A Study into the Viability of Mineral Carbonation as a means of CO_2 Sequestration in South Africa

Yogandhri Naidoo

A Research Report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in partial fulfilment of the requirements of the degree of Master of Science in Engineering

Johannesburg, 2013

Declaration

I declare that this research report is my own unaided work. It is being submitted for the degree of Master of Science to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

(Signature of candidate)

30th day of May 2013

Abstract

Long term geological storage of CO_2 is currently considered a most attractive option in the reduction of greenhouse gas emissions while continuing to utilize fossil fuels for energy production. Mineral carbonation is a long term storage option where CO_2 binds with geologic material (certain rocks minerals) to form stable environmentally benign carbonate minerals (carbonation). Rocks containing the elements calcium (Ca) and or magnesium (Mg) bound in silicate minerals are considered feasible for the process of mineral carbonation. In this study a two phase assessment of the potential for mineral carbonation as a means of CO_2 sequestration in South Africa is investigated. The desktop study investigates suitable locations of ultramafic or silicate bearing rocks in South Africa, for the purpose of mineral carbonation. Potential starting materials and reaction routes are addressed, as well as the slow kinetics of the solid –fluid mineral reaction rates. Current global projects are examined, their applicability in the South African context assessed. The investigation, though conceptual, is hoped to add value to South Africa's carbon emission mitigation strategy.

The experimental study compares the data resulting from the generation of CO_2 adsorption isotherms of a basalt and shale, to those generated from a coal and ash under similar experimental conditions. As adsorption isotherms provide information pertaining to the uptake of CO_2 by a material, and not retention, a second aim of the study attempts to determine the effect of supercritical CO_2 on mineral composition of these rocks, over a period of thirty days or so. This period of time may be insufficient for mineral carbonation to have a detectable effect; longer term samples, are anticipated in future research projects. It is hoped that this research will contribute to the advancement of mineral carbonation processes, especially in South Africa, if not globally.

Acknowledgements

My ‘blanket ‘of acknowledgment, and sincere gratitude and appreciation spreads out to envelope the following individuals, teams and establishments:

Professor Nicola Wagner, my supervisor, for her integrity in guidance and support of this work; the Coal and Carbon Research team at the University of Witwatersrand, for their unselfish and sincere assistance and support; Professor Spike McCarthy and Dr. Marion Bamford of the University of Witwatersrand School of GeoSciences, for the rock samples; Professor Dave Billing; Mr. Wilson Mogodo and Mr. Robert Richardson of the University of Witwatersrand School of Chemistry for their kind assistance with the XRD work; Mr. Gregory Onkolo of the University of Potchefstroom for his extended efforts with the BET analyses, Dr. Frederic Doucet of CGS for the integrity and kindness of both his literature and other knowledgeable contributions; Mr. David Long and especially Ms Corlien Cloete of CGS, and Ms. Frances O’ Neil of UIS for the XRF analyses.

A sincere thank you to SANEDI for the year of funding provided for this project.

To the selfless efforts of dear friends, I am ever grateful, for helping to ‘bring it all together’. To my loving Mum and siblings, for always being there. To my husband, no words can describe enough, the tireless and immense love, warmth and support- always my beam, my rock.

For Dad, whom I know, is always a guiding spirit, and; the all-encompassing Divine, for affirming time, place and above all, reason for everything and, the faith, that all will come to pass, as is meant to be.

Table of Contents

Nomenclature

List of Units

Bcf	Billion Cubic Feet
Gt	Giga Tonne
kg/m^3	Kilogram per Metre Cubed
M	Mole
Ma	Million Years
m^2/g	Metres Squared per Gram
Mt	Million Tonne
Mt/a	Million tonnes per annum
MW	Mega Watts
t	Tonne
wt%	Weight Percent

List of Symbols

℃	Degrees Celsius
Al_2O_3	Aluminium Oxide
NH_3	Ammonia
Ca	Calcium

CaO	Calcium Oxide
CH_4	Methane
CO_2	Carbon Dioxide
CO_3	Carbonate
Fe	Iron
FeO	Iron Oxide
H_2O_2	Hydrogen Peroxide
Mg	Magnesium
MgO	Magnesium Oxide
N_2	Nitrogen
O_2	Oxygen
pCO_2	Partial Pressure of Carbon dioxide
S	Sulfur
SiO_2	Silica
SO_2	Sulfur Dioxide
TiO_2	Titanium Oxide

List of Abbreviations

ARC	Albany Research Centre
BET	Brunauer-Emmett-Teller
CCS	Carbon Capture & Storage

CCT	Carbon Capture Technologies
CDM	Clean Development Mechanism
COP17	Conference of Parties No.17 held in Copenhagen
ECBM	Enhanced Coalbed Methane Recovery
EOR	Enhanced Oil & Gas Recovery
EU	European Union
FBC	Fluidised-Bed Combustion
FDG	Flue Gas Desulfurisation
IGCC	Integrated Gasification Combined Cycle
JCOP	Japan CO_2 Geosequestration of Coal Seams Project
KZN	Kwa Zulu Natal
LNG	Liquefied Natural Gas
NIST	National Instruments Standard
NOx	Oxides of Nitrogen
PGE	Platinum Group Elements
PGM	Platinum Group Metals
PXRD	Powder X-Ray Diffraction
RECOPOL	Reduction of CO_2 emissions by means of CO_2 storage
SACCCS	South African Centre for Carbon Capture & Storage
SANERI	South African Natural Energy Research Institute
SANERI	South African National Energy Research Institute
SB	Subcritical
SP	Supercritical

SCPSS	Supercritical Pulverised Coal Combustion
SEM EDS	Scanning Electron Microscope-dispersive Spectrometer
TCM	Technology Centre Mongstad
UCG	Underground Coal Gasification
VAS	Volumetric Adsorption System
WITS	University of the Witwatersrand
XRF	X-Ray Fluorescence

Chapter 1 Introduction

This chapter encompasses the background and motivation for the research. It discusses the aims, objectives, scope and hypothesis of the project as well as the report structure.

Global warming and its impact on climate change, whether regarded as theory or fact, are aspects of our life on earth that cannot be ignored. Vehement differences in opinion are held by both the sceptics who feel that it is the result of a natural climatic adjustment, and those proponents who hold the premise that industrial growth coupled with non-structured methods has created a situation where our planet is getting progressively hotter (Global Warming., 2011).

In South Africa, coal has always been, and will continue to be, the most significant energy source used to meet the country’s energy requirements to maintain and increase the level of comfort we have grown accustomed to. This indigenous resource is expected to remain as the country’s primary source of fuel to meet its increasing energy demand for the foreseeable future, making it a very ‘emissions intensive’ economy.

Generating 93% of its electricity from coal combustion (Surridge and Cloete., 2009), the environmental impact caused by coal fired processes in South Africa is enormous. Nitrogen (N) and sulfur (S) impurities in the coal are released into the air as nitrous oxide and sulfur dioxide causing problems such as acid rain and smog. Inorganic mineral matter, which does not combust, is also released into the atmosphere as particulate matter resulting in respiratory health diseases. The emission of carbon dioxide (CO_2) however, is of particular concern because of its implication in global warming. While CO_2 accounts for only 20% of the natural greenhouse effect, second to water vapour, it is thought to be responsible for 60% of the anthropogenic greenhouse gas effect that is causing the perceived crisis of the current global warming (Allianz Knowledge Partnersite., 2011).

Combustion of fossil fuels, especially coal, for electricity generation, transportation, and heating, and also the manufacture of cement, all result in the total worldwide emission of about 22 billion tons of CO_2 to the atmosphere each year (New Mexico Solar Energy Association., 2011).

South Africa generates about 420 million tonnes (Mt) of CO_2 per annum (Surridge and Cloete., 2009). This contributes to about 1% of global emissions (DME., 2009) making it one of the world's most 'emissions intensive' economies, listed within the top 20 greenhouse gas emitting countries globally (Sealthedeal., 2009) as shown in Figure 1.

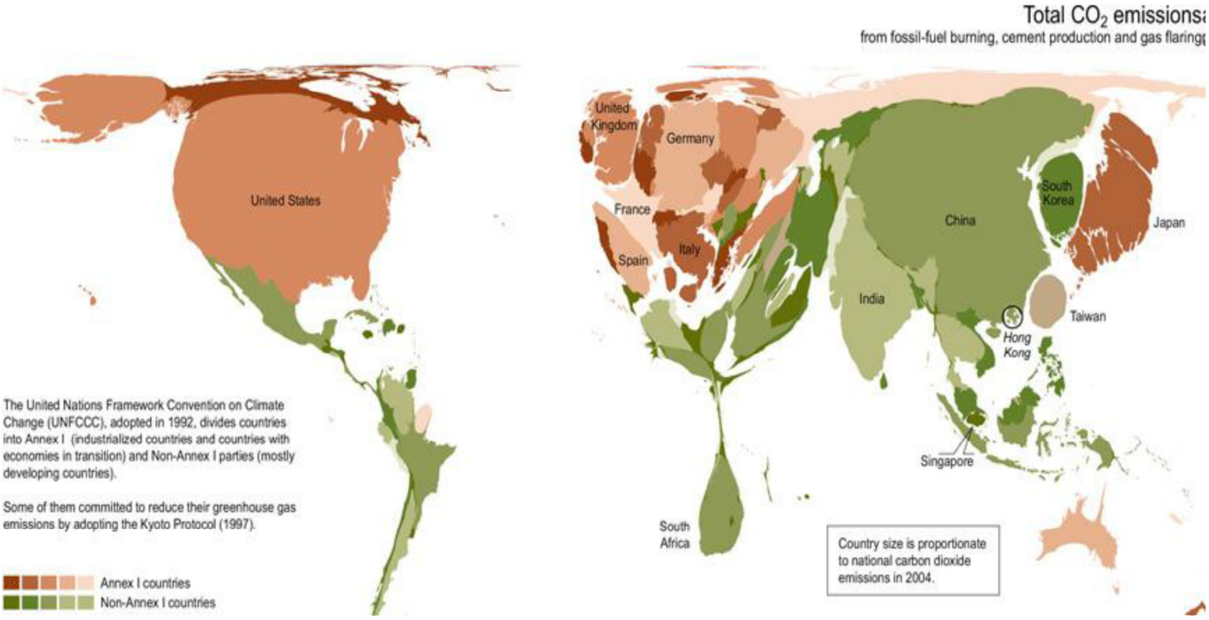


Figure 1: South Africa's Position as a Global CO_2 Emitter (Sealthedeal., 2009)

This does have serious implications for the future, however. Regardless of whether global warming and climate change are considered from a political, economic, or purely environmental consciousness standpoint, there is little doubt that the country could face intense financial and social penalties in the future, should it not adopt lower-carbon intensive energy measures (Naidoo., 2009).

1.1 Background and Motivation for Research

Efforts are under way in South Africa to adopt more conscious carbon mitigation endeavours to develop effective measures for reducing the country's CO_2 emissions. At the South African Climate Change Summit held during March 2009, it was announced that South Africa will increase its CO_2 emissions until 2020–2025, plateau for 10 years, and thereafter decrease emissions in real terms (Surridge and Cloete., 2011). Notwithstanding its increasing energy demand, South Africa has agreed as a non-Annex 1 country, to the Kyoto Protocol's global requirements, to reduce CO_2 emissions, provided international aid was made available for the implementation of such mitigation measures. South Africa's participation is primarily through the implementation of Clean Development Mechanisms (CDMs) (Engelbrecht *et al*., 2004; Viljoen *et al*., 2010).

Clean-coal technologies, such as post- combustion pollutant capture and carbon capture and storage (CCS), are being investigated, developed, and employed to mitigate the environmental impact of greenhouse gases and other air pollutants emitted during coal combustion.

The South African Centre for Carbon Capture and Storage (SACCCS) was established on 30 March 2009, under the auspices of the South African National Energy Development Institute (SANEDI), (previously, the South African National Energy Research Institute (SANERI)), and demonstrates the commitment to CO_2 mitigation in South Africa. In the recently concluded COP 17 in Durban (December 2011), CCS was officially added as a CDM project and no doubt is set to see a lot more focus in future CO_2 mitigation projects.

In September 2010, SANEDI launched the Atlas for Geological Carbon Storage in South Africa. The Atlas indicates that there is limited conventional on-shore CO_2 storage capacity (less than 2% of a total geological storage capacity of about 150 000 Mt); hence unconventional storage techniques need to be explored. These include mineral trapping or mineral carbonation, ocean storage and biomass storage.

Mineral carbonation has however, in recent years been growing in favour as a suitable unconventional stable, long-term storage mechanism for CO_2 storage. The consideration of mineral carbonation in South Africa forms the basis of this research work. Globally this sequestration option is being considered as an important part of the climate change portfolio. Attention has focused on olivine, serpentine, steel slag, and fly ash, as the main constituents in the process.

1.2 Research Aims and Objectives

1.2.1 Aim

The aim of this research project is to investigate the viability of mineral carbonation as a means of carbon sequestration in South African rocks. The investigation includes a desktop study as well as an experimental aspect to test methodologies and procedures for the sorption of CO_2 on two common indigenous rock types, namely: basalt and shale.

1.2.2 Objectives and Scope of Report

The objectives of the project are made up of two phases, namely:

i) Desktop study: A study investigating the feasibility of mineral carbonation as an option for CO_2 sequestration in South Africa. The desktop study includes an investigation of suitable locations of ultramafic or basalt host/reservoir rocks globally and in SA. Potential starting materials and reaction routes in mineral carbonation are addressed, as well as the slow kinetics of the solid–fluid mineral reaction rates. Current global projects are examined and their applicability in the South African context assessed. The study is linked to the Carbon Capture and Storage Atlas of South Africa (Cloete., 2010).

ii) Laboratory setup and equipment: The objective is to address the experimental equipment, methodologies, techniques and processes for studies on mineral carbonation, based at in the Coal and Carbon Laboratory at the University of the

Witwatersrand (Wits). The investigations at this laboratory, until recently, have been coal based.

This is the first investigation into the effect CO_2 on rocks other than coal and fly ash, using equipment available at Wits. An igneous alkaline-rich rock sample (basalt) and a sedimentary rock (shale) were tested over a period of about thirty days in a reactor to investigate the effect of supercritical CO_2 on the mineral composition, with respect to mineral carbonation. Apart from this, sorption isotherms for both rock types were investigated using a volumetric adsorption system and compared to those generated for coal and ash samples under similar experimental conditions.

It is recognized that adsorption is a physical process and its isotherms provide information pertaining to the uptake of CO_2 by a material, but not the retention. It is also appreciated mineral carbonation is a chemical bonding process and that four weeks is unlikely to be long enough to show any visible reactions using supercritical CO_2.

However the two experiments should lead to an enhanced understanding of the techniques and processes required for future studies in the field of mineral carbonation, and satisfy the following subjectives:

i) To investigate how to react the naturally occurring silicate minerals in selected rocks types found in South Africa with CO_2 to form stable carbonates.

ii) To investigate a relationship between fixation of CO_2 in relation to compositional change in the rock samples (if any are observable).

iii) To investigate the effects of pressure on the kinetic rate of observable mineral fluid reactions.

iv) To compare the sorption isotherms of the rock samples to data generated for a South African coal and ash, which have been subjected to similar experimental conditions.

v) To determine suitable analytical techniques for determining mineral carbonation.

vi) To optimize systems to determine mineral carbonation.

It is hoped that this research will contribute to the advancement of mineral carbonation globally and specially in South Africa.

1.3 Hypothesis

Mineral Carbonation using suitable indigenous rock types shows long term promise as a viable option for CO_2 sequestration in South Africa.

1.4 Research Questions

i) Are indigenous silicate and sedimentary rocks suitable for mineral carbonation?

ii) Is there a relationship between compositional change in the rock samples and CO_2 fixation?

iii) Does pressure have an effect on the kinetic rate of mineral flow reactions?

iv) How do the rock sorption isotherms compare with that of a coal and ash exposed to similar experimental conditions?

v) How can the equipment, experimental methodologies, analytical techniques and processes for studies on mineral carbonation, based at Wits, be determined and optimised?

1.5 Report Structure

The structure of the further chapters making up this research report is given below:

Chapter 2: Literature review, and presents an overview of Coal Technologies, in particular CCS options.

Chapter 3: Desktop Study of the investigation into Mineral Carbonation globally, as well as its potential in South Africa.

Chapter 4: Account of the sample preparation, characterization laboratory setup and methodologies undertaken in the CO_2 sorption experiments on the basalt and shale.

Chapter 5: Results obtained from the CO_2 sorption experiments and discussion thereof.

Chapter 6: Conclusions of the study, and recommendations for further research in the field of mineral carbonation.

Chapter 7: Reference list

Chapter 2 Clean Coal Mechanisms

The following chapter gives a literature review and an overview of various clean coal technologies, with a focus on CCS, in particular. Various trapping mechanisms and capture techniques are described as well as initiatives in South Africa are explored.

2.1 Clean Coal Technologies Overview

Efficient coal use is currently the primary means of reducing coal's harmful emission impacts. A collection of environmental control technologies are now available to improve the environmental performance of coal-fired power stations and to mitigate many of the environmental impacts.

A key strategy is to improve the energy efficiency of power plants. Efficient plants burn less coal per unit of energy produced, and consequently has lower associated environmental impacts (Philibert *et al.*, 2005). Traditional coal-fired plants suffer from two major drawbacks: overall efficiency levels are low (between 33% and 38%) (Engelbrecht *et al.*, 2008), and pollution levels are high. Efficiency improvements, particularly those related to combustion technologies, are an active area of research and an important component of a climate change mitigation strategy. A range of interventions, known as clean- coal technologies (CCT), are being developed, and, in certain instances, have already been employed in this effort. Some examples are outlined below.

- Flue gas desulfurisation (FDG) units can remove 90% of the SO_2 (sulfur dioxide). In South Africa, Eskom's Kusile plant will be the first power station in the country to have flue gas desulfurisation installed.

- Many oxides of nitrogen (NOx) reduction technologies are employed at commercial plants: low-NOx burners, water injection technology, post combustion selective catalytic reduction and selective non catalytic reduction techniques, all of which significantly reduce NOx emissions.

- Advanced combustion technologies include:

- Fluidised-Bed Combustion (FBC) which reduces emissions of sulfur dioxide (SO_2) and NOx by the controlled combustion of crushed coal in a bed fluidised with jets of air. Engelbrecht *et al.* (2008) reported gasification efficiencies in the order of 55%-75% and carbon efficiencies in the order of 65%-85% with FBC. The Komati power station is seeing a feasibility study into the implementation of FBC, using coal discards, as a means of reducing water pollution.

- Integrated Gasification Combined Cycle (IGCC) systems involve gasification of coal, usually by high temperature reaction with oxygen, cleaning the gas produced, and combusting it in a gas turbine to produce electricity. IGCC can produce efficiencies in the order of 45%-55% and lower emissions than conventional power stations (Engelbrecht *et al.*, 2008). An Eskom study is underway, into the possibility of a 2100 MW IGCC power station at the Majuba coalfields in Mpumalanga (Climate Change and Carbon Management blog., 2008).

- Supercritical pulverised coal combustion (SCPCC) plants work with the supercritical phase of water. The steam temperature can be raised to levels as high as 580 to 600°C and pressure over 300 bar. Under these conditions, boiling does not occur and, there is no phase transition from water to steam, only a gradual decrease in density. This supercritical water can dissolve a variety of organic compounds and gases, and when hydrogen per-oxide (H_2O_2) and liquid oxygen (O_2) are added, combustion is triggered. The supercritical turbines can burn low grade fossil fuels and can bring NOx emissions to near zero, and keep emissions of SO_2 to a minimum. Efficiencies are in the order of about 45%-47% (Engelbrecht *et al.*, 2008). Both Medupi and Kusile powerplants have been built to supercritical standards.

- Underground coal gasification (UCG) is a process whereby coal is pyrolised *in situ*. This relatively under applied technology is being used to exploit coal seams that are otherwise impossible to mine as produced, and combusting the gas produced in a gas turbine to produce electricity. It can also be combined with carbon capture and storage (CCS) processes where the CO_2 formed from the gasification is trapped after the coal is burnt, in the pores of the surrounding rocks, any including unburnt coal. In South Africa, Eskom's UCG pilot plant, launched in 2007, is notably, Africa's first application into UCG technology. It produced its first electricity from UCG in October 2010 through co-firing at the Majuba power plant. Sasol is conducting a preliminary feasibility study into UCG, although no pilot studies are underway yet.

- Oxy-coal combustion is a process whereby coal is burned in O_2 rather than in air. The N_2 is first extracted from the air using standard industrial equipment, so that the coal can be combusted in an atmosphere of O_2 and recycled flue gases. The result is a flue-gas stream containing almost none of the N_2 that otherwise complicates the separation of CO_2. Once the sulfur has been scrubbed using standard procedures, the flue gases consist essentially of just water vapour and CO_2. The water is separated by condensation (IEEE., 2008).

This technique is still considered developmental, in part because temperatures of pure O_2 combustion (about 3500°C) are far too high for typical power plant materials (IPPC., 2005). There are a limited number of commercial scale oxy-combustion technologies that are currently being researched around the world. Economically speaking, this method costs more than a traditional air-fired plant. The main problem has been separating O_2 from the air. This process needs lots of energy, nearly 15% of production by a coal-fired power station can be consumed for this process (SCCS). Examples of large scale pilot plants are described under Oxy-fuel Combustion Capture.

- Post combustion capture involves removing the dilute CO_2 from flue gases after hydrocarbon combustion. It is typically retrofitted into existing industrial plants and power stations without significant modifications to the original plant. There are several methods that can be used to capture the CO_2. The most common method is passing the CO_2 through a solvent and adsorbing it and amine solvents are typically used. A change in temperature and/or pressure will then release the CO_2. Another process in development is calcium (Ca) cycle capture where quicklime is used to capture the CO_2 to produce limestone, which can then be heated to drive off the CO_2 and quicklime which can then be recycled (SCCS). It is limited to large scale operating experience. This CCT has been implemented by Sasol, in South Africa. A steady stream of about 94% pure CO_2 has been captured, however a storage site is yet to be found. The Medupi and Kusile, power plants in South Africa are sub-critical in that about 12% CO_2 remain in flue gases and require capture. Sasol is involved in several experimental projects in Norway, where research into suitable capture sorbents are underway. These are discussed later in Section 2.2.

- The principals of Carbon capture and storage (CCS) have been employed over the past sixty years on a relatively small scale by the oil, gas, and chemical industries. While technically sound, none of today's commercial CO_2 capture technologies were developed for large power plants, and scaling up this technology is expensive and energy intensive (Philibert *et al.*, 2005). The SACCCS aims to implement a pilot storage project by 2017, and a fully integrated CCS demonstration plant by 2020 and highlights a government decision that all new coal power stations be CCS ready (IISD Reporting Services., 2009).

Carbon capture and storage is discussed in greater detail below.

2.2 Carbon Capture and Storage (CCS)

2.2.1 Definition

CCS involves the physical capture of CO_2 produced through coal conversion from fossil fuel combustion, and the storage of this CO_2 in such ways that it does not enter the atmosphere (IPCC., 2005).

2.2.2 Forms/Types of Storage

CO_2 storage takes three forms, namely: geological, ocean, and mineral storage.

Figure 2 illustrates the three forms of CO_2 storage, and the various storage sites as described above.

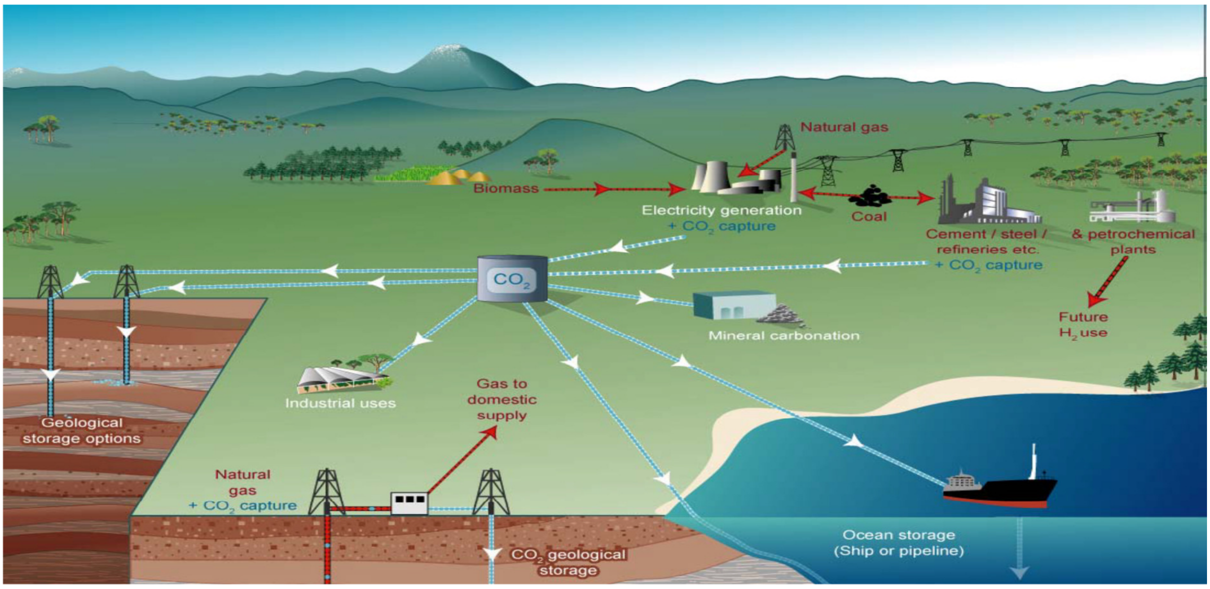


Figure 2: CO_2 Sequestration Systems, Sources and Storage Options (IPCC., 2005)

2.2.3 Geological Storage

Geological storage, or geo sequestration, is storage whereby the CO_2 is injected into and stored in suitable deep-seated porous rock strata, typically >1000m where the temperature and pressure are above critical point for CO_2 (31ºC, 7.38MPa) (Bachu., 2000). Storage may be either on land or under the seabed. In both terrains the typical storage sites are:

- saline formations
- depleted oil and gas fields
- enhanced oil and/gas recovery (EOR)
- enhanced coalbed methane recovery (ECBM)
- unmineable coal seams.

Other geological media that could provide niche options for geological storage of CO_2 are:

- basalts
- oil /gas rich shales
- salt caverns
- abandoned mines (IPCC., 2005).

Figure 3 illustrates the typical geological storage types listed above. Note: terrestrial sequestration as shown is the biological, naturally occurring CO_2 storage.

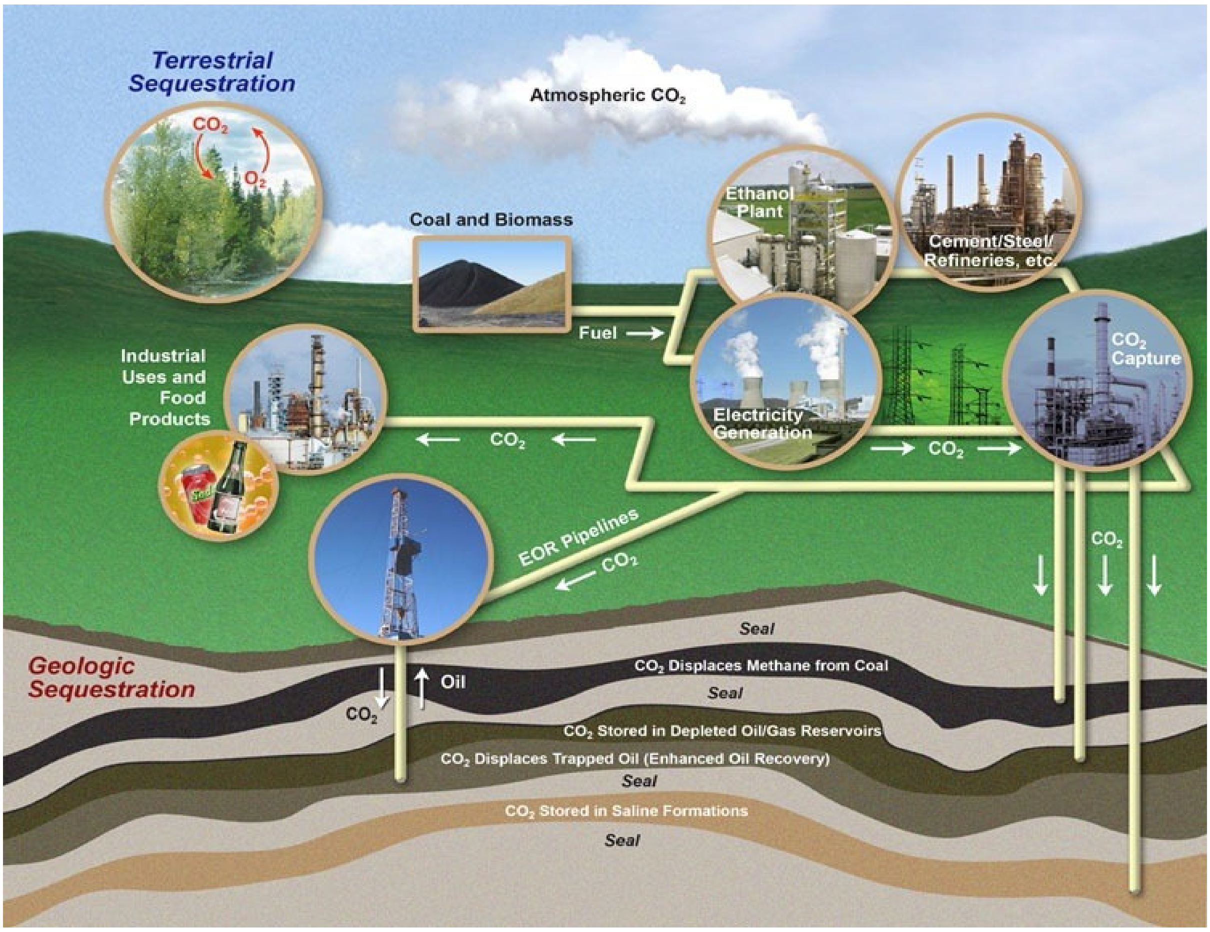


Figure 3: Schematic of CO_2 Geological Sequestration Options (Bailey and Cashman., 2010)

2.2.4 Global Analogues of Geological Storage

- The best available example of a saline formation storage project is the Sleipner West Field off Norway. It is the world's first CCS plant and has been operational since October 1996 (IISD Reporting Services., 2009). Carbon dioxide is separated off-shore from natural gas produced at a gas field in the North-Sea and is pumped into an underground aquifer below the sea bottom, at a lesser depth than the gas field.

- Weyburn-Midale is an enhanced oil recovery (EOR) operation in Canada. This project captures CO_2 from a coal gasification plant located in North Dakota, USA, transports it via a 320km pipeline across the border into Canada where it is injected into the Weyburn and Midale depleting oil fields. Since October 2000 over 20 M/t has been stored in these fields (Global CCS Institute). Perkins *et al.* (2005) estimate that over 5000 years, all the CO_2 injected into the Weyburn Oil Field will dissolve or be converted to carbonate (CO_3) minerals within the storage formation. Equally importantly, they show that the caprock and overlying rock formations have an even greater capacity for mineralization, first by adsorption. This is significant for leakage risk assessments because once CO_2 is dissolved it is unavailable for leakage as a discrete phase (IPCC., 2005).

- The In Salah onshore gas field in Algeria is the world's first large scale CO_2 storage project in a gas reservoir (Riddiford *et al.*, 2003). Since becoming operational in 2004, about 1Mt/a of CO_2 has been captured during natural gas extraction and re-injected into the Krechba geologic formation at a depth of 1,800m (Global CCS Institute., 2011).

- Snøhvit, in Norway, is an offshore gas field with CO_2 injection. The liquefied natural gas (LNG) plant is located onshore on Norway's coast. Carbon dioxide is separated from produced gas and injected in a saline aquifer below the hydrocarbon reservoir zones offshore. Since April 2008, 0.7 Mt/a CO_2 and has been captured injected into the Tubåen sandstone formation 2,600m under the seabed (Global CCS Institute., 2011).

- A CO_2-enhanced coal bed methane (ECBM) recovery demonstration project is located in the Allison field in the northern San Juan Basin of New Mexico, USA (Reeves, 2003). This pilot ECBM recovery operations commenced in April 1995. The CO_2 was sourced from the McElmo Dome in Colorado and delivered to the site through a CO_2 pipeline. A total of 181 million m^3 (6.4 Bcf) of natural CO_2 was injected into the reservoir over six years, of which 45 million m^3 (1.6 Bcf) is forecast to be ultimately produced back, resulting in a net storage volume of 277,000 t CO_2. The wells were completed in the Fruitland coal, which is capped by shale. This study provides evidence of significant coal-permeability reduction with CO_2 injection. The injection of CO_2 at the Allison Unit has resulted in an increase in methane (CH_4) recovery from an estimated 77% of original gas in place to 95% of the original gas in place within the project area. The recovery of CH_4 was in a proportion of approximately one volume of CH_4 for every three volumes of CO_2 injected (Reeves *et al.*, 2004).

- Small-scale injection projects to test CO_2 storage in coal have been carried out in Europe. RECOPOL (Reduction of CO_2 emission by means of CO_2 storage in coal seams in the Silesian Coal Basin of Poland) is a European Union (EU) funded combined research and demonstration project investigating the possibility of permanent storage of CO_2 in coal. At a selected location in Poland a pilot installation was developed for CH_4 gas production from coal beds while simultaneously storing CO_2 in the underground coal seams at depths of 1050-1090m. Injection and production took place in 2004. The produced CH_4 could become an alternative fuel that can be locally produced in Silesia. This installation is the very first of its kind in Europe, and at the moment the only one operational worldwide (RECOPOL). A similar project in Japan, called the Japan CO_2 Geosequestration in Coal Seams Project (JCOP) began in 2002 to sequester CO_2 in the Yubari coal seam of the Ishikari Field (Fujioka *et al.*, 2010).

2.2.5 Trapping Mechanisms

For all the geological storage sites, physical/structural and geochemical trapping mechanisms would prevent the CO_2 from escaping into the atmosphere. These are briefly described below.

Geological storage of CO_2 is dependent on a number of physical and geochemical trapping mechanisms and or combinations thereof (Figure 4). The most effective storage sites are those where CO_2 is immobile because it is trapped permanently under a thick, low-permeability seal or is converted to solid minerals or is adsorbed on the surfaces of coal micropores or through a combination of physical and chemical trapping mechanisms (IPCC., 2005).

1. Structural or Stratigraphic Trapping: this involves physical traps at depths greater than 800m. The free phase/immiscible CO_2 is trapped at the top of an anticline, or in a tilted fault block. It is kept from further upward movement by the seal/caprock.

There are a variety of geometrical arrangements of reservoir rock/sealing rock pairs as shown in Figure 4.

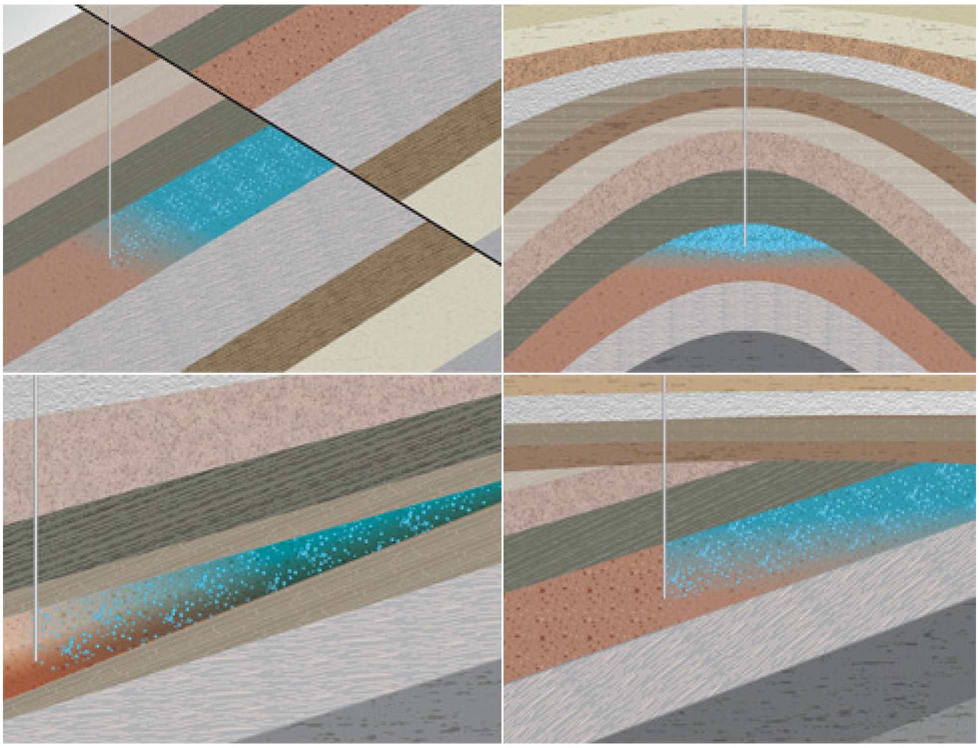


Figure 4: Schematic of Structural/Stratigraphic Trapping Mechanisms showing clockwise from top left: fault trapping; anticline or stratigraphic trapping; facies change trapping; and unconformity trapping (CO_2CRC., 2012)

If the geometry of the subsurface does not contain faults or folds, the trapping is stratigraphical. Sometimes a change in rock type within the storage layer will create a closed stratigraphical trap.

When CO_2 is injected, it is not dissolved in formation water. It is said to be free-phase or immiscible. As it is supercritical, it is less dense than the formation water and so it rises upwards. Small bumps in the seal will behave like anticlines and trap the CO_2 until it spills out and continues migrating through the reservoir rock (CO_2 CRC., 2012).

