wool. The instrument was connected to the computer, and nitrogen gas which was used during the whole process.

2.8 Inductively Coupled Plasma Mass-Spectrometry analysis (ICP-MS)

Inductively coupled plasma mass spectrometry, known as ICP-MS, is a type of mass spectrometry detecting metals and non-metals present in very low concentrations: part per million (ppm) or part per trillion (ppt).

The determination of those elements with atomic masses in the range of 7 to 250 is achieved by ionizing the sample with inductively coupled plasma, and then by using a mass-spectrometer for the separation and the quantification of the ions. The ions from the plasma are extracted into the mass spectrometer through a series of cones, usually a quadrupole. They are then separated on the basis of their mass-to-charge ratio, and the detector receives an ion signal proportional to the concentration of the element identified (Skoog et al, 2007).

Figure 2.8 shows the different components of a commercial ICP-MS system.

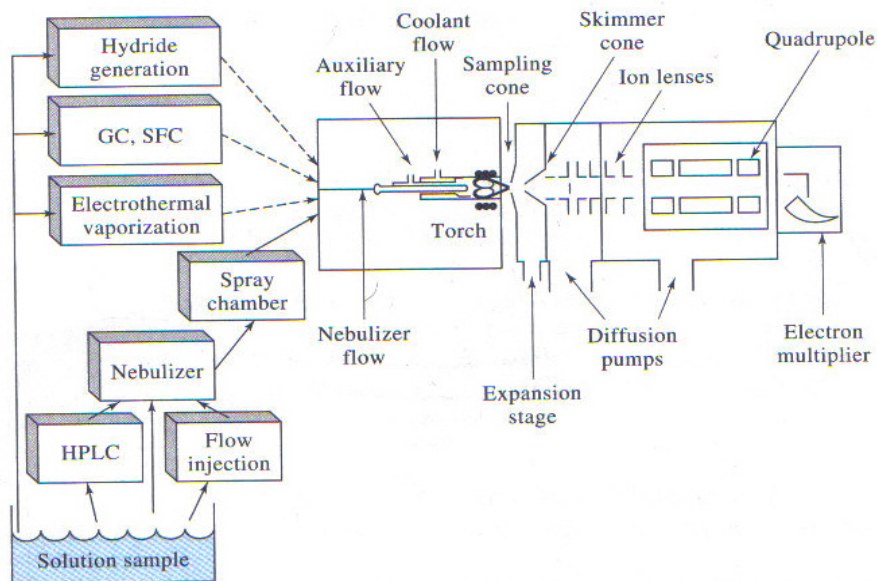


Figure 2.8 : Components of a commercial ICP-MS system (Skoog et al, 2007)

The solid lines show the introduction of liquid samples; firstly by High-performance liquid chromatography or flow injection. The sample is then inserted into the nebulizer, which conveys it into the chamber spray and finally inserts it into the system. Gaseous samples are introduced into the system via hydride generation, gas chromatography, and supercritical fluid chromatography, or by electrothermal vaporization (Skoog et al, 2007).

In this study, the following analyses were performed: 1. ICP-MS analysis of the solid sample prepared by a fusion method to determine the presence and concentrations of rare earth elements in the sample; 2. ICP-MS analysis of a solution prepared by digesting the solid sample with a mixture of 4 acids, to determine the major elements in a sample; 3. ICP-OES analysis of suitably prepared sample to determine the major element oxides and 4. Ions chromatography to determine water soluble anions such as fluorine (F^-), chlorine (Cl^-), nitrite (NO_2^-), bromine (Br^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), and sulphate (SO_4^{2-}). These methods are discussed in more details below.

2.8.1 ICP-MS for rare earth elements (REE) (CGS, 2006)

This analysis was used to determine the concentrations of the different rare earth elements a sample might contain.

It was performed using a fusion method. A PerkinElmer SCIEX ELAN[®] 6000 ICP-MS system, equipped with a standard cross-flow nebulizer and a Scott-type Rytan[®] double-pass spray chamber was used for the analysis, along with tygon peristaltic pump tubing and nickel sampler & skimmer cones. Parameters such as calibration, lens voltages, dual detector and Autolens[™] optimizations were optimized according to the manufacturer's recommendations.

Iridium was used as an internal standard, as it is the least likely element to be present in the sample solutions used during this study. It was added to samples as well as to calibration solutions for the needs of corrections of instrument drifts and other factors likely to influence physical sample introduction.

For sample preparation, 0.5g of sample was milled to below 75 microns, and 1.5g of dried AR grade 12:22 X-ray Flux (35.3% Lithium Tetraborate : 64.7% Lithium Metaborate), was weighted into a 25ml Pt-Au (5%) crucible and fused at 1000°C for approximately 30 minutes in a muffle furnace. The crucibles were allowed to cool, and the sample was then leached in a 10% HNO₃ solution in 250ml wide- mouth disposable polyethylene (PET) plastic bottles. The solution was continuously stirred on a 15 position magnetic stirrer until complete dissolution of the glass beads was reached after approximately 2 hours. The solution was then diluted directly into 16ml polypropylene (PP) autosampler tubes using ultra pure water containing the internal standard (iridium) in a 2% HNO₃ matrix and analyzed by ICP-MS. The final dilution factor was 10000.

2.8.2 Inductively Coupled Plasma 4-acid Method (CGS, 2011).

This analysis was performed on samples to determine the concentrations of the different major and trace elements they might contain once digested using a mixture of 4 acids (nitric, hydrofluoric, hydrochloric and perchloric acid).

The instrument used for this analysis was a PerkinElmer SCIEX (Concord, Ontario, Canada) Elan[®] 6000 ICP-MS system which was equipped with a standard cross-flow nebulizer and a Scott-type Rytan[®] double-pass spray chamber. The introduction of samples was done using a Type F autosampler tray capable of holding 150 samples vials, measuring 16ml each, via a Tygon[®]

peristaltic pump tubing on a Perkin Elmer AS91 autosampler. The instrument was optimized on a regular basis according to the manufacturer's recommendations

For the digestion of samples, high purity acids (analytical grade) were used: Perchloric acid (HClO_4), hydrochloric acid (HCl), nitric acid (HNO_3) and hydrofluoric acid (HF). Ultra pure water (18.2 M Ω) was used in the preparation of standard solutions as well as for the final dilution of digested samples.

The standards of this analysis were prepared using 2% (v/v) nitric acid (HNO_3) to match the sample acid matrix. 20ppb Indium (isotope 115) and 30 ppb Iridium (isotope 193) were used as internal standards to correct drift in elements in the mass range of 7 to 130 and for heavier metals (Ba to U) respectively. They were also added to samples and calibration solutions for instrument drift corrections and factors which can influence the physical introduction of the sample. The efficiency of the digestion was monitored by the recovery of elements from included certified reference materials GSD 09 and GSD 12; the repeatability of the sample preparation step was monitored using certified reference materials and in-house check sample results.

Sample preparation was performed as follows: 0.2g of sample was weighed exactly using a PFA Savillex container, and digested using 1ml of HClO_4 , 2 ml of HNO_3 , 2ml of HF and 3ml of HCl . The samples were firstly heated to almost dry at 110°C on aluminium heating blocks, then at 160°C until complete evaporation of all acid. On the next day, an extra 1 ml of HClO_4 was added to the evaporated sample which was then heated again at 160°C overnight. After the digestion was done, the samples were allowed to cool and the residue was dissolved using 1 ml of HNO_3 and 2 drops of H_2O_2 . This was followed by the addition of 19 ml of 1% HNO_3 to the sample container which was capped and heated at 100°C for 30 minutes in an oven. A 0.5ml aliquot of the digested sample was pipetted into a 16ml propylene tube to which 9.5ml of Indium- and Iridium-solution in 2% (v/v) HNO_3 was added with a bottle-top dispenser. The total volume was 10ml (a total dilution factor of 1: 2000), to reach the concentrations of 20ppb and 30ppb for Indium and Iridium respectively. Several IGGE certified reference materials (Institute of Geophysical and Geochemical Exploration, China) (GSD 09 – GSD 12) were analyzed with each batch of samples, as well as in house test soils and total method blanks.

2.9 Carbon and Sulphur analysis

Carbon and Sulphur analysis is used to determine the concentration of total carbon and sulphur in solid samples.

For the analysis, the sample is weighed in a ceramic crucible to which iron and tungsten chips were added, mixed and combusted in a stream of oxygen. During the combustion, carbon which could be present as carbonate, graphite or organic carbon combines with the oxygen to be converted into CO_2 , while sulphur, whose presence could be identified as sulphate, sulphide or elemental sulphur is converted to SO_3 when combining in turn with oxygen. The concentrations of the gases formed CO_2 and SO_3 are then detected and measured using four infrared absorption detectors (CGS, 2009a). From the concentrations of gases measured, the amounts (in weight %) of carbon (C) and sulphur (S) present in the sample are calculated.

The analysis was performed using an Eltra CS 800 Double Dual Range system using between 50 to 200mg of milled sample with particle sizes less than 75 microns. The Eltra instrument was calibrated using certified carbon and sulphur standards, (Euronorm-CRM 484-1 Whiteheart malleable iron and Leco N° 501-502); the concentration of the unknown sample was then measured by comparison with the calibration curve.

2.10 Ion chromatography for water soluble anions (CGS, 2009c)

This analysis was used to determine the concentrations of water-soluble anions samples might contain.

The anions analysis was performed using a Dionex QIC Ion Chromatograph which was equipped with an automated sampler, an IonPac AG4A guard column and an IonPac AS4A analytical column respectively. An eluant made of carbonate/bicarbonate was used along with a weak sulphuric acid regenerant solution.

Ultra pure water with a conductivity of 18.2mΩ/ cm was used in the preparation and dilution of standard solutions and samples respectively. Ultra pure salts which were firstly oven-dried overnight were used for the preparation of calibration standard.

For the preparation of calibration standards, specific amounts of salts containing NaF, NaCl, NaNO_2 , KBr, NaNO_3 , KH_2PO_4 and K_2SO_4 , the anions of interest, were weighed and dissolved in

500ml volumetric flasks. Aliquots of these solutions were further diluted to obtain the required calibration solution containing specific concentrations of 2ppm of F^- , 5ppm of Cl^- , 5ppm of NO_2^- , 20ppm of Br^- , 30ppm of NO_3^- , of PO_4^{3-} and 30ppm of SO_4^{2-} .

1.0g of the sample to be analyzed was weighed into 50ml polypropylene centrifuge tubes to which were added 20ml of ultra-pure water. The samples were agitated for 30 minutes on a roller-shaker then centrifuged for 15 minutes. The leachate was further diluted if necessary (to make sure that the conductivity peak heights fall within the detection range of the chromatograph) and analyzed for the anions listed above.

2.11 Experimental equipment

The experimental set up used to perform all the chemical reactions related to this study is shown in Figure 2.9. The set up consists of a 500ml flat-bottom flask with 5 necks, a waterbath, a carbon dioxide flow meter (Arlborg flow meter) with a maximum flow rate of 305ml/ min, an overhead stirrer, and a LABEX pH probe connected to an EUTECH INSTRUMENT pH / Ion 510 Bench pH/Ion/mv meter with a temperature probe.

The round bottom flask was immersed in a waterbath whose temperature was regulated by the temperature regulator. The overhead stirrer was inserted permanently, through one of the five-necks located on top the flask for stirring purposes. The pH-electrode and the temperature probe were also inserted on a permanent basis in the flask through two of the four necks located on of the flask. Another neck was closed on a permanent basis using a rubber stopper, while the last neck was either used to bubble carbon dioxide during the carbonation reaction or was closed using a rubber stopper.



Figure 2.9: Experimental equipment used to perform reactions in this study

2.12 References

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CHAPTER THREE: CHARACTERIZATION OF PHOSPHOGYPSUM

3.1 Sampling

A representative sample (*ca.* 20 kg) of phosphogypsum waste (PG) was collected from the phosphoric acid plant of Omnia fertilizer Ltd, located at Phokeng (near Rustenburg, North-West province, South Africa). PG is generated as a waste stream during the production of phosphoric acid (H_3PO_4) and is subsequently stockpiled on large land areas on the production site. As it comes from the production line, the PG pile is wet. Water seeping from the heap is collected in dams and pumped back to the heap to minimize the spreading of drying gypsum over large areas and distances which may be caused by strong winds. Figures 3.1 and 3.2 are photographs showing Omnia's phosphoric acid plant in Phokeng, and the PG dump respectively.



Figure 3.1: Photograph showing the phosphoric acid production plant of Omnia at Rustenburg, South-Africa (source: Omnia)



Figure 3.2: Photograph showing the phosphogypsum stockpile at OMNIA's phosphoric acid production plant in Rustenburg (source: Omnia)

Figure 3.2 shows how PG is stockpiled and is kept compact on the production site of Omnia. A small proportion of PG is sold for agricultural soil treatment, essentially as a source of calcium, sulphur and phosphorus which remains from the phosphoric acid process.

In addition to the PG sample provided by Omnia, two additional gypsum samples originating from different sources were also collected for comparison purpose:

- 'Synthetic gypsum' (SG) supplied by Merck PTY Ltd (EMSURE, calcium sulphate dihydrate);
- 'Natural gypsum' (NG), originating from the Maskam mine (Rhynsdorp, South Africa) and kindly provided by BPB Gypsum PTY Ltd.

Prior to analysis, the PG sample was firstly dried in a drying room at 25°C for 24 hours and then divided into 10 representative homogeneous sub-samples using a rotary splitter machine (Dickie and Stockler, South-Africa). The setup of the rotary splitter is shown in Figure 3.3. The NG sample contained agglomerates of the fine primary particles and was therefore mechanically sieved through a 150 μ m sieve; the sub-150 μ m fraction was characterized and subsequently used in all experiments.



Figure 3.3: Photograph showing the rotary splitter used for the splitting of phosphogypsum into representative homogeneous sub-samples.

3.2 Physicochemical characterization of phosphogypsum, synthetic gypsum and natural gypsum

Figure 3.4 shows the three type of gypsum samples collected for the purpose of this study. From top to bottom, they are phosphogypsum, synthetic gypsum, also denominated as “*Merck gypsum*” both characterized by a white color and lastly natural gypsum which is slightly brown in color. By touching the samples by hand, phosphogypsum appeared wet, while natural gypsum and Merck gypsum seemed to be dry samples.



*PG: Phosphogypsum; +SG: Synthetic gypsum; #NG: Natural gypsum

Figure 3.4: Samples of raw phosphogypsum, synthetic-gypsum and natural gypsum

The moisture content of the gypsum samples was determined gravimetrically before and after drying the samples at 25°C for 24 hours in a drying room. The samples were not dried at higher temperatures since heat treatment would have caused the removal of structural water (*i.e.* dehydration) and the subsequent conversion of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) into bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) and/or anhydrite ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) (Christensen et al, 2008). The analyses were done in triplicate for each sample and the results of the average moisture content of these samples are reported in Table 3.1 below.

Table 3.1: Summary of the moisture content present in each gypsum sample.

Sample	Moisture content (%)
Phosphogypsum	9.84 ± 0.34
Synthetic-gypsum	0.37 ± 0.12
Natural gypsum	0.49 ± 0.01

Phosphogypsum was characterized by significantly higher moisture content than synthetic-gypsum and natural gypsum. This high moisture content is explained by the fact that water was pumped on the phosphogypsum stockpile on a regular basis to prevent its spreading in the air by atmospheric conditions such as strong winds. The two other gypsum samples contained little, if any, moisture.

The structural properties of the three samples were investigated using a combination of complementary techniques (*e.g.* elemental composition by ICP-MS and ICP-OES, mineralogical composition by XRD and TGA, carbon and sulphur content, particle size distribution, specific surface area, morphology by field emission scanning electron microscopy).

3.2.1. X-ray powder diffraction analysis (XRD)

The mineral composition of each gypsum sample was determined by XRD in order to determine, semi-quantitatively, the amounts of gypsum, bassanite, anhydrite and any other minerals which may be present in these samples. The results of these analyses are expressed as weight percentage (wt %) and are summarised in Table 3.2.

Table 3.2: XRD results of untreated phosphogypsum, synthetic gypsum and natural gypsum.

Minerals	Molecular formula	Synthetic-gypsum (wt %)	Phospho-gypsum (wt %)	Natural gypsum (wt %)
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	95	97	49
Bassanite	$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	5	2	47
Calcite	CaCO_3	-	-	2
Mica	$\text{KFeMg}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	-	<1	-
Sepiolite	$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$	-	-	<1
Palygorskite	$(\text{Mg, Al})_2(\text{Si}_4\text{O}_{10})(\text{OH}) \cdot 4\text{H}_2\text{O}$	-	-	<1
Quartz	SiO_2	-	-	<1

Phosphogypsum and synthetic gypsum shared a similar mineralogy, with gypsum representing the dominant mineral phase (> 95%), and bassanite being present as a minor phase (< 5%). Phosphogypsum also contained a small amount of mica (*ca.* 1%), which could originate from the phosphate ore used during the phosphoric acid process. On the other hand, the natural gypsum sample contained similar amounts of gypsum and bassanite (49% and 47% respectively), with traces of other minerals also being present. These trace minerals could also find their origin from the clay soils and ore body from which natural gypsum was mined.

In previous studies, Rzeczycka et al (2010) found that their phosphogypsum (Wizów-Poland) consisted mainly of gypsum, bassanite and anhydrite, which together made up about 95% of the mineralogy of the material. Aliedeh and Jarrah (2012) reported that phosphogypsum contained small amounts of many of the mineral impurities that accompany phosphate rock or that had been produced in the phosphoric acid production process. Tayibi et al (2009) added that the characteristics of phosphogypsum are often strongly influenced by the composition and quality of the phosphate ore.

The contents of gypsum and bassanite reported by XRD in the three samples were used to estimate the total amount of sulphur (expressed as wt % of SO_3) present in each of the gypsum samples. Similarly, the amount of CaCO_3 was used to calculate the amount of carbon present in the samples, which were expressed as wt % of CO_2 . It was assumed that no organic carbon was present in these samples, and that calcium carbonate would be the only source of carbon. This was done to compare the semi-quantitative XRD results to data obtained from other methods (e.g. carbon and sulphur

analysis), and will be referred to again later in this chapter in Section 3.2.2. The results are summarized in Table 3.3.

Table 3.3: Estimated carbon and sulphur contents in phosphogypsum, synthetic-gypsum and natural gypsum, as calculated from XRD data

Sample	CO ₂ (wt. %)	SO ₃ (wt. %)
Phosphogypsum	-	46
Synthetic gypsum	-	47
Natural gypsum	1	49

The calculated values of SO₃ in phosphogypsum and synthetic gypsum were similar, while in natural gypsum the amount of sulphur trioxide was slightly higher as a result of its high amount of bassanite. Furthermore, natural gypsum contained about 0.8% CO₂.

3.2.2. Carbon and sulphur analysis on phosphogypsum, synthetic gypsum and natural gypsum

In most mineral samples, carbon can be present in the form of organic carbon, carbonate and/or graphite, while sulphur can be found as sulphate, sulphur trioxide, sulphides or elemental sulphur. The results obtained from the carbon and sulphur analysis are summarized in Table 3.4 and represent the total content in carbon and sulphur.

Table 3.4: Measured carbon and sulphur in phosphogypsum, synthetic gypsum and natural gypsum, as determined using the Carbon and Sulphur analyser

Sample	C (wt %)	CO ₂ (wt %)	S (wt %)	SO ₃ (wt %)
Phosphogypsum	0.06 ± 0.04	0.2	19.72 ± 0.00	49.3
Synthetic-gypsum	0.02 ± 0.00	0.1	19.76 ± 0.11	49.4
Natural gypsum	0.41 ± 0.04	1.5	15.63 ± 0.34	39.1

The weight percentage of elemental sulphur in phosphogypsum (19.72%) corresponds to a weight percentage of 49.3% of sulphur present as sulphur trioxide (SO₃) in phosphogypsum, while in synthetic gypsum, the amount of elemental sulphur (19.76%) corresponds to a percentage of 49.4% SO₃. It appears that the amount of sulphur trioxide in phosphogypsum and synthetic gypsum are similar, 49.3% for phosphogypsum and 49.4% for synthetic gypsum compared to a value of 39.1% obtained for natural gypsum. These results are higher than the values obtained from the XRD results, from which the weight percentages of SO₃ calculated in phosphogypsum and synthetic gypsum were found to be 46 % and 47% respectively, except in the case of natural gypsum where the value obtained from XRD (49%) is higher than the value obtained from the Carbon and Sulphur analysis (39.1%). The difference between the estimated and measured values was expected since XRD is a semi-quantitative method.

3.2.3 Determination of anions in the gypsum samples by ion chromatography

Ion chromatography was performed to determine the anion content of the phosphogypsum and synthetic gypsum samples. The results are reported in Table 3.5.

Table 3.5: Concentration of anions in solution for the three gypsum samples (mg /kg).

Sample	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
Phosphogypsum	328	< 0.68	< 1	< 1.82	6	< 4.6	33418
Synthetic-gypsum	< 0.48	< 0.68	< 1	< 1.82	21	< 4.6	34157
Natural gypsum	n.d*	n.d	n.d	n.d	n.d	n.d	n.d

*n.d: not determined

In general, apatite is defined as fluorapatite (Ca₁₀(PO₄)F₂), hydroxylapatite (Ca₁₀PO₄(OH)₂) and chlorapatite (Ca₁₀(PO₄)Cl₂). Fluorapatite is characterized by the presence of fluorine in solution while hydroxylapatite and chlorapatite are characterized by the presence of hydroxyl and chlorine ions respectively. The presence of fluorine (F⁻ 328 mg/kg; Table 3.5) in phosphogypsum is an impurity from the apatite rock used in the phosphoric acid manufacturing process. This means that the phosphogypsum from OMNIA used in this study probably originates from a fluoroapatite rock used during the wet phosphoric acid process. When dissolved, all untreated gypsum samples

contain mainly sulphate ions as anions in solution due to the fact that they mainly consist of gypsum and bassanite.

Table 3.6: Relationship between sulphate from ion chromatography and sulphur trioxide contents

Samples	SO ₄ ²⁻ (ppm)	SO ₃ (wt %)
Phosphogypsum	33418	55.75
Synthetic-gypsum	34157	57.01
Natural gypsum	n.d*	n.d*

*n.d: not determined

From the different concentrations of sulphate determined from the ion chromatography analysis of the phosphogypsum and synthetic gypsum samples, the amount of sulphur present as sulphur trioxide in each one of them are expected to be 55.75% for phosphogypsum and 57.01% for synthetic gypsum. These weight percentages of sulphur as sulphur trioxide are higher than the values determined by the Carbon and Sulphur analysis, which was 49.30% for phosphogypsum and 49.40% for synthetic gypsum.

3.2.4 Field Emission Scanning Microscopy of phosphogypsum, synthetic gypsum and natural gypsum

Field Emission Scanning Electron Microscopy analyses were performed on phosphogypsum, synthetic gypsum and natural gypsum to determine the morphology of their particles. Representative FESEM images of the three gypsum samples at different magnifications are given in Figures 3.5 and 3.6.

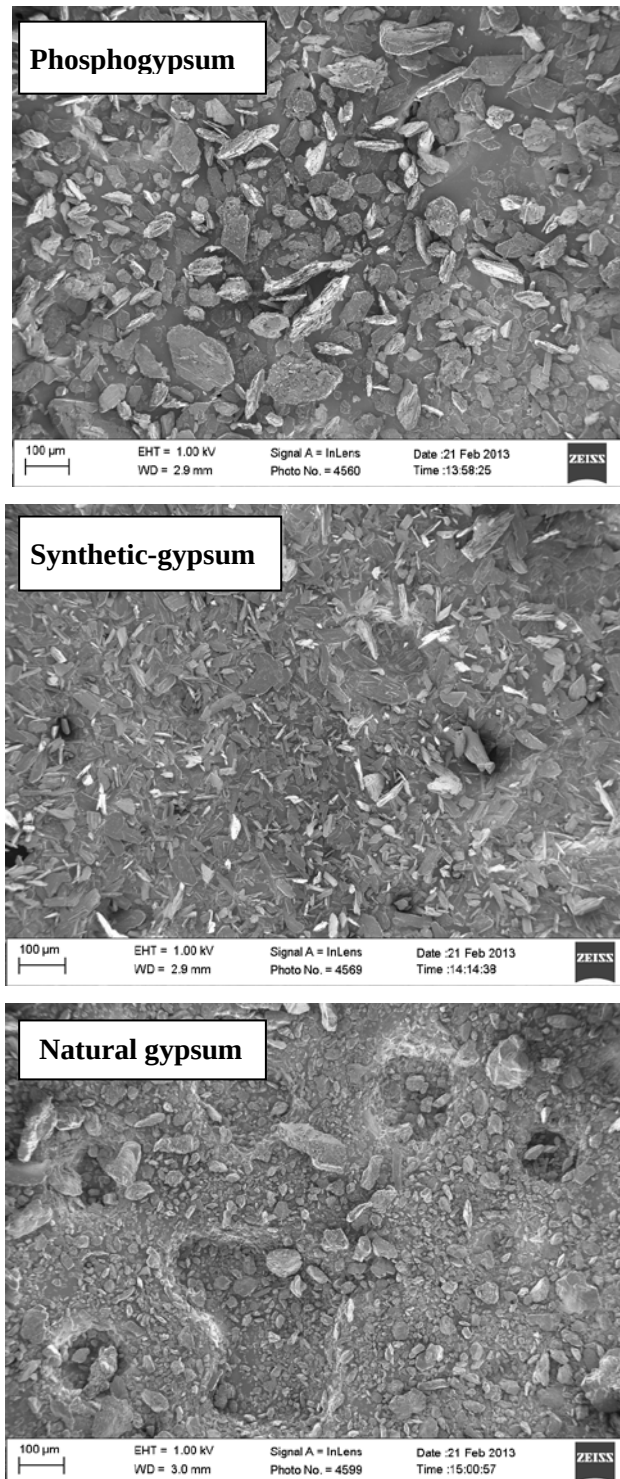


Figure 3.5: FESEM images of phosphogypsum, synthetic gypsum and natural gypsum particles.

Figure 3.5 above is an overview of the morphology of phosphogypsum, synthetic gypsum and mineral gypsum. The micrographs show that there is a significant difference in the morphology of the particles of the different gypsum samples.

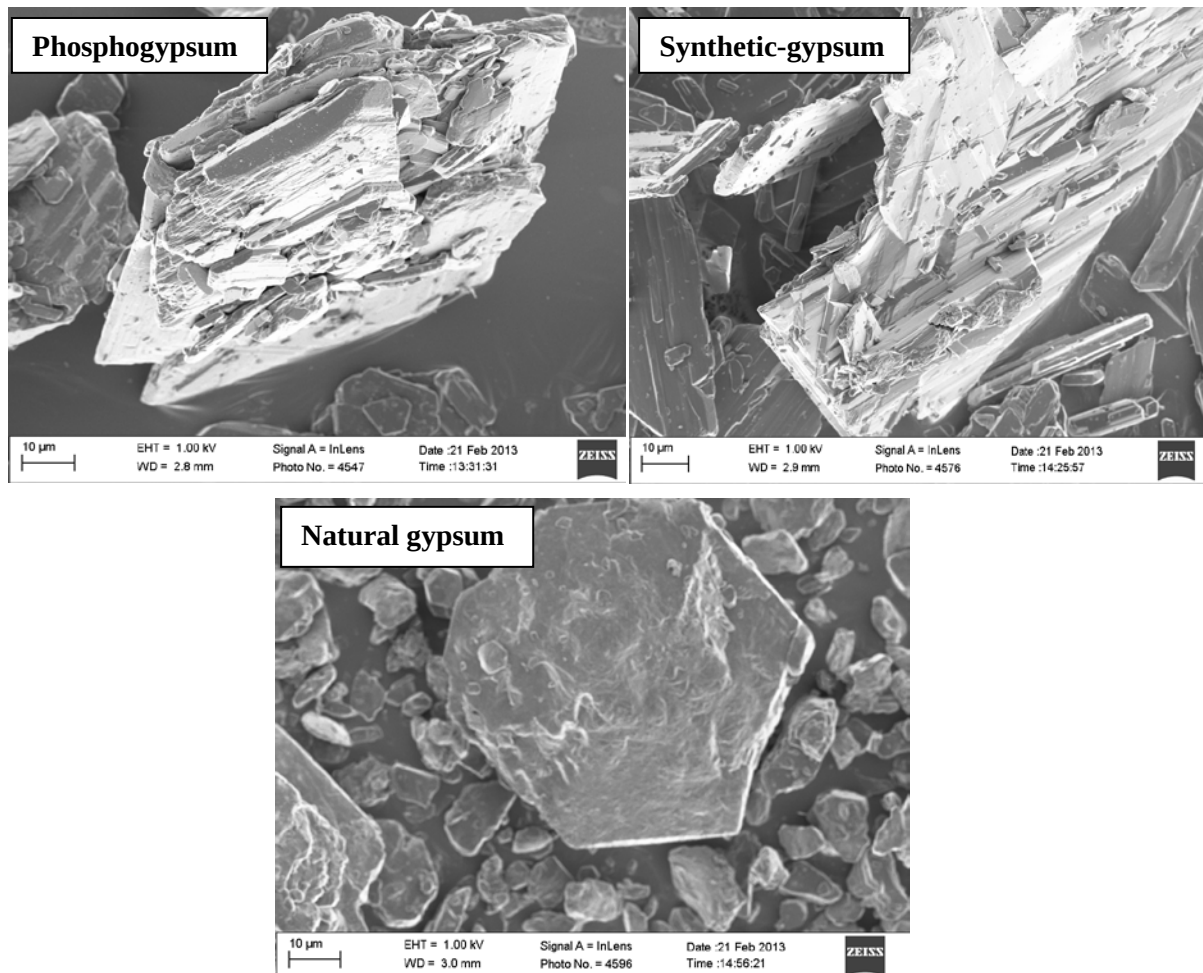


Figure 3.6: Particles of phosphogypsum, synthetic-gypsum and natural gypsum observed under scanning electron microscopy at higher magnification

Figure 3.6 shows the particle morphology of each sample at higher magnification. The FESEM images show that in phosphogypsum, the crystals look laminar (plate-like) in a prismatic arrangement, with openings like pores available between particles bounded together. Phosphogypsum has been recognized by Tayibi et al (2009) as being porous.

In synthetic-gypsum the crystals seem to grow as an agglomeration of linear particles (needle-like) with no spaces between the particles forming a crystal, while in the sieved natural gypsum sample,

the particles are smaller and seem to be more bulky and less needle-like than the particles of the other two gypsum samples.

3.2.5 Particle size distribution (PSD) of phosphogypsum, synthetic gypsum and natural gypsum.

The PSD of the three gypsum samples was determined as it affects the way samples react by having an effect on the surface area of the sample which will be exposed to the reaction. Fairhurst (2010) stated that the available particle surface area of solid particles in a suspension is a consequence of two important properties – the concentration of particles in the suspension and the size of the particles. The PSD of the gypsum samples was determined using the instrument and method described in Section 2.6. The results of the analyses are presented in the form of a frequency curve of volume percentage versus the logarithm of particle size in Figure 3.7, while Table 3.7 shows the calculated diameters obtained for the particle size distribution of all three gypsum samples.

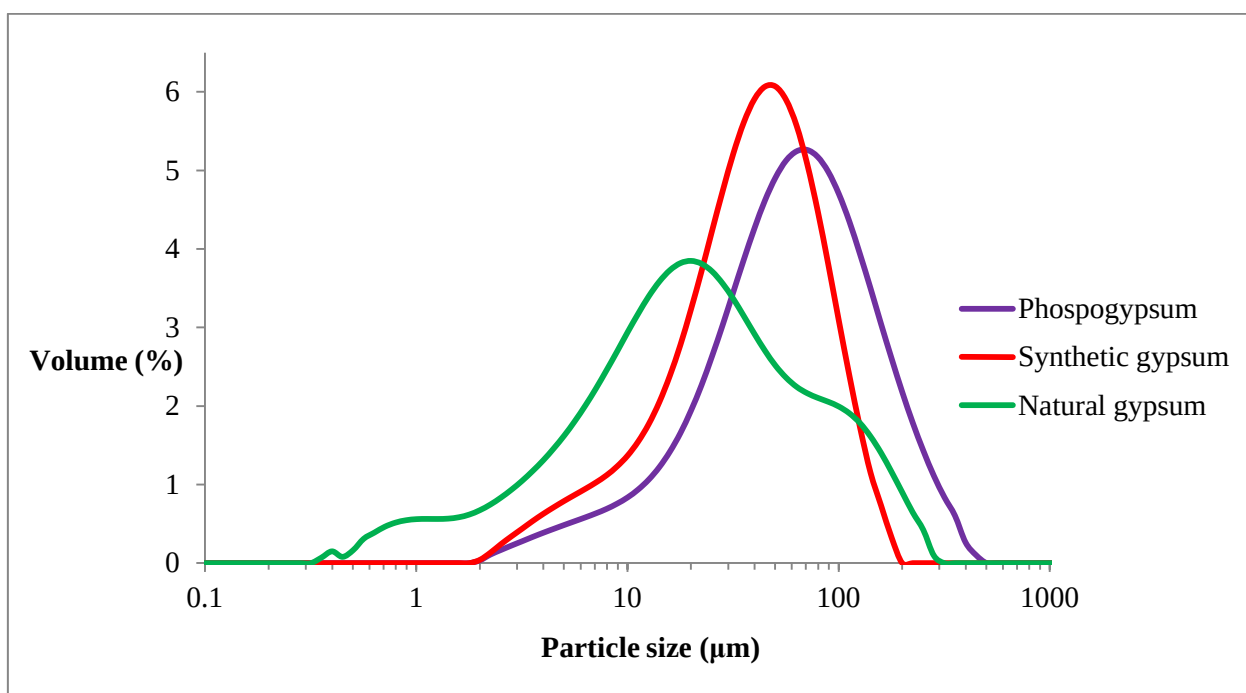


Figure 3.7: The frequency curve of the particle size distribution of phosphogypsum, synthetic-gypsum and natural gypsum.

Table 3.7: Calculated diameters of phosphogypsum, synthetic gypsum and natural gypsum particles.

Statistics	Sample		
	Natural gypsum	Synthetic-gypsum	Phosphogypsum
D (v; 0.1)	2.88 ± 0.23	9.86 ± 0.24	15.23 ± 1.02
D (v; 0.5)	17.11 ± 1.56	37.51 ± 0.43	59.45 ± 2.39
D (v; 0.9)	85.48 ± 6.24	86.06 ± 2.20	166.53 ± 2.03

The frequency curve in Figure 3.7 shows that synthetic-gypsum and phosphogypsum are both characterized by a single population. At its maximum, synthetic-gypsum has a population of 6% measuring 50.24µm. Phosphogypsum presents a maximum where 5% of its population measure 70.79µm. They are both characterized by a tail to the left of their respective frequency curves with no maxima, revealing the presence of fine particles for each sample. Unlike its two counterparts, natural gypsum presents three populations with a tail to the left of its frequency curve which reveals the presence of sub-micron particles. The extent of its tail implies that natural gypsum includes much finer particles than synthetic gypsum and phosphogypsum. The first peak for the natural gypsum sample has its maximum value located at about 1µm which represents about 1% of the total sample. The second maximum is at *ca.*20µm and represents 3.85% of the total population. The third maximum of the natural gypsum frequency curve is where 2.05% of its population measure 89.34µm.

The results in Table 3.7 show that the sieved natural gypsum sample has the particles with the smallest particle size followed by synthetic gypsum, while the particle size of phosphogypsum is the largest. 50% of the population of natural gypsum have a size below 17.11µm and 50% have a size above 17.11µm. 50% of the population of synthetic gypsum have a size below 37.51µm and 50% have a size above 37.51µm. 50% of the population of phosphogypsum have a size below 59.45µm and 50% have a size above 59.45µm. On the other hand, from the same table it is further observed that 90% of the particles in natural gypsum have a size below 85.48µm, compared to 86.06µm for synthetic gypsum and 166.53µm for phosphogypsum. This means that natural gypsum is a finer sample than synthetic gypsum which in turn is finer than phosphogypsum. This confirms the observations made from the FESEM images, where the particles of natural gypsum look

smaller than those of synthetic gypsum which in turn seems to be more needle-like than those of phosphogypsum but longer than those of natural gypsum.

3.2.6 BET surface area analysis of phosphogypsum, synthetic gypsum and natural gypsum

The BET surface area of the three gypsum samples was determined using a NOVA 1000e Surface Area and Pore Analyzer as described in Section 2.7. This analysis was done to determine the total specific surface area, including all accessible inner surfaces such as pores. Reactions involving solids with a higher surface area are expected to occur at a faster rate. The measurements were performed in triplicate, and the average of the three measurements is reported in Table 3.8:

Table 3.8: Summary of the results obtained for the BET surface area measurements of phosphogypsum, synthetic-gypsum and natural gypsum.

Sample	Surface area (m ² /g)
Phosphogypsum	8.20 ± 0.44
Natural gypsum	8.08 ± 0.92
Synthetic-gypsum	5.93 ± 0.59

The values obtained for the BET surface area of phosphogypsum and natural gypsum were similar, while that of synthetic gypsum is slightly lower. The larger surface area observed in phosphogypsum may be explained by its plate-like morphology, with pores and openings between the plates; as observed from the FESEM results (Figure 3.6). Lowell (2006) stated that voids and pores create a real surface area greater than the corresponding theoretical surface area, and that a smaller particle size may lead to an increase in the BET surface area of a sample. Since the particle size of the sieved natural gypsum sample is the smallest, it is expected that its BET surface area will be the largest. FESEM results of this sample have not shown any openings or pores. Although this sample has a smaller particle size than the phosphogypsum sample, it is possible that it contains less voids in its morphology, explaining the decreased surface area. The low surface area observed for the synthetic gypsum sample may be ascribed to its agglomerated needle-like morphology, which seemed to have very little pores or voids.

3.3 Thermogravimetric analysis (TGA)

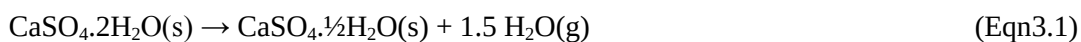
In this section, the Thermogravimetric analysis (TGA) of phosphogypsum, synthetic gypsum and natural gypsum is discussed. The main purpose of this part of the study is to confirm the composition of the gypsum samples as determined by XRD.

Prior to thermogravimetric analyses of the gypsum samples, pure samples of calcium hydroxide and calcium carbonate (both obtained from Merck) have been analysed by XRD and TGA in order to determine their composition, decomposition temperature range, and the corresponding weight loss percentages. Since the results obtained from XRD analyses have indicated the presence of CaCO_3 in the natural gypsum sample, it is important that the decomposition temperature range of CaCO_3 is known. Furthermore, TGA will be used in subsequent chapters to determine the amounts of Ca(OH)_2 and CaCO_3 in the obtained products, and therefore the thermal stability of Ca(OH)_2 is included in this discussion.

The decomposition temperature range of CaSO_4 is known to be above 1000°C (Christensen et al, 2008). Decomposition of CaCO_3 and Ca(OH)_2 occurs at much lower temperatures and may even overlap, complicating a quantitative TGA analysis of samples containing both. This aspect will also be discussed in the sections to follow.