The CO_2 will remain trapped by the seal unless the height of the layer of CO_2 creates a capillary pressure that would enable it to enter the seal. Scientists calculate this height based on the pore radius of the sealing rock and the relative densities and surface tensions of CO_2 and water to determine the safe rate of injection into the reservoir.

Where the reservoir has closed structural trapping, it is likely that much of the CO_2 remains in supercritical, free-phase state in the storage reservoir, while the rest is trapped by other mechanisms described below.

2. Hydrodynamic Trapping: occurs in saline formations that do not have a closed trap (Figure 5). The formations generally have low flow velocities (of the order of cm/year) (IPCC., 2005). CO_2 that remains free-phase migrates upwards through permeable pathways in the rock. As it is less viscous than the formation waters, CO_2 moves by a process called viscous fingering (Saffman., 1986; Weitz *et al.,* 1987). Some CO_2 is dissolved in the formation water, as in the dissolution mechanism described below. The dissolved CO_2 migrates with the formation water. The relationship between the dissolved CO_2 and the free-phase CO_2 determines how far the CO_2 will migrate before all of the CO_2 is eventually trapped residually or in solution.

Factors that have a substantial influence on the length of the migration pathway include: stratigraphic heterogeneities (e.g. siltstones, shales and coals in the reservoir rock), geochemical reactions as well as temperature (Bachu *et al.*, 1994).

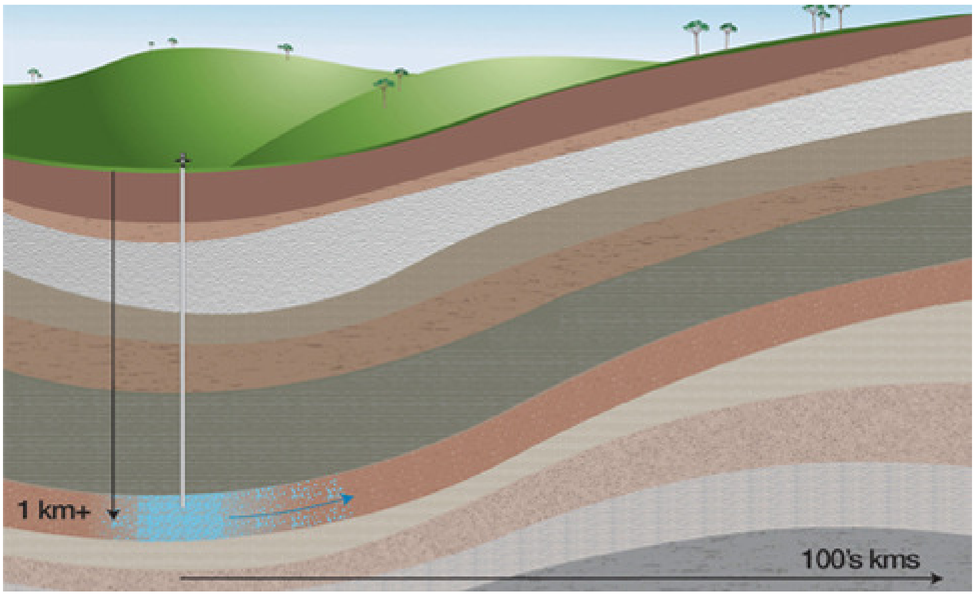


Figure 5: Schematic of Hydrodynamic Trapping Mechanism (CO_2CRC., 2012)

3. Residual Trapping: When free-phase CO_2 migrates, it forms a plume. At the back end of this plume, the concentration of the CO_2 falls below a certain level. It becomes trapped by capillary pressure from the water in the pore spaces of the rock and ceases to flow (Figure 6). This residually trapped CO_2 can dissolve into the formation water over time.

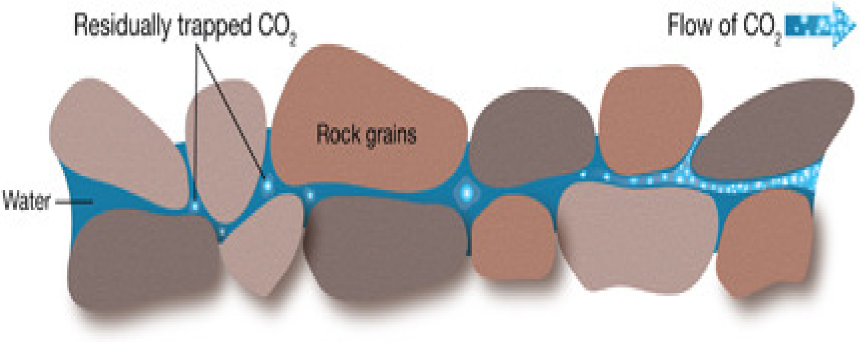


Figure 6: Schematic showing the Mechanism of Residual Trapping (CO_2CRC., 2012)

4. Solubility/Dissolution Trapping: Trapping occurs by a process of diffusion, dispersion and convection (Viljoen *et al.,* 2010). The solubility of CO_2 in the formation water increases with increasing pressure, and decreases with increasing temperature and increasing water salinity.

As some CO_2 dissolves in water, the water becomes denser, and begins to sink. This allows the CO_2 to become more dispersed in the water, and over time, the amount of CO_2 dissolved in the water can increase. If the reservoir formation is thin, the extent to which mixing occurs through a convective flow is limited.

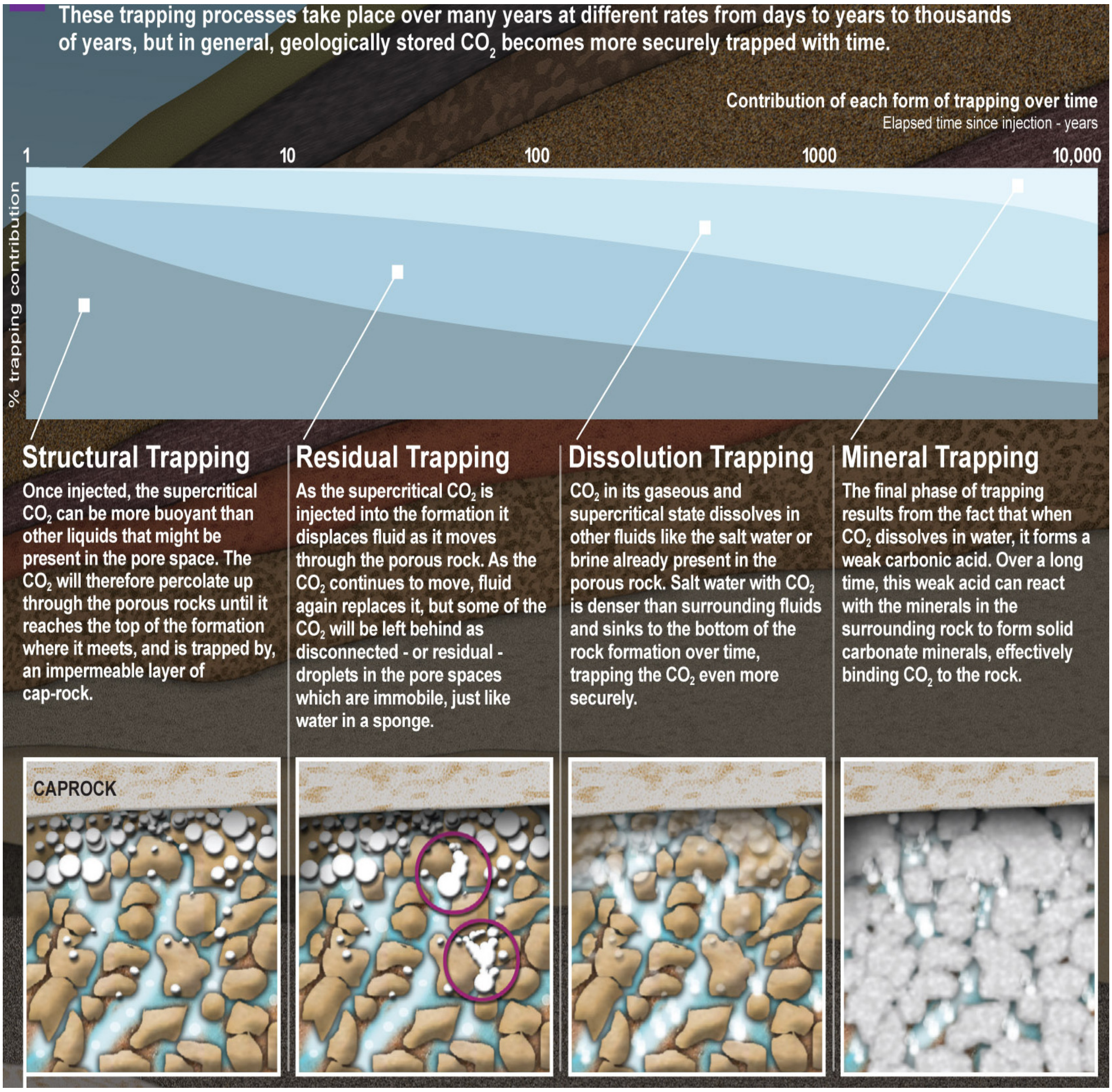
The dissolved CO_2 ceases to exist as a separate phase, eliminating the buoyant forces that propel it upwards (IPPC., 2005). It forms weak carbonic acid by dissolution in the water as shown in the following equation:

$CO_2 + H_2O <-> H_2CO_3+ = H^+ < -> CO_3^+ + 2H^+$ (1)

This is known as solubility trapping. This trapping dominates from tens to hundreds of years (IPCC., 2005). The dissolved CO_2 can eventually react with reservoir minerals if an appropriate mineralogy is encountered to form carbon-bearing ionic species– called ionic trapping. The dissolution of the rock and accompanied rise in pH, dominates from hundreds to thousands of years (IPCC., 2005).

5. Mineral Trapping: Following solution trapping and further dissolution of the rock, some fraction may be converted to stable carbonate minerals. This is a chemical bonding process which known as mineral trapping and forms the basis for the process of mineral carbonation which is the most permanent form of geological storage. This stage dominates over thousands to millions of years (IPCC., 2005). The potential for reaction to form these minerals depends on the composition of the reservoir rock, the temperature and pressure of the rock, the chemical composition of the water, the water/rock contact area and the rate of fluid flow through the rock (Viljoen *et al.,* 2010). Mineral Carbonation, the basis of this research project is discussed in greater detail in Chapter 3.

Figure 7 shows schematically the sequence or flow process of each of the trapping mechanisms described above on a time scale.



These trapping processes take place over many years at different rates from days to years to thousands of years, but in general, geologically stored CO_2 becomes more securely trapped with time.

Structural Trapping

Once injected, the supercritical CO_2 can be more buoyant than other liquids that might be present in the pore space. The CO_2 will therefore percolate up through the porous rocks until it reaches the top of the formation where it meets, and is trapped by, an impermeable layer of cap-rock.

Residual Trapping

As the supercritical CO_2 is injected into the formation it displaces fluid as it moves through the porous rock. As the CO_2 continues to move, fluid again replaces it, but some of the CO_2 will be left behind as disconnected - or residual - droplets in the pore spaces which are immobile, just like water in a sponge.

Dissolution Trapping

CO_2 in its gaseous and supercritical state dissolves in other fluids like the salt water or brine already present in the porous rock. Salt water with CO_2 is denser than surrounding fluids and sinks to the bottom of the rock formation over time, trapping the CO_2 even more securely.

Mineral Trapping

The final phase of trapping results from the fact that when CO_2 dissolves in water, it forms a weak carbonic acid. Over a long time, this weak acid can react with the minerals in the surrounding rock to form solid carbonate minerals, effectively binding CO_2 to the rock.

Figure 7: Visual Explanation of the various CO_2 Trapping Mechanisms with Time (CO_2 Capture Project, 2009)

6. Adsorption Trapping: This trapping mechanism is a purely physical process and involves the sorption of CO_2 onto a solid substrate which in the present study could be the surface of either coal, organic rich shale or other appropriate rock type. Adsorption relies on the affinity of CO_2 molecules (represented in Figure 8 as blue spheres) to the surface of the substrate under certain conditions without forming a chemical bond (CO_2 Capture Project., 2009). Adsorbents can separate CO_2 from a

stream by preferentially attracting it to the material surface at high pressures through weak interactions such as van der Waals forces (GCEP., 2005).

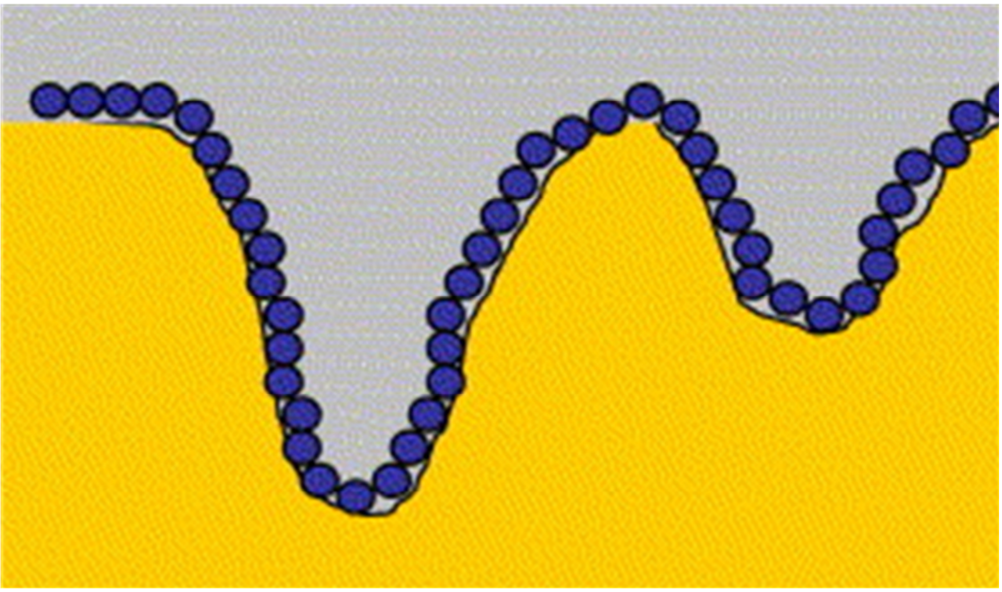


Figure 8: Principle of Adsorption (adapted from Tuan Ho and Hutmacher. (2006))

Carbon dioxide is preferentially adsorbed onto coal or organic-rich shales. This has been observed in batch and column experiments in the laboratory, as well as in field experiments at the Fenn Big Valley, Canada and the ECBM project in the San Juan Basin, USA, where the CH_4 which has a lower affinity to coal than CO_2 does, and is made free in the process. Adsorption eventually leads to absorption, and the CO_2 eventually diffuses or dissolves into the coal (IPCC., 2005).

Chapter 4, the experimental section of this research report, discusses the process of adsorption further, while Chapter 5 investigates the adsorption potential of CO_2 on shale and basalt.

2.2.6 Ocean Storage

Ocean storage involves four principle concepts whereby the CO_2 is:

- reacted with a carbonate mineral on or close to the ocean floor to form bicarbonates;

- dissolved in seawater at depths of 1000m -3000m-dissolution type storage;

- injected at depths greater than 3000m below sea level where the CO_2 liquefies with the high pressure. It becomes denser than seawater and sinks to the sea floor, where it is expected to remain for millennia-lake type storage; and

- storage in crystalline water based solids (clathrate hydrates), already existing on the ocean floor.

Figure 9 below illustrates the forms that ocean storage takes.

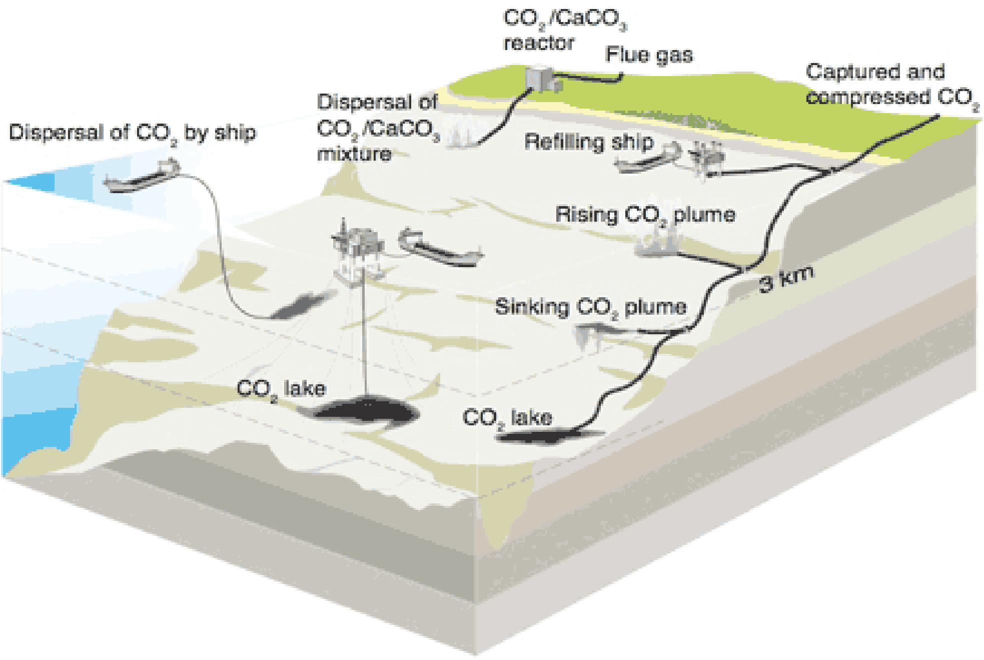


Figure 9: Forms of Ocean Storage (IPCC, 2005)

2.2.7 Mineral Storage

Mineral storage, as introduced in the Trapping Mechanism (5), and in Figure 5 above, involves the reaction of CO_2 with available metal oxides to form geologically stable environmentally benign carbonate minerals (carbonation). In nature, this process is recognized as weathering of rocks containing these metal oxides. An un/nonconventional equivalent to the above natural process is to recreate the process of carbonation on an industrial level using waste raw materials from various industrial processes such as steel slag and mine tailings. This enables the storage of CO_2 in a stable inert and solid form. Mineral Carbonation is described further in Chapter 3.

2.2.8 Capture of CO_2

The first step in direct sequestration is to produce a concentrated stream of CO_2 for transport and storage (Folger., 2007). At present, there are three significant approaches available to concentrating and capturing CO_2 from large-scale industrial facilities or power plants:

1. pre-combustion capture, where CO_2 is captured before fuel combustion,

2. oxy-fuel combustion capture, where CO_2 is captured during fuel combustion, and

3. post-combustion capture, where CO_2 is captured after fuel is burned.

For power plants, current commercial CO_2 capture systems could operate at 85%-95% capture efficiency (IPPC., 2005). Techniques for capturing CO_2 have not yet been applied to large power plants (e.g. 500 megawatts or more) (IPPC., 2005).

2.2.8.1 Pre-Combustion Capture

This process separates CO_2 from the fuel by combining it with air and/or steam to produce hydrogen for combustion, and a separate CO_2 stream that could be stored. Figure 7 is a schematic representation of the capture process.

Pre-combustion capture of CO_2 is viewed by some as a necessary requirement for coal-to-liquid fuel processes, whereby coal can be converted through a catalysed chemical reaction to a variety of liquid hydrocarbons (Folger., 2007). The coal-to-liquid process releases CO_2, and the end product liquid fuel, releases more CO_2 when combusted. Figure 10 graphically shows the pre-combustion process.

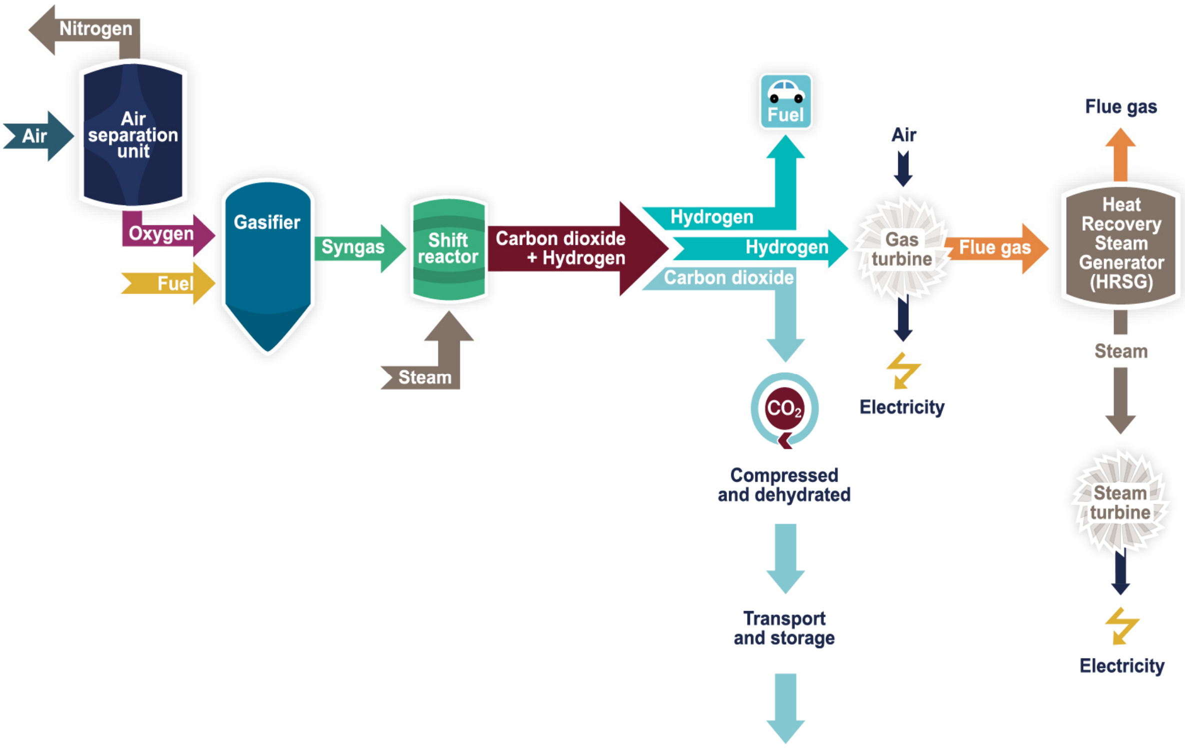


Figure 10: Pre-Combustion where CO_2 is captured before fuel is burned (ZEP.,2011)

The pre-combustion capture technology is widely applied in fertilizer, chemical, gaseous fuel (H_2, CH_4), and power production.

In Salah, Sleipner, Snøhvit and Weyburn-Midale projects discussed in 2.2.1 all involve pre-combustion CO_2 capture.

2.2.8.2 Oxy-fuel Combustion Capture

This is a CCT process and schematically shown in Figure 11. As discussed above, the process uses oxygen instead of air for combustion. After separation from the water vapour, the CO_2 can be compressed, transported, and stored.

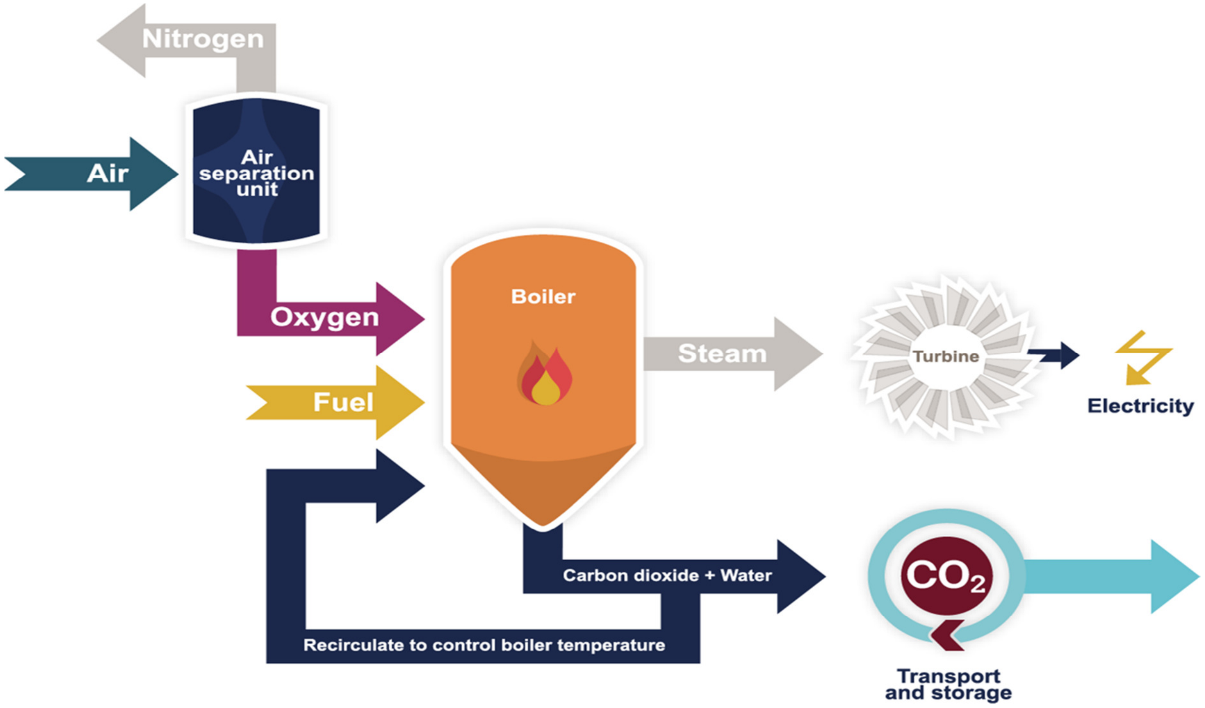


Figure 11: Oxy-Fuel Combustion Capture where CO_2 is captured during Combustion (ZEP., 2011)

Oxy-combustion is most often considered for existing coal boilers burning lower sulfur coals without any SO_2 and NOx control in the hope that these pollutants can be captured and disposed of with the CO_2. One such project is the Callide 'A' Power Station was originally built in 1962, near Biloela in central Queensland, Australia (PowerPlantCCS., 2011). This new project aims to demonstrate that new processes can be applied to old technology in order to reduce CO_2 emissions into the atmosphere, and also aims to test this project for 5 years to prove success so the technology can then be actively marketed to coal-fired power stations worldwide by 2020. The captured CO_2 will be transported (by truck) to a gas field with an impermeable caprock and in a tectonically stable area. This plant/project has the capability of reducing its CO_2 emissions by 90%, and has the means of capturing and storing up to 100,000 tonnes of CO_2 (PowerPlantCCS., 2011).

The Vattenfall Schwarze Pumpe pilot plant project is another example of oxy-fuel technology (Vattenfall., 2012). This is a 30 megawatt clean coal power plant built by Vattenfall, Sweden's national energy company in Schwarze Pumpe, Germany, came into operation in mid-2008. The purpose of the pilot plant is to validate engineering work, to gain a better understanding of the oxyfuel combustion technology on lignite and hard coal, and to demonstrate such capture technology (Vattenfall., 2012). As of November 2009, the CO_2 capture rate was reported to be nearly 100%. The CO_2 captured in the three year pilot trial, will be trucked to the depleted Altmark Gas Field (the second largest onshore gas field in Europe) for storage (MIT., 2011), and also piped to a nearby food processing plant.

2.2.8.3 Post-Combustion Capture

As described in section 2.1, post-combustion capture process involves extracting CO_2 from the flue gas following combustion of fossil fuels and/or biomass. Figure 12 shows the process. Chemical solvents of either ammonia (NH_3) or propriety amines, can in principle, be used to capture large quantities of CO_2 from flue gases (Folger., 2007).

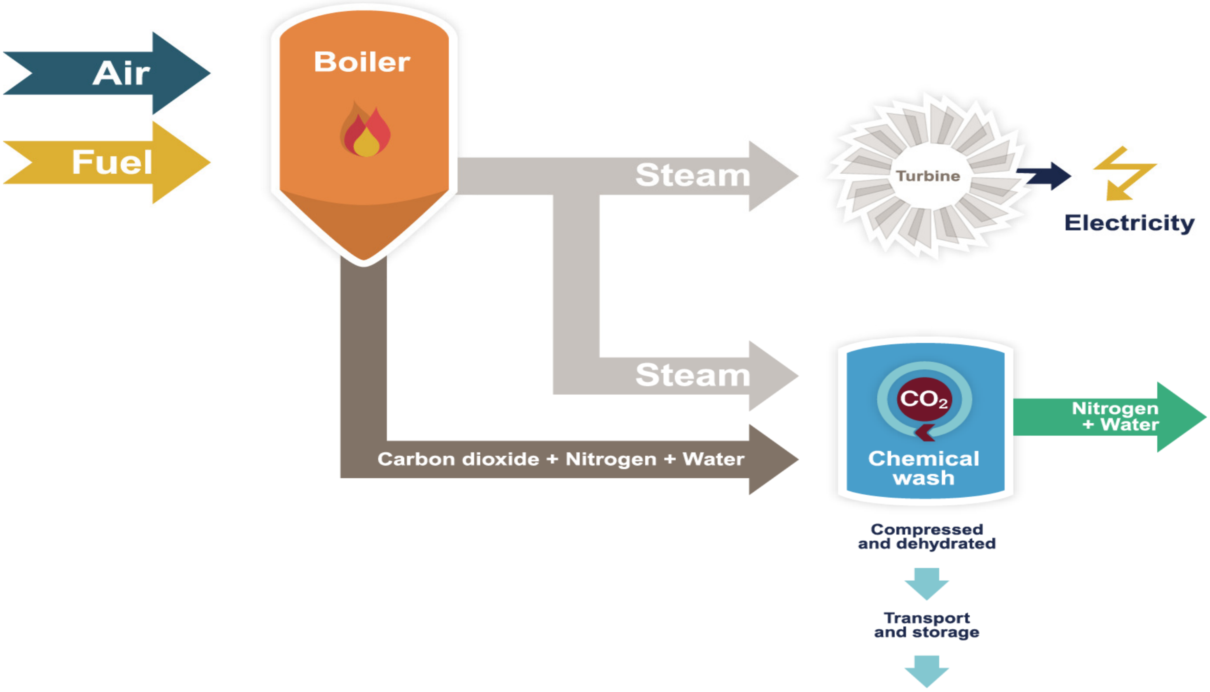


Figure 12: Post-Combustion Capture where CO_2 is captured after Combustion (ZEP., 2011)

The Norwegian Mongstad project is a retrofit of CO_2 capture at a natural gas-based combined cycle power plant, produces 280 MW electricity and 350 MW heat. Chilled NH_3 and amine based capture is employed and full scale collection of up to 1 Mt/a of

CO_2 is proposed to begin in 2020 (Global CCS Institute., 2011). Sasol has a 2.44% share of capital and operating costs in the Technology Centre Mongstad (TCM) project which was officially launched on 7th May 2012 (Naidoo., 2011). TCM is a stand-alone experimental capture plant that is fed CO_2 from a refinery and power station close by. Two capture technologies, namely; amine technology and chilled ammonia technology are to be tested. Sasol is to test and improve the CCT to prepare for full-scale CCS deployment worldwide (CO_2 Tech. Centre Mongstad., 2011). The CO_2 is to be piped offshore to be injected and stored in saline formations on the Norwegian continental shelf.

2.2.9 Transport of CO_2

If the plant locations are not above or at the geological storage site, the captured CO_2 gas (in a constant stream of 50% or more) is transported from the point source to the storage site. Pipelines are the most mature and common method used today whereby the gas is compressed, typically to a pressure above 8MPa, in order to avoid two-phase flow regimes and increase the density of the CO_2, thereby making it easier and less costly to transport (IPCC., 2005). Road/truck and rail transport, conveyor belt or ship depending on the destination to the storage site. The CO_2 is in liquid form, in insulated tanks, at much lower pressures than via pipeline and below ambient temperatures. Once at the storage site, the CO_2 is either injected into geological formations or into the ocean for storage; used in processes such as EOR; or in capacities that do not result in its emission into the atmosphere, such as mineral carbonation (IPCC., 2005).

2.3 CCS Initiatives in South Africa

Research is under way in South Africa to determine the feasibility of CCS. The SACCCS has begun working towards its vision of having a CCS demonstration plant operational in the country by 2020 (IISD Reporting Services., 2009). However, much work is still required before the SACCCS can begin work on the demonstration plant. Preparatory work includes the compilation of a carbon storage atlas, released in

August 2010, which illustrates the distribution and ranking of potential geological CO_2 storage reservoirs in South Africa, and other factors that may have a bearing on storage feasibility. Research will soon begin on the CO_2 geological injection test site, which will give scientists the opportunity to study how stored CO_2 reacts with South Africa's geological formation. First injection is expected by 2017. The South African storage atlas has indicated that there is limited existence of suitable conventional on-shore CO_2 storage capacity as shown in Figure 13.

Hence un/nonconventional storage techniques need to be explored. Mineral carbonation is one such un/nonconventional technique that has seen much research work in recent years since it was first suggested as a method of CCS by Seifritz. (1990), and may be a consideration as an option for CO_2 sequestration in South Africa. This is discussed further in Chapter 3.

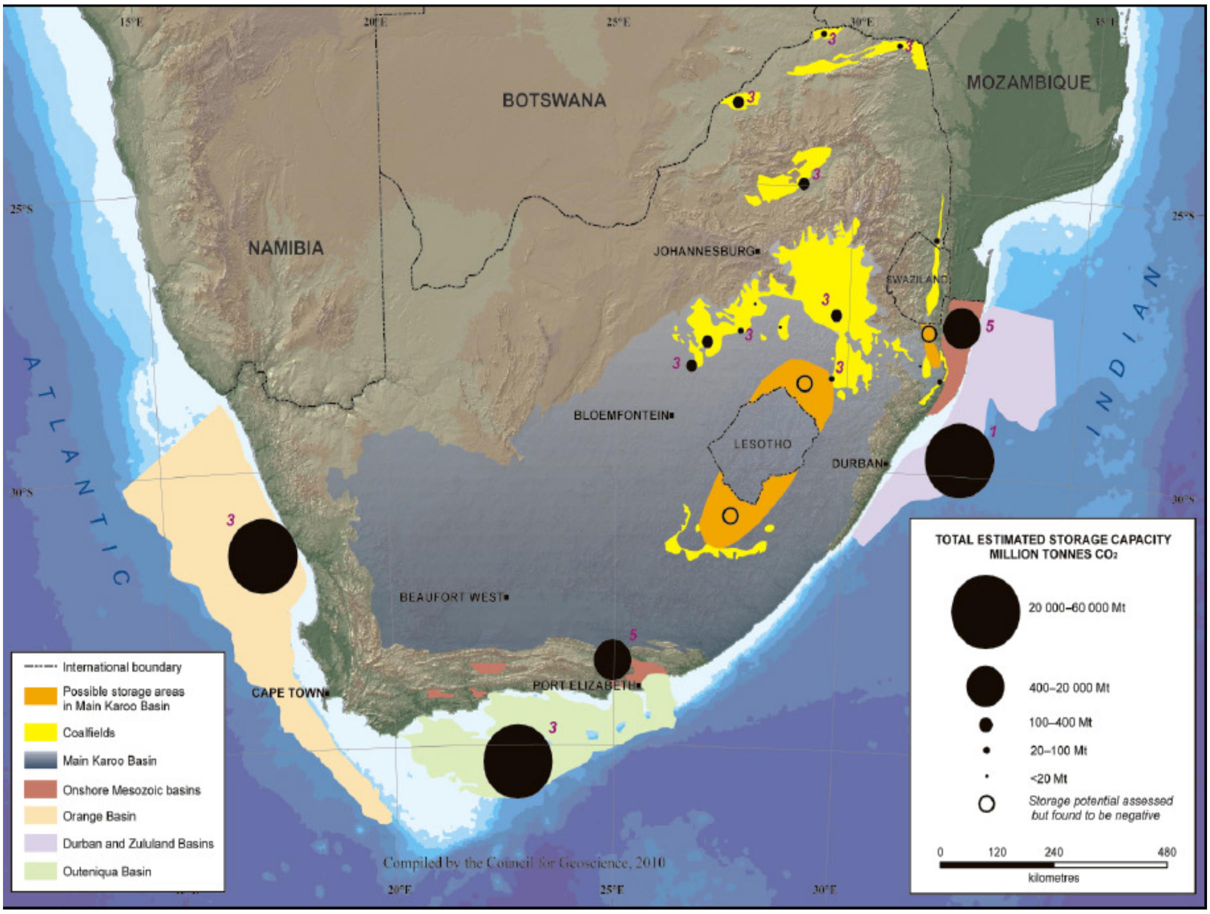


Figure 13: Carbon dioxide Storage Capacity in South Africa (Cloete., 2010)

Chapter 3 Mineral Carbonation

This chapter forms Phase One of the research: the desktop study that describes mineral carbonation in greater detail, with emphasis on the various process routes involved, global applications of the process as well as its place in the South African context.

3.1 What is Mineral Carbonation?

Mineral carbonation is based on mimicking the naturally occurring process of weathering, where the metal elements calcium (Ca) or magnesium (Mg) from alkaline silicate minerals are bound with CO_2 (dissolved in water), forming environmentally benign and stable Ca or Mg carbonates (Zevenhoven and Fagerlund., 2010). Both alkali and alkaline earth metals may be carbonated. However most of these elements are either economically valuable or form carbonates that are not stable for long term CO_2 sequestration (Doucet., 2011). Hence the alkaline earth metals Ca and Mg are most suitable elements for mineral carbonation.

3.2 Factors favouring Mineral Carbonation

1. Mineral carbonation is thermodynamically favoured. Carbonates have a lower energy state than CO_2. Therefore, theoretically, the process does not require energy inputs, but also can actually produce energy; that is, the overall process is exothermic. If properly optimized, the benefits of the favourable thermodynamics can be utilized to reduce overall energy consumption and costs of sequestration (Huijgen *et al.*, 2006). In nature, magnesite and silica are common in serpentinised /altered ultramafic rocks. The formation of these minerals is due to natural CO_2 –rich fluids that come into contact with the ultramafic rocks. The reactions are all thermodynamically favoured (Seifritz., 1990; Lackner *et al.*, 1995; Lackner., 2002) and are shown as follows:

$Mg_2SiO_4 + 2CO_2$ <=> $2MgCO_3$ + SiO_2 (2)

forsterite magnesite quartz

Apart from forsterite, other Mg based silicates suitable for carbonation include: olivine, ($(Mg,Fe)SiO_4$), and serpentine, ($Mg_3Si_2O_5(OH)_4$). Some other suitable minerals exist in smaller amounts (Zevenhoven and Kohlmann., 2001).

Calcite can be formed by a similar reaction as shown below:

$CaSiO_3$ + CO_2 <=> $CaCO_3$ + SiO_2 (3)

wollastonite calcite quartz

Reactions such as these have been observed in nature and the laboratory (Giammar *et al.*, 2005; McGrail *et al.*, 2006).

2. The second advantage is that vast capacities of raw materials for binding the CO_2 exist in vast quantities across the globe (Yegulalp *et al.*, 2000). The total mass of carbon currently in the atmosphere is approximately 800 gigatons (Gt). In contrast, ~39,000,000 Gt of C are currently present in carbonate rocks, such as marble, limestone and chalk, in the Earth's crust (Oelkers *et al.,* 2008).

3. Thirdly, mineral carbonation is the only form of carbon sequestration that is "permanent". The formed products are thermodynamically stable and therefore the sequestration of CO_2 is permanent and safe. The traditional sequestration options, namely: geologic storage (in depleted oil and gas reservoirs and saline formations) and ocean sequestration, have the potential for leakage over time, and risk compromising CCS as a climate change mitigation option. In addition, leaks may present other environmental, health, or safety issues associated with CO_2. Mineral sequestration is not regarded as having any leakage risks. The long term stability due to natural process of mineral carbonation over geological time frames is therefore a favourable option for CO_2 storage.

Ca-silicates tend to be more reactive to carbonation than Mg-silicates. This is a reason why wollastonite formed as a result of the metamorphism of impure limestone, has gained a lot of attention in mineral carbonation experiments in recent years (Lackner., 2002; Huijgen and Comans., 2003).

Mg, however, is more favoured than Ca, because it is the more abundant elemental oxide in mafic and ultramafic rocks. Ultramafic rocks like peridotite, pyroxenite or dunnite are Mg and iron (Fe) rich minerals. The earth's upper mantle is composed mainly of mainly of ultramafics, comprising the Mg bearing minerals olivine and pyroxene. Being dense, these rocks are prone to quite rapid weathering (in geological terms) (Schenk., 1984). When exposed to CO_2, they react with it to form the carbonates, limestone and chalk. These deposits tend to be restricted to the planet's more geologically active regions including the eastern Mediterranean (from Italy through to the Middle East), western North America, Japan, New Zealand, and other countries along the Pacific Ring of Fire (Schenk., 1984). In South Africa, the Barberton Greenstone Belt and Bushveld Igneous Complex, as well as the centre of the Vredefort Dome, are the areas where these magnesium rich rocks are found. The significance of ultramafic rocks such as peridotites in South Africa, with respect to mineral carbonation, is discussed further under *Ex Situ* carbon mineralisation later in this chapter.

If these ultramafic rocks are first infiltrated by water (H_2O), where they lie beneath the oceans, they may combine chemically with some of this H_2O and alter to serpentinites. These are another family of ultramafic rocks comprised mainly of three minerals: antigorite, lizardite, and chrysotile (which is rare and the troublesome form is white asbestos). The serpentinites are more resistant to weathering, so are more abundant in the earth's crust, being found even within and around the margins of geologically ancient shields such as those in Australia, Canada and South Africa (McGrail *et al.*, 2006).

Basalt is a mafic rock, composed of pyroxene and feldspar (alumino silicates), is one of the Earth's most common rock formations, making up about 10% of the continental crusts. Basalt is also found on the seafloor surrounding most continents, as well as inland. There is storage space in geologic formations worldwide for at least 2 trillion tonnes of CO_2 (IPCC., 2005). Like peridotites, basalts chemically react with CO_2-saturated water to quickly form minerals, some of which contain C, such as magnesite, calcite, and dolomite. Basalt, in terms of mineral carbonation in South Africa is discussed further under *In Situ* carbon mineralization later on in this chapter.

3.3 Previous Research Work on Mineral Carbonation

Carbon dioxide sequestration by mineral carbonation tries to mimic naturally occurring rock weathering which, is known to have played an important role in the historical reduction of the CO_2 concentration in the atmosphere after the creation of the Earth (Huijgen and Comans., 2003). The term mineral carbonation was proposed as a CO_2 binding concept by Seifritz (Seifritz., 1990) and discussed a few years later by Dunsmore (Dunsmore., 1992). Lackner *et al*. (1995) conducted the first detailed study on mineral carbonation using two types of processes, involving either direct carbonation of minerals at high temperature or processing in aqueous solution. These aim at *ex situ* processing in a dedicated processing plant as opposed to in situ carbonation by injecting the CO_2 into geological formations.

Either way, the carbonates formed by the process of mineral carbonation are the products of natural geologic processes that remain stable over geologic time scales. Both *in situ* and *ex situ* processes are discussed further under Process Routes in this chapter.

The greater part of the C in the lithosphere is held in its oxidised form, thus an enormous potential for C sequestration in solid carbonated form can be expected (Dunsmore., 1992). The reactions are also stable and environmentally safe. Lackner (2002) distinguishes three carbonate disposal strategies:

i) Introduction of bicarbonate salts into the ocean;

ii) Injection of (bi) carbonate brines into underground reservoirs and

iii) Storage of solid carbonates on the surface or underground (mineral CO_2 sequestration).

Bicarbonates are more soluble than carbonates, hence the latter option is considered more favourable for permanent CO_2 storage (Lackner., 2002).

Recent years has seen speedy development efforts in mineral carbonation being made, characterized by patent applications (Delgado., 2010) and a trend toward scale-up and demonstration. The slow deployment of large-scale underground storage of CO_2 or simply the availability of large amounts of suitable minerals seems to be the motivation and progress on mineral sequestration is being steadily made and reported by an increasing number of research teams and projects worldwide (Zevenhoven *et al.*, 2011). Also, improved assessment of usable storage capacity for underground sequestration is changing the relative positioning of different CCS methods (IEA., 2010).

3.4 Process Routes for Mineral Carbonation

Much literature has been published on different routes for mineral carbonation (Huijgen and Comans., 2003; Lackner., 2002; O'Connor *et al.*, 2003; Sipilä *et al.*, 2008; Zevenhoven *et al.*, 2011). The process routes are divided into two types namely:

- *Ex situ* process routes, and
- *In situ* process routes

Each of these process routes is discussed in further detail below.

3.4.1 *Ex Situ* Mineral Carbonation Routes

Ex situ mineral carbonation routes involve the above ground industrial processes using silicate rich rocks produced by mining activities or industrial waste products. Various pre-treatment options are available. These include size reduction by crushing and milling, magnetic separation and thermal treatment (Huijgen and Comans., 2003). The main purpose of pre-treatment is to increase the carbonation reaction rate by increasing the reaction surface area available for carbonation. The pre-treatment methods can be very energy intensive.

Figure 14 illustrates the various process steps associated with *ex-situ* carbonation.

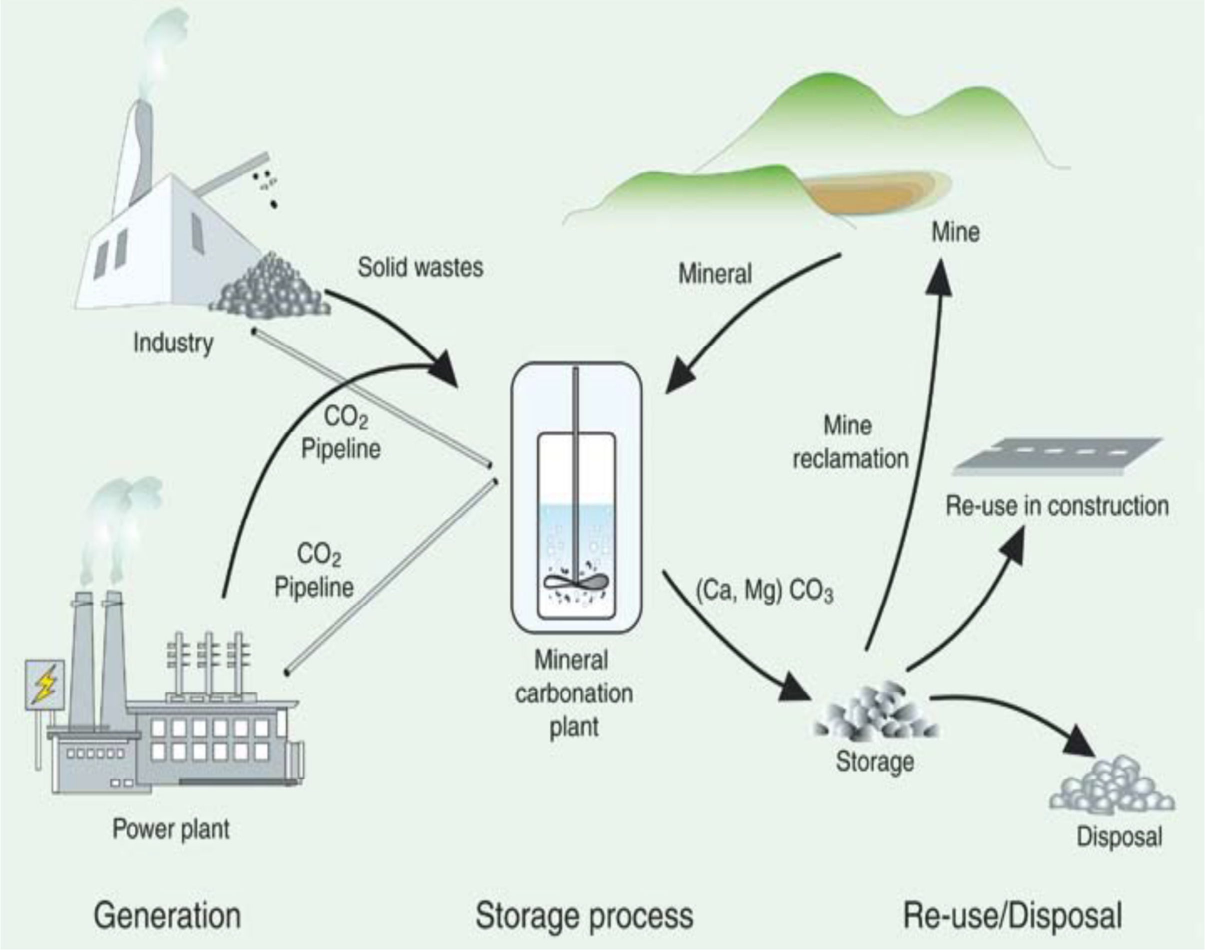


Figure 14: Material Fluxes and Process Steps associated with the Ex Situ Mineral Carbonation of Silicate Rocks or Industrial Residues (IPCC., 2005)

The *ex situ* process routes are given below. Figure 15 schematically shows these routes.

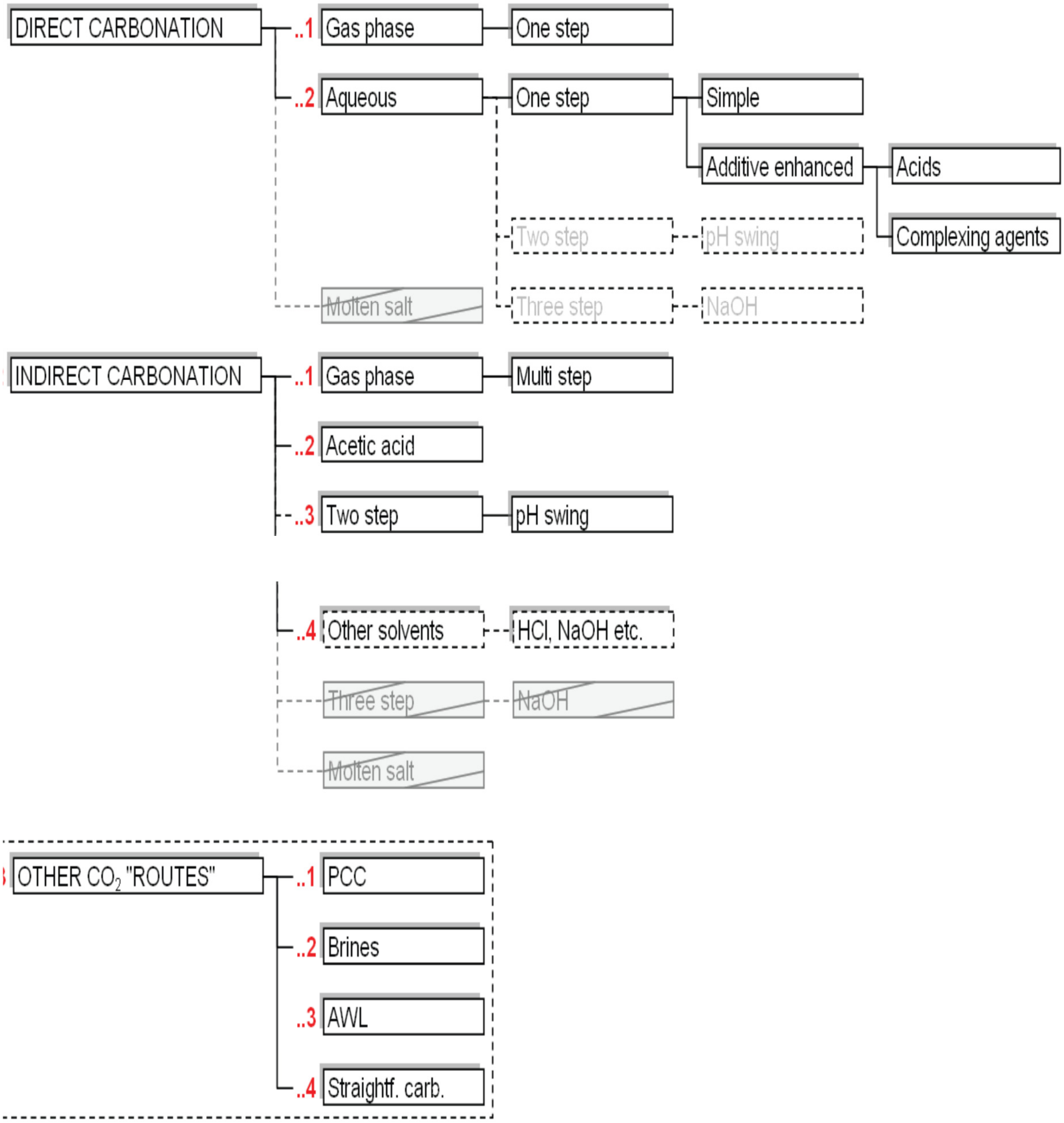


Figure 15: Chart of Various Ex Situ Mineral Carbonation Routes (Sipilä et al., 2008)

Dotted lines indicate modifications to Huijgen and Comans 2005; dotted process route boxes have been moved and grey boxes represent abandoned routes)

3.4.1.1 Direct Carbonation

Direct carbonation is the simplest approach to mineral carbonation, and the principal approach is that a suitable feedstock, such as serpentine or a Ca/Mg rich solid residue, is carbonated in a single process step (Sipilä *et al.*, 2008). The removal of metals from the feedstock and the reaction of these metals with dissolved CO_2 to form carbonates in one reactor. This applies to an aqueous process.

It has two sub routes namely:

1. Direct gas-solid carbonation with CO_2 – Gas-solid carbonation is probably the simplest approach towards mineral carbonation than any other. In this route, the metal oxides are brought into contact with CO_2 at a particular temperature and pressure (Sipilä *et al.*, 2008). This is the process used in the experiments documented in Chapter 4 of this report. 2. Aqueous-silicates slurried with water and carbonated directly with CO_2 - direct aqueous carbonation involves three coexistent mechanisms in a single reactor: (a) aqueous dissolution of CO_2, (b) aqueous dissolution of Ca- and Mg-bearing mineral phases, and (c) precipitation of carbonates. It is generally accepted that silicate dissolution is the rate-limiting step, and as a result effort has focused on improving the kinetics of silicate dissolution using a wide range of additives and by varying operating conditions such as temperature, pressure, CO_2 concentration, solid to liquid ratio, and particle size. The advances made to aqueous solution chemistry were significant, but the expensive additives need to be recycled. Otherwise the process route becomes unattractive. Nevertheless, the studies conducted on direct aqueous carbonation have improved the overall knowledge of aqueous carbonation reactions considerably (Sipilä *et al.,* 2008).

3.4.1.2 Indirect Carbonation

The process of mineral carbonation is divided into several steps. In other words, indirect carbonation means that the reactive component (usually Mg or Ca) is first extracted from the feedstock (as oxide or hydroxide) in one step and then, in another step or more, it is reacted with CO_2 to form the desired carbonates.

There are many sub-routes which are briefly listed below.

1. Multistage gas-solid carbonation - The process involves extraction of magnesium (oxide or hydroxide) in an atmospheric pressure step followed by a carbonation step at elevated temperature (>500 °C) and pressure (>20 bar) (Zevenhoven *et al.*, 2006).
2. Acetic acid - used to speed up separation of Ca from a Ca rich feedstock (Kakizawa *et al.,* 2001).
3. Two step aqueous carbonation (pH swing) - extracts the metal at low pH, and the carbonate precipitation at high pH (Kodama *et al.*, 2008).
4. Other solvents - sodium hydroxide (NaOH) application to enhance Ca extraction (Eloneva *et al.*, 2008), or Mg extraction using hydrochloric acid (HCl) (Teir et al., 2009).

3.4.1.3 Other Routes

These are a list of other processes and applications that resemble mineral carbonation.

1. Production of precipitated calcium carbonate (PCC) (Tier *et al.,* 2005)
2. Carbonation using brines - large concentration of metals are capable of forming carbonates (Druckenmiller and Maroto-Valer., 2005)
3. Accelerated weathering of limestone (AWL) - imitates natural carbonate weathering (Huijgen and Comans., 2005)
4. Straight-forward carbonation- spreading olivine on land where acidity is a problem increases the pH of the soil and capture CO_2 from surrounding air (Schuiling and Krijgsman., 2006).

3.4.1.4 Challenges and Pre-treatment Options for Ex Situ Mineral Carbonation

Increasing the slow reaction rates of mineral carbonation processes has been, and still, is a research field that receives attention. While many studies have focused on modifying the process itself, as was described in the sections above, some studies have looked towards activating the feedstock by various pre-treatment options, including heat, chemical, and/or mechanical pre-treatment. In general, mechanical activation is used for olivine, while heat activation is used for serpentine (Delgado., 2010). An alternative is combined mechanical and chemical treatment, which, when used on raw serpentine, increased the surface area from 8 m^2/g to over 330 m^2/g. (Maroto-Valer *et al.,* 2005), However, it is uncertain whether this option could balance the loss of chemicals including magnesium (up to 70%) into the solution against the improved reactivity (Huijgen and Comans., 2005).

The major problem with many of the pre-treatment options has been (or still is) the high energy input requirement and it was recently concluded that only conventional grinding of the feedstock, has been proven to be energetically and potentially economically feasible (Huijgen and Comans., 2005).

The heat activation process of serpentine was studied in the Albany Research Centre (ARC) for a quite some time (Delgado., 2010). Li *et al.*, (2009) studied the heating of serpentine at 10 ℃/min from ambient temperature to different temperatures up to 950 ℃ for 30 min and after cooled rapidly. It was observed that below 600 ℃, hydroxyl groups were still present in the heat-activated material, which became less with heating until completely disappeared at 950 ℃. The Mg solubility was found to increase first and then decrease with increasing heat-treatment temperature, with a maximum solubility at 650 ℃, which agreed with previous studies (O' Connor *et al.*, 2005). But this treatment was found to be too energy intensive (Huijgen and Comans., 2005; Sipilä *et al.*, 2008).

3.4.1.5 Current Large Scale Ex Situ Process Applications

Both direct and indirect mineral carbonation processes are still currently under development, with indirect processes offering the benefits of faster chemical kinetics and better product quality (Zevenhoven *et al.*, 2011). Below are described, some of the most promising processes to date.

1. The U.S. Department of Energy's National Energy Technology Laboratory (NETL) located in Albany, OR (formerly the Albany Research Center-ARC) developed a direct carbonation process in aqueous solutions is considered, today, to be the state-of-the-art route for mineral carbonation (O'Connor et al., 2005). This process takes advantage of the natural alteration of ultramafics. Optimization of solution chemistry (using 0.64 mole (M) $NaHCO_3$ (sodium bicarbonate) and 1 M NaCl (sodium chloride)); heat treatment (615–630℃) for serpentine to remove the chemically bound water) and high energy attrition grinding to destroy the crystal structure and; the introduction of a catalyst, all accelerated the reaction rates. The maximum extent of reaction were achieved for olivine, serpentine and wollastonite under the following conditions: 185℃/150 bar for olivine, 155℃/115 bar for heat-treated serpentine and 40 bar/100℃ for wollastonite. Higher reaction rates were achieved by decreasing the particle size to 50 microns using a METSO stirred media detritor (SMD) mill. 80% conversions were possible in one hour as reported by Gerdemann *et al* (2003).

The results of the ARC experiment showed untreated serpentine that does not react significantly. Even finely ground particles showed lower reaction rates than for olivine. This means it is expensive to treat with heat and heavy grinding. Wollastonite was more reactive in distilled water than olivine in bicarbonate ($NaHCO_3$) solution. A larger particle size was used than for either olivine or serpentine. Thus it showed wollastonite to be more reactive than the latter two minerals.

Koukouzas *et al.* (2009) tested the same process on serpentines from Greece and found only 10% of Mg was converted to carbonates. This showed that the ARC process will require optimization for each serpentine variety, although maintaining the lowest possible reaction temperature and pressure is desired for the technical and economic feasibility of the direct carbonation process (Doucet .,2011).

2. The Hunwick System (Hunwick., 2008), which combines scrubbing of CO_2 from power plant flue gas with an ammonium/water/metal silicate slurry, with serpentine as the preferred silicate does show promise of large scale development. This process gives slurry that is pumped into a reactor where at a high temperature and pressure carbonate is produced and the ammonia released to be reused.

3. A process that is being demonstrated at two process units, in California and Australia, respectively, is the Calera process (Constantz *et al.*, 2009). This invention uses sea water waste fly ash (sources of Mg and Ca) are mixed with CO_2. The CO_2 -charged acidic water passes through to a precipitation reactor while the pH is increased with addition of sodium hydroxide. The resulting carbonates serve as building materials.

4. Reddy *et al.* (2009) have recently patented a process which involves a method of simultaneously sequestering and storing mercury, SO_2, and CO_2 by reacting an alkaline material such as fly ash from a coal-fired plant (at ambient pressures and slightly elevated temperature conditions)with a flue gas containing these contaminants. A demonstration project is underway at a coal-fired power plant in Wyoming in the USA.

3.4.1.6 Ex-Situ Mineral Carbonation in South Africa

Several sites around the country have been identified by Doucet. (2011). These materials are available in large piles that have already been crushed and milled following mining activities and include diamond, chromium and phosphorous pentoxide, asbestos and platinum group metal (PGM) tailings, usually made up of ultramafic rocks such as peridotites. These mine tailings can provide an untapped resource for *ex-situ* mineral carbonation processes. Industrial alkaline waste such as steel furnace slags, phosphogypsum, and coal combustion fly ash are other waste products identified for *ex-situ* mineral carbonation. Moreover, these large quantities of readily available tailings and waste are potentially near areas of high point sources as shown in Figure 16. Figures regarding the neutralising material indicate that for a power plant producing 10 000 tonnes of CO_2 per day, approximately 25 000 tonnes/day of this material is required or approximately 9 million tonne per annum (Engelbrecht *et al.,* 2004).

Platinum Group Metals:

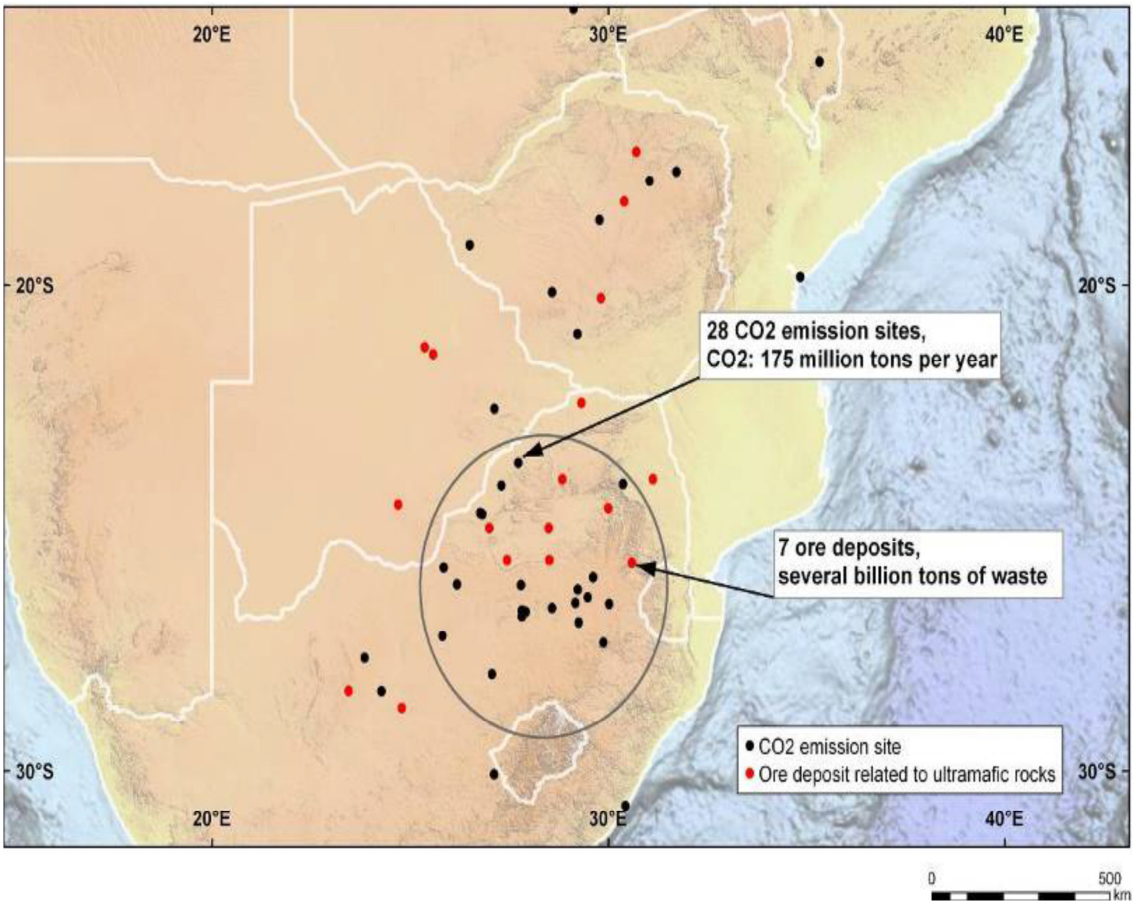
Vogeli *et al*. (2011) in their mineral carbonation study of PGM mine tailings from the Bushveld Igneous Complex, indicate that platinum group elements (PGE) are available in large amounts and contain Ca and Mg silicates in appreciable amounts and in fine grain size, for mineral carbonation .

In a project undertaken by a French consortium, Carmex aimed at assessing the worldwide potential for ex situ mineral carbonation, an evaluation of the mine tailings of South Africa is made (Doucet., 2011). Potential sites for implementing *ex situ* mineral carbonation were ranked by crossing two data sources, the world inventory of "Large and Superlarge Deposits" and CO_2 emission sites (Picot *et al*., 2010), using ArcGIS, a geographic information system designed for creating analysing and using maps, and geographic data in a range of applications.

The material that is potentially beneficial to carbonation in terms of quantity and quality is the waste from mining world-class deposits related to ultramafic (Ca,Mg,Fe > 40% by weight) and mafic (Ca,Mg > 30-40%) rocks. A number of selection criteria was used in the search, such as using only Superlarge (Class 4) ore deposits related to ultramafic rocks (i.e. chromium (Cr); copper (Cu); nickel (Ni); PGE), distance from CO_2 emissions sites, and volume of CO_2 released per annum (Picot *et al*., 2010).

The negative effect of the Carmex selection is the exclusion of PGE mine tailings from their short-list, although these materials are known to be abundant and promising resources for carbonation (Vogeli *et al*., 2011).

The Carmex finding showed that the South African sites were very favourable in terms of the concentration of ore deposits related to ultramafic rocks, very large amounts of mining waste (several billion tons), and the proximity of numerous CO_2 emission sites. Figure 16 below illustrates this.



28 CO2 emission sites,
CO2: 175 million tons per year

7 ore deposits,
several billion tons of waste

Figure 16: CO_2 Sources fixed with Ore Deposits related to Ultramafic Rocks in South Africa (Picot et al., 2010)

Kimberlite

Kimberlite is defined as a volatile-rich, potassic, ultrabasic igneous rock that occurs as small volcanic pipes, dykes and sills (De Beers Group., 2011). The mineralogy comprises olivine with several of the following: phlogopite, calcite, serpentine, diopside, monticellite, apatite, perovskite, and ilmenite. Kimberlite often contains fragments of upper-mantle derived ultramafic rocks, including xenocrysts such as pyrope garnet, picro-ilmenite, chromian spinel and chrome-diopside. Kimberlite may contain diamond, but as a very rare constituent.

Two distinct types of kimberlite are recognised:

i. Group I - CO_2 and forsteritic olivine rich, umtramafic potassic igneous rocks, and

ii. Group II - (orangeites), ultrapotassic, volatile rich - dominantly H2O.

Historically, these were respectively referred to as “basaltic” and “micaceous lamprophyric” kimberlites (Mitchell., 1995).

Only a small proportion of known kimberlites carry diamonds and of the approximately thousand or so individual kimberlite intrusions known in South Africa, only about fifty carry economically viable quantities of diamonds, and exploited for these gems (De Beers Group., 2011). Figure 17 shows the distribution of kimberlites in South Africa. It is to be noted that while diamonds are the only economically significant product extracted from kimberlite, not all kimberlite deposits are diamond bearing (Barker., 2008). Hence there are considerable tailings from this peridotite variety, available for mineral carbonation purposes.

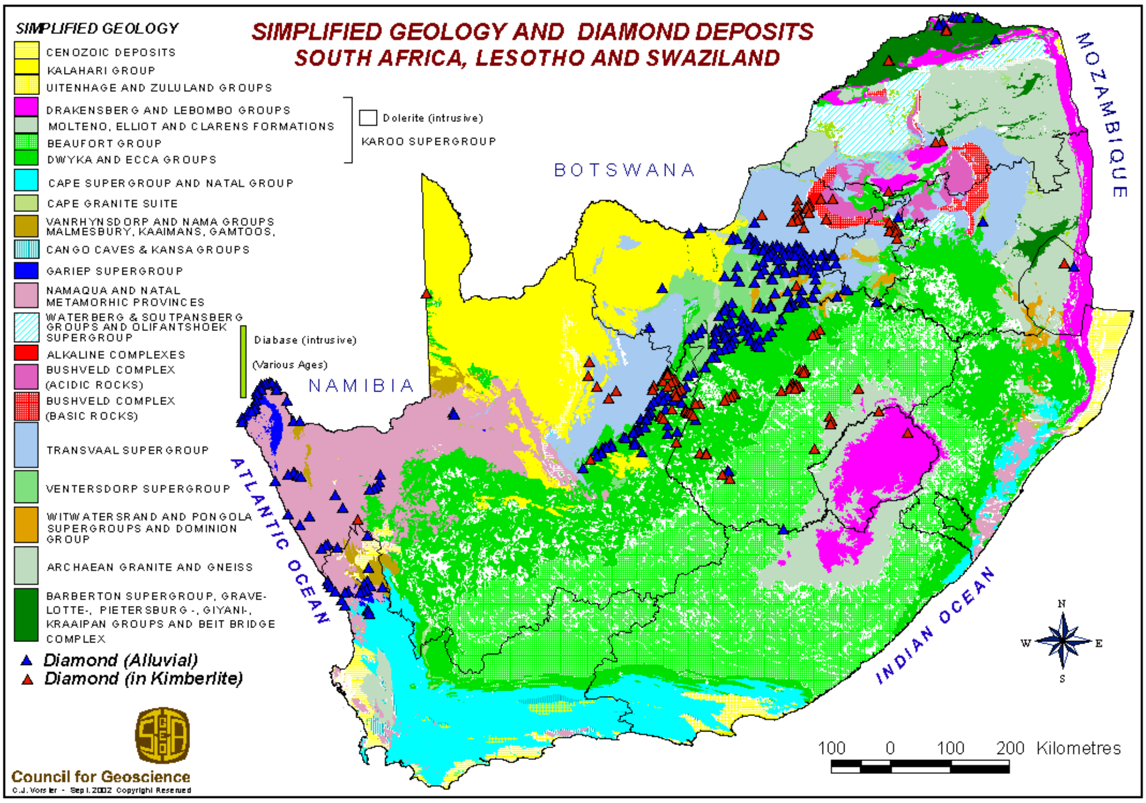


Figure 17: Kimberlite Deposits in South Africa (CGS., 2011)

In South Africa the tailings or waste products from kimberlite hosted diamond mines are in abundance, as identified by the Cullinan Premier Mine, near Pretoria that has generated over a billion tonnes of diamond mine tailings (Picot *et al.,* 2010). These tailings contain gabbro, (Doucet., 2011), the plutonic igneous rock, chemically similar to basalt, but only differ in grain size. The basalt grain size is smaller because it is extruded to the earth's surface, and cools rapidly in comparison to gabbro.

Kimberlite tailings contain serpentine, forsteritic olivine, phlogopite and magnesium ilmenite (Halenyane and Reid., 2011). From Table 1 it can be seen that the rock has an abundance of Mg-rich minerals favourable for carbonation.

Table 1: Kimberlite Chemical Analysis from Three South African Mine Tailings (Halenyane and Reid., 2011)

Mine Sample	**Major Oxide in weight percent (wt)%**			
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**MgO**
Bultfontein	47.10	7.57	7.52	21.86
Kampfersdam	44.85	6.64	7.63	22.33
Jagersfontein	47.15	6.45	7.06	21.79

These major oxide results are part of a study on kimberlite tailings of three mines, Bultfontein, Kampfersdam and Jagersfontein, in the Kimberly area, currently under investigation at the University of Cape Town (UCT). Of interest is the history of multiple re-cycling of the kimberlite tailings in the Kimberley area. Comparisons of the different generations of tailings are to be investigated. Modern tailings from a retreatment plant in the Kimberly area are considered to be totally exhausted in valuable diamonds and thus probably represent the material most likely to be released for recycling. (Halenyane and Reid., 2011). The historic tailings dumps might have experienced natural carbonation through surface weathering of Mg-Ca-Fe silicates over the several decades of existence and the scale of CO_2 absorption needs to be accurately quantified as it may prove significant.

Power *et al*. (2011) conducted interesting microcosm/microbe experiments into mineral carbonation on ultramafic mine tailings from the Diavik Diamond Mine, Canada and the Mount Keith Nickel Mine, Western Australia using a combination of chemical and biological processes. The tailings were leached using various dilute acids to produce subsaline solutions at near neutral pH. Colourless and green sulfur bacteria from stratified freshwater lakes and ponds (Overmann *et al*., 1998) capable of inducing carbonate precipitation were then introduced to the tailings. CO_2 sequestration rates are mainly limited by cation availability and the uptake of CO_2. Abundant carbonate mineral precipitation occurred when heterotrophic oxidation of acetate acted as an alternative pathway for CO_2 delivery (Power *et al*., 2011). Geochemical modelling of the experimental solutions showed up to 2.5% and 16.7% of the annual emissions for Diavik and Mount Keith mines, respectively, could be sequestered as carbonate minerals and phototrophic biomass (Power *et al*., 2011).

Tailings storage facilities could be redesigned to promote CO_2 sequestration by directing leachate waters from tailings dumps into specially designed ponds where carbonate precipitation would be mediated by both chemical and biological processes (Power *et al.,*2011).

Similar use of both chemical and biological processes of mineral carbonation may be employed on the large amount of ultramafic tailings in South African mine dumps, as an option to store carbon as stable carbonate minerals, while producing potentially valuable biomass for biofuel production at the same time.

Wollastonite

Wollastonite ($CaSiO_3$), like the mineral, forsterite ($MgSiO_3$), is a naturally occurring silicate. It is a common mineral in skarns or contact metamorphic rock and forms when impure limestones are metamorphosed (subjected to heat and pressure) or silica bearing fluids are introduced into calcareous sediments during metamorphic processes. In both cases, calcite reacts with silica to produce wollastonite and CO_2 (Virta., 2001). Refer to Equation 3 for the reaction.

Wollastonite can also crystallize directly from a magma that has unusually high carbon content, but this is a rarer occurrence. It has a theoretical composition of 48.3% calcium oxide (CaO) and 51.7% silicon dioxide (SiO_2) but may contain trace to minor amounts of aluminium (Al), iron (Fe), magnesium (Mg), manganese (Mn), potassium (K), and sodium (Na) (Virta., 2001). If they are present, these ions with the inclusion of titanium (Ti), can be absorbed to a certain extent into the wollastonite structure during its formation as shown in Table 2. If these ions are present in appreciable amounts, then minerals such as diopside and feldspars etc. may form also (Minerals Zone., 2005).