3.3.1 Literature study and calculation of the decomposition weight loss percentages of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3 and Ca(OH)_2

Considering a 100% pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ sample which decomposes as below:



The dehydration reactions of calcium sulphate dihydrate occurs in two steps between 25°C and 200°C . Between 25°C and 100°C , surface water is removed. From 100°C to 200°C is the removal of the water of crystallization of calcium sulphate dihydrate, and occurs in two steps which are described by Equations 3.1 and 3.2 above. The conversion of calcium dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) into calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) is described by Equation 3.1, and occurs between

109°C and 140°C. Thereafter, the conversion of hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) into anhydrite (CaSO_4), as described by Equation 3.2, takes place between 165°C and 172°C (Christensen et al, 2008).

According to literature (Christensen et al, 2008), a weight loss over the temperature range from 1089°C to 1400°C characterizes the decomposition of calcium sulphate (CaSO_4) into calcium oxide (CaO) and sulphur trioxide (SO_3), as shown in equation 3.3.

Knowing the molecular masses of pure calcium sulphate dihydrate and the different products into which it decomposes, the theoretical weight percentage that each one of them represents in calcium sulphate dihydrate is determined by dividing their respective molecular masses by the molecular mass of calcium sulphate dihydrate. These theoretical weight percentages are presented in the table below:

Table 3.9: Theoretical weight percentages of the decomposition products of pure calcium sulphate dihydrate.

Name	Molecular Formula	Molecular Mass (g/mol)	% in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Calcium sulphate dihydrate	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	172.17	100
Water	H_2O	18.01	20.93
Calcium Oxide	CaO	56.08	32.57
Sulphur trioxide	SO_3	80.06	46.50

Similarly, the theoretical weight loss percentages can be calculated for the decomposition of $\text{Ca}(\text{OH})_2$ and CaCO_3 , and is reported in Tables 3.10 and 3.11. The decomposition reactions are as shown below:



Table 3.10: Theoretical weight percentages of the decomposition products of Ca(OH)_2

Name	Molecular Formula	Molecular Mass (g/mol)	% in Ca(OH)_2
Calcium hydroxide	Ca(OH)_2	74.09	100
Calcium oxide	CaO	56.08	75.69
Water	H_2O	18.01	24.31

Theoretically, the weight loss that should be observed upon decomposition of pure Ca(OH)_2 should be 24.31%. However, Hudson-Lamb (1997) reported a weight loss of 18% over the temperature range 553°C - 759°C for the decomposition of pure calcium hydroxide into water and calcium oxide. For the low percentage reported, she suggested the possibilities of the overlapping of the decomposition reactions of calcium hydroxide and calcium carbonate contained as impurities in the calcium hydroxide sample and that the decomposition of calcium hydroxide, by losing water did not stop at 759°C, but carried on above that temperature. This aspect will be discussed in more details in this chapter.

Table 3.11: Theoretical weight percentages of the decomposition products of CaCO_3

Name	Molecular Formula	Molecular Mass (g/mol)	% in CaCO_3
Calcium carbonate	CaCO_3	100.08	100
Calcium oxide	CaO	56.08	56.03
Carbon dioxide	CO_2	44.01	43.97

A weight loss of 44% occurring over the temperature range 655°C-808°C should characterize the decomposition of calcite (CaCO_3) into calcium oxide and carbon dioxide (Hudson-Lamb, 1997).

3.3.2 TGA and XRD analysis of CaCO_3 and Ca(OH)_2

CaCO_3 and Ca(OH)_2 were obtained from Merck Pty Ltd. XRD analyses were performed on these samples to confirm their composition. The results are reported in Table 3.12.

Table 3.12: Quantitative XRD results of Ca(OH)_2 and CaCO_3 obtained from Merck

Minerals	Molecular formula	Ca(OH)_2 (wt %)	CaCO_3
Portlandite	Ca(OH)_2	99	-
Calcite	CaCO_3	<1	98
Aragonite	CaCO_3	-	2

From the XRD results shown in Table 3.12, it is observed that the calcium hydroxide sample contains a small amount of calcite, which could find its origin from the reaction between Ca(OH)_2 and carbon dioxide from the atmosphere (Mikhail et al, 1996). The calcium carbonate sample obtained from Merck contains two forms of CaCO_3 namely calcite and a small percentage of the less stable aragonite. The occurrence and properties of calcite and aragonite were discussed in Section 1.4.

The results obtained for the TGA analysis of the CaCO_3 and Ca(OH)_2 samples are presented in Figures 3.8 and 3.9.

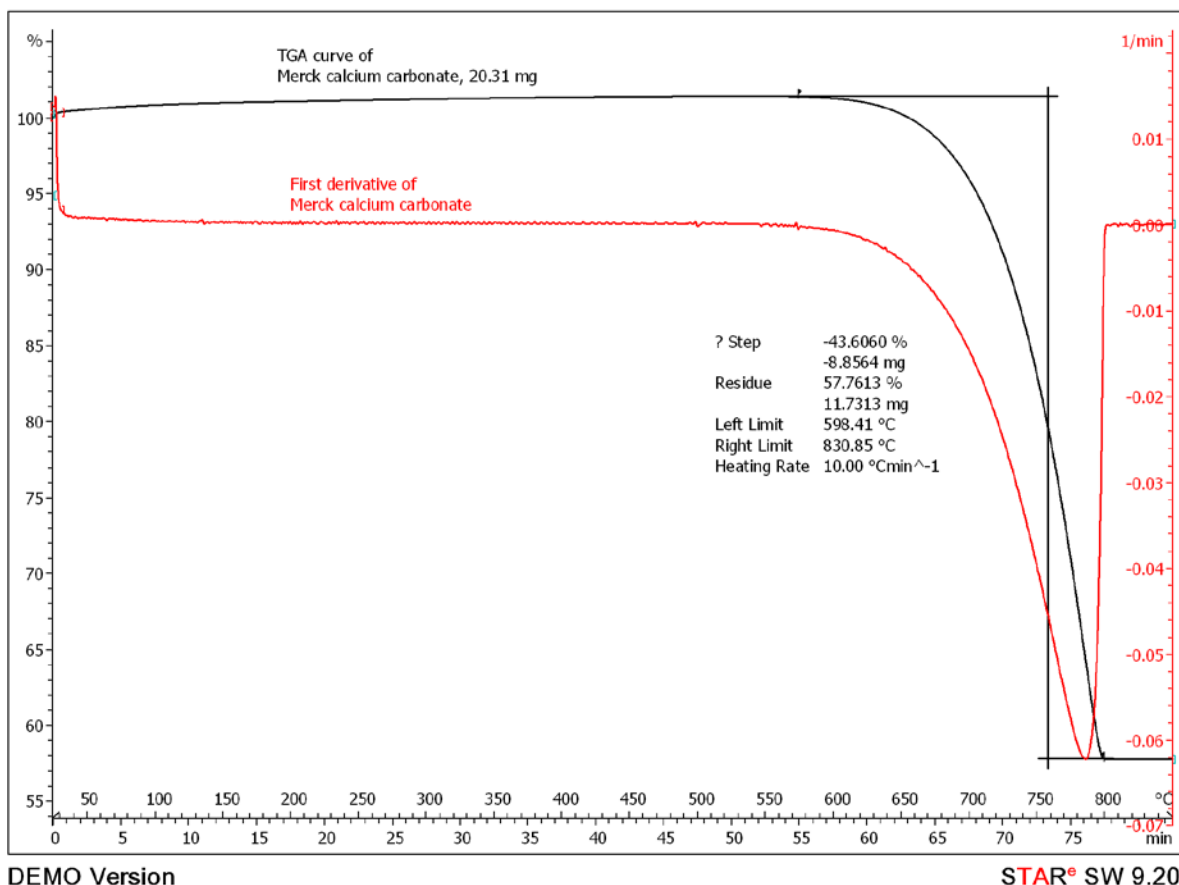


Figure 3.8: The TGA curve of CaCO_3 and its first derivative (DTG).

The thermal decomposition of the CaCO_3 sample occurs between 598°C and 831°C. This is characterized by a weight loss of CO_2 of 43.6% for a sample weight of 20.31 mg. This weight loss is close to the theoretically calculated weight loss (43.97%), and the decomposition temperature range corresponds well to the temperature range determined by Hudson-Lamb (1997), who reported it to be between 655°C and 808°C.

Using the theoretically calculated weight loss for the decomposition of CaCO_3 , a weight loss of 43.6% of carbon dioxide released for this sample corresponds to 99.2% CaCO_3 present in the sample. This percentage of calcium carbonate obtained from by TGA corresponds well to the percentage of calcium carbonate obtained from XRD analysis as the total of calcite (98%) and aragonite (2%).

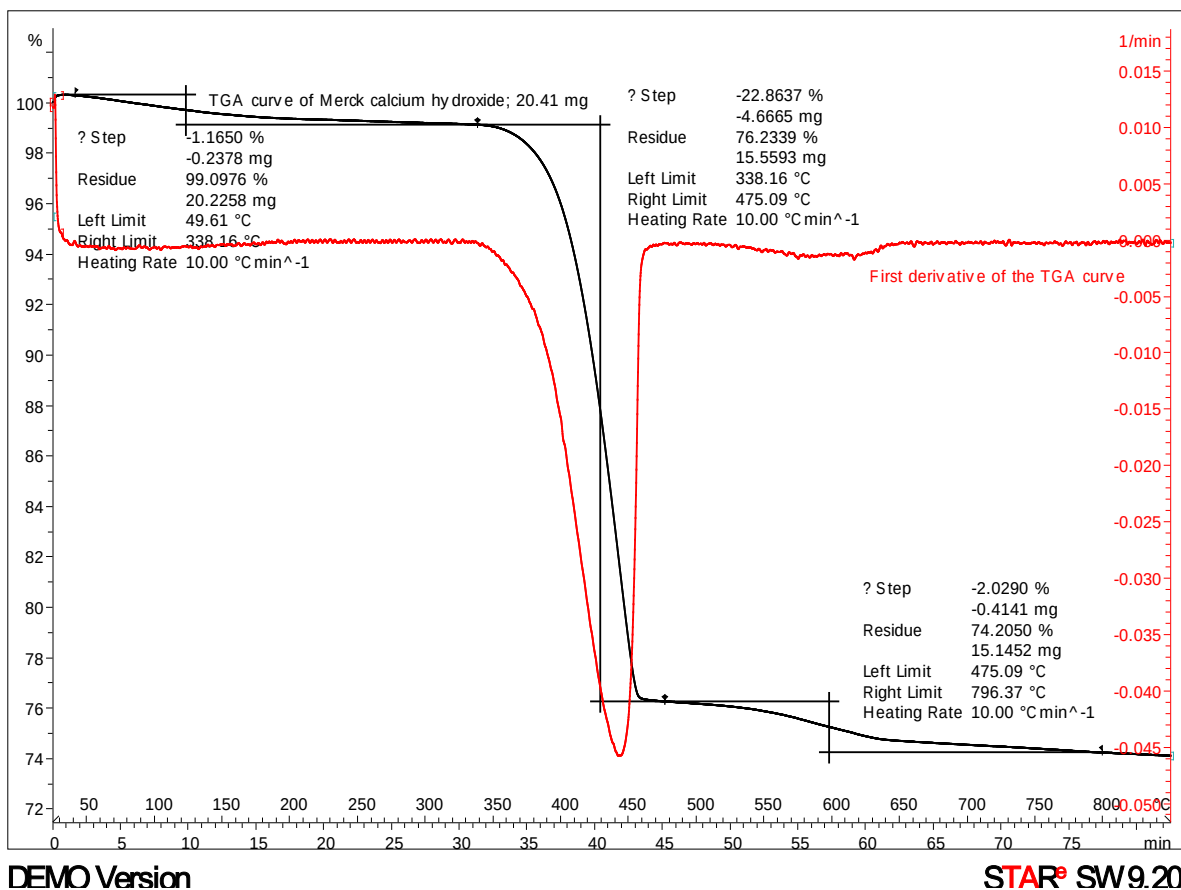


Figure 3.9: The TGA curve of CaCO_3 and its first derivative (DTG).

From the figure above, it is observed that the thermal decomposition of the $\text{Ca}(\text{OH})_2$ sample is characterized by three successive decomposition steps ranging from 49°C to 338°C, from 338°C to 475°C and from 475°C to 796°C. The first decomposition step (from 49°C to 338°C) represents the loss of adsorbed water by the sample (Chen et al, 1993). This weight loss represents 1.17% of the sample weight (20.41 mg) used for this analysis. The second weight loss (from 338°C to 475°C) corresponds to the decomposition of calcium hydroxide into calcium oxide with the release of water. This weight loss represents 23.07% of the weight residue at 338°C (20.23 mg), after the removal of adsorbed water, and compares well to the theoretical value of 24.31%. By comparing the experimentally obtained weight loss to the theoretical value, an amount of 94.7% $\text{Ca}(\text{OH})_2$ is obtained for this sample. The amount of $\text{Ca}(\text{OH})_2$ determined by TGA is lower than the result obtained from XRD analysis, which was reported to be 99%.

The last decomposition step (from 475°C to 796°C) corresponds to the decomposition of a small amount of the calcium carbonate that the sample contains as impurity, and represents 2.0% of the sample weight (20.23 mg) after the removal of adsorbed water. This calcium carbonate was

suspected to have been formed as a result of the reaction between carbon dioxide from the atmosphere and humid calcium hydroxide (Mikhail et al, 1996). Using the theoretical weight loss (43.97%), the amount of CaCO_3 contained in this sample is calculated to be 4.5%. This amount is higher than the amount obtained from XRD measurements, which was reported to be below 1%.

It has been reported before (Hudson-Lamb, 1997) that the decomposition temperature ranges for Ca(OH)_2 and CaCO_3 overlaps. Since these two compounds are the main products to be formed during this study, a TGA-FTIR analysis study was performed on the Ca(OH)_2 sample to investigate this further, and the results are summarised in Figures 3.10 - 3.13.

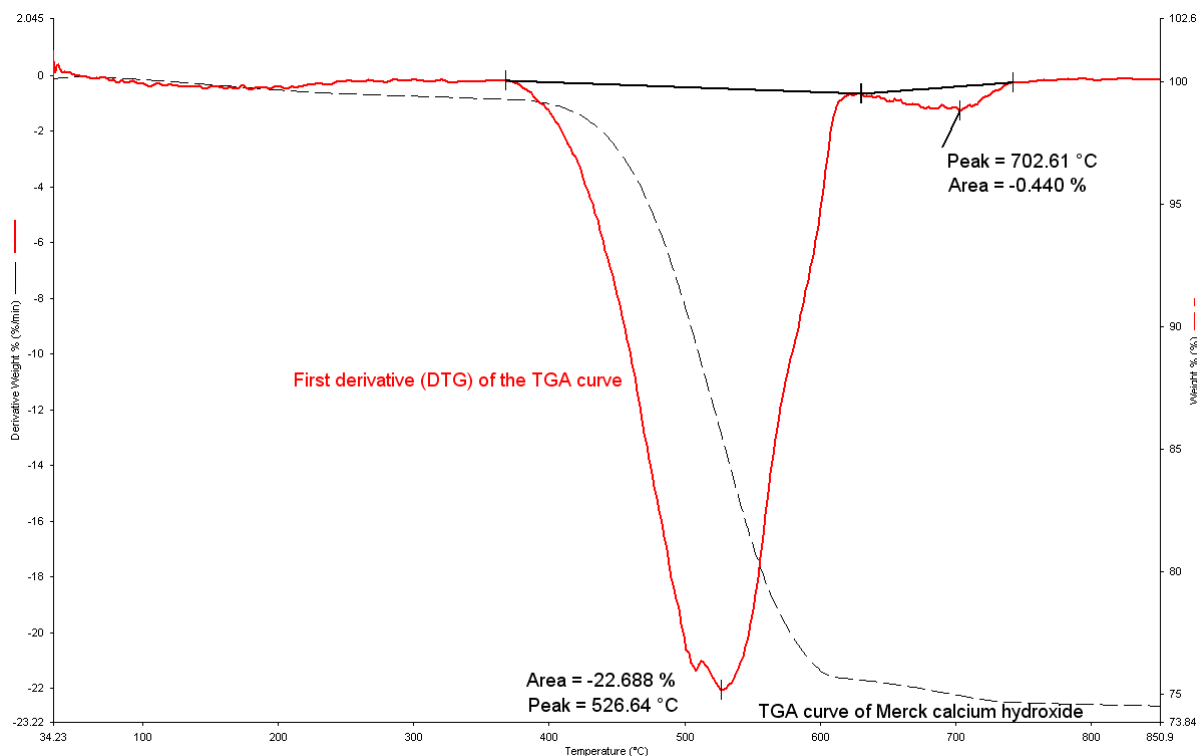


Figure 3.10: The TGA curve of Ca(OH)_2 and its first derivative (DTG) obtained from TGA-FTIR analysis.

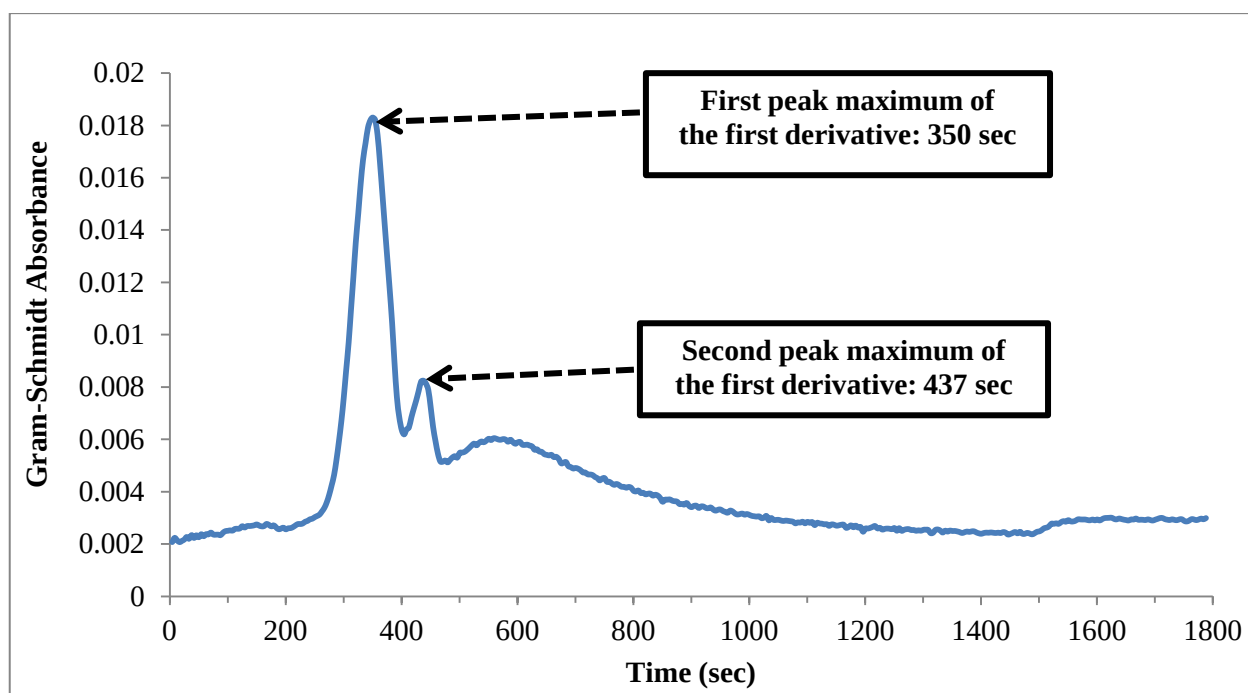


Figure 3.11: Graph of the Gram-Schmidt Absorbance versus time profile obtained for the gaseous decomposition products of the $\text{Ca}(\text{OH})_2$ sample

Figure 3.10 shows the TGA curve of the calcium hydroxide sample, obtained from Merck, and its first derivative (DTG). It shows that the first peak maximum (where the first decomposition step is at its maximum) of the DTG curve occurs at 526.6°C while the second peak maximum (where the second decomposition step is at its maximum) occurs at 702.6°C.

The Gram-Schmidt graph is a plot for the absorbance of the gaseous decomposition products obtained from the TG analysis of a sample against the time. It allows identifying the time where the weight loss of a sample during a TG analysis is at its maximum. The maximum of a peak, which also corresponds to DTG peak maximum, is the time where the decomposition of a sample is at its maximum. Then each peak is analyzed for its characteristic spectra to identify the nature of the gases released during the weight loss of the sample.

Figure 3.11 shows the Gram-Schmidt Absorbance versus time profile for the gaseous decomposition products obtained from the TGA analysis of this sample. Two peak maxima are observed in this curve. The first peak maximum, at 350 seconds, corresponds to the DTG peak maximum at 526.6°C, while the second peak maximum in the Gram-Schmidt curve at 437 seconds corresponds to the DTG curve maximum at 702.6°C. The corresponding FTIR-spectra, recorded at 350 seconds and 437 seconds are presented in Figures 3.12 and 3.13.

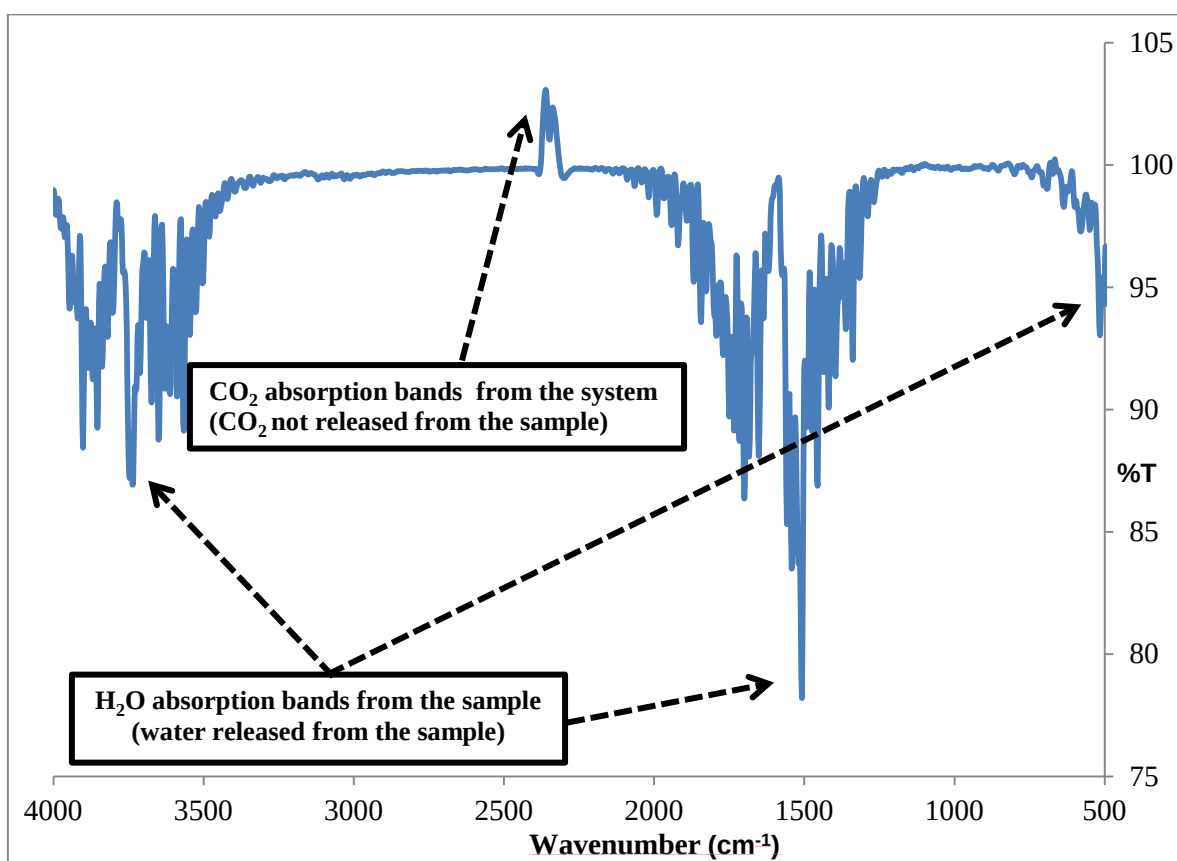


Figure 3.12: FTIR spectrum obtained from the gaseous TGA decomposition products taken at 350 seconds

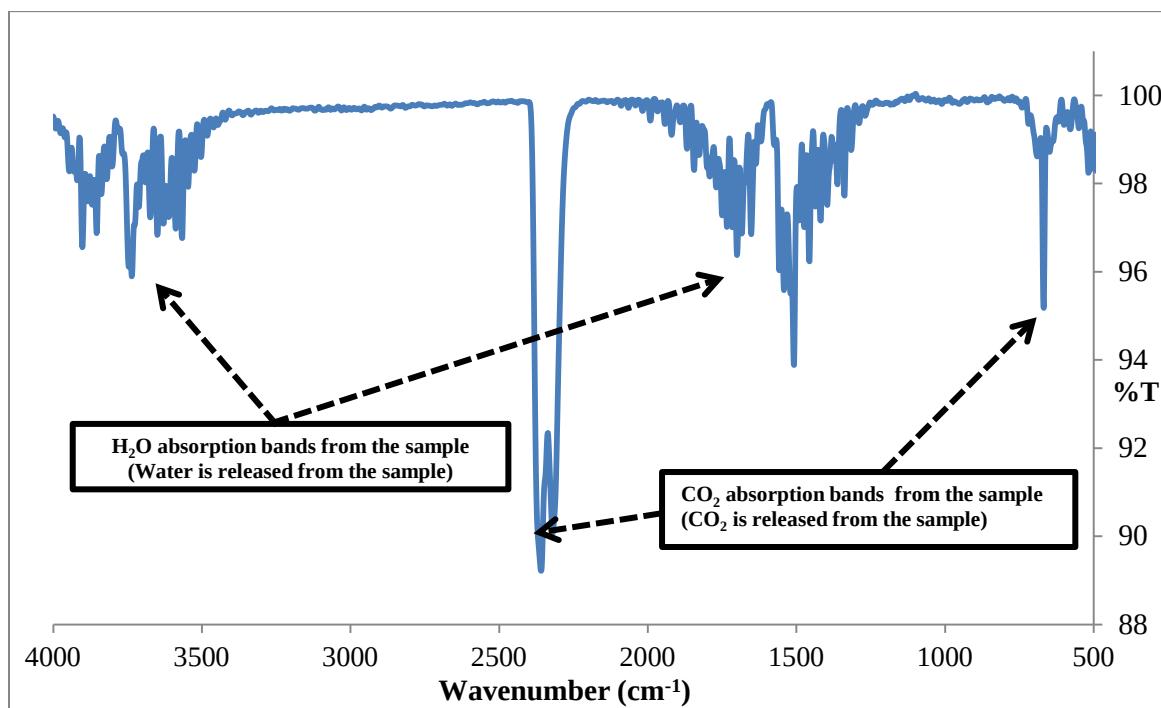


Figure 3.13: FTIR spectrum obtained from the gaseous TGA decomposition products taken at 437 seconds.

Figures 3.12 and 3.13 show the FTIR spectra of the evolved gases during the thermal decomposition of $\text{Ca}(\text{OH})_2$. Figure 3.12 shows intense bands between 3200cm^{-1} - 4000cm^{-1} , 1200 - 2000cm^{-1} , and around 500cm^{-1} , which all suggest the presence of water vapor. In their study, Mc Connell et al (2008) identified the presence of sharp bands in the range of 4000cm^{-1} to 3500cm^{-1} and from 2000cm^{-1} to 1300cm^{-1} as characteristic of the presence of H_2O vapor, while the absorption bands around 500cm^{-1} in the fingerprint region can be attributed to the presence of hydrogen bonds (McConnell et al, 2008). This results indicates that during the first weight loss in the TGA curve, only water is released as decomposition product, indicating the decomposition of only $\text{Ca}(\text{OH})_2$.

Figure 3.13 shows the FTIR spectrum taken from the decomposition product obtained at 437 seconds. In this spectrum, intense bands that can be attributed to the presence of both CO_2 and H_2O were recorded. The bands between 2200cm^{-1} - 2400cm^{-1} and around 700cm^{-1} are attributed to the presence of gaseous CO_2 while those between 3200cm^{-1} - 4000cm^{-1} , 1200cm^{-1} - 2000cm^{-1} and around 500cm^{-1} to the presence of H_2O vapor. Fermo et al (2005) identified the most intense signal in the CO_2 infrared spectrum to occur at 2350cm^{-1} while Chédin et al (2003) identified further CO_2

absorptions in the range 725cm^{-1} - 740cm^{-1} . This means that during the second decomposition step of this sample, both CO_2 and H_2O are being released as gaseous decomposition products and therefore this weight loss can be attributed to the simultaneous decomposition of Ca(OH)_2 and CaCO_3 . This result confirms the suggestions made by Hudson-Lamb (1997) who suspected the existence of an overlap in the decomposition temperature ranges of Ca(OH)_2 and CaCO_3 .

The occurrence of this overlap in the decomposition temperature range of Ca(OH)_2 and CaCO_3 should therefore be considered when using TGA as a quantitative analysis technique for samples containing both these compounds. In summary, the amount of Ca(OH)_2 determined by TGA (94.7%) in the Ca(OH)_2 sample obtained from Merck is lower than the result obtained from XRD analysis, which was reported to be 99%. This was due to the fact that the decomposition of Ca(OH)_2 takes place in two steps, and the temperature range of the second step overlaps with the decomposition temperature range of CaCO_3 . This was confirmed by the TGA-FTIR analysis of this sample. Although it is difficult to quantify the amounts of Ca(OH)_2 and CaCO_3 in a mixture thereof with great certainty, the error introduced by calculating the decomposition of the Ca(OH)_2 sample by only the first step is around 5% and is not significant for the purpose of this study.

3.3.3 Thermogravimetric analysis of the gypsum samples used in this study

Phosphogypsum, synthetic gypsum and natural gypsum were analysed by TGA to confirm their composition as determined by XRD. The temperature range where each weight loss occurs was determined using the first derivative of the thermogravimetric curve. The derivative was superimposed onto its thermogravimetric curve and the temperature range was limited from where the thermogravimetric curve started to deviate downwards from its first derivative until its return to the baseline. Figures 3.14, 3.15 and 3.15 below show the evaluation of the TGA curves of synthetic gypsum, phosphogypsum, natural gypsum and their first derivatives.

Figure 3.14 shows the thermal decomposition of synthetic gypsum. The first weight loss in synthetic gypsum occurs between 84°C and 243°C . This represents the loss of surface water and the water of crystallization contained in the structure of synthetic gypsum which consists of 95% (w/w) of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and 5% (w/w) of bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), as determined by XRD analysis. This weight loss represents 20.3% of the total sample weight (20.38 mg) used for this analysis, and corresponds well to the theoretical value calculated for the dehydration of pure gypsum (20.9%). The theoretical weight loss for the dehydration of pure hemihydrate (or bassanite) is 6.2% therefore; the small amount of bassanite contained in synthetic gypsum will make a small

contribution in lowering the dehydration weight loss percentage when compared to that of pure gypsum.

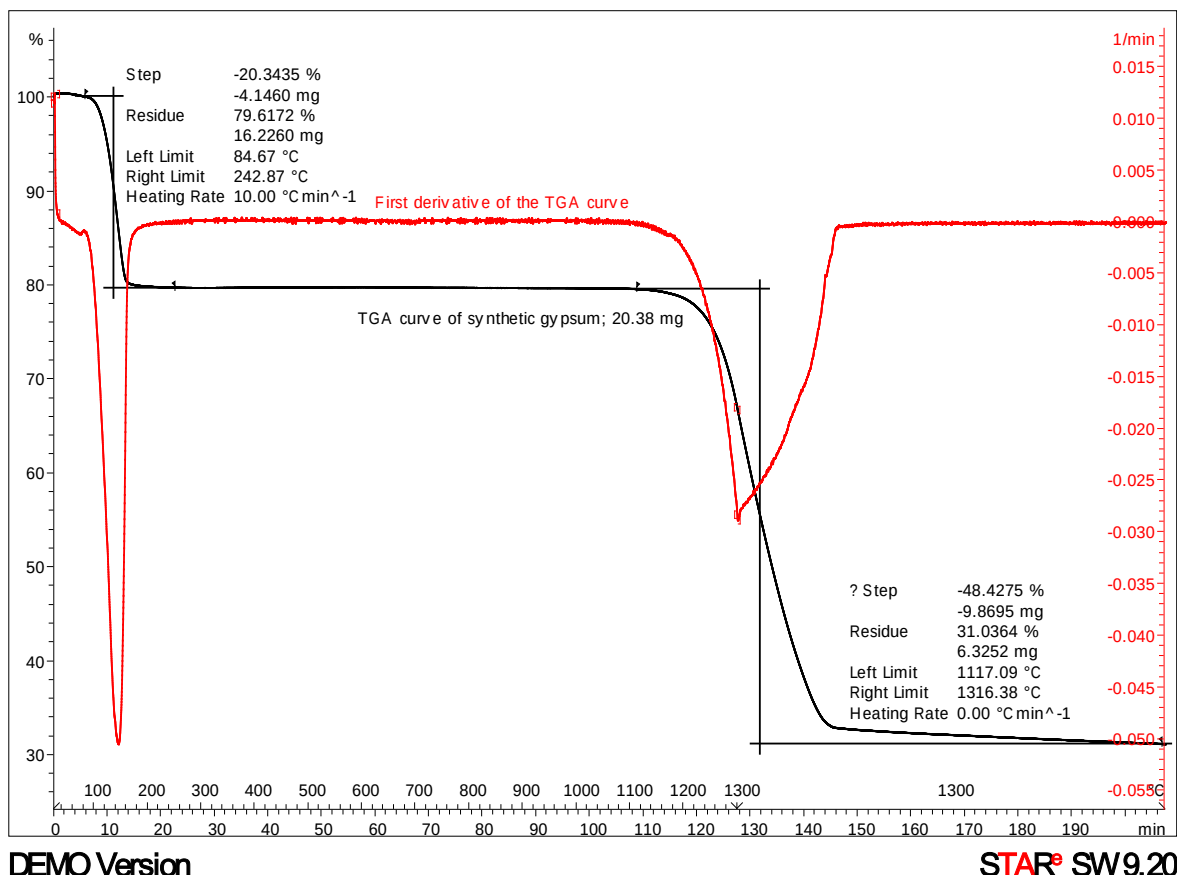


Figure 3.14: The TGA curve of synthetic gypsum and its first derivative (DTG).

The second weight loss observed for synthetic gypsum occurs between 1117°C and 1316°C. This weight loss (48.4%) corresponds to the decomposition of calcium sulphate (CaSO_4) into calcium oxide and sulphur trioxide and compares well to the theoretical value of 46.5% calculated for the decomposition of pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

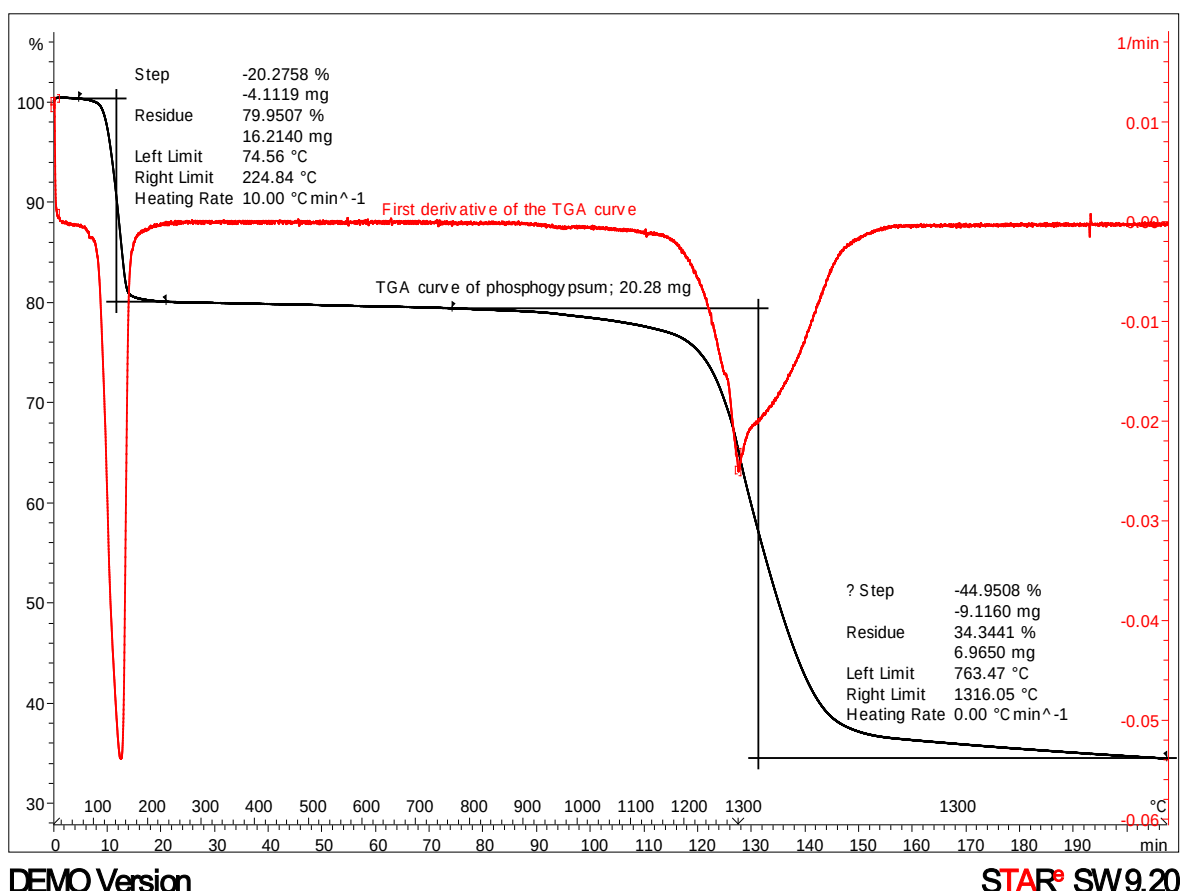


Figure 3.15: The TGA curve of phosphogypsum and its first derivative (DTG).

Figure 3.15 is an evaluation of the TGA curve of phosphogypsum. It is observed that the first weight loss in phosphogypsum occurs between 75°C and 225°C. This represents the loss of surface water and the water of crystallization contained in the structure of phosphogypsum, consisting of 97% (w/w) of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and 2% (w/w) of bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), as determined by XRD analysis. This weight loss represents 20.3% of the total sample weight used for this analysis (20.28 mg), and also corresponds well to the theoretical value calculated for the dehydration of pure gypsum (20.9%).

The value of second weight loss observed for the phosphogypsum sample occurring between 763°C and 1316°C was 44.9%, and corresponds well to the theoretical value (46.5%) for the decomposition of calcium sulphate (CaSO_4) into calcium oxide and sulphur trioxide.