Table 2: Typical Chemical Composition in wt % of a Wollastonite (Daval et al., 2009)

SiO_2	CaO	TiO_2	MnO	FeO	MgO	Total
50.3	47.77	0.03	0.03	0.05	0.03	98.31

Wollastonite is mainly distributed in Asia and America (Zhang *et al.*, 2010). China was the top producer of wollastonite with at least 50% of the world market share, followed by India, the USA, Mexico and Finland, in 2010 (US Geol. Survey., 2011). Figure 18 shows the world output of wollastonite for 2005 (Wikipedia., 2011).

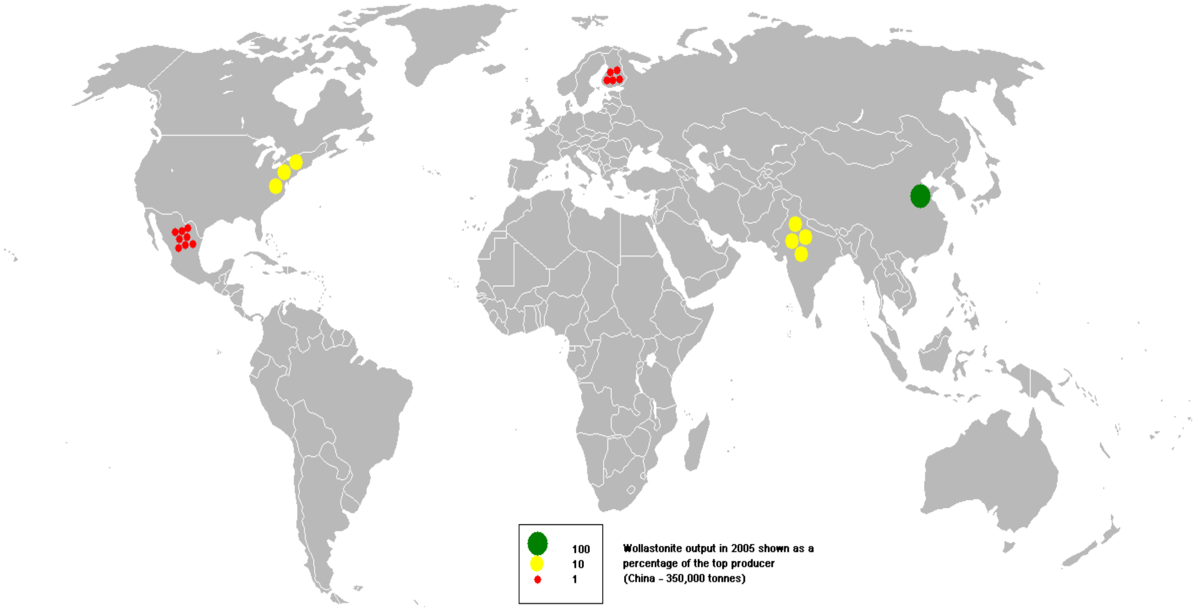


Figure 18: Global Wollastonite Production for 2005 (Wikipedia., 2011)

Due to its fluxing properties, freedom from volatile constituents, whiteness, and acicular particle shape, wollastonite is used extensively worldwide in the ceramics, plastics, rubber and paint industries as well as in a variety of construction, friction products and metallurgical applications (Wikipedia., 2011).

The researcher has found that very limited information on wollastonite deposits or production in South Africa is available. This is not surprising as Figure 18 above, shows. A search on the Council for GeoScience (CGS) website, only alluded to the exploitation of small open workings in Namaqualand (CGS., 2011). This probably in part refers to large wollastonite deposits occurring in the Northern Cape in the Namaqualand and Gordonia districts, according to the Northern Cape Province (NCP)–Mineral Sector Strategy Report. (2004). The report lists three deposits found along the boundary between the farms Wilgehout Fontein 426, Modderfontein, and Lelie Fontein 350, located 20 km to the Northeast of Garies. In addition to the Garies deposits, two further deposits have been listed in the Gordonia district. The most significant are these deposits occurs on the farms Keimoes 1152 north of Keimoes and Eksteenkuil 35, 7 km southeast of Keimoes. The deposits tend to be very siliceous, making extraction very difficult.

Mining operations started in 1963. It was reported to have had a production of 200 tonnes in 1999 with proven reserves of 3Mt (Virta., 2001). However, marketing difficulties related to quality problems, associated with high iron content, resulted in the closure of the operations (NCP., 2004).

Various mining attempts have all failed until April 2010, when Namaqua Wollastonite (Pty)Ltd began producing the metasilicate at its Magata Wollastonite Project , 14 km north east of Garies, Namaqualand in the Northern Cape (Feytus., 2010).

To the researcher's knowledge, Garies deposits are the only deposits exploited to date.

The rapid dissolution rate of wollastonite has made the mineral useful in carbonation reaction studies at elevated temperature and partial pressure of CO_2 (pCO_2). The dissolution behaviour of wollastonite has been investigated for over 20 years (Daval *et al.*, 2009). As a Ca-silicate, studies of this mineral can enable direct comparison to the carbonation of Ca-rich alkaline solid residues such as steel slag (Huijen *et al.*, 2006) and results obtained may yield useful insights for CO_2 sequestration monitoring and modelling in geological reservoirs containing important quantities of Ca-rich silicate minerals, such as in basalts (Daval *et al.*, 2009).

In spite of the perceived limited tonnages locally, the advantages that wollastonite exhibits in terms of having more reactive features towards carbonation compared to Mg silicates (Huijen and Comans., 2003 and Gerdemann *et al.*, 2003), cannot be overlooked in terms of carbon sequestration by mineral carbonation in South Africa. Perhaps on a small scale, for example, the tailings from the Magata Wollastonite Project could be harnessed for this purpose. However this must be balanced with the uses it serves, in the various industries it is being mined for at present.

Dolerite

Dolerites are a coarser grained sub-volcanic equivalent of basalts, so, is rich in divalent cation-bearing minerals such as olivine and pyroxene (rich in Mg-Ca-Fe). It is also extremely abundant and widespread throughout South Africa as shown in Figure 19. They occur as sills and dykes particularly they are encountered by miners, where they intrude into coal seams. In the Highveld and Witbank coalfields they have been described as showing evidence of mineral carbonation in parts where they penetrate coal seams (Ngwagwe., 2009; Mathivha., 2010). At New Denmark Colliery, an investigation into the dolerite dykes that penetrated the coal seams there, showed ferrous carbonate formation as a result of the hot doleritic magma reacting with the coal. The CO_2 emitted during the reaction then reacted with silicates in the dolerite to form the carbonate (Ringane., 2003; Dalwani and Smith., 2009). The high temperature magmatic intrusions were capable of igniting the coal and presumably generating significant CO_2 in what is essentially a natural fossil fuel conversion process. Some of this CO2 could have escaped, the extensive carbonate alteration of the adjacent dolerite where it intersected the coal, clearly demonstrates a form of internal self-sequestration. (Vogeli *et al.*, 2011). The alteration process appears to be volume for volume pseudomorphic replacement of the dyke from the margins inwards, with the order of preferential carbonation being olivine, followed by pyroxenes and Fe-Ti oxides, and finally feldspar (Meyer and Reid., 2011).

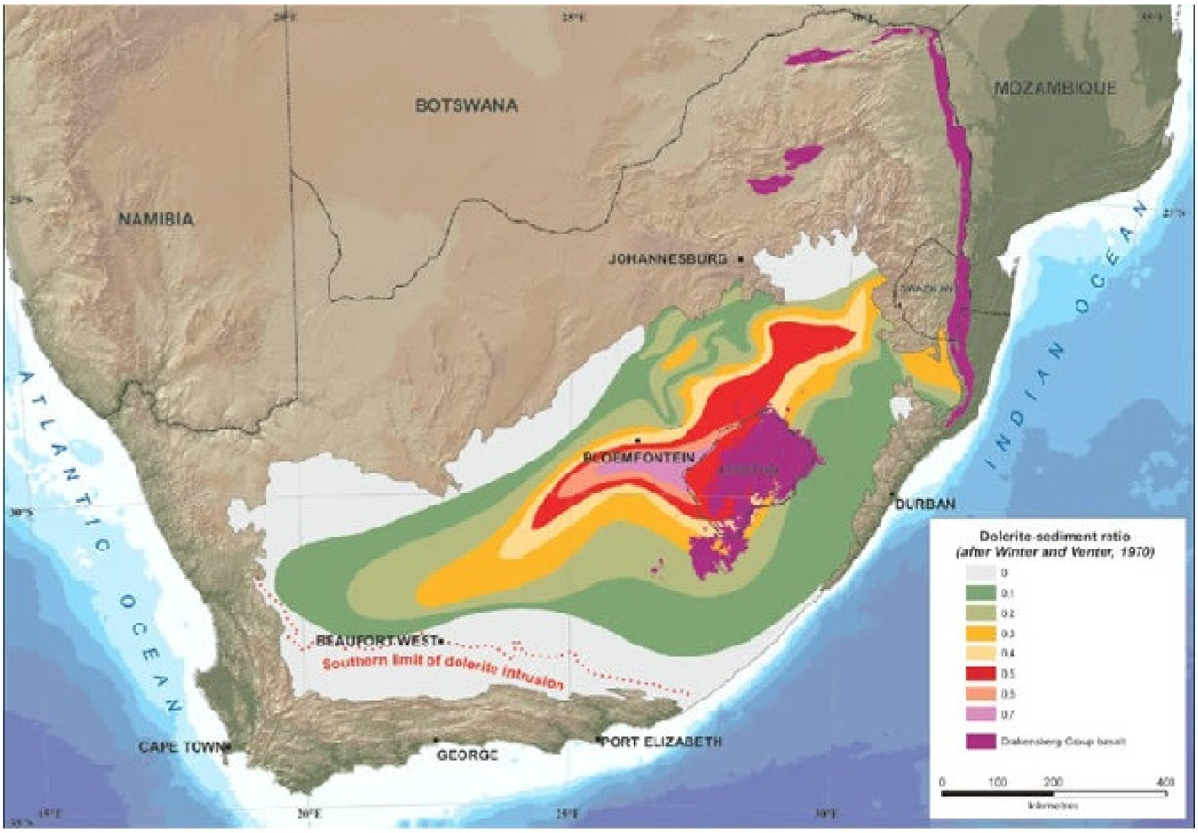


Figure 19: Extent of Karoo Flood Basalt, and Dolerite, its Sub-Volcanic Equivalent (Cloete., 2010)

Investigations into the geochemical factors of this natural carbonation process can give insight into its use in industrial applications such as the road pavement construction where 'detrimental carbonation' of the dolerite is a cause for concern (Kleyn and Bergh., 2008). Even though they are prolific over the country, they are not massive like their basalt flow equivalents, and therefore are unlikely to be suitable for in situ mineral carbonation.

Asbestos

In terms of asbestos, no quantifiable reserves with respect to CO_2 sequestration is available and total emissions in South Africa far outweigh the amount of CO_2 that can be sequestered (Doucet., 2011). Figure 20 shows the asbestos deposits for the country. Nevertheless, it is worth noting that carbonation of the existing dumps could add a benefit of remediation as asbestos is considered a respiratory hazard due to the presence of serpentine and amphibole minerals dust (Doria., 2005).

The results from the studies suggest that the ARC process as described in 3.4.1.3 may be an effective method for the remediation of asbestos wastes due to the apparent destruction of chrysotile by combined heat treatment and direct carbonation (Doucet., 2011). Figure 18 shows the various asbestos deposit localities in Southern Africa.

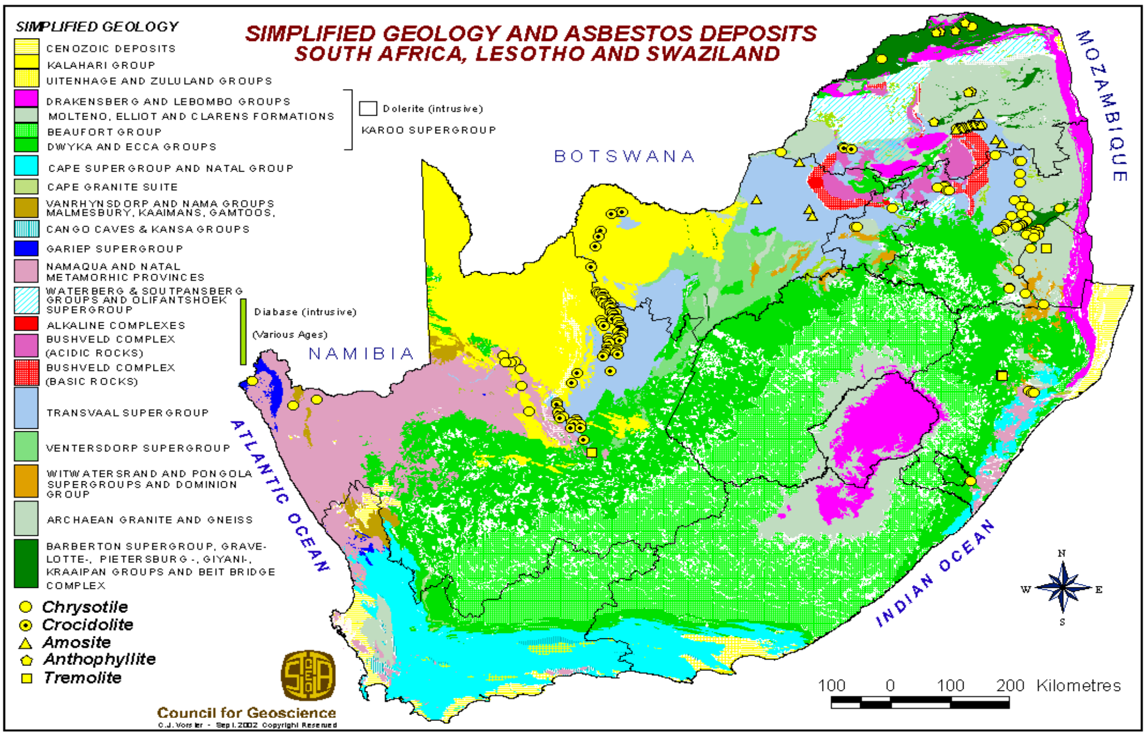


Figure 20: Asbestos Deposits in Southern Africa (GGS., 2011)

3.4.2 *In Situ* Carbonation

In situ mineral carbonation involves a direct injection of CO_2 into host rocks underground, without moving any rock material. It thus eliminates the need for transport of reactants in and end products out. It may also provide heat to accelerate the carbonation process (Oelkers *et al.*, 2008), as the mineral reactions are exothermic.

In CO_2 underground geologic sequestration, the final CO_2 fixation stage after very long times is in fact, *in situ* mineralization, as depicted by the progression over time of the various trapping mechanisms in Figure 7 of Chapter 2. Therefore, studies into mineral carbonation are mostly carried out as part of the research into the long-term consequences of geological CO_2 storage.

3.4.2.1 Host Rocks

The choice of the host rocks for in situ carbonation is of critical importance as these must contain the metal cations that are easily dissolved as well as appropriate permeability and pore volume to store the CO_2 and the product minerals of the carbonation process.

There are numerous locations in the world where large deposits of suitable mineral, usually Mg silicates (serpentine, olivine) but sometimes also Ca silicates (wollastonite) are available (which exceed the number of locations where underground CO_2 sequestration is viable) (Zevenhoven *et al.*, 2011).

Examples are found in Finland, the east coast of Australia, Portugal, and regions at the west coast of the USA (Krevor *et al.*, 2009) and Canada, as well as Oman on the Arabian Peninsula where one single deposit of olivine-containing rock is said to be able to sequester all the CO_2 that might be produced from combusting all of the coal on Earth (Lackner and Ziock., 2000; Keleman and Matter., 2008). Below is given a brief list and description of potential host rocks.

1. Sedimentary rocks (sandstones and shales): Deep aquifers in sedimentary basins are regarded as the most promising CO_2 storage sites because of their large storage capacity due to in pore space, high permeability and geographic extent. However, the dominant rocks in sedimentary basins are sandstone, siltstone, shale and limestone, which generally contain minor quantities of basic silicate minerals (Xu *et al.,* 2004).

Mineral trapping simulation of two sandstones and a peridotite made by Xu *et al.* (2004) showed that the sandstones would be almost completely carbonated in 60 000years with total CO_2 uptake being 17 kg/m3 and 90 kg/m3 for each of the sandstones. After only 1000 years the CO_2 uptake in peridotite is predicted to be about 100 kg/m^3. Models that predict limited mineral carbonation in sedimentary rocks, are complimented by field observations (Matter and Keleman., 2009).

It has been estimated that over 5000 years, all the CO_2 injected into the Weyburn Oil Field will dissolve or be converted to carbonate minerals within the storage formation (Perkins *et al.*, 2005). They also demonstrated that the caprock and overlying rock formations have an even greater capacity for mineralization. These clastic sedimentary rocks rich in alkalis have the capacity to buffer pH and to enhance CO_2 storage via solubility trapping (Gunter *et al.,* 2000).

The degree to which *in situ* CO_2 mineralisation is possible in sandstones and sandstone-shale sequences has been tested by means of reaction–transport calculations by Xu *et al.* (2005). These calculations suggest that minerals such as dawsonite ($NaAl(CO_3)(OH)_2$) and iron bearing carbonates can form but the composition of the host rock and, in particular, the presence of Fe_2 - bearing minerals such as chlorite, is important. However, these reactions appear to be relatively slow due to sluggish silicate dissolution rates (Xu *et al.,* 2005). Mineral carbonation in such rocks could require 100,000 years or more to produce 90 kg of carbonate minerals per cubic metre of sandstone, if sufficient Al, Na and Fe are present in the rock (Oelkers *et al.*, 2008).

2. Oil/Gas rich Shale: Shales are typically composed of variable amounts of clay minerals and quartz grains. The transformation of the clay minerals smectite to illite produces SiO_2; Na,; Ca; Mg; Fe; and H_2O. These result in the formation of authigenic quartz, and minor minerals such as chert; calcite; dolomite; ankerite; hematite; and albite (Harvey and Tracy., 1996). The average weight percent of the various shale constituents are typically 59% clay mineral; 20% quartz and chert; 8% feldspars; 7% carbonates; 3% Fe oxides, 1% organic matter and 2% trace minerals (Yaalon, D.H., 1961).

Deposits of oil or gas shale or organic-rich shale occur in many parts of the world. One such example is the gas shales of the Karoo that are under investigation at present in South Africa. However, the trapping mechanism for oil /gas shale is CO_2 adsorption similar to coal beds, rather than mineral carbonation. Adsorption has been has been observed in batch and column experiments in the laboratory, as well as in field experiments at the Fenn Big Valley, Canada and the San Juan Basin, USA (IPCC., 2005).

Carbon dioxide-enhanced shale-gas production such as ECBM for example, has the potential to reduce storage costs. The potential for storage of CO_2 in oil or gas shale is currently unknown, but the large volumes of shale suggest that storage capacity may be significant. Volumes could be limited, though, if minimum depth is defined and used as a site criteria and the low permeability of these shales may only allow for small volumes of CO_2 to be injected.

In the South African context, the Technical Report on geological CO_2 storage (Viljoen *et al*., 2010), makes note of shale which provides an adsorption substrate for CO_2 similar to coal seams, but it has low permeability.

3. Mafic and Ultramafic rocks (basalt and peridotite) : Enormous volumes of mafic and ultramafic rocks are present on the Earth's surface. These large volumes have a correspondingly large CO_2 sequestration capacity (McGrail *et al.,* 2006).

There is diverse evidence demonstrating the potential of CO_2 sequestration in mafic and ultramafic rocks as reactions proved far more effective in basalts or ultramafics (McGrail *et al*., 2006; Matter *et al*., 2007). Important applications for *in situ* carbonation are found for example in Iceland (Oelkers *et al.,* 2008) where the host rock is basalt, and Oman, where the CO_2 is injected into peridotite (Kelemen and Matter., 2008).

Compared with basalt, ultramafic rocks such as peridotite probably have lower porosity and permeability, dominated by fissures in the weathered upper ~50 m and fractures in the deeper subsurface (Dewandel., 2005). Peridotite contains 40–50 wt% MgO, CaO and FeO combined, compared with 20–25 wt% in basalt (Matter and Keleman., 2009).

Mg-rich compositions of the mineral olivine (Mg-end member, forsterite), which forms 60–95% of peridotite, dissolve and react more rapidly than the dominant compositional type of plagioclase (labradorite) that forms 50–70% of crystalline basalt. Studies on crystalline basalt which contain about 60% plagioclase with 40% olivine and pyroxene, showed higher rates than for the plagioclase, and moreover, basalt glass dissolves 10 to 1000 times faster than crystalline basalt (Wolff-Boenisch *et al.,* 2006). This makes for compelling evidence of basalt suitability for CO_2 storage. However more kinetic studies and field characterisation of basalts is required. The carbonation of peridotite is known to be exothermic, while the thermodynamics in basalt is unclear and is probably at slower flow rates and higher temperature owing to slower reaction and smaller enthalpy changes (Matter and Keleman., 2009).

In basalt, CO_2 takes up ~33% of all the CO_2 consumed during natural weathering of Earth's surface silicates (Dessert *et al*, 2003).

The flux of Mg and Ca liberated when CO_2 -rich water reacts with basalt is more than twice the flux than when they react with other, more crystalline or silica-rich rocks (Wolff-Boenisch *et al.*, 2006).

Several well-documented examples of carbonation of basaltic rocks are known, such as through hydrothermal alteration (Gudmundsson and Arnórsson , 2002) and surface weathering (Gislason and Eugster., 1987; Gislason et al., 1996; Gislason *et al.*, 2006).

Worth noting that in the Barberton Greenstone belt, the Weltevreden Formation is said to be made up of komatiites (ultramafic mantle derived volcanic rock) with an extremely high Mg content (34%MgO). This could prove a lucrative feedstock for mineral carbonation purposes.

Basalt is one of the most common rock types in the world. It makes up most of the world's oceanic crust but also reaches the earth's surface as lava flows. Many lava flows are porous and permeable and have enormous storage capacity.

Basalt is variable in composition with the common minerals typically being plagioclase feldspar, pyroxene, olivine, magnetite and ilmenite. On average the typical composition of a basalt is 45-55wt% SiO_2; 14wt% Al_2O_3; 5-14wt% FeO; 10wt% CaO; 5-12wt% MgO; and 0.5-2.0wt% TiO_2 (Hofmann., 2003).

As they dominate the seafloor, they provide vast *in situ* carbon-mineralization sites throughout the world (Goldberg *et al.*, 2008). Storage in basalts, therefore, is now considered to be among the best of the options for sequestering CO_2 (O'Connor *et al.*, 2003).

The locations of some of the world's major continental basalts are shown in Figure 21.

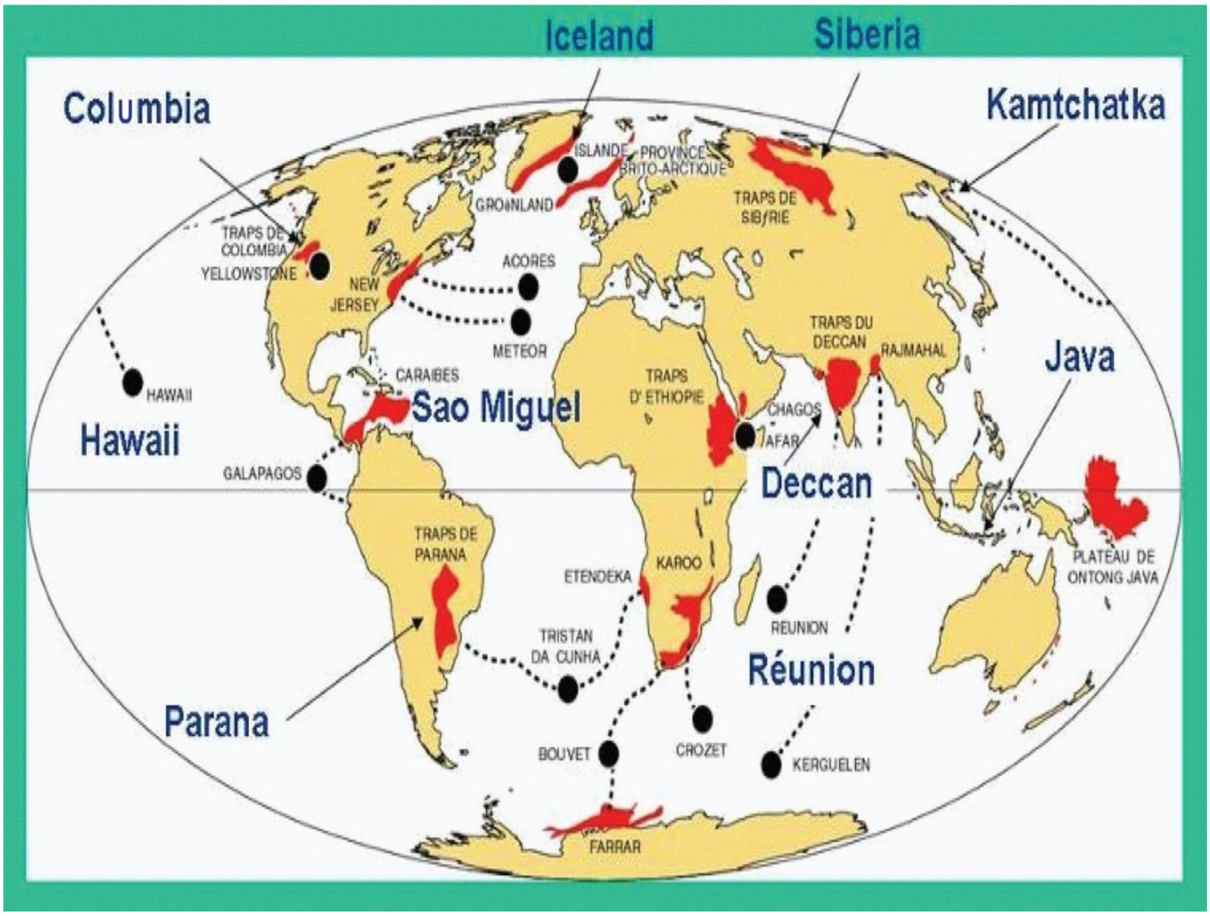


Figure 21: Extent of Global Continental Basalt Sheets (Matter., 2008)

Further insight into *in situ* mineral carbonation in basalts and ultramafic rocks comes from the results of reactive transport modelling. Marini. (2007) simulated the interaction of injected CO_2 with a number of potential host rocks. For the dissolution of basaltic glass by carbonated water, the formation of chalcedony (SiO_2), goethite (FeOOH) and clay mineral, kaolinite, are the products.

The Marnini model suggests that after approximately a year, siderite precipitates, followed by dolomite, dawsonite and magnesite. Substantial CO_2 mineralization is evident after 10–100 years of reaction.

The volume of these secondary phases is much larger than that of the basaltic glass that was initially dissolved to produce them, leading to the potential of these phases to block pore spaces available and, also to substantially decrease the permeability of the host rock (Gysi and Stefánsson., 2008).

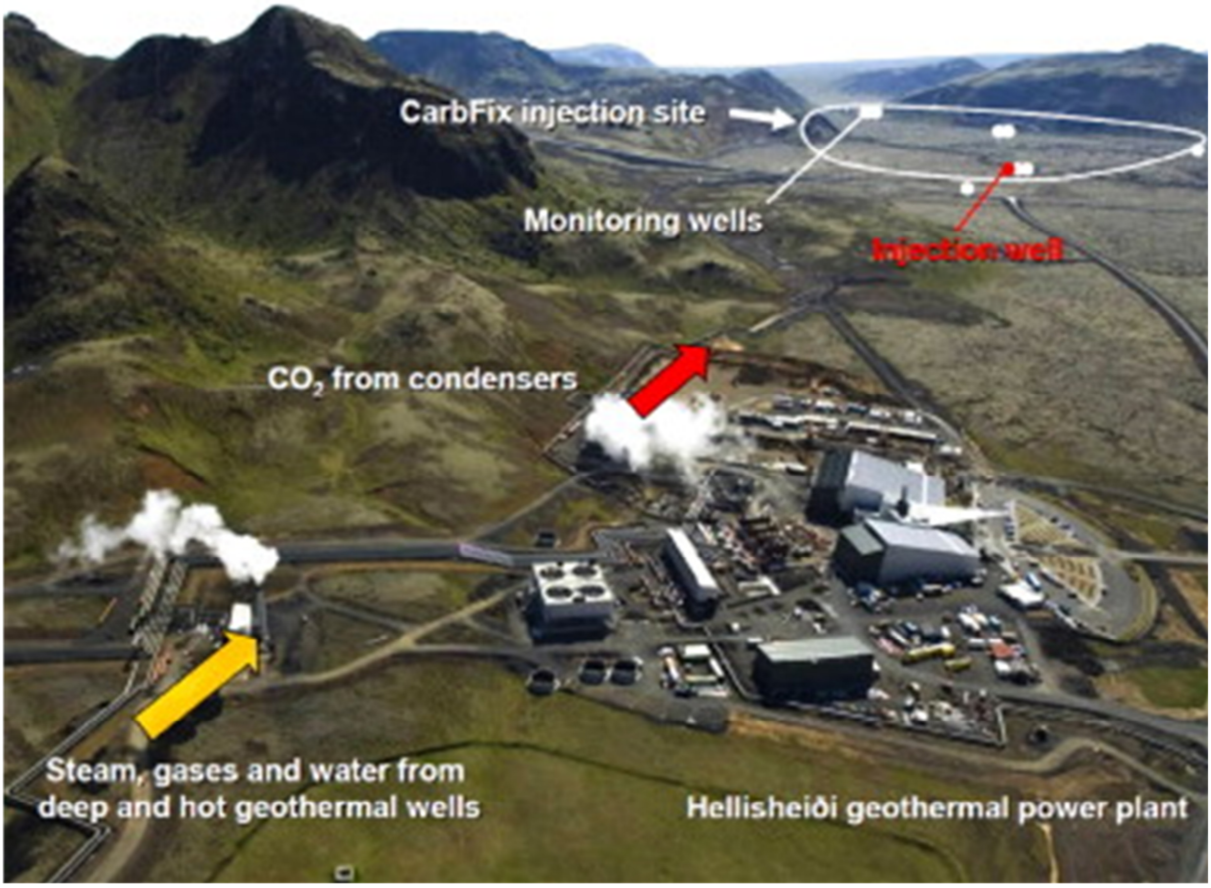


Figure 22: Aerial Photograph of Iceland's Hellisheidi Geothermal Power Plant showing Condensers which emit +30,000 tons/year of CO_2 and the CarbFix In Situ Carbonation Site in the background showing an Injection and Several Monitoring Wells (Gislason et al., 2010)

Research has been done into basalts at Hellisheidi Iceland to store CO_2 from a geothermal powerplant as solid calcium carbonate mineral in basaltic rock (Carbfix). Known as the Carbfix Project (see Figure 22), it is a field-scale project. It is an attempt to assess the feasibility of *in situ* CO_2 mineralization in basaltic rocks. CarbFix was scheduled to commence carbon injection in October 2011 at Hellisheidi, Iceland. The injection site, shown in the figure above, is adjacent to a new geothermal power plant that has 30 wells tapping into superheated steam laden with CO_2 and hydrogen sulphide (H_2S). On separation of the gases, up to 30,000 tons of CO_2 per year will be supplied for injection into subsurface basalts at a depth of 400–700 m and a temperature of about 30°C. The Hellisheidi site was chosen for a number of reasons, including a local source of CO_2, the availability of several strategically located wells for monitoring the chemical evolution of the groundwater, and the proximity to infrastructure through Reykjavik Energy, a CarbFix partner and public utility supplying the Icelandic people with electricity (Carbfix., 2011). CO_2 will be injected at a partial pressure of 25 bars and will be dissolved in water during injection. It is anticipated that the results of this project will be used to optimize the *in situ* carbon mineralization process, enabling *in situ* carbonation at sites throughout the world, and researchers hope that the technology used will be exported to other basaltic terrains (Oelkers *et al.*, 2008).

3.4.2.2 Challenges for In Situ Mineral Carbonation

The challenges facing *in situ* carbon mineralisation are:

i) *Availability of water for carbonation*: one tonne of CO_2 at 25 bars partial pressure and 25℃, requires approximately 27 tonnes of water for dissolution. This quantity increases to ~341 tonnes of water at a CO_2 partial pressure of 2 bars (Oelkers *et* al., 2008). Water is a precious commodity in South Africa and so poses a huge problem in this regard.

Direct injection of CO_2 may overcome the difficulty of finding sufficient water, but injected as a separate phase, CO_2 must dissolve into the groundwater before carbonation can begin. CO_2 diffusion into groundwater can be a slow process, depending on system hydrology and the chemical composition of the groundwater.

ii) *Impermeable cap rocks*: as both CO_2 dissolution into groundwater and coupled mineral dissolution, precipitation reactions leading to carbon mineralization may be slow, an impermeable cap rock is essential to keep the dissolved CO_2 in contact with the reactive host rock for sufficient time to allow carbonation. Cap rocks are common in oilfield reservoirs but may be missing over a basalt or ultramafic formation. A further complication is that these rock types are commonly fractured. The permeability of the cap rock itself may be altered by its reactions with the injected CO_2, leading to leaks in the originally impermeable barrier (Gaus *et al.*, 2005). In South Africa extensive mapping of basal terrains is imperative for sealing purposes.

iii) *Possible mobilization of trace and toxic metals*: The dissolution of CO_2 into water produces carbonic acid, which reacts with the host rocks to liberate the cations necessary to create carbonate minerals. These reactions may also release trace and toxic metals into solution, allowing them to migrate. The degree to which these metals move with the formation water depends on the hydrology and chemistry of the system (Oelkers *et al.,* 2008). Extensive geochemical and hydrological monitoring would be required in South Africa.

3.4.2.3 In Situ Mineral Carbonation in South Africa

The 2010 Technical Report on geological storage of CO_2 in South Africa (Viljoen *et al.,* 2010) did not give basalts much focus but attests that mineral carbonation is an option for further research.

Figure 19 illustrates the dolerite sediment ratio for South African sedimentary basins. The 2010 report makes note of shale which provides a substrate for CO_2 similar to coal seams, but it has low permeability. The dolerites, however, increase secondary porosity in baked shales which may increase capacity of CO_2 storage in the shales. However it can decrease the CO_2 potential of sandstones (Viljoen *et al.,* 2010) because heat induced chemical reactions in the sandstones can result in decrease in porosity and permeability of these rocks. As the target for geological storage is saline aquifers or sandstones with shale seals or cap rocks, the dolerites pose advantages and disadvantages.

The Doucet Scoping report (Doucet., 2011) suggested detailed mapping and evaluation of basaltic and andesitic rocks for in situ carbonation. Viljoen *et al.* (2010) further suggests an assessment of the Lebombo Group basalts in the Somkele/Lebombo area of KwaZulu Natal, where the CO_2 storage may be possible at the base of the basalts, or in the basalts themselves (which in places is more than 3000m thick) (Viljoen *et al*., 2010). It has the added advantage of being close to a point source of CO_2 emissions (see Figure 14).

Below is a brief description of the geological setting of the Lebombo Group basalts and the underlying Stormberg Sandstones.

Figure 23 is a simplified and geological map of the KwaZulu Natal area and surrounds showing the Lebombo Group Basalts.

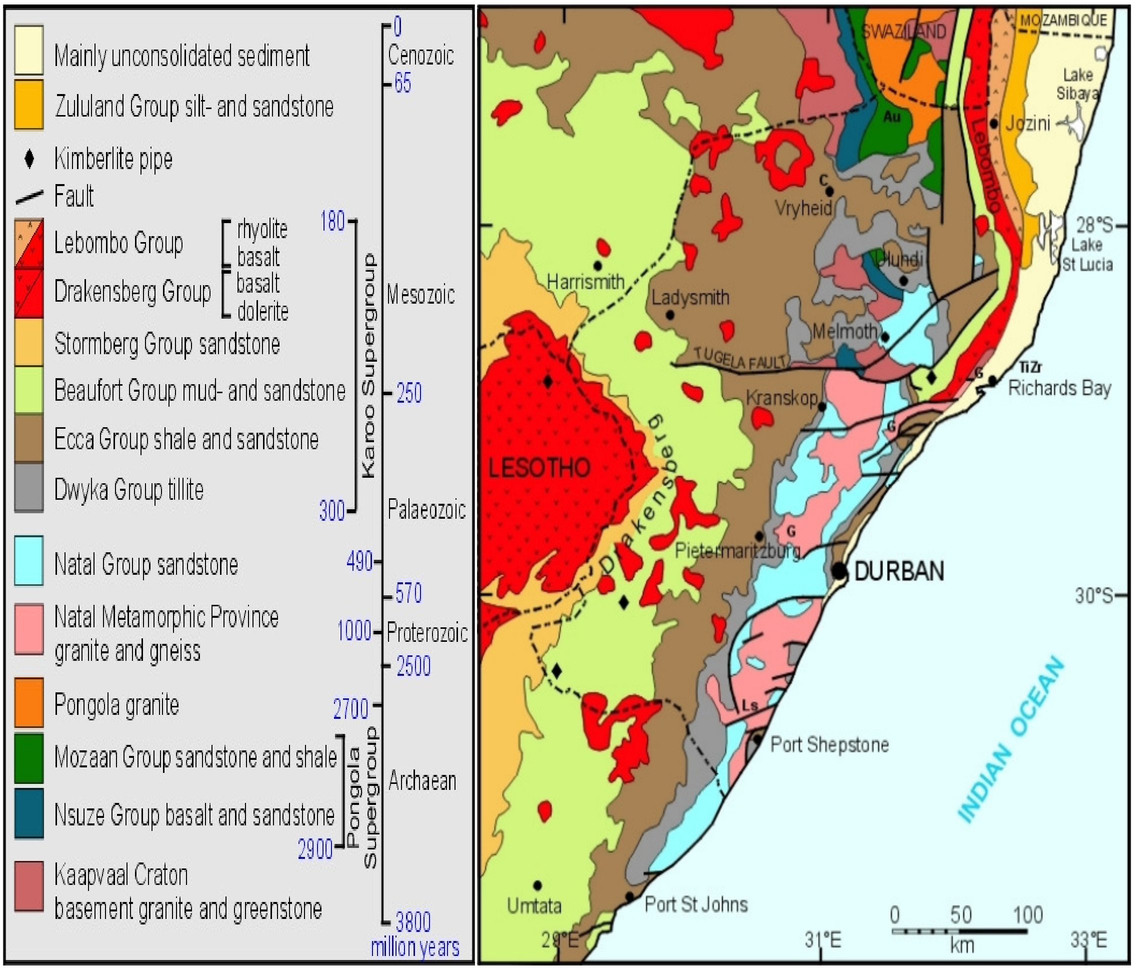


Figure 23: Simplified Geology of the Kwa Zulu Natal Area (CGS., 2011)

The oldest rocks in Kwazulu/Natal can be subdivided into two major groups. In the northern part of the province outcrops form part of the Archaean Kaapvaal Craton (+3 500Ma) and hosts numerous minor gold occurrences. In the south, the oldest rocks forming the basement are about 2000Ma with poorly exposed outcrops. These rocks have been subdivided into three distinct Terranes based on geological characteristics (Whitmore *et al*., (2006).

In the Tugela Valley, the rocks of the Tugela Terrane are in tectonic contact with the Archaean rocks. Due to the rugged topography and inaccessible nature of the remote parts of this northern Terrane, there has been sporadic exploration for new deposits in this area but there is potential for finding new orebodies. The basement is overlain by the Ordovician-Silurian aged sandstones of the Natal Group in the east, as well as by the younger Carboniferous to Jurassic sediments and volcanics of the Karoo Supergroup, which host much of the industrial mineral deposits.

The Stormberg Group is subdivided into three formations.

Sandstone of the lowermost Molteno Formation was formed by rivers in a wet environment. These are now exposed as small cliffs in the lower Drakensberg.

The Molteno Formation is in turn overlain by red mudstone of the Elliot Formation.

The overhanging white cliffs of the middle Drakensberg are composed of Clarens Formation sandstone. These sandstones were deposited as large dunes in a desert environment and preserve large internal bedding structures called crossbeds. They may be considered a viable CO_2 geological storage site (Viljoen *et al.*, 2010).

Overlying these sequences are the basalt flows of the Lebombo Group.

Numerous lava flows signified the Gondwana breakup (180Ma). Following this breakup, a period of unique igneous activity formed numerous volcanoes of kimberlite rock, commonly known to contain diamonds. The kimberlite pipes of KwaZulu-Natal have not yielded any significant diamonds (Whitmore *et al.,* 2006).

Figure 24 shows a sketch of a KZN kimberlite pipe. Carbon crystallises to form diamond under high pressure and low temperature - conditions only found beneath the Kaapvaal Craton, such as in northern Lesotho.

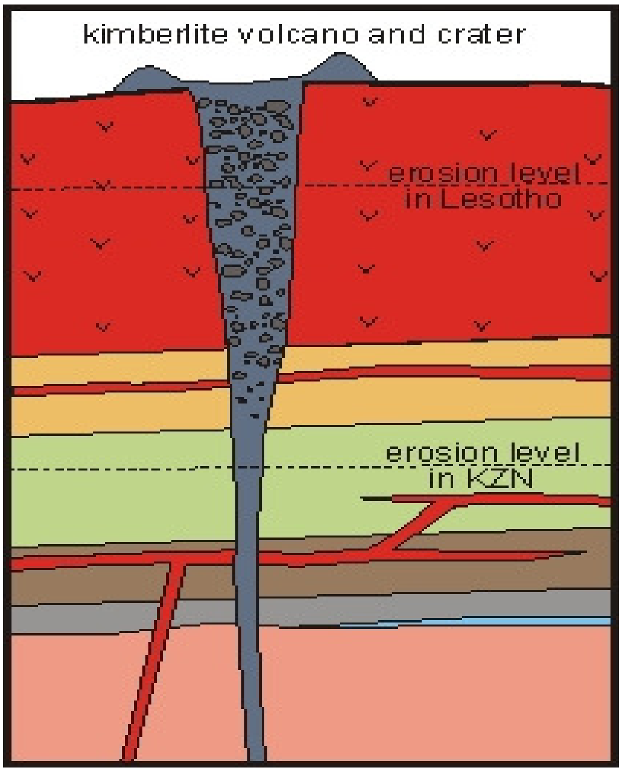


Figure 24: Schematic of the Kimberlites found in Kwa Zulu Natal (Whitmore et al., 2006)

Remnants of the once extensive lavas now form the Lesotho highlands and Lebombo mountains. Jurassic age basalt flows can be seen along the Drakensberg Escarpment (Figure 25).

Figure 25: Visual Depiction of the Drakensberg Mountainsand Stormberg Sandstone. (Whitmore et al., 2006)

Dolerite sills and plugs are common throughout inland KZN, having intruded into the sedimentary rocks of the Karoo Supergroup.

Figure 26 shows one such sill extending diagonally from top left of the picture to the bottom right.

Figure 26: Drakensberg Basalt intruded by Dolerite (Whitmore et al., 2006)

The final volcanic event produced rhyolite lava which now forms the Lebombo mountains as shown by Figure 27. These volcanic events were followed by uplift and faulting that eventually separated Africa and Antarctica.

Figure 27: Visual Extent of the Lebombo Group Basalt and Rhyolite (Whitmore et al., 2006)

A geochemical study of approximately 950 analyses of Karoo Basalt series was conducted pre 1996, showed that bulk samples of the Lebombo basalts to be potassic (Geokem., 2006).

Since then much study has been conducted on these rocks. Sweeny *et al.* (1997) identified three basalt rock types in the Central Lebombo of the Karoo Igneous Province. Duncan *et al*. (1997) found the Karoo eruptions to consist predominantly of tholeiitic basalts, while the rhyolites of the Jozini and Mbuluzi and Oribi Beds of the southern Lebombo Monocline, have been found to exhibit low H_2O contents, according to a study by Miller and Harris. (2006).

These amongst other studies point to much complexities in the Lebombo rocks with respect to composition and mantle crustal geodynamics.

Much research and analysis is needed to understand the make-up of these rocks as well as detailed mapping of the Lebombo suite to validate their suitability for *in situ* mineral carbonation.

3.5 Summary

Mineralization of CO_2 is gaining more and more ground as an important CCS method that provides an alternative for CO_2 storage in underground formations. The method offers leakage-free CO_2 storage, the benefit of thermodynamics and energy economy, and more-than-sufficient suitable mineral resources available worldwide. However, despite successes with carbonation of residues and promising process ideas for the carbonation of rock material, so far no concept for carbonation of natural minerals has matured into implementation on a large scale (say, more than 1 Mt/year) as compared with underground sequestration of CO_2 (the Sleipner project for example). However, recent and current developments and trends indicate rapid changes and stronger support for promising concepts. CO_2 mineralization applications, where a clear view exists on what to do with the products of the process, seem most viable.

Currently, both *ex situ* and *in situ* mineral carbonation processes are still under development, with indirect processes offering the benefits of faster chemical kinetics and better product quality (Zevenoven *et al*., 2011).

Many challenges in mineral carbonation must be resolved:

i) overcoming the slow kinetics of mineral–fluid reactions

ii) dealing with the large volume of source material required

iii) reducing the energy consumed to induce reactions

iv) little progress has been made when it comes to the recovery and recycling of additives

Even though both process routes exhibit reactions that are thermodynamically favoured, investigations into increasing and optimising the reaction rate of the mineral-fluid kinetics, requires much more research. Research into reduction of energy consumption and costs of the process also requires attention for it to be economically viable. Compared with other sequestration options, mineral carbonation has the advantage of being the longer term option and its theoretically vast capacity (Huijgen and Comans., 2003). Nevertheless the advantages of mineral carbonation as described earlier in this chapter, indicates that CO_2 mineralisation could play a significant role in risk mitigation strategies for CCS activities in South Africa.

The state of the art ARC process has given much in terms of ranking the minerals olivine, serpentine and wollastonite as well as ways to reduce costs speeding up the reaction process.

Both olivine and serpentine are attractive mineral reactants for mineral sequestration because of their vast reserves and relatively high Mg content.

There are significant problems with using serpentine for carbon sequestration.

- More serpentine needed to sequester the same amount of CO_2 than olivine. Considerably more serpentine would have to be mined to sequester the same amount of CO_2
- Untreated serpentine does not react to any significant extent. Even finely ground serpentine reaches only approximately 10% carbonation in an hour.
- At present, two solutions, both expensive, have been found to this problem: heat treatment and high-energy attrition grinding.

Some method must be found to speed up the carbonation of serpentine without heat treatment. Olivine requires no heat treatment but is less common than serpentine.

There is however, enough olivine that it could represent regional solution needs even though serpentine is more prevalent than olivine.

The particle size for the wollastonite does not have to be as fine as for olivine or serpentine, so it seems that wollastonite is more reactive than olivine or serpentine. Less work has been done on wollastonite, but it appears to offer the same advantages and disadvantages as olivine. Wollastonite is probably more reactive than olivine, but is only prevalent enough to represent a more localised solution in South Africa with respect to its CO_2 emissions, until more deposits are found.

A lot of research and development effort during the last decade has focused on methods of extracting Mg or Ca from minerals or industrial by-products and wastes using strong or weak acids, or alkali solutions. This could lower the energy needs for crushing and grinding, but using chemicals that cannot be completely recovered and re-used may lead to deteriorating process economics. Nevertheless, the ARC process is very useful as a reference for assessment of other methods (Zevenhoven *et al.*, 2011).

Both basalt and peridotite prove their suitability for mineral carbonation, although basalt would be more suited to *in situ* carbonation and peridotite to *ex situ* carbonation with feedstock coming from the vast number of mine tailings available.

Large quantities of kimberlite and dolerite are also readily available as feedstock for carbonation purposes (Doucet, 2011).

Sedimentary sequences are more suited for geological CO_2 storage. However the end result is mineral carbonation in these rocks as well.

Shales are less permeable and are best suited as sealing and cap rocks. However in certain instances, such as the shale gas in the Karoo, adsorption rather than mineral trapping is the choice of mechanism to be considered.

The dolerite intrusions pose a ‘double edged sword’ in that they may increase secondary porosity in baked shales which may increase capacity of CO_2 storage in the shales but it can decrease the CO_2 potential of sandstones as the heat of reactions reduce permeability and porosity of these sediments. Where dolerites are in close proximity to shales and sandstones, detailed investigations of the dolerites, including fine comb mapping, are necessary, to make these sediments viable options for mineral carbonation.

The Lebombo Rocks are complex in their geochemical makeup and a lot more research is required to consider it viable for mineral carbonation. It is attractive as it is close to a point source. The underlying Stormberg Sandstone is a viable geological storage site with the added advantage of the basalts above it in the event of leakage and upward movement of CO_2, trapping by mineral trapping mechanism in the basalt is plausible.

The non-diamond bearing kimberlites in KwaZulu Natal need investigation, for localised CO_2 storage.

Chapter 4 Experimental Work

This section forms Phase Two of the research project: experimental work and describes the various laboratory experiments and tests undertaken. It describes the methodology employed to establish these experimental set-ups, techniques, and processes in order to obtain data to support studies on mineral carbonation.

4.1 Methodology Overview

Two experiments, each with different procedures and conditions, were followed on an igneous alkaline-rich rock (basalt) as well as a sedimentary rock (shale) for comparative purposes. These were:

1) Supercritical (SP) CO_2 conditions (CO_2 at pressure (P) =/> 73.8 bar and temperature (T) =/> 31ºC): whereby a storage reactor was utilised to treat each rock sample with SP CO_2, for a period of about thirty days, to test if carbonation of silicate minerals occurred. The samples were characterised before and after exposure.

2) Subcritical (SB) and SP Conditions: utilising a high pressure volumetric adsorption system (VAS). Each pulverised rock sample was subjected to sorption tests, using the VAS, housed in the Wits Coal and Carbon Research Laboratory. In this experiment also, samples were subjected to post VAS characterisation.

At the outset, it was recognized that:

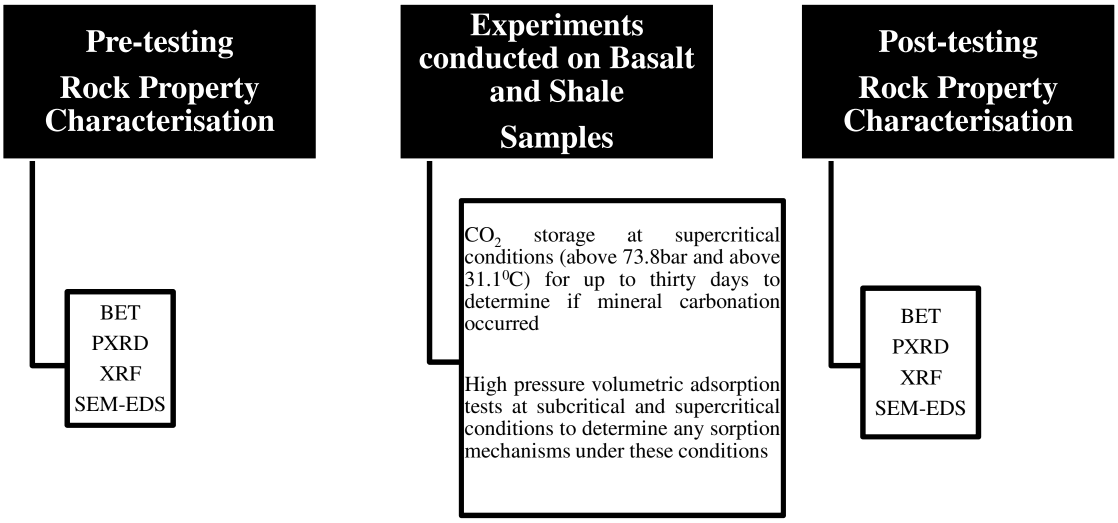
1. Thirty days may not be sufficient for any detectable carbonation reactions to occur. However, the demand for use of the storage reactors by other higher level researchers for PhD work, could not allow longer duration of the experiment.

2. The VAS had been developed to determine adsorption isotherms on coal samples and until recently, ash samples. So it was unclear what results the sorption tests on rock samples would yield. These results would be tested for

their validity on the basalt and shale samples, and the resulting isotherms and information thereof compared, to that of a coal and an ash which had been subjected to similar tests.

However, it was hoped that results from both of these different experiments would afford insight into techniques and processes for future in-depth and detailed mineral carbonation and other sorption studies of rocks, at Wits in the future.

Figure 28 below schematically illustrates the characterization, and experimental procedures carried out on both rock samples.



CO_2 storage at supercritical conditions (above 73.8bar and above 31.1^{0}C) for up to thirty days to determine if mineral carbonation occurred

High pressure volumetric adsorption tests at subcritical and supercritical conditions to determine any sorption mechanisms under these conditions

Figure 28: Schematic of Procedures Conducted in the CO_2 Sorption Experiments

4.2 Materials and Sample Preparation

4.2.1 Materials

The materials used were two local rock types namely: an igneous alkaline rich silicate rock – termed basalt and a sedimentary rock – termed shale (Figure 29a and c). These rocks were provided courtesy of Wits Geosciences Environmental Earth Sciences and Palaeobotany departments respectively.

CO_2 was used in liquid form from a dip tube cylinder.

4.2.2 Sample Preparation

The rock samples were too hard and large to be milled using the using the School's in-house centrifugal mill, which can only crush particles of about 2 mm in size. The rocks were sent to the Department of Metallurgical Engineering at the University of Johannesburg, Doorenfontein Campus, where crushers can handle particle sizes greater 10 mm. Both the basalt and shale sample were crushed to powder form (Figure 29b and d). The samples were stored in 250 ml screw top jars and flushed with N_2 to suppress any possible reactions of the pulverised samples with air.

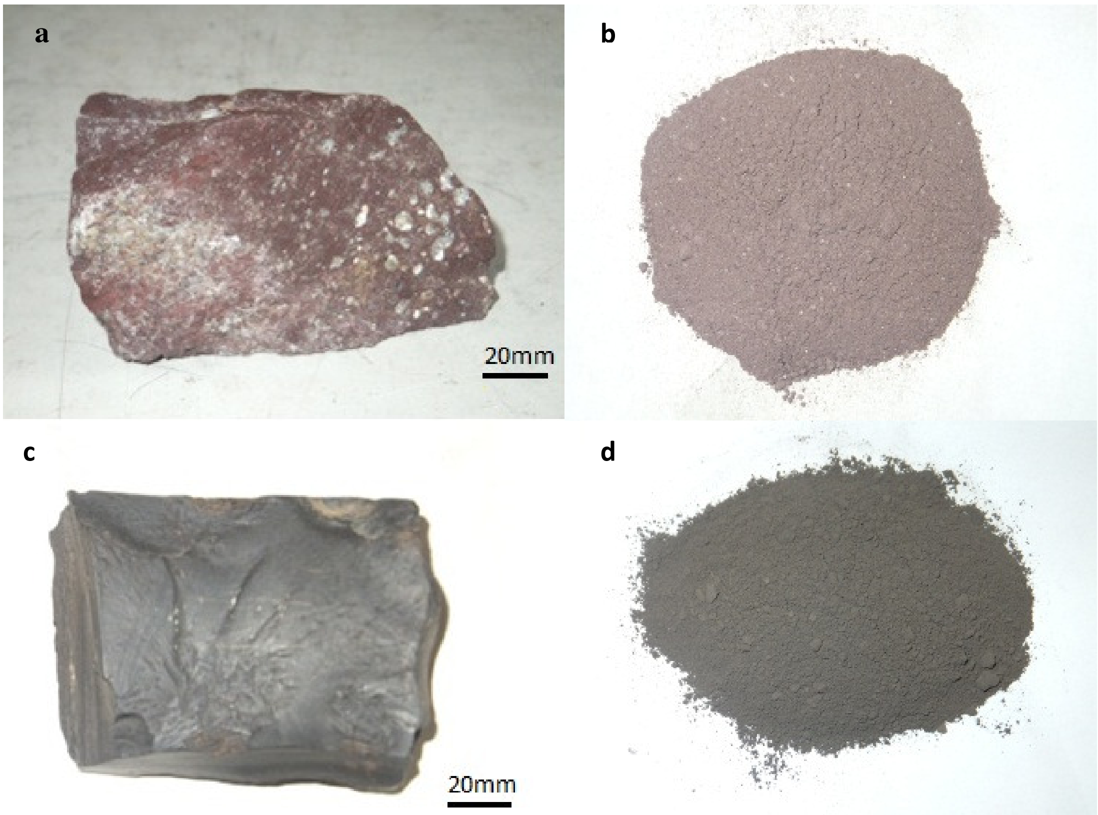


Figure 29: Rock Samples Whole and Pulverised: Basalt (a, b) and Shale (c, d) respectively

4.3 Experiments

4.3.1 Supercritical Storage Reactor

Each rock type was placed in a storage reactor for a period of four weeks each (Figure 30). An air dried sample of 10 grams of each rock type was used.

The samples in the reactor were first saturated with liquid CO_2 using the Teledyne Isco Pump shown in Figure 32a. The reactor was unplugged and placed in the thermal jacket.

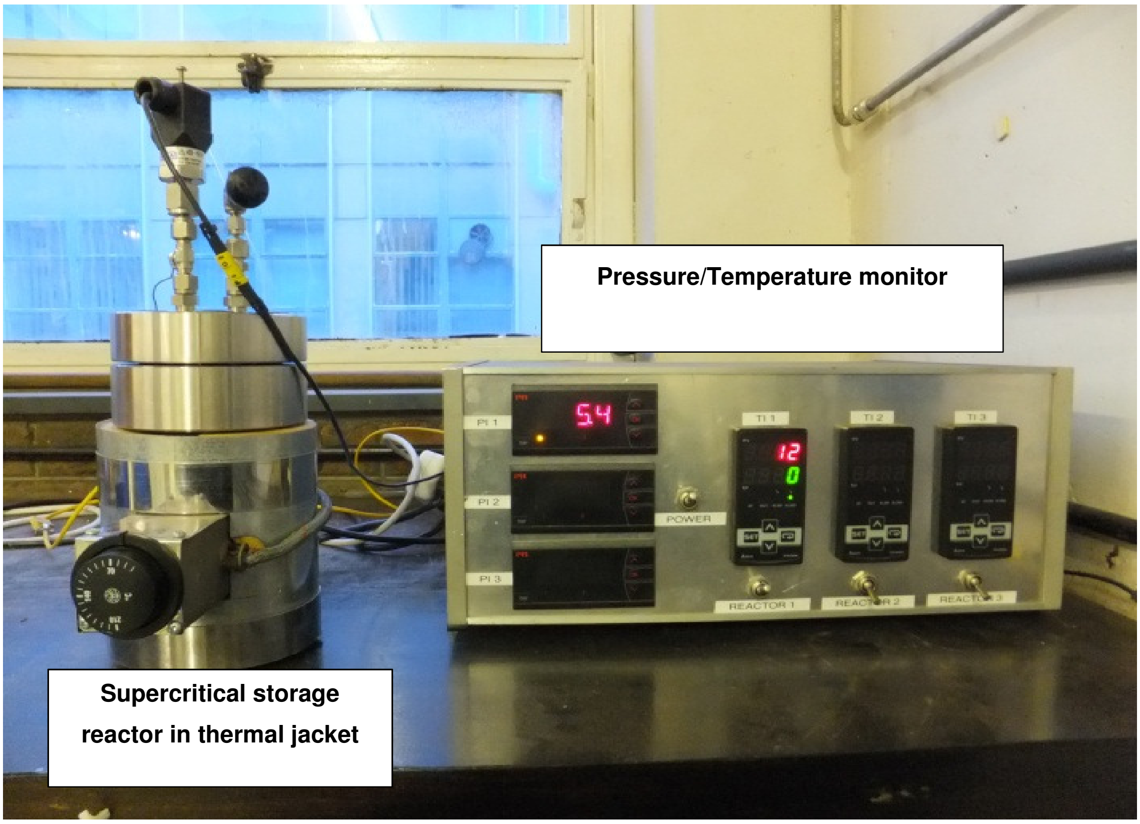


Figure 30: CO_2 Storage Reactor with Thermal Jacket connected to Pressure/Temperature Monitor (Note: Pressure and Temperature not at Supercritical at time of picture)

4.3.1.1 Procedure

Storage in the reactor was conducted under supercritical conditions (over 73.8 bars and at 31.1°C). These conditions are graphically explained by the phase diagram for CO_2 depicted in Figure 31. The supercritical phase is favoured for CO_2 injection because it has the unique physical property intermediate between gas and liquid phase (Kirk-Othmer., 1991).

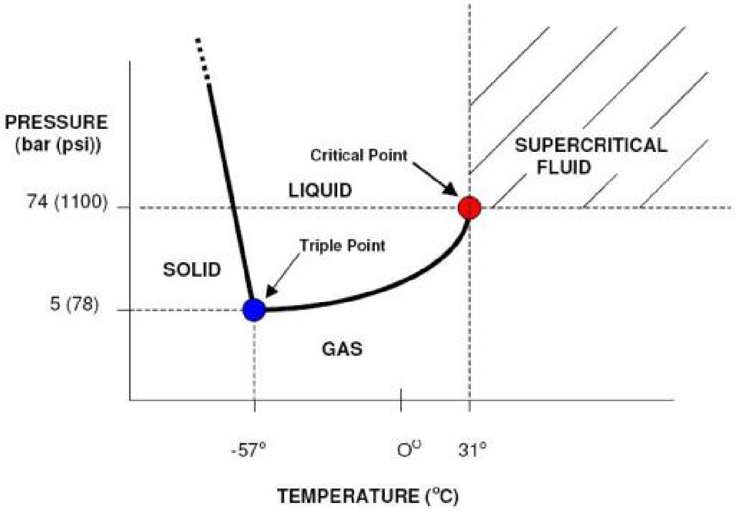


Figure 31: Phase Diagram showing Temperature and Pressure Values of Pure CO_2 (Langley., 2011)

The supercritical temperature and pressure values for each rock sample were recorded by the display unit and noted by the researcher on every alternate day during the month or so long duration of the experiment, to make sure that supercritical conditions were being maintained. After the thirty day period, each rock was then analysed by various means as described in Figure 28. These results are discussed in Chapter 5.

4.3.2 High Pressure Volumetric Adsorption System (VAS)

Figure 32 shows the VAS equipment as housed in the Wits Coal and Carbon Research Laboratory. The VAS is used to establish volumes of CO_2 fixated onto coal and ash. This secondary exercise is a first attempt using this VAS equipment to explore CO_2 sorption, if any, onto rock samples. The results are to be compared with that of the primary mineral carbonation experiment using the supercritical reactor, detailed above in Section 4.3.1.

Detailed descriptions of the equipment and it operation are found in Kholumo (2012) and Maphada (2012) and within the scope of this research, will only be briefly described here.

The VAS consists of an adsorption chamber and gas vessel linked by a tube with a valve. In order to ensure isothermal conditions during the experiment, the instrument was placed inside an air heated oven to keep the temperature constant during runs.

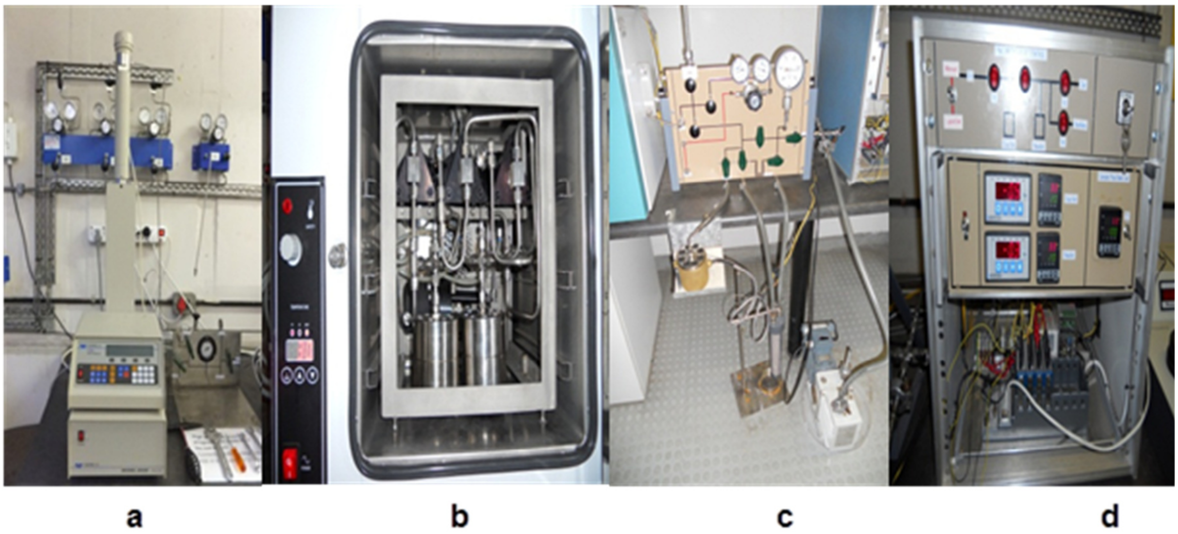


Figure 32: High Pressure VAS showing a) Teledyne Isco Pump; b) Oven Housing the Reference Cell and Sample Cell; c) Valves, Piping Equipment, Degassing Equipment and Vacuum Pump; d) Control Panel

Two grams of air dried sample was used at a time. The sample cell itself is a stainless steel electro-polished sample vessel, made to withstand the high pressures. The inside surfaces are electroplated to prevent adsorption onto the surfaces.

The samples were first degassed for just over an hour in order to remove any other gases if present, and to release pores in the sample particles. The volatiles and other gases were then sucked by a suction vacuum pump installed in the system. This degassing apparatus is shown in the lower portion (off the counter, on the floor) of Figure 32c.

4.3.2.1 Procedure

In the initial experiment, supercritical conditions could not be reached as the VAS system could not at that stage reach supercritical pressure. Two runs on the basalt and one on the shale were conducted at this stage as the leaks became too intense to continue with further runs. The isotherms for the runs conducted on the samples have been included in Appendix A, Figure A6 for the purpose of visual clarification.

At a later date, following intense and time consuming adjustments and calibrations to the system, conducted by members of the Wits Coal and Carbon Research team, the leaks could not be rectified; however, new seals for the reactors were designed and installed, to help reduce the leaks in the system. Supercritical pressures could be achieved and more runs at these conditions could be done.

Upon advisement, each sample was covered with about 0.035g of glass wool before bolting the reactor to prevent any powdered sample from blowing out of the reactor when CO_2 was introduced. This was done as a preventative measure as the powder could cause possible blockages of the valves in the VAS system.

Two further runs on each rock were completed, at a temperature of 32°C and pressures set from 20bar to 90bar, increasing in increments of 10bar at 2hour intervals. Blank runs were conducted both before and after the four runs to determine and compensate for the leak rates, and make adjustments to the adsorption isotherms obtained for each sample. It was assumed that leak rates of the two sample reactors used in the experiment, were the same as they are identical in construction.

The data acquisition is completely automated, using National instruments hardware, and Labview software to generate the algorithms describing sorption and to detect any leaks in the system.

This data is available in Appendix A.

An initial pressure of 20 bars was decided upon after taking into consideration that previous research on ash samples run on the equipment generally began to show sorption from about this pressure. It was assumed that the same would apply to both rocks because of their inorganic mineral constituents. It is noted by the researcher that shale has an appreciable amount of organic material; however the inorganic constituents in the rock would still be in larger proportion.

The volumes of CO_2 adsorbed were determined from the difference between the initial CO_2 pressure in the reference cell and the final pressure in the sample cell. Moles of CO_2 sorbed for each of the rock types were determined from the thermophysical properties of CO_2 using the NIST Standard (NIST Chemistry WebBook., 2013), for the particular temperature, and minimum and maximum pressure conditions recorded during the VAS experiments. The details of these calculations may be found in Table A1 of Appendix A.

4.3.2.2 Principle of Adsorption

This section follows through from the brief description of adsorption as a trapping mechanism described in Chapter 2 and it is found necessary to clarify particular terms associated with it.

Adsorption is defined as the concentration of gas molecules near the surface of a solid material. The adsorbed gas is called adsorbate and the solid where adsorption takes place is known as the adsorbent.

Adsorption takes place because of the presence of an intrinsic surface energy. When a material is exposed to a gas, an attractive force acts between the exposed surface of the solid and the gas molecules. The result of these forces (intermolecular forces such as Van der Waals forces are characterized as physical adsorption or physisorption (Saf Chem., 2012). The weak forces between the gas molecules and the surface make adsorption a reversible phenomenon. This is referred to as desorption.

This is in contrast to the stronger chemical attractions (valence forces such as those operating in the formation of chemical compounds) associated with chemisorption.

In literature there are several models describing the process of adsorption, of which the Freundlich isotherm, Langmuir isotherm, and Brunauer-Emmett-Teller (BET) isotherm are the best know.

Adsorption isotherms for the rock samples were determined from the data acquired from the VAS test. These are discussed in Chapter 5.

4.4 Sample Characterisation

The basalt and shale samples were characterised before and after both the SP reactor and VAS tests, so that any changes in the properties could be determined.

4.4.1 X-Ray Fluorescence (XRF)

X-ray fluorescence (XRF) is a non-destructive technique used for chemical analysis of materials. An X-ray source is used to irradiate the specimen and to cause the elements in the specimen to emit (or fluoresce) their characteristic X-rays. A detection system (wavelength dispersive) is used to measure the peaks of the emitted X-rays for qualitative/quantitative measurements of the elements and their amounts. These measurements are used to determine major and minor/trace elemental concentrations. XRF will give details as to the chemical composition of a sample but will not indicate what phases are present in the sample.

4.4.1.1 XRF Measurements

X-ray fluorescence analysis was used to indicate major and minor element concentrations of the initial rock samples as well as ash oxides, and again after experiments to determine any changes in the rocks' composition. XRF on original and SP CO_2 treated samples were overseen by UIS Analytical, in Centurion, Mid Rand. UIS is a SANAS (South African National Accreditation System) accredited laboratory, however the XRF method is not yet accredited. Below is a summary of the fusion method used, as described and supplied by UIS:

- A Thermo Scientific sequential XRF instrument with an Rh x-ray tube set at 50kV/50mA was used to perform the analysis.
- The samples received were dried at 110°C prior to performing a LOI at 1000°C.
- The roasted material was fused into a glass bead at approximately 1050°C in a 1:9 ratio with a 66:34 Litetraborate Limetaborate fluxing agent.
- The results obtained on the roasted (fully oxidized) material was back-calculated (using the LOI value) to the original sample on a dried basis.
- The XRF is calibrated with a range of certified reference materials with different oxide concentrations as well as varying mineralogy

X-ray fluorescence on the VAS sample as well as original samples were conducted by the Council for Geoscience (CGS) in Pretoria. A fusion technique was also used by CGS. A description of this fusion technique as provided by CGS is as follows:

- Glass disks were prepared by fusing about 1 g roasted sample and flux to a total mass of 10.5 g at 980° C.
- The flux consists of 35% $LiBO_2$ and 64.71% $Li_2B_4O_7$.
- The glass disks were analysed by a PANalytical Axios X-ray fluorescence spectrometer equipped with a 4 kW Rh tube.
- The quality control reference mineral used by CGS is a secondary amphibolite.

The results of the tested samples from both centres are presented in Chapter 5 show consistent and comparable oxide determinations.

4.4.2 Powder/Polycrystalline X- Ray Diffraction (PXRD)

X- ray diffraction can determine the presence and amounts of minerals species in sample, as well as identify phases. When X-rays interact with a crystalline substance (phase), one gets a diffraction pattern. The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance. The powder diffraction method is non-destructive analysis used to characterize chemical composition, crystallographic structure, grain size, and preferred orientation in polycrystalline or powder solid samples (X-ray-Diffraction., 2012). This is a preferred method of analysis for characterization of unknown crystalline materials. The main use of powder diffraction is to identify components in a sample by a search/match procedure. This is a qualitative analysis. Furthermore, the areas under the peak are related to the amount of each phase present in the sample. Compounds are identified by comparing diffraction data against a database of known materials maintained by the International Centre for Diffraction Data (ICDD) (X-ray-Diffraction., 2012).

4.4.2.1 XRD Measurements

In order to establish the occurrence of any carbonation reactions by virtue of changes in crystallographic structure and chemical composition, XRD was used to analyse the untreated, SP CO_2 treated and VAS basalt and shale samples. The evaluations were conducted by the Wits Coal and Carbon Research Group, and members of the XRD unit in Chemistry Department at Wits. Powder x-ray diffraction data for the tested samples were collected using a Bruher AXSD2 XRD apparatus. Data was collected in a 2-theta angle range of between 50 and 900 with a step size of 0.0070/min. This speed results in a counting time of about 439.2s. The comparisons between treated and untreated samples are presented in Chapter 5.

4.4.3 Scanning Electron Microscopy-Energy Dispersive Spectrometer (SEM-EDS)

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm).

Energy Dispersive Spectrometer (EDS) analyses selected point locations on the sample. This is used to qualitatively or semi-quantitatively determine chemical compositions.

4.4.3.1 SEM-EDS Measurements

Scanning electron microscope analysis was used for the purpose morphological assessment of the samples before, and following the VAS and the storage reactor tests to determine any sorption in the VAS treated samples, and any alteration and potential carbonate mineralisation on the supercritical CO_2 samples. Energy Dispersive Spectrometer (EDS) was used to determine any presence of carbon on fractures in the sample surface. SEM analysis was conducted by technicians the at Wits Microscopy Unit using the FEI ESEM Quanta 400F, (EDS). Small fractions of air dried samples were attached to double-sided carbon adhesive tape and then mounted on the microscope holder for analysis.

4.4.4 Brunauer-Emmett-Teller (BET) Analysis

Brunauer-Emmett-Teller (BET) analysis provides precise specific surface area evaluation of materials by multilayer adsorption measured as a function of relative pressure. The technique encompasses external area and pore area evaluations to determine the total specific surface area in m^2/g, yielding important information in studying the effects of surface porosity and particle size distribution.

The concept of the BET theory is an extension of the Langmuir theory (Barron., 2011). The following assumptions are held for this latter theory of monolayer molecular adsorption, to a multilayer adsorption:

(a) Gas molecules physically adsorb on a solid in layers infinitely;

(b) There is no interaction between each adsorption layer; and

(c) The Langmuir theory can be applied to each adsorption layer.

The surface area of a solid includes both the external surface and the internal surface of the pores. Adsorption occurs in two ways fashions, namely:

a. Monolayer adsorption which occurs when all the adsorbed molecules are in contact with the surface layer of the adsorbent, and

b. Multilayer adsorption which results when the adsorbent accommodates more than one layer of molecules and not all adsorbed molecules are in contact with the surface layer of the adsorption space.

Gas physisorption is considered non-selective (Saf Chem., 2012). Hence it fills the surface or layer by layer, depending on the available solid surface and the relative pressure.

Figure 33 graphically shows monolayer and multilayer gas adsorption process.