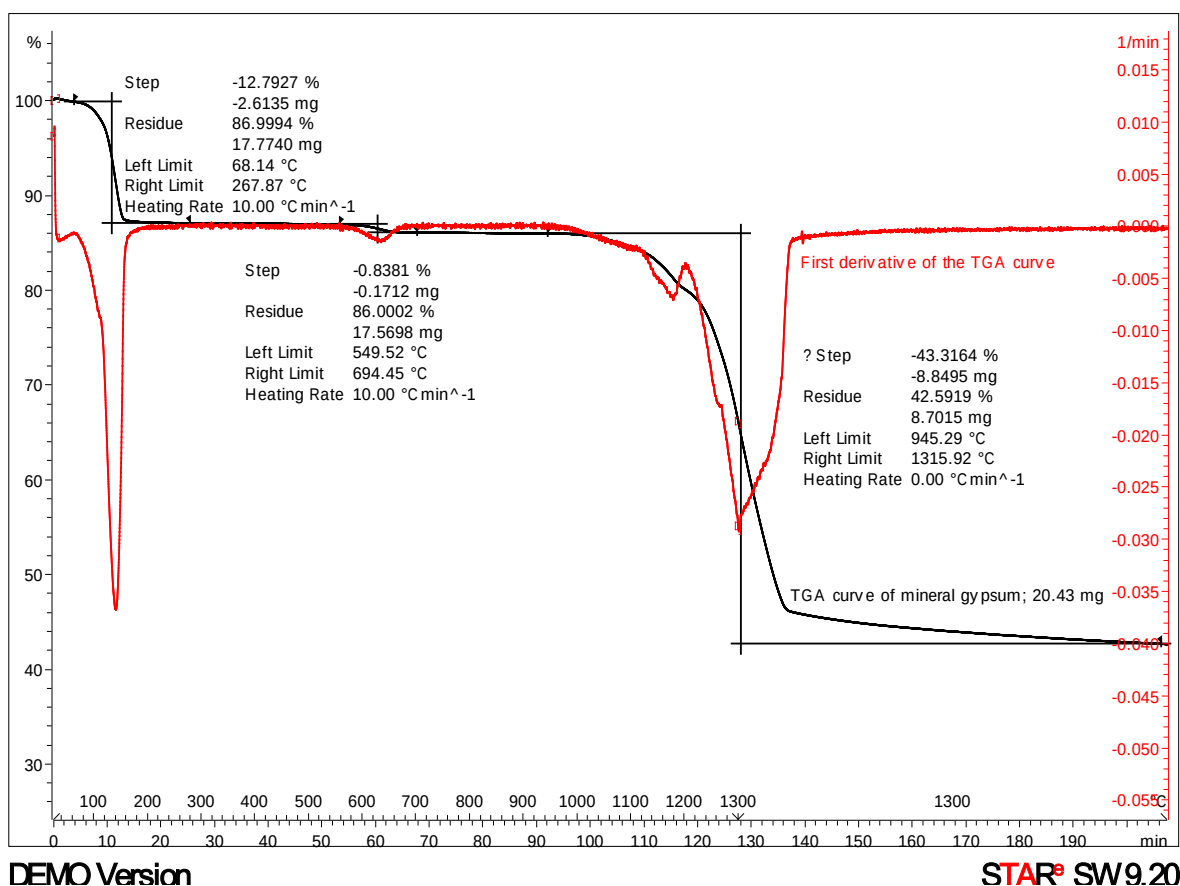


Figure 3.16: The TGA curve of natural gypsum and its first derivative (DTG).

From Figure 3.16, the first weight loss obtained for the natural gypsum sample occurs between 68°C and 268°C. This represents the loss of surface water and water of crystallization contained in the structure of mineral gypsum which consists of 49% (w/w) of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and 47% (w/w) of bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), as determined by XRD analysis. This weight loss represents 12.8% of the total sample weight used for this analysis and is significantly lower than the theoretical value calculated for the dehydration of pure gypsum (20.9%), and well above the theoretical weight loss for the dehydration of pure hemihydrate (6.2%).

Natural gypsum contains approximately the same amounts of gypsum and bassanite in its mineral composition as determined by XRD, explaining the lower weight loss for the dehydration step. Van der Merwe (2001) confirmed that the low weight loss of dehydration observed for mineral gypsum was due to the presence of bassanite (calcium sulphate hemihydrate) and/or impurities in the sample. Quantitative analysis of a mixture of gypsum and bassanite by TGA is not simple (Putnis et al, 1990) and was not the focus of this study. Therefore, the weight loss associated with the loss

of water will be disregarded when performing the quantitative analysis of this sample; and the sample weight will be considered to be 17.77 mg (residue at 268°C) in quantitative calculations, as will be discussed in more detail later.

The second weight loss for mineral gypsum occurs between 550°C and 694°C and represents the decomposition of calcium carbonate into calcium oxide (CaO) with the subsequent release of carbon dioxide. The thermal decomposition of pure CaCO₃ is discussed comprehensively later in this chapter. A weight loss of 0.84% is obtained for this step. When compared to the theoretical weight loss for the decomposition of a pure CaCO₃ sample (43.97%), this sample contains 1.91% of CaCO₃. The amount of calcium carbonate present in mineral gypsum as calculated from the TGA data corresponds well to the amount of calcite obtained from XRD results, which was reported to be 2%.

The final weight loss (8.85mg) observed for the natural gypsum sample occurs between 945°C and 1316°C and represents 49.8% of the sample weight taken after dehydration at 268°C. This weight loss corresponds to the decomposition of anhydrous calcium sulphate (CaSO₄) into calcium oxide and sulphur trioxide, for which the theoretical value is 58.8%.

The quantitative TG analysis performed on synthetic gypsum, phosphogypsum and natural gypsum is summarized in the table below:

Table 3.13: Quantitative TG analysis of the gypsum samples used in this study.

TGA weight loss	Theoretical weight loss of $x\text{H}_2\text{O}$: ($x = 1/2$ or 2) ($\pm 69^\circ\text{C} \rightarrow \pm 268^\circ\text{C}$) $\text{CaSO}_4 \cdot x\text{H}_2\text{O} \rightarrow \text{CaSO}_4 + x\text{H}_2\text{O}$		Theoretical weight loss of CO_2 : 43.97% ($\pm 549^\circ\text{C} \rightarrow \pm 831^\circ\text{C}$) $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$		Theoretical weight loss of SO_3 : % ($\pm 941^\circ\text{C} \rightarrow \pm 1316^\circ\text{C}$) $\text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_3$	
	Experimental weight loss of $x\text{H}_2\text{O}$ in %	Experimental weight loss of CO_2 in %	Experimentally determined Weight percentage of CaCO_3 using its decomposition weight loss percentage	Experimental weight loss % of SO_3 , determined from initial sample weight	Calculated weight loss % of SO_3 calculated from sample weight after dehydration at about 268°C	Experimentally determined weight percentage of CaSO_4 , using its decomposition weight loss percentage
Phosphogypsum	20.3	-	-	44.9	56.2	96.7
Synthetic gypsum	20.3	-	-	48.4	60.8	104.1
Natural gypsum	12.8	0.84	1.9	49.8	49.7	84.7

The weight losses occurring between 69°C - 268°C for the three gypsum sample correspond to the loss of adsorbed surface water and water of crystallization. However, it is difficult to determine whether the obtained weight loss originates from a loss of surface water or water of crystallization, either from bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) or gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Application of quantitative analysis by TGA over this temperature range is complicated, and has not been applied in this study. Therefore, the weight percentages that those weight losses represent as water of crystallization present in each gypsum sample could not be determined with certainty, and subsequently only the values obtained for the weight losses occurring over this temperature range is reported.

Comparing the weight loss of the three gypsum samples between 549°C – 831°C , only the mineral gypsum sample contained a small amount of calcium carbonate (1.9%). No $\text{Ca}(\text{OH})_2$ was detected in the TGA analysis of the three gypsum samples.

The final weight loss for all three gypsum samples occur in the range 941°C - 1316°C. This weight loss corresponds to the decomposition of anhydrous calcium sulphate into calcium oxide with the subsequent release of sulphur trioxide gas. The theoretical weight loss percentage for this decomposition reaction is 58.8%. Experimentally, the value of the percentage weight loss occurring over this temperature range should be calculated from the sample weight after the loss of surface water and water of crystallization. The sample weight should therefore be taken at about 268°C, depending on the dehydration temperature range of a specific sample. The percentage weight loss for the decomposition of anhydrous CaSO_4 is then calculated by dividing the weight of SO_3 lost during the last decomposition step by the sample weight taken after dehydration, and expressing the ratio as a percentage. The obtained values are reported in Table 3.13.

The weight percentage of anhydrous CaSO_4 contained in each of the three gypsum samples was calculated by comparing the weight loss percentage to the theoretical value, for which the data is summarised in Table 3.10. Since synthetic gypsum is a pure commercial product, it is expected that the amount of CaSO_4 in this sample should be close to 100%. However, the result obtained from quantitative TGA analysis was 103.4%, indicating the level of experimental error obtained for quantitative TG analysis in these experiments. For this sample, the amount of SO_3 obtained from TGA weight loss data (48.4%) compares well to the amount calculated from XRD results (47%).

The weight loss percentage calculated for the decomposition of anhydrous calcium sulphate occurring in phosphogypsum was found to be 56.2%, corresponding to 95.6% CaSO_4 present in the phosphogypsum sample. The amount of SO_3 obtained from the TGA results for this sample was 44.9%, which also compared well to a value of 46% calculated from XRD data.

Similarly, the experimentally determined weight loss percentage for the decomposition of CaSO_4 contained in mineral gypsum was 49.7%, corresponding to 84.5% CaSO_4 present in this sample. Results obtained from XRD analysis of this sample indicated a weight percentage of 49% SO_3 , compared to 43.3% as determined by TGA analysis.

In general, the TGA quantitative analysis of the three gypsum samples compare well to results obtained from XRD. It is interesting to note that, when compared to the XRD data, quantitative TGA analysis overestimate the amount of SO_3 contained in the synthetic gypsum sample but underestimates it for the phosphogypsum and mineral gypsum samples. However, the difference in results obtained from the quantitative analysis using these two techniques is below 5% (by weight) for all three gypsum samples.

3.4 Solubility studies performed phosphogypsum, synthetic gypsum and natural gypsum

Solubility is defined as the amount of substance that dissolves in a specific volume at a specific temperature (Zumdahl and Zumdahl, 2006). It depends on the relative attractions that the ions in solution have for each other and for the attraction of these ions for the solvent, which for the purpose of this study is water. For a material to be soluble in water it must dissociate itself into its different ions when in solution; as such the material needs to be polar. The different ions formed, originating from the dissociation of material in water, will then be hydrated by the water molecules.

On the other hand, the conductivity of a solution is defined as its ability to conduct an electric current. The extent to which a solution can conduct an electric current is directly proportional to the number of ions present. A material that dissolves in water to give a solution able to conduct an electric current is defined as electrolyte. A strong electrolyte is a substance that is completely ionized when dissolved in water and shows good conductivity while a weak electrolyte is one that partly ionizes in water and does not display a high value for conductivity (Zumdahl and Zumdahl, 2006). The solubility of the three gypsum sample was investigated by measuring their conductivities in ultra-pure water (18.2 M Ω .cm) as a function of time, and is reported in Figure 3.17.

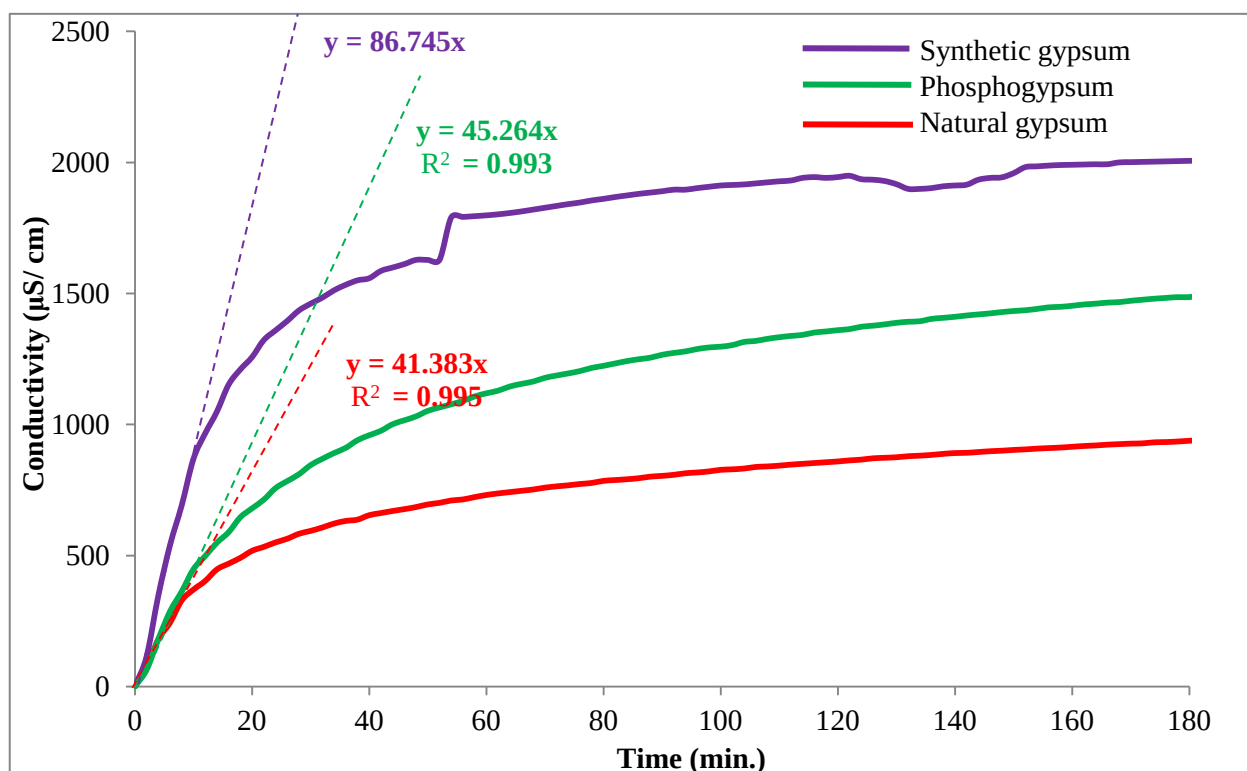


Figure 3.17: Changes in conductivity of aqueous solution upon addition of phosphogypsum, synthetic gypsum and natural gypsum over time

The solubility product is defined as the constant for the equilibrium expression representing the dissolving of an ionic solid in water (Zumdahl and Zumdahl, 2006). The solubility products of gypsum and bassanite are found to be similar. At room temperature, Christoffersen and Christoffersen (1976) reported the solubility product of gypsum as $K_s = 2.45 \cdot 10^{-5} \text{ M}^2$ while Amathieu and Boistelle (1988) reported $2.39 \cdot 10^{-5} \text{ M}^2$ as the solubility product of bassanite. These values suggest that the 3 gypsum samples will release the same amount of Ca^{2+} and SO_4^{2-} in solution. However, the 3 samples showed very different dissolution behaviour, both in terms of kinetics of dissolution (as indicated by the initial slope within the first 10 minutes of dissolution; 86.7, 45.3 and 41.4 for synthetic gypsum, phosphogypsum and natural gypsum respectively; Figure 3.17) and the extent of dissolution achieved within 180 minutes. This implies that the amount of calcium which will be available for $\text{Ca}(\text{OH})_2$ and the subsequent CaCO_3 formation (Chapter 4) will be different for each sample at any specific experimental reaction time.

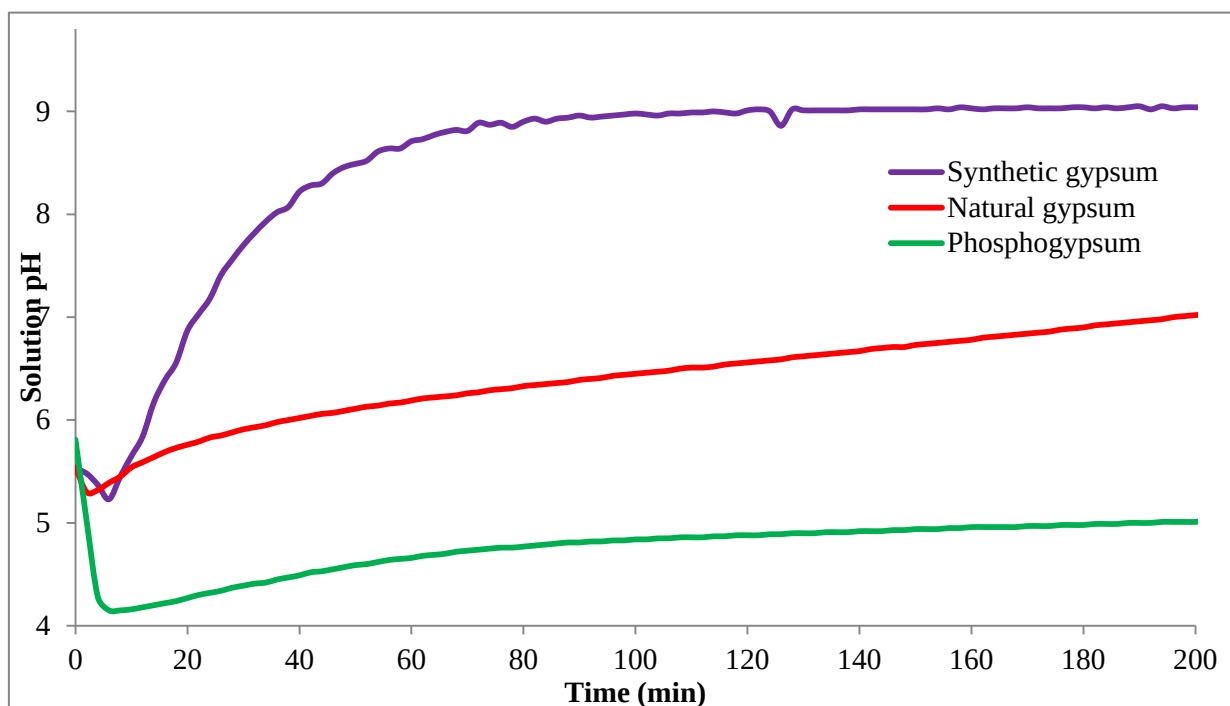
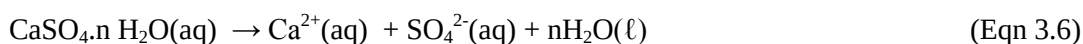


Figure 3.18: Changes in solution pH upon addition of phosphogypsum, synthetic gypsum and natural gypsum over time.

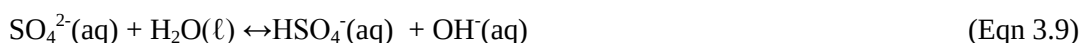
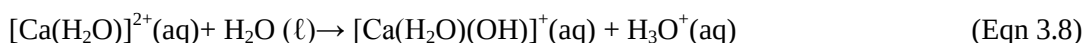
The pH variations on the solubility studies of the different gypsum samples, represented by Figure 3.18 shows that in the beginning all three pH values decrease with phosphogypsum reaching the lowest pH among the three, followed by synthetic (Merck) gypsum and natural gypsum. After decreasing for 8 minutes, the pH values then increase over the time. At time 0, the pH of ultra-pure water is reported to be slightly acidic. After addition of the gypsum samples, the acidic pH decreases shortly and then reaches an equilibrium with the OH^- ions brought by the dissolution of CaSO_4 before starting to increase. However, the decrease in pH observed in phosphogypsum is also influenced by the residual acid, originating from the phosphoric acid process, it contains within its pores.

The steady increase in pH over time for the natural gypsum sample serves as an indication that dissolution of mineral gypsum occurs steadily and at a slower rate over the time period studied. No plateau has been reached after 200 minutes, indicating that the sample is still dissolving slowly. The pH curve of synthetic-gypsum has reached a plateau after 100 minutes, while that of phosphogypsum seemed to have reached it after 200 minutes. This may be an indication that these two samples will not reach higher solubilities under these conditions. In water, calcium sulphate dissociates itself into ions Ca^{2+} and SO_4^{2-} which are then hydrated by the water molecules in

solution (Azimi et al, 2007). Ca^{2+} firstly reacts with water to form a hydrated complex which will then act as an acid in water to produce hydronium (H_3O^+) (Shriver and Atkins, 2006). On the other hand, the sulphate ions will act as a weak base which will react with water to form bisulphate ions, HSO_4^- (a weak acid) and hydroxide ions making the calcium sulphate solution basic. (Zumdahl and Zumdahl, 2006). A corresponding increase in the pH of the solution is observed upon dissolution of CaSO_4 in water. These reactions are represented by the chemical equations below:

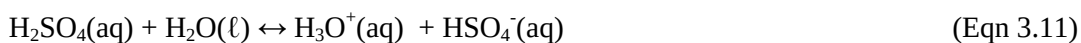
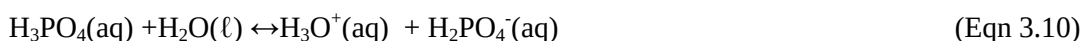


With: $n = 0.5; 2$.



The highest pH observed in synthetic-gypsum (Merck gypsum) could be explained by the fact that it has a higher kinetics of dissolution than its two counterparts. Therefore it ionizes easily in solution in such a way that more OH^- ions are being produced to make the solution more basic than the other two gypsum samples in solution as a result of the reactions between sulphate ions (SO_4^{2-}) and H_2O .

The low pH observed in phosphogypsum (all over its dissolution in water) is due to the residual acid, from the phosphoric acid process, phosphoric, sulphuric and may be hydrofluoric acids (if the phosphate ore (apatite) used during the phosphoric acid process is fluoroapatite) contained within its pores, lowering its basic pH (Tayibi et al, 2009). Therefore in solution, despite the dissolution of calcium sulphate in water which occurs to produce some bisulphate ions in solution, there is phosphoric acid, sulphuric acid and may be hydrofluoric acids which react with water to form more hydronium ions, H_3O^+ , and making the solution more acidic as shown by the dissociation equations below (Zumdahl and Zumdahl, 2006):



3.5 ICP-MS analysis performed on phosphogypsum, synthetic gypsum and natural gypsum

3.5.1 ICP-MS 4-acid analysis performed on phosphogypsum, synthetic gypsum and natural gypsum for the determination of the different major and trace elements.

An ICP-MS 4-acid analysis was performed on the gypsum samples to determine the concentrations of different major and trace elements occurring in each sample. The results obtained from these analyses are reported in Table 3.14 in parts per billion ($\mu\text{g/kg}$).

Table 3.14: Concentration of the major and trace elements in solution reported in part per billion ($\mu\text{g/kg}$)

Elements (Atomic weight)	Detection limit	Samples		
		Phosphogypsum	Synthetic-gypsum	Natural gypsum
Na (23)	50 000	72 068	756 813	1 459 525
Mg (24)	50 000	192 840	< 50 000	1 924 367
Al (27)	50 000	483 092	< 50 000	4 620 834
K (39)	50 000	< 50 000	< 50 000	1 728 256
Ca (43)	50 000	210 506 403	236 514 212	249 467 885
Cr (52)	50 000	< 10 000	11 107	13 335
Cd (114)	20	23	< 20	24
Pb (208)	500	6 739	< 500	8 283
U (238)	10	1 173	12	2 269

From the values above, it is observed that all untreated gypsum samples contain calcium in significant amount. This finds its explanation by the fact that they are mainly composed of gypsum

and bassanite which contain calcium as cation. In a 100% pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ sample, calcium contributes to 23.28% of the sample weight similarly, in a 100% pure $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ sample, calcium contributes to 27.61% of the sample weight and in a 100% pure CaCO_3 sample the same calcium will contribute to 40.04% of the sample weight. Based on the XRD results in section 3.2.1, calcium will contribute to 22.77% of the phosphogypsum sample weight and compares well to the amount of calcium presents in phosphogypsum (210 506 403 $\mu\text{g/kg}$) which corresponds to a contribution of 21.1% of calcium in phosphogypsum. Similarly with synthetic-gypsum and natural gypsum, from the XRD results, calcium contributes to 23.48% and to 25.04% of the sample weight of synthetic gypsum and natural gypsum respectively. From Table 3.14, the amount of calcium in synthetic gypsum (236 514 212 $\mu\text{g/kg}$) corresponds to a contribution of 23.65% of calcium in the synthetic gypsum sample and the amount of calcium in natural gypsum (249 467 885 $\mu\text{g/kg}$) corresponds to a contribution of 24.95% of calcium in natural gypsum. This confirmed that the data obtained from XRD and ICP-MS 4-acid analysis were in agreement.

Beside calcium which is contained in all three gypsum sample in significant amount due to the fact that they are mainly composed of gypsum and bassanite, phosphogypsum and natural gypsum contain the other elements as impurities originally contained in the phosphate rocks used during the phosphoric acid process (the case of phosphogypsum) and from the clay soil from which natural gypsum was mined (Section 3.1). Rutherford et al (1994) stated that despite the fact phosphogypsum is mainly made of calcium sulphate dihydrate; it contains elevated levels impurities which originate primarily from the phosphate rocks used in the phosphate fertilizer production. Tayibi et al (2009) added that phosphogypsum contains relatively high levels of uranium series radionuclide which are naturally present in the phosphate rock; it could contain as much as 60 times the levels normally found prior to processing.

3.5.2 ICP-MS analysis performed on phosphogypsum, synthetic gypsum and natural gypsum for the determination of Rare Earth Elements (REE)

ICP-MS analysis for rare earth elements were performed on the untreated gypsum samples to determine the amounts of these elements available in the gypsum samples. Phosphogypsum is expected to contain significant levels of these elements, due to its origin (phosphate rocks). According to Salvis and Williams-Jones (2004) apatite rocks are known to be a great source of rare earth elements. The results obtained from these analyses are reported in the Table 3.15 in parts per billion ($\mu\text{g/kg}$).

This table shows that phosphogypsum and natural gypsum contain all rare earth elements in significant amounts compared to synthetic gypsum, a commercially available product, which should be free of impurities. The presence of rare earth elements in significant amounts in phosphogypsum derives from the phosphate rocks (or apatites), used during the phosphoric acid process as stated by Salvis and Williams-Jones (2004). The rare earth elements found in natural gypsum find their origin from the ore body from which natural gypsum was mine. Synthetic gypsum is reported to contain only thorium and zirconium (in very low amount compared to phosphogypsum and natural gypsum) as rare earth elements in its elemental composition. One of the tasks during this study will be to observe whether or not the rare earth elements contain in these gypsum samples will be transferred in the products formed.

Table 3.15: Concentrations of rare earth elements in phosphogypsum, synthetic gypsum and natural gypsum as determined by ICP-MS, reported in parts per billion (µg/kg).

Elements (Atomic weight)	Detection limit	Samples		
		Phosphogypsum	Synthetic-gypsum	Natural gypsum
Y (89)	50	88 636	< 50	2 697
La (139)	500	584 475	< 500	2 919
Ce (140)	500	1 420 900	< 500	5 787
Pr (141)	50	197 297	< 50	767
Nd (146)	200	855 150	< 200	2 880
Sm (147)	20	143 259	< 20	686
Eu (151)	10	28 205	< 10	132
Gd (157)	20	95 168	< 20	557
Tb (159)	20	10 157	< 20	91
Dy (163)	10	31 824	16	536
Ho (165)	10	3 923	< 10	109
Er (167)	10	6 357	20	318
Tm (169)	10	554	< 10	48
Yb (172)	10	2 560	14	304
Lu (175)	10	212	< 10	47

3.6 Inductively Coupled Plasma-Optical Emission Spectroscopy analyses performed on phosphogypsum, synthetic gypsum and natural gypsum for major oxide elements (ICP-OES)

The major oxide elements of phosphogypsum and synthetic gypsum samples were determined by ICP-OES. The results are expressed in weight percentage (wt %) and are summarized in Table 3.16:

Table 3.16: ICP-OES of major oxide elements contained in the studied gypsum samples reported in (wt %).

Oxide element (wt %)	Sample		
	Phosphogypsum	Synthetic gypsum	Natural gypsum
Al ₂ O ₃	0.10	0.03	n.d*
CaO	33.30	36.27	n.d*
Cr ₂ O ₃	< 0.1	< 0.1	n.d*
Fe ₂ O ₃	0.03	0.00	n.d*
K ₂ O	0.00	0.03	n.d*
MgO	0.06	0.02	n.d*
MnO	0.02	0.01	n.d*
Na ₂ O	0.01	0.05	n.d*
P ₂ O ₅	0.66	0.36	n.d*
SiO ₂	0.36	0.01	n.d*
TiO ₂	0.02	0.01	n.d*
L.O.I	5.6	3.7	n.d*
H ₂ O	17.4	17.2	n.d*
Total	57.59	57.81	n.d*

*n.d: not determined

Theoretically in a 100% pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ sample, CaO will contribute to 32.5% of the sample weight while the same CaO will contribute to 38.6% of the weight of a pure sample of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. According to the XRD analyses (section 3.2.1); phosphogypsum contains gypsum at 97% and bassanite at 2%. From these results, the amount of Ca as CaO present in phosphogypsum expected from these XRD results is 32.34% and compares well with the amount of Ca expressed as CaO (33.30%) determined by the ICP-OES analysis. On the other hand for synthetic gypsum the amount of CaO expected to be present from the XRD (32.86%) compares well with the amount of CaO (36.27%) determined by the ICP-OES analysis. This confirmed that the data obtained from XRD and ICP-OES were in agreement.

The other elements such as Al_2O_3 , Cr_2O_3 , Fe_2O_3 , Na_2O , MgO , SiO_2 , P_2O_5 , are found to be present in phosphogypsum in significant amount as impurities resulting from the wet phosphoric acid process. Taha and Seals (1992) found that these elements along with CaO are the main components of phosphogypsum.

Phosphogypsum and synthetic-gypsum are reported to have a similar amount of water in their mineral composition, 17.4 % and 17.2 %, respectively. These results from ICP-OES were in fairly good agreement with the TGA data (20.3% structural water for both samples; Table 3.13). This may be explained by the amount of water of crystallization found in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_2 \cdot 0.5\text{H}_2\text{O}$ respectively since both samples were in a dry state prior to the analysis; phosphogypsum and synthetic gypsum shared a similar mineralogy, with gypsum representing the dominant mineral phase (> 95%), and bassanite being present as a minor phase (< 5%).

3.7 Conclusion

In this chapter, the three gypsum samples were characterized to determine their morphologies and chemical and mineralogical compositions. Despite the fact that they all have gypsum and bassanite in common in their respective mineral composition they are found to differ in their morphologies and particle size. However, phosphogypsum and natural gypsum are found to contain impurities which originate primarily either from the phosphate rock used during the wet phosphoric acid and/or during the wet phosphoric acid itself, in the case of natural gypsum, the impurities derive from the ore body from which it was mined.

These gypsum samples, prior to their reactions in this study, were not washed to remove the impurities they contain. One of the steps of this study will be to verify whether the impurities contain in the gypsum samples are transferred in the different products that will be formed. Chemical components of particular interest will include the rare earth elements contained in the phosphogypsum sample.

3.8 References

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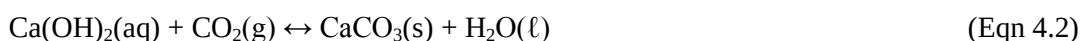
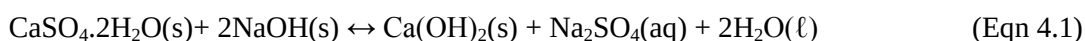
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CHAPTER FOUR: MINERAL CARBONATION OF PHOSPHOGYPSUM

4.1 Introduction

Cardenas-Escudero et al (2011) developed an indirect aqueous mineral carbonation process for the transformation of a phosphogypsum sample from Spain into CaCO_3 . The first step involved the conversion of phosphogypsum into portlandite (Ca(OH)_2) using NaOH. The two reactions describing the overall process are represented by the chemical equations below:



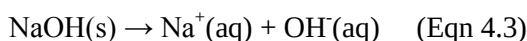
4.1.1 Cardenas-Escudero process (Cardenas-Escudero et al, 2011)

The experimental procedures followed by Cardenas-Escudero (2011) were as follows: 5g of phosphogypsum were dispersed into 20ml of pure water by magnetic stirring at room temperature and atmospheric pressure. 2.4g of NaOH were then added to the solution to reach an OH/Ca mole ratio of 2. The whole mixture was then stirred for 3 hours at a constant stirring rate. After 3 hours of reaction, the resulting white precipitate was separated by centrifugation from its supernatant; the latter was dried at 80°C on a hot plate. The dried supernatant (a transparent salt) and the white precipitate were characterized. It was found that the white precipitate consisted mainly of portlandite (Ca(OH)_2) and the salt which crystallized from the supernatant was sodium sulphate (Na_2SO_4).

During the carbonation process, 2g of the white precipitate was dispersed into 40 ml of ultrapure water under constant magnetic stirring. CO_2 was purged into the mixture at a flow of $20\text{cm}^3/\text{s}$ at a pressure of 1 bar for 15 minutes. The carbonated suspension was then left to rest overnight. The resulting precipitate was separated from its supernatant by centrifugation, dried at 80°C and characterized while the supernatant was discarded.

4.1.2 NaOH solution and hydroxide ions (OH⁻)

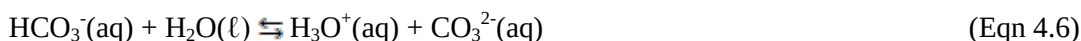
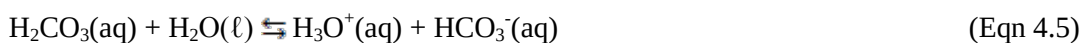
NaOH is known to be soluble in water. Its dissolution in water is known to be an exothermic reaction. Once completely dissolved, the solution is reported to be colorless and odorless with a slippery feeling. In aqueous solution, NaOH produces OH⁻, which is known to be a strong base, as described in the following chemical equation (Zumdahl and Zumdahl, 2006):



At room temperature, a concentrated NaOH solution is known to have a strong basic pH. As the temperature of a NaOH solution is increased, a decrease in pH of the solution may be observed due to a number of reasons.

When the temperature of a solution is changed, a change in the pH of the solution will be observed due to the effect of temperature on the sensor of the pH electrode. As such, Automatic Temperature Compensation (ATC) was performed for all experiments.

Dissolution of CO₂ from the atmosphere, which will react with H₂O to form carbonic acid (H₂CO₃), may also cause a decrease in the solution pH. In aqueous solutions, carbonic acid will be deprotonated by water to form hydrogen carbonate (HCO₃⁻). HCO₃⁻ in turn will be deprotonated by H₂O allowing the release of carbonate ions (CO₃²⁻) in solution (Wen et al., 2003). This mechanism is shown by the following chemical equations.



Furthermore, in the presence of NaOH, CO₂ may react immediately with OH⁻ with a subsequent release of CO₃²⁻ in solution (Xiang et al, 2002). This mechanism is shown by Equation 4.7:



The CO_3^{2-} ions formed in the NaOH solutions are expected to react with Ca^{2+} present from gypsum to form CaCO_3 .

The purpose of this chapter is to investigate the extent of carbonation and the purity of CaCO_3 that can be achieved when treating a South-African phosphogypsum using the Cardenas-Escudero process (Cardenas-Escudero, 2011).

4.2 Experimental

The experimental part of this process was performed according to the resources available for the study.

1. Firstly, the conversion of phosphogypsum into Ca(OH)_2 was investigated using NaOH.
2. The parameters of an efficient carbonation were then determined using a control; the control was Ca(OH)_2 produced from the reaction of a commercial sample of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH.
3. Finally, the Ca(OH)_2 precipitates produced from phosphogypsum were carbonated using the parameters determined using the Ca(OH)_2 produced from the reaction of a commercial sample of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH (see bullet No 2 above).

4.2.1 Conversion of gypsum into Ca(OH)_2

The effect of temperature on the conversion of South-African phosphogypsum into Ca(OH)_2 was first determined. The reactions were studied at 25°C, 40°C and 70°C for 3 hours.

200ml from a 2.9mol/l NaOH stock solution was poured into a 500ml flask with 5 necks and placed in a waterbath at the selected temperature. A pH electrode, a temperature probe and an overhead stirrer were inserted in the flask through three of the five necks available. The other two necks of the flask were closed using plastic stoppers. The NaOH solution was continuously stirred until stabilization of the pH of the NaOH solution and the selected temperature were achieved. The experimental setup used was shown in Figure 2.9.

50g of the gypsum sample (e.g. phosphogypsum) was suspended in the 200ml of NaOH solution at the selected temperature. The suspension was stirred at 750rpm for 3 hours and the pH was recorded every minute. After 3 hours of reaction, the liquid fraction was separated from the solid material by filtration, using Whatmann filter paper. The precipitate was then washed 4 times with 50ml of distilled water in order to remove any unreacted salt it might contain and was dried at 75°C for 3 hours. For each gypsum sample, the experiment was performed in duplicate at each temperature. The obtained products were weighed before further analyses were performed.

4.2.2 Synthesis of Ca(OH)_2 and CaCO_3 (controls) from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

To determine the parameters required for complete carbonation, a Ca(OH)_2 sample (control) was prepared from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH. The reaction was performed by dispersing 42.7g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ into 200ml of a NaOH solution with a molarity of 2.9M. The solution was stirred at 750 rpm at a temperature of 40°C for 3 hours. This was followed by filtration, washing, drying and weighting of the precipitate. The calcium chloride dihydrate batch used, (calcium chloride dihydrate, EMSURE) obtained from Merck Pty Ltd, as indicated by its label contained some alkaline earth metals such as magnesium (Mg) in a very low concentration (< 0.005%).

2g of the Ca(OH)_2 precipitate that was produced from the reaction at 40°C between NaOH and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, was then dispersed into 40ml of pure water at room temperature. The solution was stirred at 750rpm for an hour to obtain an homogeneous slurry mixture of Ca(OH)_2 in water, and also to ensure that the solution inside the flask reached the required temperature of 25°C and a stable pH. After stirring for an hour, CO_2 was purged into the solution at a flow of 285ml/min for 30 and 60 minutes respectively. The precipitate was then washed 3 times with 50ml of distilled water in order to remove any unreacted soluble salt it might contain and dried at 75°C for 3 hours. The experiment was performed in duplicate. The obtained products were then weighed before further analyses.

4.2.3 Carbonation of Ca(OH)_2 formed from gypsum

2g of the obtained Ca(OH)_2 product (procedure described in Section 4.2.1) was dispersed into 40 ml of water at room temperature. The solution was stirred at 750rpm for an hour to obtain an homogeneous Ca(OH)_2 solution, and to ensure that the solution inside the flask reached a temperature of 25°C and the pH was stable. After stirring for an hour, CO_2 was purged into the Ca(OH)_2 solution at a flow rate of 285ml/min for 30 minutes.

The precipitates obtained were washed 3 times with 50ml of distilled water, dried at 75°C for 3 hours and weighed before further analyses.

4.3 Results and discussion

4.3.1 Results of the reactions between gypsum and NaOH

For each temperature, the reaction was performed in duplicate and the average values were plotted against the time.

4.3.1.1 Changes in solution pH with time for the reactions of all 3 types of gypsum with NaOH

The reactions between phosphogypsum and NaOH were studied at the selected temperatures (25°C, 40°C, and 70°C) and the changes in pH over time are shown in Figure 4.1. The reaction was firstly studied at room temperature, before increasing it to 40°C and 70°C respectively.

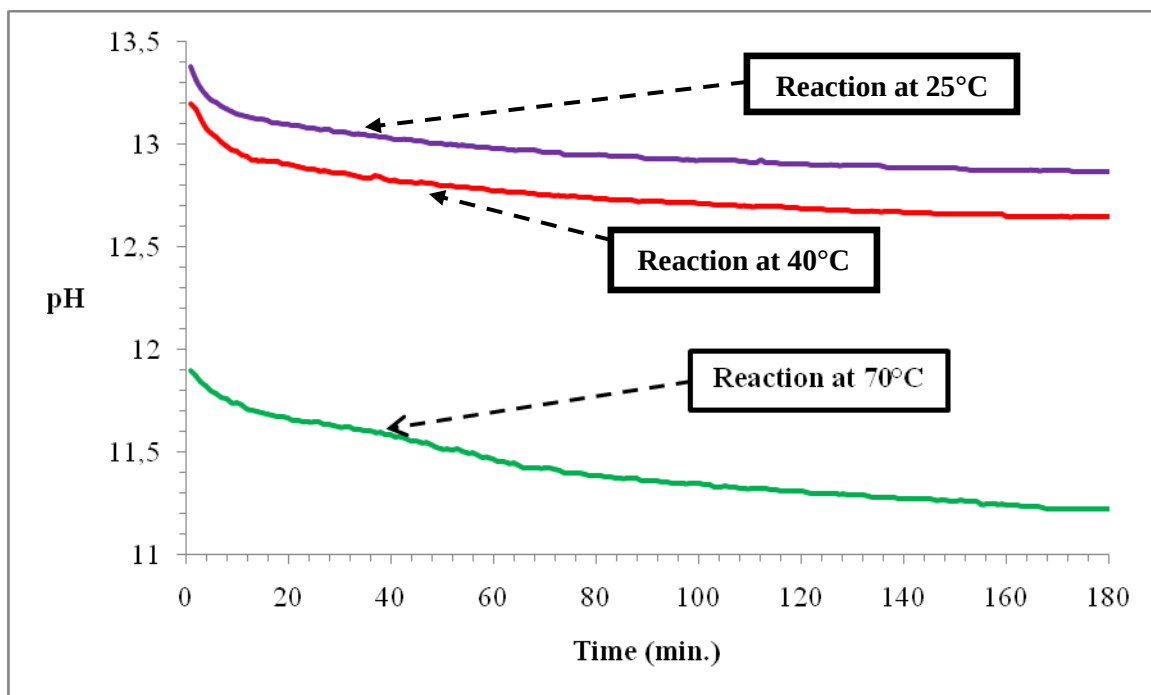


Figure 4.1: pH changes of the reaction between phosphogypsum and NaOH over time

The pH of the NaOH solution at 25°C before addition of phosphogypsum was 13.50. After addition of 50 g phosphogypsum, the pH decreased rapidly to 13.38. This decrease in pH means that OH^- ions in solution started to react with the Ca^{2+} ions from the dissociation of CaSO_4 contained in phosphogypsum to form a $\text{Ca}(\text{OH})_2$ precipitate (Equation 4.1). After complete addition of phosphogypsum, the pH value decreased continuously until the end of the reaction (3 hours). After 3 hours, the pH of the solution was not stable yet. This could indicate that the reaction was not complete after 3 hours of reaction at room temperature and that some phosphogypsum was still left unreacted.

At 40°C, the pH of the NaOH solution before addition of phosphogypsum was found to be 13.26 compared to the value at 25°C where it was at 13.50. The small decrease in pH observed for the NaOH solutions at this temperature may be due to one of the reasons explained earlier in this chapter. Upon addition of phosphogypsum, an immediate decrease in pH is observed. After the complete addition of phosphogypsum and at the end of the 3 hours of reaction, there was no stabilization of the pH values were observed. This could mean that the reaction was still not complete after 3 hours of reaction at 40°C.

At 70°C, the pH value of the NaOH solution before addition of phosphogypsum was found to be at 11.90. This further decrease in the pH of the NaOH solution may find its explanation from the

reasons listed in Section 4.1.2 above. After the complete addition of phosphogypsum, the pH decreased to 11.23 after 3 hours of reaction. The pH value reached a stable value during the last 13 minutes (from the 167th minute) of the reaction. However, 13 minutes of reaction are found to be relatively small to assert that the reaction between phosphogypsum and NaOH at 70°C was complete from the 167th minute. This would have to be confirmed by characterization of the precipitates formed by XRD which will be discussed later in this chapter.

The variations in pH at the different temperatures between synthetic gypsum and NaOH were then studied and are recorded in Figure 4.2 below.

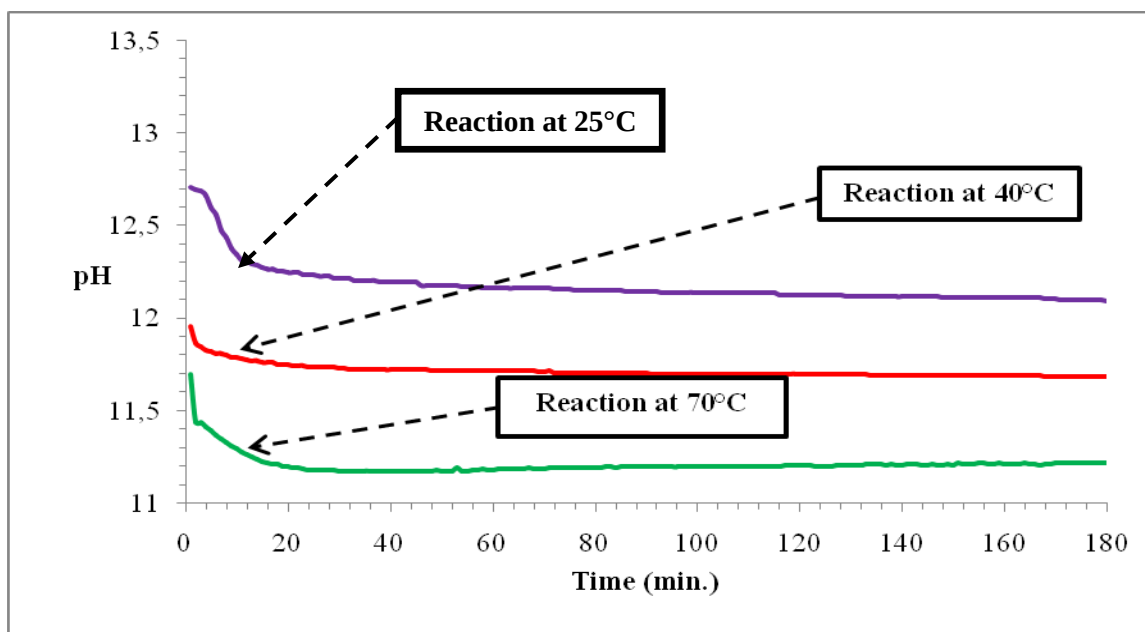


Figure 4.2: pH changes of the reaction between synthetic gypsum and NaOH over time

Upon addition of synthetic gypsum at 25°C, the pH values for both runs decreased from 13.50 (starting NaOH solution) to 12.70. This implies the immediate reaction between the hydroxide and the calcium ions present in solution. After the complete addition of synthetic gypsum, the pH curve further decreased to values around 12.10 during the 3 hours of reaction. After 3 hours of reaction, there is no clear sign that the pH has reached a stable value. The reactions between synthetic gypsum and NaOH do not seem to be complete at 25°C. There is the possibility that some synthetic gypsum was left unreacted.

At 40°C, upon addition of synthetic gypsum, the pH value decreased from 13.26 to 11.96. After complete addition of synthetic gypsum and at the end of the 3 hours of reaction, the value of the pH decreased to 11.69. After the reaction time, it is still difficult to say with certainty that the pH does

not decrease beyond 180 minutes. There is the possibility that some synthetic gypsum is still left unreacted in the flask.

At 70°C the pH values of the NaOH solution, before addition of synthetic gypsum, was 11.91. During the addition of synthetic gypsum, a decrease in pH is observed which means that the reaction between NaOH and synthetic gypsum is immediate at 70°C.

After the complete addition of synthetic gypsum, the pH decreased until the 30th minute where it seems to stabilize shortly before increasing slowly until the end of the reaction where it reaches the value of 11.20. This could mean that at 70°C, somewhere around the 56th minute of reaction, Ca(OH)_2 has stopped from being precipitated, compared to the reactions at 25°C and 40°C for synthetic gypsum. The slight increase recorded after the 56th minute, may be due to an increase of the concentration of OH^- in solution, explained by the dissolution of the Ca(OH)_2 formed during the first 30 minutes of reaction (Xiang et al, 2002). An alternative explanation to the slight increase in pH may be due to the evaporation of water from the aqueous solution at this increased temperature, also causing an increase in the concentration of OH^- .

The reactions between natural gypsum and NaOH were then studied at the same temperatures over 3 hours. The changes in pH were recorded in Figure 4.3 below.

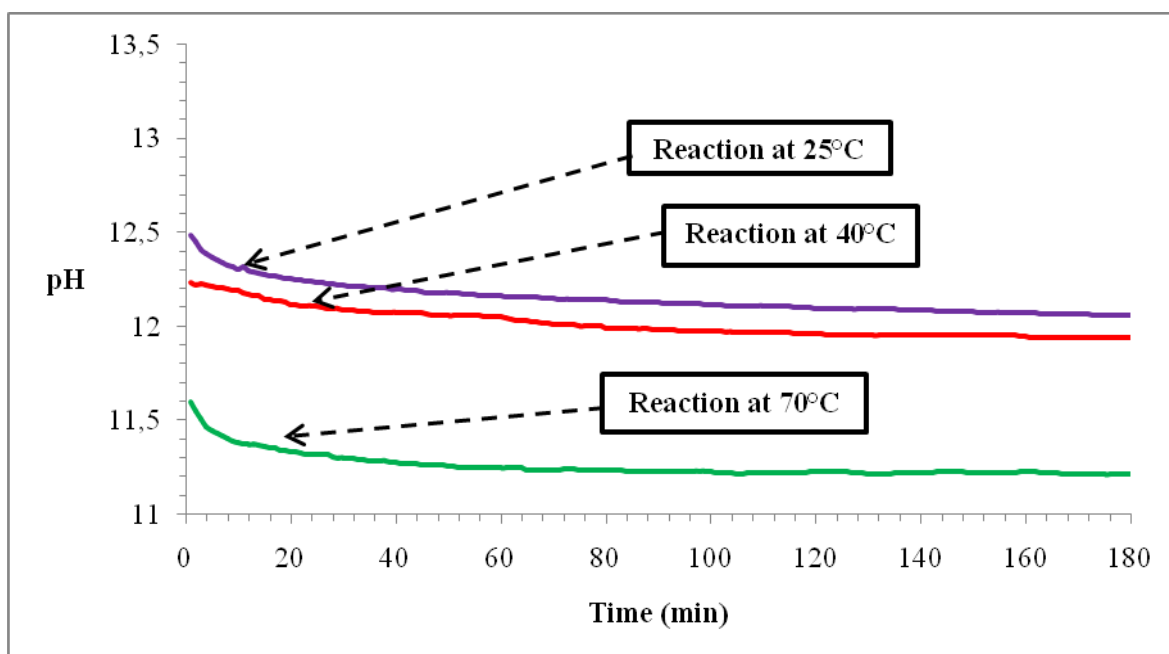


Figure 4.3: pH changes of the reaction between natural gypsum and NaOH over time

Upon addition of natural gypsum, the pH value decreased to 12.49, meaning that at 25°C, the reaction between natural gypsum and NaOH is immediate. After the complete addition of natural gypsum, the pH values decreased further over the 3 hours of reaction.

Upon addition of natural gypsum at 40°C, the pH value decreased to 12.24. After the complete addition of natural gypsum, the pH value further decreased until the end of the reaction where it reaches the value of 11.94.

The pH values of the NaOH solution before addition of natural gypsum at 70°C were found to be at 11.90. Upon addition of natural gypsum, the pH value decreased to 11.60. This means that the reaction between natural gypsum and NaOH at 70°C is immediate. After the complete addition of natural gypsum, the pH value further decreased to the value of 11.20 after the 3 hours of reaction.

4.3.1.2 Weights of the precipitates formed from the reactions between NaOH and the gypsum samples

The precipitates formed at the different temperatures between the gypsum samples and NaOH were filtered, washed, dried and weighed. The weight of each of the precipitates is reported in Table 4.1 below.

Table 4.1: Weights of the precipitates formed at the different temperatures for the reaction between the gypsum samples and NaOH

Temperature (°C)	Weight of precipitate (g)		
	Phosphogypsum + NaOH	Synthetic-gypsum + NaOH	Natural gypsum + NaOH
25	23.15	22.55	26.08
	23.06	21.78	26.14
40	22.32	21.35	27.55
	22.41	22.13	28.15
70	22.72	20.46	27.72
	22.12	22.09	27.30

Theoretically, 50g of a pure gypsum sample ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) dispersed into 200ml of NaOH (NaOH) solution should generate 21.52g of $\text{Ca}(\text{OH})_2$. On the other hand, dispersing 50g of bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) in 200ml of NaOH is expected to yield 25.55g of $\text{Ca}(\text{OH})_2$.

The experimental weights of the different precipitates formed from phosphogypsum are slightly higher than the expected theoretical weight for the formation of pure $\text{Ca}(\text{OH})_2$. Since the molecular weight of gypsum is higher than that of $\text{Ca}(\text{OH})_2$, a higher weight of the product when compared to the stoichiometrically calculated theoretical weight could be an indication of incomplete conversion of gypsum to $\text{Ca}(\text{OH})_2$. This may confirm the results obtained from the pH measurements, indicating that some of the phosphogypsum were left unreacted after 3 hours of reaction.

The weights of the different precipitates formed from synthetic gypsum are reported to be slightly closer to the theoretical weight expected for the formation of pure $\text{Ca}(\text{OH})_2$. This could mean that a

greater conversion of synthetic gypsum was reached. However some raw gypsum may still be present in the precipitates; the degree of conversion will have to be confirmed by XRD measurements.

The natural gypsum sample consists of gypsum at 49% w/w and bassanite at 47%w/w. Theoretically, for the natural gypsum sample, the weight of the product should be between 21.5g and 25.55g for a full conversion of this sample to $\text{Ca}(\text{OH})_2$. The weights of the different precipitates formed when natural gypsum reacted with NaOH are well above those theoretical weights. This could be an indication that the reactions between natural gypsum and NaOH were incomplete at all temperatures, as suspected from the behavior of the pH curves.

4.3.1.3 XRD analyses of the precipitates formed from the reaction between NaOH and the gypsum samples.

The precipitates formed were analyzed by XRD to determine their respective mineral compositions. The mineral compositions of the precipitates formed are recorded in Table 4.2.

The results show that a good extent of conversion (96-97%) of phosphogypsum into $\text{Ca}(\text{OH})_2$ is already reached at 25°C. The temperature does not seem to have a major effect on the conversion of the phosphogypsum sample.

The precipitates formed at 40°C and 70°C have the particularity to contain small amounts of calcite. CaCO_3 can possibly form from dissolution of CO_2 from the atmosphere, as discussed in section 4.1.2. It seems that the increase in temperature favors the formation of CaCO_3 . The presence of Na_2SO_4 in the mineral composition of the precipitates formed at 40°C was most probably due to insufficient washing of the precipitate after filtration. Unreacted gypsum was only found in the precipitates formed at 25°C and 70°C.

The XRD results further show that the extent of conversion for the transformation of synthetic gypsum into $\text{Ca}(\text{OH})_2$ increases directly with the temperature. However, there is no significant difference in the amount of $\text{Ca}(\text{OH})_2$ formed at 40°C and 70°C respectively. It is further observed that no CaCO_3 is formed at 25°C and 40°C, and that there is some unreacted synthetic gypsum left in all the samples.

Finally, it is observed that the conversion of natural gypsum into Ca(OH)_2 increased with temperature. The greatest extent of conversion is obtained at 70°C with an average of 88% of portlandite formed and the lowest percentage of unconverted gypsum (3%). From the XRD analysis performed on unreacted natural gypsum where the presence of calcite was already reported to be present as impurities (2%), a net increase in calcite content is observed in the precipitates formed most probably due to the dissolution of CO_2 in solutions. This analysis also reveals the presence of quartz in the precipitates as impurities due to the fact that quartz was initially present in the mineral composition of unreacted natural gypsum.

Table 4.2: Mineral compositions of the precipitates formed from the reaction between the gypsum samples and NaOH at different temperatures, reported as weight percentage (wt %)

Minerals	Molecular formula	Sample								
		PG + NaOH			SG + NaOH			NG+ NaOH		
		25°C	40°C	70°C	25°C	40°C	70°C	25°C	40°C	70°C
Portlandite	Ca(OH)_2	97	95	96	92	97	97	80	73	89
		96	93	97	90	95	95	81	70	89
Calcite	CaCO_3	-	<1	2	-	-	-	5	7	6
		-	2	-	-	-	1	7	7	7
Sodium sulphate	Na_2SO_4	-	5	-	-	-	-	-	-	-
		-	5	-	-	-	-	-	-	-
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	3	-	2	8	3	3	12	18	4
		4	-	3	10	5	4	10	21	3
Quartz	SiO_2	-	-	-	-	-	-	3	2	1
		-	-	-	-	-	-	2	2	1

4.3.1.4 Extent of conversion of the precipitates formed from the reaction between NaOH and the gypsum samples

The XRD results showed that the dominant mineral phase in the precipitates formed from the reaction between the gypsum samples and NaOH at the different temperature was portlandite. A mass balance study was then performed using the masses of the precipitates formed in order to determine the percentage of calcium in each gypsum sample that was really converted into Ca(OH)_2 . The results of this study are summarized in Table 4.3 below

Based on the assumption that 100% of the Ca contained in each gypsum sample is converted into pure Ca(OH)_2 , there is the potential to form 21.04g, 21.70g and 22.48g of pure Ca(OH)_2 that will form from phosphogypsum, synthetic gypsum and natural gypsum respectively. The masses of formed products achieved in these experiments ranged from 20.46 to 28.15g (Table 4.3), with the degree of purity reported in Table 4.2.

Table 4.3 further shows that the masses of the Ca(OH)_2 precipitates formed from the three gypsum samples are above the theoretical weights of Ca(OH)_2 explaining the extent of conversion of calcium into Ca(OH)_2 which is above 100%. This great extent of conversion of calcium into Ca(OH)_2 may be explained by the fact that some of the reactant (gypsum and/ or bassanite) may still be present in the precipitates formed and therefore explaining the high masses obtained. These high extents of conversion are in agreement with the behavior of the pH curves as well as with the XRD analyses where the presence in the precipitates formed of unreacted gypsum and/or bassanite was suspected and then confirmed by XRD.

Table: 4.3: Extent of conversion of the calcium contained in the gypsum samples into Ca(OH)_2

	Theoretical mass of Ca(OH)_2 to be formed	Temperature	Mass of Ca(OH)_2 formed in (g)	Extent of conversion in %	Average extent in %
PG + NaOH	21.04 g	25°C	23.15 23.06	110 109.6	109.8 ± 0.3
		40°C	22.32 22.41	n.d*	n.d*
		70°C	110 109.6	108 105.1	106.6 ± 2.1
SG + NaOH	21.70 g	25°C	22.55 21.78	n.d*	n.d*
		40°C	21.35 22.13	98.4 102	100.2 ± 2.5
		70°C	20.46 22.09	94.3 102	98.2 ± 5.4
NG + NaOH	22.48 g	25°C	26.08 26.14	n.d*	n.d*
		40°C	27.55 28.15	n.d*	n.d*
		70°C	27.72 27.30	n.d*	n.d*

*not determined (mass balance was only calculated for samples with more than 95% of portlandite)

4.3.1.5 Elemental compositions (majors) of the precipitates formed at different temperatures

The content of major elements in the Ca(OH)_2 precipitates formed at different temperatures between the gypsum samples and NaOH was determined by ICP-OES. The results are expressed in weight percentage (wt oxide %) and are summarized in Table 4.4, 4.6 and 4.8.

Table 4.4: ICP-OES of major elements (wt % oxide) of the precipitates formed from phosphogypsum

Samples	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO
P _{PG+NaOH25°C}	0.727	0.021	0.216	0.438	0.006	0.080	67.356
	0.830	0.018	0.209	0.215	0.003	0.073	64.334
P _{PG+NaOH40°C}	1.149	0.029	0.361	0.313	0.004	0.098	77.563
	1.237	0.021	0.367	0.331	0.004	0.108	81.487
P _{PG+NaOH70°C}	0.901	0.018	0.237	0.268	0.004	0.073	64.731
	0.815	0.019	0.230	0.251	0.006	0.076	67.338

Samples	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I	Moisture
P _{PG+NaOH25°C}	0.212	< 0.1	2.291	21.664	2.264
	1.064	< 0.1	2.223	22.056	1.494
P _{PG+NaOH40°C}	0.336	0.056	2.879	23.728	1.610
	0.390	0.017	3.136	24.057	0.997
P _{PG+NaOH70°C}	0.937	< 0.1	2.262	22.597	0.818
	1.125	< 0.1	2.305	22.845	0.636

*PG= Phosphogypsum; P = Precipitate.

**P_{PG+NaOH25°C}= Precipitate formed between Phosphogypsum and NaOH at 25°C.

Table 4.5: Amount of CaO in the $\text{Ca}(\text{OH})_2$ precipitates made from phosphogypsum as determined from XRD

Sample	Amount of CaO in the $\text{Ca}(\text{OH})_2$ precipitate expected from the XRD analysis in (wt %)
$\text{P}_{\text{PG}+\text{NaOH}25^\circ\text{C}}$	73.57%
	72.68%
$\text{P}_{\text{PG}+\text{NaOH}70^\circ\text{C}}$	72.39%
	73.09%

Table 4.5 shows that the amount of calcium (expressed as CaO) in each of the precipitates formed is double the amount of CaO reported to be present in phosphogypsum before going into reaction, which was 33.30%. The amount of CaO in the precipitate is influenced by the amounts of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{OH})_2$ and/or CaCO_3 each contain. In a sample containing 100% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ for instance, CaO can only contribute to 32.5% of the sample weight, while in a sample made up of 100% $\text{Ca}(\text{OH})_2$, CaO will contribute to 75.5% of the sample weight. Lastly in a sample of pure CaCO_3 , CaO can only contribute to 56% of the sample weight. This implies that an increased weight percentage of CaO contained in the product, may serve as an indication of a higher $\text{Ca}(\text{OH})_2$ and/or CaCO_3 content compared to the CaO content of the original gypsum sample.

The other elements are present as impurities previously contained in the untreated phosphogypsum before the reactions and are found into the $\text{Ca}(\text{OH})_2$ precipitates. Cardenas-Escudero et al (2011) also reported that there was a transfer of the impurities originally in untreated phosphogypsum to the portlandite formed.

A comparison on the amount of CaO present in the precipitates determined by ICP-OES and the amount of CaO deriving from the portlandite in the precipitates expected from the XRD analysis (Table 4.5) shows that the amount of CaO deriving from portlandite as expected from XRD (73.57% and 72.68% for the precipitates formed at 25°C ; 72.39% and 73.09% for the precipitates formed at 70°C) are higher than the amount of CaO detected by ICP-OES. The difference in the results between XRD and ICP-OES was most probably due to the fact that XRD is a semi-quantitative method and each instrument is based on a different principle of analysis and therefore comes with its own limitations. Furthermore, prior to the XRD analysis, the samples were not micronised since it was uncertain whether the sample would have been altered during the

micronisation process with ethanol. The size of the particles which were analysed by XRD may have therefore been larger than what is recommended (i.e. sub-10µm), which could have caused artefacts such as preferential orientation during the analysis.

Table 4.6: ICP-OES of major elements (wt % oxide) of the precipitates formed from synthetic gypsum

Samples	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO
P _{SG+NaOH25°C}	0.003	< 0.01	0.004	0.232	0.002	0.001	71.088
	0.274	< 0.01	0.003	0.161	0.000	0.000	69.382
P _{SG+NaOH40°C}	0.003	< 0.01	0.003	0.164	0.000	0.001	76.045
	0.039	< 0.01	0.003	0.165	0.000	0.001	72.544
P _{SG+NaOH70°C}	0.055	< 0.01	0.013	0.186	0.000	0.002	77.081
	0.101	< 0.01	0.014	0.177	0.000	0.001	69.265

Samples	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I	Moisture
P _{SG+NaOH25°C}	< 0.1	< 0.1	0.013	22.736	2.134
	0.189	< 0.1	0.002	24.224	1.254
P _{SG+NaOH40°C}	0.186	< 0.1	0.009	25.363	0.517
	0.992	< 0.1	0.006	24.204	0.358
P _{SG+NaOH70°C}	< 0.1	< 0.1	0.007	25.933	0.140
	1.262	0.199	0.007	23.016	1.276

*SG= Synthetic Gypsum; P = Precipitate.

**P_{SG+NaOH25°C}= Precipitate formed between synthetic gypsum and NaOH at 25°C.

Table 4.7: Amount of CaO in the Ca(OH)_2 precipitates made from synthetic gypsum as determined from XRD

Sample	Amount of CaO in the Ca(OH)_2 precipitate expected from the XRD analysis in (wt %)
$\text{P}_{\text{SG}+\text{NaOH}40^\circ\text{C}}$	73.31%
	72.21%
$\text{P}_{\text{SG}+\text{NaOH}70^\circ\text{C}}$	73.51%
	71.60%

The ICP-OES analysis of the major elements reported in Table 4.6 shows that the amount of calcium present as CaO in each of the precipitates formed between synthetic gypsum and NaOH is twice the amount of calcium present as CaO in synthetic gypsum (36.27%) before reaction.

A comparison on the amount of CaO present in the precipitates determined by ICP-OES and the amount of CaO deriving from the portlandite in the precipitates expected from the XRD analysis (Table 4.7) shows that the amount of CaO deriving from portlandite as expected from XRD (73.31% and 72.21% for the precipitates formed at 40°C; 73.51% and 71.60% for the precipitates formed at 70 °C) are higher than the amount of CaO detected by ICP-OES. The difference in results between XRD and ICP-OES were explained previously.

Table 4.8: ICP-OES of major elements (wt % oxide) of the precipitates formed from natural gypsum

Samples	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO
P _{NG+NaOH25°C}	6.006	0.068	1.125	0.761	0.017	0.983	61.866
	6.315	0.084	1.163	0.816	0.017	0.969	59.575
P _{NG+NaOH40°C}	5.608	0.072	1.001	0.732	0.015	0.876	55.082
	5.968	0.080	1.097	0.780	0.015	0.920	56.002
P _{NG+NaOH70°C}	6.280	0.089	1.164	0.818	0.018	0.933	56.879
	6.853	0.072	1.139	0.805	0.016	0.922	60.003

Samples	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I	Moisture
P _{NG+NaOH25°C}	0.347	0.101	0.025	23.879	1.555
	0.223	0.127	0.023	22.726	2.030
P _{NG+NaOH40°C}	0.331	0.096	0.024	20.721	3.845
	0.343	0.106	0.026	19.415	4.217
P _{NG+NaOH70°C}	1.339	0.114	0.025	22.799	1.590
	0.486	0.190	0.025	22.165	3.488

*NG= Natural gypsum; P= Precipitate.

**P_{NG+NaOH25°C}= Precipitate formed between Natural gypsum and NaOH at 25°C.

Table 4.9 shows the ICP-OES analysis of the major elements contained in the Ca(OH)₂ precipitates obtained from the reactions between natural gypsum and NaOH at the different temperatures. Natural gypsum was made of 49.0% w/w of CaSO₄.2H₂O and 46.8% w/w of CaSO₄.0.5H₂O. Theoretically, in a sample made up of 50% CaSO₄.2H₂O and 50% CaSO₄.0.5H₂O, CaO originating from CaSO₄.2H₂O will contribute to 16.25% of the sample weight while CaO obtained from CaSO₄.0.5H₂O will contribute to 19.3% of the sample weight. The amount of calcium, expressed as CaO, present in each precipitate is double the theoretical amount of CaO (35.55%) that would be present in a natural gypsum sample made up of 50% CaSO₄.2H₂O and 50% CaSO₄.0.5H₂O before reaction.

The other elements found in the Ca(OH)₂ precipitates are impurities previously contained in the untreated natural gypsum before the reactions.

4.3.1.6 Carbon and Sulphur analysis of the precipitates formed at different temperatures

Carbon and Sulphur analyses were performed on the precipitates formed from the reactions between the gypsum samples and NaOH at the different temperatures to determine the amount of sulphur present in those precipitates. The results of these analyses are summarized in Table 4.9

Table 4.9: Carbon and Sulphur analysis of the Ca(OH)_2 precipitates formed from the three gypsum samples

Samples	CO_2 (%)	SO_3 (%)	Amount of SO_3 (%) determined by XRD
$\text{P}_{\text{PG}+\text{NaOH}25^\circ\text{C}}$	1.8	6.19	1.29
	2.0	5.54	2.58
$\text{P}_{\text{PG}+\text{NaOH}40^\circ\text{C}}$	3.1	2.18	n.d*
	3.1	1.97	n.d*
$\text{P}_{\text{PG}+\text{NaOH}70^\circ\text{C}}$	2.0	4.31	2.00
	2.2	4.51	2.09
$\text{P}_{\text{SG}+\text{NaOH}25^\circ\text{C}}$	1.4	6.51	n.d*
	1.5	4.17	n.d*
$\text{P}_{\text{SG}+\text{NaOH}40^\circ\text{C}}$	1.8	2.51	1.17
	1.3	4.46	2.07
$\text{P}_{\text{SG}+\text{NaOH}70^\circ\text{C}}$	2.6	0.89	0.41
	2.1	6.62	3.08
$\text{P}_{\text{NG}+\text{NaOH}25^\circ\text{C}}$	3.2	3.56	n.d*
	3.1	5.45	n.d*
$\text{P}_{\text{NG}+\text{NaOH}40^\circ\text{C}}$	2.6	10.20	n.d*
	3.6	10.83	n.d*
$\text{P}_{\text{NG}+\text{NaOH}70^\circ\text{C}}$	3.1	4.92	n.d*
	4.2	1.59	n.d*

*not determined (The amount of CaO as determined by XRD was only calculated for samples containing more than 95% of portlandite)

A substantial decrease in the amount of sulphur (S) present as sulphur trioxide (SO₃) is observed in each one of the precipitate compared to the amount of SO₃ found in the untreated phosphogypsum sample, which was reported to be 49.30%. This strongly suggests that an efficient conversion of calcium sulphate occurred during the reactions at the different temperatures.

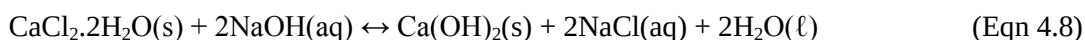
A considerable decrease in the amount of sulphur as SO₃ is recorded in each precipitate compared to its value (49.4%) in synthetic gypsum before the reaction, indicating a good conversion of calcium sulphate contained in the raw synthetic gypsum. It is also observed that the amount of carbonate in each precipitate is greater than the amount of carbonate as CO₂ (0.1%) in synthetic gypsum before it reacts with NaOH at the different temperatures. This just confirms that the formation of calcium carbonate was taking place during the reactions.

The decrease in the amount of sulphur as SO₃ in each precipitate compared to its value (39.1%) in natural gypsum before the reaction is an indication of a good conversion of the calcium sulphate contained in natural gypsum before reactions. Moreover, it is observed that the amount of carbonate in each precipitate is greater than the amount of carbonate as CO₂ (1.5%) in natural gypsum before going into reaction with NaOH at the different temperatures. This confirms the formation of calcium carbonate during the reactions.

Table 4.9 further shows that the amounts of SO₃, determined by the XRD analysis, are lower than the amounts of SO₃ determined by the Carbon and Sulphur analysis for each Ca(OH)₂ precipitate. This difference may be due to the fact that XRD is a semi-quantitative method, and the two methods of analysis rely on distinct principles of analysis.

4.3.2 Synthesis of Ca(OH)₂ and CaCO₃ from CaCl₂·2H₂O

After the formation of Ca(OH)₂ from phosphogypsum, the parameters for an efficient carbonation reaction, such as the flow rate of CO₂ and the duration of the carbonation of the Ca(OH)₂ precipitates formed from the gypsum samples, were determined on a pure Ca(OH)₂ sample. This sample was precipitated from CaCl₂·2H₂O and NaOH. The reaction between CaCl₂·2H₂O and NaOH is described by the chemical Equation 4.8.



The carbonation of the Ca(OH)_2 formed from CaCl_2 was performed at room temperature over two reaction times (30, 60 minutes) at a CO_2 flow of 285ml/min. The flow rate used in the literature to purge CO_2 into the Ca(OH)_2 solution was $20\text{cm}^3/\text{s}$ (1200ml/min) (Cardenas-Escudero et al, 2011). This CO_2 flow rate is four times higher than the maximum CO_2 flow rate of the flow meter to be used in this study.

4.3.2.1 Variations of pH with time for the reactions between $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ with NaOH

The changes in pH at 40°C of the reactions between $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH are reported in Figure 4.4. The reaction was performed in duplicate and the average values were plotted against the time.

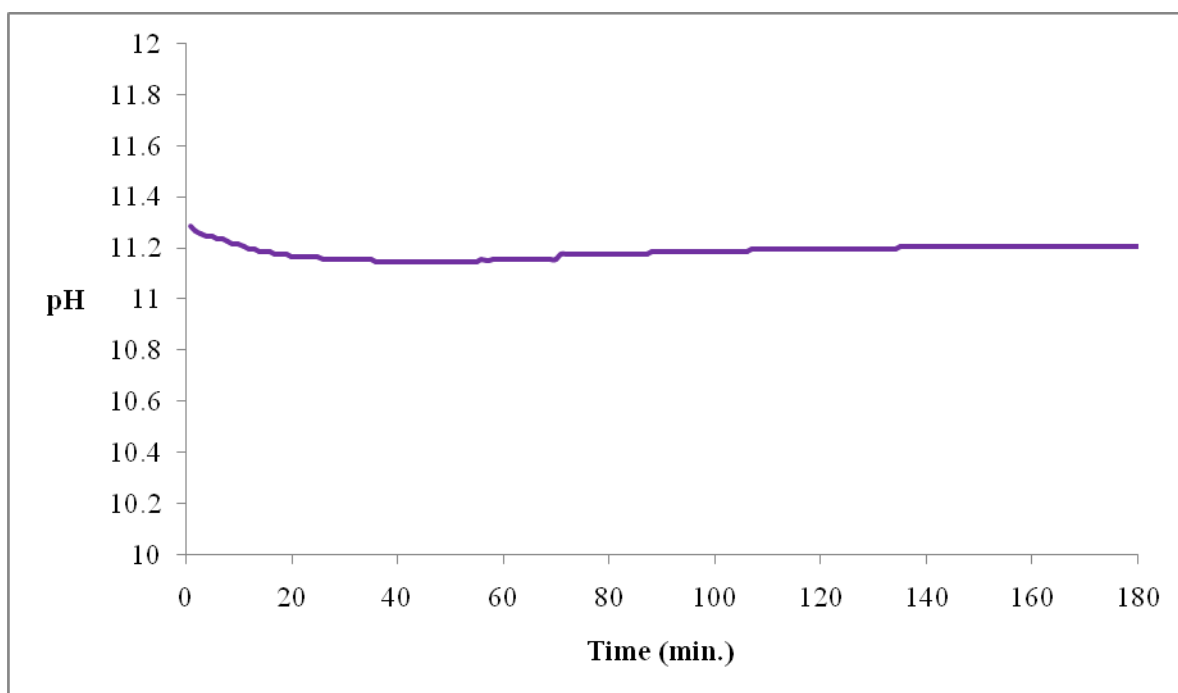


Figure 4.4: pH variations of the reaction between $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH at 40°C

The pH value of the NaOH solution at 40°C was 13.25. After the complete addition of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, the pH value decreased to 11.30. It is further decreased to 11.15 after 36 minutes of reaction. Thereafter, the pH remained stable for about 20 minutes before increasing slightly until the end of the reaction where a value 11.21 was reached.

4.3.2.2 Variations of pH with time for the carbonation of the Ca(OH)_2 precipitates made from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH

The changes in pH at 25°C for the carbonation of the Ca(OH)_2 precipitates made from the reaction at 40°C between $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH are reported in Figure 4.5. For each time (30 minutes and 60 minutes), the reaction was performed in duplicate and the average values were plotted against the time.

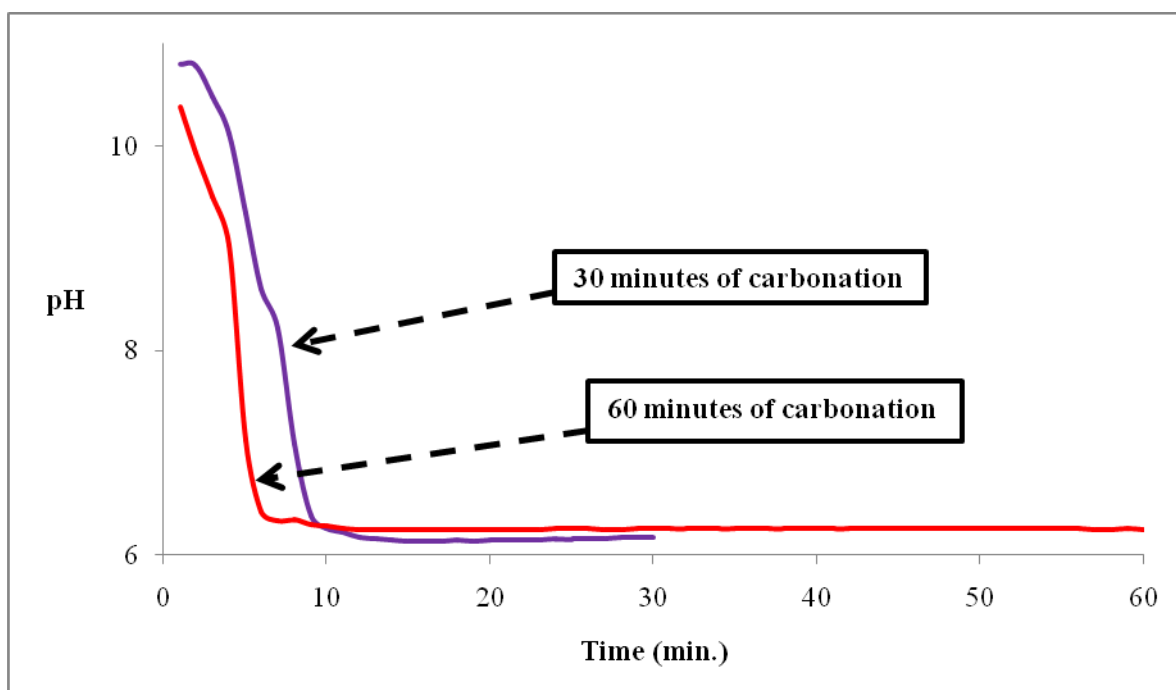


Figure 4.5: pH variations for the carbonation of the Ca(OH)_2 precipitates made at 40°C from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH .