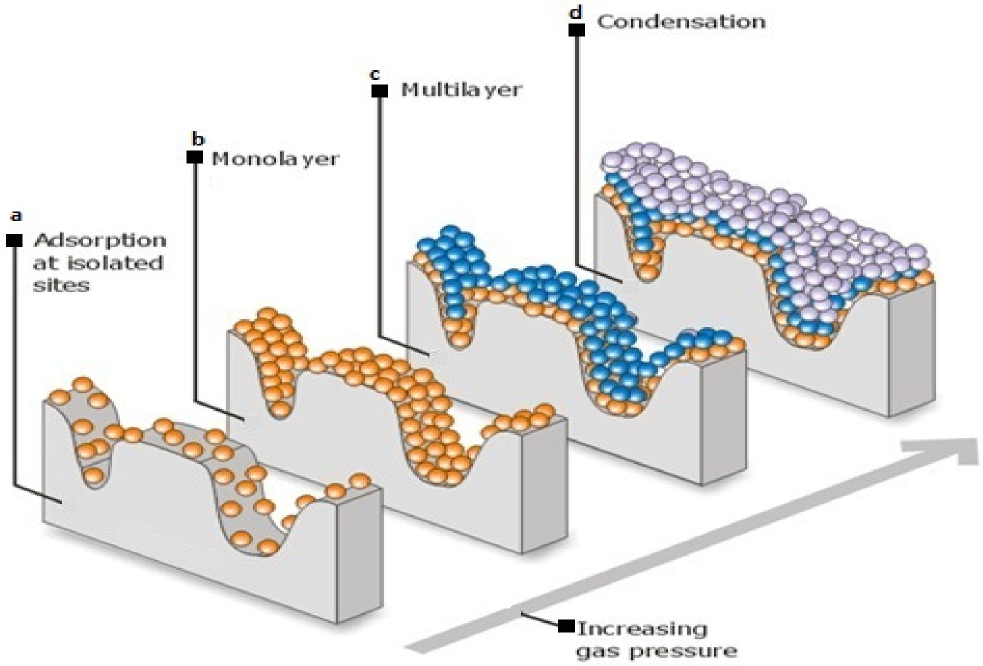


Figure 33: Schematic Explanation of Monolayer and Multilayer Physical Adsorption (Modified From Aerogel., 2003)

The process is described as follows:

a) Gas molecules are attracted to the pore surfaces.

b) They will initially form a monolayer of molecules covering it. The formation of this monolayer allows the calculation of the surface area covered by this layer because the amount of gas adsorbed when the mono-layer is saturated is proportional to the entire surface area of the sample.

c) As the adsorption process continues, multiple layer filling occurs and pore sizes can be calculated at this stage.

d) Pore characteristics, namely: total pore volume, and pore size distribution are determined near the bulk condensation point, from the fact that smaller pores will fill up quicker than the larger pores by the multiple layers being adsorbed.

In capillary condensation the residual pore space which remains after multilayer adsorption has occurred is filled with condensate separated from the gas phase by menisci. Capillary condensation is often accompanied by hysteresis. Adsorption hysteresis arises when the adsorption and desorption curves do not coincide.

The relation, at constant temperature, between the amount adsorbed and the equilibrium pressure of the gas is known as the adsorption isotherm (IUPAC .,1985).

4.4.4.1 Types of Isotherms

According to IUPAC. (1985) the majority of physisorption isotherms may be grouped into the six types.

Figure 34 schematically shows these isotherms with a brief description of each.

They differ because the systems demonstrate different gas/solid interactions.

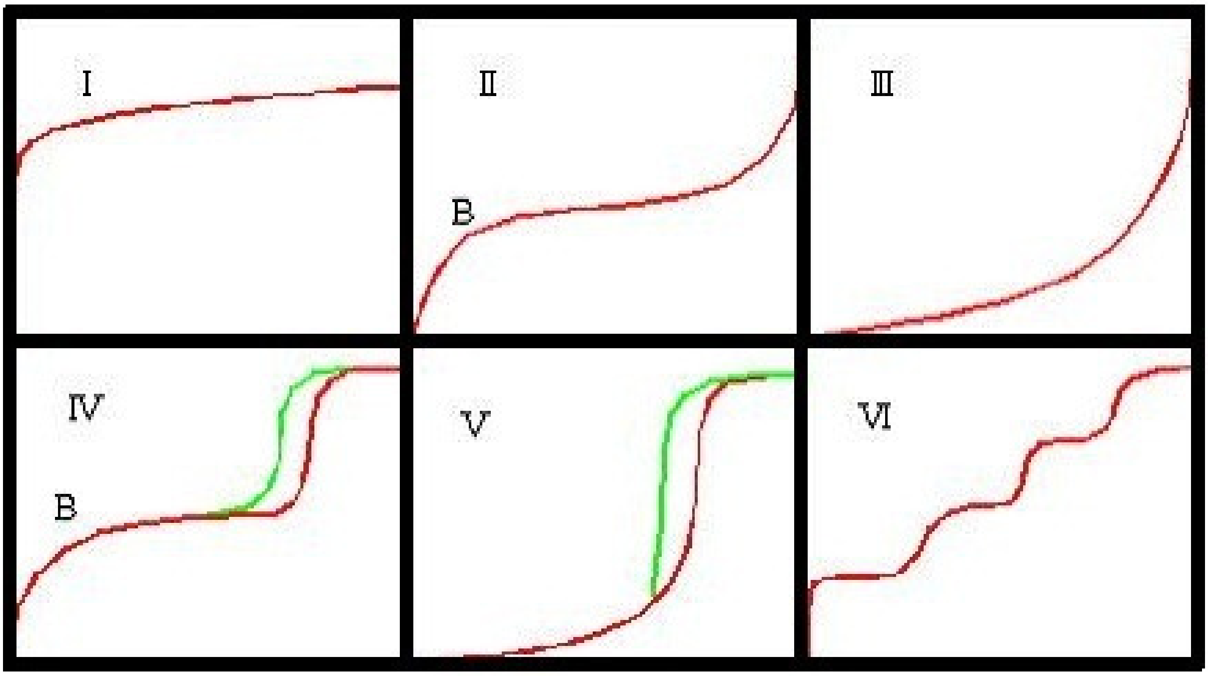


Figure 34: Isotherm Types (IUPAC., 1985)

Type I: Adsorption is limited to the completion of a single monolayer of adsorbate at the adsorbent surface. Type I isotherms are observed for the adsorption of gases on microporous solids whose pore sizes are not much larger than the molecular diameter of the adsorbate. Complete filling of these narrow pores corresponds to the completion of a molecular monolayer

Type II: This type of isotherm is reversible and indicates an indefinite multi-layer formation after completion of the monolayer and is found in adsorbents with a wide distribution of pore sizes. Near to the first point of inflexion (point B) a monolayer is completed, following which adsorption occurs in successive layers. It is exhibited by finely divided non-porous or macroporous solids.

Type III: This isotherm is also reversible and occurs when the amount of gas adsorbed increases without limit as its relative saturation approaches unity

Type IV: This is a variation of Type II, but with a finite multi-layer formation corresponding to complete filling of the capillaries (capillary condensation) , and has a hysteresis loop associated with it. The adsorption terminates near to a relative pressure of unity. These isotherms are exhibited by mesoporous industrial adsorbents.

Type V: Type V is uncommon but is similar to Type III in that the adsorbant-adsorbent interaction is weak. It is obtained with certain porous adsorbants and is typical of vapour adsorption, i.e. water vapour on hydrophobic materials.

Type VI: The rare type VI step-like isotherm represents stepwise multilayer adsorption on a uniform non-porous surface. The step-height now represents the monolayer capacity for each adsorbed layer and the sharpness of the steps depends on the system and the temperature.

Once the isotherm is obtained, a number of calculation models can be applied to different regions of the adsorption isotherm to evaluate the specific surface area.

If the adsorption isotherm shape is Type I, II or IV, adsorption can be used to separate the adsorbate from the carrier gas. If it is Type III or V, adsorption will probably not be economical for the separation (IUPAC., 1997).

4.4.4.2 BET Measurements

The surface area measurements and pore volume on the basalt and shale was conducted using the BET apparatus, Micrometrics ASAP 2020 Surface Area and Porosity Analyser located at North West University (NWU), Potchefstroom Campus. CO_2 was the probe gas used to reach micropores that could be accessed during CO_2 sequestration.

The BET test was also conducted on samples both before, and after the VAS and the SP storage reactor tests, to determine changes in surface area and/or pore volume and pore size distribution.

Chapter 5 Results and Discussion

This chapter follows through from Chapter Four in discussing the results of the various advanced techniques employed in the examination of sorption and carbonation on the basalt and shale samples are presented and discussed. The validity of the techniques is also considered.

5.1 Supercritical (SP) Reactor

The basalt sample attained a maximum pressure of close to 125bar and a maximum temperature of 64ºC over the four week period in the reactor.

The shale reached a maximum pressure of about 93bar and a maximum temperature of 62ºC was achieved.

This fully satisfied the required SP conditions as explained in Chapter 4, Figure 31.

5.2 High Pressure Volumetric Adsorption System (VAS)

The results of the VAS experiment under supercritical conditions are presented in this section.

The highest pressure attainable by the VAS system during this experiment was just over 73bar for both rocks and in all four runs.

Details of calculations for the graphs below of the basalt and shale may be found in Table A2 of Appendix A.

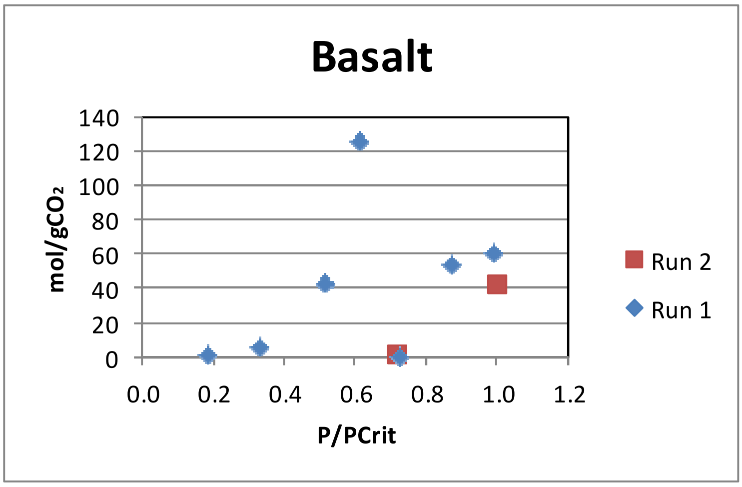


Figure 35: Supercritical CO_2 Isotherms for Basalt *(P/PCrit = Reduced Pressure)*

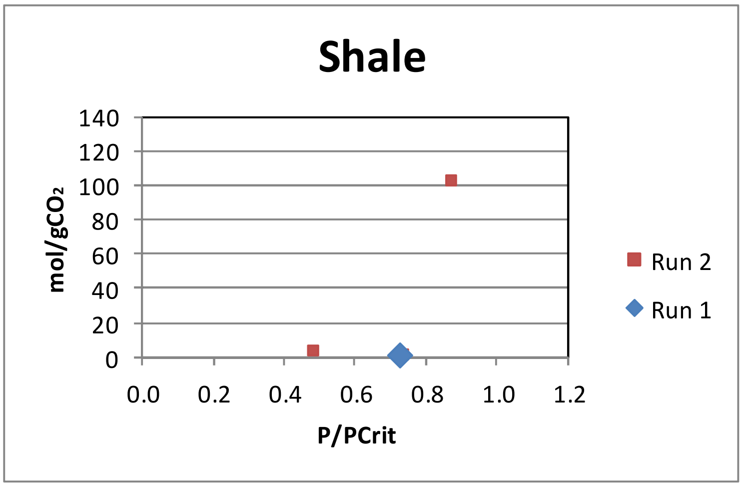


Figure 36: Supercritical CO_2 Isotherms for Shale *(P/PCrit = Reduced Pressure)*

The data points for all four runs were very scattered, and an exponential relationship was difficult to achieve. A more linear relationship seemed to fit the data even though this is not to be expected from the nature of the experiment. This could be as a result of the leaks in the VAS system.

As a point of interest worth mentioning (for the sake of future research) is the consistent spike in pressure, observed at the fifth pressure increment step (i.e. when the pressure is increased by the system to 50bar). It is not in the scope of this report to investigate the VAS system itself. However, this spike could be related to the silica contributed by the glass wool or some mechanical aspect of the VAS system and warrants further investigation.

A comparison between the isotherms in terms of adsorption capacity of CO_2, generated for the basalt and shale samples with that of a coal sample and ash sample subjected to similar experimental conditions was attempted. The initial SB CO_2, results for the rocks (Table A3 of Appendix A) were used, as only subcritical results for ash and coal were available at the time of this report.

Table 3 below shows the comparative adsorption capacity of the rocks with that of ash and coal.

Table 3: Comparison of CO_2 adsorption capacity under subcritical conditions for coal ash with that of basalt and shale. (Data for ash and coal courtesy of Kholumo, 2012 and Gertenbach, 2009 respectively)

Sample	Adsorption Capacity (mol/g)
Pulverised power plant ash	$1.87\text{x}10^{-3}$
Highveld, Waterberg coal	$0.3\text{x}10^{-3}$-$1.5\text{x}10^{-3}$
Basalt	$1.05\text{x}10^{-3}$
Shale	$1.80\text{x}10^{-3}$

From Table 3 it is seen that under subcritical conditions the pulverised coal ash indicates the highest adsorption capacity, followed by shale and coal if the maximum adsorption capacity for the latter is to be considered. Basalt ranks lowest.

It is appreciated by the researcher that the VAS results are inconclusive and that many more runs in a more detailed project, on the shale and basalt are needed to draw conclusive comparisons with ash and coal in terms of adsorption capacities. Nonetheless, the researcher is satisfied that the exercise fulfilled its purpose in demonstrating that it is possible to conduct adsorption experiments on rock samples using the adsorption equipment available at Wits.

5.3 X-ray Fluorescence (XRF)

The untreated, SP treated and VAS, basalt and shale samples were characterized chemically by XRF so that the effective oxide weight percent of the important elements could be determined in each sample.

As stated in Chapter 4, the VAS sample was sent to CGS for analysis because UIS could not/ did not want to handle the small amount (under 5g) of VAS sample that was available. Original rock sample were also sent for analysis here, as the quality control reference mineral used by both laboratories varied. No supercritical sample remained (after all other tests), to be sent to CGS as well.

Hence the adsorption test samples are compared only to the untreated samples analysed by CGS, while the SP samples are compared to those untreated samples analysed with it, by UIS.

The ash oxides generated for the major and minor elements from both UIS and CGS is presented in Tables 4 and 5, respectively.

The results from both laboratories show consistent results with each other.

From Tables 4 and 5 it is seen that the composition of the untreated, supercritical and VAS basalt samples are consistent with the compositions as discussed in Chapter 3. Quartz, represented as SiO_2, has a weight percent (wt%) of 45-55 % SiO_2, 2-6 t% total alkalis, 0.5-2.0% TiO_2, 5-14% Fe_2O_3 and 14% or more Al_2O_3. Contents of CaO are commonly near 10 %, those of MgO commonly in the range 5 to 12 % as determined by Le Maitre *et al.* (2002).

The basic mineralogy of basalt is known to be plagioclase feldspar [$(Ca,Na)Al(Al,Si)Si_2O_8$], pyroxene (a Mg-Fe-Ca silicate), and ilmenite ($FeTiO_3$).

Evidence of these elements in the sample basalt is seen from the oxides listed on Table 4 and Table 5, with the major oxides generally considered for carbonation purposes, highlighted in red. Each of these oxides contain at least one or more of the cations Fe^{3+}, Mg^{2+}, and Ca^{2+}, which is appropriate for carbonation as CaO, and MgO and Fe_2O_3 are the principal compounds traditionally expected to be carbonated in basalt.

In Fe_2O_3, iron is in its highest oxidation state. Fe_2O_3 is generally the more common compound found in basalt as opposed to FeO, an iron II oxide or ferrous oxide.

Recent experimental studies investigating the carbonation potential of different basalts from around the world, have found vastly different rates and styles of mineral carbonation that cannot be explained purely by compositional differences (Schaef *et al.*, 2010), although the release of Fe appears to be an important factor. (Maher *et al.*, 2011). O' Connor *et al.*, (2000) found that oxidation of the magnetite during heat treatment of serpentine inhibited the carbonation reaction. There seems little reason why this could not be the same case with basalt. They also added that additional study is required to determine the effect of iron oxide, which perhaps acts as a control on redox conditions (O' Connor *et al.*, 2000).

Although the above information does not directly relate to the results of this research, as evidenced in Tables 4 and 5, the researcher deemed it significant to include here, as Fe_2O_3 is one of the minerals, together with CaO and MgO, in basalt commonly expected to undergo carbonation, and the above inclusion could be beneficial to any future research into basalt carbonation processes.

The oxides CaO, MgO and Fe_2O_3 react with CO_2 to form carbonates as given by the basic stoichiometric equation below:

$$MO + CO_2 = MCO_3 \tag{4}$$

Where M = cations Fe^{3+}, Mg^{2+}, and Ca^{2+}.

From Tables 4 and 5 it is seen that for the basalt VAS sample, CaO shows an increase of 0.41% and MgO of 0.44%, with a decrease in Fe_2O_3. However, the LOI or loss on ignition (also highlighted in red in Tables 4 and 5), was also lower than the untreated basalt by 0.32%. The LOI provides information as to the amount of CO_2 or any other volatile component present in the sample. A high LOI could have been an indication of carbonates (MO_3) in the treated samples, this latter upon ignition, would have released CO_2, to form ash oxides (MO), a converse reaction to equation (4).

The SP values also saw an increase of 0.07% and 0.06% for CaO and Fe_2O_3 respectively, while a decrease in MgO was obtained. The LOI here also saw a decrease of 0.03%.

Shale, as described in Chapter 3, generally has poor porosity and permeability, making it a good caprock or seal. The expected high quartz values (> 50%) in the shale, is also typical, owing to its sedimentary provenance, but increased Al_2O_3 is much higher in the shale than the basalt as expected because of the clay mineral constituents in this rock type.

The XRF results in Table 4 showed no change in CaO and negative values for Fe_2O_3 and MgO for the SP samples. The VAS samples fared slightly better in the ash oxide values with CaO increasing by 0.04% and MgO by 0.23%, while Fe_2O_3 reflected in the negative. The LOI for the SP and VAS samples were 0.47% and -0.56% respectively.

Table 4: UIS Analytical XRF Results for Untreated and Supercritical CO_2 treated Basalt and Shale (wt%)

Sample	Al_2O_3	CaO	Cr_2O_3	Fe_2O_3	K_2O	MgO	Mn_3O_4	Na_2O	P_2O_5	SiO_2	SrO	TiO_2	V_2O_5	ZrO_2	BaO	LOI	Total
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Basalt - Untreated	14.02	9.79	0.04	10.08	0.72	6.37	0.16	2.22	0.08	49.73	0.04	0.8	0.03	0.01	0.02	6.72	100.83
Basalt - Supercritical CO_2	14.13	9.86	0.05	10.14	0.73	6.36	0.16	2.21	0.09	49.96	0.04	0.81	0.03	0.01	0.02	6.69	101.27
Shale - Untreated	18.42	0.64	0.01	7.5	4.02	2.34	0.08	0.86	0.11	54.07	0.02	0.64	0.02	0.02	0.07	11.35	100.16
Shale - Supercritical CO_2	18.35	0.64	0.01	7.47	3.95	2.32	0.08	0.89	0.11	54.24	0.02	0.63	0.02	0.02	0.07	11.82	100.63

LOI: Loss on Ignition

Data reported on DRIED BASIS

Results are only representative of sample received for testing

Identification of test method: Fusion technique

Instrument: X-ray fluorescence spectrometer

Table 5: CGS XRF Results for untreated and high pressure VAS treated Basalt and Shale (wt%)

Sample	Al_2O_3	CaO	Cr_2O_3	Fe_2O_3	K_2O	MgO	Mn_3O_4	Na_2O	P_2O_5	SiO_2	SrO	TiO_2	V_2O_5	ZrO_2	BaO	LOI	Total
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Basalt - Untreated	13.69	9.66	0.04	9.87	0.69	6.08	0.15	1.77	0.09	50.73	na	0.79	na	na	na	6.97	100.51
Basalt –VAS CO_2	13.75	10.07	0.04	9.84	0.68	6.52	0.15	1.61	0.09	49.82	na	0.74	na	na	na	6.65	100.49
Shale - Untreated	18.18	0.65	0.01	7.33	3.86	2.24	0.08	0.55	0.12	55.52	na	0.63	na	na	na	11.32	99.96
Shale –VAS CO_2	18.49	0.69	0	7.38	3.82	2.47	0.08	0.58	0.12	55.19	na	0.63	na	na	na	10.76	100.22

**na: not analysed*

LOI: Loss on Ignition

Data reported on DRIED BASIS

Results are only representative of sample received for testing

Identification of test method: Fusion technique

Instrument: X-ray fluorescence spectrometry

CGS set the limit for reporting for CaO, MgO and Fe_2O_3 is 0.01%, and UIS at 0.1. Upon further enquiry as to the smallest detectable threshold of XRF apparatus, CGS XRF division obliged with the following values for each of the above minerals, as shown in Table 6 below. The minerals under investigation appear to fall within this range of detection. An important note to make is that the Level of Detection Limit, Level of Determination Limit and Level of Quantification are very different. Hence the detection limit here is basically 3 x standard deviation of the background mean.

Table 6: XRF detectable threshold for VAS samples (Data courtesy of Corlien Cloete - CGS)

Sample	**Major Oxide in %**		
	CaO	**MgO**	**Fe_2O_3**
Basalt	0.0010	0.0034	0.0028
Shale	0.0013	0.0038	0.0038

UIS, who conducted the XRF on the SP samples did not respond to the threshold enquiry. Hence no threshold data were available for the SP sample.

In terms of moles, the increase in CaO for the VAS basalt sample, the calculation is shown below. The mass of VAS basalt samples used in the XRF test was 1g.

(0.41%/100% * 1g)/CaO molecular mass

= 0.0041g/56.0778g/mole

= 0.7.3113 * 10^{-5} moles

In similar calculations using the molecular weight of the other ash oxides, their increase in moles for VAS basalt and shale are listed below.

VAS basalt MgO = 1.0917 * 10^{-4} moles

VAS shale CaO = 5.7064 * 10^{-6} moles

VAS shale MgO = 4.5652 * 10^{-5} moles

The VAS shale mass was 0.8g. Fe_2O_3 decreased in both samples and thus is omitted here.

Increases in moles of the ash oxides in the SP basalt are shown below. A mass of 7g was used in the analysis:

SP basalt CaO = 8.7379 * 10^{-5} moles

SP shale MgO = 1.0421 * 10^{-4} moles

Fe_2O_3 was negative in both SP rocks, as was MgO in the shale. CaO in the SP shale sample showed no change.

Although, on the whole, small and/or negative values were obtained with respect to ash oxide weight percent and LOI of rock samples, whether SP or VAS treated; this exercise indicated that X-Ray Fluorescence (XRF) is an excellent quality control test method with unique capabilities including highly accurate determinations for percentage level elements and a broad elemental survey of the sample composition without standards. The XRF method is non-destructive, simple, fast, and inexpensive compared to monograph methods to determine effective oxide weight percent of the relevant elements for mineral carbonation.

5.4 Powder X-Ray Diffraction (PXRD)

Figures 37 and 38 exhibit the qualitative XRD results produced for the untreated and both treated rock samples.

For both the basalt and shale samples, the SP and VAS diffraction peaks are not too dissimilar to the untreated samples. Under the advisement from the operators of the Wits XRD facility, any shift in the treated peaks compared to the untreated are assumed to be due to possible sample packing inconsistencies (two different operators handled the samples and equipment). Care must be taken to create a flat upper surface and to achieve a random distribution of lattice orientations. The angle of incidence onto the sample surface may vary as a result of inconsistent packing, resulting in shifted diffraction peaks.

The VAS basalt sample in Figure 37 shows the most changes. However no calcite peaks were observable as with the SP basalt. The new peaks visible on the VAS diffraction pattern could be attributed to the formation of new minerals, but is unlikely, as the sample spent a much shorter time in the adsorption chamber than the SP sample did in the reactor. The peak shifts are possibly due to packing irregularities as described above.

Of the two rocks, the shale samples show virtually no detectable changes in peak geometry. The calcite peaks at D-spacing 3.035 Å (amstrong) and 2.095Å are present in all three samples.

Trace elements Ti and Cr as confirmed in the ash oxides of the XRF analysis in Section 5.1 and the EDS spot analysis in Section 5.3 below, could not be verified in the XRD, perhaps because these minerals were present at levels less than that routinely detectable by PXRD (~1% by weight). It is possible, also, in the case of carbonates, if any were formed in the treated samples, were in such minute quantities, making them undetectable by the XRD apparatus. This was verified after consultation with the XRD team that conducted the analysis on the rocks. The detectable threshold of their XRD equipment could not be accurately determined without additional experiments and follow-up calculations. A 'guesstimate' in their professional opinion would place the detectable threshold for Ca, Fe and Mg, was placed at estimates between 2% and 5% by weight for each element above. The approximate mass of each rock sample used was ~ 1g.

Thus, assuming a mineralisation rate of between 2% and 12%/fifteen weeks under SP conditions (Otheim *et al.*, 2011), would correspond to a value of 0.13% - 0.8%/thirty days (30), as was the duration of the SP study in this research. After thirty days, the expectation of mineral precipitation would hypothetically be ~ 0.1% (x). However the detection threshold of the XRD apparatus is 2% (y) (if the lowest threshold scenario were to be considered).
Therefore,
$x < y$.
The maximum mineral precipitation rate would therefore be:
$y/30 = 2\%/30$.
Converting this to moles for Ca would be:
$((2/100)*1g)/$ Ca molecular weight
$= 0.02g/40.0784g/mole$
$= 0.000499$ mole
$= 4.99*10^{-4}$ mole

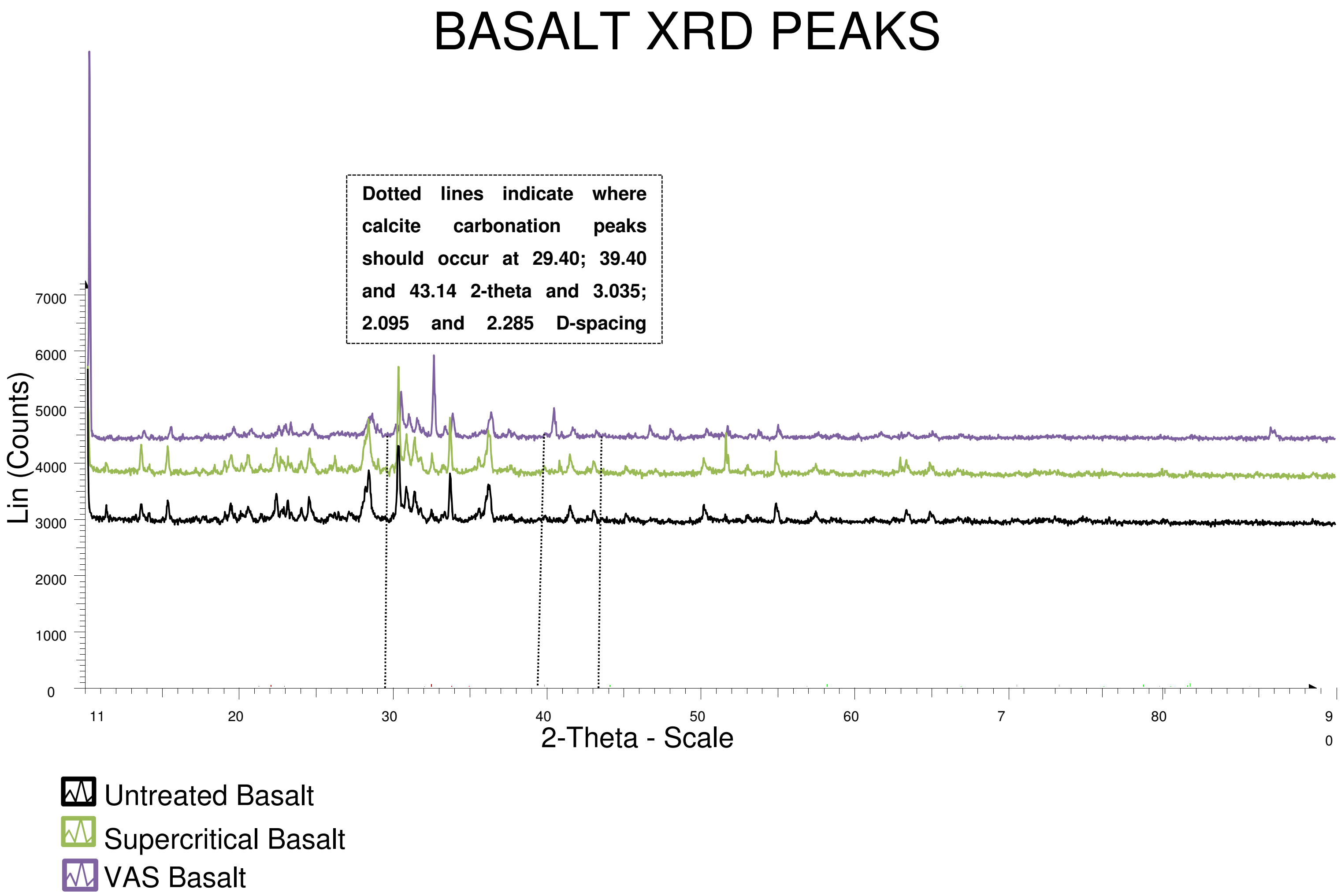
In similar fashion, the moles for Mg with a molecular weight of 24.3051g/mole
Mg = $8.228 * ^{10-4}$ mole; and

Fe, with a molecular weight of 55.8452g/mole
Fe = $3.581 *10^{-4}$ mole.

However, as stated earlier in Chapter 1, it was expected at the outset that four weeks was too short a time for carbonate formation even under SP conditions in a reactor. The VAS samples were only tested for adsorption, retention of CO_2, and possible new carbonate formation was highly unlikely to be achieved. The above calculations were based on assumptions from literature (Otheim *et al.*, 2011). Thorough estimations of mineralisation rate in basalt requires detailed information on three main areas namely; concentrations in solution of Ca, Mg and Fe needed to precipitate carbonates; the release rate of the Ca, Mg and Fe from the basalt, and the concentration of dissolved CO_2 (McGrail *et al.,* 2006).

X-ray diffraction has its merits in that it is non-destructive, sample preparation is relatively simple, small sample sizes can be analysed, and it introduces variables other than elemental composition.

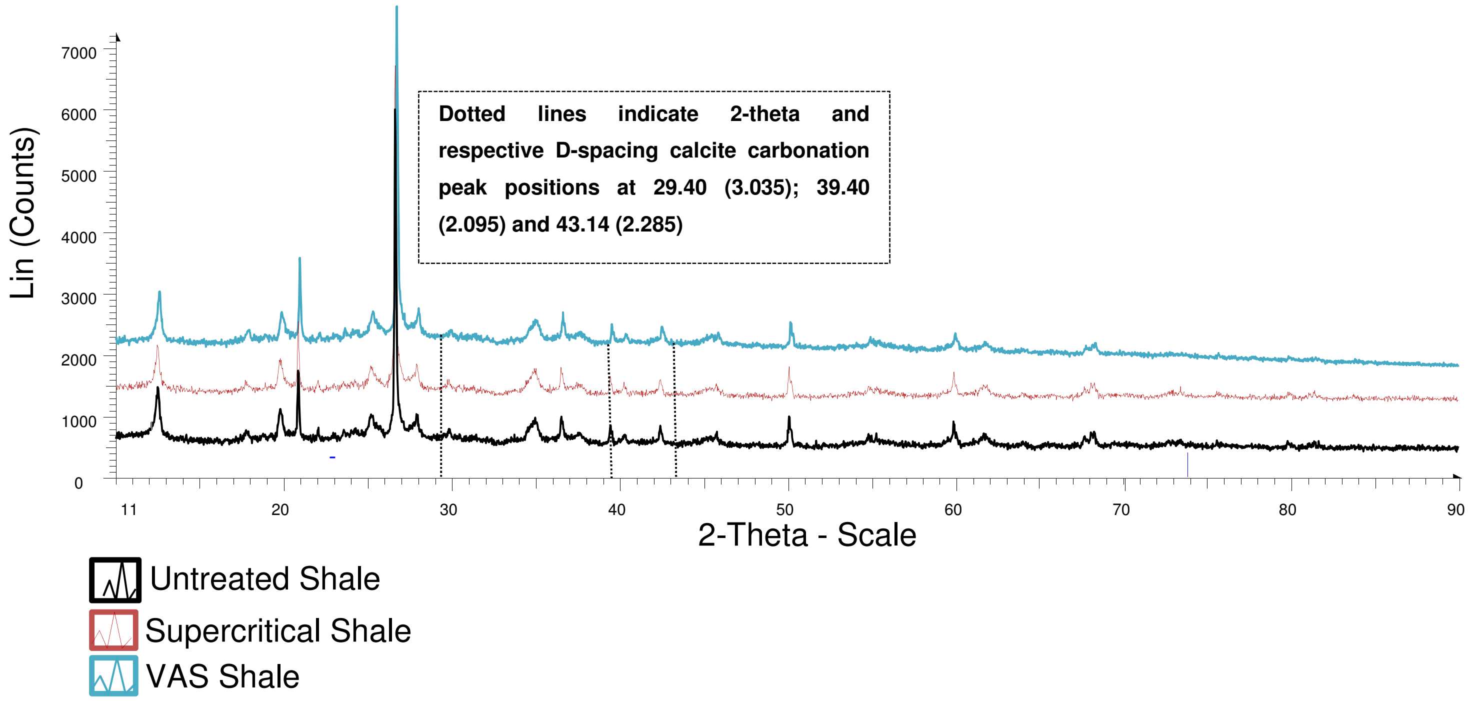
This was a qualitative analysis, where the concentration of the various species is determined by the peak intensity, and the interpretation of the diffraction pattern. Peak intensities on the samples did not show significant changes in the carbonate peaks, and their likely positions are indicated on Figures 35 and 36. A web-based phase identification tool (Cranswick., 1999), was applied to identify the D-spacing for the calcite peak positions.



Dotted lines indicate where calcite carbonation peaks should occur at 29.40; 39.40 and 43.14 2-theta and 3.035; 2.095 and 2.285 D-spacing

Figure 37: XRD Results for Untreated, Supercritical CO_2 treated and VAS treated Basalt

SHALE XRD PEAKS



Dotted lines indicate 2-theta and respective D-spacing calcite carbonation peak positions at 29.40 (3.035); 39.40 (2.095) and 43.14 (2.285)

Figure 38: XRD Results for Untreated and Supercritical CO_2 treated and VAS treated Shale

5.5 Scanning Electron Microscopy (SEM)

Results from the morphological analyses using back scattered electron imaging of SEM, on the basalt and shale samples are given in Figures 39a to c and 40a to c.

Minute amounts of powdered untreated, supercritical, as well as the VAS treated samples were all analysed. This exercise attempted to evaluate and compare any visible morphological changes (due to possible carbonation reactions and related secondary mineral phases) in the surface structure of the treated samples, with those of the untreated rock samples.

In the first booking of the SEM, clear surface imagery of the powdered rock samples could not be produced.

A second attempt at a later date, to extract more refined images was also unable to yield clear images on higher magnification on both the basalt and shale. This could not be explained by the Microscopy Unit.

The Microscopy Unit subsequently sent out a notice that the SEM was out of order and under repair, until further notice. This malfunction was taken to be the reason for the difficulties experienced in the earlier attempts to obtain higher magnifications and hence clearer images of the powdered samples.

On one micrograph, namely, Figure 40b), could the typical platy micaceous habit of phyllosilicate minerals characterising shale be vaguely observed, on a fragment to the top right of the image.

As such no visible evidence of reactions such as dissolution textures or reaction rims, if any, could be identified either.

Spot analyses using energy-dispersive spectrometry (EDS), shown in Figures 39a to c and 40a to c, was at least more fruitful. The element peaks for the basalt and shale tied in with their compositions, when compared to the XRD peaks in Figures 37 and 38 respectively. EDS showed the elements Chromium (Cr) and Titanium (Ti) which did not come up in the XRD samples but were confirmed to be present in the XRF analyses.

It is to be noted that the carbon(C) detected in the spot tests could be the detection of the carbon adhesive strip used to stick the grains onto the disk before insertion into the microscope.

Although higher magnifications could not be achieved, the researcher does not see this as a wasted exercise, as an insight into the use and function of the SEM was gained. Various researchers such as Fauth *et al*., 2002; Anjali *et al*., 2011; Lim *et al*., 2010; Schaef *et al*., 2010; Vogeli *et al*., 2011, to name a few, have documented the value of this advanced technique in detecting morphological/surface changes to rock samples as a result of mineral carbonation.