After dispersion of Ca(OH)_2 for an hour, the pH values of the Ca(OH)_2 suspensions were reported to be 12.24. At the introduction of CO_2 into the Ca(OH)_2 a sudden decrease in pH of the solutions were observed from the first minute. This decrease in pH was due to the formation of H_2CO_3 as CO_2 was dissolved into the solutions to react with H_2O as was shown by Equation 4.4.

H₂CO₃ is then deprotonated by H₂O to form HCO₃⁻ which in turn will undergo a deprotonation by water to form CO₃²⁻ as was shown by Equations 4.5 and 4.6. CO₂ may also dissolve in solution by reacting immediately with OH⁻ to release CO₃²⁻ as was shown by Equation 4.7.

In all cases, this decrease in pH will result into the formation of CO₃²⁻ which will react with the Ca²⁺ resulting from the dissociation of Ca(OH)₂, to precipitate CaCO₃ as shown by Equation 4.9.



The pH values of all suspensions further decreased during the carbonation process until a reaction time between 8 and 12 minutes after which they became stable until the end of the reaction. The stabilisation of pH values which were reached after 8 minutes or 12 minutes of reaction could be considered as an indication of completion of the reaction between Ca²⁺ and CO₃²⁻ ions for the precipitation of CaCO₃. No more CaCO₃ are expected to form after the 12th minute of the carbonation process.

4.3.2.3 XRD analysis of the precipitates formed from CaCl₂.2H₂O

The mineral compositions of the precipitates formed from CaCl₂.2H₂O were determined by XRD. Table 4.10 shows the mineralogical compositions of the Ca(OH)₂ precipitates formed at 40°C from the reactions between CaCl₂.2H₂O and NaOH while Table 4.11 shows the mineralogical compositions of the products formed after the carbonation of Ca(OH)₂.

Table 4.10: XRD results of the precipitates formed at 40°C between CaCl₂.2H₂O and NaOH

Minerals	Molecular formula	Weight %	
		Precipitate 1	Precipitate 2
Portlandite	Ca(OH) ₂	94	94
Calcite	CaCO ₃	5	4
Halite	NaCl	<1	<1
Dolomite	CaCO ₃ .MgCO ₃	<1	1

Table 4.11: Mineral compositions of the carbonated Ca(OH)₂ precipitates

Minerals	Molecular formula	Weight %			
		60 minutes of carbonation		30 minutes of carbonation	
		Precipitate 1	Precipitate 2	Precipitate 1	Precipitate 2
Calcite	CaCO ₃	97	97	100	96
Portlandite	Ca(OH) ₂	3	3	-	4

The XRD results from Table 4.10 show that the Ca(OH)₂ precipitates have the same amount of portlandite in their respective mineral compositions (94%). They are also reported to have the same amount of calcite formed during the 3 hours of reaction, possibly due to the dissolution of CO₂ from the atmosphere, as discussed in section 4.1.2. A relatively small amount of dolomite is present in both precipitates. This was due to the presence of a small amount of magnesium contained in the CaCl₂.2H₂O sample. The magnesium ions replaced part of the calcium ions contained in the crystal lattice of the calcium carbonate formed (Banth et al, 2008). The presence of halite could be attributed to insufficient washing of the precipitates.

The XRD results, shown in Table 4.11 reveal that at room temperature and after 30 minutes of carbonation, a conversion of at least 96% of Ca(OH)₂ into CaCO₃ is obtained by dissolving 2g of

Ca(OH)_2 in 40 ml of water while stirring the solution at 750rpm and purging CO_2 into the mixture at a flow rate of 285ml/min. The same result was obtained when the samples were carbonated for 60 minutes.

4.3.2.4 Extent of conversion of the precipitates formed from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

A mass balance study was then performed on the masses of the precipitates formed in order to determine the percentage of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was really converted into Ca(OH)_2 as well as the amount of Ca(OH)_2 that was then transformed into CaCO_3 . The results of this study are summarized in Tables 4.12 and 4.13

Table 4.12: Weights of the Ca(OH)_2 precipitates formed at 40°C from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH

	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O} + \text{NaOH}$	Average
	40°C	
Theoretical mass of Ca(OH)_2 to form in (g)	21.52	21.52 ± 0.00
Mass of Ca(OH)_2 formed in (g)	18.5	18.35 ± 0.21
	18.2	
Extent of conversion in %	85.97	85.27 ± 0.99
	84.57	

On weighing the precipitates, their weights were reported to be 18.5g for the precipitate deriving from the first run and 18.2g for the second precipitate. These low weights reveal that some of the precipitates were lost during the filtration process.

In a 100% pure $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, calcium will contribute to 27.27%. Therefore, from 42.7g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved into 200ml of 2.9M NaOH, calcium will contribute to 11.64% of the weight of the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ sample. This would theoretically produce a precipitate of pure Ca(OH)_2 of 21.52g. Table 4.6 shows that for 42.7g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ dispersed into 20ml of a NaOH solution, an average of 18.35g of Ca(OH)_2 is formed, which represents an extent of conversion of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ into Ca(OH)_2 of 85.27% in average. This means that a significant proportion of the calcium in solution was converted into Ca(OH)_2 .

Table 4.13: Weights of the carbonated $\text{Ca}(\text{OH})_2$ precipitates made from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

			Average
Theoretical mass of CaCO_3 to form in (g)		2.52	2.54 ± 0.02
		2.55	
Mass of CaCO_3 formed in (g)	Precipitates formed after 60 minutes of carbonation	2.22	2.13 ± 0.13
		2.04	
	Precipitates formed after 30 minutes of carbonation	2.16	2.12 ± 0.06
		2.08	
Extent of conversion in %	Precipitates formed after 60 minutes of carbonation	87.4	83.85 ± 5.02
		80.3	
	Precipitates formed after 30 minutes of carbonation	85.04	83.47 ± 2.23
		81.89	

On the other hand, when 2g of $\text{Ca}(\text{OH})_2$ is transformed into CaCO_3 , the theoretical weight of the CaCO_3 precipitate is 2.7g. However, it is observed that the experimental weights of the precipitates obtained are lower than the theoretical weight. This could be explained by the fact that some of the precipitates were lost during filtration.

Theoretically, for an average of 2g of $\text{Ca}(\text{OH})_2$ precipitate (containing an average mass of 1.02g of calcium) formed at 40°C from the reaction between $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH, dispersed into 20 ml of a NaOH solution, 2.54g of CaCO_3 should be formed. Table 4.7 shows that for 2g of $\text{Ca}(\text{OH})_2$ used during the carbonation reactions, an average mass 2.13g and 2.12g of CaCO_3 are produced after 60 minutes and 30 minutes of carbonation respectively. These masses mean that 83% of the calcium present in portlandite was converted into calcium carbonate.

4.3.3 Carbonation of $\text{Ca}(\text{OH})_2$ precipitates formed from phosphogypsum, synthetic gypsum and natural gypsum.

The $\text{Ca}(\text{OH})_2$ precipitates formed from phosphogypsum, synthetic gypsum and natural gypsum containing the highest percentage of $\text{Ca}(\text{OH})_2$ formed at the lowest temperature possible were carbonated using the parameters described in Section 4.2.3.

4.3.3.1 Variations of pH with time for the carbonation reactions of the Ca(OH)_2 formed from the gypsum samples

Figures 4.6, 4.7 and 4.8 show the variations in pH of the carbonation of the Ca(OH)_2 precipitates obtained from the reactions of phosphogypsum and NaOH at 25°C, synthetic gypsum and NaOH at 40°C and natural gypsum and NaOH at 70°C. For each Ca(OH)_2 sample selected, the carbonation process was performed in duplicate and the average values were plotted against time.

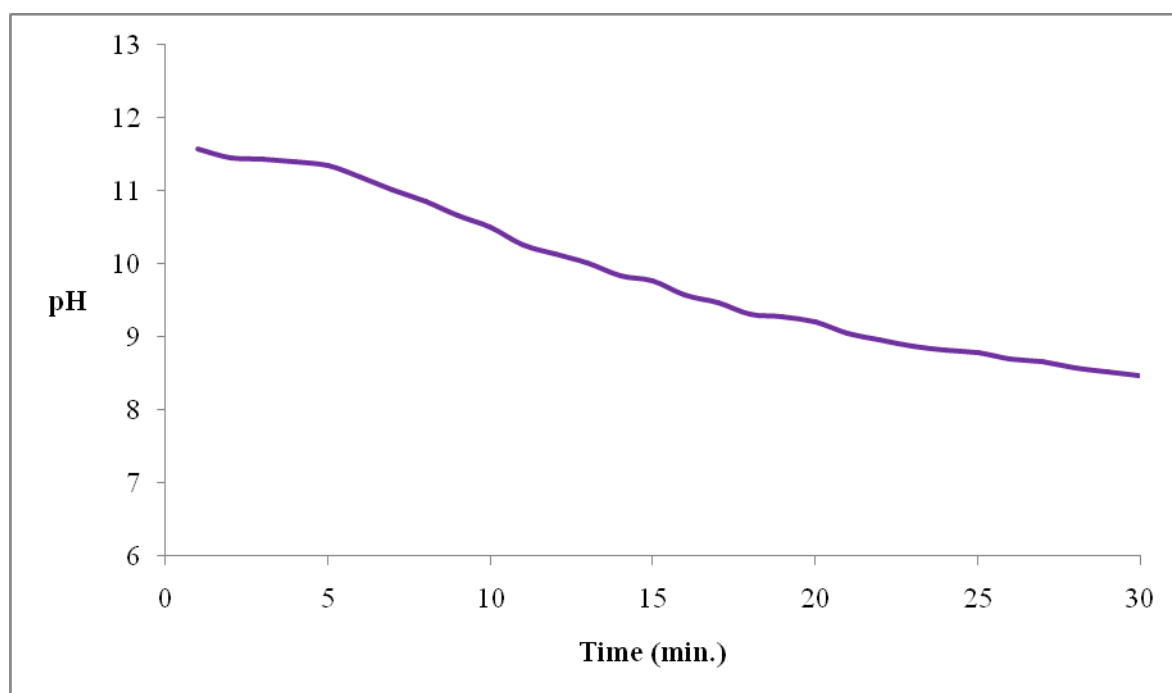


Figure 4.6: Variation of pH for the carbonation of the Ca(OH)_2 precipitates obtained at 25°C from phosphogypsum and NaOH.

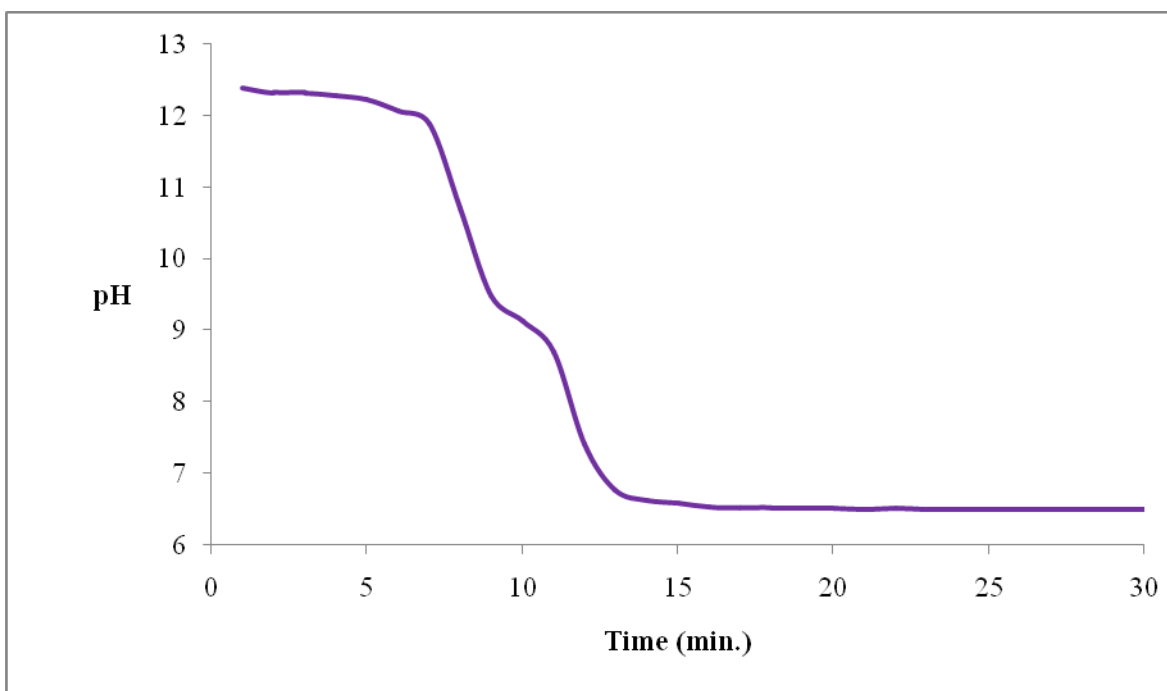


Figure 4.7: Variation of pH for the carbonation of the Ca(OH)_2 precipitates obtained at 40°C from synthetic gypsum and NaOH.

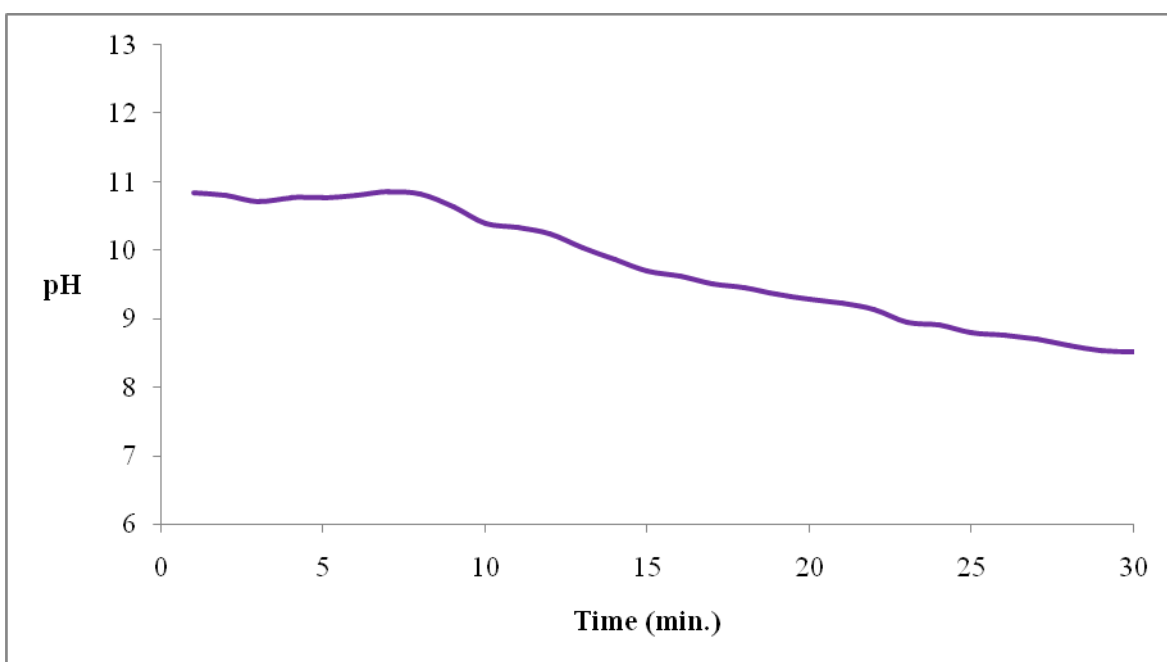


Figure 4.8: Variation of pH for the carbonation of the Ca(OH)_2 precipitates obtained at 70°C from natural gypsum and NaOH.

Figure 4.6 shows the variation of pH for the carbonation of the Ca(OH)_2 sample obtained at 25°C from the reaction between phosphogypsum and NaOH. After dispersing Ca(OH)_2 in water, the pH values of the Ca(OH)_2 solutions, before purging CO_2 , was at 12.30. Upon introduction of CO_2 in the Ca(OH)_2 suspension, the pH value rapidly decreased to 8.47 after 30 minutes. The decrease in pH is the result of the formation of CaCO_3 precipitates in solution. However, after 30 minutes of reaction, the pH curves revealed that carbonation of the Ca(OH)_2 obtained from phosphogypsum was incomplete.

Figure 4.7 shows the pH variations for the carbonation of the Ca(OH)_2 made a 40°C between synthetic gypsum and NaOH. The pH of the Ca(OH)_2 before purging CO_2 was at 12.62. Upon introduction of CO_2 , the pH value decreased to 6.53 just after 16 minutes of reaction time after which the pH values remained stable until the end of the reaction time. From these observations, it may be said that the carbonation of the Ca(OH)_2 obtained from synthetic gypsum was complete after 16 minutes of reaction and that no major CaCO_3 will be precipitated afterwards.

Figure 4.8 shows the variation in pH for the carbonation of the Ca(OH)_2 precipitates obtained at 70°C between natural gypsum and NaOH. After dispersing the Ca(OH)_2 precipitate into water, the pH values of the Ca(OH)_2 suspension was at 11.92. This slight decrease in the pH of the Ca(OH)_2 suspension deriving from natural gypsum is due to the difference in the mass of portlandite in 2g of Ca(OH)_2 precipitate. In 2g of Ca(OH)_2 precipitate, the Ca(OH)_2 made from natural gypsum contains in average 1.77g of portlandite compared to the Ca(OH)_2 precipitates deriving from phosphogypsum and synthetic gypsum containing in average 1.93g and 1.92g of portlandite respectively. Upon dissolution of the CO_2 in each solution, the pH value decreased to 8.51 after 30 minutes. Similar to the carbonation of the Ca(OH)_2 obtained from phosphogypsum, the pH curves reveal that the carbonation of the Ca(OH)_2 samples obtained from natural gypsum is incomplete after 30 minutes of reaction. No stable values of the pH were reached during the reaction time.

The new precipitates formed were then analysed by XRD to determine their respective mineralogical compositions.

4.3.3.2 XRD analyses the carbonated Ca(OH)_2 precipitates obtained from the gypsum samples

The mineral compositions of the carbonated Ca(OH)_2 precipitates obtained from phosphogypsum, synthetic gypsum and mineral gypsum were determined by XRD in order to identify the minerals present in these samples. The results of these analyses are expressed as weight percentage (wt %), and are summarized and compared in Table 4.14.

Table 4.14: XRD results of carbonated Ca(OH)_2 samples obtained from phosphogypsum, synthetic gypsum and natural gypsum.

Minerals	Molecular formula	Weight %		
		Carbonated Ca(OH)_2 from phosphogypsum	Carbonated Ca(OH)_2 from synthetic gypsum	Carbonated Ca(OH)_2 from natural gypsum
Calcite	CaCO_3	83	98	87
		82	98	88
Portlandite	Ca(OH)_2	8	2	2
		7	<1	5
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	8	-	8
		11	2	4
Quartz	SiO_2	1	-	3
		-	-	3

Table 4.14 shows the degree of purity of the precipitates formed during the carbonation reactions. It is observed that they all contain calcite as the main phase of their respective mineralogical composition. The precipitates obtained from phosphogypsum and natural gypsum contain a weight percentage of calcite below 90% while that of synthetic gypsum is above 95%. De Beer (2013) defined low grade CaCO_3 as precipitate whose purity in CaCO_3 is below 90% and high grade CaCO_3 as precipitate with purity in CaCO_3 which is above 95%. The low grade of CaCO_3 found in the first precipitates cited above then confirms that the carbonation reactions of the Ca(OH)_2 precipitates obtained from phosphogypsum and natural gypsum were incomplete as observed from

the pH curves. Furthermore, calcium carbonate precipitates obtained from phosphogypsum and natural gypsum still contain some unconverted portlandite in their mineralogical compositions while in the precipitates obtained from synthetic gypsum, the amount of unconverted portlandite is below 2%.

4.3.3.3 Extent of conversion of the Ca(OH)_2 precipitates formed from the gypsum samples into CaCO_3

A mass balance study was then performed on the masses of the precipitates formed in order to determine the percentage of calcium from portlandite really converted into CaCO_3 . The results of this study are summarized in Table 4.15.

The table shows that 78.72% of the calcium contained in portlandite was converted into fairly pure CaCO_3 . This indicates that 21.28% of calcium remained in solution. No calculations were performed on the samples with less than 95% of CaCO_3 .

Table 4.15: Weights of the carbonated Ca(OH)_2 precipitates obtained from the gypsum samples

	Theoretical mass of CaCO_3 to be formed(g)	Experimental mass of CaCO_3 formed (g)	Extent of conversion (%)
Carbonated Ca(OH)_2 from phosphogypsum	2.61 ± 0.02	2.12 2.15	n.d*
Carbonated Ca(OH)_2 from synthetic- gypsum	2.59 ± 0.03	2.04 2.04	78.72 78.72
Carbonated Ca(OH)_2 from natural gypsum	$2.39 \pm 7.07 \times 10^{-4}$	1.97 2.11	n.d*

*not determined (extent of conversion was only calculated for samples with more than 95% of CaCO_3)

4.3.3.4 Thermogravimetric analyses of the carbonated Ca(OH)_2 precipitates made from the gypsum samples.

The thermogravimetric analyses of the precipitates formed after carbonation were done using a TGA / SDTA 851^e METTLER TOLEDO instrument, using a 150 μl alumina pan. For each analysis, a sample mass of about 20 mg was used and the sample was heated between 25°C and 850°C using a heating rate of 10°C/min in an air atmosphere. The temperature range where each weight loss occurs was determined using the first derivative of each thermogravimetric curve. The derivative was superimposed onto its thermogravimetric curve and the temperature range was limited from where the thermogravimetric curve started to deviate downwards from its first derivative until its return to the baseline. Figure 4.9 shows the evaluation of the TGA curves of one of the precipitates with its first derivative.

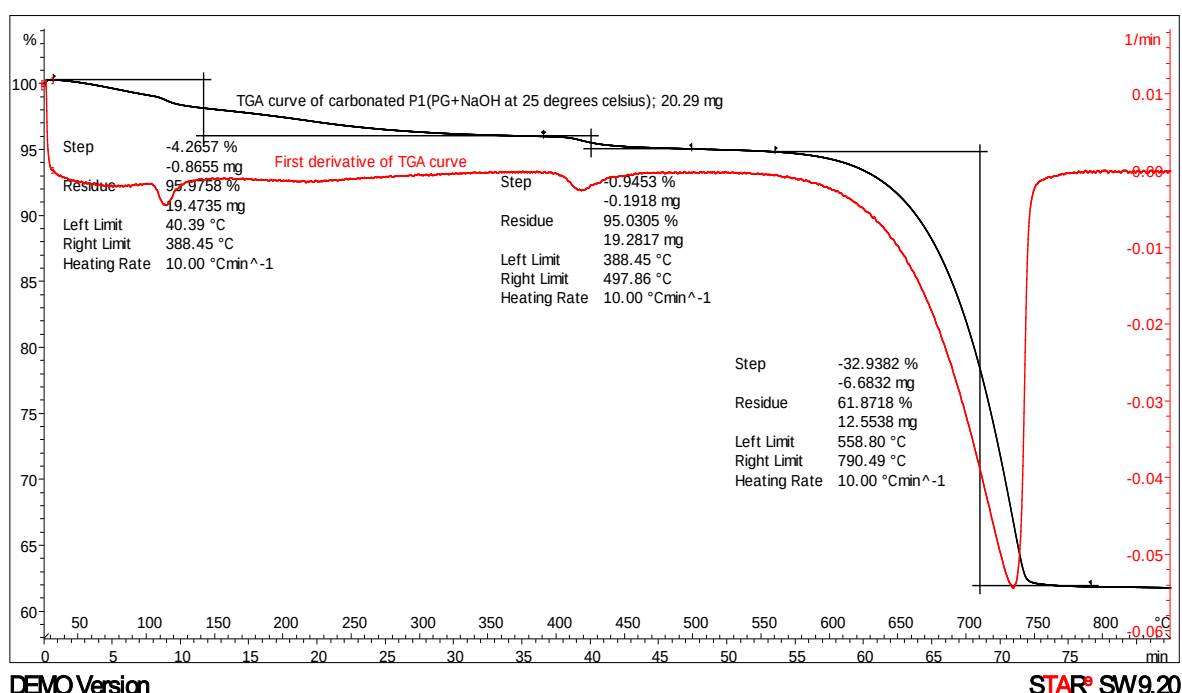


Figure 4.9: The TGA curve and the first derivative (DTG) obtained for the carbonated Ca(OH)_2 sample from the reaction between phosphogypsum and NaOH at 25°C.

The first step in the thermal decomposition of this sample occurs between 40°C and 388°C. This decomposition is characterized by a weight loss of 4.3% for a sample weight of 20.29mg and corresponds to the loss of surface water and/or water of crystallization contained in phosphogypsum.

The second thermal decomposition occurs between 388°C and 498°C. This corresponds to the decomposition of Ca(OH)_2 into CaO with the release of H_2O . Sawada and Ito (1994) identified the decomposition of calcium hydroxide in the temperature of 300°C - 460°C. This decomposition is characterized by a weight loss of H_2O of 0.95% for this sample.

The third and final weight loss in this sample occurs between 559°C and 790°C. It corresponds to the decomposition of CaCO_3 into CaO and CO_2 and is in agreement with the temperature range of the decomposition of CaCO_3 as identified by Hudson-Lamb (1997) to take place between 655°C and 808°C. It is characterized by a weight loss of 32.9%. Using the theoretical weight loss of calcium carbonate (43.97%), the amount of CaCO_3 contained in this sample is calculated to be 74.9% and is close to the amount of CaCO_3 determined by XRD, which was 83%

The quantitative TG analysis performed on the other carbonated Ca(OH)_2 samples is summarized in Table 4.16 while Table 4.17 compares the total amount of CaCO_3 detected by TGA and XRD in each of the precipitates formed from the three different gypsum samples.

Table 4.17 shows that the total amount of CaCO_3 detected by XRD corresponds well to the amount of CaCO_3 determined by TGA for each precipitate.

Table 4.16: Quantitative TG analysis of the carbonated $\text{Ca}(\text{OH})_2$ samples

TGA weight loss	Theoretical weight loss of (H_2O): 24.31 % ($\pm 334^\circ\text{C} \rightarrow \pm 542^\circ\text{C}$) $\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$		Theoretical weight loss of (CO_2): 43.97 % ($\pm 562^\circ\text{C} \rightarrow \pm 812^\circ\text{C}$) $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	
	Experimental weight loss of (H_2O) in %	Experimentally determined weight percentage of $\text{Ca}(\text{OH})_2$, using its dehydration weight loss percentage	Experimental weight loss of (CO_2) in %	Experimentally determined weight percentage of CaCO_3 using its decomposition weight loss percentage
CaCO ₃ from phosphogypsum	0.9 0.6	3.9 2.6	32.9 35.8	74.9 81.4
CaCO ₃ from Synthetic gypsum	0.4 0.1	1.6 0.6	43.3 43.2	98.5 98.3
CaCO ₃ from natural gypsum	1.4 1.3	5.9 5.5	35.9 35.2	81.6 80.1

Table 4.17: Comparisons of the total CaCO_3 as calculated from TGA versus the amount of CaCO_3 detected by XRD in each precipitate formed from the gypsum samples

		Total CaCO_3 detected by XRD	Total CaCO_3 detected by TGA
Carbonated $\text{Ca}(\text{OH})_2$ samples that were made at 25 °C between phosphogypsum and NaOH	Run 1	83	74.9
	Run 2	82	81.4
Carbonated $\text{Ca}(\text{OH})_2$ samples that were made at 40 °C between synthetic- gypsum and NaOH	Run 1	98	98.5
	Run 2	98	98.3
Carbonated $\text{Ca}(\text{OH})_2$ samples that were made at 70 °C between mineral gypsum and NaOH	Run 1	87	81.6
	Run 2	88	80.1

4.4 Conclusion

In this chapter, three different gypsum samples were converted into CaCO_3 . In the first step of the indirect aqueous carbonation process, phosphogypsum, synthetic gypsum and natural gypsum were converted into $\text{Ca}(\text{OH})_2$ in a 3 hour reaction with NaOH. An extent of conversion of 96% was obtained for the transformation of phosphogypsum and synthetic gypsum into $\text{Ca}(\text{OH})_2$ at 25°C and 40°C respectively. In the case of natural gypsum, a lower extent of conversion (88%) was obtained at 70°C. During the formation of $\text{Ca}(\text{OH})_2$ precipitates, the impurities contained in phosphogypsum and natural gypsum were found into their respective $\text{Ca}(\text{OH})_2$ precipitates, while the $\text{Ca}(\text{OH})_2$ precipitates obtained from pure synthetic gypsum were free of impurities.

The $\text{Ca}(\text{OH})_2$ precipitates formed were then carbonated for a period of 30 minutes using a CO_2 flow rate of 285ml/ min. The main phase of these carbonated precipitates was calcite. However, the time of carbonation was reported to be insufficient for the carbonation of the $\text{Ca}(\text{OH})_2$ obtained from phosphogypsum and natural gypsum. Low grade CaCO_3 was obtained from phosphogypsum and natural gypsum while high grade CaCO_3 was obtained from synthetic gypsum. 78.72% of the calcium contained in the portlandite of the $\text{Ca}(\text{OH})_2$ precipitate obtained from synthetic gypsum was converted into calcium carbonate.

4.5 Future work

For future work, it is firstly recommended to increase the reaction time to 4 hours for complete conversion of phosphogypsum and synthetic gypsum into Ca(OH)_2 . In the case of natural gypsum, a 5 hour or 6 hour reaction could be effective for its total conversion into Ca(OH)_2 . Secondly, an hour carbonation reaction could be effective for the complete conversion of Ca(OH)_2 precipitates made from phosphogypsum and natural gypsum using a minimum CO_2 flow rate of 285 ml/min. In the case of Ca(OH)_2 deriving from synthetic gypsum, a 30 minutes carbonation reaction will be effective.

The influence of the CO_2 flow rate on the morphology of the calcite particles was outside the scope of this work and may be included in future studies. Furthermore, the effect of Ca(OH)_2 particle size and specific surface area on the kinetics of the carbonation process may be studied in order to optimise the physical properties of the obtained products, and improve the kinetics of the carbonation process.

4.6 References

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CHAPTER FIVE: A FURTHER STUDY ON THE MINERAL CARBONATION OF PHOSPHOGYPSUM

5.1 Introduction

In the previous chapter, the mineral carbonation process proposed by Cardenas-Escudero (2011) was performed on a South African phosphogypsum sample, and the degree of conversion of gypsum into calcium carbonate was followed. During the process described in Chapter 4, 50g of phosphogypsum was reacted with 200ml of a 2.9M NaOH solution at room temperature during a 3 hour reaction. This resulted in the formation of a $\text{Ca}(\text{OH})_2$ precipitate which was then separated from the liquid fraction by filtration followed by drying. 2g of the $\text{Ca}(\text{OH})_2$ precipitate was then carbonated for 30 minutes in 40ml of water to precipitate CaCO_3 , where after a second filtration and drying step was performed.

The purpose of this chapter is to convert phosphogypsum into CaCO_3 using the optimised reaction conditions and CO_2 flow rate as identified in Chapter 4, but also by eliminating the intermediate filtration step. The aim would be to perform the process without the filtration process taking place after the first 3 hours of reaction, in order to limit the amounts of water and energy used during the mineral carbonation process. Since different solid to liquid ratios were used in the two steps described in Chapter 4, the influence of different solid to liquid ratios will be studied briefly in this chapter.

5.2 Experimental

Attempts were made to transform phosphogypsum (obtained from Omnia, Rustenburg) into CaCO_3 at room temperature using the following solid to liquid ratios:

1. In the first experiment at room temperature, 5g of phosphogypsum was dispersed into 20 ml of NaOH solution, and the reaction was performed for 3 hours. The resulting mixture was then carbonated for 30 minutes. Therefore, this first experiment mimics the experimental conditions used during the pre-filtration step by Cardenas-Escudero (2011), omits the solid-liquid separation step, and as a result uses a more concentrated system during the post-filtration step.

2. In the second experiment still performed at 25°C, 5g of phosphogypsum was dispersed into 20ml of NaOH solution and the reaction was performed for 3 hours. At completion of this reaction, 80 ml of deionized water was added to the resulting solution and stirred for an hour to ensure homogeneity of the solution as well as stabilization of the pH. The resulting mixture was then carbonated for 30 minutes. This experiment which was done on the basis of the mineral carbonation from Cardenas-Escudero et al (2011), was performed to test if for the same amount of phosphogypsum (5g), the volume would have an influence on the extent of conversion of phosphogypsum into CaCO_3 . The 5g of phosphogypsum was firstly dispersed into 20ml of NaOH for 3 hours as in experiment 1. The total volume of the solution was then increased to 100 ml after the first 3 hours of reaction by the addition of 80 ml of water making a solid to liquid ratio of 1/20 to replicate the solid to liquid ratio used in the second part of the mineral carbonation described by Cardenas-Escudero et al (2011) where 2g of Ca(OH)_2 was carbonated into 40 ml of water for a solid to liquid ratio of 1/20.
3. For the third experiment (at room temperature), 2g of phosphogypsum was suspended into 40ml of NaOH solution and the reaction was performed for 3 hours at 25°C. The resulting mixture was then carbonated for 30 minutes. This experiment was performed to test the effect of decreasing the starting solid-to-liquid ratio on the conversion of phosphogypsum into CaCO_3 .

For all experiments, the 2.9M NaOH solution was poured into the 5 neck 500ml flat-bottom flask, which was placed in a waterbath at a temperature of 25°C. The NaOH solution was stirred at 750 rpm for an hour to ensure that its temperature reaches 25°C and its pH stabilizes. The pH of the NaOH solution at 25°C was 13.51. The specified amount of phosphogypsum was then added into the NaOH solution, and the suspension was continuously stirred at 750 rpm for three hours. After three hours, CO_2 was purged in the resulting suspension for 30 minutes. The CO_2 flow rate was 285ml/min. Each precipitate was separated from the liquid fraction by filtration, where after it was washed three times with 50 ml of distilled water. The products were then dried in a laboratory oven at 40°C for three hours before being analyzed. The experimental setup used was identical to the setup used in Chapter 4, and was described in Figure 2.9.

5.3 Results and discussion

5.3.1 The variation of pH with time for the carbonation of phosphogypsum

The variation of pH with time for the transformation of phosphogypsum into CaCO_3 , studied at room temperature and different solid to liquid ratios are reported in Figures 5.1, 5.2 and 5.3. Each reaction was performed in duplicate and the average values were plotted against time.

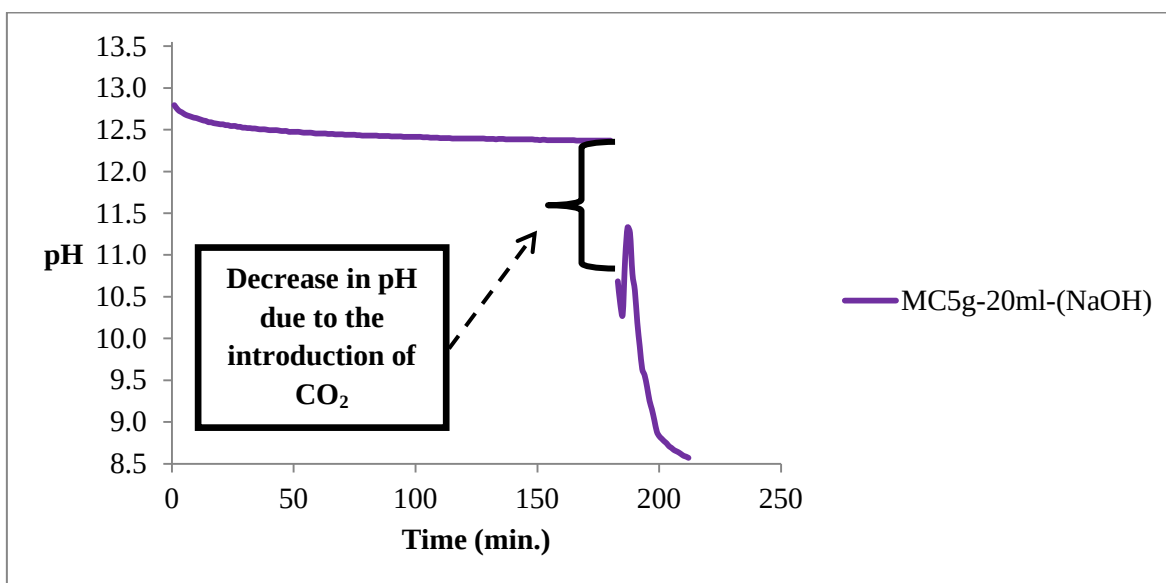


Figure 5.1: Variation in pH for the carbonation of 5g of phosphogypsum in 20 ml of NaOH solution (Experiment 1)

Figure 5.1 show the variation of pH with time for the conversion of 5 g of phosphogypsum in 20ml of NaOH solution. After complete addition of the 5g of phosphogypsum, the pH value decreased to 12.32 after three hours of reaction. This decrease in pH was caused by the decrease of the free OH^- in solution. The OH^- ions react with the Ca^{2+} coming from the dissociation of CaSO_4 contained in phosphogypsum to form $\text{Ca}(\text{OH})_2$, as described by Equation 4.1.

When CO_2 is introduced into the $\text{Ca}(\text{OH})_2$ suspension, a rapid decrease in pH to 8.52 after the 30 minutes of carbonation is observed. This decrease is due to the dissolution of CO_2 into solution. CO_2 immediately reacts with water to form H_2CO_3 thus acidifying the solution which result, after two successive deprotonation steps, into the release of CO_3^{2-} in solution that will react with the Ca^{2+} coming from the dissociation of $\text{Ca}(\text{OH})_2$ to form CaCO_3 (Xiang et al., 2002). CO_2 may also react

with the OH^- obtained from the dissociation of $\text{Ca}(\text{OH})_2$ to form HCO_3^- which will be deprotonated to release more CO_3^{2-} in solution in order to form CaCO_3 when reacting with the free Ca^{2+} (Xiang et al., 2002).

The variation of pH with time for the transformation of 5g of phosphogypsum in 100 ml of solution was then studied and reported in Figure 5.2 below.

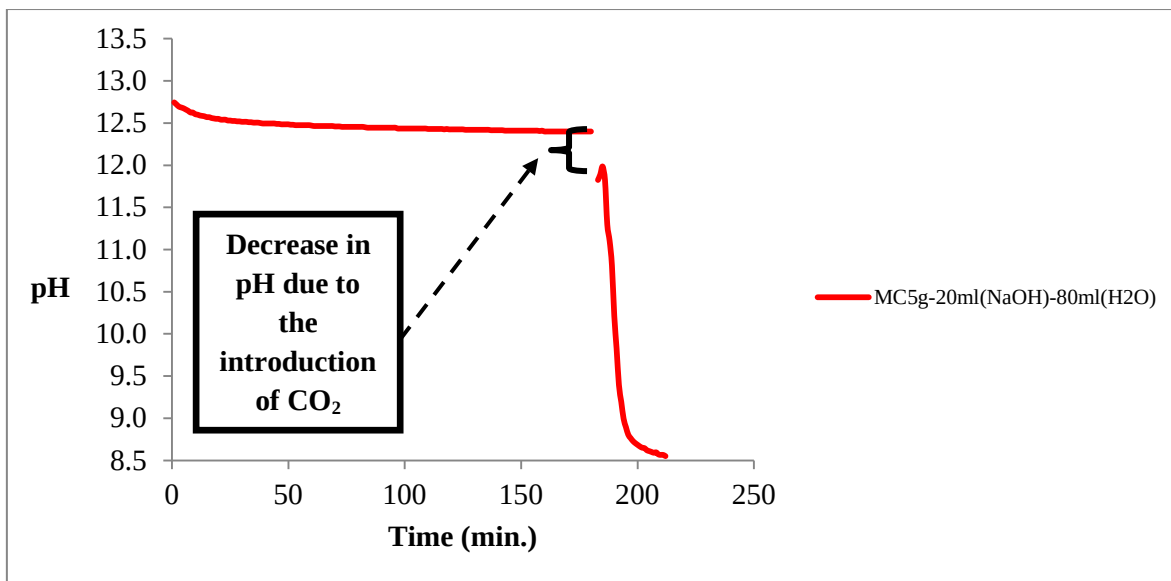


Figure 5.2: Variation in pH for the carbonation of 5g of phosphogypsum into 100 ml of NaOH solution (Experiment 2)

After the addition of 5g of phosphogypsum into NaOH, a decrease in pH was observed. The pH decreased to 12.4 after the first three hours of reaction. This decrease in pH was due to the formation of $\text{Ca}(\text{OH})_2$ in solution.

After the first three hours of reaction, 80 ml of deionised water were added and the solution was stirred at 750 rpm for an hour. Upon introduction of CO_2 , a decrease in pH as a result of the formation of H_2CO_3 and HCO_3^- was observed. This decrease in pH results into the formation of CO_3^{2-} ions in solution that will react with the Ca^{2+} ions coming from the dissociation of $\text{Ca}(\text{OH})_2$ to form CaCO_3 . The final pH of the solution (8.55) was similar to that observed for Experiment 1.

The variation of pH for the conversion of 2 g of phosphogypsum in 40 ml of solution into CaCO_3 (Experiment 3) is reported in Figure 5.3 below.

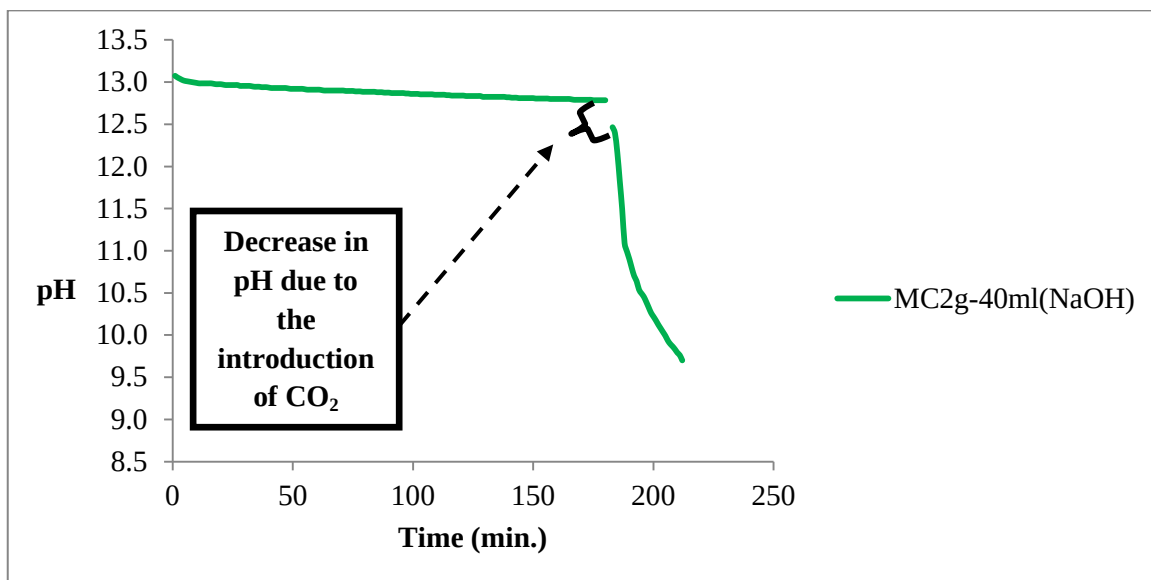


Figure 5.3: Variation of pH for the carbonation of 2 g of phosphogypsum in 40 ml of NaOH solution (Experiment 3)

After addition of the 2g of phosphogypsum in NaOH solution, a decrease in pH was observed as a result of the formation of $\text{Ca}(\text{OH})_2$. The pH decreased to 12.79 after the first 3 hours of reaction. Upon introduction of CO_2 , a continuous decrease in pH was observed until the end of the carbonation reaction. After the 30 minutes of reaction, the final pH observed for this experiment (9.7) was observed to be higher than that of the first two experiments, and no plateau was observed towards the end of the reaction. The pH curve shows that the carbonation reaction was probably incomplete, given that the pH was still decreasing. However, no attempt to increase the duration of the experiment was made since the objective of the experiment was to compare the effect of the starting solid-to-liquid ratio on the carbonation process within a set 30 minutes carbonation experiment.

5.3.2 X-ray powder diffraction analysis (XRD) of the precipitates formed

XRD analyses were performed on the precipitates formed in order to determine the amounts of calcium carbonate, calcium hydroxide, gypsum and other minerals they might contain. The results of these analyses are expressed as weight percentage (wt %) and are summarised in Table 5.1 below.

Table 5.1: XRD analyses of the precipitates formed from the mineral carbonation of phosphogypsum, using different solid to liquid ratios

Samples	runs	Minerals (wt %)				
		Calcite (CaCO ₃)	Vaterite (CaCO ₃)	Portlandite Ca(OH) ₂	Gypsum (CaSO ₄ ·2H ₂ O)	Quartz (SiO ₂)
MC _{5g-20ml-(NaOH)}	Run 1	99	-	-	-	1
	Run 2	97	-	2	-	1
	Run 3	99	-	<1	-	<1
MC _{5g-20ml(NaOH)-(80mlH₂O)}	Run 1	84	-	2	12	<1
	Run 2	81	7	-	12	-
	Run 3	95	5	-	-	<1
	Run 4	88	12	-	-	<1
MC _{2g-40ml-(NaOH)}	Run 1	30	70	-	-	-
	Run 2	43	54	-	-	3
	Run 3	15	85	-	-	-
	Run 4	14	86	-	-	-

Key to sample names:

MC_{5g-20ml(NaOH)}: Mineral carbonation of 5 g of phosphogypsum using 20 ml of NaOH solution

MC_{5g-20ml(NaOH)-(80mlH₂O)}: Mineral carbonation of 5 g of phosphogypsum using 20 ml of NaOH solution to which were added 80 ml of water

MC_{2g-40ml(NaOH)}: Mineral carbonation of 2 g of phosphogypsum using 40 ml of NaOH solution

Initially, an attempt was made to transform 5g of phosphogypsum into CaCO₃ using 20ml of NaOH solution (**MC_{5g-20ml (NaOH)}**); a solid to liquid ratio of 1:4. The XRD analysis revealed the formation of the stable polymorph of CaCO₃, calcite, with a small amount of unreacted portlandite. No crystals of gypsum were identified in the precipitates, which suggested its complete conversion. The XRD results also reveal the presence of quartz in all the precipitates.

In the second experiment, the same amount of phosphogypsum was used as in Experiment 1. An initial solid to liquid ratio of 1:4 was used, which was then increased to 1:20 by increasing the total volume of the solution to 100 ml for the carbonation step (**MC_{5g-(20mlNaOH)-80ml (H₂O)}**). The XRD results reveal that in most of the runs, vaterite is formed alongside calcite. Day et al. (2013) reported that metastable vaterite can also form alongside calcite at room temperature under elevated CO₂ pressure (6 bar). It also observed that the amount of vaterite formed is much less than the amount of calcite formed for all runs and that the amount of vaterite formed is greater than the

amount of vaterite formed in Experiment 2. The presence of vaterite in these proportions could be associated with the addition of the 80ml of deionized water just after the first three hours of reaction; consequently by diluting the concentration of ions present before the carbonation reaction. Maciejewski et al. (1994) argued that the precipitation of vaterite is influenced by the concentrations of the reactants in solution. He further added that vaterite is more reactive than calcite and transforms at low temperature in aqueous solution into calcite. From these findings, it seems that after the 30 minutes of carbonation, the transformation of vaterite into calcite was almost complete.

Finally, while maintaining a constant solid to liquid ratio of 1:20, an attempt was made to convert 2g of phosphogypsum into CaCO_3 using a total volume of 40ml, ($\text{MC}_{2\text{g-40ml (NaOH)}}$). The XRD results firstly show that phosphogypsum has been completely transformed into Ca(OH)_2 during all the runs, and that the latter was subsequently fully converted into CaCO_3 . It is important to note that vaterite was still formed alongside calcite and that the amount of vaterite in this case is greater than the amount of calcite formed. In this case, vaterite is suspected to be a precursor of the calcite formed and that at the end of the 30 minutes of carbonation more than half of the vaterite formed was not still transformed into calcite. Nehrke et al (2006) confirmed that in laboratory, vaterite was a precursor of calcite.

The CaCO_3 precipitates formed at room temperature using 5g of phosphogypsum into 20ml of solution (Experiment 1) were further characterized because full conversion of phosphogypsum into CaCO_3 was obtained. Furthermore, the CaCO_3 precipitates this solid to liquid ratio was mainly calcite, compared to the other experiments where the precipitates formed contained two polymorphs of CaCO_3 (calcite and vaterite). Additionally, full conversion of phosphogypsum was not obtained in some of the runs performed using the reaction conditions for Experiment 2 (Table 5.1).

5.3.3 Further characterization of the CaCO_3 precipitates formed using 5 g of phosphogypsum into 20 ml of solution (Experiment 1)

5.3.3.1 Extent of conversion of the calcite precipitate formed using 5 g of phosphogypsum into 20 ml of solution (Experiment 1)

The XRD results showed that the dominant mineral phase (> 96%) in the precipitates formed using 5g of phosphogypsum and 20 ml of NaOH solution was calcite. A mass balance study was then performed using the masses of the precipitates formed in order to determine the percentage of calcium present in phosphogypsum that was transformed into calcite. The results of this study are summarized in Table 5.2

Table 5.2: Extent of conversion of the calcium contained in the gypsum samples into CaCO_3

Mass of Phosphogypsum used during the mineral reaction in (g)	Mass of Calcium in 5 g of phosphogypsum in (g)	Theoretical mass of CaCO_3 to be formed from 1.97 g of Ca in (g)	Experimental mass of CaCO_3 formed in (g)	Extent of conversion of phosphogypsum into CaCO_3 in %
5	1.97	4.91	2.86	58.25
5	1.97	4.91	2.67	54.38
5	1.97	4.91	2.73	55.60
Average :			2.75 ± 0.09	56.08 ± 1.98

Table 5.2 shows that for 5g of phosphogypsum (containing 1.97g of calcium) dispersed into 20ml of a NaOH solution, 2.75g of CaCO_3 is formed, which represents an extent of conversion of phosphogypsum into CaCO_3 of 56.08% in average. This means that a significant proportion of the calcium (43.92%) in solution was unreacted and was not converted into CaCO_3 .

5.3.3.2 Field Emission Scanning Electron Microscopy (FESEM)

FESEM analyses were performed on the CaCO_3 precipitates formed using 5g of phosphogypsum and 20ml of solution in order to determine the morphology of the particles. Representative FESEM images of these CaCO_3 precipitates are given in Figures 5.4(a) and 5.4(b).

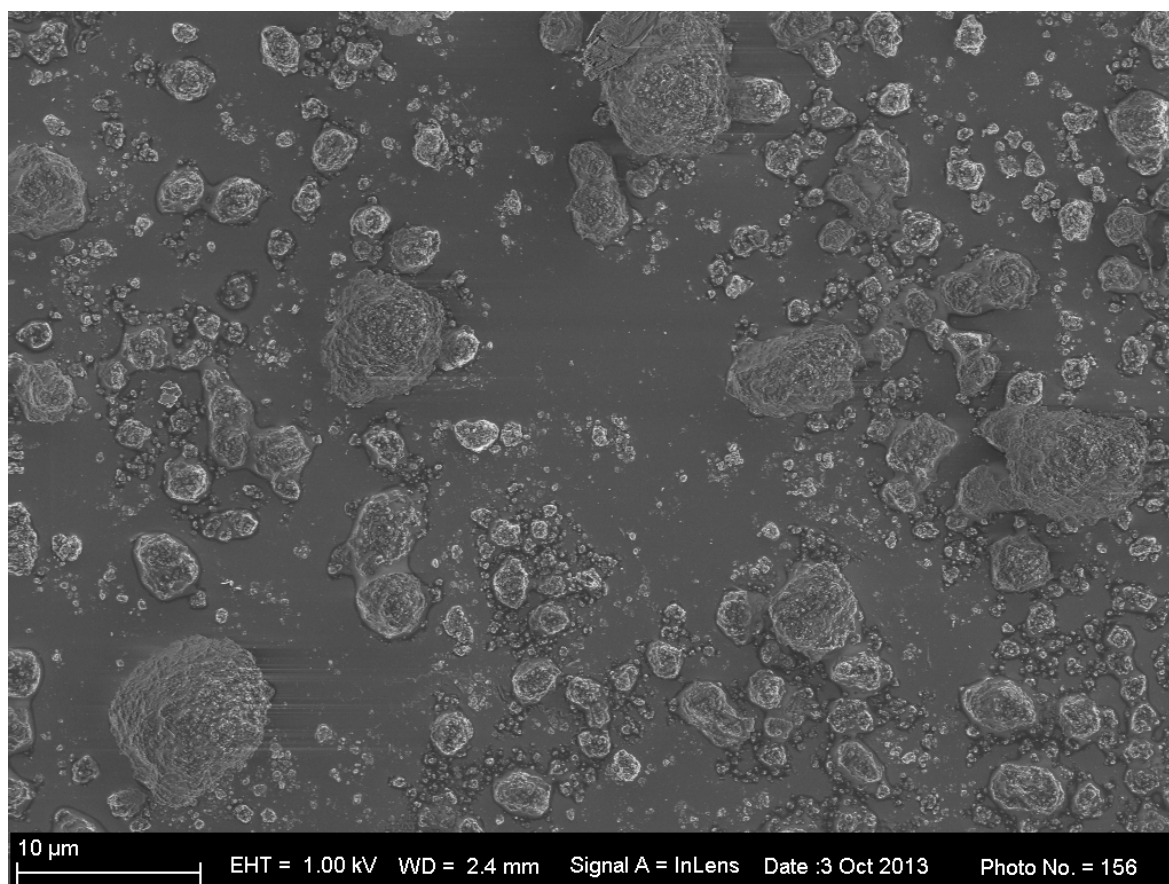


Figure 5.4(a) : FESEM images of the calcite formed using 5g of phosphogypsum in 20 ml of solution (Experiment 1) at a magnification of 3000 × (a) and 17500 × (b)

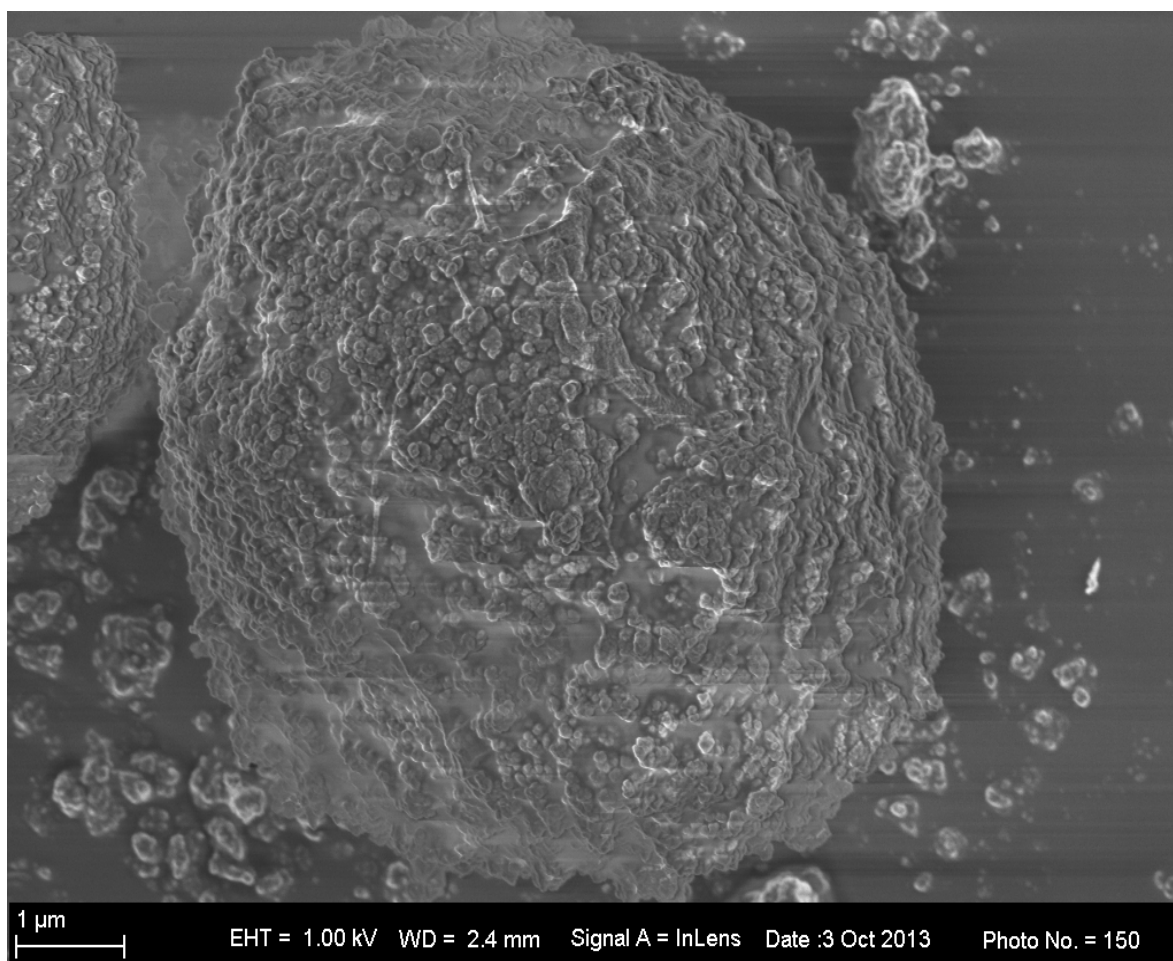


Figure 5.4(b) : FESEM image of a single crystal of calcite formed

Figure 5.4 (a) presents an overview of the particles of calcite formed while Figure 5.4 (b) shows the morphology of a single particle. Figure 5.4 (a) indicates that there is an irregular size distribution of the particles, while from Figure 5.4(b), it appears that these crystals have a spherical shape with rough surface area. Wen et al (2003) said that the morphologies of calcite particles are influenced by the concentration of Ca(OH)_2 and that spherical particles of calcite with an average diameter of about 100 nanometers are formed when the Ca(OH)_2 concentration was increased up to 0.4% (m/v).

5.3.3.3 Particle size distribution (PSD) of the precipitates obtained in Experiment 1

The PSD of the calcite samples formed at 25°C using the experimental conditions described in Experiment 1 was determined. The results of the analyses are presented in the form of a frequency curve of volume percentage versus the logarithm of particle size in Figure 5.5, while Table 5.3 shows the calculated diameters for both samples.

Figure 5.5 shows that the calcite precipitates formed using 5g of phosphogypsum and 20 ml of NaOH shows that are made of three populations with three maxima. The first maximum is located where 1.8% of the population measures 1.262 μ m. The second maximum is where 7.4% of the population measures 7.10 μ m and the third population is located where 0.3% of the population measures 39.91 μ m.

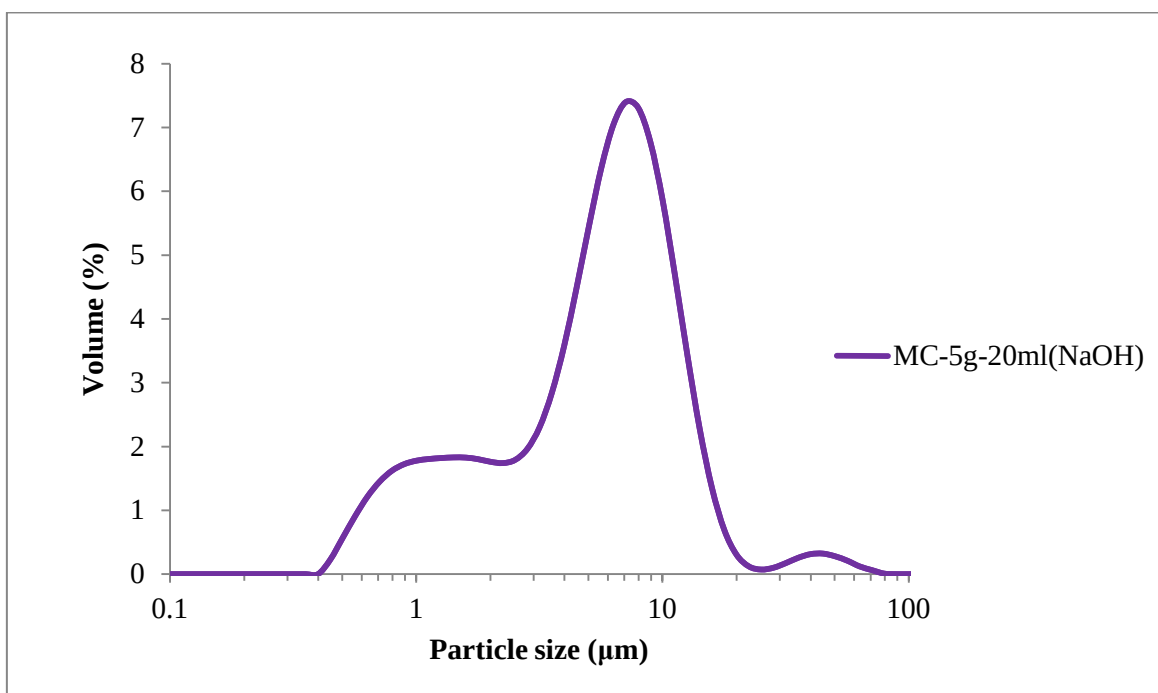


Figure 5.5: The frequency curve of the particle size distribution of calcite formed using 5g of phosphogypsum in 20 ml of NaOH solution (Experiment 1)

Table 5.3: Summary of the particle size distribution of the calcite samples formed using 5g of phosphogypsum into 20ml of solution (Experiment 1)

	Sample
Statistics	MC _{5g-20ml(NaOH)}
D (v; 0.1)	1.1 ± 0.1
D (v; 0.5)	8.3 ± 0.3
D (v; 0.9)	20.4 ± 0.6

The statistics compiled in Table 5.3 shows that 50% of the particles have a size below 8.3µm and 90% of the population have a size particle below 20.4µm. The sizes of these particles are found to be larger than the size reported by Wen et al (2003).

5.3.3.4 ICP-MS 4-acid analysis performed on the calcite precipitates formed for the determination of the different major and trace elements.

ICP-MS 4-acid digestion analysis was performed on the gypsum samples to determine the concentrations of major and trace elements present in each sample. The results obtained from these analyses were reported in Table 3.14 while the elemental composition of the formed carbonate sample is reported in Table 5.4. Table 5.5 shows the percentage of calcium in each calcite precipitate obtained using 5 g of phosphogypsum and 20 ml of solution (Experiment 1) from the XRD analysis.

Table 5.4: Concentration of the major and trace elements in the calcite precipitates formed in Experiment 1 reported in part per billion (µg/kg)

Elements (Atomic weight)	*Detection limit	Sample
		MC _{5g-20ml(NaOH)}
Na (23)	50 000	12 877 815
Mg (24)	50 000	354 049
Al (27)	50 000	310 705
K (39)	50 000	70 303
Ca (43)	50 000	452 507 418
Cr (52)	50 000	16 283
Cd (114)	20	59
Pb (208)	500	21 828
U (238)	10	1229

*The detection limit is the minimum concentration of the element which can be detected by the instrument. An element whose concentration is below the detection limit is considered as absent in the sample.

Table 5.5: Percentage of calcium in the calcite precipitates formed in Experiment 1 as estimated from the XRD data

Sample	% Ca in the calcite precipitates formed
Run 1	39.79
Run 2	38.81
Run 3	39.50
Average	39.37 ± 0.50

Table 5.5 shows that the formed precipitates contain nearly 40% of calcium. Theoretically, in a 100% calcium carbonate sample, calcium contributes to 40.04%. Based on the XRD results in section 5.3.2, calcium contributes in average to 39.37% of the calcite precipitates as shown in Table 5.5. The values generated by XRD and ICP-MS on the formed carbonate were therefore found to be in agreement.

The amount of calcium (45.3%) present in the calcite precipitates, estimated from the ICP-MS 4-acid digestion analysis (452 507 418µg/kg) reported in Table 5.4 is found to be higher than the weight percentage of calcium (39.37%) present in the calcite precipitates as determined by XRD and summarized in Table 5.5. The difference in the results between XRD and the ICP-MS analysis was most probably due to the fact that XRD is a semi-quantitative method and each instrument is based on a different principle of analysis and therefore comes with its own limitations. Furthermore, prior to the XRD analysis, the samples were not micronised since it was uncertain whether the sample would have been altered during the micronisation process with ethanol. The size of the particles which were analysed by XRD may have therefore been larger than what is recommended (i.e. sub-10 µm), which could have caused artefacts such as preferential orientation during the analysis.

The other elements found in the calcite precipitate are impurities that were previously contained in the phosphogypsum sample before going into reaction as described in section 3.5.1

5.3.3.5 ICP-MS analysis performed on the calcite precipitates obtained from (Experiment 1) for the determination of Rare Earth Elements (REE)

ICP-MS analysis for rare earth elements were performed on the calcite precipitates formed in Experiment 1 to determine the amounts of these elements present in the precipitates and assess the percentage of REE elements originally present in the phosphogypsum which were transferred to the formed carbonate product. The results obtained from these analyses are reported in Table 5.6.

Table 5.6: Concentrations of rare earth elements in the calcite precipitates obtained from Experiment 1as determined by ICP-MS, reported in parts per billion (µg/kg).

Elements (Atomic weight)	Detection limit	Sample
		MC_{5g-20ml(NaOH)}
Y (89)	50	134 120
La (139)	500	992 576
Ce (140)	500	2 377 132
Pr (141)	50	351 473
Nd (146)	200	1 446 003
Sm (147)	20	251 182
Eu (151)	10	47 512
Gd (157)	20	176 318
Tb (159)	20	18 075
Dy (163)	10	55 748
Ho (165)	10	6 558
Er (167)	10	10 754
Tm (169)	10	826
Yb (172)	10	4 473
Lu (175)	10	429

*The detection limit is the minimum concentration of the element which can be detected by the instrument. An element whose concentration is below the detection limit is considered as absent in the sample.

Every rare earth element that had been identified in the untreated phosphogypsum sample (Section 3.5.2) was found in the carbonate sample obtained using 5 g of phosphogypsum and 20 ml of solution. The histogram represented in Figure 5.6 represents the quantification of the rare earth elements that were transferred in the calcite precipitates.

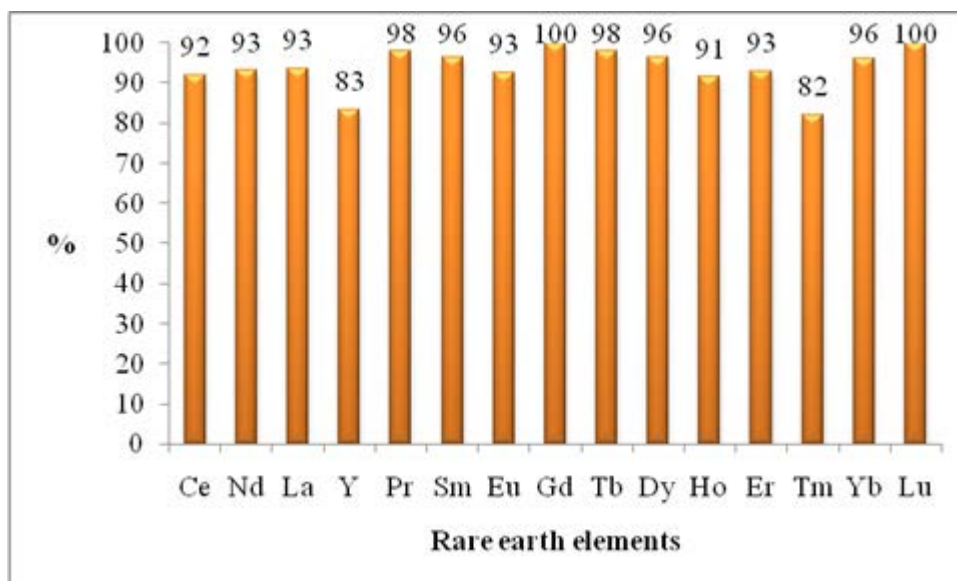


Figure 5.6: Calculated percentage of rare earth elements which was transferred from phosphogypsum to the calcite precipitate

Figure 5.6 shows that most of the rare earth elements (*i.e.* 82% to 100%) contained in the phosphogypsum sample before treatment were identified in the calcite precipitate formed during Experiment 1. An assessment as to whether their presence in calcite is a problem for specific applications will have to be addressed in future works.

5.3.3.6 Carbon and Sulphur analysis of the calcite precipitates formed in Experiment 1

Carbon and Sulphur analysis was performed on the precipitates obtained from using 5 g of phosphogypsum and 20 ml of solution in order to determine the amount of carbon and sulphur they contain. The results of this analysis are summarized in Table 5.7.

Table 5.7: Carbon and Sulphur analysis of the CaCO_3 precipitates obtained from 5 g of phosphogypsum and 20 ml of solution expressed in weight percentage (wt%)

Sample	C (wt %)	C (wt %) as determined by XRD	SO_3 (wt %)	SO_3 (wt %) as determined by XRD
$\text{MC}_{5\text{g}-20\text{ml}(\text{NaOH})}$	10.34	11.80 ± 0.15	0.19	*n.d

*not determined

Table 5.7 shows that the amount of carbon detected by Carbon & Sulphur analysis (10.34%) in the formed carbonate precipitate was close to, and therefore in agreement with the amount of carbon estimated from the phases identified by XRD (11.80%; Table 5.8). Little sulphur (0.19 wt % SO_3) was identified, which may have indicated the presence of a small amount of unconverted gypsum in the precipitate, which was not detected by XRD, or of and sulphur impurity due to insufficient washing following filtration.

5.4 Conclusion

In this chapter, the mineral carbonation of phosphogypsum was further studied at room temperature by eliminating the intermediate filtration and drying step, and by varying the solid to liquid ratio of phosphogypsum to the NaOH solution.

An XRD analysis performed on the formed precipitates revealed that only Experiment 1 (involving 5 g of phosphogypsum in 20 ml of solution) was effective in producing a single polymorph of CaCO_3 (in the form of calcite) from phosphogypsum. This process was therefore successful in yielding calcite as a single CaCO_3 polymorph and in inducing a complete conversion of phosphogypsum into carbonate. Most of the rare earth elements present in the phosphogypsum, as well as other elements (*e.g.* Al, Cr) was however transferred into the carbonate compound.

5.5 Future work

The following actions are recommended for future work:

1. To study the effect of CO_2 flow rate on the extent and kinetics of conversion of intermediately-formed $\text{Ca}(\text{OH})_2$ into calcite.
2. To control particle size, shape and the uniformity of the size distribution of the formed CaCO_3 , for instance by replacing and/or combining mechanical stirring by/with sonication, or by reducing the size of CO_2 gas bubbles used in the carbonation experiments.
3. To control the fate of the rare earth elements in the process.

4. The mass balance can be improved on as long as the energy penalty which will be associated with an improved mass balance is acceptable.

5.6 References

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CHAPTER SIX: THE MERSEBURG PROCESS

6.1 Introduction

The Merseburg process is a very old technology that was firstly developed by I.G. Farben industries before 1914 for the production of ammonium sulphate $(\text{NH}_4)_2\text{SO}_3$ (Gopinath, 1968; Burnett et al, 1996). In this process, gypsum or by-product phosphogypsum is made to react with ammonium carbonate to form ammonium sulphate and calcium carbonate. The reaction describing this process is represented by the chemical equation below:

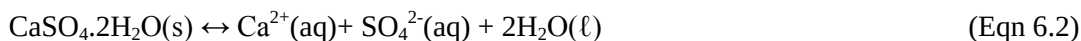


6.1.1 Description of the Merseburg process (Burnett et al, 1996)

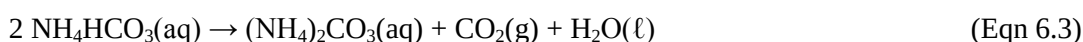
After being produced from the phosphoric acid process, phosphogypsum is firstly washed with water to remove all the impurities it might contain such as silica, phosphate and organic matter. Phosphogypsum is then treated with a 0.125N ammonium carbonate solution made from liquid ammonia and carbon dioxide for an hour at room temperature (Chen, 1990). The resulting mixture consists of slurry calcium carbonate precipitate in an ammonium sulphate solution. The calcium carbonate is then separated from the ammonium sulphate solution which is concentrated and then crystallized. Any ammonium carbonate in excess is neutralized using sulphuric acid.

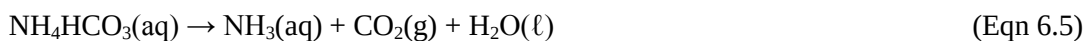
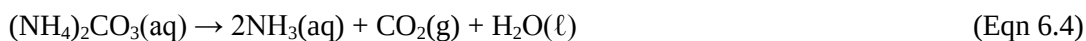
6.1.2 Ionic species in solution during the reaction between gypsum and ammonium carbonate

When dissolved, phosphogypsum produces Ca^{2+} and SO_4^{2-} ions which are then available to react with other ionic species present in solution (Ping et al, 2012):



On the other hand, ammonium bicarbonate $(\text{NH}_4\text{HCO}_3)$ dissociates in water to produce ammonia (NH_3) and carbon dioxide (CO_2) gases in three possible mechanisms (Qing et al., 2010):

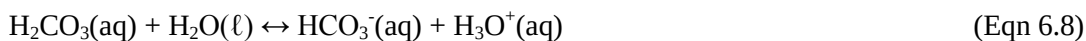




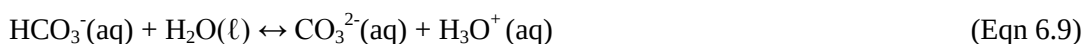
NH_3 and CO_2 , may then react with water as shown by Equations 6.6 and 6.7:



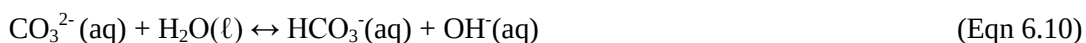
Carbonic acid (H_2CO_3) may undergo a deprotonation reaction to form hydrogen carbonate (HCO_3^-):



Hydrogen carbonate (HCO_3^-) is in turn deprotonated to release carbonate ions (CO_3^{2-}):



Some of the free carbonate ions (CO_3^{2-}) in solution could react with water to form HCO_3^- and hydroxide ions (OH^-) which will contribute to an increase of the pH of the solution. This mechanism is summarized by the equation below:



Therefore, the dissociation of ammonium carbonate in solution will result the formation of NH_4^+ , and CO_3^{2-} which may react with Ca^{2+} and SO_4^{2-} ions from phosphogypsum to form CaCO_3 as a precipitate and $(\text{NH}_4)_2\text{SO}_4$ as a soluble salt.

The purpose of this chapter is to investigate the extent of carbonation and the purity of CaCO_3 that can be achieved when treating a South-African phosphogypsum with a solution of ammonium carbonate using the Merseburg process.

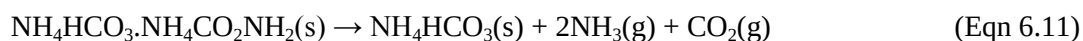
6.2 Experimental

Attempts were made to transform phosphogypsum (obtained from Omnia, Rustenburg) into CaCO_3 while studying the effect of the temperature and the time.

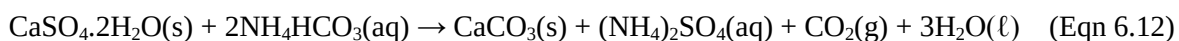
1. Firstly, the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$ was studied at room temperature for 1 hour 2 hours, 3 hours and 4 hours of reaction.
2. Secondly, the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$ was studied at 40°C during 1 hour, 1 hour and 30 minutes and 2 hours of reaction.
3. Lastly the same reaction was studied at 65°C for the same period of time as listed in the reaction at 40°C

6.2.1 Chemistry of commercial-grade ammonium carbonate

According to Sclar and Carrison (1963), commercial-grade ammonium carbonate $((\text{NH}_4)_2\text{CO}_3)$ consists of equivalent parts of mixture of ammonium bicarbonate $(\text{NH}_4\text{HCO}_3)$ and ammonium carbamate $(\text{NH}_4\text{CO}_2\text{NH}_2)$. It is generally presented with the molecular formula $(\text{NH}_4\text{HCO}_3.\text{NH}_4\text{CO}_2\text{NH}_2)$. When exposed to air, it transforms rapidly into ammonium bicarbonate $(\text{NH}_4\text{HCO}_3)$ with subsequent evolution of ammonia, as shown by Equation 6.11:



Ammonium bicarbonate will then participate in the reaction with gypsum to produce a mixture of a calcium carbonate precipitate and ammonium sulfate in solution:



Theoretically, 7.8g of commercial-grade ammonium carbonate to prepare 200ml of a 0.125N ammonium carbonate solution. 7.8g of ammonium bicarbonate is required. An excess of 2.2g of commercial-grade ammonium was added to prepare a 200ml of ammonium carbonate solution to increase the solubility of phosphogypsum during the reaction. Burnett et al (1996) said that phosphogypsum had low conversion efficiency and Ping et al (2012) added that the solubility of calcium sulfate dihydrate increases with an increased concentration of ammonium salts. A new stock solution was prepared for each temperature studied; using 100g of commercial-grade ammonium in 2000ml of deionized water.

6.2.2 Conversion of phosphogypsum into CaCO_3

200ml from a $(\text{NH}_4)_2\text{CO}_3$ stock solution with a concentration of 0.52M was poured into a 500ml flask with 5 necks and placed in a waterbath at the selected temperature. A pH electrode, a temperature probe and an overhead stirrer were inserted in the flask through three of the five necks available. The other two necks of the flask were closed using plastic stoppers. The $(\text{NH}_4)_2\text{CO}_3$ solution was continuously stirred until stabilization of the pH of the $(\text{NH}_4)_2\text{CO}_3$ solution and the selected temperature were achieved. The experimental setup used was shown in Figure 2.9.