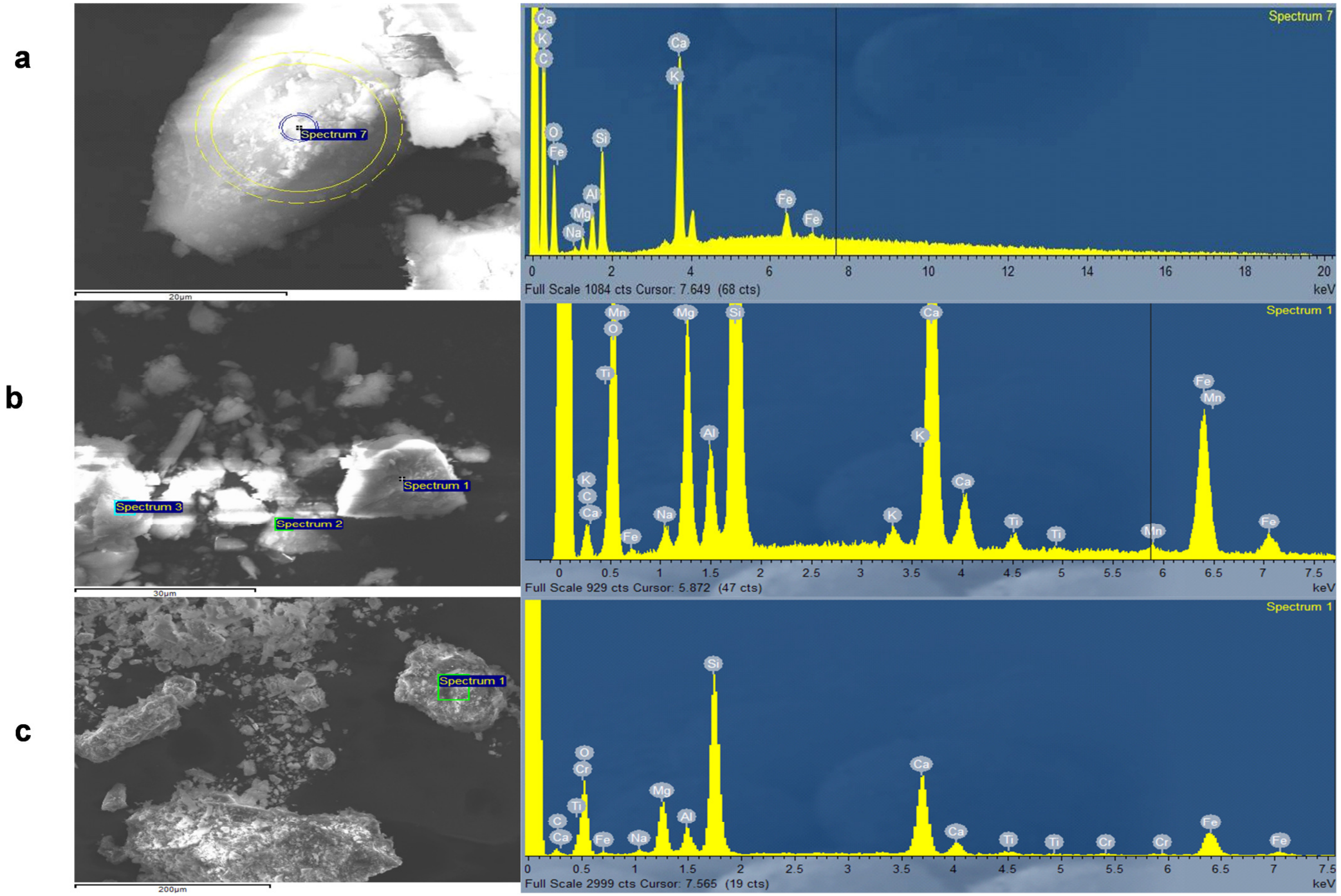


Figure 39: SEM-EDS Results of Basalt – a) Untreated Sample; b) Supercritical CO_2 Storage Reactor Sample; c) VAS Sample

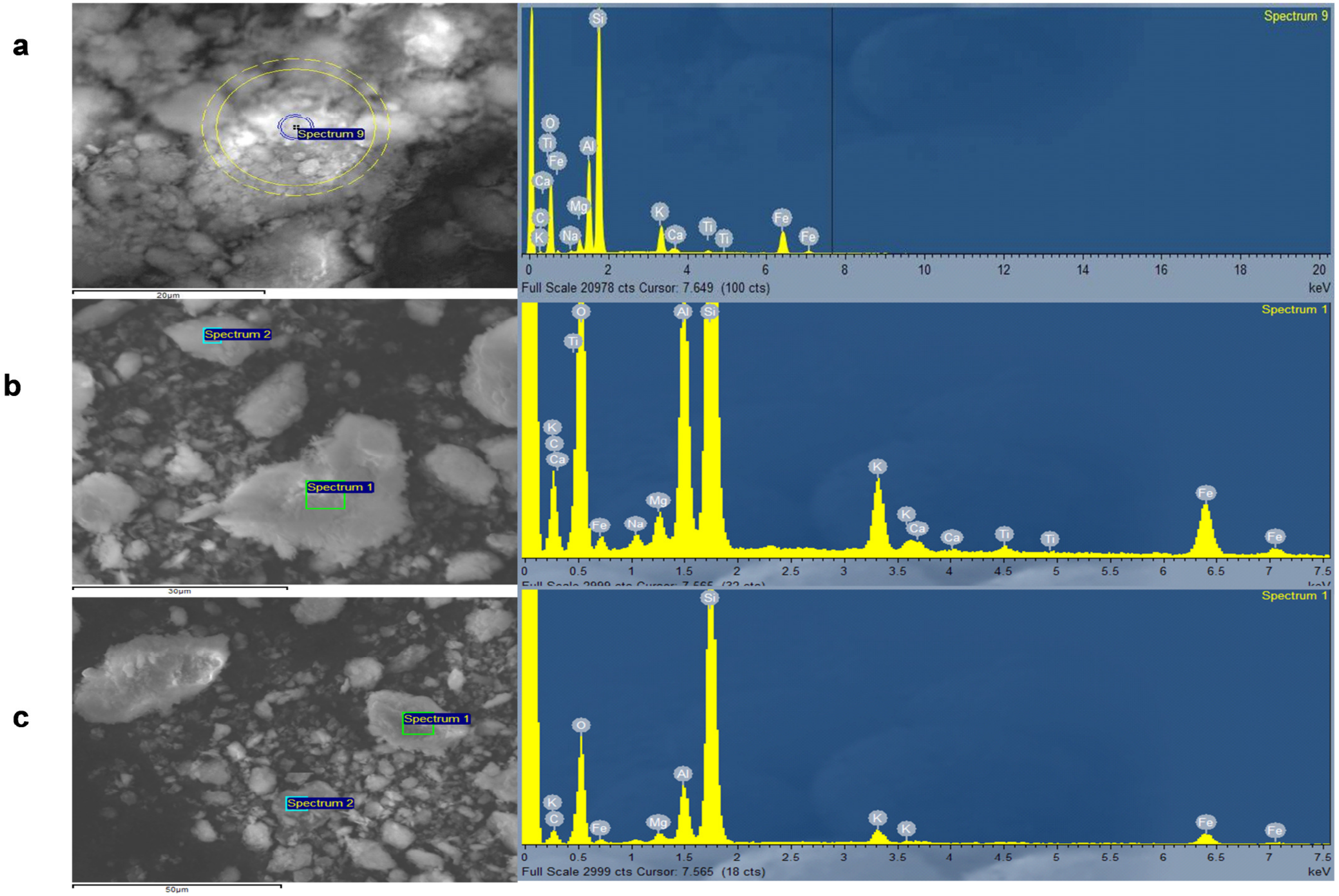


Figure 40: SEM-EDS Results of Shale– a) Untreated Sample; b) Supercritical CO_2 Storage Reactor Sample; c) VAS Sample

5.6 BET RESULTS

This section presents the results of the BET tests as performed at the University of the North West. Tests were conducted on all three batches of samples of both rock types, namely: each of the untreated samples; the supercritical storage reactor samples and the VAS treated samples.

With respect to BET characteristics, for each, the basalt results will first be presented first, followed by the results of the shale samples.

5.6.1 Basalt Physical and Structural Changes

Figures 41a and b show the surface area and pore volume results of the BET. Median pore width results for both rocks showed inconclusive results for untreated and treated samples. The values for these appear in Appendix B.

The supercritical basalt sample exhibits a marked increase in surface area. If sorption of CO_2 in/onto the rock (and possible carbonation) had taken place, this would result in a decrease in surface area.

Pore volume of the supercritical sample (Figure 41b) also shows an increase, indicating that the rock has opened up. If carbonates had formed they would have filled the pores, thus decreasing the pore volume.

These structural changes, namely; increase in surface area and pore volume can indicate dissolution of the CO_2 and minerals in the SP basalt, with the release of Ca, Mg and Fe ions, ahead of carbonation. This can be related to the dissolution trapping mechanism explained and shown in Figure 7 of Chapter 2.

The VAS sample exhibits slight decrease in surface area from the untreated sample, but the pore volume shows a marked increase which could indicate the ‘opening up’ of the rock.

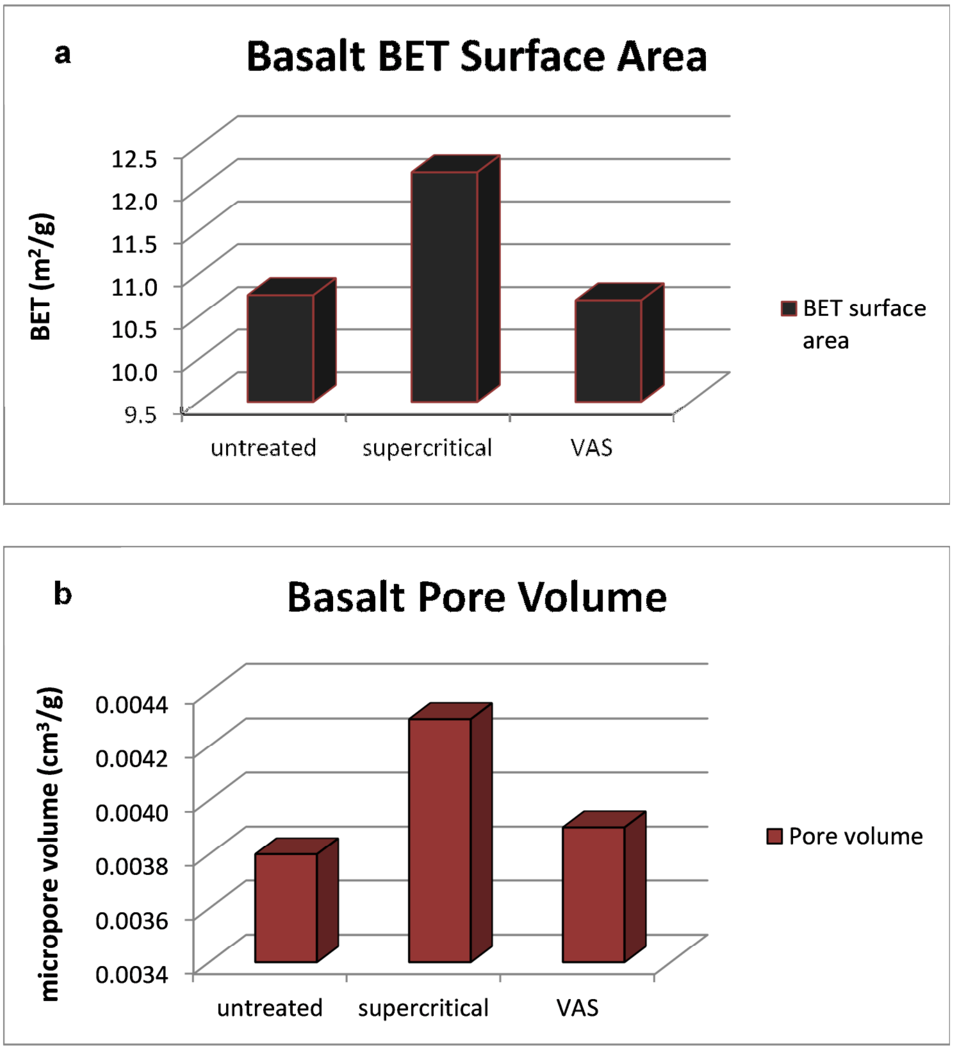


Figure 41: Basalt Physical and Structural Changes

5.6.2 Shale Physical and Structural Changes

The physical and structural changes to the shale samples are graphically shown in Figures 42a and b.

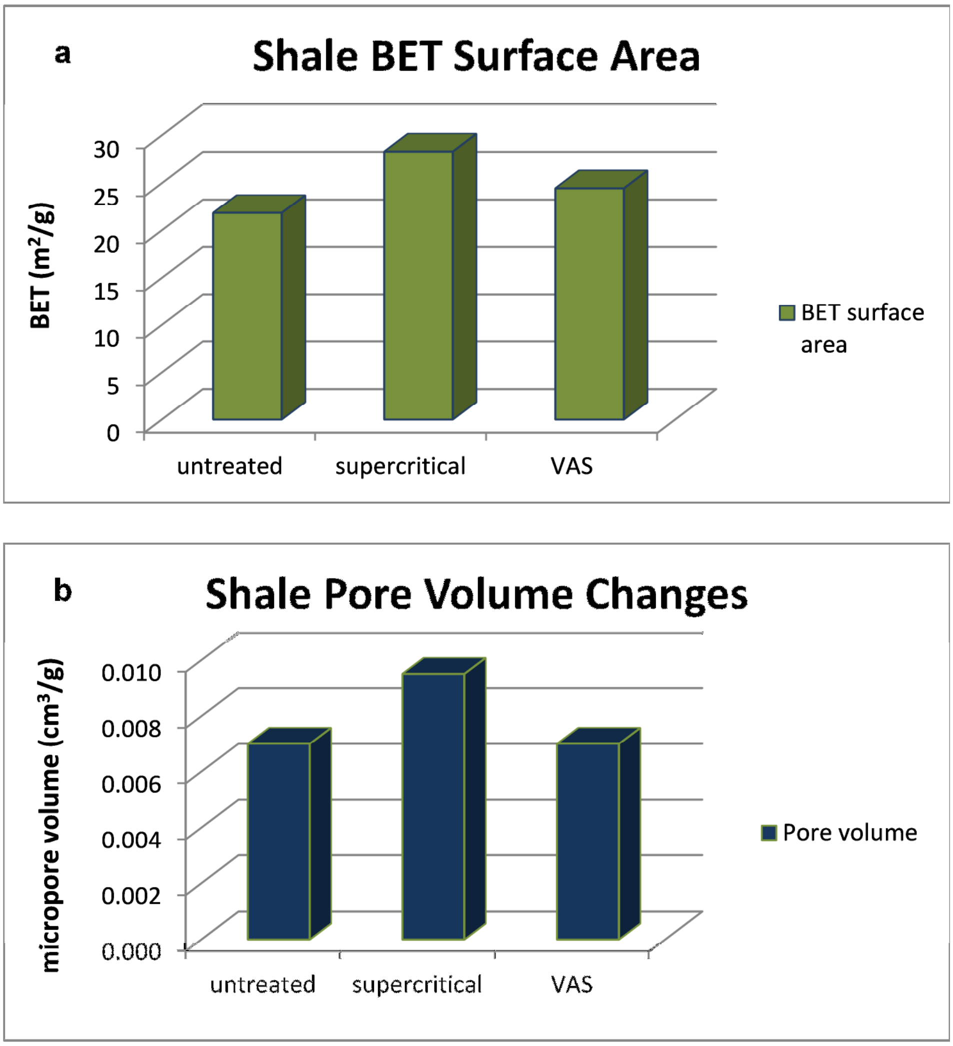


Figure 42: Shale Physical and Structural Changes

Surface area of both SP and VAS shale samples appear to have increased compared to the untreated sample.

The untreated and VAS samples show virtually no change in and pore volume. This is to be expected as the VAS sample would achieve CO_2 uptake but not retention.

The exercise showed that BET can be satisfactorily demonstrated on basalt and shale.

Chapter 6 Conclusions and Recommendations

This chapter concludes the project, with recommendations given for further future work in the field of mineral carbonation.

The South African storage atlas has indicated that there is limited existence of suitable conventional on-shore CO_2 storage capacity. Hence, un/nonconventional storage techniques need to be explored. Mineral carbonation as an un/nonconventional technique formed the basis of this study.

This report entailed a two phase assessment of the potential for mineral carbonation as a means of CO_2 sequestration in South Africa. The desktop study investigated suitable locations of ultramafic or silicate bearing rocks in South Africa, for the purpose of mineral carbonation. The second phase of the study compared the data resulting from the generation of CO_2 adsorption isotherms of a basalt and a shale sample, to those generated from a coal and ash under similar experimental conditions. In addition, the effect of supercritical CO_2 on mineral composition of these rocks was tested.

Ex situ mineral carbonation routes involve the above ground industrial processes using silicate rich rocks produced by mining activities or industrial waste products, with various pre-treatment options available.

With respects to *ex situ* carbonation, below are some conclusions and recommendations drawn.

1. Suitable raw materials from waste rock and mine tailings are to be found at various sites throughout the country. These raw materials are suitable for ex-situ mineral carbonation. They have the added advantage of already being crushed and milled during mining as well as being close to high CO_2 point sources.
2. Of the known kimberlite pipes in the country, only a small proportion of these are diamond bearing, and are available for carbonation purposes as they have

abundant Mg- rich minerals. The non-diamond bearing kimberlites in KwaZulu Natal, warrants investigation, for localised CO_2 storage.

3. Tailings storage facilities could be redesigned to promote CO_2 sequestration by directing leachate waters from tailings dumps into specially designed ponds where carbonate precipitation would be mediated by both chemical and biological processes.

4. Similar use of both chemical and biological processes of mineral carbonation may be employed on the large amount of ultramafic tailings in South African mine dumps, as an option to store carbon as stable carbonate minerals, while producing potentially valuable biomass for biofuel production at the same time.

5. Although wollastonite is found to exhibit more reactive features in terms of carbonation, limited exploited reserves have been identified in South Africa. The Magata Wollastonite Project tailings could be a source of raw material for this purpose.

6. The sub-volcanic equivalent of basalt – dolerite, is widespread across the country. They are not massive like basalt flow equivalents, but occur as sills and dykes, usually found in close proximity to or intersecting coal seams. They are therefore not suitable for *in situ* carbonation but could be suitable for *ex-situ* carbonation if extracted as a waste product from coal mining.

7. Although CO_2 emissions in South Africa far outweigh asbestos deposits, heat treatment and direct carbonation of the existing asbestos dumps could be a means of remediation of asbestos as a respiratory hazard.

In situ mineral carbonation involves a direct injection of CO_2 into host rocks underground, without moving any rock material. It thus eliminates the need for transportation of reactants and end products.

In terms of *in situ* carbonation, the following conclusions and recommendations are drawn.

1. Rocks of significance in South Africa are shales which provide a similar adsorption substrate as coal, but of lower permeability. However, in close proximity to dolerites, baked shales have increased porosity and therefore its capacity to store CO_2 may be improved. However, the heat of the dolerites, can decrease the CO_2 potential of sandstones because heat induced chemical reactions in the sandstones can result in decrease in porosity and permeability of the sandstones. Where dolerites are in close proximity to shales and sandstones, detailed investigations of the dolerites, including fine comb mapping, are necessary, to make these sediments viable options for mineral carbonation.

2. The Lebombo Group basalts in the Somkele/Lebombo area of KwaZulu Natal, where CO_2 storage may be possible at the base of the basalts, or in the basalts themselves, is advantageous in being close to a point source of CO_2 emissions. The Stormberg Sandstone underneath the basalt is another storage site with the added benefit of the overlying basalt in the event of leakage.

3. The Barberton Greenstone belt can provide an attractive feedstock due to its high Mg content.

4. The Clarens Formation Sandstone may be considered a viable CO_2 geological storage site as its high permeability; large pore space; and favourable geographic extent, all account for a high storage capacity.

In the experimental phase of the research, two rock samples, namely: basalt and shale were subjected to subcritical and supercritical conditions using equipment at the University of the Witwatersrand. This was the first attempt at investigating adsorption onto rocks using the equipment at the University of the Witwatersrand. All previous work involved coal and ash. The following conclusions and recommendations are made.

1. The VAS system enabled the researcher to acquire isotherms for the basalt and shale. However, the system needs greater calibration methods to identify

leaks and control them. The results of the VAS tests on the rocks can provide sensible information for future detailed work, especially the sharp spike encountered at the 50bar increment. Also worth looking into is the use of the glass wool and its effects if any, on the results.

2. Values for adsorption capacity were attained at subcritical conditions for the basalt and shale. These show comparable results to ash and coal under similar temperature and pressure conditions. Many more runs over longer periods in, an in-depth study will validate these results, which time constraints on this research would not allow.
3. X-ray fluorescence for ash oxide determination, even though conducted by two separate laboratories showed not too dissimilar results.
4. Powder x-ray diffraction also proved a reliable test, even if no detectable carbonate peaks were defined. Diligence in packing of samples in preparation for analysis though, is an important factor in maintaining authenticity of the peaks obtained.
5. Literature revealed SEM to be a reliable source for surface texture investigation. Even though at the time of this research, equipment malfunction could not allow higher magnification of samples to be achieved, the exercise allowed the researcher access to the facility and procedures involved in SEM work.
6. Although no visible carbonation reactions were observed in other tests, the surface area and pore volume changes on the supercritical and VAS samples, indicate significant structural changes in the SP basalt possibly related to dissolution mechanisms. This renders the viability of BET as an investigative tool for observation of such changes.
7. The reaction rates of the gas-solid CO_2 carbonation route, as applied in this research, have notably been too slow, or too miniscule to be observed, and the process suffers from thermodynamic limitations (Zevenhoven and Kavaliauskaite., 2004).

8. It is clear that thirty days is not long enough a time period for visible carbonation reactions to be detected. Longer periods for future research is advised and dedicated reactors assigned for a period of 180 days or longer be made available for supercritical studies on rocks.
9. It should also be noted that literature shows carbonation reactions to be hastened by dissolving the CO_2 in water or slurry. The use of brines and amines also enhanced carbonation reactions.
10. Future in-depth studies should look into developing a supercritical system that made use of CO_2 in this form, in a laboratory context. However, in the case of simulating in situ carbonation in real life terms, cost is an issue with respect to the application of additives.
11. An important fact to bear in mind, is that South Africa is a drought ridden country and use of the precious commodity of water to dissolve the tonnes of CO_2 emitted from the burning of fossil fuels, is a defeating exercise in terms of environmental consciousness.

More in-depth, detailed research with adequate resources and funding made available, can take future research to the level required where innovative ideas can make mineral carbonation a possible viable solution to the build-up of CO_2 in the atmosphere. This investigation, it is hoped, though conceptual, adds value to South Africa's carbon emission mitigation strategy.

Chapter 7 References

Aerogel., (2003). Union College Mechanical Engineering Senior Project 2003. Available at: http://www.vu.union.edu/~bakranis/aerogels/results.htm Accessed on 3rd Jan 2012

Allianz Knowledge Partnersite. Focus on Climate Change, Energy, Microfinance, Demographic Change, Mobility, and Health. Available at: http://knowledge.allianz.com Accessed on 5th Oct 2011

Anjali, G., Bhavya, M., Kumar, N.A., (2011). CO_2 Sequestration Potential of construction demolition alkaline waste material in Indian perspective. World Academy of Science, Eng. And Tech. 78: 947-952

Bachu, S., (2000), Sequestration of CO_2 in geological media: Criteria and approach for site selection in response to climate change, Energy Conver. Manage. 41: 953–970

Bachu, S., Gunter W.D., Perkins, E.H., (1994). Aquifer disposal of CO_2: hydrodynamic and mineral trapping, Energy Conversion and Management, 35(4): 269–279

Bailey, A., and Cashman, K., (2010). Lowest-cost CO_2 technology still too pricey. Available at: http://www.greeningofoil.com/post/Lowest-cost-CO_2-technology-still-too-pricey.aspx Accessed on 3rd Dec 2011

Barker, D.S., (2008). Kimberlite. AccessScience, ©McGraw-Hill Companies, 2008. Available at: http://accessscience.com/content/Kimberlite/757584 Accessed on 3rd Jan 2012

Barron, A.R., (2011). Physical methods in inorganic and nano chemistry. Connections. Available at: http://cnx/org/content/coll0699/1.12/ Accessed on 2nd Feb 2012

Carbfix. Available at: http://www.or.is/English/Projects/CarbFix/ Accessed on 4th June 2011

CGS. (Council for GeoScience). Available at: http://www.geoscience.org.za/ Accessed on 3rd Jan 2011

Climate Change and Carbon Management Blog., (2008). IGCC Study Taking Place in South Africa- International Policy/Programs. Available at: http://climate.alston.com/blog.aspx?entry=481 Accessed on 14th June 2011

Cloete, M., (2010). Atlas on Geological Storage of CO_2 in South Africa. Council for Geosciences. Pretoria, South Africa.

CO_2 Capture Project (2009). © Copyright CO_2 Capture Project. www.co2captureproject.com Available at : http://www.co2captureproject.org/image_library.html Accessed on 5th Jan 2012

CO_2 CRC (CRC for Greenhouse Gas technologies). Available at: http://www.co2crc.com.au/aboutccs/stor_trapping.html Accessed on 3rd Jan 2012

CO_2 Tec. Centre Mongstad. Available at: http://www.tcmda.com/en/Press-center/News/2011/The-operators-arrive-at-TCM-/ Accessed on 4th Apr 2011

Constantz, B.R., Youngs, A., Holland, T.C., (2009). Methods of Sequestering CO_2. US Patent No. 20090169452A1

Cranswick, L.M.D., (1999). Hints on Phase Identification Using Powder X-ray Diffraction. Available at: http://www.ccp14.ac.uk/poster-talks/phase-id-1999/html/phaseid.htm Accessed on 3th Jan 2012

Dalwani, I., and Smith C.L., (2009). Sequestration of CO_2 by means of Carbonation of Mineral Industry Tailings. Fourth Research Project . University of Cape Town, Dept. of Chem Eng.

Daval, D., Martinez, I., Corvisier, J., Findling, N., Goffe', B., Guyot, F., (2009). Carbonation of Ca-bearing silicates, the case of wollastonite: Experimental investigations and kinetic modelling. Chemical Geology. 262: 262-277

De Beers Group. Diamond Geology. Published on: www.debeersgroup.com Available at: http://www.coastofdiamonds.co.za/getting_around/diamondGeology.pdf Accessed on 5th Aug 2011

Delgado, T. M., (2010). Assessing the Mineral Carbonation Science and Technology, MSc (Eng.) Thesis. ETH Zürich, Switzerland. 51

Dessert, C., Dupre´, B., Gaillardet, J., Francois, L.M., Alle´gre, C.J., (2003). Basalt weathering laws and the impact of basalt weathering on the global carbon cycle. Chem. Geol. 202, 257–273

Dewandel, B., (2005). A conceptual hydrogeological model of ophiolite hard-rock aquifers in Oman based on a multiscale and a multidisciplinary approach. Hydrogeol. Jnl. 13, 708–726

DME (Department of Minerals and Energy), (2009). Digest of South African Energy Statistics. Directorate Energy Information Management, Process Design and Publications, Department of Energy, Republic of South Africa.

Doria, L.R., (2005) .Belvidere asbestos mine: mine suitability for CO_2 sequestration through mineral carbonation. BHon. Thesis, Department of Geology, Middleburg College, USA, .60

Doucet, F.J., (2011). Scoping Study on CO_2 Mineralisation Technologies. Council for GeoScience (CGS) Report No: 2011-007. Prepared for South African Centre for Carbon Capture and Storage (SACCCS)

Druckenmiller, M.L., and Maroto-Valer, M.M., (2005) Carbon sequestration using brine of adjusted pH to form mineral carbonates, Fuel Processing Technology. 86. 1599-1614

Duncan, R.A., Hooper, P.R., Rehacek, J, Marsh, J.S., Duncan, A.R., (1997). The timing and duration of the Karoo igneous event, southern Gondwana. Journal of Geophysical Research. 102, 18127-18138

Dunsmore, H. E., (1992). A Geological Perspective on Global Warming and the Possibility of CO_2 Removal as Calcium Carbonate Mineral. Energy Convers. Mgmt. 33: 5-8,565-72

Eloneva, S., Teir, S., Salminen, J., Fogelholm, C.J., and Zevenhoven, R., (2008) Fixation of CO_2 by carbonating calcium derived from blast furnace slag, Energy 33: 1461-1467

Engelbrecht, A.D., Golding, A., Hietkamp, S., Scholes, B., (2004). The potential for sequestration of CO_2 in South Africa, CSIR and DME

Engelbrecht, A.D., North, B.C., Hadley, T.D., (2008). Clrean Coal Technology: Gasification of South African Coals. Industrial Fluidization South Africa (IFSA). 188-202

Fauth, D.J., Soong, Y., White, C.M., (2002). Carbon Sequestration utilising industrial solid residues. US Dept. of Energy Nat. Energy Tech. Lab (NETL), Fuel Chemistry Division 47(1): 37-38

Feytus, A., (2010). South Africa re-enters wollastonite [Industrial Minerals]. Available at: http://www.indmin.com/Article/2398492/S-Africa-re-enters-wollastonite.html Accessed on 6th June 2011

Folger, P., (2007). Direct Carbon Sequestration: Capturing and Storing CO_2. Congressional Research Service Report for Congress

Fujioka, M., Yamaguchi, S., Nako, M., (2010). CO_2-ECBM field tests in the Ishikari Coal Basin of Japan. International Journal of Coal Geology (2010). 82: 287-298

Gaus, I., Azaroual, M., Czernichowski-Lauriol, I., (2005). Reactive transport modelling of the impact of CO_2 injection on the clayey cap rock at Sleipner (North Sea). Chemical Geology. 217: 319-337

GCEP (Global Climate Energy Project). (2005). An Assessment of Carbon Capture Technology and Research Opportunities. Stanford University Technical Assessment Report (2005). Available at: http://gcep.stanford.edu Accessed on: 3rd Jan 2012

Geokem, (2006). Geochemistry of Igneous Rocks. Available at: http://www.geokem.com/flood-basalts-1.html Accessed on 3rd Aug 2011.

Gerdemann, S. J. Dahlin, D. C., O'Connor W. K., Penner, L. R., (2003). Carbon di Oxide Sequestration by aqueous Mineral Carbonation of Magnesium Silicate Minerals. Albany Research Centre, Office of Fossil Fuel Energy, US DOE. Available at: http://www.osti.gov/bridge/purl.cover.jsp?purl=/898299-wXwUr6/ Accessed on 9th July 2011

Gertenbach, R.G., (2009). Methane and CO_2 sorption studies on South African coals. Masters dissertation. University of Stellenbosch

Giammar, D.E., Bruant, R.G. Jr., Peters, C.A., (2005). Forsterite dissolution and magnesite precipitation at conditions relevant for deep saline aquifer storage and sequestration of CO_2. Chemical Geology. 217: 257-276

Gislason, S.R., and Eugster, H.P., (1987). Meteoric water-basalt interactions: II. A field study in NE Iceland. Geochimica et Cosmochimica Acta. 51: 2841-2855.

Gislason, S.R., Arnórsson, S., Ármannsson, H., (1996). Chemical weathering of basalt in Southwest Iceland: Effects of runoff, age of rocks and vegetative/glacial cover. American Jnl. of Science. 296: 837-907

Gislason, S.R., Oelkers, E.H., Snorrason, Á., (2006). Role of river-suspended material in the global carbon cycle. Geology. 34: 49-52

Gislason, S.R., Wolff-Boenisch, D., Stefansson, A., Oelkers, E.H., Gunnlaugsson, E., Sigurdardottir, H., Sigfusson, B., Broecker, W.S., Matter, J.M., Stute, M., Axelsson, G., Fridriksson, T., (2010). Mineral sequestration of CO_2 in basalt: A pre-injection overview of the CarbFix project. Int. Jnl. of Greenhouse Gas Control.4: 537–545

Global CCS Institute. Available at: http://www.globalccsinstitute.com/ccs/key-projects Accessed on 5th Oct 2011

Global Warming: Climate Change News, Facts, and Solutions. Available at: http://globalwarming.com/ Accessed on 5th Oct 2011

Goldberg, D.S., Takahashi, T., Slagle, A.L., (2008). Carbon dioxide sequestration in deep-sea basalt. Proceedings of the National Academy of Sciences. 105: 9920-9925

Gudmundsson, B.T, and Arnórsson ,S., (2002). Geochemical monitoring of the Krafla and Námafjall geothermal areas, N-Iceland. Geothermics. 31: 195-243

Gunter, W. D., Perkins, E. H., Hutcheon, I., (2000). Aquifer disposal of acid gases: modelling of water-rock reactions for trapping of acid wastes. Appl. Geochem.15: 1085–1095

Gysi, A.P., and Stefánsson, A., (2008). Numerical modelling of CO_2-water-basalt interaction. Mineralogical Magazine. 72(1): 55-59

Halenyane, K., and Reid, D.L., (2011). Kimberlite mine tailings and their suitability as a mineral storage reservoir for CO_2 sequestration. Presented at: Inkaba ye Africa-Earth Systems Science Wksp 8-Cape Town, 28th Aug-2 Sept 2011. Available at: http://www.inkaba.org/member-area/presentations/77-workshop-8-cape-town-28-august-2-september-2011.html Accessed on 3rd Jan 2012

Harvey, B., and Tracy R.J., (1996). Petrology: Igneous, Sedimentary and Metamorphic, 2nd ed., Freeman281-292

Hofmann A.W., (2003). Sampling mantle heterogeneity through oceanic basalts: isotopes and trace elements. Treatise on Geochemistry. 2: 61-101

Huijgen W.J.J., and Comans R.N.J., (2003). Carbon Dioxide Sequestration by Mineral Carbonation. Report No. ECN-C--03-016. ECN (Energy research Centre of the Netherlands), the Netherlands

Huijgen, W.J.J., and Comans, R.N.J., (2005). Carbon dioxide sequestration by mineral carbonation: Literature review update 2003-2004, ECN-C--05-022, Energy Research Centre of The Netherlands, Petten, The Netherlands

Huijgen W.J.J., Witkamp G.J., Comans R.N.J., (2006). Mechanisms of aqueous wollastonite carbonation as a possible CO_2 sequestration process. Chemical Engineering Science. 61: 4242-4251

Hunwick, R.J. (2008). Patent. System, Apparatus and Method CO_2 sequestration. WO200810293 (A1), AU2008000232

IEA, Carbon Capture and Storage – Progress and Next Steps. (2010). IEA/CSLF Report to the Muskoka 2010 G8 Summit. IEA, Paris. 39

IEEE (Spectrum IEEE), (2008), Green Tech, Winner: Restoring Coal's Sheen. Available at: http://spectrum.ieee.org/green-tech/clean-coal/winner-restoring-coals-sheen Accessed on 5th Oct 2011.

IISD Reporting Services., (2009). Carbon Capture and storage Bulletin. A Summary of the high level Conference on Fighting Climate Change with Carbon Capture and Storage. Available at: http://www.iisd.ca/ymb/climate/ccs/ Accessed on 5th Oct 2011.

IPCC., (2005). Special Report on CO_2 Capture and Storage, ed. by Metz B., Davidson O., de Coninck H.C., Mand L., Meyer L.A. Cambridge University Press, UK

IUPAC (International Union of Pure and Applied Chemistry)., (1985). Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure & Appl. Chem. 57(4): 603—619

IUPAC (International Union of Pure and Applied Chemistry),. (1997). Compendium of Chemical Terminology 2nd ed. Compiled by McNaught, A. D., and Wilkinson, A. Blackwell Scientific Publications, Oxford (1997). Available at: http://goldbook.iupac.org (2006). Accessed on: 3rd Jan 2012

Kakizawa, M., Yamasaki, A., Yanagisawa, Y., (2001). A new CO_2 disposal process via artificial weathering of calcium silicate accelerated by acetic acid, Energy 26: 341-354

Kelemen P.B., and Matter J., (2008). In-situ carbonation of peridotite for CO_2 storage. P Natl Acad Sci USA .105: 17295–17300

Kholumo M., (2012). A study of the adsorption potential of South African ash. Masters 50/50 report. University of Witwatersrand.

Kirk-Othmer., (1991). Kirk-Othmer Encyclopaedia of Chemical Technology. 4th ed. John Wiley and Sons, Inc, New York

Kleyn, E.G., and Bergh, A. O., (2008). Some aspects regarding the handling of dolerite for base and sub-base construction. Proceedings of the 27th S. African Transport Conf. (SATC 2008)

Kodama, S., Nishimoto, T., Yamamoto, N., Yogo, K., Yamada, K., (2008) Development of a new pH-swing CO_2 mineralization process with a recyclable reaction solution. Energy. 33: 776-784

Koukouzas, N., Gemeni, V., Ziock, H.J., (2009). Sequestration of CO_2 in Magnesium Silicates in W. Macedonia, Greece. Int. Jnl .Min.Process. 93:179-186.

Krevor S.C., Graves C.R., Van Gosen B.S., McCafferty A.E., (2009). U.S Geological Survey Digital Data Series 414. Available at: http://pubs.usgs.gov/ds/414/ Accessed on 3rd Aug 2011

Lackner, K.S., Wendt, C.H., Butt, D.P., Joyce, E.L. Jr, Sharp, D.H., (1995). Carbon dioxide disposal in carbonate minerals. Energy 20: 1153-1170

Lackner K.S., and Ziock H., (2000). From low to no emissions. Modern Power Systems. 20 (31): 32

Lackner, K.S., (2002). Carbonate chemistry for sequestering fossil carbon. Annual Review of Energy and the Environment. 27: 193-232

Langley, G.J., Herniman, J., Ratsameepakai, W., Patel, K., Wicking, C., Galezowska, A., Thite, M., Holman, S., Wronska, L., Gassiot, A.M., Ball, R., Klagkou, K., (2011). Supercritical Fluid Chromatography (SFC) (Mass Spectrometry and

Supercritical Fluid Chromatography-University of Southampton). Available at: http://www.soton.ac.uk/~gjl/Research/sfc.htm Accessed on 24th June 2011

Le Maitre R.W.(editor), Streckeisen, A., Zanettin B, Le Bas, M.J., Bonin, B., Bateman, P., Bellieni, G., Dudek, A., Efremova, S,, Keller, J., Lamere, J., Sabine, P.A., Schmid, R., Sorensen, H., Woolley, A.R., (2002). Igneous Rocks: A Classification and Glossary of Terms, Recommendations of the International Union of Geological Sciences, Subcommission of the Systematics of Igneous Rocks. Cambridge University Press

Li, W., Li, B., Bai, Z., (2009). Electrolysis and heat pre-treatment methods to promote CO_2 sequestration by mineral carbonation. Chemical Engineering Research and Design. 87: 210-215

Lim, M., Han, G.C., Ahn, J.W., You, K.S., (2010). Environmental Remediation and conservation of CO_2 into useful green products by accelerated carbon technology. Int Jnl Environ Res. Public Health. 7: 203-228

Maher, K., Bird, D.K., Brown, G.E., Rosenbauer, R.J., Kharaka, Y., Johnson, N., Garci'a del Real, P., Kang, S.H., Nelson, J., Thomas, D., (2011). Reactivity of CO_2 in the Subsurface. 2011 GCEP Progress Report. Available at: http://gcep.stanford.edu/research/technical_report/2011.html Accessed on 11th Aug 2011.