4.3g of the phosphogypsum sample was suspended in the 200 ml of $(\text{NH}_4)_2\text{CO}_3$ solution at the selected temperature. The suspension was stirred at 750 rpm during the required reaction time. After the elapsed time, the liquid fraction was separated from the solid material by filtration, using Whatmann filter paper. The precipitate was then washed 3 times with 50ml of distilled water in order to remove any unreacted salt it might contain and was dried at 75°C for 3 hours. For each run, the experiment was performed four times for reproducibility purposes. The obtained products were weighed before further analyses were performed.

6.3 Results and discussion

The reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$ was studied at the selected temperatures over different periods of time. The reaction was firstly studied at room temperature, before increasing it to 40°C and 65°C respectively. The reaction time was increased as long as full conversion was not achieved, based on the XRD results. For a specific temperature at a specific time, the reaction was performed in quadruplicate.

6.3.1 XRD analysis of the precipitates formed from the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$.

The mineralogical composition of each of the precipitates formed was determined by XRD to assess the extent of conversion of phosphogypsum into calcium carbonate. The results of these analyses, expressed as weight percentage (wt %), are summarized in Tables 6.1, 6.2 and 6.3.

Table 6.1: XRD analyses of the precipitates formed from the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$ at 25°C

Reaction time	Run number	Mineral			
		Calcite (CaCO_3)	Vaterite (CaCO_3)	Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	Quartz (SiO_2)
1 hour ($\text{M}_{25^\circ\text{C}-1\text{hour}}$)	Run 1	81	8	10	1
	Run 2	56	13	30	1
	Run 3	61	20	18	1
	Run 4	87	-	12	1
2 hours ($\text{M}_{25^\circ\text{C}-2\text{hours}}$)	Run 1	45	8	46	1
	Run 2	65	22	12	1
	Run 3	61	25	13	1
	Run 4	97	-	2	1
3 hours ($\text{M}_{25^\circ\text{C}-3\text{hours}}$)	Run 1	51	15	33	1
	Run 2	54	23	22	1
	Run 3	99	-	-	1
	Run 4	78	-	21	1
	Run 5	99	-	-	1
4 hours ($\text{M}_{25^\circ\text{C}-4\text{hours}}$)	Run 1	68	23	8	1
	Run 2	63	29	7	1
	Run 3	99	-	-	1
	Run 4	99	-	-	1

Table 6.2: XRD analyses of the precipitates formed from the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$ at 40°C

Reaction time	Run number	Mineral			
		Calcite (CaCO_3)	Vaterite (CaCO_3)	Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	Quartz (SiO_2)
1 hour ($\text{M}_{40^\circ\text{C}-1\text{hour}}$)	Run 1	71	19	9	1
	Run 2	78	14	7	1
	Run 3	57	42	-	1
	Run 4	53	47	-	-
1 hour 30 min. ($\text{M}_{40^\circ\text{C}-1\text{hour and 30 minutes}}$)	Run 1	76	9	14	1
	Run 2	73	18	8	1
	Run 3	57	42	-	1
	Run 4	57	43	-	-
2 hours ($\text{M}_{40^\circ\text{C}-2\text{hours}}$)	Run 1	68	23	8	1
	Run 2	74	25	-	1
	Run 3	57	43	-	-
	Run 4	73	27	-	-

Table 6.3: XRD analyses of the precipitates formed from the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$ at 65°C

Reaction time	Run number	Mineral			
		Calcite (CaCO_3)	Vaterite (CaCO_3)	Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	Quartz (SiO_2)
1 hour ($\text{M}_{65^\circ\text{C}-1\text{hour}}$)	Run 1	99	-	-	1
	Run 2	98	-	1	1
	Run 3	96	3	-	1
	Run 4	99	-	-	1
1 hour 30 min. ($\text{M}_{65^\circ\text{C}-1\text{hour and 30 minutes}}$)	Run 1	98	-	1	1
	Run 2	99	-	-	1
	Run 3	99	-	-	1
	Run 4	96	-	3	1
2 hours ($\text{M}_{65^\circ\text{C}-2\text{hours}}$)	Run 1	98	-	1	1
	Run 2	99	-	-	1
	Run 3	99	-	-	1
	Run 4	99	-	-	1

Table 6.1 shows the XRD results of the precipitates formed at 25°C. At this temperature, calcite co-exists with vaterite under all reaction times tested, although not in every replicate. It is also observed that calcite is consistently present in excess over vaterite for all samples produced. The total amount of calcium carbonate (calcite + vaterite) formed varies greatly between replicates, regardless of the reaction time studied. In a similar way, the amount of unreacted gypsum also varies significantly between runs. In a study where $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ was reacted with NH_3 and CO_2 at room temperature and converted into calcite, Nehrke et al (2006) found that vaterite can serve as a precursor phase for the calcite. A similar mechanism may have taken place under the current experimental conditions, which is further supported by the experiments run at higher temperatures (40°C and 65°C; see below). All the precipitates formed at 25°C contain about 1% quartz. Given the significant variations in mineralogical composition observed between the carbonate samples produced at 25°C for different replicates, reaction time does not appear to play an important role under these conditions. This may be due to the metastable nature of the reactions, where little differences in solution composition as well as temperature and time may favor different equilibrium positions between chemical species.

Similar observations were made at 40°C (Table 6.2). For instance, vaterite is formed alongside calcite, although the former is more prominent than at 25°C. The difference in temperature between 25°C and 40°C had a significant influence on the amount of unreacted gypsum identified in the final product ($\leq 46\%$ at 25°C vs $\leq 14\%$ at 40°C). Similar mineralogical compositions were found for the carbonates formed between 1 and 2 hours. Quartz is still present in the precipitates formed at 40°C.

At 65°C calcite was the only polymorph of calcium carbonate identified in all but one run, where less than 3% of vaterite had been formed (Table 6.3). This confirmed that temperature plays an important role during the transformation of phosphogypsum into calcium carbonate using the Merseburg process. No significant difference exists between the products formed after 1 or 2 hours of reaction. High-grade calcite, defined as precipitates containing more than 95% CaCO_3 (De Beer, 2013), was therefore only formed at 65°C.

6.3.2 Thermogravimetric analyses of the precipitates formed from the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$ at different temperatures

Thermogravimetric analyses of the precipitates formed from the reaction between phosphogypsum and ammonium carbonate at the different temperatures were also performed and the findings were compared with those obtained by XRD. Figure 6.1 below shows the evaluation of the TGA curves of one of the precipitates formed, and its first derivative (DTG).

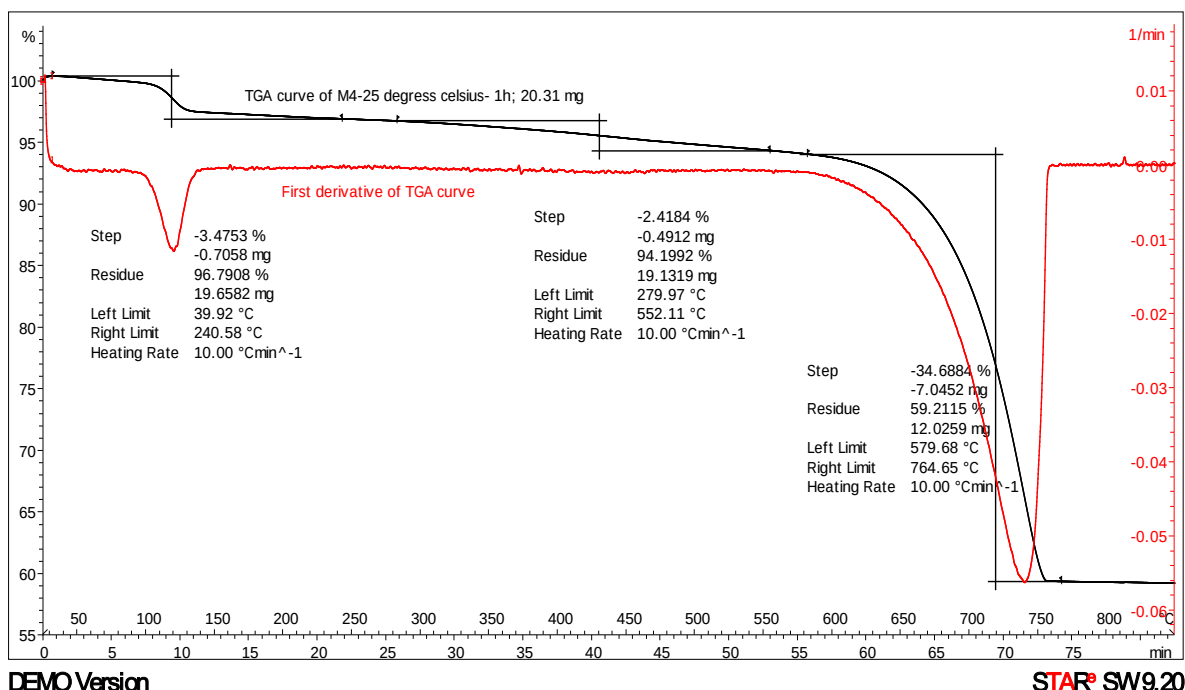


Figure 6.1: The TGA curve of a precipitate formed from the reaction between phosphogypsum and $(\text{NH}_4)_2\text{CO}_3$ at 25°C during 1 hour of reaction (M4-25°C-1h) and its first derivative (DTG).

Figure 6.1 exhibits the thermal decomposition of the precipitate formed from the reaction between phosphogypsum and ammonium carbonate at 25°C, which is characterized by three successive decomposition steps, ranging from 40°C to 241°C, from 280°C to 552°C and from 580°C to 765°C respectively.

The first decomposition step (from 40°C to 241°C) may represent the loss of surface water and/ or water of crystallization contained in the unreacted phosphogypsum. This weight loss represents 3.5% of the sample weight (20.31mg) used for this analysis.

The second weight loss takes place between 280°C and 552°C may correspond to an overlap for the decompositions of calcium carbonate and the continued loss water of crystallization from unreacted gypsum. The decompositions taking place just after 241°C have been investigated by TGA-FTIR in order to identify the nature of the gases evolving between 280°C and 552°C.

The last decomposition step (from 580°C to 765°C) corresponds to the decomposition of calcium carbonate formed during the reaction. Hudson-Lamb (1997) identified the range of decomposition

of calcium carbonate between 655°C and 808°C. This weight loss represents 34.7% for a sample weight of 20.31mg. This weight loss corresponds to 78.9% of CaCO_3 . This makes up to a total of 84.3% of CaCO_3 present in this precipitate.

The TGA-FTIR analysis was performed on the precipitate “ $\text{M}_{4-25^\circ\text{C}-1\text{h}}$ ” to investigate the nature of the gases which evolve between 280°C and 552°C. The analysis is summarized in Figures 6.2 and 6.3.

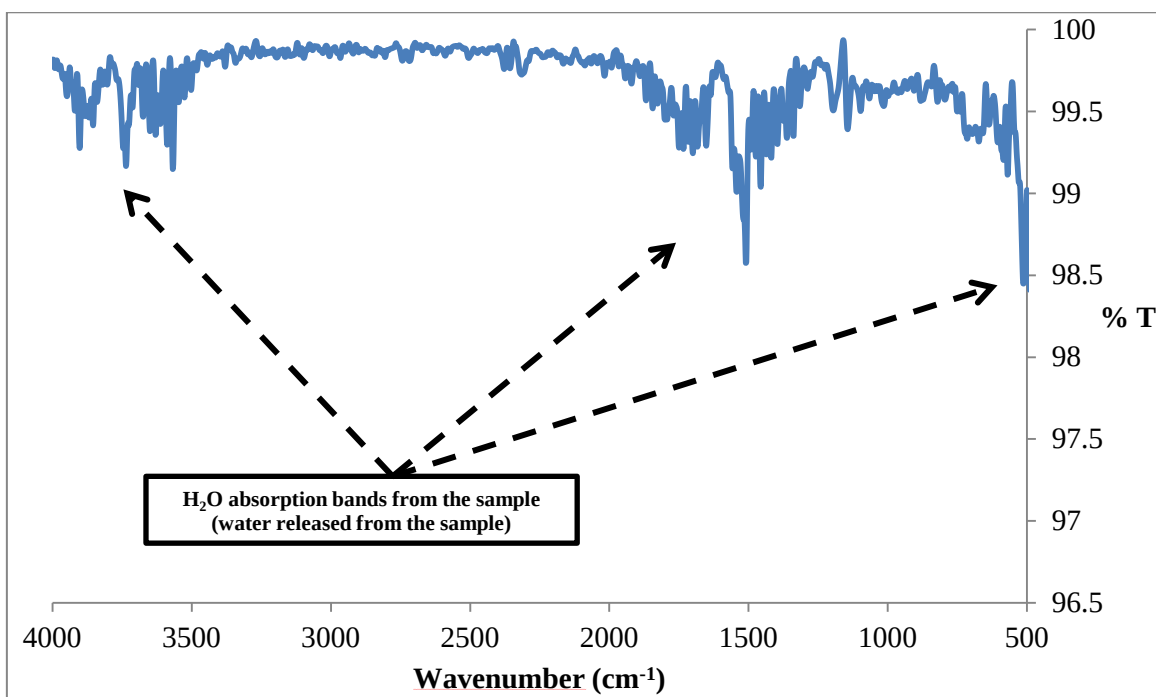


Figure 6.2: FTIR spectrum obtained from the gaseous TGA decomposition between 40°C and 241°C of the precipitate($\text{M}_{4-25^\circ\text{C}-1\text{h}}$) formed at 25°C during an 1 hour reaction

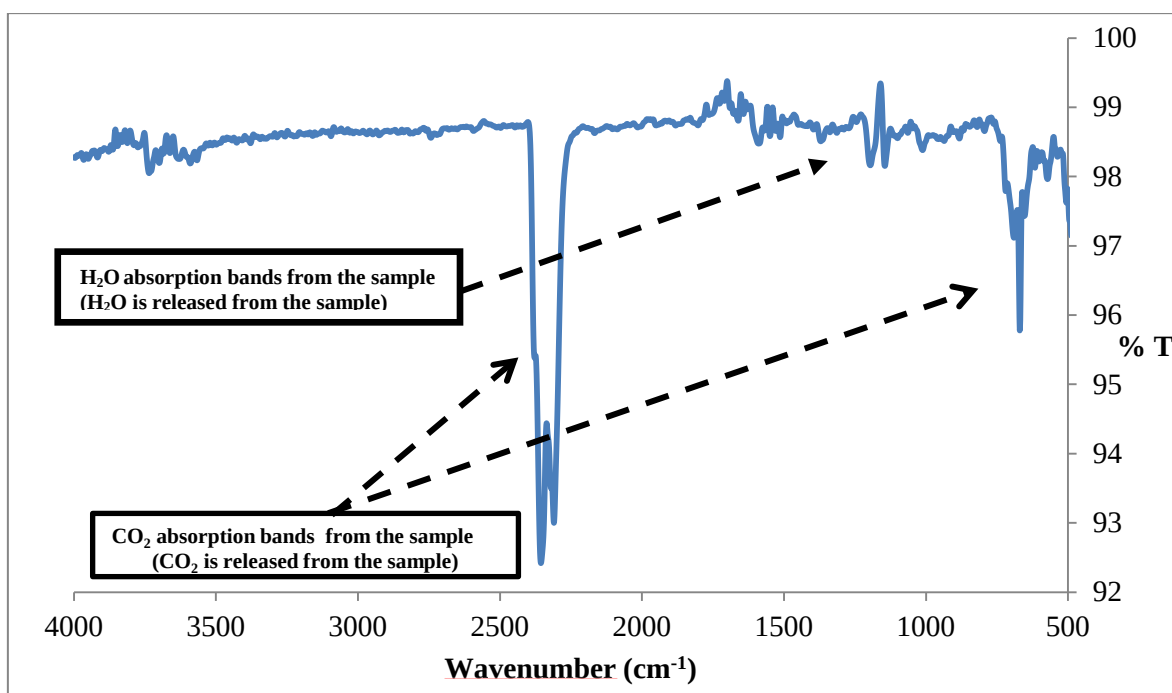


Figure 6.3: FTIR spectrum obtained from the gaseous TGA decomposition taking place after 241°C of the precipitate ($M_{4-25^{\circ}\text{C}-1\text{h}}$) formed at 25°C during an 1 hour reaction

Figure 6.2 and Figure 6.3 show the FTIR spectra of the evolved gases during the thermal decomposition of the precipitate “ $M_{4-25^{\circ}\text{C}-1\text{h}}$ ” that was formed at 25°C from the reaction between phosphogypsum and ammonium carbonate.

Figure 6.2 shows the FTIR spectrum taken from the decomposition product of the sample occurring between 40°C and 241°C. It shows intense bands between 3400 - 4000 cm^{-1} , 1400 - 1900 cm^{-1} , and around 500 cm^{-1} , suggesting the presence of water vapor. In their study, Mc Connell et al (2008) identified the presence of sharp bands in the range of 4000 cm^{-1} to 3500 cm^{-1} and from 2000 cm^{-1} to 1300 cm^{-1} as characteristic of the presence of H_2O vapor, and Barrett (2005) identified absorption bands between 400 cm^{-1} and 600 cm^{-1} as those of H_2O . These results indicate that during the first weight loss (between 40°C and 241°C) in the TGA curve, only water is released as decomposition product. This confirms the presence of surface water and/ or the presence of water of crystallization contained in unreacted gypsum.

Figure 6.3 shows the FTIR spectrum taken from the decomposition of the sample occurring after 241°C. It shows intense bands around 2400 cm^{-1} as well as around 700 cm^{-1} which are attributed to the presence of CO_2 . Fermo et al (2005) identified the most intense signal in the CO_2 infrared spectrum to occur at 2350 cm^{-1} while Barrett (2005) identified CO_2 absorptions between 600 cm^{-1} and

800cm⁻¹. However, the spectrum shows the presence of small band in the region of 996cm⁻¹ and 1796cm⁻¹ which according to Mc Connell et al (2008) are characteristic of the presence of H₂O vapor. This means that at temperatures above 241°C, the loss of a small amount of water continues concurrently with the onset of decomposition of calcium carbonate.

The quantitative TG analysis performed on all the precipitates formed at the different temperatures is summarized in Tables 6.4 to 6.6, while Tables 6.7, 6.8 and 6.9 compare the total amount of CaCO₃ determined TGA and XRD analyses for each precipitate at the different temperatures.

Table 6.7 shows that for each precipitate formed at 25°C, the total amount of CaCO₃ detected by TGA compares well to the total amount of CaCO₃ reported by XRD. This confirms the amount of CaCO₃ formed in each generated sample. However, a discrepancy (a difference greater than 5%) is observed in “Run 2” of “M_{25°C-3hours}” where the amount of CaCO₃ detected by TGA (69.1%) is lower than the amount of CaCO₃ detected by XRD (77%). Another difference greater than 5% is observed in “Run 3” of “M_{25°C- 2hours}”, where the amount detected by TGA (91.9%) is greater than the amount of CaCO₃ detected by XRD (86%). In this specific case, the difference may suggest that “Run 3” of “M_{25°C- 2hours}” contains some amorphous CaCO₃.

Tables 6.8 and 6.9 show that for each precipitate formed at 40°C and 65°C, the total amount of CaCO₃ detected by TGA compares well with the amounts of CaCO₃ determined by XRD. However, the presence of small amounts of water in the early temperature decompositions of the precipitates made at 65°C may indicate the presence of amorphous phosphogypsum not detected by XRD.

Table 6.4: Quantitative TG analysis of the precipitates formed at 25°C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 2 hours 3 hours and 4 hours of reaction.

TGA Weight loss	Theoretical weight loss of CO₂: 43.97% (±252°C→±580°C) CaCO₃ → CaO+CO₂		Theoretical weight loss of CO₂: 43.97% (±580°C→±850°C) CaCO₃ → CaO+CO₂	
	Weight Loss of CO ₂ (%)	Weight % CaCO ₃	Weight Loss of CO ₂ (%)	Weight % percentage CaCO ₃
M _{25°C-1hour}	2.7	6.1	35.9	81.6
	1.3	2.9	27.6	62.8
	3.2	7.3	31.2	70.9
	2.4	5.5	34.7	78.9
M _{25°C-2hours}	1.1	2.5	22.9	52.1
	1.4	3.2	35.0	79.6
	1.8	4.1	38.6	87.8
	2.3	5.2	39.7	90.3
M _{25°C-3hours}	1.7	3.9	27.9	63.5
	1.9	4.3	28.5	64.8
	1.6	3.6	40.7	92.6
	1.7	3.9	30.0	68.2
	1.9	4.3	40.8	92.8
M _{25°C-4hours}	1.8	4.1	36.7	83.5
	2.1	4.8	37.3	84.8
	2.4	5.5	40.3	91.6
	1.8	4.1	41.3	93.9

Table 6.5: Quantitative TG analysis of the precipitates formed at 40°C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 1 hour and 30 minutes and 2 hours of reaction.

TGA weight loss	Theoretical weight loss of CO₂: 43.97% (±192°C→±580°C) CaCO₃ → CaO+CO₂		Theoretical weight loss of CO₂: 43.97% (±580°C→±850°C) CaCO₃ → CaO+CO₂	
	Experimental weight loss of (CO ₂) in %	Experimentally determined Weight percentage of CaCO ₃ using its decomposition weight loss percentage	Experimental weight loss of (CO ₂) in %	Experimentally determined Weight percentage of CaCO ₃ using its decomposition weight loss percentage
M_{40°C-1hour}	2.3	5.2	37.2	84.6
	2.3	5.2	37.8	86.0
	1.7	3.9	40.2	91.5
	0.7	1.7	40.7	93.0
M_{40°C-1hour and 30 minutes}	2.0	4.7	33.8	77.0
	0.0	0.0	39.3	89.4
	2.3	5.3	40.1	91.2
	2.1	4.7	39.6	90.1
M_{40°C-2hours}	2.1	4.8	37.7	85.7
	1.8	4.1	39.6	90.1
	2.2	5.0	39.7	90.3
	2.7	6.1	39.9	90.7

Table 6.6: Quantitative TG analysis of the precipitates formed at 65°C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 1 hour and 30 minutes and 2 hours of reaction.

TGA weight loss	Theoretical weight loss of CO₂: 43.97% (±223°C→±580°C) CaCO₃ → CaO+CO₂		Theoretical weight loss of CO₂: 43.97% (±580°C→±831°C) CaCO₃ → CaO+CO₂	
	Experimental weight loss of (CO ₂) in %	Experimentally determined Weight percentage of CaCO ₃ using its decomposition weight loss percentage	Experimental weight loss of (CO ₂) in %	Experimentally determined Weight percentage of CaCO ₃ using its decomposition weight loss percentage
M_{65°C-1hour}	1.9	4.3	39.7	90.3
	1.8	4.1	39.6	90.1
	3.1	7.1	39.9	91.0
	2.9	6.6	39.4	90.0
M_{65°C-1hour and 30 minutes}	1.9	4.3	38.7	88.0
	1.5	3.4	39.8	91.0
	3.5	8.0	39.7	90.3
	0.0	0.0	39.3	89.3
M_{65°C-2hours}	0.2	0.5	42.7	97.1
	2.0	5.0	40.3	91.7
	2.1	4.8	39.0	88.7
	2.2	5.0	39.5	90.0

Table 6.7: Comparisons of the total CaCO₃ detected by TGA against the total CaCO₃ detected by XRD of the precipitates formed at 25°C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 2 hours 3 hours and 4 hours of reaction.

		Total CaCO ₃ detected by XRD	Total CaCO ₃ detected by TGA
M _{25°C-1hour}	Run 1	89	87.7
	Run 2	69	65.7
	Run 3	81	78.2
	Run 4	87	84.4
M _{25°C-2hours}	Run 1	54	54.6
	Run 2	87	82.8
	Run 3	86	91.9
	Run 4	97	95.5
M _{25°C-3hours}	Run 1	66	67.4
	Run 2	77	69.1
	Run 3	99	96.2
	Run 4	79	72.1
	Run 5	99	97.1
M _{25°C-4hours}	Run 1	91	87.6
	Run 2	92	89.6
	Run 3	99	97.1
	Run 4	99	98.1

Table 6.8: Comparisons of the total CaCO₃ detected by TGA against the total CaCO₃ detected by XRD of the precipitates formed at 40°C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 1 hour and 30 minutes and 2 hours of reaction.

		Total CaCO ₃ detected by XRD	Total CaCO ₃ detected by TGA
M _{40°C-1hour}	Run 1	90	89.8
	Run 2	92	91.2
	Run 3	99	95.4
	Run 4	100	98.7
M _{40°C-1hour and 30 minutes}	Run 1	85	81.7
	Run 2	91	89.4
	Run 3	99	94.8
	Run 4	100	96.42
M _{40°C-2hours}	Run 1	91	90.5
	Run 2	99	94.2
	Run 3	100	95.3
	Run 4	100	96.8

Table 6.9: Comparisons of the total CaCO_3 detected by TGA against the total CaCO_3 detected by XRD of the precipitates formed at 65°C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 1 hour and 30 minutes and 2 hours of reaction.

		Total CaCO_3 detected by XRD	Total CaCO_3 detected by TGA
$M_{65^\circ\text{C}-1\text{hour}}$	Run 1	99	94.6
	Run 2	98	94.2
	Run 3	99	98.1
	Run 4	99	96.6
$M_{65^\circ\text{C}-1\text{hour and 30 minutes}}$	Run 1	98	92.3
	Run 2	99	94.4
	Run 3	99	98.3
	Run 4	96	89.3
$M_{65^\circ\text{C}-2\text{hours}}$	Run 1	98	97.6
	Run 2	99	96.7
	Run 3	99	93.5
	Run 4	99	95.0

6.3.3 Further characterization of the calcite precipitates formed at 65°C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 1 hour and 30 minutes and 2 hours of reaction.

The CaCO_3 precipitates formed at 65°C were further characterized firstly due to the fact that full conversion of phosphogypsum into CaCO_3 was obtained and secondly because they consist of a single phase of calcium carbonate (the stable calcite) compared to the precipitates formed at 25°C and 40°C where the precipitates contained two polymorphs of CaCO_3 (calcite and vaterite). Furthermore, the amount of unconverted gypsum was still significant in most of the experiments performed below 65°C .

6.3.3.1 Extent of conversion of the calcite precipitates formed at 65°C.

The XRD results showed that the dominant mineral phase (> 96%) in the precipitates formed using 4.3g of phosphogypsum and 200ml of $(\text{NH}_4)_2\text{CO}_3$ solution at 65°C was calcite. A mass balance study was then performed using the masses of the precipitates formed in order to determine the percentage of calcium present in phosphogypsum that was transformed into calcite. The results of this study are summarized in Table 6.10

Table 6.10: Extent of conversion of the calcium contained in the gypsum samples into CaCO_3

Sample	Mass of Calcium in 4.3 g of phosphogypsum in (g)	Theoretical mass of CaCO_3 to be formed from 1.97g of Ca in (g)	Experimental mass of CaCO_3 formed in (g)	Extent of conversion of phosphogypsum into CaCO_3 in %
M _{65°C-1hour}	1.69	4.23	2.30	54.37
M _{65°C-1hour and 30 minutes}	1.69	4.23	2.18	51.54
M _{65°C-2hours}	1.69	4.23	2.19	51.77

Table 6.10 shows that for 4.3g of phosphogypsum (containing 1.69g of calcium) dispersed into 200ml of a $(\text{NH}_4)_2\text{CO}_3$ solution, 2.30g of CaCO_3 is formed after 1 hour of reaction, 2.18g of CaCO_3 is formed after 1 hour and 30 minutes of reaction and 2.19g of CaCO_3 is formed after 2 hours of reaction. These represent an extent of conversion of phosphogypsum into CaCO_3 of 54.37% after 1 hour of reaction; 51.54% after 1 hour and 30 minutes of reaction and 51.77% after two hours of reaction. This means that a significant proportion of the calcium in solution (45.63% after 1 hour of reaction, 48.46% after 1 hour and 30 minutes and 48.23% after 2 hours of reaction) was unreacted and was not converted into CaCO_3 .

6.3.3.2 Field Emission Scanning Electron Microscopy (FESEM) of the calcite precipitates formed at 65°C.

FESEM analyses were performed on the CaCO_3 precipitates formed at 65°C in order to examine the size and morphology of the particles. Representative micrographs of the CaCO_3 precipitates formed after 1 hour, 1 hour and 30 minutes and 2 hours of reaction are shown in Figures 6.4a, 6.4b, and 6.4c respectively.

From these figures, it is firstly observed that the size of the particles formed at the three different times is below 10 μm . Furthermore, it is observed the existence of two types of particles: particles with rough surface area and particles with smooth surface area.

The particles formed after 1 hour (Figure 6.4a) and 1 hour and 30 minutes (Figure 6.4b) contains more particles with rough surfaces than those present in the sample obtained after 2 hours of reaction (Figure 6.4c).

A closer examination of the crystals with smooth surface areas (Figures 6.5a, 6.5b and 6.5c) reveals that they are in fact made of two different structures: a cube-like structure made by the aggregation of rectangular plate-like crystals, and a cube-like structure made from thick crystals. It seems that the plate-like crystals are formed at the surface of crystals with rough surface areas and those plate-like crystals then become thicker, adopting the shape of a cube. In another mineral carbonation route where CO_2 was purged into $\text{Ca}(\text{OH})_2$ suspension, Wen et al (2003) found that the rectangular CaCO_3 particles formed became bigger and thicker as the flow rate of CO_2 was increased from 100 to 600ml/min.

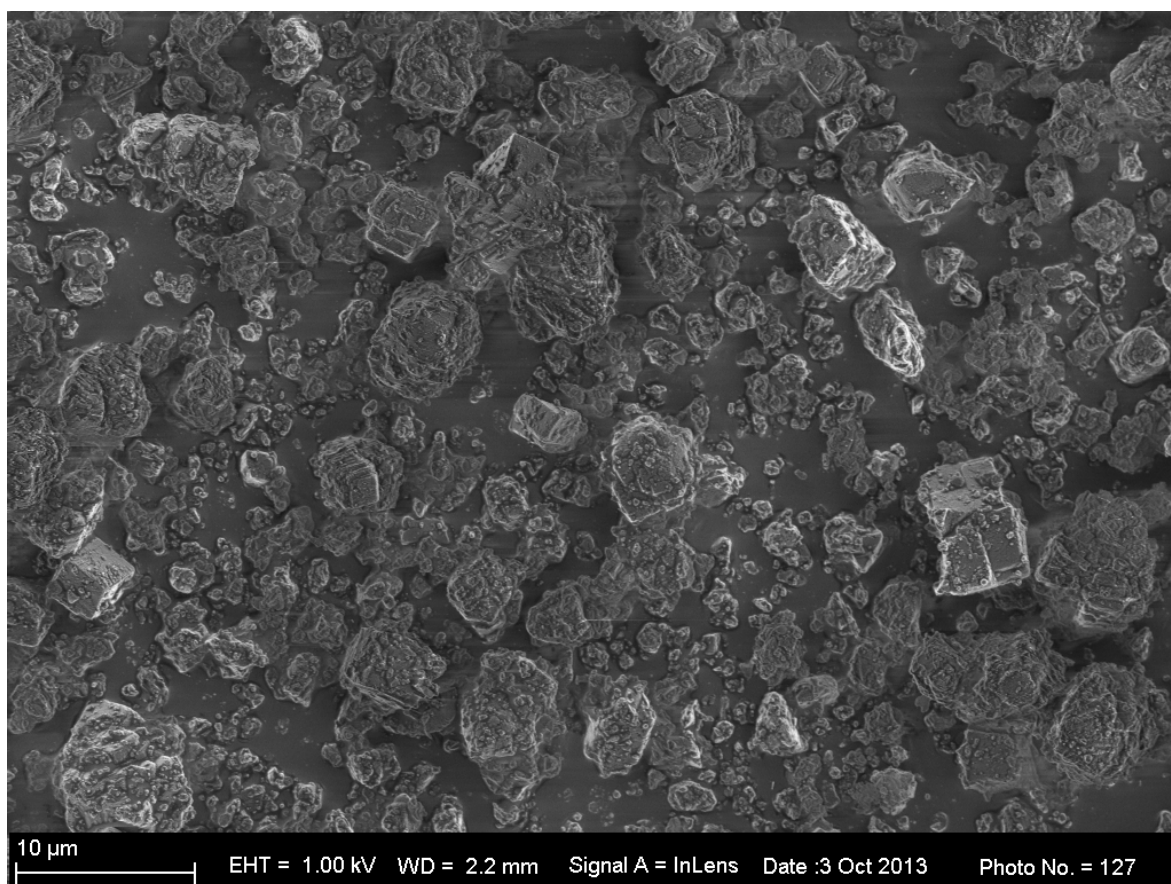


Figure 6.4a: FESEM images of the calcite crystals formed at 65°C after 1 hour of reaction at a magnification of 3200 ×

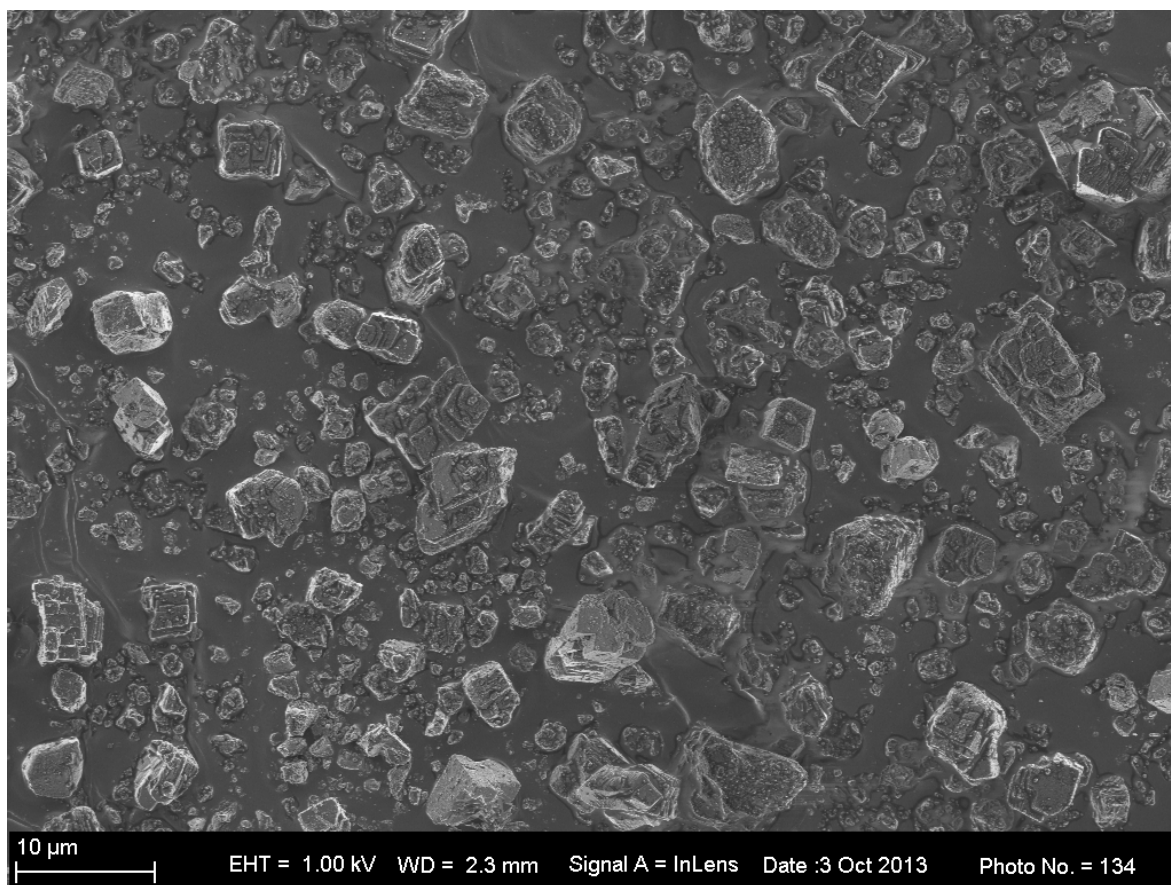


Figure 6.4b: FESEM images of the calcite crystals formed at 65°C after 1hour and 30 minutes of reaction at a magnification of 2500 ×

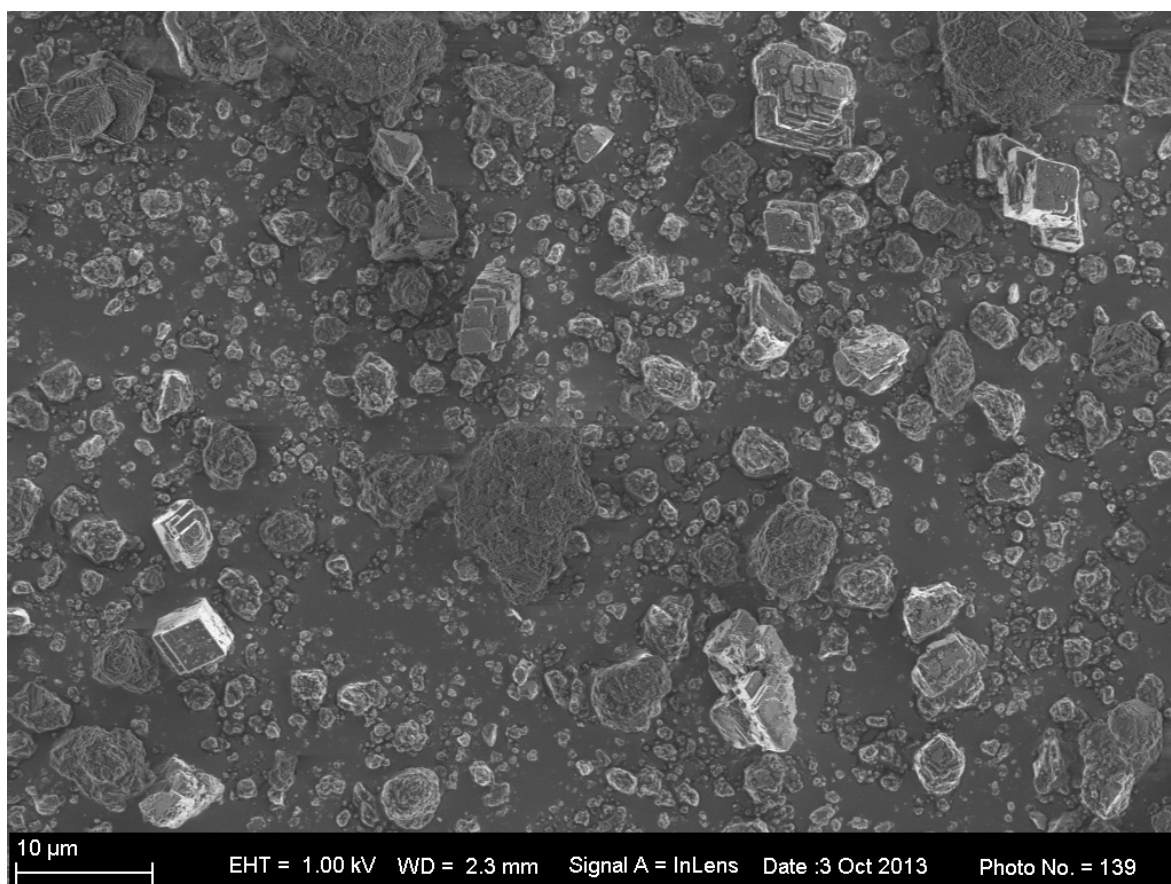


Figure 6.4c: FESEM images of the calcite crystals formed at 65°C after 2 hours of reaction at a magnification of 2500 ×

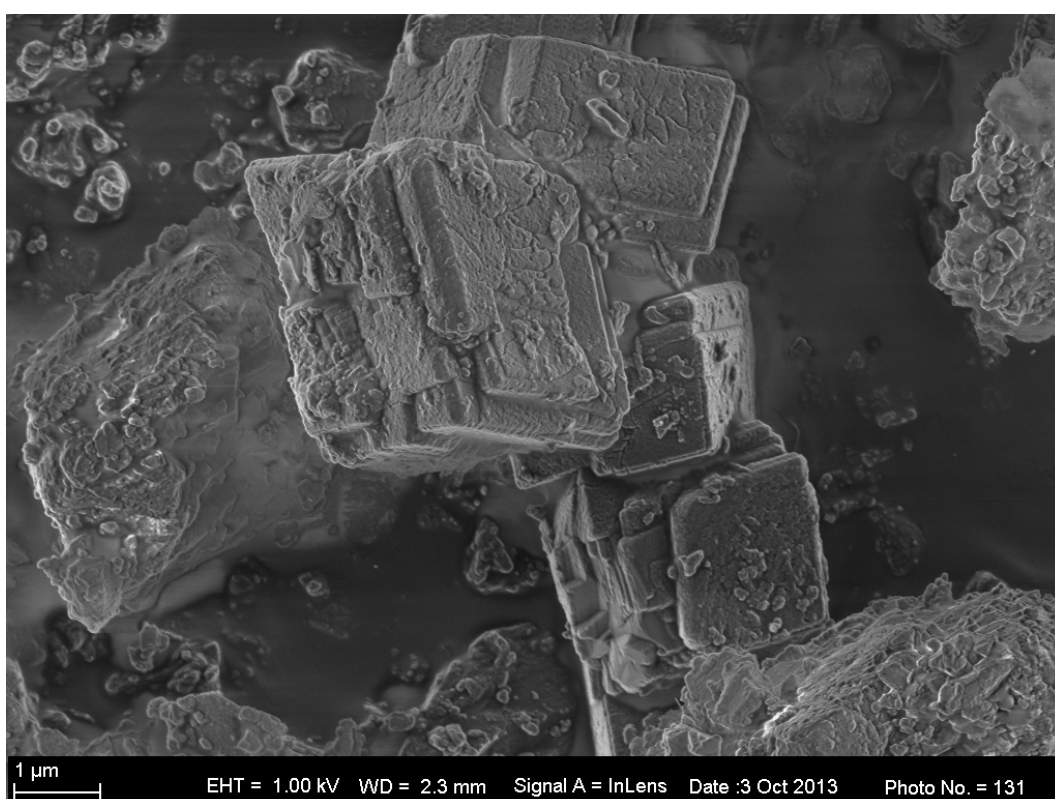
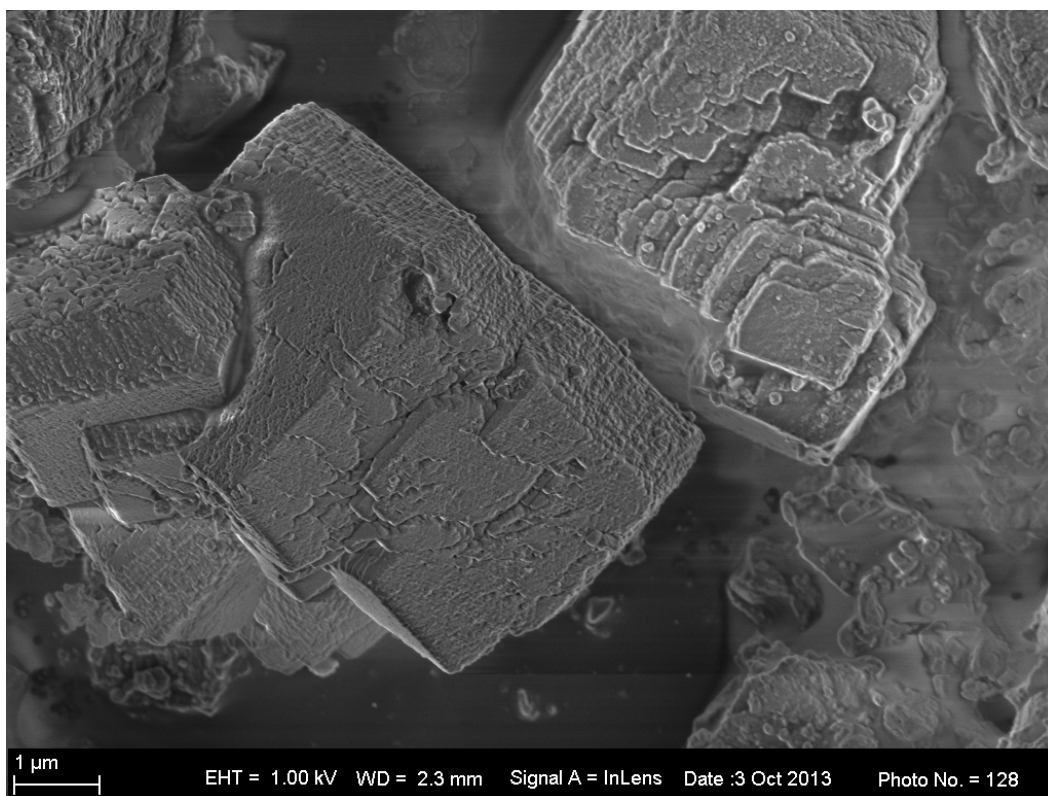


Figure 6.5a: Cubic and plate-like crystals formed from the reactions at 65°C between phosphogypsum and ammonium carbonate during an 1 hour reaction at a magnification of 16000 ×

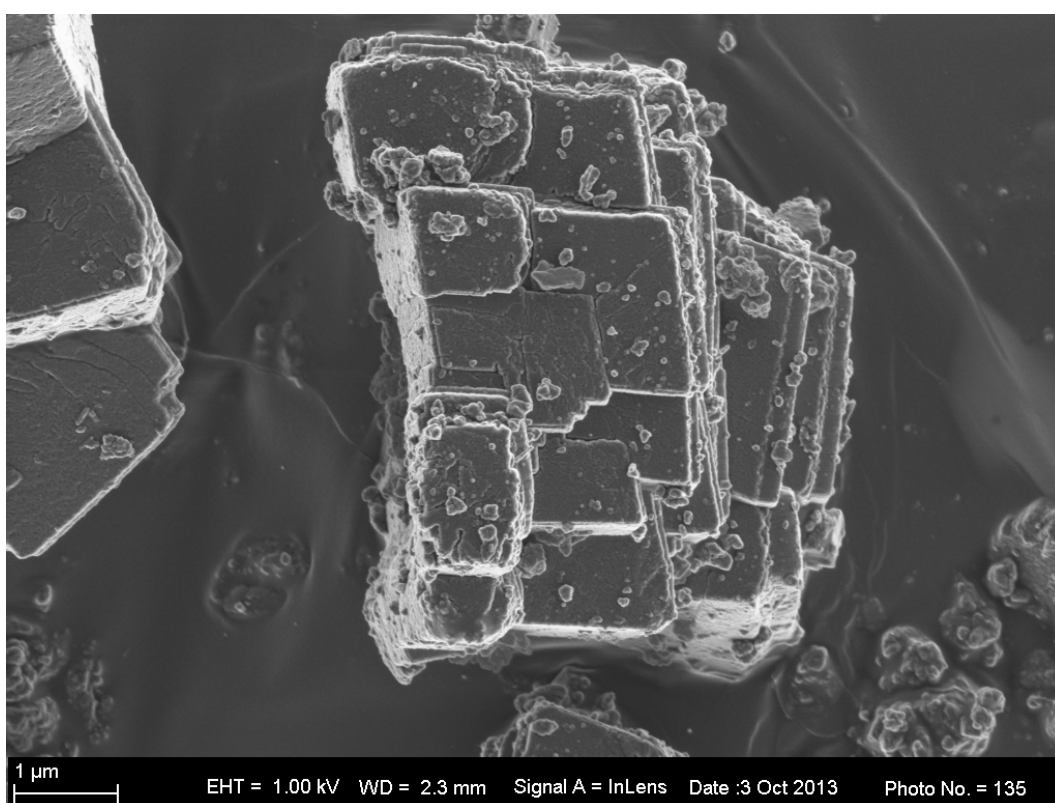
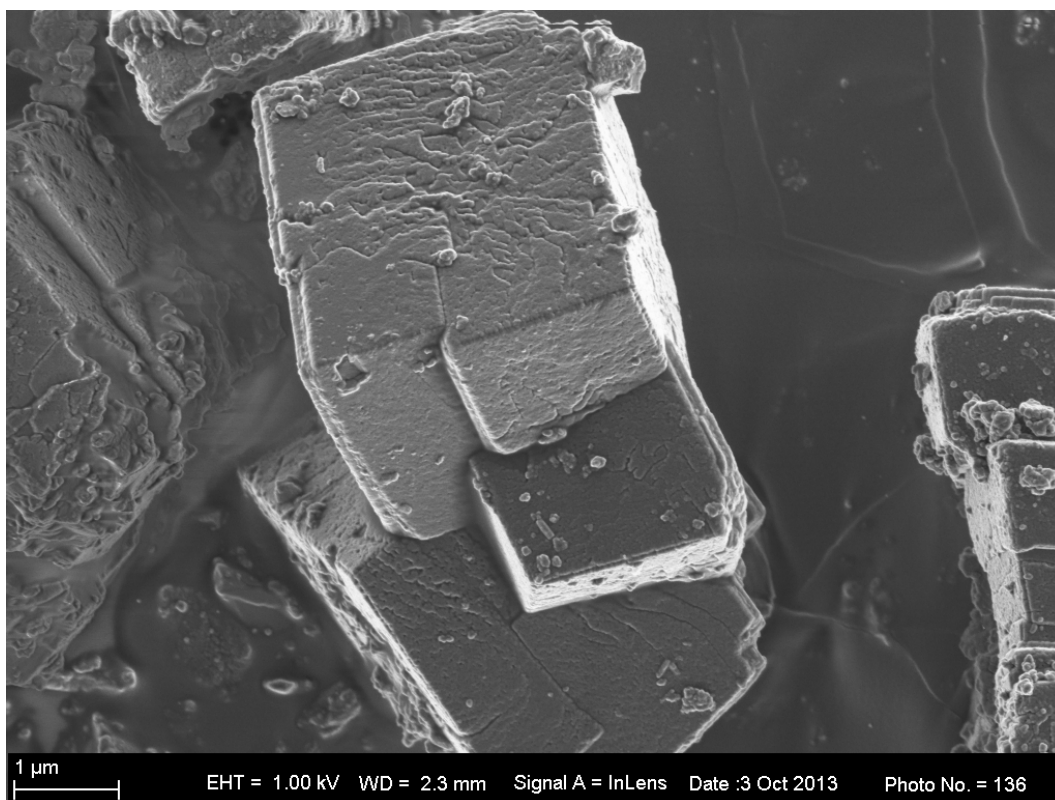


Figure 6.5b: Cubic and plate-like crystals formed from the reactions at 65°C between phosphogypsum and ammonium carbonate during an 1 hour and 30 minutes of reaction at a magnification of 19000 ×

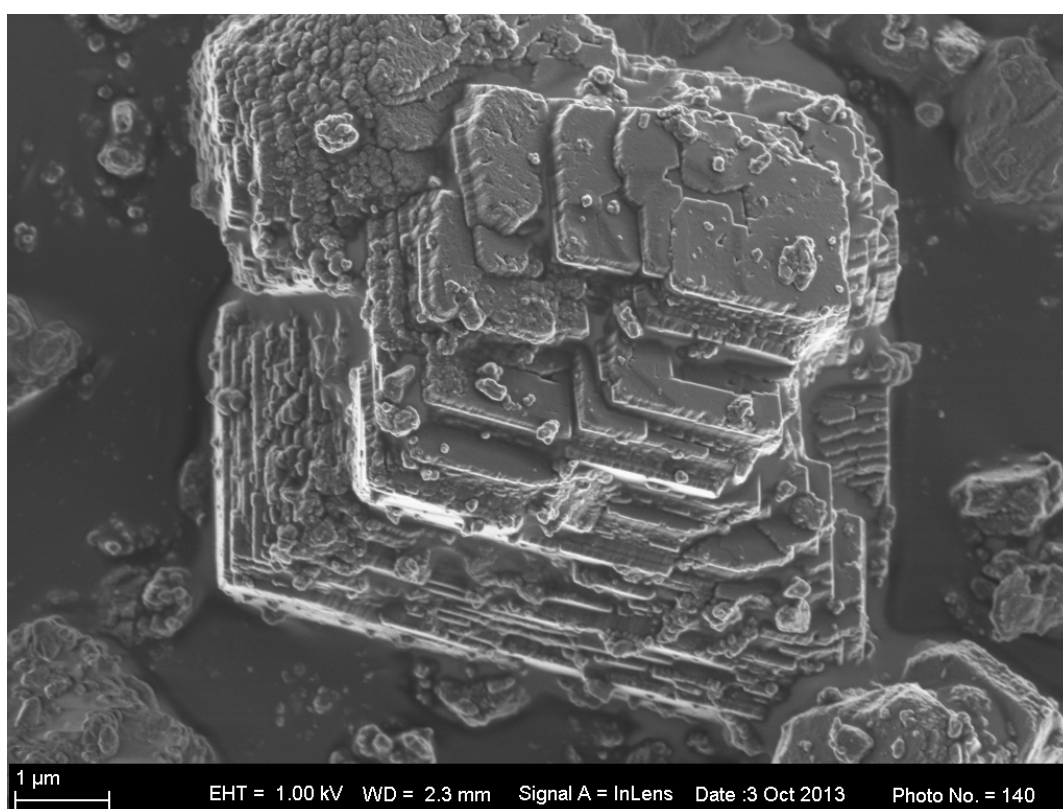
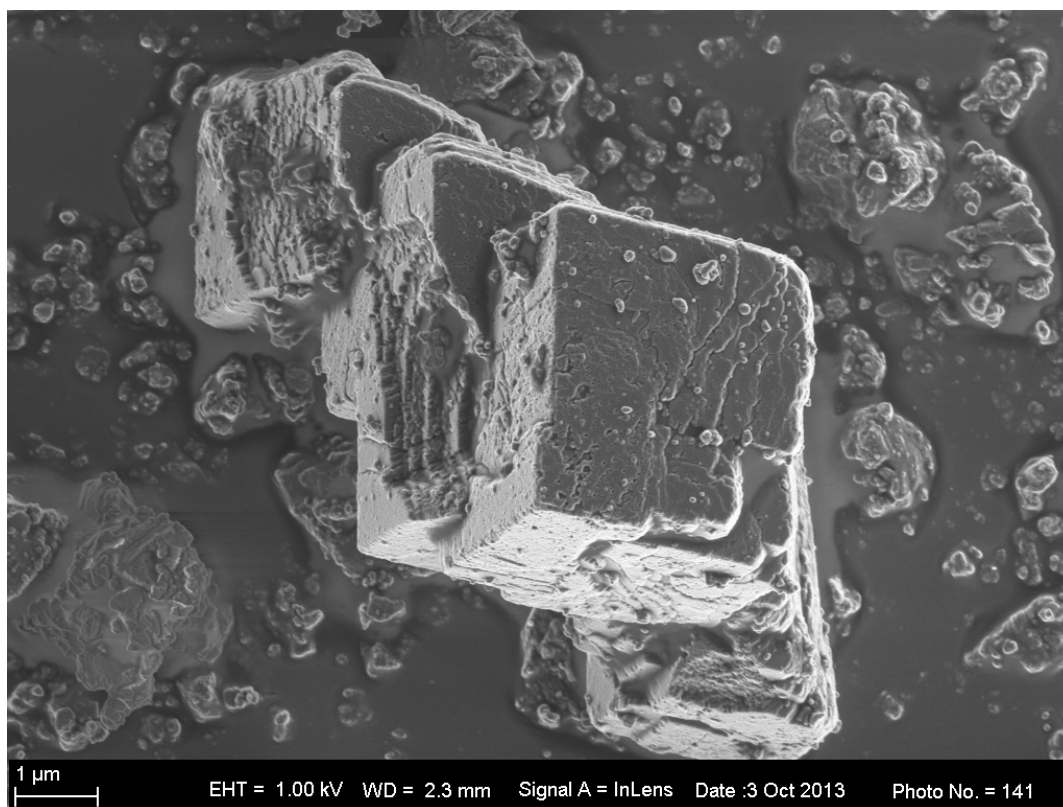


Figure 6.5c: Cubic and plate-like crystals formed from the reactions at 65°C between phosphogypsum and ammonium carbonate during an 2 hours of reaction at a magnification of 17000 ×

6.3.3.3 Particle size distribution (PSD) analysis of the calcite precipitates formed at 65°C.

The PSD of the calcite samples formed at 65°C was determined to investigate the effect of reaction time on the size of the particles. Furthermore, this analysis was done to confirm the pattern observed by FESEM analysis. The results of the analyses are presented in the form of a frequency curve of volume percentage versus the logarithm of particle size in Figure 6.6, while Table 6.11 shows the calculated diameters for all three calcite samples.

Figure 6.6 shows that the calcite precipitates obtained at 65°C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 1 hour and 30 minutes and 2 hours of reaction are made of two populations each. The first population of the calcite precipitate formed after an hour of reaction is located where 2.4% of the population measures 0.796µm. Its second population is where 7.4% of the particles measure 5.637µm. The calcite precipitates formed after 1 hour and 30 minutes of reaction have a first population where 2% of the particles measure 0.796µm; and a second population where 6.6% of the particles measure 5.637µm. Finally, the calcite precipitates obtained after 2 hours of reaction have a first population where 2.3% of the particles measure 0.796µm and a second population located where 6.2% of the particles measure 6.325µm.

Table 6.11 shows that 10% of the particles formed after 1 hour and 2 hours have a size below 0.8µm while 10% of the particles formed after 1 hour and 30 minutes have sizes below 0.9µm.

On the other hand, 50% of the calcite particles obtained after 1 hour and 1 hour and 30 minutes of reaction have a size below 6.9µm while 50% of the calcite particles obtained after 2 hours of reaction have a size below 7.3µm. This confirms that the size of 50% of the particles is of the same order of magnitude as the size observed from the FESEM pictures (particle size below 10µm).

Finally, 90% of the particles of the calcite formed after 1 hour of reaction have a size below 16µm, while the particles of the calcite formed after 1 hour and 30 minutes of reaction have a size below 19µm, and the particles of the calcite formed after 2 hours of reaction have a size below 22.9µm. The change in $D(v, 0.9)$ over time indicates the growth of the particles as the time of the reaction is increased.

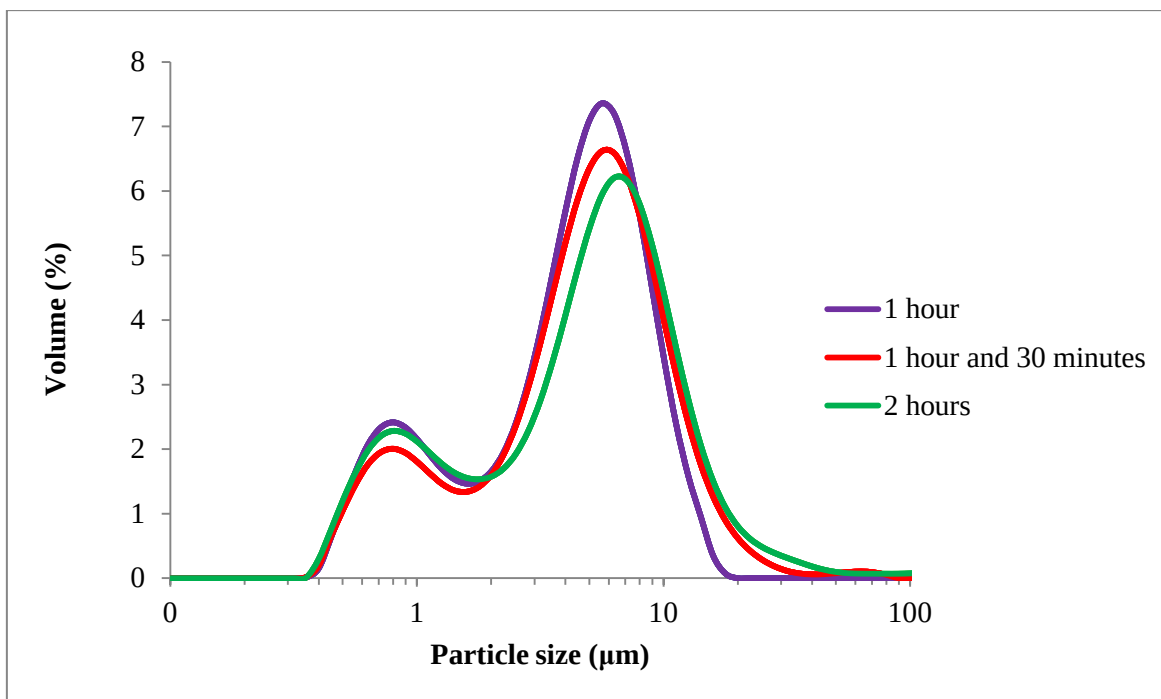


Figure 6.6: The frequency curve of the calcite precipitates formed at 65°C from the reactions between phosphogypsum and ammonium carbonate during 1 hour, 1 hour and 30 minutes and 2 hours of reaction.

Table 6.11: Summary of the particle size distribution of the calcite samples formed at 65°C

Statistics	Samples		
	$M_{65^{\circ}\text{C-1hour}}$	$M_{65^{\circ}\text{C-1hour and 30 minutes}}$	$M_{65^{\circ}\text{C-2hours}}$
D (v; 0.1)	0.8 ± 0.0	0.9 ± 0.0	0.8 ± 0.0
D (v; 0.5)	6.9 ± 0.9	6.9 ± 0.1	7.3 ± 0.1
D (v; 0.9)	16.0 ± 2.1	19.0 ± 0.5	22.9 ± 2.0

6.3.3.4 ICP-MS 4-acid analysis performed on the calcite precipitates formed at 65°C for the determination of the different major and trace elements.

ICP-MS 4-acid digestion analysis was performed on the calcite precipitates obtained at 65°C to determine the concentrations of major and trace elements they contain. The results obtained from these analyses were reported in Table 6.12. Table 6.13 shows the percentage of calcium in each calcite precipitate obtained after 1 hour, 1 hour and 30 minutes and 2 hours of reaction as determined from the XRD analysis.

Table 6.12: Concentration of the different major and trace elements contained in the calcite precipitates obtained at 65°C in part per billion (µg/kg)

Elements (Atomic weight)	*Detection limit	Samples		
		M _{65°C-1hour}	M _{65°C-1hour and 30 minutes}	M _{65°C-2hours}
Na (23)	50 000	104 723	82 114	69 423
Mg (24)	50 000	228 228	263 177	236 293
Al (27)	50 000	741 145	885 189	744 143
K (39)	50 000	199 092	140 726	134 284
Ca (43)	50 000	491 094 886	482 223 581	466 474 741
Cr (52)	50 000	27 333	17 279	73 657
Cd (114)	20	47	95	64
U (238)	10	1371	1353	1 271

*The detection limit is the minimum concentration of the element which can be detected by the instrument. An element whose concentration is below the detection limit is considered as absent in the sample.

Table 6.13: Percentage of calcium in the calcite precipitates obtained at 65°C as estimated from the XRD data

Sample	% Ca in the calcite precipitates formed as estimated from the XRD data
M _{65°C-1hour}	38.99
M _{65°C-1hour and 30 minutes}	39.31
M _{65°C-2hours}	39.54

Table 6.14: Percentage of calcium in the calcite precipitates obtained at 65°C as estimated from the ICP-MS 4-acid analysis

Sample	% Ca in the calcite precipitates formed as estimated from the ICP-MS 4-acid analysis
M _{65°C-1hour}	49.1
M _{65°C-1hour and 30 minutes}	48.2
M _{65°C-2hours}	46.6

Theoretically, in a 100% calcium carbonate sample, calcium contributes to 40.04%. Table 6.13 shows that the calcite precipitates formed obtained at 65°C after 1 hour, 1 hour and 30 minutes and 2 hours of reaction between phosphogypsum and ammonium carbonate contain nearly 40% of calcium as estimated by the XRD data.

Table 6.14 shows that the percentage of calcium in each precipitate obtained at 65°C as determined from the ICP-MS 4-acid analysis is higher than the percentage of calcium in the same precipitates as determined from the XRD data (Table 6.13). The difference in the results between XRD and the ICP-MS analysis was most probably due to the fact that XRD is a semi-quantitative method and each instrument is based on a different principle of analysis and therefore comes with its own limitations. Furthermore, prior to the XRD analysis, the samples were not micronised since it was uncertain whether the sample would have been altered during the micronisation process with ethanol. The size of the particles which were analysed by XRD may have therefore been larger than

what is recommended (i.e. sub-10µm), which could have caused artefacts such as preferential orientation during the analysis.

The other elements found in the calcite precipitates are impurities that were previously contained in the phosphogypsum sample before going into reaction as described in Section 3.5.1

6.3.3.5 ICP-MS analysis performed on the calcite precipitates formed at 65°C for the determination of rare earth elements (REE)

ICP-MS analysis for rare earth elements were performed on the calcite precipitates obtained at 65°C to determine the amounts of these elements present in the precipitates and assess the percentage of rare earth elements originally present in the phosphogypsum which were transferred to the formed carbonate products. The results obtained from these analyses are reported in Table 6.15.

Every rare earth element that had been identified in the untreated phosphogypsum sample (section 3.5.2) was found in the carbonate products obtained at 65°C after 1 hour, 1 hour and 30 minutes and 2 hours of reaction between 4.3 g of phosphogypsum and 200 ml of ammonium carbonate solution. The histograms represented in Figures 6.7, 6.8 and 6.9 represent the quantification of the rare earth elements that were transferred in the calcite precipitates.

Figure 6.17 shows that most of the rare earth elements (*i.e.* 75% to 100%) contained in the phosphogypsum sample before treatment were identified in the calcite precipitate formed after 1 hour of reaction at 65°C between phosphogypsum and ammonium carbonate.

Similarly, Figure 6.8 and Figure 6.9 show that the rare earth elements (*i.e.* 74% to 99% for the precipitates obtained after 1 hour and 30 minutes of reaction; *i.e.* 72% to 100% for the precipitates obtained after 2 hours of reaction) contained in the phosphogypsum sample before going into reaction with ammonium carbonate were identified in the calcite precipitates

An assessment as to whether their presence in calcite is a problem for specific applications will have to be addressed in future works.

Table 6.15: Concentration of rare earth elements contained in the calcite precipitates obtained at 65°C, reported in parts per billion (µg/kg)

Elements (Atomic weight)	Detection limit	Samples		
		M_{65°C-1hour}	M_{65°C-1hour and 30 minutes}	M_{65°C-2hours}
Y (89)	50	134 345	128 808	133 536
La (139)	500	980 111	968 126	984 531
Ce (140)	500	2 398 834	2 364 737	2 371 009
Pr (141)	50	349 874	344 159	350 127
Nd (146)	200	1 455 170	1 430 562	1 451 463
Sm (147)	20	249 870	248 196	250 447
Eu (151)	10	47 428	47 436	47 846
Gd (157)	20	168 964	168 196	169 693
Tb (159)	20	18 025	18 056	17 999
Dy (163)	10	55 353	54 762	55 205
Ho (165)	10	6 589	6 526	6 542
Er (167)	10	10 600	10 504	10 500
Tm (169)	10	864	817	787
Yb (172)	10	4 381	4 314	4 370
Lu (175)	10	427	414	455

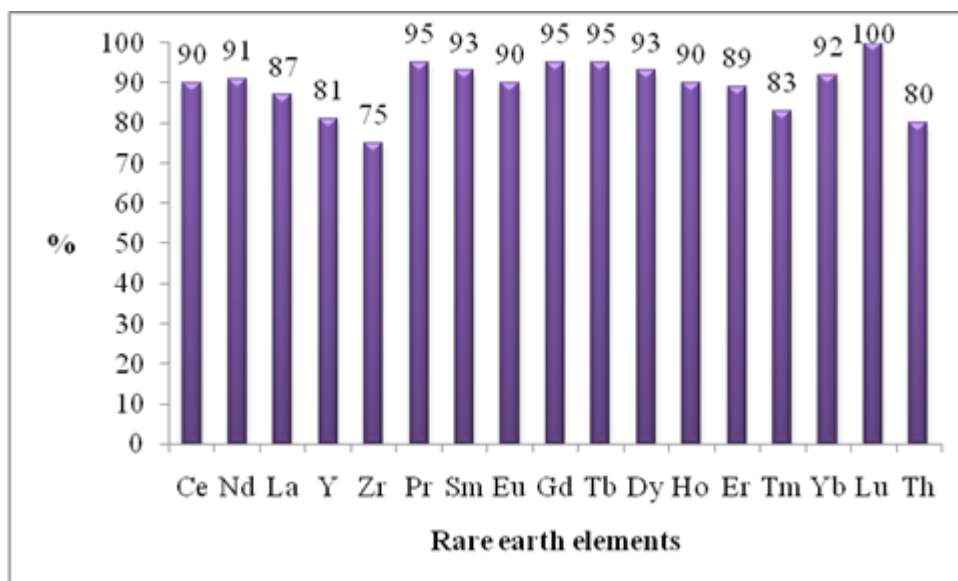


Figure 6.7: Calculated percentage of rare earth elements which was transferred from phosphogypsum to the calcite precipitate obtained at 65°C after 1 hour of reaction

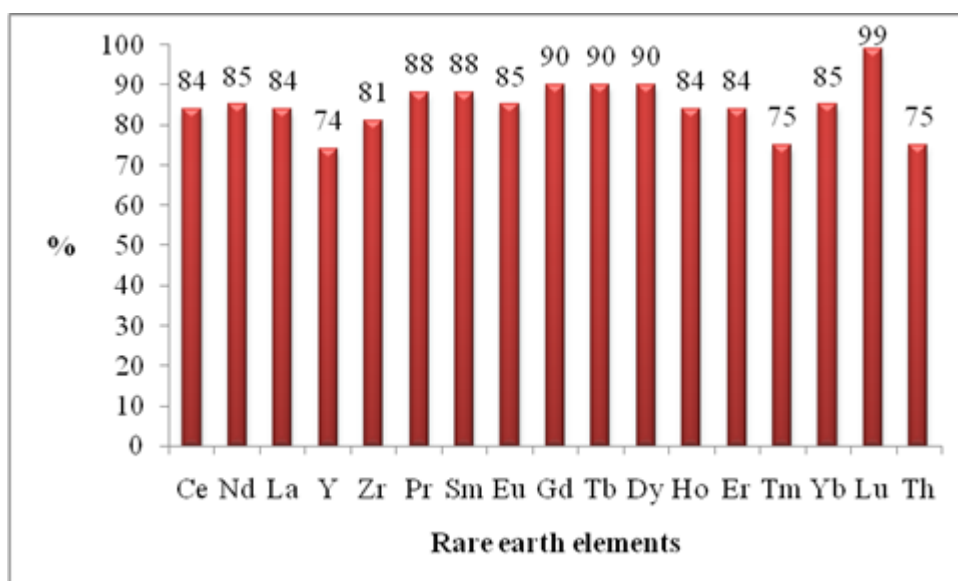


Figure 6.8: Calculated percentage of rare earth elements which was transferred from phosphogypsum to the calcite precipitate obtained at 65°C after 1 hour and 30 minutes of reaction

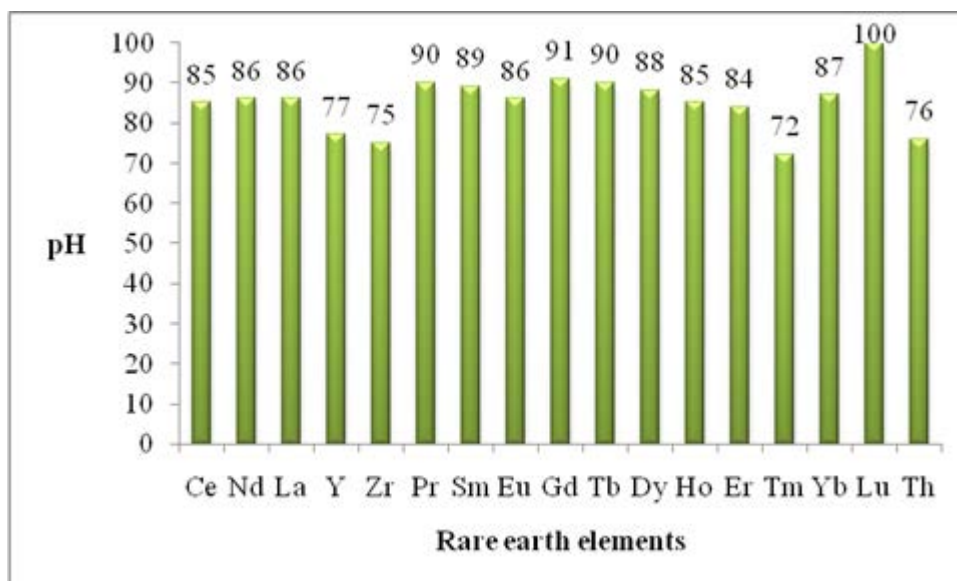


Figure 6.9: Calculated percentage of rare earth elements which was transferred from phosphogypsum to the calcite precipitate obtained at 65°C after 2 hours of reaction

6.3.3.6 Carbon and Sulphur analysis of the calcite precipitates formed at 65°C

Carbon and Sulphur analysis was performed on the calcite precipitates obtained at 65°C in order to determine the amount of carbon and sulphur they contain. The results of this analysis are summarized in Table 6.16.

Table 6.16: Carbon & Sulphur analysis of the calcite precipitates obtained at 65°C

Sample	CO ₂ (wt %)	CO ₂ (wt%) as determined by XRD	SO ₃ (wt %)
M _{65°C-1hour}	38.66	43.10 ± 0.66	1.63
M _{65°C-1hour and 30 minutes}	38.88	43.17 ± 0.59	1.40
M _{65°C-2hours}	38.40	43.97 ± 0.27	1.65

Table 6.16 shows that the amount of CO₂ as determined by XRD is greater than the amount of CO₂ as determined by the Carbon & Sulphur analysis in each sample. These results were expected due to the fact that XRD is a semi-quantitative method and each instrument is based on a different principle of analysis and therefore comes with its own limitations

6.4 Conclusion

In this chapter, attempts were made to convert phosphogypsum into calcium carbonate at different temperatures (25°C, 40°C and 65°C) using the Merseburg process.

The XRD analyses revealed that only the reaction at 65°C was effective in transforming phosphogypsum into a single polymorph of calcium carbonate (calcite). At this temperature (65°C) the time of the reaction had an impact on the size and the shape of the particles. As the time of the reaction was increased from 1 hour to 2 hours, the particles became larger in size adopting more cube and plate-like structures.

Most of the rare earth elements present in the phosphogypsum, as well as other elements (*e.g.* Al, Cr) were transferred into the calcite precipitates.

6.5 Future work

For future work, to study the influence of the time and the temperature on the morphology and the phases of the CaCO₃ precipitates formed, the following are recommended:

1. To perform the Merseburg process at 65°C by replacing (NH₄)₂CO₃ with liquid NH₃ and gaseous CO₂ at higher pressure (6 bar) to favour the dissolution of gaseous CO₂
2. To control particle size, shape and the uniformity of the size distribution of the formed CaCO₃, for instance by replacing and/or combining mechanical stirring by/with sonication, or by reducing the size of CO₂ gas bubbles used in the carbonation experiments.
3. To control the fate of the rare earth elements in the process.

6.6 References

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CHAPTER SEVEN: CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions and recommendations

This project studied the conversion of phosphogypsum into precipitated calcium carbonate using two separate mineral carbonation processes. The first process followed an indirect aqueous mineral carbonation route where an aqueous NaOH solution was initially used to chemically transform phosphogypsum into calcium hydroxide ($\text{Ca}(\text{OH})_2$), which was in turn converted into calcium carbonate (CaCO_3) using CO_2 . The second process involved the direct aqueous mineral carbonation of phosphogypsum with ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$).

In the first process, the best conversion was achieved for 5 g of phosphogypsum into 20 ml of a 2.9M NaOH solution at room temperature for 3 hours followed by 30 minutes of carbonation using a CO_2 flow rate of 285ml/min. The calcium carbonate product obtained was defined as high-grade because of its content in calcite which was close to 100%. Approximately 56% of the calcium contained in the phosphogypsum sample was converted into calcite. The calcite particles had a spherical shape with an average particle size below 8.3 μm .

In the second process, the best result was obtained with 4.3 g of phosphogypsum into 200 ml of a 0.52M $(\text{NH}_4)_2\text{CO}_3$ solution at 65°C. After as little as 1h of reaction, high-grade ($\text{CaCO}_3 > 99\%$) calcium carbonate was formed, with calcite representing nearly 100% of the formed product. The extent of conversion was 54.37%

Both processes produced calcite particles which contained most of the rare earth elements (REE) originally present in the untreated phosphogypsum sample, in spite of the washing of the products. This is a significant finding. REE are used in, for example, wind turbines, solar panels, electric cars and lithium batteries as well as light-emitting diodes (LEDs) and fluorescent materials. There is a risk that the availability of critical rare earth metals will become a significant limiting factor for competitiveness and economic growth in the future (McLellan et al., 2013). The recovery of REE from phosphogypsum (e.g. Jarosinski et al., 1993; Lokshin et al., 2004) or from phosphoric acid leaching solutions (Wang et al., 2010) has been studied by several groups. Although none of these processes are currently economically viable, it is conceivable to develop a process which, under the current and forthcoming market conditions, may become economical.

The first mineral carbonation process studied, which involves the use of NaOH, may not be suitable for large-scale development as it might be costly and NaOH cannot be regenerated. The second process, however, may be more promising. $(\text{NH}_4)_2\text{CO}_3$ could be replaced by aqueous ammonia (NH_4OH) and CO_2 , where NH_4OH could be regenerated as part of the process, and where CO_2 could originate for industrial emissions; phosphogypsum could therefore be used for the sequestration of CO_2 in addition to the synthesis of useful carbonate products. If the temperature needs to be increased to improve on the purity of CaCO_3 formed (e.g. single polymorph of calcite), it will impair the dissolution of CO_2 , which could become a rate-limiting step. This could be overcome by increasing the working pressure to a few bars since the dissolution of CO_2 improves with increasing pressure. On the other hand, improvement to the process is also required in terms of the control of particle size and shape, and the uniformity of the size distribution of the formed CaCO_3 . This could be done by replacing mechanical stirring by sonication, or by combination these two forms of solution mixing. Reducing the size of CO_2 gas bubbles entering the solution could also have a positive effect on the physical properties of the formed product.

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