Maphada, M., (2012). Verification of an automated volumetric adsorption system. MSc dissertation. University of Witwatersrand

Marini L., (2007). Geological Sequestration of CO_2: Thermodynamics, Kinetics, and Reaction Path Modelling. Elsevier, Amsterdam. 470

Maroto-Valer, M.M., Fauth, D.J., Kuchta, M.E., Zhang, Y., Andrésen, J.M., (2005). Activation of magnesium rich minerals as carbonation feedstock materials for CO_2 sequestration. Fuel Processing Technology. 86: 1627-1645

Mathivha, R., (2010). Mineralogical characterisation of natural CO_2 sequestration processes and their relevance to industrial efforts utilising mineral reservoirs. Thesis for Degree of Bachelor of Science with Honours, University of Cape Town, Dept. of Geol.Sc.

Matter J.M., Takahashi T., Goldberg D., (2007). Experimental evaluation of in situ CO_2-water-rock reactions during CO_2 injection in basaltic rocks. Implications for geological CO_2 sequestration. Geochemistry, Geophysics, Geosystems. 8: doi 10.1029/2006GC001427

Matter J.M., (2008). Permanent CO_2 Storage in Basaltic Rock. Presentation-Lamont-Doherty Earth Observatory, Earth Institute, Columbia Univ. Available at: http://www.netl.doe.gov/publications/proceedings/08/CO_2E/PDF/session%205/Juerg%20Matter%20May%2030%2097-2003v.pdf Accessed on: 3rd Jan 2012

Matter, J. M., and Keleman, P. M., (2009). Permanent storage of CO_2 in geological reservoirs by mineral carbonation. Nature GeoScience. 2: 837-842. Available online at: www.nature.com/naturegeoscience.

McGrail B.P., Schaef H.T., Ho, A.M., Chien, Y.J., Dooley, J.J., Davidson, C.L., (2006). Potential for CO_2 sequestration in flood basalts. Journal of Geophysical research. 111: B12201

Meyer, N., and Reid, D., (2011). Natural mineral carbonation of Karoo dolerite as a guide to a possible industrial CO_2 sequestration process. Presented at: Inkaba ye Africa-Earth Systems Science Wksp 8-Cape Town, 28th Aug-2 Sept 2011. Available at: http://www.inkaba.org/member-area/presentations/77-workshop-8-cape-town-28-august-2-september-2011.html Accessed on 3rd Jan 2012

Miller, J. A., Harris, C., (2007). Petrogenesis of the Swaziland and Northern Natal Rhyolites of the Lebombo Rifted Volcanic Margin, South East Africa. J. Petrology. 48(1): 185-218

Minerals Zone., (2005). World Mineral Exchange. Available at: http://www.mineralszone.com/minerals/wollastonite.html Accessed on 3rd Jan 2012

MIT (Massachusetts Institute of Technology), Carbon Capture and Sequestration Technologies @ MIT. Available at: http://sequestration.mit.edu/tools/projects/index_capture.html Accessed on 1st Dec 2011

Mitchell, R.H., (1995). Kimberlites, Orangeites, and Related Rocks. Plenum Press, New York

Naidoo B., (2009). South Africa pushes ahead with CO_2 storage Atlas project, but scepticism persists [Engineering News]. Available at: http://www.engineeringnews.co.za/article/south-africa-pushes-ahead-with-carbon-dioxide-storage-atlas-project-but-scepticism-persists .Accessed on 6th June 2011

Naidoo B., (2011). Norway to commission $1bn carbon capture and storage project in 2012 [Engineering News]. Available at: http://www.engineeringnews.co.za/article/norway-to-commission-1bn-carbon-capture-and-storage-project-in-2012-2011-12-01 Accessed on 3rd Jan 2012

NCP (Northern Cape Province)–Mineral Sector Strategy Report., (2004). Available at: http://www.northern-cape.gov/oldsite/ncpgds/mining/sec6.pdf Accessed on 5th Aug 2011

New Mexico Solar Energy Assoc. What is Global Warming. Available at: http://www.nmsea.org/Curriculum/Primer/energy_physics_primer.htm Accessed on 5th Oct 2011

Ngwagwe, M., (2009). Dolerite intrusions within the new Denmark coal mine, Mpumalanga. Thesis for Degree of Bachelor of Science with Honours, University of Cape Town, Dept. of Geol.Sc.

NIST Chemistry Webbook. Available at: http://webbook.nist.gov/chemistry/fluid/ Accessed on 1st Jan 2013

O'Connor, W.K., Dahlin, D.C., Nilsen, D.N., Walters, R.P., Turner, P.C., (2000). CO_2 sequestration by direct mineral carbonation with carbonic acid, in Proceedings of the

25th International Technical Conference on Coal Utilization and Fuel Systems. March 9–13, 1998. Clearwater, FL

O'Connor, W.K., Rush, G.E., Dahlin, D.C. (2003). Laboratory studies on the Carbonation potential of basalt: applications to geological sequestration of CO_2 in the Columbia River Basalt Group. AAPG Annual Meeting Expanded Abstracts. 12: 129-130

O'Connor, W.K., Dahlin, D.C., Rush, G.E,. Gerdemann, S.J., Penner, L.R., Nilsen, R.P., (2005). Aqueous Mineral Carbonation: Mineral Availability, Pre-treatment, Reaction Parametrics, and Process Studies. DOE/ARC-TR-04-002. Albany Research Centre, Albany, OR.USA

Oelkers. E.H., Gislason. S.R., Matter J., (2008). Mineral carbonation of CO_2. Elements. 4:333–337

Otheim, T.L., Adam, L., van Wijk, K., Batzle, M.L., McLing, T., Podgorney, R., (2011). CO2 sequestration in basalt: carbonate mineralization and fluid substitution. The Leading Edge 30 - 12: 1354–1359

Overmann, J., Tuschak, C., Fröstl, J.M., Sass, H. ,(1998). The ecological niche of the consortium "Pelochromatium roseum." Arch. Microbiol. 169:120-128

Perkins, E., Czernichowski-Lauriol, I., Azaroual, M., Durst, P. (2005). Long term predictions of CO_2 storage by mineral and solubility trapping in the Weyburn Midale Reservoir. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada 2: 2093-2096

Philibert, C., and Podkanski, J., (2005). Case Study 4: Clean Coal Technologies: International Energy Technology Collaboration and Climate Change Mitigation. OECD Environment Directorate International Energy Agency

Picot, J.C., Cassard, D., Maldan, F., Greffié, C., Bodénan, F., (2010), Worldwide potential for ex-situ mineral carbonation. (Carmex project), in GHGT-10 – 10th

International Conference on Greenhouse Gas Control Technologies, Amsterdam, The Netherlands. 19-23 Sept

Power, I.M., Wilsion, S.A., Small, D.P., Dipple, G.M., Wan, W., Southam, G., (2011). Microbially Mediated Mineral Carbonation: Roles of Phototrophy and Heterotrophy. Environ. Sci. Technol. 45 (20): 9061–9068

PowerPlantCCS. Available at: www.powerplantccs.com Accessed on 5th Oct 2011

RECOPOL. Available at: http://recopol.nitg.tno.nl/ .Accessed on 3rd Jan 2012

Reddy, K., Argyle, M., (2009). Apparatus and method to sequester contaminants. US Patent No. 20090280046A1

Reeves, S., (2003). Coal-Seq. project update: field studies of ECBM recovery/ CO_2 sequestration in coal seams. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon. I: 557–562

Reeves, S., Davis, D., Oudinot, A., (2004). A Technical and Economic Sensitivity Study of Enhanced Coalbed Methane Recovery and Carbon Sequestration in Coal. DOE Topical Report. March, 2004

Riddiford, F.A., Tourqui, A., Bishop, C.D., Taylor B., Smith M., (2003). A cleaner development: The In Salah Gas Project, Algeria. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya, (eds.), 1–4 October 2002, Kyoto, Japan. I: 601–606

Ringane B., (2003). Impact of alteration on the detectability of dolerite dykes by aeromagnetics, New Denmark Colliery, Mpumalanga. Thesis for Degree of Bachelor of Science with Honours, University of Cape Town, Dept. of Geol.S.

Saf Chem. Available at: http://saf.chem.ox.ac.uk/Instruments/BET/sorpoptprin.html Accessed on 5th Jan 2012

Saffman, P.G., (1986). Viscous Fingering in Hele-Shaw cells. California Institute of Technology. Applied Mathematics. 217-250

SCCS, (Scottish Carbon Capture and Storage). Available at: http://www.geos.ed.ac.uk/sccs/capture/oxyfuel.html Accessed on 5th Feb 2012

Schaef, H.T., McGrail, B.P., Owen, A.T., (2010). Carbonate mineralization of volcanic province basalts, International Journal of Greenhouse Gas Control. 4(2): 249-261

Schenk V., (1984). Petrology of Felsic Granulites, Metapelites, Metabasics, Ultramafics, and Metacarbonates from Southern Calabria (Italy): Prograde Metamorphism, Uplift and Cooling of a Former Lower Crust J. Petrology. 25(1): 255-296

Schuiling, R.D., and Krijgsman, P., (2006). Enhanced weathering: An effective and cheap tool to sequester CO_2, Climatic Change. 74: 349-354

Sealthedeal., (2009). UN Worldwide Campaign on Climate Change. Available at: http://www.sealthedeal2009.org/climate-change-south-africa Accessed on 6th June 2011

Seifritz W., (1990). CO_2 disposal by means of silicates. Nature. 345: 486.

Sipilä, J., Teir, S., Zevenhoven, R., (2008). CO_2 sequestration by mineral carbonation Literature review update 2005 – 2007. Environmental Protection

Surridge, A. D., Cloete, M., (2009). Carbon Capture and Storage in South Africa. Energy Procedia. 1: 2741-2744

Surridge, A. D., and Cloete, M., (2011). The Geological Storage of CO_2 and Disposal of Nuclear Waste in South Africa. Geological Disposal of CO_2 and Radioactive Waste: A Comparative Assesment .44: 569-588

Sweeny, R.J., Duncan, A.R., Erlank, A.J., (1997). The timing and duration of the Karoo igneous event, southern Gondwana. Journal of Geophysical Research. 10: 18127-18138

Teir, S., Eloneva, S., Fogelholm, C.J., and Zevenhoven, R., (2009). Fixation of CO_2 by producing hydromagnesite from serpentinite, Applied Energy. 86: 214-218

Teir, S., Eloneva, S., Zevenhoven, R., (2005). Production of precipitated calcium carbonate from calcium silicates and CO_2, Energy Conversion and Management. 46: 2954-2979

Tuan Ho, S., and Hutmacher, D.W., (2006). A comparison of micro CT with other techniques used in the characterization of scaffold. Biomaterials,.27(8): 1362-1376

U.S. Geological Survey., (2011). USGC Mineral Commodity Summaries, January 2011. Available at: http://minerals.usgs.gov/minerals/pubs/commodity/wollastonite/mcs-2011-wolla.pdf .Accessed on 3rd Jan 2012

Vattenvall. Carbon Capture and Storage-A Bridging Technology. Available at: http://www.vattenfall.com/en/ccs/pilot-plant.htm Accessed on 9th Feb 2012

Viljoen, J., Stapelberg, F., Cloete, M., (2010). Technical Report on the Geological Storage of CO_2 in South Africa. Council for Geosciences. Pretoria, South Africa

Virta, R. L., (2001). USGC Mineral Minerals Yearbook 2001. Available at: http://minerals.usgs.gov/minerals/pubs/commodity/wollastonite/860401.pdf . Accessed on 3rd Jan 2012

Vogeli J., Reid D.L., Becker M., Broadhurst J., Franzidis J.P., (2011). Investigation of the potential for mineral carbonation of South African PGM tailings. Minerals Engineering

Weiz, D.A., Stokes, J.P., ball, R.C., Kushnick, A.P., (1987). Dynamic Pressure in Porous Media: Origin of the Viscous-Fingering Length Scale. American Physical Society Review Letters 1987. 59 (26): 2967- 2970

Whitemore, G., Meth, D., Uken, R.,Reinhardt, T. , (2006). Geology of KwaZulu Natal. © School of Geological Sciences, University of KwaZulu-Natal. Available at: http://www.geology.ukzn.ac.za/GEM/kzngeol/kzngeol.htm Accessed on 3rd Jan 2012

Wikipedia . Available at: http://en.wikipedia.org/wiki/Wollastonite . Accessed on 3rd Jan 2011

Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., (2006). The effect of crystallinity on dissolution rates and CO_2 consumption capacity of silicates. Geochimica et Cosmochimica Acta. 70: 858-870

X-Ray Diffraction. Available at: http://en.wikipedia.org/wiki/X-ray_Diffraction Accessed on 17th Jan 2012

Xu, T..F, Apps J.A., Pruess, K., (2005). Mineral sequestration of CO_2 in a sandstone–shale system. Chemical Geology. 217: 295-318

Xu, T., Apps, J. A., Pruess, K., (2004). Numerical simulation of CO_2 disposal by mineral trapping in deep aquifers. Appl. Geochem. 19: 917–936

Yaalon, D.H., (1961). Mineral composition of the average shale. Dept. of Geology, the Hebrew University, Jerusalem. Available at: www.minnersoc.org/pages/Archive-CM/Volume_5/5-27-31.pdf Accessed on 25th Jan. 2012

Yegulalp T.M., Lackner K.S., and Ziock H.J., (2000). A Review of Engineering Technologies for Sustainable use of Coal for Power Generation, presented at sixth International Symposium on Environmental and Waste Management in Energy and Mineral Production, Alberta, Canada

ZEP-Zero Emissions Platform. CO_2 Capture and Storage. Available at: http://www.zeroemissionsplatform.eu/ . Accessed on 4th Oct 2011

Zevenhoven R., Fagerlund J., (2010). Fixation of CO_2 into inorganic carbonates: the natural and artificial "weathering of silicates", CO_2 as Chemical Feedstock, ed. by Aresta M.Wiley VCH Verlag, Germany. 353–367.

Zevenhoven, R., Kohlmann, J.,(2001). CO_2 Sequestration by Mg Silicate Carbonation in Finland. Second Nordic Minisymposium on CO_2 Capture and Storage, Göteborg, 2001. Available at: http://www.entek.chalmers.se/~anly/symp/symp2001.html Accessed on 3rd Jan 2012

Zevenhoven, R., Fagerlund, J., Songok, J.K., (2011). Review: CO_2 mineral sequestration: developments towards large scale application. Greenhouse Gas Sci Technol. 1:48–57

Zevenhoven, R., and Kavaliauskaite, I., (2004), Mineral carbonation for long-term CO_2 storage: An energy analysis, International Journal of Thermodynamics. 7: 22-31

Zevenhoven, R., Teir, S., Eloneva, S., (2006). Heat optimisation of a staged gas-solid mineral carbonation process for long-term CO_2 storage, Proceedings of ECOS 2006, 12-14 July 2006, Crete, Greece, 1661-1669, in revised form Energy, 2008. 33: 362-370

Zhang, J., Zhang, R., Geerlings, H., (2010). A novel indirect wollastonite carbonation route for CO_2 sequestration. Chemical Engineering and Technology. 33(7): 1177-1183

Appendices

Appendix A: Volumetric Adsorption Data

Table A1: PVT Data

Table 1. PVT data for CO2, T= 32; P range = (20 to 100bar); Pincrement 10bar)
CO2: Pcritical ~73.8 bar, Tcritical~31 degC
Data courtesy of NIST website

T	P	Density	Volume	ernal Ener	Enthalpy	Entropy	Cv	Cp	Sound Spd	le-Thoms	Viscosity	herm. Con	Phase
°C	bar	ml/l	l/mol	kJ/mol	kJ/mol	J/mol*K	J/mol*K	J/mol*K	m/s	K/bar	uPa*s	W/m*K	Phase
32	20	0.87433	1.1437	19.436	21.723	94.643	31.334	44.552	257.15	1.0366	15.526	0.01831	vapor
32	30	1.3975	0.71557	19.087	21.234	90.087	32.693	50.055	248.81	1.0372	15.786	0.019227	vapor
32	40	2.0097	0.49758	18.686	20.676	86.304	34.353	58.218	239.69	1.0336	16.186	0.020587	vapor
32	50	2.761	0.36218	18.203	20.014	82.74	36.527	71.905	229.45	1.0218	16.821	0.0228	vapor
32	60	3.769	0.26533	17.573	19.165	78.937	39.753	100.81	217.32	0.99165	17.919	0.027041	vapor
32	70	5.491	0.18212	16.548	17.823	73.805	46.436	217.58	200.1	0.90262	20.453	0.039212	vapor
32	80	14.818	0.067487	12.506	13.046	57.767	47.882	334.89	251.62	0.27864	50.097	0.076521	vapor
32	80	14.818	0.067487	12.506	13.046	57.767	47.882	334.89	251.62	0.27864	50.097	0.076521	supercritical
32	80	14.818	0.067487	12.506	13.046	57.767	47.882	334.89	251.62	0.27864	50.097	0.076521	supercritical
32	90	16.277	0.061436	11.962	12.515	55.819	44.014	188.65	319.63	0.17867	58.066	0.078637	supercritical
32	100	17.041	0.058681	11.664	12.25	54.756	42.64	153.62	361.41	0.13778	62.83	0.082029	supercritical

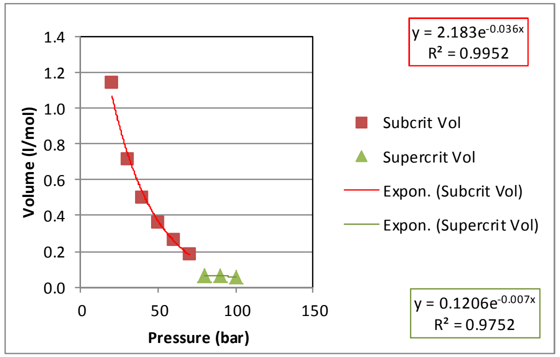


Table A2: VAS Results

Table 2. VAS Results

Step			Pav	B1	B2	S1	S2
1	Pstart	bar, guage		12.321	11.816	12.042	12.258
	Pend	bar, guage		12.203	11.823	12.085	12.282
2				23.265	23.101	23.119	34.704
				23.199	23.153	23.157	34.477
3				36.929	38.598	37.951	42.798
				36.912	38.599	37.965	42.989
4				44.060	44.502	43.983	47.510
				44.052	44.624	44.036	47.572
5				52.876	52.949	52.961	54.122
				51.876	51.900	52.017	52.557
6				63.276	62.829	62.947	63.512
				63.241	62.940	62.950	63.494
7				71.854	71.974	72.126	71.989
				71.812	72.231	72.166	72.081
8				73.314	73.267	73.371	73.306
				73.423	73.203	73.376	73.528
1	Vstart	l/mol		1.35	1.38	1.37	1.35
	Vend	l/mol		1.36	1.38	1.36	1.35
2				0.91	0.92	0.92	0.60
				0.91	0.92	0.91	0.61
3				0.56	0.52	0.54	0.45
				0.56	0.52	0.54	0.45
4				0.43	0.42	0.43	0.38
				0.43	0.42	0.43	0.38
5				0.31	0.31	0.31	0.30
				0.33	0.33	0.32	0.32
6				0.22	0.22	0.22	0.21
				0.22	0.22	0.22	0.21
7				0.16	0.16	0.16	0.16
				0.16	0.16	0.16	0.16
8				0.15	0.15	0.15	0.15
				0.15	0.15	0.15	0.15
1	delta V	l/mol		0.006	0.000	-0.002	-0.001
2				0.002	-0.002	-0.001	0.005
3				0.000	0.000	0.000	-0.003
4				0.000	-0.002	-0.001	-0.001
5				0.011	0.012	0.011	0.017
6				0.000	-0.001	0.000	0.000
7				0.000	-0.001	0.000	-0.001
8				-0.001	0.000	0.000	-0.001
1	moles			5	-92	-14	-26
2				13	-17	-23	6
3				89	-1237	-109	-9
4				253	-16	-35	-34
5				3	2	3	2
6				109	-34	-1198	205
7				122	-20	-130	-56
8				-49	84	-1291	-24
1	Paverage			13.3	12.8	13.1	13.3
2				24.2	24.1	24.1	35.6
3				37.9	39.6	39.0	43.9
4				45.1	45.6	45.0	48.5
5				53.4	53.4	53.5	54.3
6				64.3	63.9	63.9	64.5
7				72.8	73.1	73.1	73.0
8				74.4	74.2	74.4	74.4
1	moles/g			2.5	-45.9	-6.9	-12.8
2				6.7	-8.6	-11.6	2.9
3				44.3	-618.6	-54.6	-4.7
4				126.4	-7.8	-17.6	-17.1
5				1.3	1.2	1.3	0.8
6				54.6	-16.8	-599.1	102.7
7				61.1	-10.0	-65.2	-28.1
8				-24.7	42.1	-645.6	-12.1
1	P/Pcrit, Pcrit=73.8			0.2	0.2	0.2	0.2
2	73.8			0.3	0.3	0.3	0.5
3				0.5	0.5	0.5	0.6
4				0.6	0.6	0.6	0.7
5				0.7	0.7	0.7	0.7
6				0.9	0.9	0.9	0.9
7				1.0	1.0	1.0	1.0
8				1.0	1.0	1.0	1.0

vol estim sample cell(l)	0.02913
mass of sample(g)	2.00000

NOTES this sheet correct
assume measured P in guage
all P charted as absolute pressure
no errorbars
no negative values included
no leak correction on subcritical data

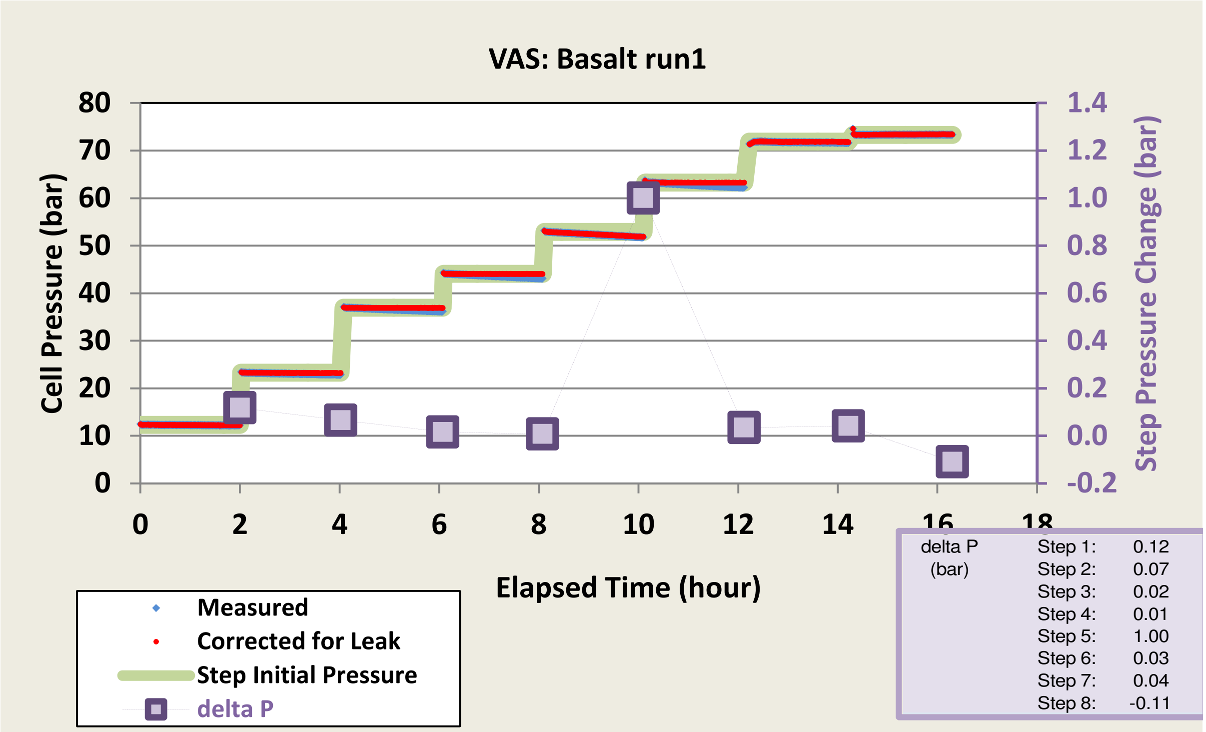


Figure A1: Basalt Run 1

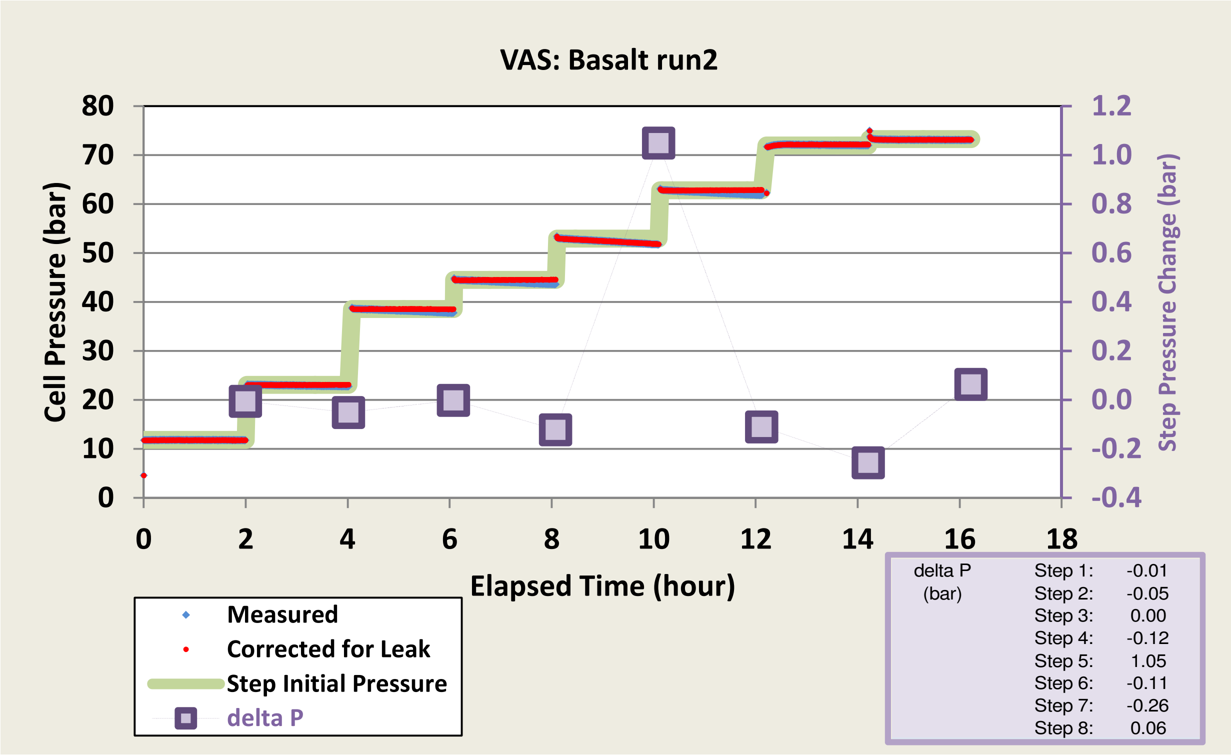


Figure A2: Basalt Run 2

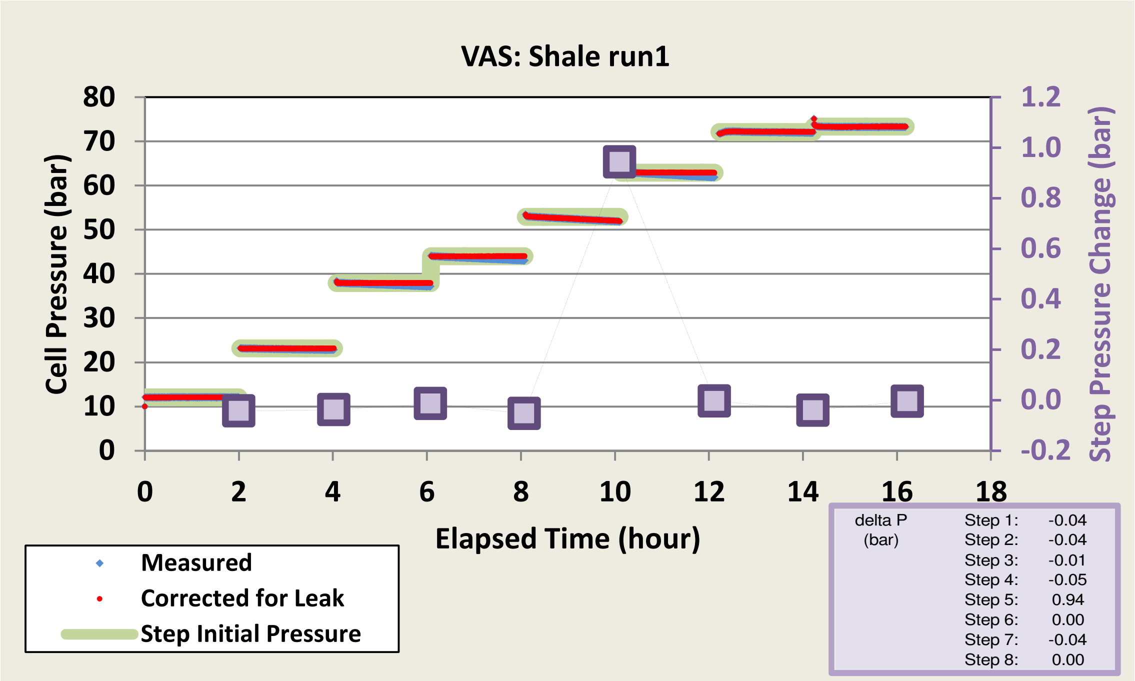


Figure A3: Shale Run 1

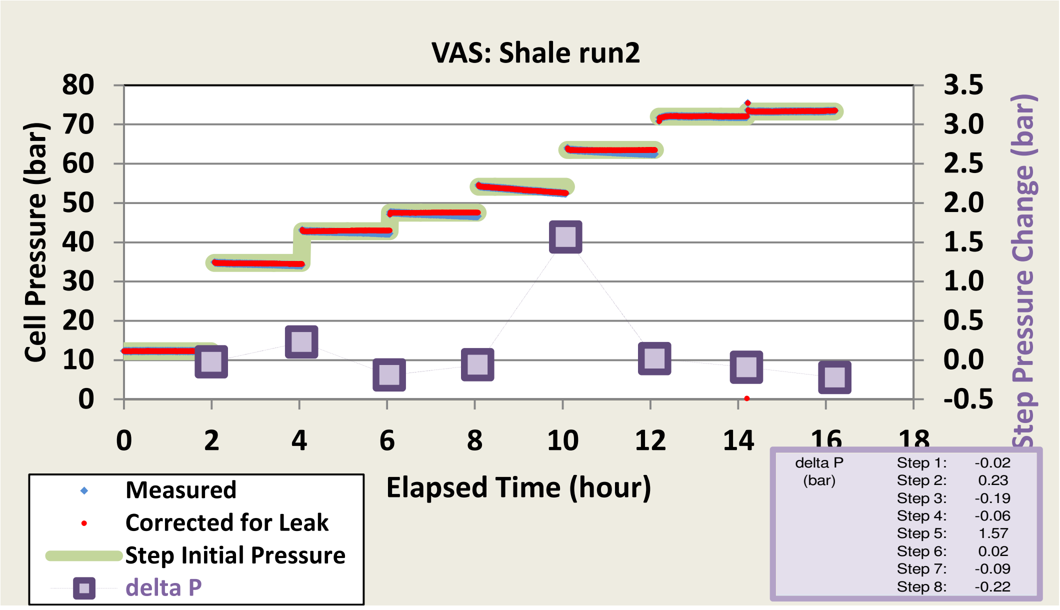


Figure A4: Shale Run 2

Table A3 Subcritical Data

REFERENCE		**CALCULATIONS**								**EXPERIMENTAL DATA**					
								vol estim sample cell(l)	0.02913						
								mass of sample(g)	2.00000						
File	**Sheet**	**Paverage**	**P** initial	final	**Mol Vol** initial	final	**Mol V**	**Moles**	**Moles/g**	**Index** **start**	**end**	**P2** **start**	**end**	**P1** **start**	**end**
2011-08-01 shale Test 1		21.9	21.78	20.45	1.020	1.100	0.080	2.33E-03	1.17E-03	160	3520	21.78	20.45	21.84	21.87
Test 2		31.4	31.23	28.76	0.664	0.732	0.069	2.00E-03	1.00E-03	3660	7040	31.23	28.76	31.45	31.38
Test 3		41.4	41.53	37.98	0.472	0.525	0.053	1.55E-03	7.74E-04	7300	10800	41.53	37.98	41.49	41.35
Test 4		43.8	44.41	28.90	0.436	0.728	0.29215	8.51E-03	4.26E-03	11000	29220	44.41	28.90	44.20	43.46
2011-12-16 basalt Test 1	14-00-52	8.2	7.68	7.40	3.548	3.708	0.15937	4.64E-03	2.32E-03	20	3110	7.68	7.40	8.20	8.18
Test 2	15-02-27	15.3	14.87	14.22	1.611	1.699	0.08819	2.57E-03	1.28E-03	3200	6280	14.87	14.22	15.53	15.17
Test 3	16-04-03	24.0	23.56	22.20	0.929	0.997	0.06835	1.99E-03	9.96E-04	6370	9440	23.56	22.20	24.36	23.57
Test 4	17-07-39	37.1	36.83	34.39	0.545	0.591	0.04645	1.35E-03	6.77E-04	9570	12590	36.83	34.39	37.87	36.35
Test 5	18-08-16	43.7	43.37	40.45	0.448	0.487	0.03882	1.13E-03	5.65E-04	12720	15720	43.37	40.45	44.59	42.83
Test 6	19-09-50	52.7	52.16	48.81	0.359	0.389	0.02968	8.65E-04	4.32E-04	15825	18860	52.16	48.81	53.80	51.70
2011-07-29-13 basalt															
Test 1		20.4	20.47	19.98	1.099	1.131	0.03249	9.47E-04	4.73E-04	450	3940	20.47	19.98	20.38	20.33
Test 2		29.9	30.07	28.36	0.694	0.744	0.05018	1.46E-03	7.31E-04	4075	8440	30.07	28.36	29.94	29.82
Test 3		36.6	36.99	34.36	0.542	0.592	0.04982	1.45E-03	7.26E-04	8610	13800	36.99	34.36	36.70	36.52
Test 4		36.9	37.44	30.10	0.534	0.693	0.15904	4.63E-03	2.32E-03	14000	30160	37.44	30.10	37.19	36.64

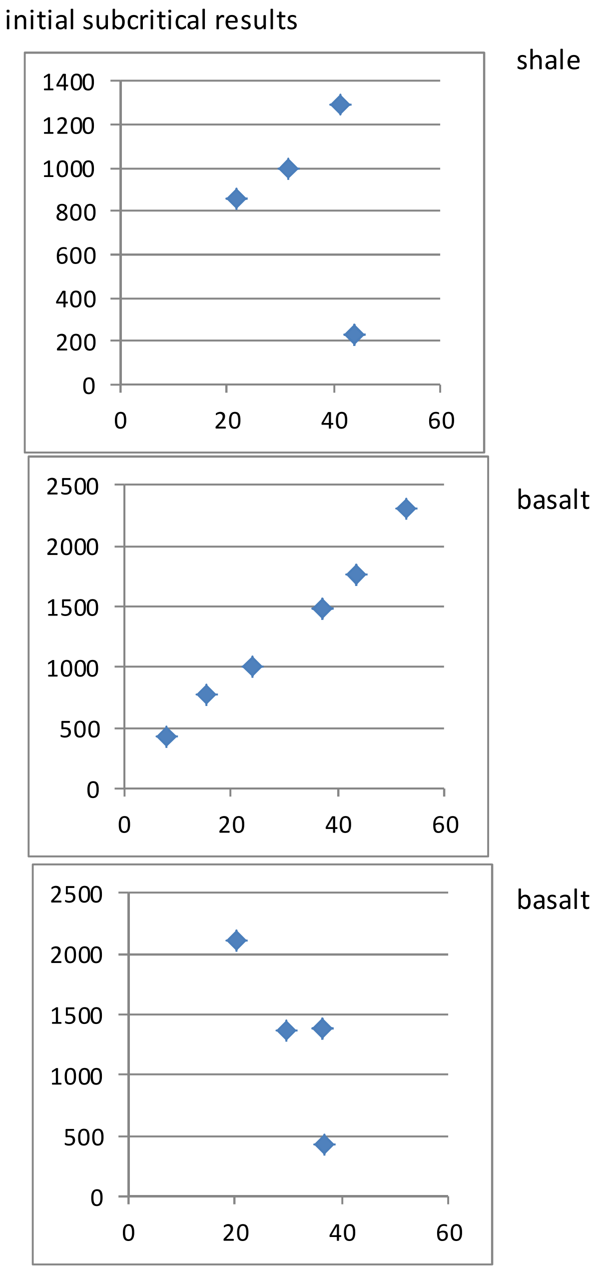


Figure A6: Initial VAS Subcritical Results (uncorrected for leaks): x = Moles of CO_2/gram sample and y = Pressure in bar

Appendix B: BET Data

Table B1 Shale BET Results

		m²/g BET surface area	cm³/g Pore volume	Median Pore Width
	untreated	21.8419	0.0070	4.234 Å
Shale	supercritical	28.2831	0.0095	4.177 Å
	VAS	24.4519	0.0070	4.203 Å

Table B2 Basalt BET Results

		m²/g BET surface area	cm³/g Pore volume	Median Pore Width
Basalt	untreated	10.7534	0.0038	4.304 Å
	supercritical	12.1922	0.0043	4.322 Å
	VAS	10.6927	0.0039	4.226 Å